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A Unified Approach to Failure and Its Application to Highly Filled Polymers

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Synopsis

Two interrelated general approaches to the study of structural failure of highly filled polymeric materials, e.g., a solid propellant, are described. These consist of the macroscopic (thermodynamics and continuum mechanics) and microscopic (molecular model) methods of analysis in conjunction with solid propellant experimental data. The thermodynamic investigation indicates that propellant material under loading goes through stages of stable and unstable behavior which depend upon the rate at which work is absorbed and dissipated by the material. The instability point seems to correlate with results from subscale motors. The thermodynamic investigation is then extended by a functional analysis of failure treated from a viewpoint of continuum mechanics. Since fracture, per se, is a physical observable, it is represented by a "state vector" in n-dimensional space. The number of dimensions of this space depends upon the basic variables involved in fracture. Since the correct failure criteria must be tensorally consistent with the tensor rank of fracture, distinct sets of functions can be applied to experimental data. The data are compared to the classical scalar functions of failure. They were obtained from uniaxial and biaxial creep and relaxation tests to failure, uniaxial and biaxial tension tests conducted under constant rates of loading and of strain, with and without superimposed hydrostatic pressure, and pure shear tests to failure. The correlation between the different types of induced failure is demonstrated through the microscopic approach by use of molecular models and the application of statistical mechanics.

INTRODUCTION

The prediction of structural reliability of any propellant grain design requires the use of an appropriate failure criterion. If this criterion is to be consistent, it must be capable of explaining failure under various types of loading conditions. Hence, a consistent "unified" failure theory would be capable of predicting the magnitude of the stress or strain for rupture of a material under loading enviornments of constant stress or strain, cyclic stress or strain and constant rates of loading. It must also include the effects of history, temperature, humidity, etc., upon the ultimate capacity of the material. This failure theory would then allow the calculation of the reliability of a solid propellant motor under any given history of loading and environment. In this paper a preliminary investigation into this "unified" failure theory is described, and its application to solid propellant materials is demonstrated.

Material rupture begins on the atomistic scale and then propagates internally until the propagation becomes unstable and the material actually separates. Hence, a general theory can only be established through the use of two interrelated approaches, the microscopic and macroscopic ones. Included in the macroscopic approach are thermodynamics and continuum mechanics, while the microscopic approach consists of molecular models used in conjunction with quantum and statistical mechanics. Each of these methods of analysis will be considered.

Thermodynamic Investigation

While thermodynamics by definition applies only to equilibrium states, it has been extended to nonequilibrium behavior by investigations such as Onsanger. Using Onsanger's theory of irreversible thermodynamics, various authors such as Biot,[1] Schapery,[2] Staverman and Schwartzl,[3] and Lianis[4] have interpreted linear viscoelastic theory. However, in this investigation, interest exists only in obtaining the thermodynamic equation of state in terms of the energy which a material point experiences. Therefore, the propellant material is being treated as if it were devoid of thermodynamic sinks, and the material is considered to be a region in space consisting of a domain and its boundary (Fig. 1). Therefore, the thermodynamic system is closed, and, as such, the entropy must be positive definite. The resulting thermodynamic analysis is found in Appendix A, and the final equation is

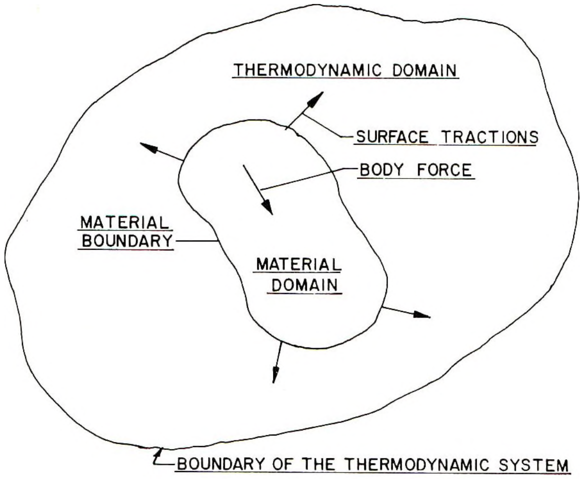

Fig. 1. Thermodynamic system.

$$\sigma_{ij}\dot{\epsilon}_{ij} + \rho(t)\,\dot{v}_i v_i + q_{i,i} = \frac{d}{dt}\left\{\rho(t)\left[E_i + \eta + K.E.\right]\right\} \qquad (1)$$

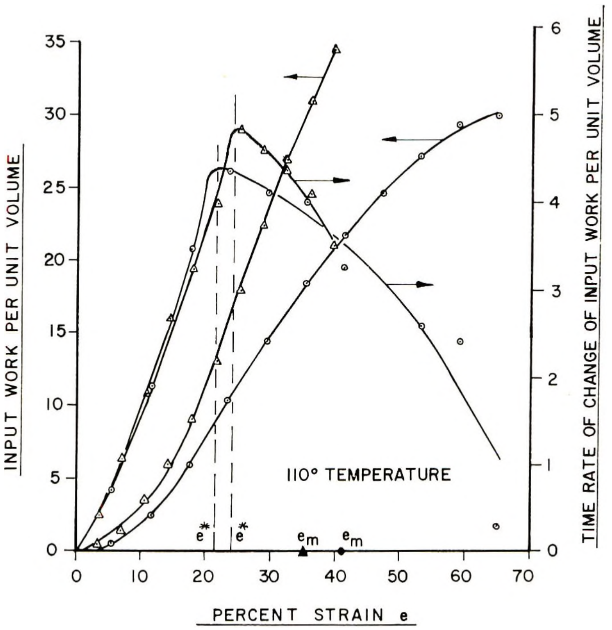

Fig. 2. Experimental input work and power curves: (⊙) uniaxial, 0.74 in./in./min.; (△) biaxial, 0.74 in./in./min. Solid points denote strain at σ_m; arrows indicate ordinate axis.

Here σ_{ij} and ϵ_{ij} are, respectively, stress and strain in the ijth direction, $\rho(t)$ is mass density at time t, v_i is the velocity in the ith direction, q_i denotes the rate of energy input in the system by heat transfer per unit area in the ith direction, E_i is the internal (stored) energy per unit mass, η is the internal dissipative energy per unit mass, and $K.E.$ is total kinetic energy.

The quantity inside the brackets of the right-hand side of eq. (1) is the total energy per unit volume at some specific location and time. From conservation of energy, however, this total energy must equal the input energy. Hence, the time-rate of change of the total input energy must equal the left-hand side. In this equation the heat flux is outwards and $q_{i,i}$ becomes negative. Because power is defined as the rate of transfer of energy, the right-hand side of the above equation is the power that the material is capable of absorbing at a specific time and location.

Equation (1) is the equation of state which will be used for comparison with experimental data. The latter consist of stress versus strain data obtained at various loading rates and various temperatures. The tests were conducted on end bonded uniaxial and modified-strip biaxial specimens.

The actual external work was computed by multiplying the force on the specimen by its corresponding displacement. The input work can be written in the form of stress and strain as

$$w/A_0L_0 = \sigma\epsilon \qquad (2)$$

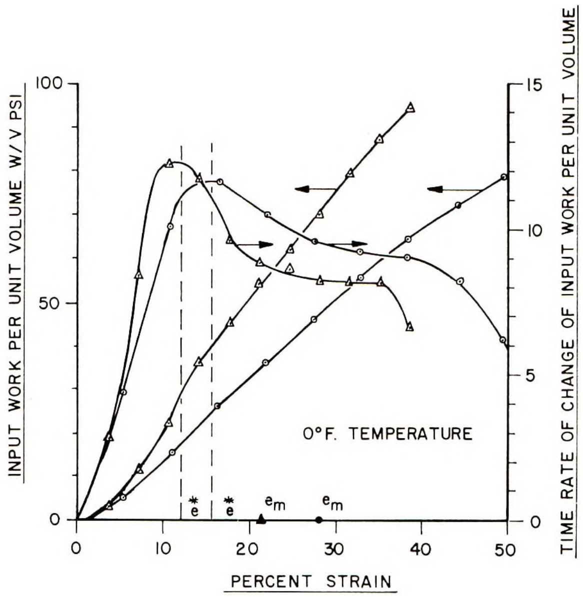

Fig. 3. Experimental input work and power curves: (⊙) uniaxial, 0.74 in./in./min.; (△) biaxial, 0.74 in./in./min. Solid points indiate strain σ_m; arrows indicate ordinate axis.

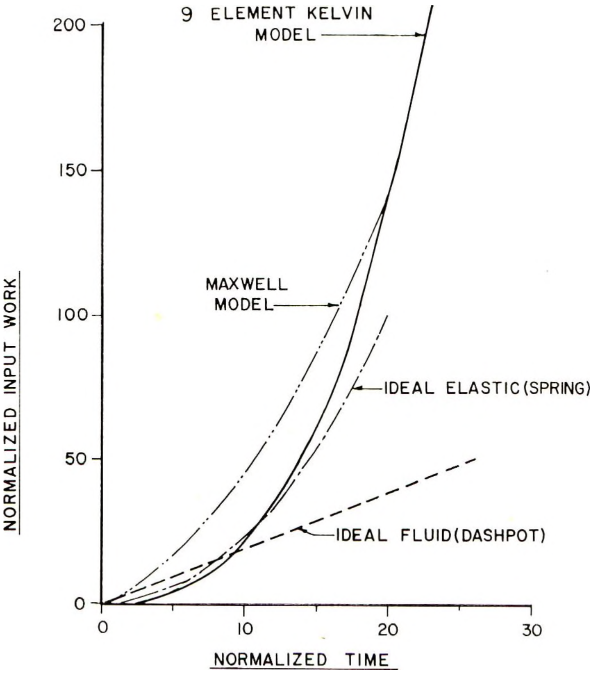

Fig. 4. Input work for model materials.

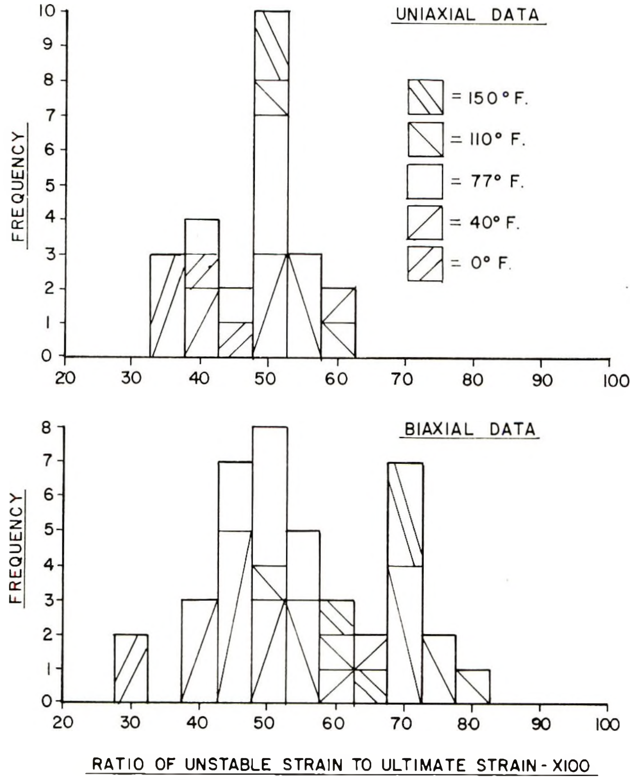

Fig. 5. Histogram of normalized strain for uniaxial and biaxial data.

where w = total input energy, A_0 is the initial cross-sectional area of the specimen, L_0 is the length, σ is axial stress, and ϵ is strain.

The left-hand side of eq. (2) is input work per unit volume. A_0L_0 is the original volume and if the assumption of incompressibility is made, it remains constant. Since input force is used, either true stress and actual cross-sectional area, or nominal stress and original cross-sectional area, are applicable definitions. Typical curves of experimental input work are shown in Figures 2 and 3. The time derivative of the work is the slope of the work curve since under constant strain rate, the strain is a constant multiplied by time.

To compare these curves of experimental input work with predictions of model materials, nondimensional work versus displacement curves are shown in Figure 4 for various material idealizations. The nine-element Kelvin model behavior was predicted by using the equations derived in Appendix B and material characterization obtained from relaxation tests. This and the other models indicate that up to the inflection point, the material responds similarly to a grouping of springs and dashpots (linear or nonlinear). Beyond this point the work input response is first linear and then monotonically decreasing to material rupture. The behavior

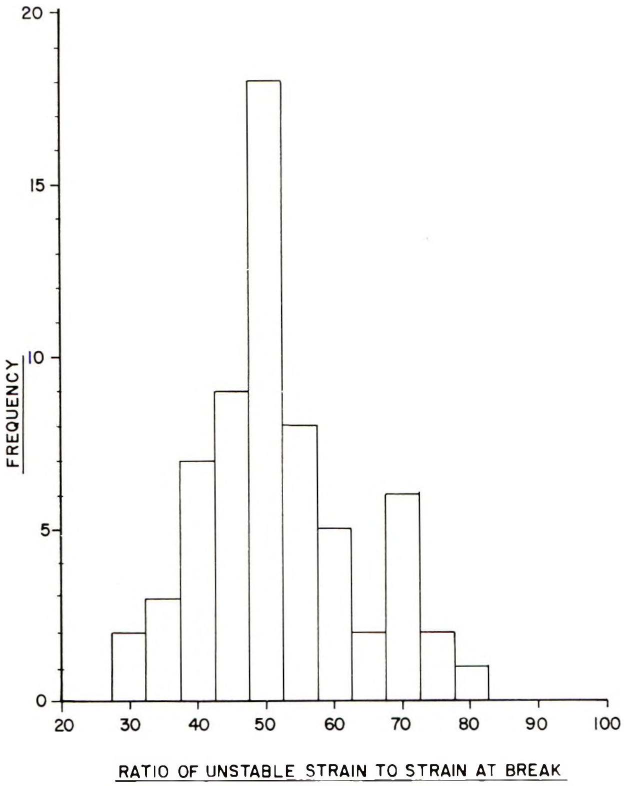

Fig. 6. Histogram of normalized strain for combined uniaxial and biaxial data.

illustrates that from the inflection point onwards, the internal mechanism goes through states of molecular motion or flow (dashpot response) and progressive tearing (decreasing capability) by coalescence of vacuoles. Dilatational data illustrate that these three states also exhibit different volumetric response. The shape of the input power curves indicates that the material is capable of stable equilibrium up to the inflection point. At the inflection point, it is in neutral equilibrium, and beyond this point, the material is in a stage of unstable equilibrium.

In terms of mechanics, the above implies that for stress–strain combinations below the inflection point, the material can relax or creep to a stable condition. Because material rupture is a molecular stability problem, the material will not fail if the input work is less than the neutral equilibrium value. Hence, "relaxation failure" will not occur if upon straining to the specified constant level, the input work is less than the inflection value. For input work beyond this value, the material is in a state of unstable behavior and failure will eventually occur. For creep to failure the strains continually increase with time until the unstable region is reached and failure occurs after a sufficient lapse of time. Both of these hypotheses are borne out by experiments at constant stress and at constant strain.[5] Re-

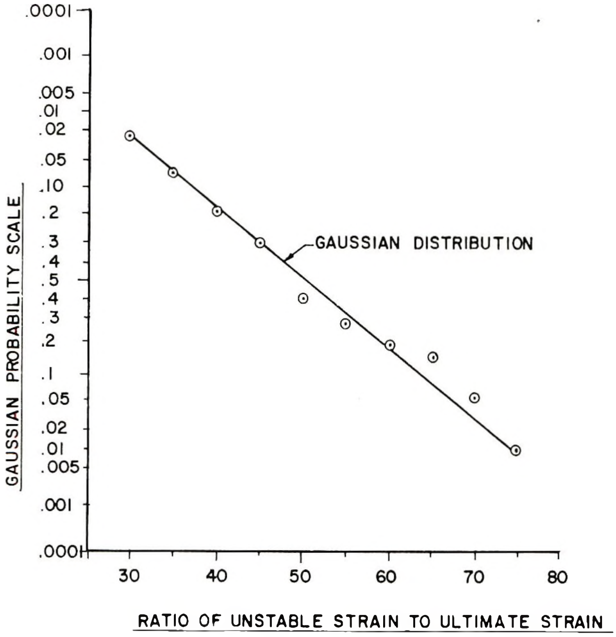

Fig. 7. Comparison of experimental distribution of ratio of unstable strain to a Gaussian distribution.

healing experiments by Colodny[6] have shown that samples strained below ϵ_m (strain at maximum stress) can essentially be rehealed to their original properties by recovery at various temperatures. Figures 2 and 3 illustrate that the strain corresponding to the maximum input power is less than the strain ϵ_m. The effect of input work on the cyclic behavior is discussed in the microscopic analysis.

With only the first terms of the left-hand side of eq. (1), the maximum in the input power occurs at the strain corresponding to the maximum stress. The heat flux term $q_{i,i}$ will shift the strain ϵ^* (strain corresponding to the inflection point in the input work curves) away from the strain ϵ_m. Hence, for the experimental data, the heat flux had a substantial effect on the material's ability to withstand deformation. This indicates that the heat-generating process from viscous flow is detrimental to the propellant's resistance to rupture. The average power term $\rho(t)\ \dot{v}_i v_i$ will either shift the strain ϵ^* away from or towards the ϵ_m value, depending upon dilatation $[\rho(t)]$ and rate of straining (v_i). Thus, as the strain rate increases, ϵ^* will approach the ϵ_m value and may exceed this value if the decrease in density due to dilatation is not too large.

The statistical variation of the strain ϵ^* (Figs. 5 and 6) shows that the mode is one-half of the ultimate strain and the histogram for the biaxial data is heavily skewed to the right (histograms also indicate that, as the temperature decreases, the mode shifts to lower fractions of the ultimate strain and vice versa).

A plot of the normalized strains on probability paper (Fig. 7), shows that the distribution is approximately Gaussian. This is analogous to the distribution of failures due to thermal cycling.[7]

Functional Investigation

The thermodynamic analysis illustrated that the rate at which work is absorbed and dissipated by a material is an indication of its ability to resist rupture. It is of interest to establish the functional form of this failure criterion. Since fracture, *per se*, is a physical observable, it can be represented by a "state vector" in an n-dimensional space. This state vector is not a vector in the ordinary sense, but rather a vector of a functional space. Any family of functions having a common domain is called a function space. "Points" of this space are the individual functions. This space is linear if, and only if, a linear combination of functions is also a member of the space.

Assuming a field f of complex scalars, and a collection V of mathematical objects which are defined as "vectors"—not necessarily geometric vectors—then V is called a vector space over f if, and only if, it satisfies certain operation rules.[8] Hence, linear spaces are alternately called vector spaces and their elements are vectors. From the operation rules, it can be seen that any set of matrices or order n and elements of the complex number field form a vector space. The vector space is called a finite dimensional space of dimension k if there exist k elements V_i such that any function g of this space can be written as

$$g = \sum_{i=1}^{k} C_i V_i \tag{3}$$

where C_i is an experimentally determined coefficient.

These V_i vectors are called the basis of g. It can be shown that any vector space of nth-order matrices has a dimension n^2. The n^2 matrices defining the basis are of the form $\epsilon_{\alpha\beta}$ $(\alpha,\beta = 1, 2,\ldots, k)$ where $\epsilon_{\alpha\beta}$ is a kth-order matrix which has unity in the αth row and βth column with all other elements equal to zero. In this definition the basis vectors can be treated as constant, but their coefficients are time-dependent, since the functions are time-dependent.

Consequently, the basis vectors used for the n-dimensional failure space will be the $\epsilon_{\alpha\beta}$. The dimension of this space is dependent upon the fundamental variables involved in the phenomenon of rupture. If the chosen variables form a complete set, then the basis is complete. However, this can only be established by theoretical consistency with experimental results. The completeness of the basis insures that some functional within this domain is capable of predicting material failure under any type of environment, i.e., a "unified" failure theory.

Extensive experimental tests have shown that propellant failure, as measured in terms of ultimate stress or strain, depends upon the material properties, environment and surface treatment. The ultimate stress for constant strain behavior differs from that observed from constant rate of loading and from cycling loading. Even cyclic behavior has exhibited path dependency.[9] Hence, in general, failure can be treated as depending upon three characteristics, including such factors as anisotropy of the propellant materials and volume effects. The mechanical characteristics contain factors such as strain, rotation, and velocity. The physical variables are moduli, density, temperature, etc. Functionally, this can be written as

$$\text{Failure} = f_1(\varphi_i, \epsilon_{ij}, V, t) \qquad (4)$$

where φ_i are material variables. Each of these variables is associated with a dimension of the failure space. Since each set of points within this space defines failure for certain specific conditions, the locus of all these points determines an n-dimensional surface. This surface is a generalized extension of the failure surfaces of classicial failure theories. Because only the set of points determines the vector, its norm is unimportant and the basis vectors can be normalized without affecting the end results. Thus, the failure state can be represented by a linear polynomial of n rank matrices with time-dependent coefficients. The actual form of this state vector will depend upon its tensor rank. This gives rise to the question as to whether fracture *per se* is a scalar, vector, or higher rank tensor. The tensor rank of the state vector is determined by its transformation law from one set of basis vectors to another set. Since the correct failure criterion must be tensorally consistent with the tensor rank of fracture, distinct sets of functions exist for each tensor rank.

A scalar quantity can be considered as having only magnitude and sense, whereas a vector has direction besides magnitude and sense. The second rank tensor has the above properties plus an associated area, volume, or length. In the normal engineering experience, fracture is observed as a scalar quantity in terms of stress or strain magnitudes. While stress or strain are second rank tensors, the principal values are invariants, hence, scalars. The classical theories treat failure as a scalar quantity. However, experimental data with propellant show that the principal stress value at failure depends upon the environmental history.

Experimental data for a particular propellant was obtained from uniaxial and biaxial tension tests conducted under constant rates of stress and strain, with and without hydrostatic pressure. Uniaxial compression tests, with and without hydrostatic pressure, were also conducted. In addition, data obtained from uniaxial and biaxial creep and relaxation tests to failure and triaxial tension (modified poker chip) tests were also compared. The stress distribution within the modified poker chip and the biaxial strip was obtained from photoelastic analyses.[10,11] While the actual stresses differ, the analyses indicated the normalized ratio of principal stresses. A typical plot of the principal failure stresses for a constant temperature is shown in Figure 8. Although the ultimate stresses for the same rate of loading fall essentially on the same failure surface, the ulti-

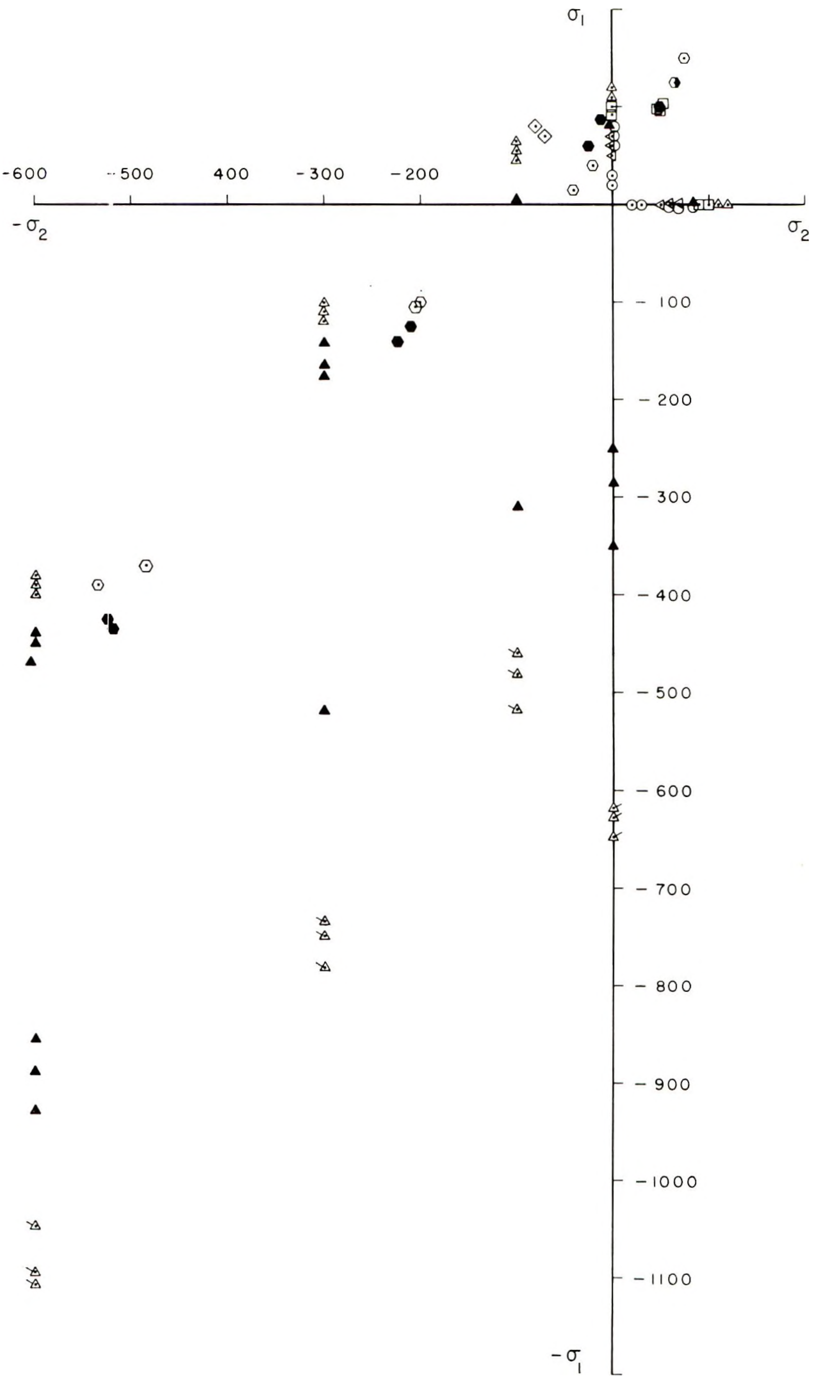

Fig. 8. Two-dimensional plots of failure stresses for ANB3066 propellant (filled, 88 wt.-% polybutadiene rubber), 77°C.: (△) uniaxial failure at 1800 psi/min.; (⊙) biaxial failure at 800 psi/min.; (⊡) biaxial failure at 0.72 in./in./min.; (⊙) uniaxial failure at constant strain; (◁) uniaxial failure at constant stress; (◇) shear failure at 45°/min.; (△) limit of testing device with respect to strain (specimen exhibited hairline cracks); (△) compressive failure due to crushing. Solid points denote stress at which the constant loading rate response deviated from linearity.

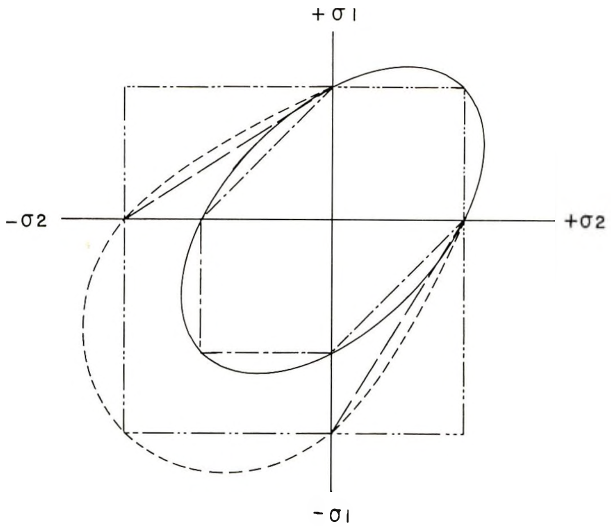

Fig. 9. Two dimensional representation of classical failure surfaces: (—) stassi or quadratic internal friction; (— -- —) maximum principal stress; (— - —) maximum shear stress; (——) octahedral shear stress; (— —) linear internal friction.

mate stresses for the other types of induced failure do not agree. The shape of the failure surface does not correspond to any of the predictions of the classical or modified classicial failure theories (Fig. 9). This deviation from the classical theories of brittle failure or failure by yielding can be due to the effect of the variables, e.g., time, etc., or because failure, *per se*, is not a scalar quantity. There is an indication that it is not the magnitude of stress or strain at a point that is critical, but rather the tensor fields or gradients within the material. However, this problem is highly complicated by the time variable and is under further investigation.

Molecular Investigation

The previous discussion illustrated that variables other than stress or strain magnitude enter into the process of fracture. The use of group symmetry and tensor analysis can determine distinct sets of functions.[12] However, for propellant, the type of material group symmetry must be kept general to account for inhomogeneities and strain-induced anisotropy. The great number of possible variables leads to a large variety of functions within any particular tensor group. Consequently, the actual variables to be used as the basis for the n-dimensional space must be established from the molecular structure of the propellant. Since fracture is a physical entity, correlation must exist between the different types of induced failures. It has already been demonstrated that these failures do not correlate with respect to principal stresses. However, a positive correlation appears to exist between constant load failures and cyclic fatigue failures (Fig. 10), indicating that the failure mechanism is governed by the micro-

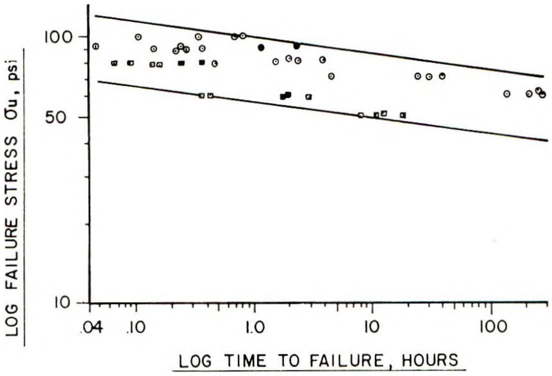

Fig. 10. Comparison of time to failure for fatigue and constant load: (●) triaxial tension fatigue, 5 cycles/sec.; (○) triaxial tension; (■) shear fatigue, 5 cycles/sec.; (□) shear.

scopic kinetics between molecular bond failure and rehealing. This parallels the findings of the thermodynamic investigation that the rate at which work is absorbed or dissipated by the material is critical, i.e., it is a problem of molecular stability.

Stuart, et al.[13] have applied a nonequilibrium rate process to the problem of static fatigue of glass. This involves the hypothesis that, while the chemical bonds are incessantly being broken and reformed by molecular vibration, the rate of breaking is greater than the rate of formation. However, since glass is an almost perfect elastic material, the molecular potential energy is not time-dependent, and the kinetic equation is very simple. Various other kinetic equations have been used for the nonequilibrium rate process such as Coleman's theory of breaking kinetics,[14] but they do not account for the accumulation of damage as evidenced by loading histories or various other influences. In practice, the basic kinetic equation can only be established from a microscopic approach.

Macroscopic results are obtained from a microscopic analysis by application of statistical mechanics[15] (either quantum or classical) to account for the statistical possibilities of atomic arrangements or the uncertainty of quantum mechanics.[16] This involves establishing the allowable energy values and using these values in the appropriate distribution function to establish the partition function. Because the propellant reaction is time-dependent, non-equilibrium behavior must be considered. This requires finding the allowable energy levels from the solution to the time-dependent Schrödinger equation and using them with the "master equation" of non-equilibrium statistical mechanics.[17]

The first step in solving the quantum mechanical problem is the establishing of the molecular model for solid propellant materials. This involves treating the molecules as atomic masses interconnected by molecular potential energy, i.e., a molecular model. The molecular model can be established by means of spectrographic analysis[18] and by thermodynamic

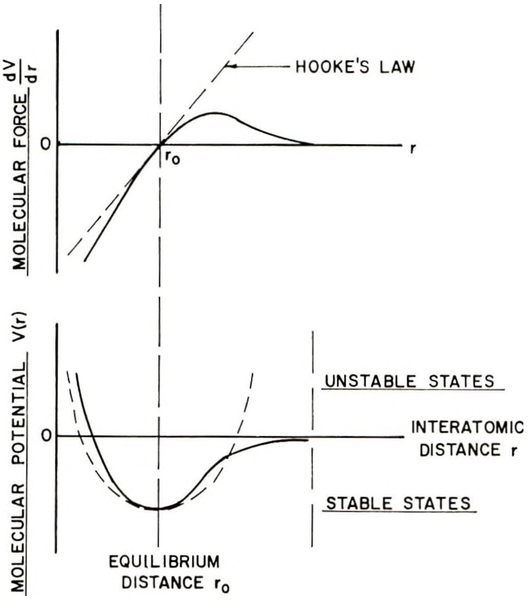

Fig. 11. Typical molecular potential as a function of interatiomic distance.

data,[19] e.g., specific heat as a function of temperature. This consists of computing the molecular model's free energy from which all thermodynamic quantities can be predicted and compared with experimental data. The simplest model for comparison with experimental data is that of an ensemble of N independent linear harmonic oscillators (point masses interconnected by elastic springs). This model[15] predicts a free energy F, given by

$$F = M\epsilon_0 + kT \sum_{j=1}^{N} \ln \left(1 - e^{-h\omega_j/kT}\right) \tag{5}$$

where ϵ_0 is the lowest allowable energy state, K is Boltzmann's content, h is Planck's constant, T is temperature, M is the number of molecules in the material body, ω_j is the frequency of vibration of the jth spring. The summation is accomplished by treating the vibrations as sound waves at low temperatures and approximating the exponential at high temperatures. This model has been used for crystal representation with fair quantitative results at extremely high or low temperatures, i.e., the Dulong and Petit law of specific heat. A somewhat better crystal representation is obtained by use of an anharmonic oscillator[20] which accounts for different properties in tension and compression. However, for intermediate temperatures, the above summation procedure cannot be used since the sum depends upon the actual distribution of frequencies in the oscillatory spectrum of the material. An interpolation formula for these intermediate temperatures (including the extreme working range of solid propellant materials) was obtained by the introduction of a "characteristic" temperature Θ by Debye.[21]

His interpolation equation has led to good experimental correlation for materials with a simple crystal lattice, e.g., NaCl. Lifshitz[22] extended the idea of a characteristic temperature of the vibration spectrum to more complex crystals by using a series of characteristic temperatures.

All these models are elastic in nature, however, and do not account for time-dependent damping. The other extreme is a fluid which does not exhibit any elastic characteristics and it is completely time-dependent. In actuality, propellant is a biphased system exhibiting both time-dependent and elastic properties, whose tensile properties are governed by interfacial bonding of the matrix and solids. Experiments have shown that properties in compression are greater in magnitude than those in tension. This is typical of materials with large "solid loadings" bound together by a cohesive matrix, e.g., concrete, silt, etc. Most solid materials would exhibit this behavior if the strains were large enough, as evidenced by the typical potential between particles (Fig. 11). While the slope is approximately linear for small deformations, with larger displacements the repulsive force increases more rapidly than the attractive force. The allowable states of the atomic system are represented by discrete levels within this "potential well." The effect of temperature is to raise the level within the well, thus increasing its probability of "escaping," i.e., it becomes unstable. The effect of time is to change the shape of the potential curve by distortion along the r axis. This accounts for the fact that the stress relaxes with time since the force of molecular resistance equals the slope of the potential curve.

The above description presents a qualitative picture of the actual atomic potential of the propellant. Its rubber matrix consists of electronically bound atoms forming long chain molecules and the solid oxidizer particles are actually atoms arranged in random crystallite form. However, in the composite, the resulting molecular formation is complicated by the influence of the oxidizer upon chemical bond formation, crosslinking and chemical bonding between oxidizer and matrix. Hence, the time-dependent atomic potential at any location within the material differs depending on its location within the matrix, the oxidizer, or at the matrix-oxidizer interface. The statistical behavior of these potentials, under a particular strain field and environment, determines whether or not rupture will occur. If the resulting molecular energy level occurs within its potential well, the molecule is bound and stable. If the molecular energy is greater than the potential energy, the molecule is unstable and in a free state, i.e., a vacuole will start to form. The rate of coalescence of these vacuoles determines the rate with which the material becomes unstable and ruptures. This thermodynamic instability can be calculated by statistical mechanics once the molecular potential is defined.

Conclusions

A preliminary investigation into the establishment of a "unified" failure theory indicated that various methods of approach must be attached to substantiate one another. To establish the important variables for continuum analysis and determine the kinetic equation by which these variables change, the molecular behavior must be investigated. Thermodynamics in the form of statistical mechanics plays the connecting role between the microscopic and macroscopic (continuum) analyses. For design purposes, the failure criterion must be defined in terms that can be readily computed from the results of continuum mechanics, hence, the criterion is in terms of stress and strain. However, the physical chemist who prescribes appropriate formulations for given environmental conditions is interested in thermodynamic quantities. The combined microscopic and macroscopic approaches fulfill both of these needs.

The thermodynamic investigation coupled with propellant experimental data illustrates that the propellant under mechanical loading goes through stages of stable and unstable equilibrium. The value of strain at neutral energetic equilibrium seems to correlate with abrupt changes in dilatation data and its normalized distribution is analogous to results from subscale motor failures. Values of input work which are smaller than that required for neutral equilibrium do not seem to precipitate to material rupture. Hence, it is concluded that the ability of a material to absorb and dissipate input energy at a certain rate is an indication of its overall ability to resist rupture.

Study of propellant failure data indicates that the normal three-dimensional failure surface of classical theories is inadequate for a propellant failure surface. Hence, a hyperspace (linear vector space) is introduced in which the loci of the state vector, representing rupture, form the n-dimensional failure surface. The time-dependent evaluation of this state vector depends upon the governing kinetic equation of allowable molecular configurations. Actual dimensions of this space are determined by the number of independent variables involved in propellant failure. These variables belong to three groups: geometrical, mechanical, and physical. Establishment of the independent variables and determination of the governing kinetic equation requires a microscopic investigation.

This microscopic study indicated that the classical models of solid materials cannot be used since there are three molecular potentials involved and these are time-dependent for perturbed energy states. Hence, the propellant can be treated as an ensemble of pseudo-particles interconnected by various time-dependent molecular potentials. The form of the potential for equilibrium behavior is established from propellant thermodynamic data. The distortion of the molecular potential for perturbed states is qualitatively found from quasi-static (relaxation and creep) response. Once the appropriate molecular potential is defined, the independent variables are obtained from molecular stability considerations.

Having obtained the fundamental variables, the various rank tensor functions can be investigated. The functions when compared to experimental data will determine whether fracture *per se* is a scalar or higher rank tensor. However, for design purposes, the problems of thermal cycling pressurization upon firing and slump may be such that all tensoral properties are unimportant except for their magnitude. This would greatly simplify any analysis and will be investigated in future studies.

APPENDIX A

Derivation of Equation of State

As outlined above, it is of interest to obtain the equation of state in terms of the total energy. Using the thermodynamic system depicted in Figure 1, the total energy balance will be investigated. A Galilean reference system neglecting relativistic effects will be used for this analysis. Thus, the kinetic energy of the total region C can be written as

$$K.E. = {}^1/_2 \int_D \rho(t) v_i v_i dV \tag{A-1}$$

where D denotes the material domain and V is the total volume. The total internal elastic energy is given by

$$I.E. = \int_D \rho(t) E_i dV \tag{A-2}$$

The total internal dissipative energy is given by

$$D.E. = \int_D \rho(t) \eta dV \tag{A-3}$$

The rate of work done by the body forces is given by

$$\dot{w} = \int_D \rho(t) F_i v_i dV \tag{A-4}$$

where F_i are the body force components per unit mass. The surface tractions do work on the region C at the rate

$$\dot{w}_s = \int_B \sigma_{ij} \eta_j v_i dA \tag{A-5}$$

where n_j is the surface normal vector, A is the area, and B denotes the material boundary. The rate at which energy is transferred across the boundary due to heat transfer is given by

$$Q = \int_B q dA \tag{A-6}$$

where q is the rate at which energy is put into the system by heat transfer per unit area. Neglecting all electromagnetic energy transfers, the rate at which the surface tractions and body forces do work on a body plus the rate of energy transfer into it by heat transfer is equal to the rate of increase of the sum of its kinetic and internal energies. Therefore,

$$\dot{w}_s + \dot{w} + Q = \frac{d}{dt}\,[K.E. + I.E. + D.E.] \tag{A-7}$$

Substituting eqs. (A-1)–(A-6) into eq. (A-7) yields

$$\int_D \rho(t)F_i v_i dV + \int_B \sigma_{ij} n_j v_i dA + \int_B q dA = \frac{d}{dt}\left[\frac{1}{2}\int_D \rho(t) v_i v_i dV + \int_D \rho(t) E_i dV + \int_D \rho(t)\eta dV\right] \tag{A-8}$$

From the divergence theory, it follows that

$$\int_B \sigma_{ij} n_j v_i dA = \int_D (\sigma_{ij} v_i)_{,j} dV \tag{A-9}$$

where the comma denotes differentiation. By moving the differential inside the integral of eq. (A-8)

$$\left\{\frac{1}{2}\int_D \frac{d}{dt}\,[\rho(t) v_i^2]dV + \int_D \frac{d}{dt}\,[\rho(t)E_i]dV + \int_D \frac{d}{dt}\,[\rho(t)\eta]dV\right\} \tag{A-10}$$

and then applying the differential of eq. (A-10), the eq. (A-11) is obtained:

$$\left\{\frac{1}{2}\int_D [\dot{\rho}(t)v_i^2 + \rho(t)2\,v_i\dot{v}_i]dV + \int_D [\dot{\rho}(t)E_i + \rho(t)\dot{E}_i]dV + \int_D [\dot{\rho}(t)\eta + \dot{\eta}\rho(t)]dV\right. \tag{A-11}$$

Introducing a heat flux vector $q = q_i n_i$ into eq. (A-6) and applying the divergence theorem yields

$$\int_B q dA = \int_D q_{i,i} dV \tag{A-12}$$

Equations (A-8), (A-11), and (A-12) become

$$\int_D [F_i\rho(t) + \sigma_{ij,j} - \rho(t)\dot{v}_i]v_i dV + \int_D \{\sigma_{ij}v_{i,j} - \rho(t)(\dot{E}_i + \dot{\eta}) + q_{i,i}\}dV - \int_D \{{}^1\!/_2\,\dot{\rho}(t)v_i^2 + \dot{\rho}(t)(E_i + \eta)\}dV = 0 \tag{A-13}$$

The equation of motion requires that the terms inside the first bracket must equal zero, therefore,

$$\int_D \{[\sigma_{ij}v_{i,j} - \rho(t)(\dot{E}_i + \dot{\eta}) + q_{i,i}] - [{}^1\!/_2\,\dot{\rho}(t)v_i^2 + \dot{\rho}(t)(E_i + \eta)]\}dV = 0 \tag{A-14}$$

Because eq. (A-14) applies to any portion of the body, the integral must be identically zero at every point in the body. Thus,

$$[\sigma_{ij}v_{i,j} - \rho(t)(\dot{E}_i + \eta) + q_{i,i}] = [\dot{\rho}(t)/2(v_i^2) + \dot{\rho}(t)(E_i + \eta)] \qquad \text{(A-15)}$$

Introducing the following definitions,

$$du_i \equiv v_i dt \qquad \text{(A-16a)}$$

$$\epsilon_{ij} \equiv {}^1/_2\,(u_{i,j} + u_{j,i}) \qquad \text{(A-16b)}$$

$$w_{ij} \equiv {}^1/_2(u_{i,j} - u_{j,i}) \qquad \text{(A-16c)}$$

where u_i is the displacement in the ith direction, differentiation of eqs. (A-16b) and (A-16c) and substitution of equation (A-16a) leads to

$$d\epsilon_{ij} = {}^1/_2(v_{i,j}dt + v_{j,i}dt) \qquad \text{(A-17)}$$

$$d\omega_{ij} = {}^1/_2(v_{i,j}dt - v_{j,i}dt)$$

Now because

$$v_{i,j} = {}^1/_2(v_{i,j} + v_{j,i}) + {}^1/_2(v_{i,j} - v_{j,i}) \qquad \text{(A-18)}$$

eq. (A-15) becomes

$$\sigma_{ij}[(d\epsilon_{ij}/dt) + (dw_{ij}/dt)] - \rho(t)(\dot{E}_i + \dot{\eta}) + q_{i,i}$$
$$= \dot{\rho}(t)/2\ (du_i/dt)^2 + \rho(t)(E_i + \eta) \qquad \text{(A-19)}$$

Since the contraction of a symmetric tensor with an antisymmetric tensor is zero,

$$\sigma_{ij}\omega_{ij} = 0 \qquad \text{(A-20)}$$

and eq. (A-19) now can be rewritten as

$$\sigma_{ij}\dot{\epsilon}_{ij} - \frac{\dot{\rho}(t)}{2}\left(\frac{du_i}{dt}\right)^2 + q_{i,i} = \frac{d}{dt}\,[\rho(t)(E_i + \eta)] \qquad \text{(A-21)}$$

The addition of $[-\ \rho(t)\dot{v}_i v_i]$ to both sides of eq. (A-21) gives

$$\sigma_{ij}\dot{\epsilon}_{ij} - \frac{\dot{\rho}(t)}{2}v_i^2 - \rho(t)\dot{v}_i v_i + q_{i,i} = \frac{d}{dt}\,[\rho(t)(E_i + \eta)] - \rho(t)\dot{v}_i v_i \qquad \text{(A-22)}$$

After introducing an expression for kinetic energy and rearranging the terms, this equation becomes

$$\sigma_{ij}\dot{\epsilon}_{ij} + \rho(t)\dot{v}_i v_i + q_{i,i} = \frac{d}{dt}\,[\rho(t)(E_i + \eta + K.E.)] \qquad \text{(A-23)}$$

From the principle of conservation of mass

$$\rho(t)V(t) = \rho_0 V_0 \qquad \text{(A-24)}$$

where ρ_0 is the initial mass density. In terms of density this is:

$$\rho(t) = \rho_0 V_0/\Pi\lambda_i(t) \qquad \text{(A-25)}$$

where λ_i is the extension ratio in the ith direction, $\lambda_i = 1 + \epsilon_i$. Since the product of the extension ratios is equal to the invariant I_3

$$\rho(t) = \rho_0 V_0/I_3 \tag{A-26}$$

which, when differentiated, becomes

$$\dot{\rho}(t) = -\rho_0 V_0[\dot{I}_3(t)/I_3^2(t)] \tag{A-27}$$

The negative sign indicates that the density decreases with time. This expression can be evaluated by using dilatation data.

APPENDIX B

Input Work Function for Linear Viscoelastic Material

Input work is defined as force times displacement. The necessary force F for an axially loaded specimen is given as

$$F = \sigma A \tag{B-1}$$

and the displacement is

$$u_x = L\epsilon \tag{B-2}$$

With these quantities, the input work becomes

$$w = (\sigma A)(L\epsilon) \tag{B-3}$$

Since AL is the volume, the work per unit volume is

$$W = W/AL = \sigma\epsilon \tag{B-4}$$

In terms of strains eq. (B-4) is

$$W = E\epsilon^2 \tag{B-5}$$

Application of the correspondence principle of linear viscoelasticity to Equation (B-5) results in

$$\bar{W} = \bar{E}\,\bar{\epsilon}^2 \tag{B-6}$$

where the bars denote Laplace transforms of corresponding quantities.

For a constant strain rate test, the strain is $\epsilon = a\,t$, where a is the strain rate. Therefore, the transform becomes

$$\bar{\epsilon} = a/p^2 \tag{B-7}$$

(p being a transform parameter) and the transform of the work is

$$\bar{W} = \bar{E}(p)(a^2/p^4) \tag{B-8}$$

The transform of the modulus $\bar{E}(_p)$ can be expressed as

$$\bar{E}(_p) = E_{c0}\left[1 + \sum_{n=1}^{N} \frac{C_n}{p + \gamma_n}\right] \tag{B-9}$$

where the C_n and γ_n are obtained from relaxation tests.[23] Therefore

$$W = (a^2/p_4)\left\{E_{c0}\left[1 + \sum_{n=1}^{N} C_n/(p + \gamma_n)\right]\right\} \tag{B-10}$$

Inverting eq. (B-10) by expanding the second term by means of partial fractions, we obtain

$$W = E_{b0}a^2\left\{(t^3/6) + \sum_{n=1}^{N} \frac{C_n}{\gamma_n{}^4}\left[(e^{-\gamma_n t} - 1) + \frac{\gamma_n t^3}{6} + \gamma_n t - (\gamma_n{}^2 t^2/2)\right]\right\} \tag{B-11}$$

Consequently, we see that the input work depends upon the square of the strain rate for a linear viscoelastic material.

References

1. Biot, M. A., *J. Appl. Phys.*, **25**, 1385 (1954).
2. Schapery, R. A., Ph.D. Dissertation, California Institute of Technology, Pasadena, 1962.
3. Staverman, A. J., and F. Schwarzl, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B55**, 474 (1952).
4. Lianis, G., Purdue University Report A and ES 64-J, January 1964.
5. Svob, G. J., Aerojet-General Corporation Tech. Memo. No. 232 SRP, August 1963.
6. Wiegand, J. H., Report 0411-10F, Aerojet-General Corporation, 1962.
7. Briar, H. P., and J. H. Wiegand, Aerojet-General Corporation SRP Memo. No. MLP-1, 1964.
8. Hohn, F. E., *Elementary Matrix Algebra*, Macmillan, New York, 1958.
9. Majerus, J. N., and Masao Tamekuni, Aerojet-General Corporation SRO Report, August 1964.
10. Dixon, J. D., AGC Report PEL-47, February 1964.
11. Dixon, J. D., AGC Report PEL-44, January, 1964.
12. Lolchin, V. V., *Soviet Phys. Doklady*, **8**, (1963).
13. Stuart, D. A., and O. L. Anderson, *J. Am. Ceramic Soc.*, **36**, 416 (1953).
14. Coleman, B. D., *J. Appl. Phys.*, **29**, 968 (1958).
15. Landau, L. D., and E. M. Lifshitz, *Statistical Physics*, Addison-Wesley, Reading, Mass., 1958.
16. Messiah, A., *Quantum Mechanics*, Vols. I, II, Wiley, New York, 1961.
17. Prigogine, I., *Non-Equilibrium Statistical Mechanics*, Vol. I, Interscience, New York, 1962.
18. Barrow, G. M., *The Structure of Molecules*, Benjamin, New York, 1964.
19. MacDonald, D. K. C., *Introductory Statistical Mechanics for Physicists*, Wiley, New York, 1963.
20. Weiss, R. J., U. S. Army Materials Research Agency TR 63-20, AD 4228682.
21. Debye, P., *Ann. Phys.*, **35**, 789 (1912).
22. Lifshitz, E. M., *Zh. Exptl. Teor. Fiz. USSR*, **22**, 471 (1952).
23. Hilton, H. H., J. N. Majerus, and M. Tamekuni, Aerojet-General Corporation, Tech. Mem. No. 226 SRP, August 1963.

Résumé

On décrit deux voies expérimentales générales et liées entre elles pour étudier de défaut de structure de matériaux polymèriqus fortement chargés, par ex., un agent de propulsion solide. Ce sont des méthodes d'analyses macrose copiques (thermodynamiques et mé-

caniques en continu) et micoscopiques (modèle moléculaire) conjointement avec les résultats expérimentaux sur les agents de propulsions solides. L'étude thermodynamique montre que l'agent de propulsion soumis à la charge passe par des étages de comportement stable et instable dépendant de la vitesse à laquelle le travail est absorbé et dissipé par les matériaux. Le point d'instabilité semble être relié avec les résultats obtenus à partir de moteurs pilotes. L'étudethermodynamique est alors étendue au moyen d'une analyse fonctionelle du défaut, traité du point de vue de la mécanique en continu. Puisque la cassure est en soi observable physiquement, elle est représentée par un "vesteur d'état" dans un espace à n-dimensions. Le nombre de dimensions de cet espace dépend des variables fondamentales comprises dans la cassure. Puisque les critères corrects de la cassure doivent être tensoriellement compatibles avec l'ordre dutenseur de la cassure, des séries distinctes de fonctions peuvent être appliquées aux résultats expérimentaux. Les résultats sont comparés aux fonctions scalaires classiques de la cassure. Elles sont obtenues à partir du fluage uniaxial et biaxial et des tests de relaxation, les tests de tension uniaxiale et biaxiale étant effectués à vitesses constantes de charge et de tension, avec et sans pression hydrostatique supplémentaire, et à partir d'essais de cissaillement pur. La relation entre les différentes types de défauts provoqués est démontrée par la méthode microscopique au moyen de modèles moléculaires et par l'application de la mécanique statique.

Zusammenfassung

Zwei zueinander in Beziehung stehende allgemeine Verfahren zur Untersuchung des strukturellen Bruches hochgradig gefüllter polymerer Stoffe, z.B. eines festen Treibstoffes werden beschrieben. Sie bestehen aus der makroskopischen (Thermodynamik und Kontinuumsmechanik) und der mikroskopischen (Molekülmodell) Analysenmethode im Verein mit Versuchsdaten über feste Treibstoffe. Die thermodynamische Untersuchung zeigt, dass das Treibstoffmaterial beim Beladen durch stabile und instabile Verhaltensbereiche geht, welche von der Geschwindigkeit abhängen, mit welcher vom Material Arbeit absorbiert und dissipiert wird. Der Instabilitätspunkt scheint in Korrelation zu Ergebnissen an Modellmotoren zu stehen. Die thermodynamische Untersuchung wird dann durch fuktionalanlytische Behandlung des Bruches vom Gesichtspunkt der Kontinuumsmechanik ausgedehnt. Da der Bruch, per se, eine physikalische Beobachtungsgrösse ist, wird er durch einen "Zustandsvektor" im n-dimensionalen Raum wiedergegeben. Die Dimensionszahl dieses Raums hängt von den am Bruch beteiligten unabhängigen Variablen ab. Da das korrekte Bruchkriterium tensoriell mit der tensoriellen Ordnung des Bruches konsistent sein muss, können verschiedene Funktionssysteme auf die Versuchsergebnisse angewendet werden. Die Daten werden mit den klassischen skalaren Bruchfunktionen verglichen. Sie wurden aus uniaxialen und biaxialen Kreichund Relaxationstests bis zum Bruch, uniaxialen und biaxialen bei konstanter Belastungs- und Verformungsgeschwindigket, mit und ohne überlagerten hydrostatischem Druck ausgeführten Spannungstests und reinen Scherungstests bis zum Bruch erhalten. Die Korrelation zwischen den verschiedenen Typen von induziertem Bruch wird durch das mikroskopische Verfahren, durch Verwendung von Molekülmodellen und durch die Anwendung der statistischen Mechanik gezeigt.

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Vinyl Polymerization. XCI. Polymerization of Styrene Initiated by Nickel Peroxide

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Synopsis

A study of the radical polymerization of styrene initiated by nickel peroxide (Ni-PO) as a solid initiator has been made. The rate of polymerization (R_p) was found to be expressed by the equation: $R_p = k[\text{Ni-PO}]^{1/2}[\text{Styrene}]^{3/2}$. This equation could be understood by considering that the radical polymerization by Ni-PO is initiated through the interaction between the monomer and the Ni-PO initiator and terminated by the ordinary bimolecular termination mechanism. By extracting the resulting polystyrene with methyl ethyl ketone (MEK), the MEK-insoluble polymer, which was confirmed by infrared spectra and x-ray diffraction analyses to be isotactic polystyrene, was isolated. The amount of the isotactic polymer increased as the polymerization temperature decreased. The results obtained in the present study indicate that the stereospecific absorption (π-complex formation) of the monomer on the solid Ni-PO initiator might be important for producing an isotactic polystyrene.

INTRODUCTION

It is known that some vinyl monomers, such as vinyl chloride,[1] methyl methacrylate,[2] vinyl formate,[3] and vinyl trifluoroacetate[3] polymerize through radical mechanism at low temperatures to give syndiotactic polymers. However, no successful results on the stereospecific radical polymerization of various kinds of vinyl monomers at rather high temperatures have been reported.

In 1960, Burleigh and co-workers[4,5] found that in the polymerization of vinyl chloride initiated by α,α'-azobisisobutyronitrile (AIBN) at 50°C., a stereoregular polymer is obtained by the presence of aldehydes, especially n-butyraldehyde. In 1961, we obtained the same results by using a number of organic compounds which have π-electrons.[6,7] However, the poly(vinyl chlorides) obtained by both research groups were of quite low molecular weight.

In the stereospecific polymerization of α-olefins by Ziegler-Natta catalyst, it has been suggested that the formation of a complex of the reacting monomer with the catalyst on the solid surface in the transition state of propagation process is significant for producing a stereoregular polymer. Contrary to the coordinated ionic polymerization, in the ordinary radical polymerization it is not possible to consider the interaction between growing polymer end and the initiator in the propagation process. If a radical initiator is solid and has the ability to form a complex with the monomer, such an initiator may lead to stereospecific polymerization.

Recently, Nakagawa and co-workers[8,9] have reported that nickel peroxide shows selectivity for the oxidation of some organic compounds as the result of the complex formation. On the basis of the above-mentioned consideration, it has been found that some solid metal peroxides, of which nickel peroxide is the best initiator, can serve as a radical initiator of stereospecific polymerization of styrene.[10] The present paper deals with the radical polymerization of styrene initiated by solid nickel peroxide.

EXPERIMENTAL

Nickel Peroxide (Ni-PO) and Other Reagents

Ni-PO was prepared by oxidation of nickel sulfate with sodium hypochlorite in water, followed by drying in a stream of nitrogen at room temperature. The detailed procedure has been described in previous papers.[8,9,11] Nickel oxide was a commercial sample used without further purification. Styrene and other reagents were purified by the usual methods.

Determination of Physical and Chemical Properties of Ni-PO

The active oxygen content in Ni-PO was determined as follows.[6,8] A given amount of Ni-PO (about 0.2 g.) was introduced into a titration flask containing 20 ml. of 36% aqueous acetic acid solution and 2 g. of potassium iodide. The flask was stoppered and then allowed to stand to dissolve the Ni-PO. Then, the liberated iodine was titrated with 0.1*N* sodium thiosulfate solution with the use of starch indicator. The active oxygen content (in gram-atoms per gram of Ni-PO) was used as the initiator concentration available for polymerization.

The specific surface area of the Ni-PO was determined from the adsorption isotherm of nitrogen according to the B.E.T. method.[12] The crystallinity of the Ni-PO was investigated by means of x-ray diffraction, electron microscopy, and electron diffraction.

The chemical composition of the Ni-PO was deduced by the determinations of nickel, chlorine (alkali fusion method), sodium hydroxide, water, and oxygen (differential thermal analysis) contents. The nickel content was determined by the dimethyl glyoxime method following the correction of the impurity, mainly silicon oxide, determined by the Treadwell-Hall method.[13] Sodium hydroxide adhering to the Ni-PO was determined by titrating the filtrate, which was extracted by boiling water, with acid.

Determination of Decomposition Rate of Ni-PO

The rate of decomposition of Ni-PO in styrene was determined as follows. In a hard glass tube were placed 1 g. of Ni-PO and 5 ml. of styrene, and the tube was sealed off under nitrogen atmosphere. The tube was then shaken in a thermostat maintained at constant temperatures from 0 to 80°C. After reaction for a given time, the tube was removed from the thermostat and its contents poured into a mixture of 15 ml. of diethyl ether, 2 ml. of water, and trace of hydroquinone to recover the Ni-PO. After the Ni-PO was filtered and washed with diethyl ether, its active oxygen content was determined iodometrically. The rate of decomposition was calculated from the amount of consumed active oxygen in the recovered Ni-PO.

Polymerization Procedure

Polymerizations and copolymerizations were carried out in a sealed glass tube under shaking in a thermostat maintained at given temperatures. After polymerization for a given time, the polymerization mixture was poured into a large amount of methanol containing hydrochloric acid to precipitate the polymer and to decompose the Ni-PO initiator. The polymer which still contained the Ni-PO was purified several times by further decomposing the Ni-PO with a methanol–hydrochloric acid mixture. The resulting polymer was then purified by reprecipitation from benzene with methanol.

In the case of kinetic study, the rate of polymerization was determined from the amount of unreacted styrene monomer (bromination method) in the polymerization mixture.

Analysis of the Polymers

The chemical composition of the resulting polymers and of copolymers with vinyl acetate was determined from the results of their elementary analyses. All of the resulting polymers contained no inorganic impurities arising from the Ni-PO and its decomposition products.

The stereoregular polystyrene was separated by extracting the resulting polymer with methyl ethyl ketone (MEK). The MEK-insoluble polymer thus obtained was reprecipitated from boiling toluene with methanol. Crystallization of the polymer was performed by refluxing it overnight in *n*-heptane.

The tacticity of the MEK-insoluble polystyrenes was checked by their infrared spectra (film) and x-ray powder diffraction patterns using nickel-filtered CuKα radiation. It was also confirmed by their melting points T_m, glass transition temperatures T_g, and densities which were determined by the hot-plate method, dilatometric method and the gradient method, respectively.

The intrinsic viscosity of the polymers was determined by viscosity measurement on their dilute toluene solutions at 25°C. in an Ubbelohde viscometer. Number-average molecular weight $\bar{M}_n$ was calculated from intrinsic viscosity $[\eta]$ by applying the following equations.

For ordinary polystyrene:[14]

$$[\eta] = 1.7 \times 10^{-4}\bar{M}_n^{0.69}$$

For isotactic polystyrene:[15]

$$[\eta] = 1.1 \times 10^{-4}\bar{M}_n^{0.725}$$

RESULTS

Physical and Chemical Properties of Ni-PO

The chemical composition of the Ni-PO and its physical and chemical properties are shown in Table I, in which the results on nickel oxide are also indicated. Figure 1 shows the x-ray diffraction patterns of Ni-PO and nickel oxide (Ni_2O_3). The electron microscopic and electron diffraction diagrams of Ni-PO are also shown in Figure 2.

As can be seen from Table I and Figures 1 and 2, it is clear that active Ni-PO (Nos. 1 and 2) is an amorphous and nonstoichiometric compound containing more than about 3×10^{-3} g.-atom of active oxygen per gram of Ni-PO. The commercial nickel oxide is known to be a stoichiometric and highly cubic crystalline compound as is also shown by Figure 1. The Ni-PO sample heated at 180°C. (No. 3 in Table I) is seen to have almost the same properties and chemical composition as nickel oxide, except for the content of active oxygen.

Figure 3 shows the results of differential thermal analysis of active Ni-PO. Two pronounced endothermic peaks were observed at about 150 and 250°C.; these peaks were found by chemical analyses to arise from water and oxygen, respectively. The Ni-PO is not soluble in most organic

TABLE I

Chemical Compositions and Properties of Ni-PO and Nickel Oxide (Ni_2O_3)

	Ni-PO-1	Ni-PO-2	Ni-PO-3[a]	Ni_2O_3
Specific surface area, m.^{2}/g.	40	50	188	204
Crystallinity	Amorph.	Amorph.	Cryst.	Cryst.
Active oxygen, g.-atom/g. of Ni-PO × 10^3	3.21	3.90	1.50	0
Ni, %	55.8	55.9	70.6	70.8
H_2O content, %	23.9	23.9	4.6	0
Cl impurity, %	0.15	Trace	0.20	0
NaOH impurity, %	0.14	Trace	0.77	0
Catalytic activity for telomerization (as telomer yield), %[b]	91.3	90.7	23.8	0
Presumed empirical formula	$Ni_4H_6O_{11}$	$Ni_4H_6O_{11}$	$Ni_3H_3O_{7.5}$	(Ni_2O_3)

[a] This sample was obtained by heating Ni-PO-1 at 180°C. for 2 hr.

[b] Expressed by the yield of 1:1 adduct on the telomerization of octene-1 (1 mole) with $CBrCl_3$ (0.4 mole) at 70°C. for 4 hr.

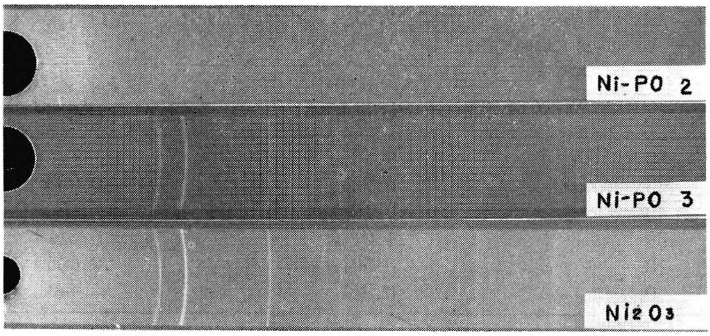

Fig. 1. X-ray diffraction patterns of Ni-PO and Ni_2O_3.

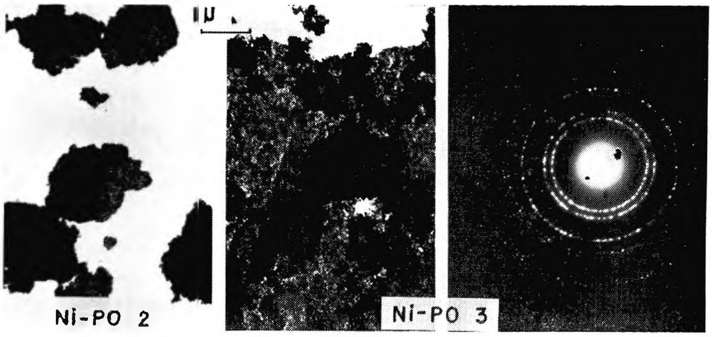

Fig. 2. Electron microscopic and electron diffraction diagrams of Ni-PO.

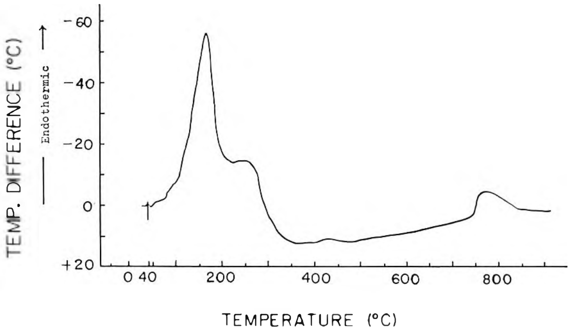

Fig. 3. Differential thermal analysis of Ni-PO-2.

solvents and does not lose its active oxygen on standing in the solid state at room temperature for about a month. It is obvious from Table I that the content of active oxygen atom in Ni-PO is a measure of catalytic activity for telomerization or polymerization, as described in a later section.

Decomposition of Ni-PO

The rate of decomposition of Ni-PO in styrene was measured iodometrically at the temperatures between 80 and 0°C. The result indicated

TABLE II
Decomposition Rate Constants for Ni-PO in Styrene

Temperature, °C.	$k_d \times 10^6$, sec.$^{-1}$	$k_d f \times 10^6$, sec.$^{-1}$[a]
80	9.12	—
60	5.22	0.033
40	2.10	—
30	1.21	0.0118
10	0.501	0.0049
0	0.311	—

[a] These values were calculated from eq. (2).

TABLE III
Results of the Polymerization of Styrene Initiated by Ni-PO

[M], mole/l.	[Ni-PO], g.-atom/l.	[Benzene], mole/l.	Temp., °C.	$R_p \times 10^5$, mole/l.-sec.	$\bar{P}_n$
8.72	0.930	0	60	4.50	1130
8.72	0.320	0	60	2.73	2110
8.72	0.161	0	60	2.00	2890
8.72	0.080	0	60	1.34	4170
8.72	0.023	0	60	0.793	6520
8.72	0.928	0	30	1.04	—
8.72	0.316	0	30	0.693	—
8.72	0.161	0	30	0.495	—
8.72	0.080	0	30	0.364	—
8.72	0.040	0	30	0.252	—
8.72	0.936	0	10	0.320	—
8.72	0.535	0	10	0.238	—
8.72	0.197	0	10	0.141	—
7.64	0.927	1.34	60	3.19	1120
6.53	0.929	2.78	60	3.09	1120
5.79	0.927	3.75	60	2.63	1100
4.56	0.935	5.33	60	2.07	1100
3.87	0.935	6.24	60	1.56	1090
3.10	0.935	7.23	60	1.14	1070
2.05	0.924	8.59	60	0.716	1070

that the rate followed first-order kinetics. The first-order rate constants k_d are shown in Table II.

From a plot of log k_d against $1/T$ based on the results of Table II, a straight line was obtained as shown in Figure 4, from which the following relationship was drawn:

$$k_d(\text{sec.}^{-1}) = 9.49 \exp\{-9.53 \text{ kcal.}/RT\} \quad (1)$$

It is noted that the activation energy and the frequency factor for decomposition of Ni-PO are quite small values, compared with those for benzoyl peroxide[16] (29.6 kcal./mole and 3.0×10^{13}) and for di-*tert*-butyl peroxide[17] (34.5 kcal./mole and 4.31×10^{14}).

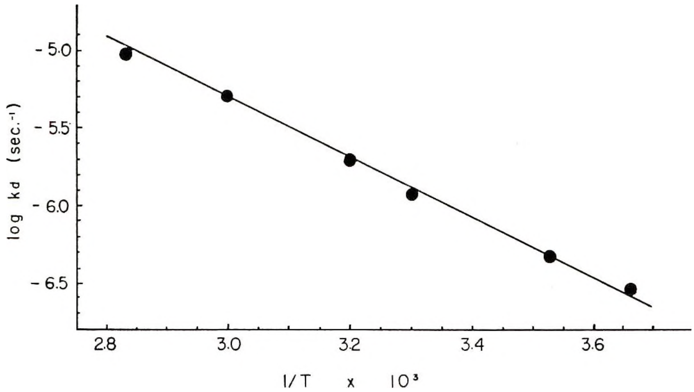

Fig. 4. Arrhenius plot for decomposition of Ni–PO.

Kinetics of the Polymerization by Ni-PO

The kinetic results of the polymerization of styrene initiated by Ni-PO in bulk or in benzene at 60, 30, and 10°C. are summarized in Table III.

From the results of Table III, the linear relationship between the rate of polymerization R_p and the square root concentration of Ni-PO initiator is shown in Figure 5, The results indicate that the polymerization by Ni-PO proceeds through a radical intermediate and terminates by bimolecular interaction of the growing radicals just as in ordinary radical polymerization.

As also shown in Figure 6, a linear relationship between R_p and the $^3/_2$ power of the concentration of monomer [M] was observed and the following rate equation was obtained:

$$R_p = k\,[\mathrm{M}]^{3/2}[\mathrm{Ni\text{-}PO}]^{1/2} \tag{2}$$

The result of the dependence of the monomer concentration in eq. (2) might be understood by supposing that the initiation occurred through

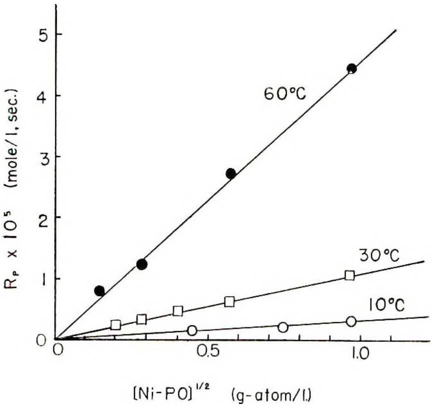

Fig. 5. Relationship between R_p and $[\mathrm{Ni\text{-}PO}]^{1/2}$ on bulk polymerization of styrene.

formation of a complex between the solid Ni-PO initiator and the monomer, as suggested by Mark,[18] Schulz,[19] and Tobolsky and Mattack[20] for homogeneous polymerization.

In eq. (2), $k = k_p(k_df/k_t)^{1/2}$, in which k_d,k_p and k_t are the rate constants for decomposition, propagation and termination, and f is the efficiency of the initiator. Although the Ni-PO-initiated polymerization proceeds heterogeneously, the values of k_df are calculated as indicated in Table II, assuming that the values of $k_p/k_t^{1/2}$ for homogeneous system of styrene reported by Tobolsky and Baysal[21] can apply. From the values of observed k_d and the k_df which may be not based on an accurate treatment, the apparent efficiency of the Ni-PO initiator was found to be a small value (6.32×10^{-3}) at 60°C.

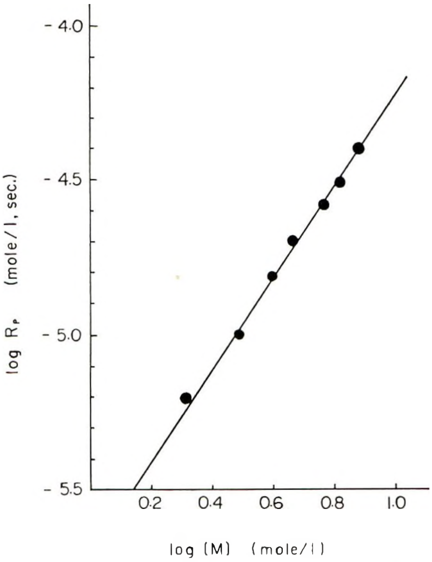

Fig. 6. Relationship between log R_p and [M] on polymerization of styrene in benzene at 60°C.

In order to determine the chain transfer reactivity to the Ni-PO, relationship between $1/\bar{P}_n - AR_p$ and [Ni-PO]/[M] according to the following eq. (3) was plotted:

$$(1/\bar{P}_n) - AR_p = C_m + C_i[\text{Ni-PO}]/[\text{M}] \tag{3}$$

Here $C_m(= k_{trm}/k_p)$ is chain transfer constant to monomer, $C_i(= k_{tri}/k_p)$ is chain transfer constant to Ni-PO, and $A = k_t/k_p^2[\text{M}]^2$ is a constant. From a slope of the resulting straight line shown in Figure 7, C_i was calculated as 2.65×10^{-3}. From the results in benzene, the same C_i value was observed as also plotted in Figure 7. The C_i value for Ni-PO is a rather small value as compared with the reported value for benzoyl peroxide[22] ($C_i = 4.8$–5.5×10^{-2} at 60°C.).

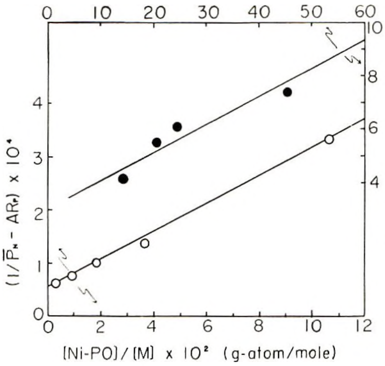

Fig. 7. Relationship between $1/\bar{P}_n - AR_p$ and [Ni-PO]/[M] on polymerization of styrene at 60°C.: (○) in bulk; or (●) in benzene. C_s indicates the chain transfer constant to benzene (S).

Endgroup Analysis of the Polymer

In order to deduce the initiating radical by Ni-PO, the endgroup in the low molecular weight polystyrene was determined. The low molecular weight polystyrene was prepared through the polymerization of styrene by a large amount of Ni-PO at 60°C. and a fraction boiling at 110°C./1 mm Hg collected. The analytical results of molecular weight of this fraction were in agreement with those calculated for the hydroxystyrene dimer.

ANAL. Calcd. for $(C_8H_8OH)_2$: C, 79.34%; H, 7.44%; Mol. Wt. 242. Found: C, 78.90%; H, 8.02%; Mol. Wt. 234.

The infrared spectrum of this fraction showed an intense hydroxyl band at 3320–3280 cm.$^{-1}$. When this material was reacted with 3,5-dinitrobenzoyl chloride, its crystalline derivative was isolated. After cystallization three times, the nitrogen content of the pure derivative (m.p. 106–110°C.) agreed with the calculated value.

ANAL. Calcd. for $C_{30}H_{22}O_{12}N_4$: N, 8.88%. Found: N, 8.69%.

The infrared spectrum of this derivative was also found to show no hydroxyl band. Accordingly, if this result can be applied to the ordinary high polymerization, it is concluded that Ni-PO can initiate through the hydroxyl radical and terminate bimolecularly.

Formation of Isotactic Polystyrene

In order to check whether stereospecific polymerization by Ni-PO takes place, the polymerization of styrene was carried out in bulk or in *n*-hexane at various temperatures. The results are shown in Table IV.

As understood from Table IV, it was observed that the amount of MEK-insoluble polymer increased as the polymerization temperature decreased. Table V shows the melting point T_m, glass transition temperature T_g and density of the MEK-insoluble polystyrene thus obtained. The observed

TABLE IV
Results of the Extraction of the Polystyrene with MEK

Polymerization	Temperature, °C.	Time, hr.	Yield, %	Soluble fraction %	Soluble fraction $\bar{P}_n$	Insoluble fraction %	Insoluble fraction $\bar{P}_n$
In *n*-hexane ([M] = 3.4 mole/l.)[a]	80	8	25.8	~100	—	~0	—
	60	10	17.2	~100	—	~0	—
	30	20	7.4	98.7	210	1.3	—
	10	100	12.5	82.4	830	14.4	1200
	0	240	8.5	69.5	530	29.3	5300
	−10	240	3.1	38.7	—	61.0	7400
In bulk ([M] = 8.7 mole/l.)[b]	60	31	20.0	97.9	—	2.1	—
	35	90	15.4	98.1	—	1.9	—
	0	175	3.3	89.5	—	10.5	—

[a] Polymerized by Ni-PO (0.34 g.-atom/l.)
[b] Polymerized by Ni-PO (0.4 g.-atom/l.)

TABLE V
Some Properties of the MEK-Insoluble Polystyrene (PSt) Obtained with Ni-PO

Polymer sample	Polymerization temperature, °C.	Melting point T_m, °C.	Glass transition temperature T_g, °C.	Density at 30°C., g./cc.
PSt by Ni-PO	10	218–221	82	—
	0	229	85	1.08
	−10	229	85	1.08
Isotactic PSt[a]	—	230	85	1.085

[a] From data of Natta.[23]

values were in good agreement with those reported by Natta[23] for isotactic polystyrene.

The x-ray powder diffraction patterns of the MEK-soluble and insoluble polymers are shown in Figure 8. The Bragg *d* spacings estimated for the MEK-insoluble polymer are 5.63 (m), 4.85 (s), 4.17 (s), and 3.48 (w) A., which also agreed with the values calculated from the data of Natta.[23] Figure 9 shows infrared spectra of the unoriented film of these polymers. As seen from this figure, crystalline absorption bands at 1301, 1054, and 734 cm.$^{-1}$ were found for the MEK-insoluble polymer. Accordingly, it was concluded that the MEK-insoluble polystyrene consisted of an isotactic polymer chain.

Polymerization in the Presence of Nickel Oxide (Ni_2O_3)

In order to check whether the π-complex formation of the Ni-PO with the monomer is the key point in stereoregularity of the resulting polymer, the polymerization of styrene initiated by AIBN was carried out in the

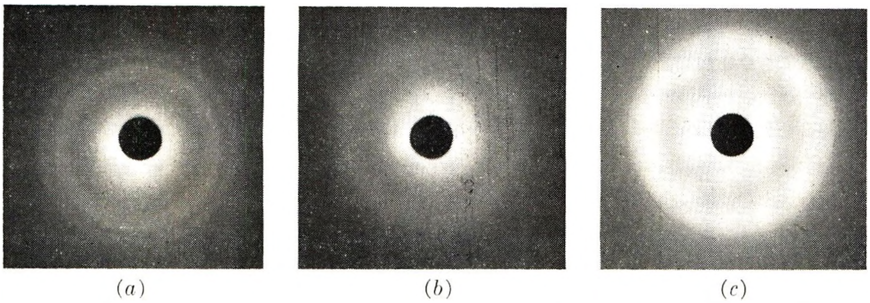
(a) (b) (c)

Fig. 8. X-ray diffraction patterns of polystyrenes obtained by Ni-PO: (*a*) MEK-insoluble polystyrene obtained at 10°C.; (*b*) MEK-soluble polystyrene obtained at 80°C.; (*c*) MEK-soluble polystyrene obtained at 10°C.

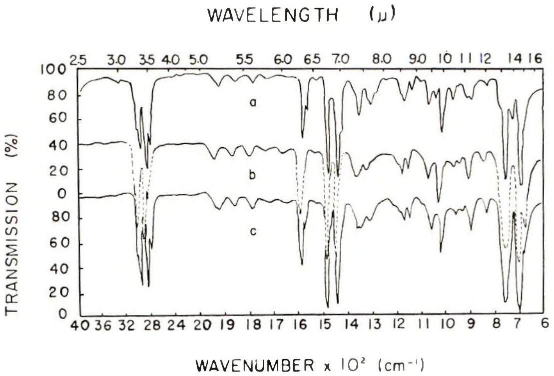

Fig. 9. Infrared spectra of polystyrene obtained by Ni-PO: (*a*), (*b*), and (*c*) are the same as those indicated in Fig. 8.

presence of nickel oxide at 60 and 0°C. The results are shown in Table VI, in which the results by Ni-PO are also indicated for comparison.

TABLE VI

Results of Polymerization of Styrene in the Presence of Ni-PO or Ni_2O_3[a]

Styrene, ml.	Ni-PO, g.	Ni_2O_3, g.	Temp., °C.	Time, hr.	Yield, %	MEK-insoluble portion, %
10	1.0[b]	0	60	31	20.0	2.1
10	0	2.0	60	7	10.7	0
10	0	4.0	60	7	9.6	0
10	0	6.0	60	7	7.9	0
10	1.0[b]	0	0	175	3.3	10.5
10	0	2.0[c]	0	4	0.85	1.0
10	0	4.0[c]	0	4	0.81	2.5
10	0	6.0[c]	0	4	0.72	4.2

[a] [Ni-PO] = 4.0×10^{-3} g.-atom/g.; [AIBN] = 4.36×10^{-3} mole/l.

[b] Polymerized in the absence of AIBN.

[c] Polymerized with ultraviolet irradiation.

As can be seen from Table VI, the polymerization of styrene in the presence of solid nickel oxide at 0°C. was found to give an MEK-insoluble polymer which was confirmed by its infrared spectrum to be isotactic polystyrene. The yield of the MEK-insoluble polymer was less than that obtained by using Ni-PO. However, it was clear that the yield increased with increasing concentration of the solid nickel oxide.

Copolymerization of Styrene with Vinyl Acetate by Ni-PO

If two monomers are presented, the concentration of the monomer having the greater complex-forming ability with Ni-PO may be expected to increase in the neighborhood of the Ni-PO initiator. In order to test this point, copolymerizations of styrene and vinyl acetate initiated by Ni-PO and AIBN was carried out at 60 and 0°C The resulting monomer–copolymer composition curves are shown in Figure 10, in which monomer reactivity ratios for both monomers calculated by the Fineman-Ross method[24] are indicated.

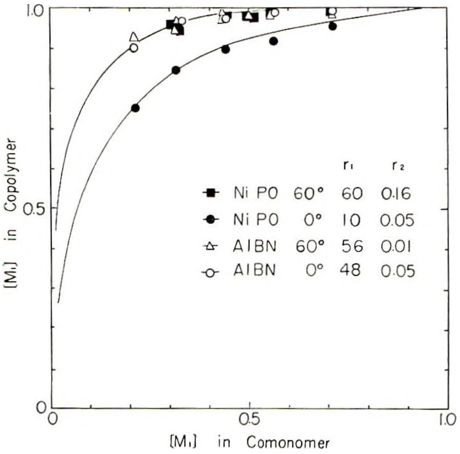

Fig. 10. Monomer–copolymer composition curves for copolymerization of styrene (M_1) with vinyl acetate (M_2) initiated by Ni-PO or AIBN.

As can be seen from this figure, at 60°C. almost similar curves are found for the copolymerization by both initiators. At 0°C., however, curves for the two initiators were little different. Such a difference might be explained by an increased concentration of vinyl acetate monomer in the neighborhood of the solid Ni-PO initiator at 0°C.

DISCUSSION

The results shown in Table I, indicate that active Ni-PO is an amorphous and nonstoichiometric compound consisting of nickel, oxygen, and hydrogen. It could also be converted to a stoichiometric nickel oxide on heating. The results on the polymerization and copolymerization indicated that the Ni-PO could serve as a radical initiator. However, unlike soluble radical initiators such as AIBN, the solid Ni-PO initiator might be characterized by an increase of the radical concentration in the neighborhood of its solid phase.

The $^3/_2$ power dependence of the monomer concentration on R_p as shown in eq. (2) might be related to the small values in activation energy of the decomposition of Ni-PO as compared with those of benzoyl peroxide, and these facts might be interpreted as indicating that the initiation occurred through formation of a complex between the reacting monomer and the Ni-PO initiator, as is the case in homogeneous radical polymerizations.[18–20]

Since Ni-PO is a nonstoichiometric compound and eliminates water and oxygen on heating at 180°C., Ni-PO is expected to contain various kinds of functional groups which are available to liberate the iodine from potassium iodide. Accordingly, from the small values of apparent initiator efficiency it may be assumed that only specified functional groups in the Ni-PO which can produce a hydroxyl radical are available to chain initiation.

If chain propagation were to proceed through the reaction of the sterically ordered monomers by complexing with Ni-PO, it may to be a possible route for producing a stereoregular polymer. As shown in Tables IV and V, the polystyrenes obtained by Ni-PO at rather low temperatures were found to contain MEK-insoluble polymer, which was confirmed by infrared spectra, x-ray diffraction, and other physical property analyses to be an isotactic polystyrene.

In the stereospecific polymerization by Ziegler-Natta catalyst, it is clear that the counterion interaction between the growing polymer end and the transition metal on the solid catalyst is significant for producing a stereoregularity of the resulting polymer chain. Since the polymerization by Ni-PO is induced by a radical mechanism, such a counterion interaction might be impossible in this case.

The fact that the yield of the MEK-insoluble polymer decreased with increasing polymerization temperature indicated that the stereospecific adsorption (π-complex formation) of the monomer on the solid Ni-PO initiator may be important for producing a stereoregular polymer. At rather high temperatures, the monomers adsorbed stereoregularly on the Ni-PO might be easily exchanged with the other free monomers. This would lead to conversion from isotactic propagation to atactic propagation. At the present time, however, it is impossible to explain the exact manner of such stereospecific adsorption.

As can be seen from Table VI, the fact that a small amount of the MEK-insoluble polymer was produced through the polymerization by AIBN in the presence of nickel oxide at 0°C. indicated that nickel oxide could also serve as the stereospecific adsorption bed for producing an isotactic polymer. In this case, however, the yield of isotactic polymer is quite low as compared with the case of Ni-PO. Accordingly, these results suggest that chain initiation must occur through the interaction with the monomer on the amorphous solid phase of Ni-PO.

The importance of the adsorption of the monomer on the solid Ni-PO was also shown by the copolymerization of styrene with vinyl acetate: The vinyl acetate content in the copolymer obtained with Ni-PO at 0°C. was much greater than that with AIBN under similar conditions (Fig. 10). The interpretation of this result is that an increased concentration of vinyl acetate monomer in the neighborhood of the solid Ni-PO initiator occurs if the Ni-PO can form a π-complex with vinyl acetate more easily than with styrene.

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References

1. Fordham, J. W. L., P. H. Burleigh, and C. L. Sturn, *J. Polymer Sci.*, **41**, 73 (1959).
2. Fordham, J. W. L., and G. H. McCain, *J. Polymer Sci.*, **39**, 355 (1959).
3. Rosen, I., G. H. McCain, A. L. Endrey, and C. L. Sturn, *J. Polymer Sci.*, **A1**, 951 (1963).
4. Burleigh, P. H., *J. Am. Chem. Soc.*, **82**, 749 (1960).
5. Rosen, I., P. H. Burleigh, and J. F. Gillespie, *J. Polymer Sci.*, **54**, 31 (1961).
6. Imoto, M., K. Takemoto, and Y. Nakai, *Makromol. Chem.*, **48**, 80 (1961).
7. Sumi, M., and M. Imoto, *Makromol. Chem.*, **50**, 161 (1961).
8. Nakagawa, K., R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).
9. Nakagawa, K., and T. Tsuji, *Chem. Pharm. Bull. (Japan)*, **11**, 296 (1963).
10. Imoto, M., T. Otsu, T. Nakata, and Y. Kinoshita, *J. Polymer Sci.*, **B2**, 227 (1964).
11. Nakata, T., *Kogyo Kagaku Zasshi*, **65**, 1044 (1962).
12. Brunauer, S., P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
13. Treadwell, F. P., and W. F. Hall, *Analytical Chemistry*, Wiley, New York, 1935, Vol. II, p. 193.
14. Outer, P., C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
15. Danusso, F., and G. Moraglio, *J. Polymer Sci.*, **9**, 171 (1952).
16. Brown, C. E. H., and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).
17. Offenbach, J. A., and A. V. Tobolsky, *J. Am. Chem. Soc.*, **79**, 278 (1957).
18. Mark, H., and D. Josefowitz, *Polymer Bull.*, **1**, 140 (1945).
19. Schulz, G. V., A. Dinglinger, and E. Husemann, *Z. Physik. Chem.*, **B39**, 246 (1938).
20. Tobolsky, A. V., and L. R. Matlack, *J. Polymer Sci.*, **55**, 49 (1961).
21. Tobolsky, A. V., and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).
22. Baysal, B., and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).
23. Natta, G., *Angew. Chem.*, **68**, 393 (1956).
24. Fineman, M., and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).

Résumé

On étudie la polymérisation radicalaire du styrène, initiée par un initiateur solide, le peroxyde de nickel (Ni-PO). La vitesse de polymérisation, R_p, peut être exprimée par l'équation: $R_p = k[\text{Ni-PO}]^{1/2} [\text{styrène}]^{3/2}$. L'on peut comprendre cette relation si l'on considère que la polymérisation radicalaire est initiée par une réaction interne entre le monomère et l'initiateur, Ni-PO, et se termine par un mécanisme ordinaire de terminaison bimoléculaire. Si l'on extrait le polystyrène par la méthyl-éthylacétone (MEK), on isole un polymère insoluble dans le MEK que les analyses par spectrométrie infrar-rouge et par diffraction aux rayons-X ont confirmé être un polystyrène isotactique. Lorsqu'on diminue la température, il se forme une quantité plus grande de polymère isotactique. Les présents résultats indiquent que l'absorption stéréospécifique (formation de complexe π) du monomère sur l'initiateur solide Ni-PO, peut être importante pour la production de polystyrène isotactique.

Zusammenfassung

Eine Untersuchung der radikalischen, durch Nickelperoxyd (Ni-PO) als festen Initiator gestarten Styrolpolymerisation wurde durchgeführt. Die Polymerisationsgeschwindigkeit (R_p) lässt sich durch die Gleichung $R_p = k[\text{Ni-PO}]^{1/2}\ [\text{Styrol}]^{3/2}$ darstellen. Diese Gleichung wird verständlich, wenn man annimmt, dass die radikalische Polymerisation durch Ni-PO durch Wechselwirkung zwischem dem Monomeren und Ni-PO gestartet und durch den gewöhnlichen bimolekularen Abbruchsmechanismus beendet wird. Durch Extraktion des erhaltenen Polystyrols mit Methyläthylketon (MÄK) wurde MÄK-unlösliches Polymeres isoliert, das sich durch Infrarotspektrum und Röntgenbeugungsanalyse als isotaktisches Polystyrol erwies. Die Menge des isotaktischen Polymeren nahm mit fallender Polymerisationstemperatur zu. Die Ergebnisse der vorliegenden Arbeit zeigen, dass eine stereospezifische Adsorption (π-Komplexbildung) des Monomeren am festen Ni-PO-Starter für die Entstehung eines isotaktischen Polystyrols von Bedeutung sein kann.

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Preparation and Properties of Crystalline, Low Molecular Weight Poly(vinyl Chloride)

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Synopsis

The preparation of low molecular weight (DP $<$ 52) poly(vinyl chloride) by free radical solution polymerization in chain transfer agents, e.g., butyraldehyde, chloroform, tetrahydronaphthalene, and tetrahydrofuran, is described. It is found that such polymers are crystalline and that the degree of crystallinity increases with decreasing molecular weight.

Introduction

It has recently been claimed that certain aldehydes exert a stereoregulating effect on the free radical polymerization of vinyl chloride.[1,2] Thus, poly(vinyl chloride) (PVC) prepared by free radical-initiated solution polymerization in *n*-butyraldehyde is a highly crystalline material, with an x-ray diffraction pattern and infrared bands suggesting that such PVC is at least partially syndiotactic.[3] All such crystalline PVC samples described are, however, of low molecular weight ($\overline{DP} < 60$).

This "aldehyde effect" has been further discussed in a series of papers by Minsker and co-workers. Of 31 different solvents screened for this effect only acetaldehyde and butyraldehyde gave rise to highly crystalline poly(vinyl chloride).[4] The effect was attributed to the formation of six-membered ring intermediate complexes between the aldehyde and the monomer,[4] and this theory has been further elaborated in recent papers.[5-7]

Imoto has also screened solvents for this aldehyde effect, and he found that vinyl chloride when polymerized in alkyl phosphites gave crystalline, low molecular weight poly(vinyl chloride).[8] He also observed that similar crystalline PVC could be prepared by polymerizing vinyl chloride in tetrahydrofuran containing acetaldehyde.[9] Patents have also been published, claiming that the crystallinity of poly(vinyl chloride) may be enhanced by performing the polymerization in acetonitrile[10] or various aliphatic halides.[11,12] The aldehyde effect has also been noticed in the polymerization of acrylonitrile,[13] vinyl formate,[14] vinyl bromide, and vinyl fluoride.[7]

Bovey and Tiers have also investigated the poly(vinyl chloride) formed by free radical polymerization at 50°C. in butyraldehyde, and found that the NMR spectra of such polymers were essentially indistinguishable from that of commercial PVC. They therefore rejected the claim made for the stereoregulating effect of butyraldehyde, and proposed that the crystallinity might be due to increased linearity of the polymer.[15] A similar explanation has been suggested by Alexandru, Opris, and Ciocanel[16] for the crystallinity of poly(vinyl acetate) prepared by free radical solution polymerization in ketones, e.g., acetone.[17]

The results of Bovey and Tiers, together with the fact that all the crystalline poly(vinyl chloride) samples prepared by utilizing the aldehyde effect were of low molecular weight, suggested that a high degree of crystallinity might be a typical feature of PVC with DP < 60, and perhaps of other polymers too. The crystallinity could also be independent of the nature of the chain transfer agent used for preparing the low molecular weight polymers. However, Minsker and co-workers have made a low molecular weight poly(vinyl chloride) by free radical polymerization in chloroform solution, and described the polymer as amorphous.[4] We therefore decided to reinvestigate the properties of this and similar low molecular weight poly(vinyl chloride).

Experimental

Vinyl chloride, polymerization grade, was used as obtained from the production line (Norsk Hydro-Elektrisk Kvælstofaktieselskab, Porsgrunn).

Azobisisobutyronitrile (Genitron LM) was supplied by Whiffen & Sons Ltd.

n-Butyraldehyde (reagent grade, B.D.H), chloroform (Merck), tetrahydronaphthalene (Riedel de Haen), and tetrahydrofuran (chromatographic grade, from Merck) were used as supplied.

The polymerizations were carried out essentially as described by Rosen,[3] 175 ml. soda bottles being used as pressure vessels. Each bottle was charged with 164 mg. azobisisobutyronitrile and the required amount of solvent, then cooled to -20°C. The vinyl chloride was then added while flushing the bottle with nitrogen. The polymerization was carried out at 52°C. for 4 hr. The polymer was precipitated with methanol, dissolved in tetrahydrofuran, and reprecipitated by the addition of methanol. The proportions of reagents, yields, and polymer properties are tabulated in Table I. The viscosities of 0.5, 1, 1.5, and 2% solutions of the polymer in cyclohexanone were determined at 25°C. Films for x-ray diffraction measurements were prepared by casting solutions of 134 mg. polymer in 2 ml. tetrahydrofuran onto a mercury surface (diameter 3.5 cm.). The films were mounted while still moist with solvent, as the dry films were extremely brittle. The films were dried and annealed[18] by heating at 125°C. for 1.5 hr., then cooled at a rate of 0.45°C./min. The diffraction pattern was recorded by a flat-plate camera, Cu$K\alpha$-radiation being used. The heating time and cooling rate did not appear to influence the observed crystallinity of the samples. The NMR spectra were recorded on a dual-purpose Varian

TABLE I
Crystallinity and $\overline{DP}$ of Low Molecular Weight Poly(vinyl Chloride) Prepared by Free Radical Solution Polymerization in Chain Transfer Agents

Sample no.	Solvent	Solvent, g.	Vinyl chloride, g.	Polymer yield, %	[η]	$\overline{DP}$	Crystallinity
1	*n*-Butyraldehyde	39	85	16	0.122	52	Medium
2	"	67	58	6	0.078	30	High
3	Chloroform	165	25	20	0.115	50	Medium
4	"	190	8	1.7	0.071	26	High
5	Tetralin	75	60	0.9	0.111	46	Medium
6	Tetrahydrofuran	110	16	2.4	0.090	35	High

60MC spectrometer. The samples were examined in 10–20% chlorobenzene solution at 170°C.

Results and Discussion

Preliminary experiments showed that low molecular weight poly(vinyl chloride) prepared by using butyraldehyde, chloroform, tetrahydronaphthalene, tetrahydrofuran, carbon tetrachloride, and isopropanol as chain transfer agents in the free radical-initiated polymerization all showed a high degree of crystallinity. The crystallinity of the polymers, as judged by the intensity and sharpness of the diffraction lines appeared to be determined mainly by the molecular weight of the samples. We therefore prepared two series of polymers, using *n*-butyraldehyde, chloroform, tetrahydronaphthalene, and tetrahydrofuran as chain transfer agents. The ratio transfer agent/monomer was adjusted to give polymers of about equal crystallinity. The results are described in Table I.

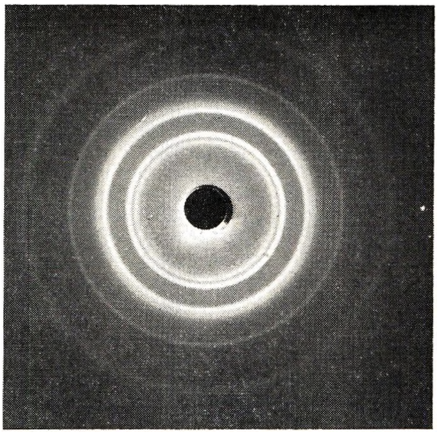

Fig. 1. X-ray diffraction pattern of sample 4, a low molecular weight poly(vinyl chloride) prepared by free radical solution polymerization in chloroform.

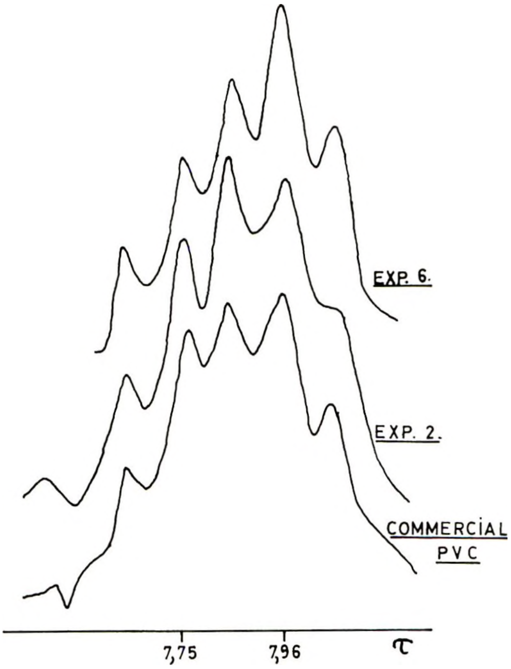

Fig. 2. CH_2 NMR signals from commercial, and from crystalline, low molecular weight poly(vinyl chloride).

The molecular weights of the polymers were estimated from the viscosity data by using the method of Rosen, Burleigh, and Gillespie,[2] and it was found that the three samples with a medium degree of crystallinity had $\overline{DP}$ in the range 52–46, while the three samples which had a high degree of crystallinity had $\overline{DP}$ in the range 35–25. Of these six samples, the sharpest diffraction pattern, (with *d* spacings about the same as those reported by Natta[19]) were found for sample 4, prepared by polymerization in chloroform. This sample also had the lowest molecular weight. The x-ray diffraction pattern of this sample is recorded in Figure 1. The crystallinity of the polymers prepared in chloroform was neither affected by an increase in polymerization rate (9-fold increase in initiator concentration) nor by an increase in polymerization time (for up to 24 hr.). The degree of crystallinity for commercial PVC, when judged by this method, was found to be low, in agreement with data published in the literature.

The NMR spectra of samples 2, 3, 5, and 6 were also recorded and compared with that of a commercial PVC (Norsk Hydro-Elektrisk Kvælstofaktieselskab, Norvinyl S-1-70). The results were in general agreement with those of Bovey and Tiers, though there seemed to be some increase in the area under the peaks at $\tau = 7.96$ ascribed to the syndiotactic diads. The spectra of samples 2, 6, and Norvinyl S-1-70 are recorded in Figure 2. Although there is still no general agreement on the detailed interpretation of the PVC NMR spectra in terms of tacticity,[15,20–23] we interpret our results as indicating that the highly crystalline low molecular weight poly(vinyl chloride) prepared by free-radical polymerization in a chain transfer agent has essentially the same tacticity as that of the conventional polymer prepared at the same temperature. The isolation and purification procedure may have caused some fractionation of the polymer, thus explaining the slight increase in syndiotacticity observed for the crystalline poly(vinyl chloride).

It further seems that the crystallinity is determined by the molecular weight alone. Rosen, Burleigh, and Gillespie[2] have found that the infrared absorbance ratio $D_{635\text{ cm.}^{-1}}/D_{692\text{ cm.}^{-1}}$ is dependent on the $\overline{\text{DP}}$ of the polymer for a series of polymers by using various aldehydes as polymerization solvents. If this ratio is taken to be a measure of the crystallinity (and not of the stereoregularity) of the polymers, their results agree very well with our findings and indicate that poly(vinyl chloride) of $\text{DP} < 60$ should show increasing crystallinity with decreasing molecular weight. Thus, there seems to be no special aldehyde effect.

It should be added that our results indicate that caution should be exercised in estimating the stereoregularity of very low molecular weight poly(vinyl chloride) from infrared or x-ray data. It is thus possible that the stereoregular poly(vinyl chloride) prepared by Minsker and co-workers[18] using Ziegler-Natta catalysts, and the similiar polymers prepared by Guyot and Pham Quang Tho[24] using Grignard reagent initiation are crystalline mainly because of their very low molecular weight.

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References

1. Burleigh, P. H., *J. Am. Chem. Soc.*, **82,** 749 (1960).

2. Rosen, I., P. H. Burleigh, and J. F. Gillespie, *J. Polymer Sci.*, **54,** 31 (1961).

3. Rosen, I., *Macromol. Syntheses*, **1,** 55 (1963).

4. Minsker, K. S., A. G. Kronman, B. F. Teplov, E. E. Rylov, and D. N. Bort, *Vysokomol. Soedin.*, **4,** 383 (1962).

5. Razuvaev, G. A., K. S. Minsker, A. G. Kronman, Yu. A. Sangalov, and D. N. Bort, *Dokl. Akad. Nauk SSSR*, **143,** 1116 (1962).

6. Razuvaev, G. A., K. S. Minsker, A. G. Kronman, and Yu. A. Sangalov, *Vysokomol. Soedin.*, **5,** 1615 (1963).

7. Sangalov, Yu. A., K. S. Minsker, G. A. Razuvaev, and A. S. Shevlyakov, *Plaste Kautschuk*, **10,** 464 (1963).

8. Imoto, M., *Makromol. Chem.*, **50,** 161 (1961).

9. Imoto, M., K. Takemoto, and Y. Nakai, *Makromol. Chem.*, **48,** 80 (1961).

10. Tanaka, H., A. Tomioka, U. Kaga, M. Katsura, and M. Fujihara, Japan Pat. 11,542 (1962).

11. Tanaka, H., K. Okamura, S. Tomioka, and U. Kaga. Japan Pat. 15,935 (1962).

12. Tanaka, H., S. Tomioka, U. Kaga, and Y. Komatsu, Japan Pat. 15,937 (1962).

13. Rosen, I., and P. H. Burleigh, *J. Polymer Sci.*, **62,** S160 (1962).

14. Fujii, K., T. Mochizuki, S. Imoto, J. Ukida, and M. Matsumoto, *Makromol. Chem.*, **51,** 225 (1962).

15. Bovey, F. A., and G. V. D. Tiers, *Chem. Ind.* (*London*), **1962,** 1826.

16. Alexandru, L., M. Opris, and A. Ciocanel, *Vysokomol. Soedin.*, **4,** 613 (1962).

17. Alexandru, L., and M. Opris, French Pat. 1,334,037.

18. Minsker, K. S., V. S. Etlis, E. E. Riber, and D. N. Bort, *Vysokomol. Soedin.*, **1,** 1403 (1959).

19. Natta, G., and P. Corradini, *J. Polymer Sci.*, **20,** 251 (1956).

20. Bovey, F. A., E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39,** 1199 (1963).

21. Johnsen, U., *J. Polymer Sci.*, **54,** S6 (1961).

22. Tincher, W. C., *J. Polymer Sci.*, **62,** S148 (1962).

23. Doskočilovà, D., *J. Polymer Sci.*, **B2,** 421 (1964).

24. Guyot, A., and Pham Quang Tho, *J. Polymer Sci.*, **C4,** 299 (1964).

Résumé

On décrit la préparation du chlorure de polyvinyle de bas poids moléculaire (DP < 52) par polymérisation radicalaire en solution dans des agents de transfert de chaîne, p. ex. le butyraldéhyde, le chloroforme, le tétrahydronaphtalène et le tétrahydropyrane. On a trouvé que de tels polymères sont cristallins et que le degré de cristallinité augmente avec la diminution du poids moléculaire.

Zusammenfassung

Die Darstellung eines niedermolekularen (DP < 52) Polyvinylchlorids durch radikalische Lösungspolymerisation in Kettenüberträgern, z.B. Butyraldehyd, Chloroform, Tetrahydronaphthalin und Tetrahydrofuran wird beschrieben. Diese Polymeren sind kristallin und der Kristallisationsgrad steigt mit abnehmendem Molekulargewicht an.

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Radiation Crosslinking of Nylon 66 and Poly(vinyl Alcohol)*

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Synopsis

Low dose Co^{60} radiation of nylon 66 and poly(vinyl alcohol) in the presence of methanol-water-allyl methacrylate (AMA) mixtures allows crosslinking of the polymers. In both cases, crosslinking is facilitated by the presence of the polyfunctional monomer and does not occur in its absence. Nylon gel fractions of 40% have been obtained after a dose of 3 Mrad; poly(vinyl alcohol) gel fractions of over 75% have been obtained after 5 Mrad. With both polymers, the gel fraction is dependent upon the radiation dose, AMA level, and water level during radiation.

INTRODUCTION

The radiation crosslinking of hydrocarbon polymers in the presence of allyl methacrylate monomer has been discussed in earlier communications from this laboratory.[1,2] Efficient crosslinking at low doses via this technique can be induced in hydrocarbon polymers that normally respond to γ-radiation by either predominantly undergoing degradation (e.g., polyisobutylene) or crosslinking (e.g., polyethylene). In the latter case, crosslinking efficiency is enhanced and gelation occurs at doses considerably lower than those normally required. This process of radiation-induced crosslinking in the presence of polyfunctional monomers is extended here to the polyamide nylon 66 and to poly(vinyl alcohol).

The determination of the polymer gel fraction is an excellent method for evaluating the extent to which crosslinking occurs. Gelation results upon radiation when the polymer molecular weight has increased to the point where there is one crosslinked unit per weight-average molecule; i.e., $(P_c)_{\text{crit}}\,\bar{P}_w = 1$, where $(P_c)_{\text{crit}}$ is the probability of a monomer unit being crosslinked at incipient gelation, and $\bar{P}_w$ is the weight-average degree of polymerization of the original polymer. Polymers undergoing simultaneous crosslinking and scission will show a gel fraction as long as the rate of crosslinking exceeds that of scission ($\beta/\alpha \leq 2$). After the gel point is

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reached, crosslinking will continue to an extent determined by the β/α ratio. Upon straight radiation, polymer crosslinking occurs in proportion to the radiation dose; $(P_c)_{\text{crit}}$ and $\bar{P}_w$ are fixed quantities determined by the polymer nature, molecular weight, molecular weight distribution, and physical state. When an additive is present, $(P_c)_{\text{crit}}$ can be altered; when the additive has been consumed by the radiation treatment, the polymer will then respond as under straight radiation conditions (assuming no significant alterations have been induced by the additive). A polyfunctional monomer such as allyl methacrylate (AMA) reduces $(P_c)_{\text{crit}}$ and therefore the incipient gelation dose of the system; at the dose normally required for the polymer to reach incipient gelation in the absence of the AMA, $(P_c)\bar{P}_w > 1$.

Concern about the incipient gelation dose and total gel fraction is of importance since it is only when the polymer has passed the former point to give large solvent-insoluble fractions that sought-after property improvements can be anticipated. Efficient crosslinking of nylon 66 or poly(vinyl alcohol) in the absence of degradation or where degradation is of little or no significance has been impossible to attain upon straight radiation.

EXPERIMENTAL

The nylon 66 used was DuPont's Zytel 101, obtained as 0.127 cm. thick, 1.60 cm. wide extruded tape from the Polymer Corporation of America. Allyl methacrylate was obtained from Sartomer Resins, Inc. The polymer was cut into strips ca. 2.5 cm. in length, swollen to equilibrium in volume mixtures of methanol–water–monomer, flushed with nitrogen, sealed, and subjected to mutual irradiation employing the RAI Co^{60} source at 0.02–0.06 Mrad/hr. After irradiation, the strips were vacuum-dried at 120°C. for 16 hr. and weighed. Machine irradiations were performed as described earlier.[1] White, fluffy, fibrous gel fractions were obtained by immersion of the irradiated strips in 97–100% formic acid. Extraction was continued for 8–12 days at room temperature (the solvent being changed at 3–4 day intervals); gels were collected by filtering through a fritted glass crucible. Unirradiated and monomer-free specimens irradiated in methanol or nitrogen and treated similarly, completely dissolved in less than one day via this formic acid treatment.

DuPont's Elvanol 72-60 poly(vinyl alcohol) ($\bar{M}_w = 1.7\text{–}2.2 \times 10^5$; 99% hydrolyzed) was cast from 7% aqueous solutions into 0.008–0.010 cm. thick films and dried. The films were placed into methanol–water–allyl methacrylate solutions, purged with nitrogen, sealed, and then irradiated via Co^{60} at 0.04 Mrad/hr. After irradiation, the films were washed with cold water, dried, and weighed. Gel fractions were determined by extraction for 4 days either in refluxing water or room temperature triethylenetetramine.

The per cent monomer incorporated into the polymer was expressed as one hundred times the weight increase divided by the initial polymer weight. The per cent gel is expressed as one hundred times the nonextractable fraction divided by the irradiated film weight.

RESULTS AND DISCUSSION

Nylon 66

The primary effect of radiation on nylon 66 is crosslinking;[3,4] the phenomenon is accompanied by considerable degradation and the loss of crystallinity.[5-7] The $G_{\text{crosslink}}$ value as derived from modulus data is reported to be 0.3.[4] Incipient gelation upon irradiation *in vacuo* is reported to occur after about 50 Mrad.[7] Zimmerman[5] has reported that electron irradiation followed by 25°C. conditioning induces incipient gelation after 80 Mrad, and has concluded that radiation crosslinking is facilitated by increasing dose, temperature, and water content during radiation; water decreased the incipient gelation point from 80 to 30 Mrad. High doses have similarly been required to crosslink other polyamides. A 40/20/40 nylon 66–nylon 6–nylon 610 terpolymer irradiated at −78°C. and conditioned at 125°C. showed a gel fraction after 40 Mrad.[5] Majury and Pinner,[8] employing a polycaprolactam of $\overline{M}_n = 2 \times 10^4$, calculated an incipient gelation dose of 35 Mrad.

Figure 1 shows the results obtained by swelling and irradiating nylon 66 to 2.9 Mrad in 90/0/10, 80/10/10, and 65/25/10 methanol–water–allyl methacrylate solutions. It is seen that 3% weight gain occurs after this dose. In the absence of water, 27% gel fraction is obtained; the gel fraction increases to 30% when water is present at the 10% level in solution, and further increases to 36% at the 25% water level. Straight irradiation of the polymer either in nitrogen or in methanol–water mixtures in the absence of the polyfunctional monomer fails to yield a gel fraction after this dose. It is seen, therefore, that methanol–AMA mixtures reduce the gelation dose and water aids in increasing the total gel fraction.

Figure 2 shows the results obtained by varying the radiation dose in the 65/25/10 methanol–water–AMA system. Over the 1–4 Mrad range, the per cent gel increases with dose; 18% gel is obtained after 1 Mrad, and the gel fraction increases to 38% after 4 Mrad. The per cent weight gain of AMA is also dose-dependent and reaches $3^1/_2$% after 4 Mrad. The crosslinking of nylon 66 in this liquid mixture is therefore dose-dependent. Figure 3 shows the effect of varied AMA concentration (5–20%) in the 10% water initial system. The 70/10/20 methanol–water–AMA system is seen to give 38% gel after 3.0 Mrad. Increasing the AMA content in the initial system causes an increase in the gel fraction.

It is seen, therefore, that nylon 66 can be crosslinked via radiation in the presence of allyl methacrylate monomer. The crosslinking is total dose-dependent, and water aids in increasing the gel fraction slightly. Gel fractions have been obtained at the lowest dose studied, 1 Mrad. Gel fractions could also be obtained by replacing AMA with commercial 50–55% divinylbenzene (DVB) as the polyfunctional monomer. In all experiments, the gel contents obtained were greater than could be accounted for by monomer homopolymerization alone.

The results indicate the feasibility of crosslinking nylon 66 at low radiation doses by use of Co^{60}. Multifunctional monomer presence during radia-

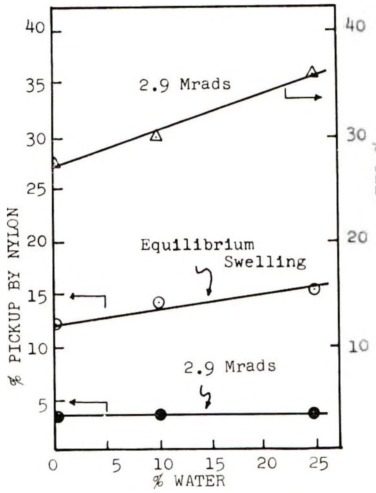

Fig. 1. Nylon 66 behavior in 10% allyl methacrylate solutions of methanol–water–AMA. (⊙) per cent weight gain after equilibrium swelling; (●) per cent weight gain after irradiation to 2.9 Mrad; (△) per cent gel after irradiation to 2.9 Mrad at 0.04 Mrad/hr.

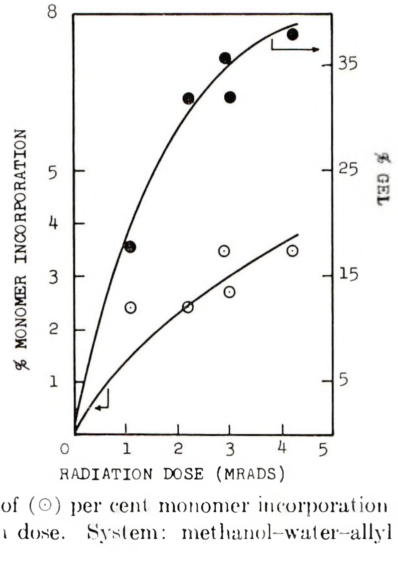

Fig. 2. Dependence of (⊙) per cent monomer incorporation and (●) per cent gel of nylon 66 on irradiation dose. System: methanol–water–allyl methacrylate, 65/25/10 at 0.02–0.06 Mrad/hr.

tion facilitates incipient gelation and post-gelation crosslinking of the polyamide.

For a predominantly crosslinking polymer such as polyethylene, electron-beam radiation following Co^{60} treatment of polymer–polyfunctional monomer systems has been shown to increase substantially the solvent-insoluble fraction of the polymer.[1] A degrading polymer like polyisobutylene, however, is observed to undergo a decrease in gel fraction after all the monomer has been polymerized.[2] In attempting to upgrade this polyamide further after the low dose polyfunctional monomer crosslinking treatment, speci-

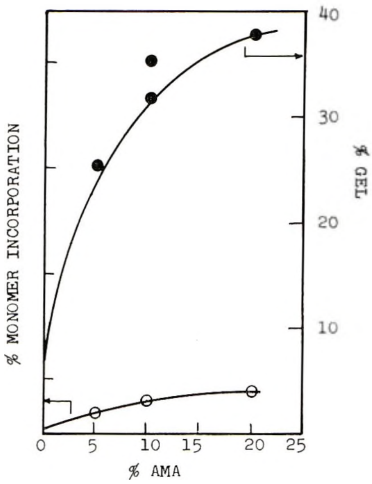

Fig. 3. Dependence of (⊙) per cent monomer incorporation and (●) per cent gel of nylon 66 on AMA level in initial system (10% water). Dose: 3.0 Mrad at 0.04 Mrad/hr.

mens of nylon–AMA and Nylon–DVB mixtures initially irradiated via Co^{60} to the low doses discussed above, were further irradiated via machine to impart additional doses of 28–164 Mrad. Such a process, it was reasoned, would serve to increase the gel if the β/α ratio of the polyfunctional monomer–crosslinked polymer were sufficiently low to facilitate further crosslinking. It was observed that little, if any, further increase in gel fraction occurs via this process. Thus, an additional 56 Mrad dose imparted to a 3.0 Mrad nylon–4% AMA system increased the gel fraction to 45%. The reasons for the failure of the polyfunctional monomer–crosslinked polyamide to show substantial increases in gel fractions via the machine radiation treatment after the initial Co^{60} graft-crosslinking process are equivocal; however, it is probable that the crosslinked nylon is simply exhibiting a normal response to machine radiation. Monomer-free nylon 66 specimens failed to yield any gel fraction over this entire dose range via this machine irradiation procedure.

Poly(vinyl Alcohol)

The effect of radiation on poly(vinyl alcohol) is highly dependent on the exact experimental conditions. Chain scission has been reported to be the most significant result upon radiation of the solid, regardless of whether the environment is air or vacuum.[9,10] However, various heat treatments either during or after irradiation are reported to aid gelation.[11,12] Radiation crosslinking can be induced in water solutions of the polymer;[13] however, the effect of water on the crosslinking of solid poly(vinyl alcohol) is unclear. Sakurada[14] reports the complete lack of gel formation for water-swollen films after 12 Mrad, while Shinohara[15] reports incipient gelation after 5 Mrad. In any case, efficient low dose radiation crosslinking of solid poly(vinyl alcohol) (e.g., the formation of 50–75% gel after 5 Mrad or less) has not been attained.

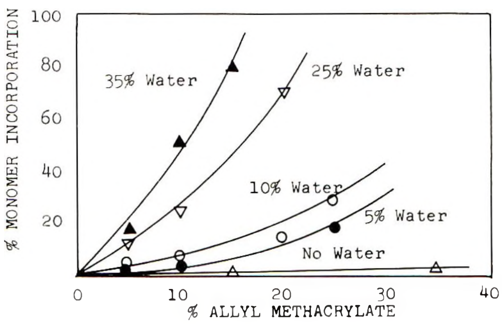

Fig. 4. Dependence of per cent monomer incorporation onto poly(vinyl alcohol) on AMA level at various water concentrations. Dose: 0.7 Mrad at 0.04 Mrad/hr.

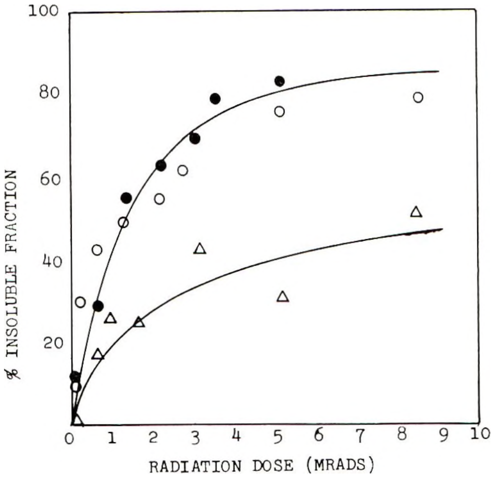

Fig. 5. Gel vs. dose for Elvanol 72-60 poly(vinyl alcohol) irradiated in presence of methanol–water–AMA system: (○) 19% monomer incorporation from 60/35/5; (●) 6% monomer incorporaton from 60/35/5; (△) 6% monomer incorporation from 85/5/10.

A series of irradiations was performed by using various methanol–water–allyl methacrylate mixtures at a total dose of 0.7 Mrad. These results are shown in Figure 4. It is seen that the presence of water markedly affects the amount of allyl methacrylate which is incorporated into the poly(vinyl alcohol). This is similar to the effect of water on the grafting of methyl methacrylate to poly(vinyl alcohol).[16] The 60/35/5 system was then chosen for a gel versus dose study at two monomer concentrations to determine the effect of monomer on the gelation process. Monomer concentrations were 6% and 19%. The first series was performed in the experimental manner described above with total dose being varied. The allyl methacrylate level of incorporation reached 19% after 0.3 Mrad (and remained at that level after increased radiation dosage due, very likely, to monomer depletion). In the second series of experiments, the radiation was interrupted after 0.1 Mrad to maintain the level of allyl methacrylate incorporation at 6%. For this second series, the films were removed from the methanol–water–AMA solutions after the initial dose, placed into water, flushed with nitrogen, resealed, and the irradiation continued. In this manner the crosslinking reaction could be observed at the two different monomer levels.

The results of these experiments (Fig. 5) show that the use of allyl methacrylate via methanol–water–allyl methacrylate solutions brings about very rapid crosslinking of solid poly(vinyl alcohol) film at low doses, e.g., 75% gel is obtained after only 4–5 Mrad of radiation. In the absence of allyl methacrylate, (in the methanol–water system), a gel fraction was not observed under similar radiation conditions. It is seen from Figure 5 that the gel content is essentially the same for the two monomer levels. This effect is similar to that observed in work with other polymer systems, in that monomer above a certain level is ineffective for crosslinking.[1]

That water plays a significant role in this polyfunctional monomer-crosslinking process was demonstrated by a third series of experiments: a gel versus dose study of the 85/5/10 system in the standard manner. This system allows a maximum allyl methacrylate incorporation level of 6%. It is seen from Figure 5 that this system is less efficient than either 65/35/5 system with regard to the amount of crosslinking per unit of radiation dose. This effect is likely to be due to an increased indirect effect, i.e., attack on the poly(vinyl alcohol) by radicals formed from water radiolysis, in the latter system.

CONCLUSIONS

These results clearly indicate the feasibility of crosslinking a polyamide and a poly-ol via the polyfunctional monomer–Co^{60} radiation technique. As with hydrocarbon polymers, the incipient gelation dose is reduced and higher gel fractions are obtained per unit dose when radiation is performed in the presence of allyl methacrylate monomer. The presence of water facilitates the radiation-induced crosslinking process for both of these polymers. Gel fractions of ca. 40% have been obtained by irradiation of nylon 66 to only 3 Mrad; gel fractions of 70% have been obtained by radiation of poly(vinyl alcohol) to the same dose. The level of polyfunctional monomer incorporation and total gel fraction can be controlled by varying the water/monomer ratio as well as the total dose.

The mechanism of Co^{60} radiation–polyfunctional monomer crosslinking has been discussed for polyethylene.[1] The process here can be visualized as occurring via radiation-induced radical formation on the polymer backbone via either a direct or indirect effect, followed by radical interaction with polyfunctional monomer. The grafted chains grow in length and interact to form a three-dimensional crosslinked network.

These results represent the first successful radiation crosslinking treatment of a polyamide and a polyol at these low doses. The early crosslinking process is likely to occur without being accompanied by simultaneous degradation.

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References

1. Odian, G., and B. S. Bernstein, *J. Polymer Sci.*, **A2,** 2835 (1964).
2. Odian, G., and B. S. Bernstein, *J. Polymer Sci.*, **B2,** 819 (1964).
3. Valentine, L., *J. Polymer Sci.*, **23,** 297 (1957).
4. Deeley, C. W., A. E. Woodward, and J. A. Sauer, *J. Appl. Phys.*, **28,** 1124 (1957).
5. Zimmerman, J., *J. Polymer Sci.*, **46,** 151 (1960).
6. Harmon, D. J., *Textile Res. J.*, **27,** 378 (1957).
7. Okamura, S., et al., *Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy, Geneva,* **29,** 176 (1958).
8. Majury, T. C., and S. H. Pinner, *J. Appl. Chem.*, **8,** 168 (1958).
9. Sakurada, I., and S. Matsuzawa, *Kobunshi Kagaku*, **17,** 687, 693 (1960).
10. Danno, A., *J. Phys. Soc. Japan*, **13,** 609, 614 (1958).
11. Matsumoto, M., and A. Danno, *Large Radiation Sources in Industry*, Intern. Atomic Energy Commission, Vienna, 1960, p. 331.
12. Danno, A., M. Koike, K. Nagoshi, and M. Inonue, paper presented at 4th Japanese Conference on Radioisotopes, Tokyo, 1962.
13. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon Press, London, 1960, ch. 25.
14. Sakurada, I., and S. Matsuzawa, *Kobunshi Kagaku*, **17,** 268 (1960).
15. Shinohara, K., A. Amemiya, M. Matsumoto, Y. Shinohara, and S. Onishi, *Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy, Geneva,* **29,** 186 (1958).
16. Chapiro, A., and V. Stannett, *Intern. J. Appl. Radiation Isotopes*, **8,** 164 (1960).

Résumé

L'irradiation à faible dose par le Co^{60} du Nylon 6,6 et de l'alcool polyvinylique en présence de mélanges méthanol-eau-méthacrylate d'allyl permet le pontage des polymères. Dans chacun des cas, le pontage est favorisé par la présence du monomère polyfonctionnel, et ne se fait pas en son absence. On obtient des fractions de 40% de gel de Nylon après une dose de trois Mrads, des fractions de 75% de gel d'alcool polyvinylique après 5 Mrads. Pour les deux polymères, la fraction de gel dépend de la dose d'irradiation, de la quantité d'AMA et d'eau pendant l'irradiation.

Zusammenfassung

Co^{60}-Bestrahlung in niedriger Dosis von Nylon 66 und Polyvinylalkohol in Gegenwart von Methanol/Wasser/Allylmethacrylat-Mischungen gestattet eine Vernetzung der Polymeren. In beiden Fällen wird die Vernetzung durch die Gegenwart polyfunktioneller Monomerer erleichtert und findet in ihrer Abwesenheit nicht statt. Nach einer Dosis von 3 Mrad wurden nur Gelfraktionen von 40% erhalten; Polyvinylalkoholgelfraktionen von über 75% wurden nach 5 Mrad erhalten. Bei beiden Polymeren hängt die Gelfraktion von Bestrahlungsdosis, AMA-Konzentration und Wassergehalt während der Bestrahlung ab.

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Probability of Cyclopolymerization

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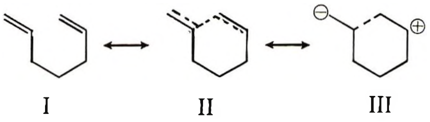
Synopsis

A statistical approach to the mechanistic problem of cyclopolymerization was taken. The model for this calculation was based on a stepwise mechanism for polymerization of 1,6-dienes. The assumption was made that a reaction site was formed at the second carbon of the chain C_2, and the probability of C_7 being in a volume element surrounding this position was calculated. The results, which indicate that on a statistical basis only, monomer concentrations must be reduced to <0.10 mole/l. in order to attain $>95\%$ cyclization, were compared with numerous experimental results in which 95–100% cyclization was obtained at monomer concentrations of 1.9–8.0 mole/l.

The principle of cyclopolymerization or intra-intermolecular polymerization has now been well established.[1,2] Although various theories have been proposed to explain the selectivity of the intramolecular propagation step in the reaction under discussion, none of them have received a widespread acceptance. These theories may be grouped into two general categories: (*1*) interspatial activated state and/or ground state interactions, and (*2*) statistical. The first category is, of course, also statistical, but the differentiation used here should be perceived from the discussion which follows.

The activated state–ground state interactions theory, proposed earlier[2] and recently supported by ultraviolet absorption evidence[3,4] is based upon an across space homoconjugation interaction between the double bonds in a monomer molecule. This effect, for 1,6-heptadiene, has been depicted as shown in eq. (1).



(1)

If 1,6-heptadiene can be appropriately represented by structure II, this molecule would require only a small entropy change in going from the ground state to the activated state for the intramolecular propagation reaction. Aside from this desirable entropy effect, the energy of both the ground and activated states would be decreased.

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Several pieces of evidence have been published recently which support the interspatial activated state and/or ground state interaction. Mikulasova and Hvirik[5] calculated the total activation energy for the radica polymerization of diallyldimethylsilane and found it to be ca. 9 kcal./mole double bond less than that for allyltrimethylsilane; however, Gibbs' showed that this lowering of the activation energy did not apply to al 1,6-heptadiene polymerizations. He found that in the case of methacrylic anhydride versus methacrylic acid, there was essentially no difference in the total activation energies in the polymerizations. On the other hand Marvel and Stille[7] obtained a cyclic polymer from 2,5-dimethyl-1,5-hexadiene, but could get only a low molecular weight oil from attempted polymerization of 2-methyl-1-pentene, suggesting an unusual driving force from diene monomer to cyclic polymer.

One would expect such a phenomenon to manifest itself in the ultraviolet region of the spectrum, and abnormalities in this spectral region for certain monomers which are known to undergo cyclopolymerization have been pointed out.[3,4] Interpretation of the data in terms of an excited state interaction appears reasonable; however, certain aspects of these studies permit a more reasonable explanation on the basis of interactions in both the ground and excited states.

Winstein[8] has published a paper concerning the ultraviolet spectrum for bicycloheptadiene showing absorption bands at 205, (E = 2100), 214, (E = 1480), and 220 mμ, (E = 870) and a shoulder at 230 mμ (E = 200). By assuming a slight interaction in the excited state, he calculated a theoretical absorption spectrum in good agreement with the observed one. It should be mentioned that this compound adds one mole of such reagents as bromine to yield predominately a saturated product having a nortricyclenic structure.[9]

It is of interest in this connection that carbethoxy derivatives of bicycloheptadiene have now been polymerized,[10] and evidence was presented that this type of polymerization requires activation of the double bonds and resonance stabilization of radicals formed during the polymerization.

Results and Discussion

It was the purpose of this study to undertake a statistical approach to this mechanistic problem, and to compare the results of these calculations with experimental observations. The model for this determination was based on a stepwise mechanism for the polymerization of 1,6-heptadiene. It was assumed that a reaction site was formed at the second carbon of the chain, C_2, and the probability of C_7 being in a volume element surrounding this position was then calculated.

Treloar[11] has previously solved a similar problem for a one-dimensional five-link chain. The carbon–carbon single bond distance was used for the length of each link, and the approximate tetrahedral angle of 109.5° for the angle between links. Completely free rotation about this fixed angle was assumed. The probability that the chain will have a certain length is not

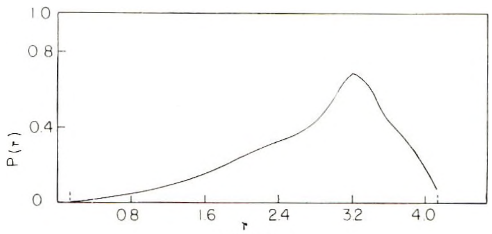


FIGURE 1.
DISTRIBUTION FUNCTION FOR LENGTH OF A FIVE-LINK CHAIN

Fig. 1. Distribution function for length of a five-link chain.

expressed by a single equation but rather by a complex series of equations. The graphical solution of this model in terms of the relative probability of specific end-to-end distance is given in Figure 1. This distribution function was used in this work to calculate the ratio of intramolecular to intermolecular propagation. Reaction was assumed to take place at 1.3 bond lengths, and the distribution function between the limits of 0.33 and one bond length was integrated. The number of double bonds furnished by adjacent molecules within this same volume element were then calculated. The results obtained are given in Table I. For comparison, the results of some typical cyclopolymerization experiments are recorded in Table II.[12–19] These results could be used to explain the high degree of cyclization in dilute solution, but they do not correlate with the experimental evidence that many monomers of this type can be polymerized in high concentration (ca. $6M$) to yield polymers which have undergone in excess of 90% cyclization.

Returning to the case of the interspatial interaction, the fundamental question is whether or not this phenomenon would necessarily lead to a cyclization step. If this interaction is purely of the across-space type, both interactions in the ground and excited states would, presumably, be related only to the distance and orientation of other double bonds with respect to the reaction site. But for polymerization at high concentrations, the results of Table I show statistically that there is a greater probability of a double bond from another monomer molecule to lie within the volume element with a radius of one bond length around the reaction site, than for the other end of this same molecule to lie within

TABLE I
Probability of Cyclization in 1,6-Dienes

Concentration of monomer, mole/l.	P_1/P_2	Cyclization, %
7.43	0.34	25
1.00	2.50	71
0.10	25.00	96
0.01	250.00	99.6
0.001	2500.00	ca. 100.00

TABLE II
Extent of Cyclization in Polymerization of 1,6-Heptadienes

Monomer	Concentration of monomer, mole/l.	Soluble polymer, %	Estimated cyclization, %	Reference
Diallyl quaternary ammonium salts	>5.0	100	96–100	12
Diallyl silanes	1.2–2.3	92–100	>95	13,14
1,6-Heptadiene	1.9–6.2	100	90–96	7
1,6-Heptadiyne	3.1	10	100	15
N,*N*-Diallylmelamine	(Solid state)	100	99	16
Diallylphosphine oxides	Bulk (melt)	100	100	17
Acrylic anhydride	~ 8.0	100	98–100	18,19

this same volume element. It would, therefore, appear that if this explanation is valid it would be primarily due to an orientation effect.

For a strong π–π interaction the nodal planes of all of the *p*-orbitals must lie in a common plane. An examination of a molecular model of 1,6-heptadiene reveals there are two such conformations with a reasonably close approach between the double bonds. One of these conformations is with the closest approach between atoms C_2 and C_7, and this is the conformation which could act as a precursor to the formation of a six-membered ring. However, in this geometry one of the terminal hydrogens lies in the nodal plane directly between the number two and number seven carbon atoms. It seems highly unlikely that a strong π–π interaction could take place through a bonded hydrogen. The other conformation which meets the π–π interaction requirement is with the closest approach between the carbons C_2 and C_6. In this conformation, measurements on the models indicate a closest approach of approximately 2A. (center-to-center). There is a slight steric interference at this distance from one of the internal chain hydrogens. Of course, the most serious objection to this conformation is that if it leads to ring closure, the resulting ring would be five-membered.

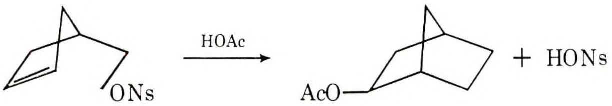
Another type of interaction which is applicable to this molecule is of the so-called π–σ type. In this case the restriction of having the *p*-orbital nodal planes coplanar is removed, and the molecular model indicates that this type interaction, in a conformation which might act as a precursor to the formation of a six-membered ring, is possible.

Since double bonds furnished by other molecules in close proximity to a particular olefinic bond would have, neglecting any induced effects, random orientation, the probability of a given orientation would be controlled by factors beyond the scope of the present discussion.

Another way in which the reaction site might distinguish that one of the many double bonds in its vicinity is unique would be by an inductive effect. It is conceivable that a very weak inductive effect would be operable even at a position four carbons removed from the reaction site. However, this effect would not explain the cyclization since, if this effect was the controlling factor, it would likely lead to the formation of five-membered rings, as well as six-membered rings.

If one assumes a ground state in which there is no interaction, then for the molecule to go from this state to the activated state would involve a relatively large entropy change. This factor would be extremely important in deciding which of two possible reaction paths a reaction would take, assuming an approximately equal activation energy for both paths. Of the two paths, for the reaction under consideration, the intramolecular propagation would involve primarily the change in entropy due to rotational degrees of freedom about the various bond axes, whereas the intermolecular step would be primarily concerned with translational motion. A qualitative answer as to the magnitude of these two effects could be derived from the relative contribution of these two modes to the total entropy for molecules of this type in solution.

In recent years, there have been a number of publications concerning a phenomenon that is, in certain respects, similar to the intramolecular–intermolecular polymerization mechanism. Bartlett and Bank[20] have observed that the rate of solvolysis of β-(cyclopentene-3-yl)-ethyl *p*-nitrobenzenesulfonate in acetic acid is 95 times faster than the solvolysis of the corresponding saturated *p*-nitrobenzenesulfonate. The product from the solvolysis of the unsaturated ester is the acetate of *exo*-norborneol-2. The reaction is shown in eq. (2). (Ns = *p*-nitrobenzenesulfonate.)



(2)

IV V

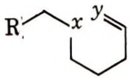
Similar results have been obtained[21] by Closson in open chain systems. He has reported that the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in acetic acid yields 34% cyclic and 39% noncyclic acetate. This reaction is 71% faster than the rate of solvolysis of the *n*-hexyl ester. However, this type closure has been demonstrated only in the cases where a carbonium ion is formed during the course of the reaction. On the other hand, certain 1,6-heptadienes have been converted to cyclic polymers with all known types of initiators.[22]

Probability Calculations

During the polymerization of an unconjugated diene, there is a certain probability that the monomer will cyclize. This probability may be calculated and, along with it, the per cent cyclization that may be expected on as statistical basis.

Treloar[11] has calculated the distribution function for the length r of a paraffin chain having five links. The probability that the chain will have a certain length, r, is not expressed by a single equation, but rather by a complex series of equations. These were solved graphically to give the distribution curve in Figure 1.

Consider a 1,6-diene undergoing polymerization: in order to calculate the probability P of intermolecular versus intramolecular reaction, we must be able to calculate the probability P_1 that x and y (see VI) will approach to within a distance $r = Dr$, within which, we will assume reaction to take place.



VI

We may then calculate the probability P_2 of x approaching within this distance to any other double bond in the system and compare P_1 and P_2.

We will first assume that the five-link chain from x and y may be treated as a saturated paraffin chain, i.e., that the differences in bond angle and bond length for the double bond portion do not greatly change the distance r. Second, we are only concerned with the probability that r will be equal to or less than Dr. We will assume Dr to be less than 1.3 bond lengths (2A.).

We may now use the following approximation for the probability equation:

$$P(r) = 0.09(r - 0.33) \pm 0.01 \tag{3}$$

Assuming $Dr = 1$ bond length, we may integrate eq. (3) and obtain P_1:

$$P_1 = \int_{0.33}^{1} P(r)\,dr$$

$$= 0.9 \int_{0.33}^{1} r dr - 0.09 \int_{0.33}^{1} 0.33\,dr \pm 0.01 \int_{0.33}^{1} dr$$

$$= 0.030 \pm 0.006$$

We may now calculate the probability, P_e, of x approaching to within a distance r of any other double bond in the system by merely calculating the density of double bonds. For 1,6-heptadiene the molecular weight is 96.2 g./mole, and the density is 0.714 g./cc. Therefore, the number of molecules per cubic Angstrom (N) for pure monomer is:

$$N = \left(\frac{0.714 \text{ g./cc.}}{1 \text{ cc.}}\right)\left(\frac{6.023 \times 10^{23} \text{ molecules}}{\text{mole}}\right)\left(\frac{\text{mole}}{96.2 \text{ g.}}\right)\left(\frac{1 \text{ cc.}}{10^{24}} \text{A.}^3\right)$$

The number of double bonds per cubic Angstrom equals $2N$.

For solution of monomer:

$$N = \left(\frac{\text{moles}}{\text{liter}}\right)\left(\frac{6.023 \times 10^{23} \text{ molecules}}{\text{mole}}\right)\left(\frac{\text{liter}}{10^3 \text{ cc.}}\right)\left(\frac{1 \text{ cc.}}{10^{24}} \text{A.}^3\right)$$

The probability of x approaching within the distance r is:

$$P_e = (2N)4/3r^3$$

If we express the concentration, C, in moles per liter, we have

$$P_e = 5.05 \times 10^{-3}Cr^3 \tag{4}$$

Letting r = 1.54 A. (1 bond length),

$$P_2 = 1.2 \times 10^{-2}C$$

The ratio of intramolecular to intermolecular propagation is then equal to the ratio:

$$P_1/P_2 = 3.0 \times 10^{-2}/1.2 \times 10^{-2}C = 2.5/C \tag{5}$$

By substituting values into eq. (5) for C, we obtain the results in Table I.

In the calculations the effect of the orientation of the double bond to x on its reactivity is neglected. The only unfavorable orientation would occur when the methylene group attached to the double bond lies between it and x.

In arbitrarily choosing a distance of one bond length for Dr, we are within the distance at which repulsive forces between the molecules exist. It is assumed that these forces will affect intermolecular and intramolecular approach of a double bond to x in the same way.

The results in Table I neglected cyclization which may occur when x reacts with the pendent double bond of a previously added, uncyclized monomer unit. Since the six-membered ring is the most favorable size, the probability of forming any other size will be considerably less.

In calculating the per cent cyclization for large rings (10–12 members), Haward[23] obtained a value of 31% cyclization. He then made a rough calculation to determine what the per cent cyclization would be if the probability of formation of the larger ring sizes was included. This resulted in a value of 75% cyclization.

Since the probability of ring formation does not change as greatly from one large ring size to the next large ring size as it does in going from a six-membered ring to a seven or eight-membered ring, it is assumed that for the present problem, the effect of including all the possible cyclizations will not be as great as in Haward's case. We may then estimate that there will be less than 50% cyclization for pure monomer on a purely statistical basis.

The results summarized in Table II which show that complete cyclization may occur at high monomer concentrations, even though statistically the extent of cyclization should be less than 50%, are interpreted to mean that a more energetically favorable pathway from 1,6-diene to cyclic polymer exists than would be predicted on a purely statistical basis.

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References

1. Butler, G. B., and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).
2. Butler, G. B., *J. Polymer Sci.*, **48**, 279 (1960).
3. Butler, G. B., and T. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).
4. Butler, G. B., and M. A. Raymond, *J. Org. Chem.*, **30**, 2410 (1965).
5. Mikulasova, O., and A. Hvirik, *Chem. Zvesti*, **11**, 641 (1962).
6. Gibbs, W. E., and J. T. Murray, *J. Polymer Sci.*, **58**, 1211 (1962).
7. Marvel, C. S., and J. K. Stille, *J. Am. Chem. Soc.*, **80**, 1740 (1958).
8. Winstein, S., *J. Am. Chem. Soc.*, **82**, 5450 (1960).
9. Winstein, S., and M. Shatavsky, *Chem. Ind.* (*London*), **1956**, 56.
10. Graham, P. J., E. L. Buhle, and N. Pappas, *J. Org. Chem.*, **26**, 4658 (1961).
11. Treloar, L. G. R., *Proc. Phys. Soc.*, **55**, 345 (1943).
12. Butler, G. B., A. Crawshaw, and W. L. Miller, *J. Am. Chem. Soc.*, **80**, 3615 (1958).
13. Butler, G. B., and R. W. Stackman, *J. Org. Chem.*, **25**, 1643 (1960).
14. Marvel, C. S., and R. G. Woolford, *J. Org. Chem.*, **25**, 1641 (1960).
15. Stille, J. K., and D. A. Frey, *J. Am. Chem. Soc.*, **83**, 1679 (1961).
16. Gibbs, W. E., *J. Polymer Sci.*, **54**, 51 (1961).
17. Butler, G. B., and K. D. Berlin, *J. Am. Chem. Soc.*, **82**, 2712 (1960).
18. Crawshaw, A., and G. B. Butler, *J. Am. Chem. Soc.*, **80**, 5464 (1958).
19. Jones, J. F., *J. Polymer Sci.*, **33**, 15 (1958).
20. Bartlett, P. D., and S. Bank, *J. Am. Chem. Soc.*, **83**, 2591 (1961).
21. Bartlett, P. D., *Ann. Chem.*, **653**, 45 (1962) (see Table 2, p. 53 for results attributed to Dr. W. D. Closson.).
22. Field, N. D., *J. Org. Chem.*, **25**, 1006 (1960).
23. Haward, R. N., *J. Polymer Sci.*, **14**, 535 (1954).

Résumé

On a employé une méthode statistique pour résoudre le problème mécanistique de la cyclopolymérisation. On a basé le modèle de ce calcul sur un mécanisme par étapes pour la polymérisation des diènes-1,6. On a supposé qu'un site réactionnel était formé sur le second carbon de la chaîne C_2 et on a calculé la probabilité qu'avait C_7 d'être dans un élément de volume aux environs de cette position. Les résultats obtenus sur une base statistique seule indiquent que les concentrations en monomères doivent être résuites à moins de 10 moles/litre pour obtenir plus de 95% de cyclisation. On a comparé ces résultats avec de nombreuses résultats expérimentaux où l'on obtenait 95 à 100% de cyclisation avec des concentrations en monomères de 1,9 à 8 moles/litre.

Zusammenfassung

Das mechanistische Problem der Zyklopolymerisation wurde auf statistischem Weg behandelt. Das Modell für diese Berechnung beruht auf einem schrittweisen Mechanismus für die Polymerisation von 1,6-Dienen. Es wird angenommen, dass ein Reaktionsort am zweiten Kohlenstoffatom C_2 der Kette gebildet wird und die Wahrscheinlichkeit für die Anwesenheit des C_7 in einem diese Stellung umgebenden Volums-element berechnet. Die Ergebnisse, welche zeigen, dass auf rein statistischer Grundlage die Monomerkonzentration auf $<0{,}10$ Mol/l herabgesetzt werden muss, um $>95\%$ Zyklisierung zu erreichen, wurde mit zahlreichen Versuchsergebnissen verglichen, bei welchen 95–100% Zyklisierung bei Monomer konzentrationen von 1,9-8,0 Mol/l erhalten wurden.

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Radiation-Induced Polymerization of 1,2-Cyclohexene Oxide

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Synopsis

Radiation-induced polymerization of 1,2-cyclohexene oxide was investigated in the liquid and in the solid state. Addition of water drastically reduces the rate of polymerization and the molecular weight of the obtained polymer. The results have been interpreted according to an ionic mechanism.

INTRODUCTION

In the course of a study on the polymerizability of linear and cyclic oxides induced by ionizing radiation[1,2] it has been found that 1,2-cyclohexene oxide may rapidly polymerize in the liquid and in the solid state to give a solid, amorphous polymer. From the literature it is seen that this monomer undergoes polymerization only by ionic catalysts such as strontium carbonate, organometallic compounds, and ferric chloride.[3-5]

This paper describes a study of the polymerization of this monomer induced by γ-rays and examines the effect of the temperature and of added water on the rate of the reaction. In the radiation-induced polymerization of this compound a difference in behavior is observed, depending on whether the monomer is irradiated in the liquid or in the solid state.

EXPERIMENTAL

Materials

The 1,2-cyclohexene oxide was prepared by treating 2-chlorocyclohexanol with an aqueous solution of sodium hydroxide.[6] The product was purified by distillation, dried on anhydrous sodium sulfate, and redistilled on a Vigreux column. The fraction boiling at 131°C. was collected and kept for a few days on molecular sieves (BDH type 5A).

Polymerization

The polymerization reactions were carried out in dilatometers filled under vacuum by distilling the monomer after degassing by the usual technique of freezing and melting operations. The samples were irradiated in a thermostat with γ-rays from a 5000-curie Co^{60} source.[7] The dose rate was measured by Fricke dosimetry ($G_{\mathrm{Fe}^{+++}} = 15.6$).

At the end of the reaction, the polymer was recovered by evaporation of the monomer under vacuum to constant weight. The addition of water has been effected by introducing a known amount of vapor into a dilatometer containing the monomer and connected to a vacuum line. Polymerization in the solid state was performed in dilatometers. The samples were frozen in liquid nitrogen and irradiated at the desired temperature in a Dewar flask containing the freezing mixture.

Viscosity and Molecular Weight Determinations

Viscosity measurements of benzene solutions of the polymer were carried out in an Ubbelohde viscometer at 25°C. Molecular weights were determined in the same solvent by the vapor pressure method by using a Model 301 A Mechrolab apparatus.

RESULTS

Preliminary experiments showed that 1,2-cyclohexene oxide may be completely polymerized by bulk irradiation. It soon appeared that the polymerization rate was affected by factors which could not be easily controlled. Samples of monomer prepared apparently under the same conditions did not give reproducible results. This difficulty was encountered in most experiments, and the data reported in Table I show that the polymerization rate, at a given temperature, may vary over a wide range. However, it may be noted from Table I that the molecular weight of the polymer increases with the rate of polymerization, and it does not seem to depend

TABLE I
Polymerization of Cyclohexene Oxide by γ-Irradiation

50°C.			25°C.			0°C.		
Rate of polymerization, %/hr.	Conversion, %	[η]	Rate of polymerization, %/hr.	Conversion, %	[η]	Rate of polymerization, %/hr.	Conversion, %	[η]
6.7	16.8	0.240	11.0	24.2	0.410	0.9	20.8	0.175
8.4	16.8	0.265	14.7	29.4	0.490	3.9	22.3	0.290
14.6	29.2	0.355	16.8	11.3	0.600	4.4	31.2	0.275
19.8	19.8	0.450	21.3	28.4	0.700	9.7	25.2	0.440
21.4	21.4	0.500	24.7	22.6	0.770	12.1	42.1	0.555
37.4	31.2	0.495	27.0	45.1	0.750	13.6	47.5	0.500
			1.46[a]	13.2	0.100			
			0.06[b]	6.2	<0.010			

[a] Sample with the addition of 0.02% water.

[b] Sample with the addition of 0.5% water.

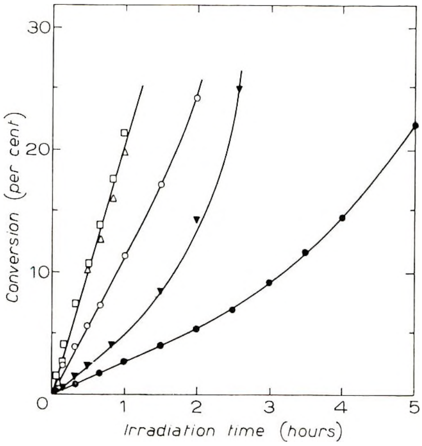

Fig. 1. Polymerization of 1,2-cyclohexene oxide in liquid state with irradiation at various temperatures and viscosities: (●) −22.8°C., [η] = 0.435; (▼) 0°C., [η] = 0.440; (○) 25°C., [η] = 0.410; (△, □) 50°C., [η] = 0.450.

on the degree of conversion. This behavior may be simply explained by supposing the presence of some fortuitous substance which acts as a retarder interrupting the chain growth.

The retarding effect is very likely due to the presence of water. In fact its addition to pure monomer drastically reduces the polymerization rate. At 25°C. a decrease of the rate by factors of about 250 and 10 times is observed for the addition by 0.5 and 0.02% of water, respectively. At the same time, the molecular weight of the polymer obtained in the presence of water is much lower.

On the other hand, pretreatment of the monomer with molecular sieves produces an increase of the polymerization rate. Thus, the longer the time of pretreatment, the greater the rate of polymerization, and this process could never be effectively brought to completion even after prolonged treatment (several months).

It was therefore decided to prepare a certain amount of monomer which was kept on molecular sieves for a given time (3 days). The monomer was partly polymerized, but this treatment led to results reproducible within experimental error.

A plot of the polymerization yield against time of irradiation of samples of liquid 1,2-cyclohexene oxide thus treated is reported in Figure 1. The data are for irradiation at various temperatures. The straight line at 50°C. is obtained by interpolating the results of two runs. All experiments in this work were carried out at a fixed dose rate of 350,000 r/hr.

By examining these kinetic data it may be observed that at low conversion the yield of the polymer increases linearly with time of irradiation. At high conversion, the polymerization rates show a tendency to accelerate for the experiments at 0°C. and −23°C. This deviation from linearity may be attributed either to the consumption of the retarder in the course

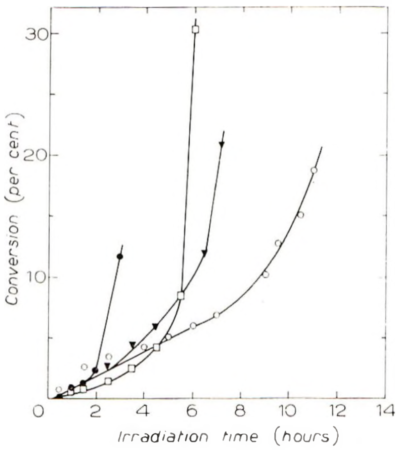

Fig. 2. Polymerization of 1,2-cyclohexene oxide in solid state with irradiation at various temperatures: (○, ▼) −78°C.; (□) −56°C.; (●) −35°C.

of the reaction or to a gel effect that may be more effective at low temperatures. The intrinsic viscosity of the polymer samples obtained at the four temperatures is practically the same. Incidentally, the values of the molecular weight of a few samples determined by vapor pressure measurements are in the range of 10,000–20,000. A quantitative relation between molecular weight and viscosity has not been determined.

The behavior of 1,2-cyclohexene oxide to polymerization in the solid state seems more complex. It may be noted from the curves of Figure 2 that initially the polymerization yield increases slowly with time of irradiation. The rate of polymerization remains very low in this initial stage, regardless of the temperature of irradiation. Thereafter an abrupt increase of the polymerization rate occurs. Further in these experiments it has been observed that while the frozen pure monomer has a crystalline aspect, as polymerization proceeds the solid system has the appearance of a glassy, homogeneous substance.

The various attempts to reproduce these kinetic curves failed. The two runs at −78°C. show completely different trends, although they were performed under the same conditions and with samples treated in the same manner. The effect of the crystalline state on the polymerizability of solid monomers is well known.[2,8,9] As the reaction proceeds, more imperfections are formed in the solid because of the presence of the polymer, and a higher rate of polymerization may result. The crystalline perfection of the frozen monomer depends naturally also on many other factors which may alter the course of the reaction.

DISCUSSION

The experiments carried out in this laboratory on a large number of epoxides have confirmed that radiation-induced polymerization of this type of monomer may occur only in a few cases.[1,2,9] The polymerization of 1,2-cyclohexene oxide, unlike other alicyclic and linear epoxides, may be due to its higher propagation rate, caused by release of strain during the polymerization process.[10]

As for the active species inducing the polymerization reaction, the behavior of this monomer to polymerization is more consistent with an ionic mechanism. This monomer in fact polymerizes only with ionic catalysts; further the effect of water on the polymerization rate is generally interpreted by an ionic deactivation due to the well known reactivity of water molecules with ionic species.[11] This would lead to a decrease of the polymerization rate and of the molecular weight of the polymer, as found in the present work. Analogous results have been found also for polymerization of α-methyl styrene by γ-rays.[12] Addition of water in this latter case also reduces the polymerization rate but it does not affect the molecular weight of the polymer.

The value of 5.3 kcal./mole for the activation energy for the polymerization of 1,2-cyclohexene oxide, calculated from the data of Figure 1, and the near invariance of the molecular weight with temperature are of little significance for the interpretation of the reaction mechanism. Too many factors influence this system to be discriminated and analyzed separately. The value of the apparent activation energy may be affected, for instance, by a different rate of consumption of the retarder at different temperatures.

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References

1. Cordischi, D., A. Mele, and R. Sassoli, unpublished results.
2. Barnaba, P., D. Cordischi, M. Lenzi, and A. Mele, *Chim. Ind.* (*Milan*), in press.
3. Bailey, F. E., and F. N. Hill, U. S. Pat. 2,897,489 (June 6, 1961).
4. Vandenberg, E. J., *J. Polymer Sci.*, **47**, 489 (1960).
5. Newth, F. H., and D. Y. Wadden, Brit. Pat. 878,033 (Mars 4, 1960).
6. Osterberg, A. E., *Organic Syntheses*, Coll. Vol. I, Wiley, New York (1932), p. 179.
7. Cordischi, D., A. Delle Site, M. Lenzi, and A. Mele, *Chim. Ind.* (*Milan*), **44**, 1101 (1962).
8. Eastmond, G. G., *J. Appl. Chem.*, **13**, 221 (1963).
9. Okamura, S., K. Hayashi, and H. Watanabe, *Isotopes Radiation*, **3**, 510 (1960).
10. Bacskai, R., *J. Polymer Sci.*, **A1**, 2777 (1963).
11. Dainton, F. S., *Discussions Faraday Soc.*, **14**, 239 (1953).
12. Best, J. B. F., T. H. Bates, and T. F. Williams, *Trans. Faraday Soc.*, **58**, 192 (1962).

Résumé

On a étudié la polymérisation initiée par des radiations, de l'oxyde de 1,2-cyclohexène à l'état liquide et à l'état solide. L'addition d'eau réduit de façon drastique la vitesse de polymérisation et le poids moléculaire du polymère obtenu. On a interprété les résultats sur la base d'un mécanisme ionique.

Zusammenfassung

Die strahlungsinduzierte Polymerisation von 1,2-Zyklohexenoxyd wurde im flüssigen und festen Zustand untersucht. Zusatz von Wasser setzte die Polymerisationsgeschwindigkeit sowie das Molekulargewicht des erhaltenen Polymeren stark herab. Den Ergebnissen wurde ein ionischer Mechanismus zu Grunde gelegt.

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Preparation and Polymerization of Addition Compounds of Unsaturated Tertiary Phosphine Oxides

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Synopsis

Complexes of vinyldiphenylphosphine oxide, vinyldi-*n*-butylphosphine oxide, and *trans*-1-propenyldiphenylphosphine oxide have been prepared with salts of Zn(II), Hg(I), Sb(III), Sn(IV), Ti(IV), Fe(III), and U(VI). The observed shifts in the phosphoryl stretching frequency on complex formation were similar to the values reported for corresponding complexes with triphenylphosphine oxide. The polymerization behavior of these compounds in the presence of free-radical and ionic intiators is similar to that of the unsaturated phosphine oxides themselves. In spite of high salt content, the polymers form clear plaques on molding, and they are completely soluble in appropriate organic solvents.

INTRODUCTION

The free-radical polymerization of vinyldialkylphosphine oxides is very sluggish under normal polymerization conditions and gives low molecular weight products.[1,2] In copolymerizations with the common vinyl monomers, vinylphosphine oxides exert a deleterious effect on both the rate of polymerization and the molecular weights of the polymers formed. These monomers are polymerized readily by anionic catalysts, however.[3] While the phosphoryl group mildly activates the double bond toward radical addition, it does not exert a strong conjugative stabilization of an adjacent carbon radical.[2,4] One of the characteristic properties of tertiary phosphine oxides is their ability to form coordination compounds with many salts.[5-11] Formation of complexes of vinyldiphenylphosphine oxide has been noted but the products were not characterized.[3] We have prepared complexes of several vinyldialkylphosphine oxides with a variety of salts and explored their polymerization behavior and the properties of their polymers.

RESULTS

Properties of the Complexes

In Table I, the properties of several complexes of vinyldiphenylphosphine oxide (VPO), vinyldi-*n*-butylphosphine oxide (VBO), and *trans*-1-

TABLE I
Complexes of Unsaturated Tertiary Phosphine Oxides

Complex	Color	Melting point, °C.	Δν, cm.$^{-1a}$	Calcd.				Found			
				C, %	H, %	P, %	Cl, %	C, %	H, %	P, %	Cl, %
$ZnCl_2 \cdot 2VPO$	White	132	−30	56.8	4.5	10.4	11.9	57.0	4.5	10.6	11.8
$Zn(NO_3)_2 \cdot 2VPO$	White	95–99	−39	52.1	4.1	9.6		52.6	4.1	9.3	
$HgCl_2 \cdot VPO$	White	104–106	−26	33.6	2.6	6.0	14.0	33.5	2.7	5.9	14.4
$SbCl_3 \cdot 2VPO$	White	75–78	−46	49.2	3.8		15.5	48.8	3.7		15.3
$SnCl_4 \cdot 2VPO$	White	203–204	−53	47.0	3.6		19.8	46.8	3.5		19.7
$TiCl_4 \cdot 2VPO$	Yellow	150–155	−55	52.3	4.0		22.0	52.0	4.1		21.2
$FeCl_3 \cdot 2VPO$	Yellow	118–122	−44	54.3	4.2	10.0	17.2	54.2	4.2	9.9	17.4
$UO_2Cl_2 \cdot 2VPO$	Yellow	205–207	−52	42.2	3.3		8.9	42.5	3.3		8.3
$HgCl_2 \cdot PPO$	White	84	−38			6.0	13.8			5.9	13.2
$SnCl_4 \cdot 2PPO$	White	185–189	−57	48.3	4.6	8.3	19.1	48.9	4.3	7.5	19.1
$ZnCl_2 \cdot 2VBO$	White	Oil	−50	Residue product (not analyzed)							
$UO_2Cl_2 \cdot 2VBO$	Yellow	Oil	−58	Residue product (not analyzed)							

[a] Shift of P=O stretching frequency from 1180 cm.$^{-1}$ for VPO and PPO and 1170 cm^{-1} for VBO.

propenyldiphenylphosphine oxide (PPO) are summarized. Except for the complexes of VBO which were oils, all were obtained as crystalline solids. In agreement with previous studies,[5–11] complexes containing two moles of the ligand were usually formed, although only 1:1 complexes were prepared with mercuric chloride. The compounds were soluble in polar organic solvents, and, although they were stable in air and not hygroscopic, they were hydrolyzed in water to their components.

The decrease in the phosphoryl stretching frequency on complex formation is indicated in Table I. The spectra of the crystalline complexes were obtained on Nujol mulls or potassium bromide plaques. In some cases the shifted band was skewed toward higher frequencies, resulting in a rather broad band for a phosphoryl group absorption. The frequency of maximum absorption[6] rather than the average frequency of the absorption,[5] which was difficult to assign because of the skewed shape of the band, was used to determine $\Delta\nu$. Assuming that the magnitude of the shift is related to the strength of the coordinate bond formed between the cation and the oxygen of the phosphoryl group, VBO complexes more strongly than does VPO (note $ZnCl_2$ and UO_2Cl_2 complexes in Table I), and it appears that the β-methyl group in PPO may increase slightly the strength of the coordinate bond over that in VPO (note $HgCl_2$ and $SnCl_4$ complexes in Table I). Both effects are to be expected from the positive inductive effect of alkyl groups and are in line with the greater shifts observed for complexes of trimethylphosphine oxide[7] than for corresponding complexes of triphenylphosphine oxide (TPO). As expected, the magnitudes of $\Delta\nu$ observed for the VPO complexes are generally similar to the values for the corresponding complexes of triphenylphosphine oxide that have been reported. For comparison, these include −37 cm.$^{-1}$ for $ZnCl_2 \cdot 2TPO$,[5] −37 cm.$^{-1}$ for $HgCl_2 \cdot TPO$,[7] −63 to −90 cm.$^{-1}$ for $SbCl_3 \cdot 2TPO$,[5] −42 (av.) and −55 cm.$^{-1}$ for $SnCl_4 \cdot 2TPO$,[5,6] −42 (av.) and −50 cm.$^{-1}$ for $TiCl_4 \cdot 2TPO$,[5,6] and −43^{-1} for $FeCl_3 \cdot 2TPO$.[5] There appeared to be little if any shift in the P=O stretching frequency on polymerization of the complexes of this study.

No shift of the C=C stretching frequency (1604 cm.$^{-1}$) was observed on complex formation with the two vinylphosphine oxides, and only slight changes to higher frequencies ($\Delta\nu < 15$ cm.$^{-1}$) were noticed in the vinyl-hydrogen bending absorptions at 974 and 1390 cm.$^{-1}$ for VPO and 990 and 797 cm.$^{-1}$ for VBO. However, the C=C stretching band of PPO (1622 cm.$^{-1}$) was split to a doublet in $SnCl_4 \cdot 2PPO$ (1622 and 1640 cm.$^{-1}$), and the =C—H bending bands at 998 and 797 cm.$^{-1}$ were shifted to 970 and 823 cm.$^{-1}$, respectively. Similarly, these latter absorptions appeared at 970 and 812 cm.$^{-1}$, respectively, in the spectrum of $HgCl_2 \cdot PPO$, and a doublet appeared at 1615 and 1635 cm.$^{-1}$.

Formation of complexes between VPO and $CuCl_2$, $TiCl_3$, $NiCl_2$, $ZrOCl_2$, $AlCl_3$, and $MgCl_2$ was examined cursorily. From the infrared spectra of the crude residue products it was evident that complex formation occurred (Table II).

TABLE II

Other Complexes of Vinylidphenylphosphine Oxide

Complex	Color	State	$\Delta\nu$, cm.$^{-1a}$
$MgCl_2 \cdot VPO$	White	Solid	−18
$AlCl_3 \cdot VPO$	White	Oil	−27
$TiCl_3 \cdot 2VPO$	Green	Solid	−29
$CuCl_2 \cdot 2VPO$	Yellow	Oil	−30
$NiBr_2 \cdot 2VPO$	Blue	Oil	−28
$Fe(NO_3)_3 \cdot 2VPO$	Brown	Oil	−53
$ZrOCl_2 \cdot 2VPO$	White	Solid	−53

[a] Shift of P=O stretching frequency from 1180 cm.$^{-1}$ in VPO.

Polymerization of the Complexes

Heating molten $ZnCl_2 \cdot 2VPO$ at 150°C. with di-*tert*-butyl peroxide gave a low molecular weight solid polymer in a few hours. Although the monomer contains two polymerizable vinyl groups, the product was soluble in organic solvents and softened to a viscous liquid at 90°C., which indicated the polymer was not crosslinked. The infrared spectrum indicated that some double bonds remained in the product. Under these conditions VPO polymerized in a similar manner.[1,2] Homopolymerization of the complex below 100° was very sluggish.

Copolymers of complexes of vinylphosphine oxides with many common vinyl monomers were prepared readily, provided that the concentration of complex did not exceed about 40 wt.-% of the monomer composition. In Table III, the preparation and properties of representative copolymers of several of the complexes are summarized. In all cases, the copolymers were soluble in appropriate solvents and fusible, in spite of the difunctional nature of the complexes. Apparently the 2:1 complexes did not cause appreciable crosslinking. Even those copolymers containing substantial amounts of salt formed clear, homogeneous moldings with no evidence of separation of the salts from solution in the polymer. Thermal stability, refractive index, density, and softening temperature were similar to the properties of corresponding copolymers lacking the complexed salt. Copolymers containing more than 15–20 wt.-% of the complexes were self-extinguishing. The flame-retardant efficiency varied with the composition of the complex; usually those having the highest phosphorus content were the most efficient. In general, the properties of the copolymers were in line with those to be expected from the base polymer system, e.g., styrene copolymers were hard and brittle (Table IV) and ethyl acrylate copolymers were soft and rubbery (Table V). In spite of the susceptibility of the complex monomers to hydrolysis, molded plaques of the styrene copolymers were not noticeably affected by immersion in water.

Polymers could not be prepared from $FeCl_3 \cdot 2VPO$ or the other complexes of iron, copper, or nickel salts. In fact, these compounds were effective polymerization inhibitors.

TABLE III

Copolymerization of Complexes of Unsaturated Tertiary Phosphine Oxides[a]

Charge								
Complex	Amt. complex, g.	Comonomer[b]	Amt. co-monomer, g.	Solvent	Amt. solvent, ml.	Yield, %	Copolymer composition, wt.-% complex	Reduced viscosity[c]
$ZnCl_2 \cdot 2VPO$	5.0	St	9.0	Acetonitrile	15	60	25	0.13
$ZnCl_2 \cdot 2VPO$	3.0	MMA	12.0	Ethanol	15	80	3.0	0.52
$ZnCl_2 \cdot 2VBP$	20.0	AN	50.0	Acetonitrile	40	67	10	3.0[d]
$Zn(NO_3)_2 . 2VPO$	2.0	AN	6.4	Ethanol	10	58	16	0.63[d]
$HgCl_2 \cdot VPO$	2.5	St	8.0	Ethanol	10	25	9.9	0.28
$SbCl_3 \cdot 2VBO$	5.0	St	9.0	—		48	28	0.48
$SnCl_4 \cdot 2VPO$	6.0	St	14.0	DMF	30	50	14	0.15
$SnCl_4 \cdot 2PPO$	2.0	St	8.0	—		50	6.8	0.36
$SnCl_4 \cdot 2PPO$	2.0	AN	8.0	Acetonitrile	10	70	3.6	2.03[d]
$TiCl_4 \cdot 2VPO$	2.0	AN	6.4	DMF	20	34	6.2	0.52[d]
$UO_2Cl_2 \cdot 2VPO$	6.0	St	17.0	DMF	30	65	16	0.18[d]
$UO_2Cl_2 \cdot 2VBO$	15.0	EA	25.0	—		73	23	0.39

[a] See Experimental section for polymerization procedure.

[b] St = styrene; MMA = methyl methacrylate; AN = acrylonitrile; EA = ethyl acrylate.

[c] Measured at 30°C. for a 0.2% solution in ethylene dichloride.

[d] Measured on a dimethylformamide solution.

TABLE IV
Properties of Styrene Copolymers with Complexes of Vinyldiphenylphosphine Oxide

Styrene copolymer composition, wt.-% complex	Reduced viscosity[a]	Density, g./ml.[b]	Softening point, °C.[c]
25% $ZnCl_2\cdot 2VPO$	0.13	1.06	160
28% $SbCl_3\cdot 2VPO$	0.48	1.04	140
14% $SnCl_4\cdot 2VPO$	0.15	1.05	134
16% $UO_2Cl_2\cdot 2VPO$	0.18	1.07	130
8% VPO	0.66	1.06	139
Polystyrene	1.06	1.02	120

[a] Measured at 30°C. for a 0.2% solution in ethylene dichloride.

[b] Determined by measuring volume and weight of 3 × 0.03 in. molded plaques.

[c] Temperature at which film heated on Koffler melting point bench could be bent without breaking.

TABLE V
Properties of Ethyl Acrylate Copolymers with Vinyldi-*n*-butylphosphine Oxide and Its Zinc Chloride Complex

Polymer Sample	Ethyl acrylate copolymer composition	$ZnCl_2$, wt.-%	Reduced viscosity[a]	Stiffness modulus, psi[b]	Tensile strength, psi[b,c]	Elongation, %[b,c]	Clarity
A	32% $ZnCl_2\cdot 2VBO$	8.6	1.5	50	60	>3000	Transparent
B	12% VBO	—	3.0	34	—	>3000	"
C	Sample B + $ZnCl_2$	8.5	2.2	350	500	600	"
D	Poly(ethyl acrylate) + $ZnCl_2$	10.0	1.5	25	1400	>3000	Opaque

[a] Measured at 30°C. for a 0.2% solution in ethylene dichloride.

[b] Measured at 25°C. on 30-mil plaques by using an Instron tester.

[c] At break.

1-Propenyldiphenylphosphine oxide polymerizes more sluggishly than do the vinylphosphine oxides,[12] and complexes of this monomer also polymerize poorly. Not more than about 5 wt.-% of $SnCl_4\cdot 2PPO$ could be incorporated into copolymers with styrene or acrylonitrile. An attempt to polymerize $HgCl_2\cdot PPO$ by using ethylmagnesium chloride as initiator was unsuccessful.

DISCUSSION

Although the complexes generally contained two presumably equivalent double bonds per molecule, polymers prepared from them were fusible and soluble in selected solvents and showed no evidence of crosslinking. Soluble polymers can result from polyfunctional vinyl monomers if the degree of polymerization is low and reaction is stopped short of the gel point or if polymerization proceeds through both vinyl groups by an intramolecular-intermolecular cyclic polymerization process.[13,14] The former process seems plausible for the formation of homopolymers of the complexes, since molecular weights were low and substantial amounts of unsaturation remained in the products In many cases, however, high molecular weight copolymers containing substantial amounts of the complexes were obtained which also showed no evidence of crosslinking (Table III). On the other hand, a cyclic polymerization process seems unlikely, because of the large size of the rings which would necessarily result.

A third possibility is that both vinyl groups participate in polymerization forming crosslinks, but the coordinate-bond crosslinks are weak and readily dissociate, permitting fusion of the polymer and dissolution in appropriate solvents. However, the infrared spectra of 20% solutions of $ZnCl_2 \cdot 2VPO$ in several organic solvents, including methanol, ethanol, acetonitrile, and tetrahydrofuran, at 50°C. indicate that little dissociation of the complex occurs, as evident by little absorption at 1180 cm.$^{-1}$ characteristic of the free phosphoryl group. Moreover, copolymers of $ZnCl_2 \cdot 2VBO$–ethyl acrylate and VBP–ethyl acrylate were similar in appearance and physical properties to poly(ethyl acrylate) homopolymer (Table V), indicating similar intermolecular polymer interactions in all cases. On mixing a solution of the VBO–ethyl acrylate copolymer with a solution of excess zinc chloride and precipitating the polymer by mixing with a nonsolvent, however, a product was obtained (polymer D, Table V) which was much stiffer than the other copolymers, indicating considerable interaction between the salt and the polymer chains. The high ratio of $ZnCl_2$ to VBP incorporated into the polymer under these conditions, approximately 1:1 rather than 1:2, may account for the fact that the polymer remained soluble. That the properties of polymer C result from interaction between the salt and VBO units in the polymer and not from an inert reinforcing action is apparent by comparing the properties of polymer C with those of polymer D which was prepared in a similar fashion from poly(ethyl acrylate) (Table V). Finally, rigorous washing of an ethyl acrylate–$ZnCl_2 \cdot 2VBO$ copolymer containing 2.8% P with water not only removed the $ZnCl_2$ from the polymer but also substantially reduced the phosphorus content to 1.1% without reducing the degree of polymerization of the polymer (the reduced viscosity increased from 1.3 to 1.9), showing that some of the vinylphosphine oxide was bound in the polymer by coordinate bonds. Consequently, the coordinate bonds are sufficiently strong to effect crosslinking if the two vinyl groups were attached to different polymer chains. Ease of dissociation of coordinate-bond crosslinks, therefore, can not be responsible for the solubility of these copolymers.

Perhaps a more satisfactory explanation is that due to the low polymerization activity of the complexes, the probability of both vinyl groups taking part in the polymerization is low. Moreover, the steric effect of the coordinated cation may reduce the accessibility of the pendant vinyl groups to further polymerization so that, in effect, the two vinyl groups are not of equivalent reactivity. In agreement with this argument, infrared analysis of the copolymers shows that substantial amounts of vinyl unsaturation remains.

EXPERIMENTAL

Vinyldiphenylphosphine Oxide

This compound was prepared by a modification of the procedures of Rabinowitz and Pellon[15] and of Cooper.[16] Ethylene oxide (220 g.) was slowly added to a stirred solution of 660 g. (3.0 mole) of diphenylchlorophosphine in 600 ml. of dry xylene. The temperature of the exothermic reaction was controlled at 40–60°C. After the addition was complete, the mixture was heated 1 hr. at 50–55°C. and then the temperature was raised slowly to reflux (140°C.). A crystal of iodine was added to catalyze the isomerization, and reflux was maintained for 4.5 hr. The solution was cooled to 70°C., and 2 liters of 1.65N sodium hydroxide was added with stirring. (If temperatures higher than 70°C. or excess of strong caustic is used to effect dehydrohalogenation, the formation of resinous products will greatly reduce the yield of the vinylphosphine oxide.) After 30 min., the slurry was added to 2 liters of water and cooled. The crude product, which crystallized, was recovered by filtration and dried. It was purified by distillation (b.p. 180–210°C./1 mm.) giving 532 g. (78%) of distillate which crystallized on cooling. The residue, 46 g., was crude 1,2-ethanebis-(diphenylphosphine oxide).

Recrystallization of the product from toluene gave pure vinyldiphenylphosphine oxide, m.p. 117°C.

trans-1-Propenyldiphenylphosphine Oxide

The procedure for the preparation of this compound is reported elsewhere;[12] the product melted at 125°C.

Vinyldi-*n*-butylphosphine Oxide

Preparation from 2-Chloroethylphosphonyl Dichloride.[17] A solution of 345 g. (1.90 mole) of 2-chloroethylphosphonyl dichloride (prepared by reaction of bis-2-chlorethyl-2-chlorethylphosphonate with phosphorus pentachloride) in 2.5 liters of anhydrous tetrahydrofuran that had been purified by distillation from $LiAlH_4$ was cooled to −78°C. under nitrogen by a Dry Ice–acetone bath. To this solution was added dropwise with stirring at −60 to −78°C. 1400 ml. (4.20 mole) of a 3.0M solution of *n*-butylmagnesium chloride in ether (Arapahoe Chemical Co.). The mixture was then warmed to 0°C. and hydrolyzed with a solution of 160 g. of NH_4Cl in 1.6 liters of water. The organic layer was separated, and the aqueous layer was extracted with two 100-ml. portions of toluene. The organic layers were combined and evaporated to dryness at room temperature, giving 399 g. (93.5% yield) of crude 2-chloroethyldi-*n*-butylphosphine oxide.

A solution of 357 g. (1.46 mole) of this product in 1785 ml. of toluene was mixed with a solution of 90 g. of KOH in 900 ml. of water, and with rapid stirring the mixture was heated slowly to 70°C. and then allowed to cool again to room temperature over a 2-hr. period. The layers were separated and the aqueous layer was extracted with 750 ml. of ethylene dichloride. On evaporation of the combined organic layers at room temperature, a 229-g. residue of vinyldi-*n*-butylphosphine oxide was obtained which crystallized on standing. Purification by distillation gave 222 g. (57% overall yield) of a white solid, b.p. 103°C./1.8 mm., n_D^{30} 1.4650 (super-cooled), m.p. 35°C.

Preparation from Di-*n*-butylphosphinyl Chloride. A solution of 1.30 mole of vinylmagnesium chloride in 600 ml. of tetrahydrofuran was added dropwise over a 2-hr. period to a solution of 255 g. (1.30 mole) of di-*n*-butylphosphinyl chloride[18] in 1.3 liters of tetrahydrofuran at 20–30°C. (Since Grignard reagents are excellent catalysts for the polymerization of vinylphosphine oxides, it is necessary that excess vinylmagnesium chloride be prevented from accumulating in the system or the entire product will be lost to polymer.)

A 310-ml. portion of 2.6*N* hydrochloric acid was added, followed by the addition of 60 g. of NH_4Cl and 200 ml. of ether to effect separation of layers. The organic layer was recovered and distilled to give 164 g. of vinyldi-*n*-butylphosphine oxide (67%), b.p. 118°C./2–3 mm., m.p. 32–34°C., n_D^{30} 1.4692.

Preparation of the Complexes

The complexes were prepared by mixing appropriate proportions of the reactants in either hot ethanol solution or hot toluene solution. In some cases, the complexes precipitated from the hot solutions on mixing ($SnCl_4 \cdot 2VPO$, $TiCl_4 \cdot 2VPO$, and $UO_2Cl_2 \cdot 2VPO$) or they crystallized on cooling the solutions ($SbCl_3 \cdot 2VPO$, $HgCl_2 \cdot VPO$, and $HgCl_2 \cdot PPO$). In other cases, the solvent was evaporated and the residue was recrystallized from isopropyl alcohol ($ZnCl_2 \cdot 2VPO$ and $FeCl_3 \cdot 2VPO$) or toluene [$Zn(NO_3)_2 \cdot 2VPO$]. The complexes of VBO could not be crystallized and were used as residue products. Infrared spectra were obtained with a Perkin–Elmer Model 157 (Infracord) on Nujol mulls or a Baird Model 4–55 or AB-2 Spectrometer on KBr plaques. Analytical data and properties of the compounds are listed in Table I. It is believed that the error in the frequency shifts reported in Table I is about ±5 cm.$^{-1}$.

Free-Radical Polymerization of $ZnCl_2 \cdot 2VPO$

A molten mixture of 6.0 g. of $ZnCl_2 \cdot 2VPO$ and 0.1 g. of di-*tert*-butyl peroxide was heated at 150°C. for 6 hr. The mixture was cooled and triturated with 200 ml. of ether to remove unreacted monomer. The solid product, 6.0 g., softened at about 90°C. and had a reduced viscosity of 0.02

in ethylene dichloride at a 0.2 wt.-% concentration at 30°C. The vinyl absorption band (1604 cm.$^{-1}$) was greatly diminished over that of the monomer.

Copolymerization Procedures

Comonomer and 0.1–0.4 g. of azobisisobutyronitrile were added to the complex dissolved in a suitable solvent in a Pyrex tube or bottle. The vessel was flushed with nitrogen, capped and rotated end-over-end for 20–40 hr. in a water bath at 50°C. The polymer was precipitated by a suitable nonsolvent, washed free of unreacted monomers, and dried in a vacuum desiccator. Generally, the copolymer composition was based on phosphorus analysis. Several copolymers were analyzed for both phosphorus and chlorine, and the close agreement between the two values for copolymer composition indicated that little, if any, of the metal salt was lost on polymerization.

Ionic Polymerization of $ZnCl_2 \cdot 2VPO$

Under a nitrogen atmosphere, 6.0 g. of $ZnCl_2 \cdot 2VPO$ was dissolved in 25 ml. of refluxing anhydrous tetrahydrofuran in a carefully dried, 100-ml. flask. The solution was cooled to 30°C., and 2.2 ml. of 1.2M n-butylmagnesium chloride solution in ethyl ether was added in three increments to the stirred solution over a 30-min. period. The catalyst was added from a hypodermic syringe through an opening sealed by a serum cap. Each addition of catalyst caused a small temperature increase, which quickly subsided, and the formation of a precipitate. An additional 1.0 ml. of catalyst solution was added after 45 min. without causing further temperature rise nor additional precipitation. The white solid product (6 g.) was removed by filtration and dried. It softened at about 145°C. (monomer m.p., 132°C.) and it was not birefringent, indicating it was not the crystalline monomer. The presence of weak vinyl absorption at 1604 and 980 cm.$^{-1}$ and the low reduced viscosity (0.03 in ethylene dichloride solution at 0.2% concentration at 30°C.) indicated the polymer was of low molecular weight.

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References

1. Berlin, K. D., and G. B. Butler, *J. Org. Chem.*, **26**, 2537 (1961).
2. Rabinowitz, R., R. Marcus, and J. Pellon, *J. Polymer Sci.*, **A2**, 1233 (1964).
3. Allcock, H. R., and R. L. Kugel, *J. Polymer Sci.*, **A1**, 3627 (1963).
4. Kabachnik, M. I., *Tetrahedron*, **20**, 655 (1964).
5. Frazer, M. J., W. Gerrard, and R. Twaits, *J. Inorg. Nucl. Chem.*, **25**, 637 (1963).
6. Sheldon, J. C., and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).
7. Alden, K. I., and M. Zackrisson, *Acta Chem. Scand.*, **14**, 994 (1960).
8. Cotton, F. A., and D. M. L. Goodgame, *J. Chem. Soc.*, **1961**, 3735.
9. Issleib, V. K., and B. Mitscherling, *Z. Anorg. Allg. Chem.*, **304**, 73, (1960).
10. Lindquist, I., and G. Olofsson, *Acta Chem. Scand.*, **13**, 1753 (1959).
11. Goodgame, D. M. L., and F. A. Cotton, *J. Chem. Soc.*, **1961**, 2298.

12. Welch, F. J., and H. J. Paxton, *J. Polymer Sci.*, **A3,** 3439 (1965).
13. Kolesnikov, G. S., and S. L. Davydova, *Russ. Chem. Rev.*, **1960,** 670 (in English).
14. Butler, G. B., *J. Polymer Sci.*, **48,** 279 (1960).
15. Rabinowitz, R., and J. Pellon, *J. Org. Chem.*, **26,** 4623 (1961).
16. Cooper, R. S., U. S. Pat. 3,035,096 (1962).
17. Kabachnik, M. I., C. Y. Chang, and E. N. Tsvetkov, *Dokl. Akad. Nauk SSSR,* **135,** 603 (1960).
18. Kasolopoff, G. M., and R. F. Struck, *J. Chem. Soc.*, **1959,** 3950.

Résumé

On a préparé des complexes de l'oxyde de vinyldiphénylphosphine, de l'oxyde vinyldi-*n*-butylphosphine et de l'oxyde *trans*-1-propényl-di-phénylphosphine avec des sels de Zn(II), Hg(I), Sb(III), Sn(IV), Ti(IV), Fe(III), et U(VI). Les glissements observés dans la fréquence d'élongation du phosphoryle par formation de complexes sont identiques aux valeurs rapportées pour les complexes correspondants avec l'oxyde de triphénylphosphine. La polymérisation de ces composés en présence de radical libre et d'initiateurs ioniques est identique à celle des oxydes de phosphines in saturées elles-mêmes. Malgré leur teneur élevée en sel, les polymères forment des plaques claires par moulage; et ils sont complétement solubles dans les solvants organiques appropriés.

Zusammenfassung

Vinyldiphenylphosphinoxyd-, Vinyldi-*n*-butylphosphinoxyd und *trans*-1-Propenyldiphenylphosphinoxydkomplexe wurden mit Salzen von Zn(II), Hg (I),Sb(III), Sn(IV), Ti(IV), Fe(III), und U(VI) dargestellt. Die beobachtete Verschiebung der Phosphorylvalenzfrequenz bei der Komplexbildung war von ähnlicher Grösse wie die für entsprechende Komplexe mit Triphenylphosphinoxyd gefundene. Das Polymerisationsverhalten dieser Verbindungen in Gegenwart radikalischer und ionischer Initiatoren ist demjenigen der ungesättigten Phosphinoxyde selbst ähnlich. Ungeachtet des hohen Salzgehalts biden die Polymeren beim Pressen klare Platten; sie sind in geeigneten organischen Lösungsmitteln vollständig löslich.

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Preparation and Polymerization of Propenyldiphenylphosphine Oxide Isomers

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Synopsis

Isopropenyldiphenylphosphine oxide (I) and both *cis*- and *trans-n*-propenyldiphenylphosphine oxides (II) have been prepared and their structures assigned primarily on the basis of infrared and NMR analyses. Like vinyldiphenylphosphine oxide, these monomers are polymerized sluggishly by free radical catalysts although copolymers with many common vinyl monomers can be prepared. Grignard reagents polymerize (I) very rapidly to low molecular weight products, but the polymerization of II by these catalysts is slower and requires larger amounts of catalyst. Evidence is presented which indicates that in the polymerization of vinyldiphenylphosphine oxide by Grignard reagents molecular weight may be limited by a chain transfer to monomer process.

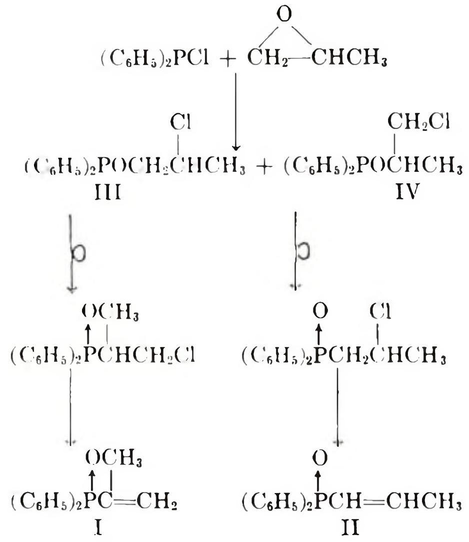
INTRODUCTION

In the presence of free-radical catalysts vinyldiphenylphosphine oxide polymerizes reluctantly to low molecular weight polymers,[1,2] and only relatively minor amounts of this monomer can be incorporated into copolymers with the common vinyl monomers.[2] Anionic polymerization is rapid but also leads to low molecular weight polymers.[3] Somewhat higher polymers seem to be formed in the presence of ionizing radiation.[4] To determine to what extent the polymerization behavior of vinylphosphine oxides is affected by the presence of hydrogen atoms adjacent to the phosphoryl group, we undertook the synthesis of isopropenyldiphenylphosphine oxide for polymerization studies. Neither this monomer nor polymers derived from it has hydrogen atoms activated by phosphoryl groups. In the course of this investigation the isomeric *cis*- and *trans-n*-propenyldiphenylphosphine oxides were prepared also and their polymerization studied.

RESULTS

Monomer Preparation

Since vinyldiphenylphosphine oxide is easily obtained by the reaction of diphenylchlorophosphine with ethylene oxide followed by thermal isomerization and dehydrohalogenation,[5-7] the analogous process for the preparation of isopropenyldiphenylphosphine oxide from propylene oxide was investigated. With propylene oxide, however, the reaction can take two courses leading to the *n*-propenyl isomer II as well as the desired isopropenyl isomer I.



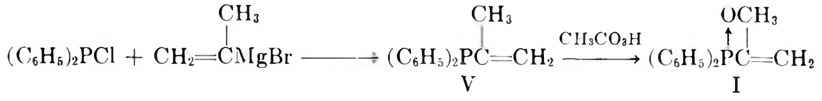
(1)

A slight excess of propylene oxide was added to diphenylchlorophosphine at 50–60°C. The Arbuzov isomerization was effected by heating the initial reaction product in refluxing decalin at 188°C., and dehydrochlorination was accomplished by using triethylamine. The crude product was recovered as a crystalline solid by vacuum distillation. Elemental analysis, the NMR spectrum, and the infrared spectrum (Table I) confirmed that the product was a propenyldiphenylphosphine oxide, but it was not clear whether it was I or II. Hydrogenation of a sample of the product gave *n*-propyldiphenylphosphine oxide, identified by NMR, indicating clearly that the product was the *n*-propenyl isomer II.

Although only the one product was obtained in pure form from this reaction, it is very likely that both isomers were actually produced in the reaction. In fact, the infrared spectrum of the initial reaction product of propylene oxide and diphenylchlorophosphine indicated both phosphinite isomers III and IV were probably present at this stage in the synthesis (see Experimental section).

Because of the high solubility of I in aromatic solvents and the difficulty in crystallizing it, it is likely that it would have been lost in the workup procedure.

The more direct procedure involving the intermediate V was used for the preparation of isopropenyldiphenylphosphine oxide.

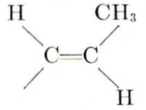
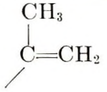
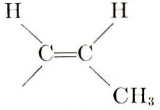


$$(C_6H_5)_2PCl + CH_2{=}\overset{CH_3}{\overset{|}{C}}MgBr \longrightarrow \underset{V}{(C_6H_5)_2P\overset{CH_3}{\overset{|}{C}}{=}CH_2} \xrightarrow{CH_3CO_3H} \underset{I}{(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}\overset{CH_3}{\overset{|}{C}}{=}CH_2}$$

(2)

TABLE I

Some Characteristic Infrared Frequencies of $(C_6H_5)_2P(O)R$[a,b]

Frequency, cm.$^{-1}$			
 (*trans*-II)	 (I)	 (*cis*-II)	Assignment
3080(m), 2980(m)	3080(m), 2940(w)	3080(m), 2970(w)	C—H stretching[c]
1625(s)	1618(w)	1625(s)	C═C stretching[c]
1587(w), 1486(w)	1590(w), 1482(m)	1592(w), 1488(m)	Phenyl[c]
1440(s)	1440(s)	1440(s)	P—phenyl[d]
1180(s)	1184(s)	1182(s)	P → O stretching[e]
1122(s)	1118(s)	1118(s)	Unassigned
—	1100(m)	—	Unassigned
1072(w)	1074(w)	1072(w)	Unassigned
1000(s), 797(s)	949(m), 937(m)	731(s)	═C—H deformation[e]
—	1000(w)	995(w)	P—phenyl[d]
756(s), 695(s)	757(s), 693(s)	755(m,d), 697(s)	Phenyl[c]
719(s), 744(s)	714(s), 734(s)	974(w), 723(s)	Unassigned

[a] Spectra were determined on 1% KBr plaques using a Baird-Atomic spectrophotometer with a sodium chloride prism.

[b] (w) = weak; (m) = medium; (s) = strong; (d) = doublet.

[c] Data of Bellamy.[8]

[d] Data of Corbrige.[12]

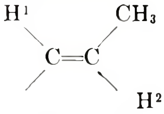
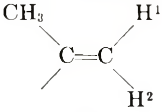
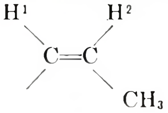
[e] Tentative assignment.

The Grignard reagent was prepared from 2-bromopropene in tetrahydrofuran and the reaction with the chlorophosphine was carried out at −70°C. Several attempts to prepare the Grignard reagent from 2-chloropropene were unsuccessful. Oxidation of the intermediate phosphine with peracetic acid in ethyl acetate solution afforded a 93% yield of a low melting solid product. On recrystallization I was obtained in 65% yield together with a 10% yield of *cis*-1-propenyldiphenylphosphine oxide. This compound arose from 10% *cis*-1-bromopropene present as a contaminant in the 2-bromopropene starting material. Since some *trans*-1-bromopropene was also present in the starting material, it would be expected that *trans*-1-propenyldiphenylphosphine oxide should also have been formed in the reaction. None was isolated, however.

Structure assignments for the *cis* and *trans* isomers were based primarily on comparison of the infrared spectra (Table I). The =C—H deformation in *trans*-olefins normally occurs at about 970 cm.$^{-1}$, whereas this absorption in *cis*-olefins occurs at about 690 cm.$^{-1}$. Conjugation of the double bond with an electronegative group shifts this absorption to higher frequency.[8]

TABLE II

Coupling Constant Assignments for $(C_6H_5)_2P(O)R$[a]

	J, cycle/sec.		
Coupling	 (*trans*-II)	 (I)	 (*cis*-II)
P, CH_3	2.5	12.5	3.2
P, H^1	—	41.3[b]	—
P, H^2	—	19.8[b]	—
CH_3, H^1	1.0	1.6	1.5
CH_3, H^2	5.5	1.2	7.0

[a] Spectra were determined at 60 Mcycles in $CDCl_3$ solutions with tetramethylsilane as an internal standard with a Varian Model A-60 spectrometer.

[b] It is assumed that *trans* coupling is larger than *cis* coupling.[11]

In the propenylphosphine oxide isomer, this =C—H deformation appears at 1000 cm.$^{-1}$ for *trans* and 731 cm.$^{-1}$ for *cis*. In addition as is usually the case, the *cis* isomer has a lower melting point than the *trans* isomer.

Furthermore, reaction of *cis*-1-bromopropene with magnesium and subsequent reaction of the Grignard reagent are expected to proceed with retention of configuration,[9] whereas the *trans* isomer would be the isomer expected to be formed on dehydrohalogenation.[10] Finally, the chemical shift for the methyl group in *cis*-II (δ 2.08 ppm) is farther downfield than that in *trans*-II (δ 1.95 ppm), in agreement with other observations of relative chemical shifts of methyl groups *cis* and *trans* to an electronegative group[11] (Table II).

Polymerization

Polymerization of these monomers by using the usual free-radical initiators was very sluggish. No polymer was formed with any of these monomers on heating several days at 60°C. with azobisisobutyronitrile catalyst. Low molecular weight polymers could be formed by heating the monomers with di-*tert*-butyl peroxide to temperatures above 100°C. (Table III). Isopropenyldiphenylphosphine oxide did copolymerize readily with many vinyl monomers when present as a minor component of the monomer mixture. Copolymers containing 10–20 wt.-% of the phosphorus component were prepared with acrylamide, acrylonitrile (Table IV), ethyl acrylate, and styrene (Table V). On the other hand, both *cis* and *trans*-II were extremely sluggish toward copolymerization. No more than about 5 wt.-% could be incorporated into copolymers with styrene or acrylonitrile.

TABLE III

Polymerization of Substituted Vinyldiphenylphosphine Oxides[a]

$(C_6H_5)_2P(O)R$	Time, hr.	Yield, %	η_{sp}/c[b]
$—CH{=}CH_2$	1[c]	88	0.029
$—C(CH_3){=}CH_2$	24	20	0.036
$—CH{=}CH—CH_3$(*trans*)	13	75[d]	0.024
$—CH{=}CH—CH_3$(*cis*)	32	18	0.030

[a] To 5.0 g. of monomer was added 0.15 g. of di-*tert*-butyl peroxide in three increments at 140–150°C. over a 6-hr. period. The product was diluted with 20 ml. of toluene and precipitated with 200 ml. of ether.

[b] In ethylene dichloride at 30°C. at a concentration of 1.0%.

[c] On addition of 0.1 g. of catalyst to 11 g. of molten monomer at 150°C. the temperature rose spontaneously to 205°C. The product was diluted with 50 ml. of toluene and precipitated with 800 ml. of heptane.

[d] The toluene solution of the product was precipitated with 200 ml. of heptane.

TABLE IV

Copolymers with Acrylonitrile[a]

$(C_6H_5)_2P(O)R$	$(C_6H_5)_2P(O)R$ in monomer, %	Yield of polymers, %	$(C_6H_5)_2P(O)R$ in polymer, %	η_{sp}/c[b]
$—CH{=}CH_2$	20	70	14.7	2.4
$—C(CH_3){=}CH_2$	25	60	21	0.32
$—CH{=}CH—CH_3$(*trans*)	20	30	4.1	0.19
$—CH{=}CH—CH_3$(*cis*)	20	63	3.1	2.3

[a] Polymerizations were run with 10 g. of monomer, 10 ml. of benzene, 0.2 g. of azobisisobutyronitrile in Pyrex polymerization tubes sealed with crown caps at 50°C. for 20 hr. The polymers were recovered by filtering from the resulting suspension, washing free of unreacted monomers, and drying at 50°C. under vacuum.

[b] In dimethylformamide at 30°C. at a concentration of 0.2%.

TABLE V
Copolymers with Styrene[a]

$(C_6H_5)_2P(O)R$	$(C_6H_5)_2P(O)R$ in monomer, %	Yield of polymers, %	$(C_6H_5)_2P(O)R$ in polymer, %	η_{sp}/c[b]
$—CH{=}CH_2$	10	45	7.8	0.18
$—CH{=}CH_2$	25	54	11.8	0.15
$—C(CH_3){=}CH_2$	25	35	8.8	0.22
$—CH{=}CH—CH_3$(*trans*)	20	30	4.1	0.19
$—CH{=}CH—CH_3$(*cis*)	25	47	4.7	0.16

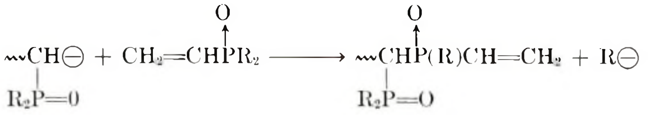
[a] Polymerizations run with 10 g. of monomer, 10 ml. of benzene, and 0.2 g. of azobisisobutyronitrile in Pyrex polymerization tubes sealed by crown caps at 50°C. for 20–36 hr. Polymers were recovered by precipitating into 100 ml. of methanol, washing free of monomer with methanol, and drying under vacuum at 50°C.

[b] In benzene or ethylene dichloride at 30°C. at a concentration of 0.2%.

The polymerization of I and *trans*-II by *n*-butylmagnesium chloride catalyst was compared with the polymerization of vinyldiphenylphosphine oxide[3] (Table VI). All formed low molecular weight polymers, but the polymerization of *trans*-II was much slower and required more catalyst than did the polymerization of the other monomers. Isopropenyldiphenylphosphine oxide polymerized as readily as did the vinylphosphine oxide to a product of very similar molecular weight. Slightly more catalyst was required, however, probably because the monomer was not quite as pure.

The polymers were molded to transparent, rigid but quite brittle plaques which were nonflammable. The polymers were soluble in polar organic solvents.

Allcock and Kugel reported that poly(vinyldiphenylphosphine oxide) was crystalline when prepared with Grignard catalysts (other than *n*-butylmagnesium chloride!) in toluene and the polymer chain length corresponded to approximately one polymer chain per catalyst molecule.[3] This polymer prepared in refluxing benzene (Table VI) gave a crystalline x-ray pattern. About 200 monomer molecules were converted to polymer per initiator molecule, which would require that the polymer have a molecular weight of about 50,000 if each catalyst molecule formed one polymer chain. However, the low reduced viscosity and relatively low melting point[3] indicate that the molecular weight of polymer was probably not over 5,000. Therefore, in this experiment about ten polymer molecules were formed from each molecule of catalyst added. Consequently, under these conditions molecular weight is limited apparently by a chain transfer process. It is proposed that transfer to monomer resulting from a displacement reaction on phosphorus is responsible for the low molecular weights.



$$\sim\underset{\substack{|\\R_2P{=}O}}{CH}^{\ominus} + CH_2{=}CH\overset{\substack{O\\\uparrow}}{P}R_2 \longrightarrow \sim\underset{\substack{|\\R_2P{=}O}}{CH}\overset{\substack{O\\\uparrow}}{P}(R)CH{=}CH_2 + R^{\ominus} \qquad (3)$$

TABLE VI

Polymerization of Substituted Vinyldiphenylphosphine Oxides by Butylmagnesium Chloride[a]

$(C_6H_5)_2P(O)R$	Monomer concn., mole/l.	BuMgCl concn., mole-%[b]	Temperature, °C.	Time, hr.	Yield, %	η_{sp}/c[c]	Polymer softening point, °C.[d]	Anal. Found (and calcd.) C, %	H, %	P, %
$—CH=CH_2$[e]	0.68[f]	0.45	70–82	1	89	0.055	215	72.7 (73.8)	5.7 (5.7)	13.3 (13.6)
$—C(CH_3)=CH_2$	1.0[g]	2.4	25–43	2	61	0.051	147	74.1 (74.4)	6.3 (6.2)	12.7 (12.8)
$—CH=CH—CH_3$(*trans*)	0.85[f]	24[h]	80	20	72	0.040	182	63.7[i] (74.4)	6.3 (6.2)	10.6[i] (12.8)

[a] See Experimental section for procedure.

[b] Based on monomer.

[c] Determined at 30°C. on 0.2% ethylene dichloride solutions.

[d] Measured on a Koffler melting point bench.

[e] Data of Welch and Paxton.[7]

[f] Benzene solution.

[g] Toluene solution.

[h] Two-thirds of catalyst was added over 3-hr. period; mixture was refluxed 15 hr., and remaining catalyst was added over final 2-hr. period.

[i] The polymer was contaminated by magnesium residues from the catalyst.

EXPERIMENTAL

trans-n-Propenyldiphenylphosphine Oxide (*trans*-II)

To 220 g. (1.00 mole) of diphenylchlorophosphine (Victor Chemical Company, distilled before use, b.p. 115°C./0.5 mm.) in a 1-liter flask fitted with a stirrer and condenser was added dropwise 64 g. (1.1 mole) of propylene oxide at 50–60°C. under a dry nitrogen atmosphere. After addition was complete, the solution was stirred an additional 2 hr. at 60°C., giving 260 g. of an oil. The infrared spectrum was that expected for a mixture of the chloropropyl diphenylphosphinites, III and IV; some characteristic bands of neat oil include 1440(s) and 1000(m) cm.$^{-1}$, (C_6H_5–P);[12] 1182(w), 1137, 1100(m), and 965(s) cm.$^{-1}$, ($>$CH–O–P^{III});[13] and 1064(s), 1030, and 892(m) cm.$^{-1}$ (probably –CH_2O–P^{III}).[13]

This oil was added slowly over a 35-min. period to 200 ml. of refluxing anhydrous decalin (174–188°C.), and the solution was refluxed an additional 25 min. When a few crystals of iodine were added at 170°C. to insure completion of the isomerization, evolution of hydrogen chloride occurred. After 30 min. the solution was cooled to 30°C., whereupon it separated into two layers. The upper decalin layer was decanted and discarded. The product layer was mixed with 110 g. of triethylamine and 200 ml. of toluene, and the mixture was refluxed for 3 hr. The mixture was cooled and extracted with 200 ml. of water to remove triethylamine hydrochloride. The aqueous solution was extracted with two 100-ml. portions of ethylene dichloride, and the combined organic fractions were evaporated under reduced pressure. The residue was distilled to give 163 g. (67% yield) of distillate, b.p. 190–210°C./1 mm., which crystallized in the receiver, and a brown, viscous residue which was discarded. By recrystallization from toluene 88 g. of *trans-n*-propenyldiphenylphosphine oxide, m.p. 124–125°C., and 53 g. of less pure material, m.p. 81–118°C., was recovered.

ANAL. Calcd. for $C_{15}H_{15}PO$: C, 74.4%; H, 6.2%; P, 12.8%. Found: C, 74.3%; H, 6.6%; P, 12.1%.

The NMR spectrum showed a complex doublet centered at δ 1.95 ppm (tetramethylsilane internal reference), a series of bands from δ 5.9 to 6.9 ppm, and a multiplet centered about δ 7.6 ppm in a ratio of 3:2:10. These were assigned to an allylic methyl group, two vinyl hydrogens, and the phenyl hydrogens, respectively.

Infrared bands at 1625, 1000, and 797 cm.$^{-1}$ disappeared on hydrogenation, and the methyl resonance appeared as a triplet centered at δ 1.0 ppm, indicating the methyl group was adjacent to a methylene group. There were two broad resonance bands in the range δ 1.4–2.6 ppm which were centered at δ 1.7 and 2.3 ppm, respectively, attributable to methylene groups, and a phenyl complex centered about δ 7.6 ppm. The ratio of phenyl protons to methyl protons was 10:3. This clearly indicates that the product is *n*-propyldiphenylphosphine oxide and not the isopropyl isomer.

Isopropenyldiphenylphosphine (V)

Isopropenylmagnesium bromide was prepared from 363 g. (3.0 mole) of 2-bromopropene (Columbia Organic Chemicals Co., Columbia, S. C.) and 90 g. (3.7 mole) of magnesium turnings in 1200 ml. of tetrahydrofuran. Vapor-phase chromatography showed the sample to be 84% 2-bromopropene, 10% *cis*-1-bromopropene, and 5% *trans*-1-bromopropene. Structures of these isomers were assigned from their infrared spectra.[14] After formation of the Grignard reagent it was necessary to add an additional 1000 ml. of tetrahydrofuran to prevent precipitation of the product on cooling. The yield by titration was 2.67 mole (89%).

The Grignard solution was cooled to −70°C., and 500 g. (2.50 mole) of diphenylchlorophosphine was added dropwise under a nitrogen atmosphere while the temperature was kept below −60°C. The mixture was then warmed to room temperature and hydrolyzed with a solution of 300 g. of ammonium chloride in 2000 ml. of water. The organic layer which separated was extracted with 200 ml. of water and the combined aqueous layers were extracted with two 200-ml. portions of toluene. The toluene extracts were combined with the original organic layer and distilled under reduced pressure. All operations were carried out under a nitrogen atmosphere with minimum exposure to air. Crude propenyldiphenylphosphine (513 g.) was recovered as a liquid, b.p. 105–120°C./1 mm., in 91% yield. It was not further characterized.

Isopropenyldiphenylphosphine Oxide (I) and *cis*-*n*-propenyldiphenylphosphine Oxide (*cis*-II)

A solution of 503 g. (2.22 moles) of the crude isopropenyldiphenylphosphine in 500 ml. of ethyl acetate was cooled to −20°C. under nitrogen and 710 g. (2.30 mole) of a 24.6% solution of peracetic acid in ethyl acetate[15] was added slowly over 1.5 hr. The solution was warmed to 25°C., diluted with 200 ml. of ethylbenzene, and extracted successively with two 330-ml. portions of water, 100 ml. of 10% sodium bisulfite solution, and 200 ml. of water to remove acetic acid and destroy any unreacted peracetic acid. The organic layer was evaporated under reduced pressure; the residue was dissolved in 500 ml. of toluene; and the solution was heated at reflux to remove water. The hot solution was filtered and evaporated to dryness, and the residue was distilled rapidly at reduced pressure. A 20-g. forerun having the odor of acetic acid was discarded, and the crude product, 502 g., (93% yield) was obtained boiling at a pot temperature of 167–175°C./0.1 mm. The crude product, which crystallized in the receiver, was dissolved in a refluxing mixture of 450 ml. of toluene and 600 ml. of heptane and allowed to cool to room temperature overnight. One crop of white crystals was recovered, 84 g., m.p. 72–100°C. On recrystallization from 500 ml. of toluene, 35 g. of white crystalline *cis*-II was obtained, m.p. 113–116°C., mixed m.p. with *trans* isomer, 92–100°C.

ANAL. Calcd. for $C_{15}H_{15}PO$: C, 74.4%; H, 6.2%; P, 12.8%. Found: C, 74.0%, H, 6.1%; P, 13.0%.

An additional 15 g. of crystalline solid was recovered from the filtrate. The methyl group in the NMR spectrum appeared as a doublet centered at δ 2.08 ppm (weight 3), each band of which was split into two doublets. The vinyl proton resonance was split into a complex of about 12 bands spaced between δ 5.7 and 7.3 ppm (weight 2), and the phenyl proton complex was centered about δ 7.5 ppm (weight 10).

The filtrate was evaporated to dryness, and the residual oil was crystallized from a mixture of cyclohexane and toluene. Although oiling caused considerable difficulty, four crops of crystalline solid totaling 364 g. was recovered, m.p. 40–60°C. Careful recrystallization from a 1:1 mixture of cyclohexane and cyclohexene gave isopropenyldiphenylphosphine oxide as large platelets, m.p. 55–56°C.

ANAL. Calcd. for $C_{15}H_{15}PO$: C, 74.4%; H, 6.3%; P, 12.8%. Found: C, 74.2%; 6.3%; P, 12.5%.

The methyl proton resonance was split into a doublet centered at δ 2.00 ppm. Each band of the doublet was in turn split into two overlapping doublets by the *cis* and *trans* vinylene protons. Four multiplets appeared in the vinyl proton region at δ 5.50, 5.62, 5.83, and 6.31 ppm. The phenyl proton complex was centered at δ 7.6 ppm, and the methyl/vinyl/phenyl proton ratios were 3:2:10.

Free Radical Polymerization

The polymerization procedure and results are described in Tables III–V.

Anionic Polymerization

Solutions of the monomers in benzene or tetrahydrofuran were stored over calcium hydride under a nitrogen atmosphere. They were transferred through glass tubing by nitrogen pressure directly into the polymerization vessel with minimum exposure to the atmosphere. Polymerizations were conducted in four-necked, 125- or 250-ml. flasks which were dried by heating at 120°C./1 mm. pressure and purging several times with nitrogen. Agitation was provided by a magnetic stirring bar or a glass paddle stirrer. *n*-Butylmagnesium chloride catalyst (1.0*M*) was added dropwise over the duration of polymerization with a hypodermic syringe through a rubber serum cap into the monomer solution. The polymers of vinyldiphenylphosphine oxide and I precipitated from solution as formed and were separated simply by filtration; the polymer from *trans*-II was recovered by precipitation with 500 ml. of ether. The products were washed free of monomer with ethyl ether and dried under vacuum at 50°. The polymerization data are summarized in Table VI.

CONCLUSIONS

Isopropenyldiphenylphosphine oxide is very similar to vinyldiphenylphosphine oxide in its response to radical and ionic catalysts, and it gives products in the same molecular weight range. Both *cis*- and *trans*-*n*-propenyldiphenylphosphine oxide are much more difficult to polymerize, although homopolymers can be formed.

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References

1. Berlin, K. D., and G. B. Butler, *J. Org. Chem.*, **26**, 2537 (1961).
2. Rabinowitz, R., R. Marcus, and J. Pellon, *J. Polymer Sci.*, **A2**, 1233 (1964).
3. Allcock, H. R., and R. L. Kugel, *J. Polymer Sci.*, **A1**, 3627 (1963).
4. Tsetlin, B. L., T. Y. Medved, Y. G. Chikishev, Y. M. Polykarpov, S. R. Rafikov, and M. I. Kabachnik, *Vysokomol. Soedin.*, **3**, 1117 (1961).
5. Kabachnik, M. I., T. Y. Medved, and Y. M. Polykarpov, *Dokl. Akad. Nauk SSSR*, **135**, 849 (1960).
6. Cooper, R. S., U. S. Pat. 3,005,000 (1962); U. S. Pat. 3,035,096 (1962).
7. Welch, F. J., and H. J. Paxton, *J. Polymer Sci.*, **A3**, 3427 (1965).
8. Bellamy, L. J., *The Infra-Red Spectra of Complex Molecules*, Wiley, New York, 1958.
9. Normant, H., and P. Maitte, *Bull. Soc. Chim. France*, **1956**, 1439.
10. Hine, J., *Physical Organic Chemistry*, McGraw-Hill, New York, 1962, p. 191.
11. Reilly, C. A., *J. Chem. Phys.*, **37**, 456 (1962).
12. Corbrige, D. E. C., *J. Appl. Chem.* (*London*), **6**, 456 (1956).
13. Thomas, L. C., and R. A. Chittenden, *Spectrochim. Acta*, **20**, 489 (1964).
14. Harwell, K. E., and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).
15. Phillips, B., F. C. Frostick, and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

Résumé

L'oxyde d'isopropényldiphénylphosphine (I) et les deux oxydes cis et trans-*n*-propényldiphénylphosphine (II) ont été préparés et leurs structures déterminées sur la base des analyses infra-rouge et RNM. Semblablement à l'oxyde de vinyldiphénylphosphine, ces monomères sont polymérises lentement par des catalyseurs à base de radicaux libres bien que des copolymères peuvent aussi être préparés avec des monomères vinyliques quelconques. Les réactifs de Grignard polymérisent (I) très rapidement et donnent des produits de bas poids moléculaire, par contre la polymérisation de (II) par des mêmes catalyseurs, est plus lente et requiére de plus grandes quantités de catalyseur. On a mis en évidence que dans la polymérisation de l'oxyde de vinyldiphénylphosphine par les réactifs de Grignard, le poids moléculaire peut être limité par un processus de transfert de chaîne sur monomère.

Zusammenfassung

Isopropenyldiphenylphosphinoxyd (I) sowie cis- und trans-*n*-Propenyldiphenylphosphinoxyd (II) wurden dargestellt und ihre Struktur hauptsächlich auf Grundlage von Infrarot- und NMR-Analyse ermittelt. So wie Vinyldiphenylphosphinoxyd werden diese Monomeren durch radikalische Katalysatoren nur zögernd polymerisiert, es können aber Kopolymere mit vielen üblichen Vinylmonomeren dargestellt werden. Grignardreagentien polymerisieren (I) sehr rasch zu niedermolekularen Produkten, die Polymerisation von (II) durch diese Katalysatoren verläuft jedoch langsamer und erfordert grössere Mengen an Katalysator. Es scheint, dass bei der Polymerisation von Vinyldiphenylphosphinoxyd durch Grignardreagentien das Molekulargewicht durch eine Kettenüber tragung zum Monomeren begrenzt wird.

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Polymerization Studies on Methyl and Ethyl α-Fluoromethylacrylate

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Synopsis

Ethyl α-fluoromethylacrylate was prepared from ethyl α-chloromethylacrylate by reaction with potassium fluoride in sulfolane. The methyl ester was prepared by transesterification. The ethyl ester was found to be unexpectedly quite toxic. Homopolymers and copolymers of both monomers were found to have lower softening temperatures than polymers from the corresponding methacrylate monomers. Reactivity ratios were determined for ethyl α-fluoromethylacrylate (M_2) with styrene ($r_1 = 0.34, r_2 = 0.09$) and with methyl methacrylate ($r_1 = 1.05, r_2 = 0.51$).

The recent papers of Baldwin and Reed[1,2] reporting the polymerization behavior of a series of ethyl α-(substituted methyl)acrylates prompt us to report our related studies concerning heat distortion temperatures of homo- and copolymers of methyl (I) and ethyl α-fluoromethylacrylate (II). Poly(methyl α-fluoroacrylate) has been reported[3] to exhibit a heat distortion temperature of 114°C., slightly higher than that of poly(methyl methacrylate) (PMMA), and more than 100°C. higher than that of poly(methyl acrylate). However, copolymers of methyl α-trifluoromethylacrylate with MMA, methyl α-fluoroacrylate, and methyl α-chloroacrylate were reported[3] to soften at lower temperatures than the corresponding homopolymers. We wished to determine the effect of replacement by fluorine of a single hydrogen attached to the α-methyl carbon on the glass temperature and other properties of PMMA. Toxicity data and copolymerization parameters for II are also reported.

RESULTS AND DISCUSSION

Monomer Synthesis

Previous syntheses[4,5] of methyl α-fluoromethylacrylate have involved synthesis of fluoroacetone, formation of the cyanhydrin, conversion to methyl α-hydroxy-β-fluoroisobutyrate, acetylation, and pyrolysis. Reed and Baldwin[2] utilized the commercially available ethyl α-hydroxymethylacrylate,[6] which they converted first to the bromomethylacrylate with PBr_3 or HBr, and then to the fluoro compound with silver fluoride. We have found it simpler to convert ethyl α-chloromethylacrylate[2,7] to II with potassium fluoride in sulfolane. Since the corresponding methyl α-hydroxymethylacrylate was not readily available, we prepared I by transesterification of II with excess methanol and sulfuric acid.

The LD_{50} value of II with male albino rats was found to be between 7 and 20 mg./kg., which is unexpectedly low, being near that for monofluoroacetic acid.[8] The monomer is also a potent lachrymator, and should be handled with great caution.

Homopolymerization

Reed and Baldwin[2] have reported monomer II to polymerize more than twice as fast as MMA with equivalent amounts of azobisisobutyronitrile initiator in ethyl acetate at 60°C. Neither normal nor degradative chain transfer processes were found to be of any significance in its homopolymerization. We have prepared homopolymers of I and II in solution and of II in bulk. Table I summarizes the results; it can be seen that the fluorine group appears to depress the softening temperature in both instances. This is contrary to the effect noted[3] when fluorine replaces the α-hydrogen in poly (methyl acrylate). Comparative results for the trifluoromethyl group are not available, as Anspon[3a] was not able to homopolymerize methyl α-trifluoromethylacrylate, contrary to disclosures of an earlier patent.[9]

TABLE I
Properties of Homopolymers of Alkyl Methacrylates and Alkyl α-Fluoromethylacrylates

Monomer	Reduced specific viscosity, dl./g.[a]	Vicat softening temperature, °C.	α-Peak, °C.[b]
I	0.36	95	108
II[c]	0.68	54	63
MMA	0.39	118	124
EMA[d]	—	65	83

[a] Reduced specific viscosity at 2 g./l. in ethylene dichloride at 30°C.
[b] Dielectric α-softening peak as described by Steck.[10]
[c] Prepared in solution; all other polymers prepared in bulk.
[d] Ethyl methacrylate.

The results can be rationalized somewhat if we compare the relative effects of a fluorine group compared to a methyl group, rather than considering fluorine as replacement for hydrogen. This is done in Table II for replacement at sites directly on the polymer chain, sites one —CH_2— group removed, and at sites on the ester function.

It appears that the fluorine group has the same general effect as methyl in all three instances, stiffening the polymer chain when directly substituted on the backbone site, causing a decrease in glass temperature when the α-substituted group is enlarged beyond methyl, and raising the glass temperature when side chain branching is involved. Fuller explana-

TABLE II
Comparison of Effects of Fluorine, Hydrogen, and Methyl on Glass Temperature

Structure	R	T_g, °C.[a]	Reference
$CH_2{=}CR{-}COOCH_3$	H	8	11
	F	108, 114[b]	3
	CH_3	106	11
$CH_2{=}C(CH_2R){-}COOC_2H_5$	H	65	11
	F	43[c]	11
	CH_3	33[d]	11
$CH_2{=}CH{-}COOCH_2CR_3$	H	−22	11
	F	−10[e]	12
	CH_3	+21	11

[a] Dilatometrically determined unless otherwise noted.
[b] ASTM D648-45T; a PMMA sample measured by these authors had a value of 106°C.
[c] Sample prepared by Reed and Baldwin of unknown molecular weight.
[d] Actual value 27°C. for M_n = 40,000; arbitrarily adjusted from data[13] on PMMA.
[e] Refractive index change.

tion of this unexpected effect would require more careful glass temperature determinations on a wider variety of polymers.

Comparison of polymers of methyl methacrylate and of methyl α-fluoromethylacrylate prepared in bulk with *n*-dodecyl mercaptan as chain transfer agent show the latter polymer to be more stable to thermal degradation as measured by weight loss in air at 260°C. Comparison of the same polymers by utilizing the thermovolatilimetric apparatus of Noel[14] showed the two to be about equivalent in stability in an air atmosphere and for PMMA to be slightly more stable in helium.

Copolymerization

Bulk copolymers of MMA/and II at 75/25 and 50/50 ratios of monomers were prepared and compared with equivalent copolymers of MMA and EMA. As expected from the homopolymerization results, the Vicat softening temperatures and α-peak values from dielectric measurements[10] were depressed when the fluorinated monomer was substituted for EMA. The 50/50 copolymer of MMA and II was approximately equal to the 50/50 MMA–EMA copolymer in flexural properties, impact strength, and burning rate, but both softening temperature determinations were 4–5°C. lower for the fluorine-containing polymer.

It is difficult to make direct comparisons between MMA–ethyl α-fluoromethylacrylate copolymers and MMA–methyl α-trifluoromethylacrylate copolymers reported by Anspon,[3] but qualitatively it appears that the replacement of three hydrogens by fluorine will depress the heat distortion temperature at least three times the amount imparted by replacement of only one hydrogen with fluorine.

Copolymerization parameters for II with methyl methacrylate were evaluated from a study of relative monomer disappearance as followed by gas chromatographic analysis (GLC). The values with styrene were

TABLE III
Copolymerization Parameters for Ethyl α-Fluoromethylacrylate

Monomer M_1	Method	r_1	r_2	Q_1	e_1	Q_2	e_2
Methyl methacrylate	GLC	1.05 ± 0.04	0.513 ± 0.046	0.74	0.40	0.97	1.19
Styrene	Carbon	0.341 ± 0.013	0.091 ± 0.017	1.0	−0.80	0.66	1.06

obtained from elemental analysis of the low conversion copolymers (Table III).

The enhanced e value of II over MMA and EMA ($e = 0.50$)[11] presumably reflects the inductive electron-attracting influence of the carbon–fluorine bond on the carbon–carbon double bond. Suitable e values for alkyl di- and trifluoromethylacrylates are not available for comparison, but examination of relative e values[15] for ethylene (−0.20) versus vinyl fluoride (1.28), for vinyl acetate (−0.22) versus vinyl trifluoroacetate (1.06), for *p*-methylstyrene (−0.98) versus *p*-trifluoromethylstyrene (−0.29), and for styrene (−0.80) versus *p*-fluorostyrene (−0.12) reveals a consistent trend.

EXPERIMENTAL

Ethyl α-hydroxymethylacrylate was purchased from the Koppers Company, Inc., and employed without further purification. Ethyl α-chloromethylacrylate[7] was prepared by a modification of the synthesis described by Reed and Baldwin,[2] b.p. 53–54°C./5 mm., n_D^{20} 1.4485.

Preparation of Ethyl α-Fluoromethylacrylate (II)

A one-liter, three-necked creased flask was fitted with a high speed stirrer, pressure-equalized dropping funnel, thermometer, and a 12-in. Vigreaux column connected to a distilling head. The flask was charged with 500 ml. of sulfolane and 250 g. (4.3 moles) of anhydrous potassium fluoride. The reaction mixture was stirred at 170°C. and the pressure reduced to 90 mm. Ethyl α-chloromethylacrylate (228 g., 1.53 mole) was added dropwise over a period of 9.5 hr. After discarding a small forerun containing azeotroped water, all material (196 g.) which distilled at a temperature less than 85°C./90 mm. was collected. Analysis by gas-liquid chromatography indicated the mixture consisted of 152 g. ethyl α-fluoromethylacrylate and 44 g. ethyl α-chloromethylacrylate. The mixture was inhibited with diphenylpicrylhydrazyl and redistilled through a 24-in. gold-plated spinning band column to give ethyl α-fluoromethylacrylate, b.p. 65–66°C./75 mm., n_D^{23} 1.4102 (literature:[2] b.p. 59–60°C./58 mm., n_D^{20} 1.4084).

The NMR spectrum in carbon tetrachloride showed four multiplets of equal area τ 3.62 and 4.07 (β-hydrogens), τ 4.50 and 5.27 (α-hydrogens) with a $J_{HF} = 46$ cycle/sec. The rest of the spectrum consisted of a quadriplet at τ 5.70 and a triplet at τ 8.72 in the area ratio of two to three (ethyl group).

ANAL. Calcd. for $C_6H_9O_2F$: C, 54.55%; H, 6.82%; F, 14.39%. Found: C, 55.17%; H, 7.07%; F, 14.55%.

Preparation of Methyl α-Fluoromethylacrylate

A two-liter flask, fitted with a reflux condenser, was charged with 98 g. (0.74 mole) of ethyl α-fluoromethylacrylate, 480 g. (15 moles) of methanol, 2 ml. of concentrated sulfuric acid, and 0.1 g. of chloranil. The solution was heated at the refluxing temperature for 65 hr. to allow the establishment of equilibrium conditions. At this time a GLC analysis of the solution indicated that at equilibrium there was 82% methyl α-fluoromethylacrylate, 14% ethyl α-fluoromethylacrylate, and 4% of a by-product (III) present. The solution was cooled to room temperature and neutralized with a 5% sodium carbonate solution. The solution was extracted with methylene dichloride and the resulting solution was then dried over anhydrous magnesium sulfate. The methylene dichloride and excess methanol were removed by distillation through a 10-plate Oldershaw column. The residue was then inhibited with diphenylpicrylhydrazyl and distilled through a 24-in. gold-plated spinning band column to yield 53 g. (60%) of methyl α-fluoromethylacrylate, b.p. 69–70°C./145 mm., n_D^{23} 1.4077 (literature:[10,11] b.p. 47°C./41 mm., 123–125°C./760 mm., n_D^{20} 1.4094, 1.4092).

ANAL. Calcd. for $C_5H_7O_2F$: C, 50.85%; H, 5.93%; F, 16.10%; Found: C, 51.07%. H, 6.04%; F, 15.52, 15.73%.

The NMR spectrum of the pot residue showed multiplets equivalent to two hydrogens at τ 3.87 and 4.28 (vinyl hydrogens), a triplet at τ 6.017 ($=CH-CH_2-O-$) equivalent to two hydrogens, and two singlets each equivalent to three hydrogens at τ 6.35 and 6.70 (methyl ester and methyl ether, respectively). On this evidence the by-product (III) was identified as methyl α-methoxymethylacrylate.

Toxicity of Ethyl α-Fluoromethylacrylate

Tests were conducted by LaWall and Harrisson Research Laboratories, Inc., Philadelphia, on male albino rats. Monomer was administered orally as a dilute aqueous solution. A variable dose response was encountered, which indicated the LD_{50} value to range between 7 and 20 mg./kg.

Homopolymerizations

Polymerizations were carried out in solution at 60°C. in toluene with azobisisobutyronitrile as initiator. The polymers were precipitated by addition to a large excess of methanol.

Bulk polymerizations were carried out at 66°C. in glass or cellophane after careful degassing. Lauroyl peroxide was the initiator (0.02 wt.-%), and n-dodecyl mercaptan (0.025 mole/mole monomer) was the chain transfer agent. Copolymerizations in bulk were carried out under similar conditions.

Copolymerization Parameters

Mixtures of methyl methacrylate and ethyl α-fluoromethylacrylate were copolymerized with ca. 1 mole-% azobisisobutyronitrile as initiator in toluene at 60°C. under helium. Total monomer concentration was ca. $2M$. Benzene (ca. $1M$) was used as an internal standard. Samples were removed with a syringe approximately every ten minutes, placed in small vials containing a few crystals of diphenylpicrylhydrazyl, and refrigerated until analyzed.

Samples were injected into an Aerograph A-350 gas chromatograph onto a 4-ft. column containing 20% SE-30 silicone rubber on a Chromasorb support under helium at isothermal conditions (93°C.). Ratios of peak heights were used to determine concentrations. At least three determinations on each sample were made. It was independently shown that plots of peak height ratios (relative to benzene) for either monomer were linear with monomer concentration. From a linear plot of relative peak heights before polymerization commenced, a calibration curve was constructed from which monomer concentrations at the time of sampling were determined. Plots of M_1 versus M_2 were constructed. In this instance, the plots were linear over most of the range, and dM_1/dM_2 was determined by a least-squares fit. Although only three values are reported (Table IV), each value is based on 10 to 20 experimental samples, each checked at least three times.

Mixtures of styrene and ethyl α-fluoromethylacrylate were copolymerized in toluene solutions at 60°C. with ca. 1 mole-% azobisisobutyronitrile as

TABLE IV
Copolymerization of Methyl Methacrylate (M_1) and Ethyl α-Fluoromethylmethacrylate (M_2)

M_1/M_2	dM_1/dM_2
0.987	1.295
2.56	3.079
0.331	0.542

TABLE V
Copolymerization of Styrene (M_1) and Ethyl α-Fluoromethylacrylate (M_2)

			m_1/m_2	
M_1/M_2	C, %	F, %	From % C	From % F
0.974	73.16	7.15	1.231	1.284
0.518	71.26	7.92	1.006	1.037
1.892	75.58	7.55	1.552	1.138
2.647	77.15	5.65	1.890	1.954

initiator. Results are shown in Table V. Total monomer concentration was ca. $2M$. A helium atmosphere was used for degassing. Conversions to polymer were kept below 5% by isolating the polymer after 100 min. Polymer was isolated by precipitation into petroleum ether, followed by reprecipitation and drying *in vacuo*.

For both series, r_1 and r_2 were evaluated by the best least-squares fit to the Fineman-Ross equation. Values based on fluorine elemental analysis are less reliable and are not reported here.

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References

1. Baldwin, M. G., and S. F. Reed, *J. Polymer Sci.*, **A1**, 1919 (1963).
2. Reed, S. F., and M. G. Baldwin, *J. Polymer Sci.*, **A2**, 1355 (1964).
3. Anspon, H. D., and J. J. Baron, Jr., WADC Technical Report 57-24, (a) Part I (1957); (b) *ibid.*, Part II (1958).
4. Iakubovitch, A. I., N. A. Bogoslovskiĭ, E. P. Pravova, and S. M. Rosenshteĭn, *J. Gen. Chem. USSR*, **28**, 2325 (1958).
5. Voong, S. T., and T. C. Chiang, *Hua Hsüeh Hsüeh Pao*, **24**, 155 (1958); *Chem. Abstr.*, **53**, 6064g (1959).
6. Rosenthal, R. W., L. H. Schwartzman, N. P. Greco, and R. Proper, *J. Org. Chem.*, **28**, 2835 (1953).
7. Ferris, A. F., *J. Org. Chem.*, **20**, 780 (1955).
8. Pattison, F. L. M., *Toxic Aliphatic Fluorine Compounds*, Elsevier, Amsterdam, 1959.
9. Dickey, J. B., U. S. Pat. 2,472,811 (1959).
10. Steck, N. S., *SPE Trans.*, 4, 34 (1964).
11. Rohm & Haas Company, unpublished results.
12. Bovey, F. A., J. F. Abere, G. B. Rathman, and C. L. Sanberg, *J. Polymer Sci.*, **15**, 520 (1955).
13. Beevers, R. B., and E. F. White, *Trans. Faraday Soc.*, **56**, 744 (1960).
14. Noel, C. J., presented to Division of Polymer Chemistry, 144th Meeting, American Chemical Society, Los Angeles, April 1963; *Polymer Preprints*, **4**, 378 (1963).
15. Ham, G. E., Ed., *Copolymerization*, Interscience, New York, 1964, Appendix B.

Résumé

L'α-fluorométhylacrylate d'éthyle a été préparé à partir d'α-chlorométhylacrylate d'éthyle par réaction avec le fluorure de potassium dans le sulfolane. L'ester methylique a été préparé par transestérification. Nous avons été surpri de constater que l'esters éthylique était toxique. On a trouvé que les homopolymères et les copolymères ont de plus basses températures de ramollissement que les polymères issus des méthacrylates correspondants. Les rapports de réactivité sont déterminés pour l'α-fluorométhylacrylate d'éthyle (M_2) avec le styrène ($r_1 = 0.34$, $r_2 = 0.09$) et avec le méthacrylate de méthyle ($r_1 = 1.05$, $r_2 = 0.51$).

Zusammenfassung

Äthyl-α-fluoromethylacrylat wurde aus Äthyl-α-chloromethylacrylat durch Reaktion mit Kaliumfluorid in Sulfolan dagestellt. Der Methylester wurde durch Umesterung gewonnen. Der Äthylester erwies sich unerwarteterweise als recht giftig. Homo- und

Copolymere beider Monomerer bessassen niedrigere Erweichungstemperaturen als Polymere aus den entsprechenden Methacrylatmonomeren. Reaktivitätsverhältnisse wurden für Äthyl-α-fluoromethylacrylat (M_2) mit Styrol ($r_1 = 0{,}34$; $r_2 = 0{,}09$) und mit Methylmethacrylat ($r_1 = 1{,}05$; $r_2 = 0{,}51$) bestimmt.

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Polymerization of Acrolein by Redox Initiation*

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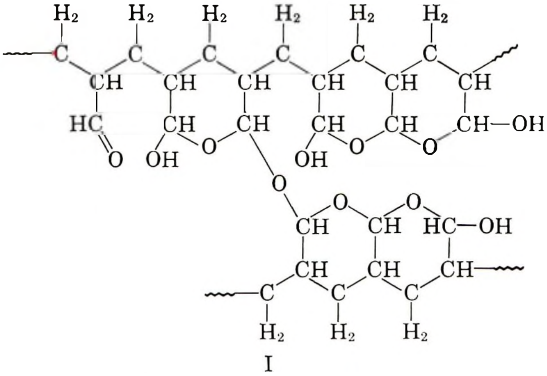
Synopsis

The kinetics of the free-radical-catalyzed redox polymerization of aqueous acrolein have been examined. The reaction was found to be second-order in acrolein, half-order in instantaneous concentration of reducing agent, and independent of peroxide as long as sufficient amount was present. The reaction has a negative temperature coefficient, decreasing in rate as the temperature is raised. The redox system used was *tert*-butyl hydroperoxide–polyacrolein hydroxysulfonic acid, and the rate of initiation was observed to vary directly with the pH and the temperature. Polymer molecular weight varied directly with acrolein concentration and indirectly with polyacrolein hydroxysulfonic acid concentration and the temperature. An empirical relationship may be represented as: $[\eta] = K[M_0]/[C_0]^{1/4}$, where $[\eta]$ is intrinsic viscosity (in deciliters per gram), $[M_0]$ is the initial acrolein concentration, $[C_0]$ is the initial reducing agent concentration; and K is a temperature-dependent variable. The effect of trace impurities in acrolein on polyacrolein preparation was examined. Acetaldehyde and propionaldehyde had a retarding effect on polymerization rate. The effect of these components in reducing the molecular weight of the product increased in the order: acetaldehyde, propionaldehyde, and acetone.

INTRODUCTION

The first homopolymer of acrolein was prepared by Redtenbacher[1] over one hundred years ago. The polyacrolein chain may be represented by the structure I:



I

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A related polyacetal structure has been reported by Overberger[2] resulting from the cyclopolymerization of glutaraldehyde.

As the polyacrolein is obtained from a polymerization system, it is in a form which is highly crosslinked through intermolecular acetal linkages.[3] Solutions of the polymer may be obtained only by causing the polymer to undergo reaction with various reagents capable of breaking the acetal links and reacting with the liberated carbonyl groups thereby rendering them unable to recombine to a crosslinked structure.

Very low molecular weight (250–1000) free-radical polymers of acrolein have been prepared[4] and found to be soluble in water–pyridine mixtures. Soluble homopolymers of methacrolein are discussed by Marks.[5]

EXPERIMENTAL

Description of System

In a typical polymerization experiment, the monomer concentration is kept low enough that its solubility in water is not exceeded, that is, less than about 23 wt.-%. Initially the acrolein, water, and catalyst form a single phase; however, as polymerization proceeds, the polyacrolein first shows up as a turbidity; then, as particles coalesce, solid polymer settles out (in the absence of agitation). When the reaction has progressed to the point where about 8 wt.-% polymer is present in the system, all of the water and unconverted monomer are adsorbed by the polymer forming a semisolid mass. Since this viscous suspension is difficult to sample, an experimental technique was devised to analyze an entire reactor full of polymer for each data point obtained. An ampule of the type utilized for bromine number determination was used as a reactor. Thus, equal portions of ice-cold reaction mixture were added by a syringe to 12–15 ampules which were sealed with a torch immediately upon being filled and stored at 0°C. until the start of the polymerization. They were then placed in a small wire basket and immersed in a constant temperature bath. Ampules were withdrawn at various intervals and analyzed for acrolein by the bromine number method.[6] Values for acrolein concentration were found to be quite reproducible by this method and were unaffected by the presence of polymer.

In a typical experiment 156.9 g. water, 41.6 g. acrolein (99% purity), 0.0635 g. *tert*-butyl hydroperoxide (TBHP), and 3.1 cc. polyacrolein hydroxysulfonic acid solution containing 0.71×10^{-3} mole available bisulfite ion were mixed at 0°C. Fifteen nitrogen-filled ampules were each loaded with 1 cc. of this solution, sealed with a torch, and placed in a 25°C. bath. At intervals, an ampule was removed from the bath and analyzed by bromine number. The results are plotted in Figure 6. Comparison of this method of analysis to sampling a polymerization conducted in a stirred flask showed that essentially identical results were obtained in each case.

Catalyst System

Various catalyst systems have been investigated in the aqueous polymerization of acrolein. Since the molecular weight of the product is very dependent upon polymerization temperature, process conditions were limited to 30°C. or lower. This limitation essentially precluded thermal decomposition of a peroxide as a source of initiating free radicals and necessitated the use of various redox systems. Considerable work has been carried out at Mainz by Schulz, Kern, et al., dealing with the use of various oxidation–reduction systems to supply free radicals to initiate the polymerization of acrolein in aqueous solution.[3,7] Ionic polymerization of acrolein is extensively discussed by Schulz and Passmann.[8]

Polyacrolein hydroxysulfonic acid was chosen as the reducing agent for this investigation. The reducing agent used in most of the studies was the solution of polyacrolein in sulfurous acid from which the excess sulfur dioxide has been removed by sparging with inert gas. During polymerization sulfur dioxide is slowly liberated and reacts with the peroxide immediately upon release. This continues as long as there is peroxide remaining, and in the presence of sufficient peroxide this reaction has been shown to have a half-life of about 3 hr. at 25°C.

RESULTS

Rate of Dissociation of Polyacrolein Hydroxysulfonic Acid

By measuring the changes in the *tert*-butyl hydroperoxide concentration, one in effect measures the rate of liberation of bisulfite ion from the polyacrolein hydroxysulfonic acid because of instantaneous reaction between bisulfite and peroxide. The maximum amount capable of dissociation is identical to the amount of peroxide decomposed over an extended period (24 hr.) in contact with the reducing agent. By taking advantage of this fact we have followed the dissociation of polyacrolein hydroxysulfonic acid in its role as initiator, and have evaluated the dissociation constant, k_1, as a function of temperature and pH. The dissociation was established as a first-order reaction, since a plot (Fig. 1) of the log of the concentration of bisulfite ion (actually total bisulfite capable of dissociation minus amount decomposed) versus time gave a straight line with a slope equal to the rate constant, k_1, for the reaction:

$$\text{Poly AN(OH)SO}_3^- \overset{k_1}{\rightleftharpoons} \text{HSO}_3^- + \text{poly AN}$$

where poly AN represents polyacrolein. Several experiments were carried out at different polyacrolein hydroxysulfonic acid concentrations and temperatures, and the rate of dissociation was found to be essentially independent of *tert*-butyl hydroperoxide concentration over a broad range as long as sufficient was present to react with the bisulfite ion liberated. The rate of dissociation was not affected by the presence of acrolein or hy-

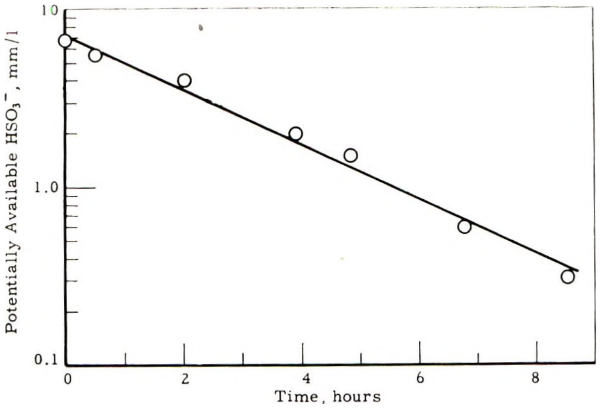

Fig. 1. Dissociation of polyacrolein hydroxysulfonic acid.

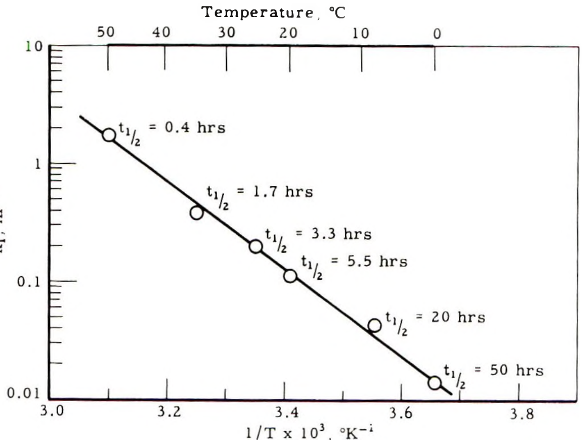

Fig. 2. Polyacrolein hydroxysulfonic acid dissociation rate constant vs. temperature

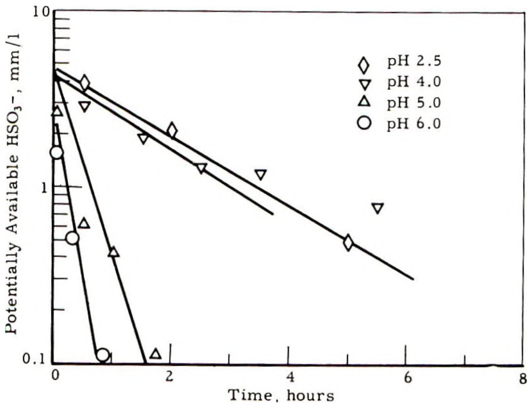

Fig. 3. Dissociation of polyacrolein hydroxysulfonic acid as a function of pH.

droquinone, but was increased by an increase in temperature and an increase in pH (Figs. 2 and 3).

Acrolein Disappearance Rate Measurements

Analysis of the experimental data obtained in the polymerization of acrolein at various concentration levels show that when the reciprocal of the monomer concentration is plotted against the estimated catalyst concentration at time t, fairly straight lines are obtained up to about 60% acrolein conversion. The reaction is therefore second order with respect to instantaneous acrolein concentration.

Assumed Kinetics

The kinetics may be described by

$$d[c]/dt = -k_1[\mathrm{C}] \tag{1}$$

where $[\mathrm{C}] = [\mathrm{C}_0] \exp \{-k_1t\}$, $[\mathrm{C}_0]$ = bisulfite ion potentially available in polyacrolein hydroxy sulfonic acid, k_1 = dissociation constant for polyacrolein hydroxysulfonic acid; and by

$$d[\mathrm{M}]/dt = -k_2(k_1[\mathrm{C}])^{1/2}[\mathrm{M}]^2 \tag{2}$$

where k_2 is the polymerization rate constant and $[\mathrm{M}]$ refers to the acrolein concentration at time t. Thus,

$$d[\mathrm{M}]/dt = -k_2(k_1[\mathrm{C}_0])^{1/2}\exp\{-k_1t/2\}[\mathrm{M}]^2 \tag{3}$$

Integration yields

$$1/[\mathrm{M}] = (1/[\mathrm{M}_0]) + 2k_2([\mathrm{C}_0]/k_1)^{1/2}(\exp\{-k_1t_D/2\} - \exp\{-k_1t/2\}) \tag{4}$$

where $[\mathrm{M}_0]$ is the initial acrolein concentration and t_D is the true time polymerization actually starts after delay due to induction period brought about by hydroquinone. By rearranging terms we obtain

$$\begin{aligned}1/[\mathrm{M}] = (1/[\mathrm{M}_0]) - 2k_2(\mathrm{C}_0]/k_1)^{1/2}(1 - \exp\{-k_1t_D/2\})\\ + 2k_2([\mathrm{C}_0]/k_1)^{1/2}(1 - \exp\{-k_1t/2\})\end{aligned} \tag{5}$$

Hence, a plot of $1/[\mathrm{M}]$ versus $(1 - \exp\{-k_1t/2\})$ will have as slope $2k_2([\mathrm{C}_0]/k_1)^{1/2}$ from which k_2 may be readily obtained. The intercept of this curve with the vertical axis will have a value $b = (1/[\mathrm{M}_0]) - 2k_2([\mathrm{C}_0]/k_1)^{1/2}(1 - \exp\{-k_1t_D/2\})$. Typical results plotted in this manner are shown in Figure 4 and listed in Table I. The straight lines in Figure 4 have been moved to the left sufficiently to eliminate the appearance of the induction period.

As seen from the parallel slopes at fixed initiator concentration, the second-order dependency and similar rate constant hold for a severalfold increase in the initial acrolein concentration. Usually in a polymerization catalyzed by a free-radical source, the reaction rate is first order with respect to

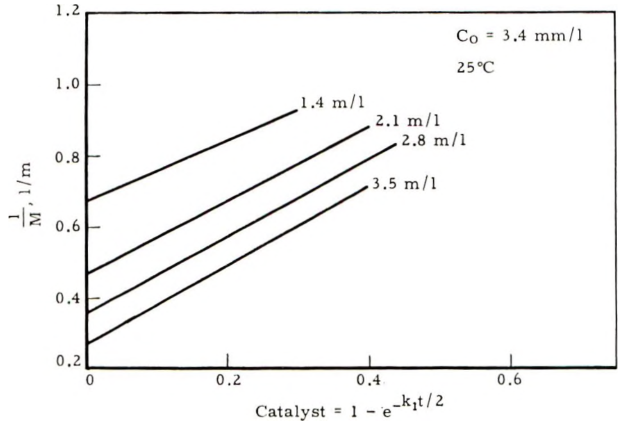

Fig. 4. Effect of acrolein cocentration at $[C_0] = 3.4 \times 10^{-3}$ mole/l., 25°C.

TABLE I
Acrolein Polymerization at Variable Monomer and Initiator Concentration

Expt. no.	$[C_0]$, mole/l. × 10^3	$[M_0]$, mole/l.	Slope	k_2, $l.^{1/2}$-mole$^{1/2}$-hr.
1	3.4	3.48	1.09	4.9
2	3.4	2.82	1.07	4.8
3	3.4	2.11	0.96	4.4
4	3.4	1.44	0.71	3.2
5	3.4	0.84	0.80	3.9
6	1.8	3.43	0.78	4.8
7	1.8	2.73	0.83	5.1
8	1.8	2.15	0.77	4.7
9	1.8	1.77	0.80	5.0

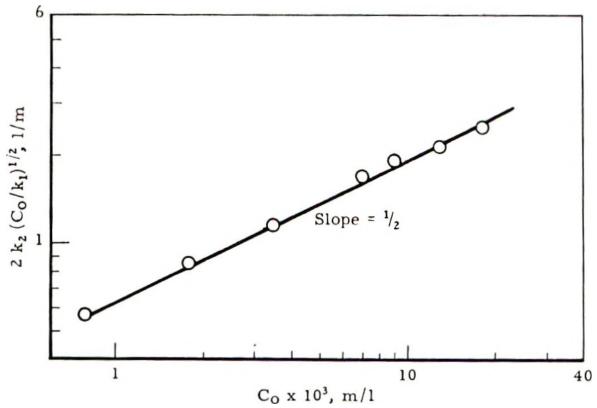

Fig. 5. Plot of $2k_2([C_0]/k_1)^{1/2}$ vs. initial concentration of polyacrolein hydroxysulfonic acid at $[M_0] = 3.5$ mole/l., 25°C.

monomer. The second-order dependence found in this study could be brought about by the reaction:

$$RO\cdot + CH_2{=}CHCHO \rightarrow ROH + CH_2{=}CH\dot{C}O$$

It has been established that *tert*-butoxy free radicals abstract the aldehyde hydrogen of acrolein to generate acrylyl radicals which then perform the function of initiating the polymer chains. Thus the generation of rapidly propagating polymer chains may well involve the relatively slow addition of acrolein to the intermediate acrylyl radicals, thereby bringing about second order dependency on monomer concentration.

TABLE II
Rate Constant k_2 at Various Conditions, 25°C.

$[M_0]$, mole/l.	$[C_0]$, mole/l. × 10^3	TBHP, mole/l. × 10^3	k_2, $l^{1/2}$-mole$^{1/2}$-hr.
3.5	1	2	5.1
3.5	3.5	7	4.8
3.5	9	3	5.0
2.7	2	3	4.9
1.8	2	3	4.8
0.6	4.5	3.5	5.0

Since the concentration of the polyacrolein hydroxysulfonic acid decreased by 75% during the course of the polymerization, the reciprocal of the acrolein concentration is plotted as a function of the half-power of the calculated initiator concentrations, $1 - \exp\{-k_1t/2\}$. In this manner one may compare the results of experiments carried out at different initial initiator levels and at different temperatures. The slopes of these curves which are proportional to the rate constants k_2 are plotted against the

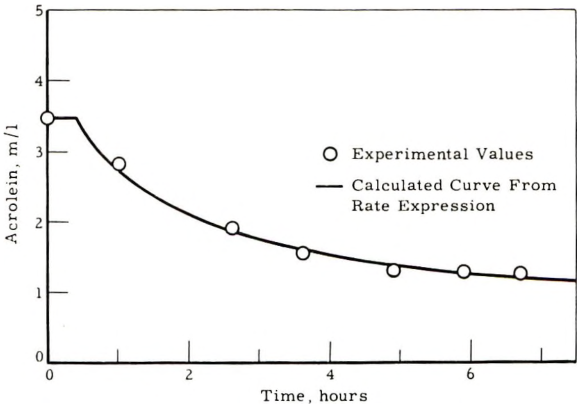

Fig. 6. Experimental verification of rate expression at $[C_0] = 3.4 \times 10^{-3}$ mole/l, $[M_0] = 3.48$ mole/l., 26°C.: (○) experimental values; (——) curve calculated from rate expression.

initial initiator concentration as shown in Figure 5. The straight line has a slope of one half, showing the half-order dependency of rate on polyacrolein hydroxysulfonic acid concentration. It may be observed that good agreement is obtained over a 25-fold change in concentration.

Data confirming the applicability of the rate equation at several different initiator and monomer concentrations for polymerization at 25°C. are shown in Table II. These data again illustrate the independence of rate on peroxide concentration and the overall consistency of the rate constant.

A more elegant demonstration of the validity of the rate equation is shown in Figure 6. As may be seen, the experimental points, representing measured acrolein concentrations, fall on the curve calculated from the rate expression (4). Experimentally, t_D was found equal to $1.3/[M_0]$.

Temperature Dependence

Similar consistency in the rate equation was found in polymerizations carried out at temperatures up to 50°C. Surprisingly, the overall rate constants k_2 were found to decrease with increasing temperature, and a plot of $1/T$ versus log k_2 gave a straight line with a positive slope, i.e., a negative activation energy of about 7 kcal./mole. These data (shown in Fig. 7) suggest that chain transfer and termination reactions have a greater temperature coefficient than does the chain propagation reaction.

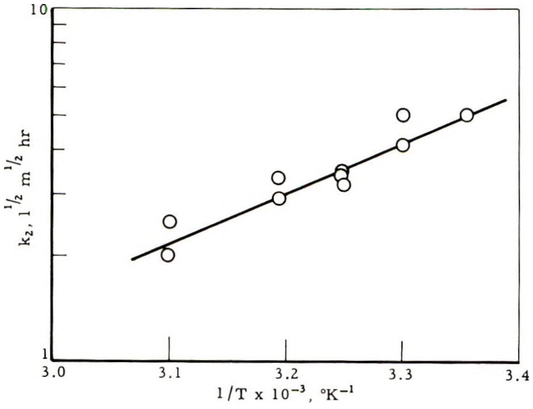

Fig. 7. Plot of log k_2 as a function of temperature.

Molecular Weight

The crosslinking ability of sodium bisulfite solutions of polyacrolein has been found useful in improving the wet and dry physical properties of cellulosic products such as paper, paperboard and hardboard. These solutions are also effective starch-insolubilizing agents, have potential as a permanent warp size or durable textile finishing agent, and hold promise in the formulation of new adhesives. They have a positive leather-tanning action and may prove valuable in the modification of wool or hair as well

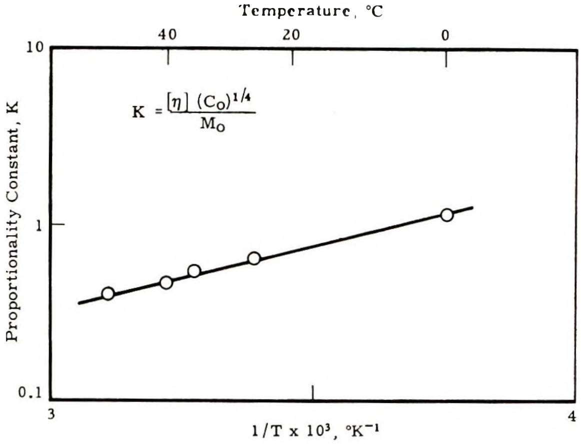

Fig. 8. Values of K as a function of temperature.

as soluble protein base materials. As polyelectrolytes, polyacrolein solutions may be useful in water treatment, latex modification, or drilling mud applications. For each of these applications, polyacrolein of a certain molecular weight range is most effective.

For this reason, one of the more important aspects of the present work was to determine the direction and magnitude of the effect of the several process variables on the intrinsic viscosity, i.e., the molecular weight, of the product. The intrinsic viscosity of the polyacrolein was found to vary directly as the acrolein concentration and indirectly with the polyacrolein hydroxysulfonic acid concentration and the temperature. The peroxide concentration was without effect on the product molecular weight as long as sufficient was present to react with all the reducing agent. In each case it is seen that the higher the rate of polymerization, the lower is the intrinsic viscosity of the polymer. An empirical relationship may be represented as

$$[\eta] = K[M_0]/[C_0]^{1/4}$$

where the value of K depends on temperature. A plot of K versus the reciprocal of temperature is shown in Figure 8.

Polyacroleins of intrinsic viscosity ranging from 0.5 to 3.0, corresponding to light-scattering molecular weights of 8×10^4–4×10^6, were prepared in this work.

Acrolein Impurity Effects

In a commercial polymerization process, unconverted monomer would be recovered from the polymer product and recycled. Consequently the recycled acrolein will contain the trace impurities initially present in the feed acrolein, assuming they do not enter into the polymerization. An experimental program was therefore carried out in the same manner as described earlier with small ampules in which highly purified acrolein was used as feed to which varying known amounts of the impurities were added. These impurities included acetone, methanol, propionaldehyde, acetaldehyde, 2-propanol, 1-propanol, and ethanol. The impurity levels investigated were 0, 1, 5, 10, and 20 wt.-% (basis charged acrolein). The rate of polymerization was measured over the initial 50% conversion when possible, and the intrinsic viscosity was determined for the polymer produced from the monomer charge polymerized at 25 and 0°C. Selected impurities were also evaluated as described above at 35 and 50°C. An estimate was made of the amount of impurity consumed in the course of the polymerization.

At a polymerization temperature of 25°C., there was essentially no effect on reaction rate by the presence of up to 10% based on acrolein of the following impurities: acetone, 2-propanol, and ethanol. At a level of 10% addition based on acrolein, methanol, and 1-propanol reduced the polymerization rate to 80% of the base rate. Propionaldehyde and acetaldehyde (10%) reduced the reaction rate to one-fifth that observed with the pure monomer.

A measure of the molecular weight of the various products was obtained by determining the intrinsic viscosity. At the 10% impurity level no effect on intrinsic viscosity was observed due to the presence of acetaldehyde, 2-propanol, 1-propanol, or ethanol in the monomer feed. A drop in intrinsic viscosity of greater than 20% took place when the monomer contained 10% methanol. At this level, propionaldehyde, and acetone brought about a 30% drop in intrinsic viscosity. When these same polymerizations were carried out at 0°C., all intrinsic viscosities were about the same, whether or not chain transfer impurity was present.

Similar effects on rate of polymerization and intrinsic viscosity were noted at 35 and 50°C.

The fraction of impurity at each concentration that was consumed during the polymerization was also determined. The results indicated that the acetone would react to a large extent while propionaldehyde, acetaldehyde, 1-propanol, 2-propanol, and ethanol would build up in recycle.

The authors are deeply indebted to J. C. Hayward as the major contributor to the kinetic interpretation of the experimental data.

References

1. Redtenbacher, J., *Ann.*, **47**, 113 (1843).
2. Overberger, C. G., S. Ishida, and H. Ringsdorf, *J. Polymer Sci.*, **62**, 81 (1962).
3. Schulz, R. C., *Kuntstoffe*, **47**, 303 (1957).
4. Schulz, R. C., J. Kovacs, and W. Kern. *Makromol. Chem.*, **52**, 236 (1962).
5. Marks, B. M., U. S. Pat. 2,993,878 (1961).
6. Smith, C. W., *Acrolein*, Wiley, New York, 1962, p. 244.
7. Schulz, R. C., H. Cherdron, and W. Kern, *Makromol. Chem.*, **24**, 141 (1957).
8. Schulz, R. C., and W. Passmann, *Makromol. Chem.*, **60**, 139 (1963).

Résumé

On a examiné les cinétiques de polymérisation radicalaire de l'acroléine en solution aqueuse, catalysée par un système rédox. On a trouvé que la réaction est du second ordre par rapport à l'acroléine, d'ordre un demi par rapport à la concentration instantaneé en agent réducteur et indépendante vis-à vis du peroxyde aussi longtemps qu'une quantité suffisante est présente. La réaction possède un coefficient de température négatif, la vitesse diminuant lorsque la température augmente. Le système rédox employé est la tert-butyl-hydroperoxyde-acide polyhydroxacroléine sulfonique et on a observé que le vitesse d'initiation variait directement avec le pH et la température. Le poids moléculaire du polymère varie directement avec la concentration en acroléine et indirectement avec la concentration en acide polyhydroxyacroléine- sulfonique ainsi qu'avec la température. On peut présenter la relation empirique suivante: $[\eta] = K[M_0]/[C_0]^{1/4}$ où viscosité intrinsègue; $[M_0]$ = concentration initiale en acroléine; $[C_0]$ = concentration initiale en agent réducteur; K = variable dépendant de la température. On examine l'influence des traces d'impuretés de l'acroléine sur la préparation de la polyacroléine. L'acétaldéhyde et le propionaldéhyde ont un effet retardateur sur la vitesse de polymérisation. L'influence de ces composés dans la réduction du poids moléculaire du polymère augmente dans l'ordre suivant: acétaldéhyde, propionaldéhyde et acétone.

Zusammenfassung

Die Kinetik der radikalisch katalysierten Redoxpolymerisation von wässrigem Acrolein wurde untersucht. Die Reaktion ist von zweiter Ordnung in Bezug auf Acrolein, von der Ordnung 1/2 in Bezug auf die Momentankonzentration des Reduktionsmittels und unabhangig vom Peroxyd, solange eine genügende Menge vorhanden ist. Die Reaktion besitzt einen negativen Temperaturkoeffizienten, d.h. ihre Geschwindigkeit nimmt mit steigender Temperatur ab. Als Redoxsystem wurde tert-Butylhydroperoxyd-Poly(acrolein)hydroxysulfonsäure verwendet, wobei sich die Startgeschwindigkeit gleichsinnig mit dem pH-Wert und der Temperatur änderte. Das Molekulargewicht des Polymeren hängt direkt von der Acroleinkonzentration und umgekehrt von der Poly(acrolein)hydroxysulfonsäurekonzentration und der Temperatur ab. Folgende empirische Beziehung wurde aufgestellt: $[\eta]$, $dl/g = KM_0/C_0^{1/4}$, wo $[\eta]$ = Viskositätszahl; M_0 = Anfangskonzentration an Acrolein; C_0 = Anfangskonzentration des Reduktionsmittel; K = temperaturabhängige Variable. Der Einfluss von Verunreinigungsspuren in Acrolein auf die Polyacroleindarstellung wurde untersucht. Acetaldehyd und Propionaldehyd hatten einen verzögernden Einfluss auf die Polymerisationsgeschwindigkeit, der Einfluss dieser Komponenten auf die Herabsetzung des Molekulargewichts des Produkts nahmen in folgender Reihenfolge zu: Acetaldehyd, Propionaldhyd und Aceton.

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Structural Investigation of Polyacrolein by Fractional Dehydration

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Synopsis

The utilization of a specially developed technique for the low temperature pyrolysis of polyacrolein, and the accurate measurement of the waterr eleased thereby from the polymer have demonstrated the presence of well-defined inflection points in the curve of water evolution versus dehydration (pyrolysis) temperature. These are postulated to indicate the presence of water in polyacrolein from a number of different sources, e.g., structural, hydrogen-bonded, and free. A correlation of the measured water evolution between inflection point temperatures with the concurrently developing free carbonyl groups, measured by an infrared technique, has provided information on the type and proportion of various structural subunits in the polyacrolein molecule. This information has been used to construct a partial structural formula for the particular polyacrolein sample under examination. As a practical outgrowth of this work, the concept of the activation of polyacrolein by dehydration at elevated temperatures has proved useful in facilitating reaction of the polymer with a number of carbonyl reagents such as sodium bisulfite, SO_2, etc.

INTRODUCTION

Polyacrolein, the free-radical polymer of acrolein, often referred to as disacryl, was first described in 1843.[1] The insoluble nature of the white powdery polymer long discouraged detailed study of the structure and chemistry of the material. Only in the last ten years, and through the brilliant efforts of Kern, Schulz, and their co-workers at the University of Mainz, has the structure of the acrolein polymer been gradually unravelled.

According to Schulz,[2] acrolein polymers prepared by free-radical methods are essentially head-to-tail vinyl polymers modified by cyclization of the pendant aldehyde functions in varying degrees. Thus among the structural subunits thought to be present are, in addition to the simple aldehyde unit (I), individually hydrated aldehyde groups (II), dihydroxytetrahydropyran rings (III), and fused tetrahydropyran rings (IV). Similar hemiacetal ether bridges (V) also connect between chains.[3] It should be noted that all these substructures represent various degrees of hydration of the basic acrolein unit.

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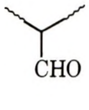
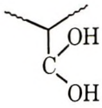


(I)



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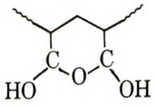

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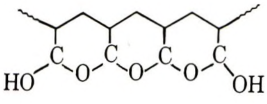

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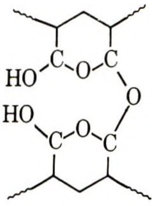


(V)

Polyacrolein samples contain these structural units in varying proportions. Unfortunately, while such variations may have important effects on the physical properties of the polymer and consequently on its applicational behavior, little progress has been made in obtaining estimates

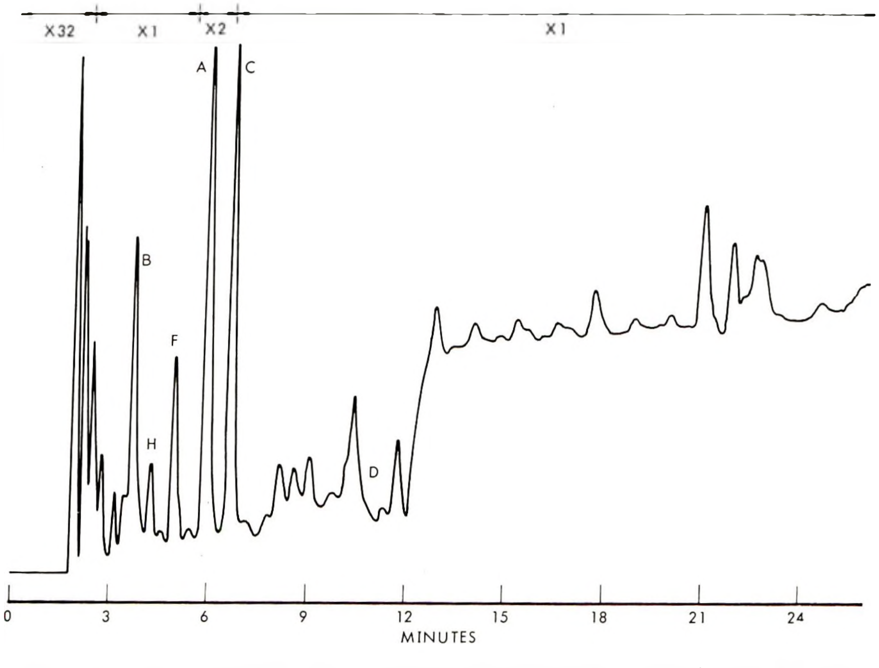


Fig. 1. Pyrolysis (600°C.) chromatogram of polyacrolein. Sample size, 3.7 mg.; pyrolysis temperature, 600°C.; 15 ft. Carbowax 20 M–Chromosorb W; column temperature, 50–250°C. at 7.9°C./min.; detector temperature, 300°C.; He flow rate, 60 ml./min.

of the likely proportions of the subunits in a given polymer sample. The present paper describes the application of the recently introduced technique of pyrolysis gas chromatography to provide at a minimum a partial solution to this problem.

Pyrolysis gas chromatography in its present form, in which a tiny sample of the material under examination is pyrolyzed directly in the inlet of a gas chromatograph, was introduced as recently as 1959 by Lehrle and Robb.[4] Since that time the convenience and general applicability of this technique to polymeric materials has led to the appearance of a great many papers on the subject. However it is apparent from the literature that most of the experiments have involved complete pyrolysis of the material at relatively high temperatures. Part of the reason for this has been the lack of a convenient means for measuring and controlling the actual temperature of the pyrolysis device.

Advantages accruing from a more precise knowledge and control of the pyrolysis temperature are the following: (*1*) it would yield information on the thermal stability of polymers; (*2*) comparisons could be made between the pyrolysis patterns of a polymer fired at different known temperatures, and thus thermally unstable parts of a polymer such as side chains, weak links in the backbone, etc., might be identified from lower temperature chromatograms with a smaller number of peaks; (*3*) low-temperature firing would yield information on any monomeric materials which might be held strongly by and possibly loosely chemically combined with polymeric materials. This last feature has proved to be particularly applicable in the polyacrolein field.

In the subsequent experimental section the construction of a modified pyrolyzer unit capable of supplying this kind of information is described.

In the initial stages of this work the pyrolysis of polyacrolein both at high temperatures and low was used merely as an analytical tool in an attempt to observe differences between polymer samples. At high temperatures (>400°C.) complete degradation took place, yielding the very complex chromatogram with at least 43 components as shown in Figure 1. At lower temperatures there was an abrupt change to a much simpler chromatogram with only three components, namely, acrolein, a "light ends" peak, and water, with the latter predominating.

The presence of water as the main pyrolysis product at temperatures as high as 250°C. suggested that structural water associated with one or more of the structural units shown above was being driven from the polymer in addition to the large quantity of physically adsorbed "free" water always associated with polyacrolein samples. Since there were obviously different energy requirements for the release of these various types of water it was postulated that different temperature thresholds should exist for each type and that, provided these temperatures were sufficiently far apart, the separate measurement of at least some of the water types and hence, hopefully, the structures associated with them might be possible.

The remainder of this paper describes the experiments made to establish the existence of the various water types from the presence of inflections in a water evolution versus pyrolysis temperature curve and the subsequent use of this information in conjunction with infrared studies of the pyrolyzed polymer samples to identify and estimate at least approximately the polymer subunits involved.

EXPERIMENTAL

Pyrolyzer Unit

This unit (Fig. 2) was a modified version of the electrically heated coiled filament type.[5] The filament was made from a 2-in. length of platinum wire (diameter, 0.012 in.) and was coiled in a cylindrical form slightly greater than $^1/_{16}$ in. diameter and closed by a half-turn at one end. Fabricated in this fashion it would accept cylindrical pellets ($^1/_{16}$ in. diameter) of polyacrolein made in a specially constructed die. Advantages of pelleting included: (*1*) eliminating the loss of the polymer, often very light and fluffy, during loading and before firing; (*2*) increasing the mass of the sample to 2–3 mg., a size convenient for measurements with the hot-wire type of chromatograph detector; (*3*) facilitating weighing the pyrolysis sample accurately and directly prior to insertion in the pyrolyzer.

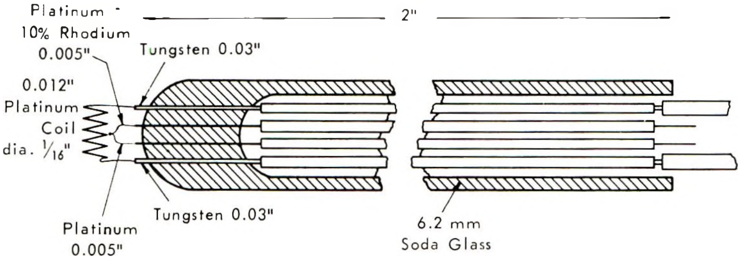


Fig. 2. Controlled temperature pyrolysis unit.

A major feature of our pyrolysis filament was the presence of a thermocouple for measuring the pyrolysis temperature. A fine wire (0.005 in.) platinum–platinumrhodium (10%) thermocouple junction was welded to the outer perimeter of the center turn of the filament. The four leads (filament and thermocouple) were sealed through a 2–3 in. length of soda glass tubing. The injection port of most gas chromatographs could readily be modified, for example, by the addition of a Swagelok T, to accept the pyrolyzer.

Current for the filament was supplied from the mains via a Powerstat variable transformer connected in turn to the primary of a radio-tube filament transformer. Depending on the temperature range to be covered by the pyrolysis unit the secondary winding could be tapped at the ends or middle to supply the necessary voltage. The millivolt-range thermocouple signal was displayed on a 1 mv. recorder using a potentiometer box to buck out the excess voltage over 1 mv. A two-channel recorder proved very convenient, in that the pyrolysis chromatogram and the temperature of the pyrolysis unit could be displayed side by side.

During a preliminary test of the pyrolysis unit at 750°C., samples of polyacrolein were pyrolyzed to give the complex chromatogram in Figure 1 which proved to be very reproducible, both with regard to the number of peaks and their relative heights. The desired temperature was attained in approximately 4 sec. For this "instantaneous" type of pyrolysis temperature was maintained for a further 12 sec. It proved to be equally easy and convenient to maintain a fixed temperature for as long as 15–20 min. The latter procedure was particularly useful in the low-temperature dehydration experiments on polyacrolein.

Gas Chromatograph

An F and M Model 500 gas chromatograph was used to detect and measure the pyrolysis products. Slight modification of the injection port was all that was necessary to enable it to accept our pyrolyzer.

The quantitative analysis of water by gas–liquid chromatography (GLC) poses many problems due to its highly polar nature. Highly unsymmetrical peaks or even mere "humps" as in Figure 1 (at 12 min.) accompanied by excessive tailing are typically found with most column packings. From a number of suggestions in the literature for dealing with highly polar compounds[6] the use of a Teflon carrier was adopted as most convenient for our purpose. With Carbowax 20 M as liquid phase, virtually symmetrical water peaks with only slight tailing were readily obtained. Moreover the light ends, acrolein, and water peaks characteristic of the low-temperature pyrolysis of polyacrolein were completely separated on a 10 ft. Carbowax 20 M column operated at 100°C. with a helium flow rate of 60 ml./min.

The water response of the chromatograph detector was found to be nearly linear in the region of 0–2 mg. H_2O. Partial water retention was indicated by the fact that the line did not quite pass through the origin. The problem of adventitious water was solved by operating the column at a fixed temperature, thus allowing equilibration with any water in the helium gas.

The procedure was checked by pyrolyzing a pelleted sample of calcium hydroxide at 500°C., the temperature at which the hydroxide is reported to lose water quantitatively to form the oxide. The water content of 22.7% measured from the resulting water peak was within 3% of the published value of 23.4% for the sample.

Infrared Data

The pelleted polyacrolein samples were mulled with Fluorolube S-30 (Hooker Chemical Co.) and the resulting suspensions applied between special micro NaCl windows. The spectra were obtained on a Beckman IR-4 spectrophotometer.

Polyacrolein

The samples examined had intrinsic viscosities ranging from 0.5 to 4 dl./g. and were prepared by the free-radical polymerization of acrolein. Typical procedures with the redox system consisting of *tert*-butyl hydroperoxide and the bisulfite adduct of polyacrolein are described in the paper by Ryder and Pezzaglia.[8]

RESULTS AND DISCUSSION

A preliminary series of firings was carried out at temperatures ranging up to 250°C. From these studies it was quickly established that the limit of water, releasable at any one temperature, was reached after only two or three repeated 17 sec. firings at that temperature or alternatively after one continuous firing of 15–20 min. The latter method was more accurate, since all the water was measured as one GLC peak; after exhaustively removing all the water releasable at any given temperature, further quantities of water could be driven off merely by raising the pyrolysis temperature 5–10°C.

This information indicated that it was possible to construct a plot of evolved water versus pyrolysis temperature by pyrolyzing polyacrolein pellets from the same polymer sample at various temperatures up to 250–300°C., where complete polymer breakdown began to take place. The

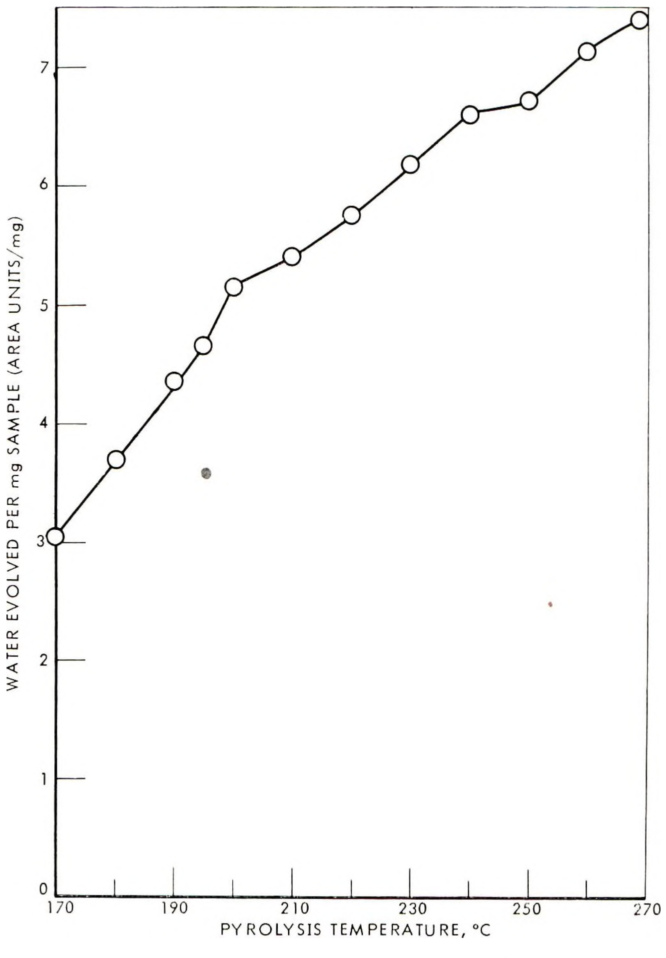


Fig. 3. Polyacrolein water evolution curve, 170–270°C.

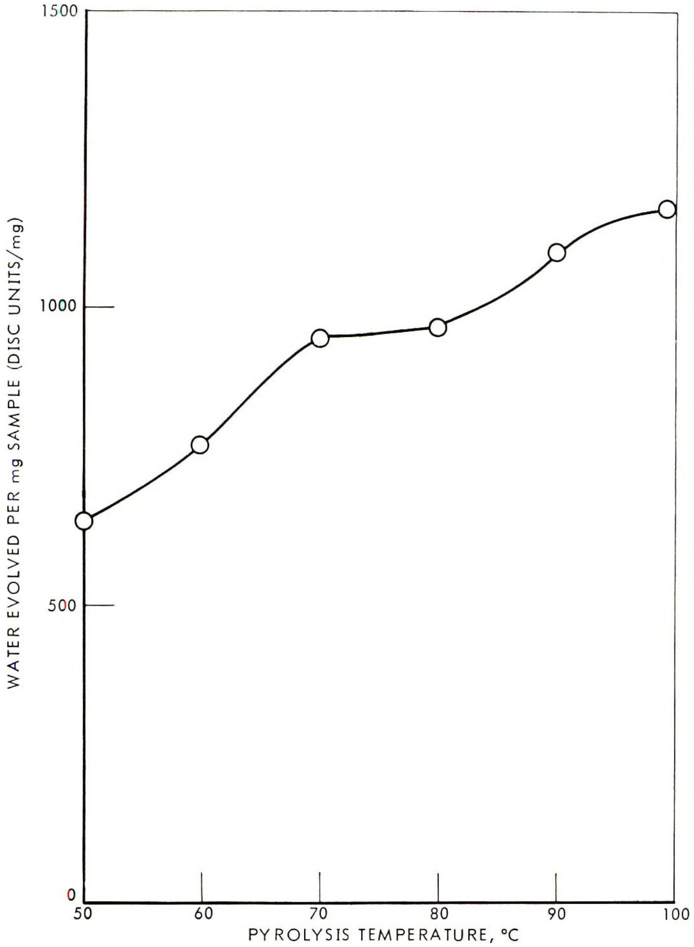


Fig. 4. Polyacrolein water evolution curve, 50–100°C.

presence of inflection points on such a curve would be indicative of water from different sources within the polymer.

Proceeding from this base it was found that a pronounced inflection point existed, not unexpectedly, at 100–105°C. On exploring temperatures above and below 100°C., we found inflection points at 205, 245, and 75°C. The relevant portions of the water–temperature curve are shown in Figures 3 and 4. An interesting point is the distinct difference in the appearance of the 205°C. point of inflection compared with the 245 and 75°C. points. Thus, whereas the latter both show definite "flats," there is a pronounced increase in slope in the 200°C. region. This is brought out by the data in Table I.

It is concluded that there is an overlap of different water types at 200 205°C. leading to the situation diagrammed in simplified form in Figure 5. By applying a construction of this type to the actual data it was calculated

TABLE I
Variation in Slope of Water Evolution Curve Between 170 and 240°C.

Temperature range, °C.	Slope
170–180	0.07
180–190	0.06
190–195	0.06
195–200	0.10
200–210	0.03
210–220	0.03
220–230	0.05
230–240	0.04

that as much as 30% of the relatively small amount of water associated with the structural change taking place in the 200–250°C. region was being included in the total 105–205°C. water measured at 205°C.

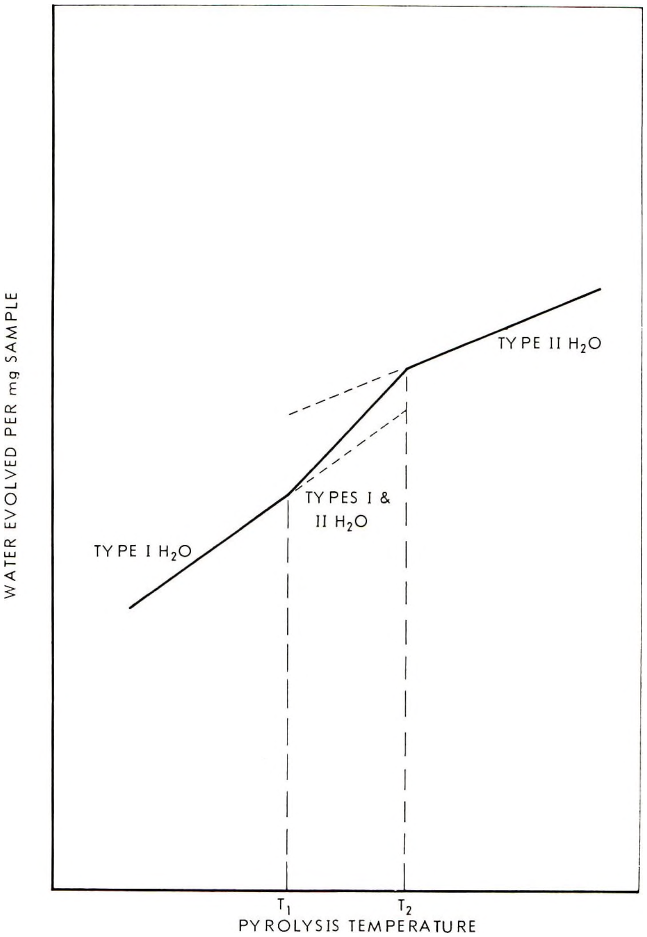


Fig. 5. Overlapping water types. Hypothetical curve (simplified).

TABLE II
Comparison of Polyacrolein Samples by Triple Pyrolysis[a]

Sample designation	105°C. water, %	205°C. water, %	245°C. water, %
6928-82-2LH1	2.0 ± 0.1	6.4 ± 0.2	0.8 ± 0.1
PR 19	0.8 ± 0.1	3.8 ± 0.2	1.6 ± 0.2
6770-51	2.0	6.8 ± 0.1	0
7126-7-1	1.4 ± 0.1	3.6 ± 0.05	1.75 ± 0.15
6928-143	3.7 ± 0.2	5.05 ± 0.05	0.85 ± 0.25

[a] Inflection point at 75°C. not located at time these analyses were conducted.

The location of four inflection points at 75, 105, 205, and 245°C. on the water–pyrolysis temperature curve confirmed that the water was coming from at least four different sources in the polyacrolein polymer. By firing a single pellet of the polymer successively at each of these temperatures the amount of each water type could be measured, thus allowing comparisons to be made between different polyacrolein samples with regard to the proportions of a number of substructures as yet unknown. Comparisons of this type proved to be a very sensitive measure of differences between various polyacrolein samples as illustrated by the data given in Table II for five polymers prepared by different techniques.

Rehydration experiments on pellets which had been dehydrated at one or other of the inflection temperatures served to demonstrate the difference between the various types of water. Thus after dehydration at 105°C., over 80% of this water could be taken up again, whereas only 8% of the water released at 205°C. and none of the water released at 245°C. was reassimilated. This clearly suggests that the bulk of the 105°C. water is free or at most hydrogen-bonded, while the loss of the higher temperature water results from the irreversible destruction of structural groups in the polymer.

In an effort to relate the inflection points to specific structural groups in the polymer the infrared spectra of pellets pyrolyzed at the various temperatures were compared. The special technique for handling the mulling of the tiny (2–4 mg.) pellet samples is described in the experimental section. Pronounced and distinct changes were observed in a number of bands. These included, in addition to the expected decreases in the water band at 6.1 μ and the OH stretching band at 2.9 μ, changes in the carbonyl band at 5.8 μ and the C—O—C (ether) band near 8 μ. For example, carbonyl absorption increased progressively with increasing dehydration temperatures but appeared to show its greatest increase, relative to the amount of water released, at lower temperatures. Ether absorption, indicative of hemiacetal groupings and chain-to-chain ether bridges, experienced its major decrease during the 105°C. dehydration. At 245°C. the main spectral event associated with the loss of water appeared to be the development of unsaturation. This suggested that water was being abstracted from the basic polyacrolein structure.

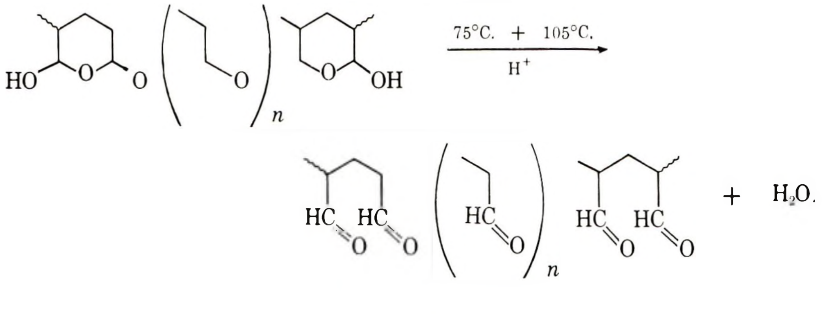
It is interesting to note that whereas free carbonyl absorption could be developed at room temperature simply by allowing the pellet to sit for an extended period (50–60 hr.) in a very dry helium stream the carbonyl band intensity could be raised to, but never made to exceed, the value resulting from firing the pellet at the 75°C. inflection point. This suggested that 75°C. constituted the upper temperature limit of the structure responsible for this carbonyl, and the very labile nature of this group strongly indicated that it was the singly hydrated carbonyl group (II).

In order to obtain a more quantitative picture of the relationship between carbonyl and liberated water the carbonyl changes were expressed in moles per 100 g. absorptivities of 14 being used for the CH_2 bending mode (necessary for normalizing the values from different pellets) and 80 for the C=O band.[8] By expressing the measured water in the same fashion the moles carbonyl generated per mole water liberated could be calculated. Table III is typical of the data obtained.

The wide variation in the amount of carbonyl generated per molecule of water released amply confirms the varied origins of the evolved water. Considered in the light of the various structural units thought to be present in polyacrolein a number of tentative conclusions can be drawn.

(*1*) The carbonyl/water ratio at 75°C. is less than 1.0 because of the free water known to be present in this temperature range. Although the true ratio, excluding free water, could not be determined, there is good reason to suspect as mentioned earlier that the dehydration of singly hydrated carbonyl groups was involved and that the ratio therefore should be 1.0.

(*2*) In the 75–105°C. range a multiplicity of carbonyl was generated per unit of water lost although again the value was probably depressed by the inclusion of free water. This strongly suggests that the unzipping of the fused tetrahydropyran rings is taking place:

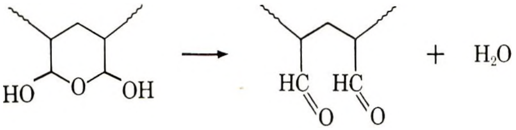


Such behavior would not be incompatible with the well-known tendency for the related aldehyde polymers, particularly in their uncapped state, to undergo degradation by chain unzipping. The fact mentioned earlier that the major reduction in ether linkages also takes place in this temperature range lends further support to this structural assignment.

TABLE III
Relationship between Free Carbonyl and Evolved Water in Dehydrated Polyacrolein

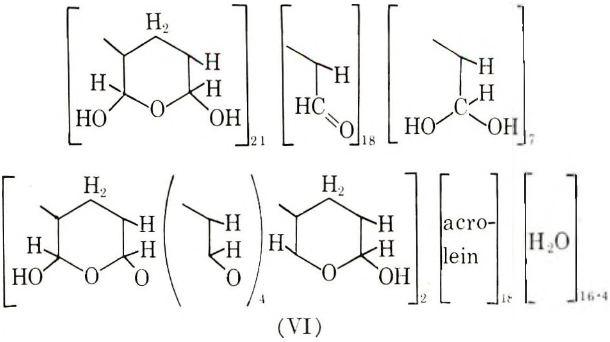
Polymer treatment	Free carbonyl, mole/100 g.		Evolved water, mole/100 g.		Ratio $\frac{\text{carbonyl}}{\text{water}}$
	Total	Increase	Total	Increase	
Untreated	0.32	—	—	—	—
75°C.	0.45	0.13	0.38	0.38	0.34
75°C. + 105°C.	0.72	0.27	0.42	0.04	6.7
75°C. + 105°C. + 205°C.	1.47	0.75	0.83	0.41	1.8

(*3*) In the 105–205°C. range approximately two carbonyl groups were generated for every water molecule. This is the result to be expected from the elimination of water from isolated dihydroxytetrahydropyran rings:



(*4*) Between 205 and 245°C., after making due allowance for overlap of the 105–205°C. elimination reaction, no further carbonyl-generating reactions appeared to be taking place. In this range the major feature was the appearance of unsaturation within the polymer. Since repeated carbon and hydrogen analyses have shown that the values for theoretical polyacrolein are approached after dehydration to 205°C., the water eliminated in the 205–245°C. range does not appear to be part of the extra water incorporated in the various hydrated structural groups but may derive from the aldehyde groups themselves, perhaps in their enol form. Hence it is of minor interest in the present investigation.

On accepting the above assignments and by using the carbonyl, developed at each stage and expressed as a percentage of the theoretical total carbonyl in polyacrolein, as a measure of the amount of each associated structural unit it was possible to develop a partial structure for the polymer. Based on a hundred acrolein units plus 12–13% extra water (the amount liberated before the elemental analysis matched that for the theoretical acrolein polymer) formula VI was arrived at.



(VI)

This formula is in good accord with most of the information available on polyacrolein. Of course, the suggested structure is undoubtedly greatly oversimplified. For example, no indication is given of the percentage of hemiacetal ether bridges between chains. The latter would merely represent special forms of the hydrated structures shown above which incorporate hemiacetal ether bridges such as the dihydroxytetrahydropyran rings or the fused ring system. Their breakdown could occur within the same temperature range as their associated structure and therefore would probably not be separately identifiable.

The eighteen [acrolein] units out of one hundred which are not accounted for are a consequence of the fact that the free carbonyl figure could not be raised to the theoretical value by dehydration, at least under the conditions tried. While some of the eighteen were no doubt associated with unknown structure elements it is likely that a number of them were originally associated with structural units of the above type which upon heating underwent reactions other than the elimination of water to give free carbonyl groups. Since the elimination reactions are pH-sensitive (the polyacrolein samples were all adjusted to the same pH—substantially neutral—for this investigation) it is not unlikely that under different conditions a more complete approach to the theoretical polyacrolein structure could be achieved.

Notwithstanding these objections the formula does provide for the first time a rough idea of the likely proportions of some of the structural elements in the polymer. Such information may be of considerable value in the future when it is desired to modify one or more of these structures to secure certain changes in the properties of the polymer for applicational purposes.

It is to be emphasized that the above formula strictly applies only to the particular polymer sample under examination. As the data in Table II indicate, there is considerable variation among various samples, presumably due to variations in the proportions of the different structural subunits.

Polyacrolein in most of its potential applications in the papermaking and textile industries is used as a solution. Because of its insoluble nature, solutions can generally be only prepared by chemical reaction with various reagents to produce soluble derivatives of the parent polymer. A typical example is the polyacrolein–bisulfite adduct prepared by reaction with sodium bisulfite or sulfur dioxide in aqueous media.

As a practical outgrowth of the work described above it has been found that the greatly increased free carbonyl resulting from the dehydration ("activation") of the polymer at elevated temperatures greatly facilitates its reaction with a number of carbonyl reagents. As a striking example, polyacrolein samples which are or have become, on aging, virtually insoluble in aqueous sodium bisulfite solution can be made to dissolve readily and completely after such activation. Soluble samples dissolve faster and give clearer solutions of increased mobility. The molecular weight of the polymer appears to be virtually unchanged. Intrinsic viscosities, measured on solutions of the SO_2 adducts, have been 1.07 dl./g. before dehydration, as compared to 1.04 dl./g. after treatment.

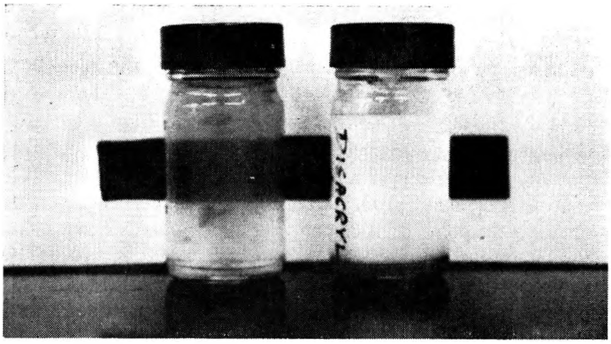


Fig. 6. Effect of dehydration ("activation") on reaction of polyacrolein with aqueous Girard's reagent T: (*left*) activated polyacrolein; (*right*) untreated polyacrolein.

Other reactions have been similarly improved. For example, Girard's reagent T, $[(CH_3)_3NCH_2CONHNH_2]^+ Cl^-$, used to convert carbonyl compounds to water-soluble derivatives, forms an opaque white emulsion in water with untreated polymer. Upon activation a clear solution is readily obtained (Fig. 6).

In the Cannizzaro reaction with base, high molecular weight poly-acroleins generally give 20% or less of base-soluble product. After dehydration, base solubility can be raised to 60–80%.

In summary, the dehydration of polyacrolein at controlled temperatures has proven to be a sensitive method for the analysis of the polymer by measuring the evolved water and in combination with infrared has thrown considerable light on the proportions of a number of structural units known to exist in the polymer. As a practical offshoot, the dehydration procedure has been shown to have an activating effect with regard to reaction with various solubilizing reagents important for various potential applications of this interesting polymer.

The skilled assistance of H. E. Melling and E. Meyer of our Glassblowing Shop in the construction of the pyrolyzer unit is gratefully acknowledged.

References

1. Redtenbacher, J., *Ann.*, **47**, 113 (1843).
2. Schulz, R. C., *Kuntstoffe*, **47**, 303 (1957).
3. Schulz, R. C., and W. Kern, *Makromol. Chem.*, **18/19**, 4 (1956).
4. Lehrle, R. S., and J. C. Robb, *Nature*, **183**, 1671 (1959).
5. Janak, J., *Nature*, **185**, 684 (1960); *Coll. Czech. Chem. Commun.*, **25**, 1780 (1960).
6. Knight, H. S., *Anal. Chem.*, **30**, 2030 (1958).
7. Kirkland, J. J., *Anal. Chem.*, **35**, 2003, (1913).
8. Ryder, E. E., Jr., and Pezzaglia, P., paper presented to Division of Polymer Chemistry, 148th Meeting, American Chemical Society, Chicago, September 1964; *J. Polymer Sci.*, **A3**, 3459 (1965).
9. Forbes, J. W., and Schissler, D. O., paper presented to Divisions of Analytical Chemistry and Polymer Chemistry, 148th Meeting, American Chemical Society, Chicago, September 1964.

Résumé

L'utilisation d'une technique spéciale pour la pyrolyse à basse température de la polyacroléine et la mesure précise de l'eau libérée de ce fait par le polymère ont démontré la présence de points d'inflexion bien définis dans la courbe du dégagement d'eau en fonction de la température de déshydratation pyrolyse. Ces faits indiquent la présence d'eau dans la polyacroléine, eau provenant d'un certain nombre de sources différentes, par ex structurale, liée à l'hydrogène et libre. Une relation entre le dégagement d'eau mesuré entre les températures du point d'inflexion et les groupements carbonyles libres, engendrés en même temps, mesurés par spectrographie infrarouge, a procuré des informations sur le type et la proportion des différentes sous-unités structurales dans la molécule de polyacroléine. Cette information a été employée pour établir une formule de structure partielle pour l'échantillon particulier de polyacroléine examiné. Comme conséquence pratique de ce travail, le concept d'activation de la polyacroléine par déshydratation à température élevée s'est montré utile en facilitant la réaction du polymère avec un certain nombre de réactifs du groupe carbonyle tel que le bisulfite de sodium, SO_2, etc.

Zusammenfassung

Die Verwendung einer speziell entwickelten Versuchstechnik für die Tieftemperatur pyrolyse von Polyacrolein und die genaue Bestimmung des dabei aus dem Polymeren freigesetzten Wassers liessen die Anwesenheit wohldenfinierter Wendepunkte in der Kurve Wasserentwicklung-Dehydratations ("Pyrolyse") temperatur erkennen. Es wird angenommen, dass diese durch die Anwesenheit von Wasser in Polyacrolein aus verschiedenen Quellen, z.B. strukturell, wasserstoffgebunden und frei, bedingt sind. Eine Korrelation der gemessenen Wasserentwicklung zwischen Wendepunktstemperaturen und den gleichzeitig auftreteden, nach einem IR-Verfahren bestimmten Carbonylgruppen liefert Aufschlüsse über den Typ und den Anteil an verschiedenen Struktur-Untereinheiten im Polyacroleinmolekül. Diese Information wurde zur Aufstellung einer partiellen Strukturformel für die speziellen hier untersuchten Polyacrolein probe verwendet. Als praktisches Ergebnis dieser Arbeit wurde die Brauchbarkeit des Konzepts der Aktivierung von Polyacrolein durch Dehydratation bei erhöhter Temperatur zur Erleichterung der Reaktion des Polymeren mit einer Anzahl von Carbonylreagentien wie Natriumbisulfit, SO_2 usw. gezeigt.

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Reactions of High Molecular Weight Polyacrolein*

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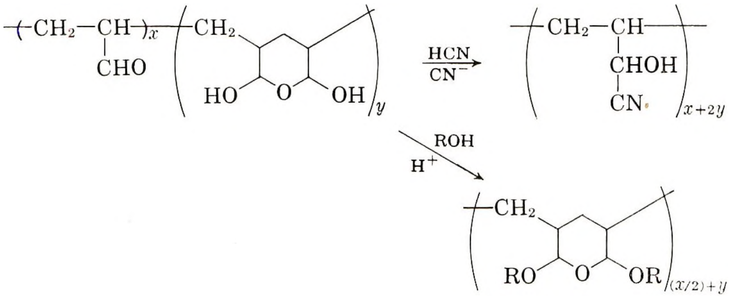
Synopsis

High molecular weight polyacrolein reacts readily with a variety of aldehyde reagents to form soluble derivatives. The reactions proceed at a measurable rate at room temperature when suitably catalyzed by acid or base. Gentle warming is occasionally required to attain useful reaction rates. The reactions of polyacrolein are conveniently divided into those involving (*a*) the aldehyde function alone or (*b*) the active hydrogen alpha to the carbonyl. The first class includes reactions with HCN, $NaHSO_3$ (SO_2), $Na_2S_2O_4$, primary and secondary amines, alcohols, thiols, and aqueous base. The second type reaction includes additions to the α-carbanion and oxidations involving chain scission. Depending on the reagent employed and conditions, reaction of polyacrolein gives open-chain derivatives or the 2,6-disubstituted tetrahydropyran structure which is present to a large extent in hydrated polyacrolein.



Base-catalyzed disproportionation of polyacrolein yields a polymethylol polycarboxylic acid via internal Cannizzaro reaction. In the presence of formaldehyde, α-methylol groups are introduced during the disproportionation.

INTRODUCTION

Polyacrolein, formed by spontaneous polymerization of acrolein, was first described in 1843.[1] Such polymers were termed disacryls and were infusible, highly insoluble materials. Recently Schulz and Kern[2-4], in their pioneering work on polyacrolein, prepared relatively low molecular weight polymers by free radical and ionic catalysis. The free radical polymers were found to be soluble in a variety of reactive media: aqueous SO_2 (or

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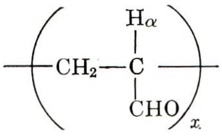
$NaHSO_3$), hydroxylamine hydrochloride in pyridine and organic solvents containing alcohols or mercaptans and an acid catalyst.[2]

The present work deals with the solution reactions of high molecular weight polyacrolein produced under controlled conditions by redox[5] or x-ray[6] initiation. Such materials are of high functional purity. They contain close to 100% of the theoretical carbonyl groups (free and combined) as indicated by analysis with hydroxylamine hydrochloride. They have viscosity-average molecular weights of $> 200{,}000$ and intrinsic viscosities (IV) $\geqq 1.0$ dl./g. as measured at 25°C. in aqueous SO_2 containing Na_2SO_4.

RESULTS AND DISCUSSION

High molecular weight polyacrolein (I) was found to be insoluble in a wide variety of polymer solvents (up to 100°C.). It did dissolve at 25°C. in 70% aqueous dichloroacetic acid, with severe degradation, the IV going from 1.0 to 0.35. Several solvents (dimethyl sulfoxide, methyl *n*-butyl sulfoxide, sulfolane hexamethylphosphoramide, dimethylformamide, and ethylene carbonate) dissolved and degraded polyacrolein at 150°C.

In order to obtain useful derivatives, reactions were carried out during which polyacrolein went into solution, usually at or near 25°C. with a suitable reagent and catalyst. The solution reactions can be divided into polyacrolein reactions involving (*a*) the carbonyl or potential carbonyl function alone, (*b*) the acidic α-hydrogen, or both.



$$\left(-CH_2-\overset{\overset{H_\alpha}{|}}{\underset{\underset{CHO}{|}}{C}}- \right)_x$$

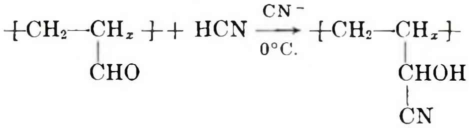
I

The first class includes reactions with HCN, $NaHSO_3$ (or SO_2), $Na_2S_2O_4$, primary and secondary amines, alcohols, thiols, and aqueous base (Cannizzaro reaction). The second type reaction includes addition to the α-carbanion and oxidations involving chain scission.

Depending on the reagent employed and conditions, reaction of polyacrolein gives open chain derivatives (favored by basic reagents) or the 2,6-disubstituted tetrahydropyran structure (favored by acidic reagents or acid catalyzed reactions) which is present to a large extent in hydrated polyacrolein.

Reactions of the Carbonyl Function of Polyacrolein

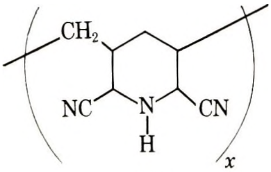
HCN. Low molecular weight polyacrolein was reported not to react with HCN,[4] although cyanohydrin type produces were obtained indirectly by reaction of poly acrolein sodium bisulfite with NaCN.[7] We have found that polyacroleins of IV up to 2.2 dl./g. react rapidly with HCN catalyzed by CN^- at 0–25°C. [eq.(1)]. This is the fastest solution reaction observed with polyacrolein to date. With a polyacrolein of 1.3 IV in 40% aqueous HCN, solution times at 0–15°C. were 5 and 40 min. with ratios of CN^-/acrolein of 0.19 and 0.015, respectively. It was found that polymer isolated immediately after the polyacrolein went into solution and 5.5 hr. later had the same analysis. No reaction was observed in the absence of CN^- or in the presence of *p*-toluenesulfonic acid.



$$\underset{\displaystyle \underset{|}{}\text{CHO}}{\left[\!-\text{CH}_2\text{—CH}_x-\!\right]} + \text{HCN} \xrightarrow[0^\circ\text{C.}]{CN^-} \underset{\displaystyle \underset{|}{}\text{CHOH}\atop{|\atop \text{CN}}}{\left[\!-\text{CH}_2\text{—CH}_x-\!\right]} \qquad (1)$$

II

The product was characterized as the open-chain polyacrolein cyanohydrin (II) by its analysis and spectrum. The polymer is unstable if traces of CN^- are left in it. When quenched in aqueous solution containing strong acids (HCl, H_2SO_4, or H_3PO_4), the precipitated polymer is relatively stable. It will redissolve in polymer solvents and does not give off detectable amounts of HCN. Dioxane solutions of stabilized polyacrolein cyanohydrin were stored for over a year without gelation. Solutions containing traces of base (even acetate) gelled in several days. The polymer reacts with ammonia to give what appears to be the 2,6-dicyanopiperidine structure (III). It can be hydrolyzed to give polyamide and polycarboxylic acid.



III

NaHSO$_3$ (or SO$_2$) and Na$_2$S$_2$O$_4$. Low molecular weight polyacroleins were first reported by Schulz[2] to dissolve in aqueous $NaHSO_3$ and SO_2. High molecular weight polyacroleins, likewise, dissolve in these reagents to give water-soluble products. The "equilibrium" composition of the solution depends on temperature, pH, and SO_2/C_6-unit ratio. Free SO_2 (or HSO_3^-) was titrated with KI_3; the dissociation of the polysulfonic acid at acid pH and 35°C. was too slow to cause interference with this analysis (half life 381 min. for first 18% of unimolecular dissociation). Table I tabulates the extent of reaction of a polyacrolein of 1.5 IV with SO_2 in water.

It is likely that for bound SO_2/C_6 unit ratios of about 1.0, the polymer exists in the pyranose form. However, it is clear that in the presence of excess SO_2, open-chain hydroxysulfonic acid forms. It was also observed that additional SO_2 (or HSO_3^-) was very slowly bound on allowing the solutions to stand for several months. The reaction could be reversed by heat-

TABLE I
Equilibrium between Polyacrolein (IV 1.5) and SO_2 (or N_2HSO_3)
$RCHO + H_2SO_3 \rightleftharpoons RCHOHSO_3H$; $K_{eq} = [RCHOHSO_3H]/([RCHO][SO_2])$

SO_2/C_6 unit	SO_2 molarity	SO_2/C_6 unit (3 weeks)	K_{eq} (3 weeks)	HSO_3/C_6 unit	HSO_3^-/C_6 unit (1 week)	K_{eq} (1 week)
0.72	0.20	0.69	70	—	—	—
0.84	0.20	0.77	36	—	—	—
1.14	0.20	0.94	25	1.14	1.04	60
1.88	0.40	1.31	16	1.50	1.14	34
2.26	0.40	1.47	19	2.26	1.40	31

ing the solution with a nitrogen stream running through to remove SO_2 or by evaporation which led to sulfur containing insoluble films.

The acid form of the sulfonic acid is sensitive to temperature and concentration. Solutions of 20 wt.-% gel, even at room temperature, by acetal crosslinking. This is reversed by subsequent dilution with water but is kinetically slow (several months at 25°C. for polymers with IV > 1).

The sodium salt is much less sensitive and can even be spray-dried at 150°C. to a 100% solids content, water-soluble powder.

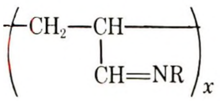
Polyacrolein sulfonic acid is stable at 25°C. up to pH 8 but dissociates and reacts with base rapidly in the pH 9–14 region.

By analogy to $NaHSO_3$, $Na_2S_2O_4$ dissolves polyacroleins at room temperature. Polymers of IV 0.8–1.8 dissolve at $S_2O_4^=/C_6$ ratios of 0.50–2.0 in aqueous solution. The polymer, after removal of unreacted $S_2O_4^=$ and HSO_3^- (with iodine), reduces methylene blue rapidly at room temperature, unlike polyacrolein bisulfite. Its structure is indicated to contain $-SO_2Na$ as well as $-SO_3Na$ groups.

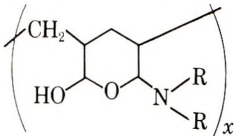
Primary and Secondary Amines. Polyacroleins of IV up to 2.1 dissolved in a wide variety of primary and secondary amines. For primary aliphatic amines, the solution rate increased with basicity: $C_2H_5OCH_2CH_2CH_2NH_2 > CH_2{=}CH{-}CH_2NH_2 > C_6H_5CH_2NH_2 \gg C_6H_5NH_2$. For secondary amines, solution rates were slower than for the primary amines, requiring several days to weeks at room temperature. Cyclic secondary amines reacted faster than acylic, the approximate order being pyrrolidine > morpholine > piperidine > diethylamine N >-methylbenzylamine ≫ *N*-methylaniline. Aromatic primary and secondary amines generally reacted so slowly that they merely swelled the polyacrolein. Ammonia and diamines, such as ethylenediamine, generally swelled and crosslinked polyacrolein unless the reaction was run with large excesses of amine.

Several tertiary amines dissolved polyacrolein at elevated temperatures, probably by Cannizzaro reaction. *N*-Methylmorpholine was effective at 100°C., quinoline at 150°C.

The amine products varied in composition depending on reaction conditions. When large excesses of amine were employed, primary amines gave products indicated to be mainly imine (IV) while secondary amines gave aminols (V).



IV



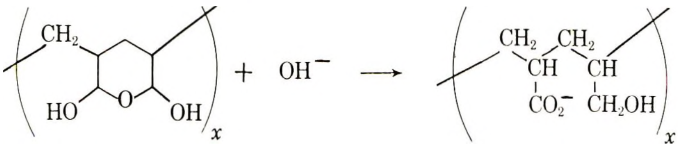
V

The amine products were generally soluble in solvents such as chloroform, THF, DMSO. They dissolved in dilute acid and aqueous SO_2.

Reaction of Polyacrolein With Base (Cannizzaro Reaction)

Treatment of wet polyacrolein with 0.75–5.0N NaOH, with the use of 1.5 mole of base per acrolein unit, gave a rapid solution reaction at 5°C. in which a portion of the aldehyde groups is converted to carboxylate. The polymer dissolved long before reaction is complete. A reaction short-stopped 1 hr. after solution was attained (at 5°C.) gave a product containing only 0.20 eq./100 g. acid. (On completion of reaction at 25°C., acidity is ca 0.5 eq./100 g.)

If less concentrated base is used, reaction proceeds at a measurable rate at 25°C. but the polyacrolein never dissolves. Presumably it crosslinks by aldol condensation between chains. In 0.10N NaOH, with 1.0 moles of base per acrolein unit, 50% and 65% reaction was reached in 60 and 240 hr., respectively, for the reaction [eq. (2)].

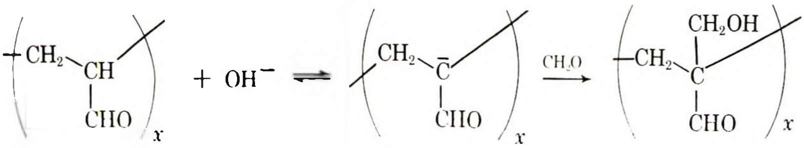


(2)

The water-soluble sodium salts produced by the reaction of base with polyacrolein behave as thickening agents similar to sodium polyacrylate.

Reactions of the α-Hydrogen of Polyacrolein

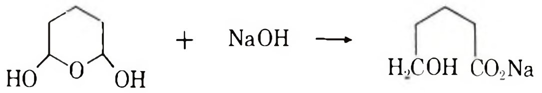
Reaction of Polyacrolein With Base and Formaldehyde. If formaldehyde is present during the Cannizzaro reaction, conversion of some of the α-hydrogens to methylol takes place [eq. (3)].



(3)

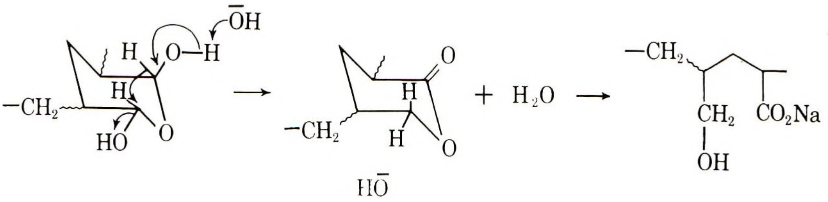
By varying the ratio of CH_2O/acrolein unit and the base concentration, products were obtained, as water-soluble sodium polycarboxylates, which contained hydroxyl (0.8–1.6 eq./100 g.), carboxyl (0.31–0.40 eq./100 g.), unreacted carbonyl (0.28–0.37 eq./100 g.) and water (2–11%). Under all conditions studied in aqueous systems, the Cannizzaro reaction was so fast that complete conversion of all α-hydrogens to methylol was not possible. Recently, Schulz, Kovacs, and Kern[8] reported that reaction of polyacrolein of very low intrinsic viscosity with formaldehyde and base in aqueous pyridine gave highly methylolated products containing ca. 0.1 eq./100 g. of carboxyl. Hydroxyl values were not given, however.

The model reaction of hydrated glutaraldehyde with aqueous NaOH was studied to obtain a quantitative measure of the rapidity of the Cannizzaro reaction in the 1,5-dialdehyde system present in polyacrolein. On mixing equal volumes of 1.0*M* glutaraldehyde and 1.0*M* NaOH at 25°C. and tapping a sample immediately, ca. 75% reaction occurred [eq. (4)].



(4)

It is believed that the very facile Cannizzaro reaction of polyacrolein with base [eq. (5)] results from the high pyranose content of the polymer.



(5)

Table II summarizes the results of some of the reactions of high molecular weight polyacrolein with formaldehyde and base.

TABLE II
Preparation of Polyacrolein–Formaldehyde–Base Reaction Products[a]

Normality of NaOH	NaOH, mole-/mole acrolein	CH_2O, mole-/mole acrolein	Reaction time at 25°C., hr.	Product analysis, eq./100 g.	
				$-CO_2H$	$-OH$
1.0	2.0	0.5	96	0.40	0.80
1.0	2.0	0.5	120	0.39	1.40
0.5	1.5	1.5	48	0.35	1.61
0.2	1.5	1.5	72	0.38	1.26
0.1	0.7	0.7	96	0.35	0.79
0.1	1.0	5.0	120	0.31	0.84
1.0	1.3	2.5	72	0.35	1.02

[a] From polyacrolein 1.6 IV.

Reactions Involving Chain Scission. Polyacrolein reacts and dissolves in warm 30% HNO_3 or in 5% NaOCl at room temperature. In both cases, severe degradation to lower molecular weight polycarboxylic acids occurs.

For example, a polyacrolein of 1.4 IV dissolved in aqueous NaOCl (OCl^-/acrolein = 1.65; pH 12) in 40 min. at 25°C. Acidification gave a fairly water-soluble, low molecular weight polycarboxylic acid containing 8.7% chlorine.

EXPERIMENTAL

Preparation of High Molecular Weight Polyacrolein

The polyacrolein samples used in this study were prepared by redox[5] or x-ray[6] -initiated polymerization. They were finely divided white powders containing 10–15% water. Polyacrolein remained a free-flowing powder even when hydrated to 60% weight H_2O.

Preparation of Polyacrolein Sulfonic Acid

To a solution of 650 g. (10.2 mole) of SO_2 in 10 liters water was added 1100 g. of a 1.2 IV polyacrolein (containing 980 g. or 17.5 mole acrolein and 120 g. H_2O) over a 5-min. period. The mixture was stirred in a 5-gal. glass carboy until it set solid (40 min.) and redissolved (additional 120 min.). The reaction was mildly exothermic (20 → 27°C.) and was completed by allowing the solution to stand at room temperature.

The clear product solution had an acidity of 0.124 eq./100 g. and had 0.88 mole bound SO_2/C_6 unit. It had a viscosity of 0.795 poise (25°C.) and a pH of 0.3.

Preparation of Polyacrolein Sodium Sulfonate. A 5-gal. carboy was swept with N_2, charged with a solution of 1425 g. $Na_2S_2O_5$ (15.0 mole) in 1244 g. of a 1.8 IV polyacrolein (containing 1120 g. acrolein or 20 mole) was added. The suspension gelled in 1.5 hr. but no exotherm was noted. After 4 hr. the gel softened, but 14 hr. was required before stirring could be resumed. After 22 hr. solution was complete. KI_3 titration at this time and 16 hr. later solution was complete. KI_3 titration at this time and 16 hr. later indicated reaction to be complete (bound HSO_3^-/C_6 unit = 1.30). The solution pH was ca 2.3 and its viscosity was 48.54 poise (25°C.).

The sodium salt could be isolated by spray drying at an inlet temperature of 140–160°C. in a Nicols Engineering laboratory model spray dryer. The product was an asbestoslike powder which dissolved readily in water and was nonhygroscopic. The water content was 0.8–2.6%.

ANAL. Calcd. for $C_3H_4O \cdot {}^3/_4\ NaHSO_3$: S, 17.9%; C, 26.8%; H, 3.64%. Found (for four fractions): S, 14.4–16.2%; C, 24.7–28.9%; H, 4.0–4.3%.

Preparation of Polyacrolein Cyanohydrin. A 10-g. portion of a 1.25 IV polyacrolein was suspended in a solution of 35 g. HCN in 124 g. H_2O at 0°C. After stirring for several minutes, to soak the polymer, 4.4 meq. NaOH was added. Dissolution of the polymer began immediately and was complete in ca 30 min. After warming to 25°C., the clear, colorless solution was precipitated, by pouring into water containing excess acetic acid, to give a tacky solid which was vacuum-dried at 25°C./1 mm. The colorless glassy product (80% yield) was powdered. It was soluble in dioxane, DMF, and DMSO when freshly prepared but gradually lost solubility, presumably by crosslinking with the loss of HCN. The infrared spectrum had sharp 4.50 μ nitrile band and a 2.99 μ hydroxyl band.

Anal. Calcd. for $(C_4H_5NO)_x$: C, 57.9%; H, 6.06%; N, 16.9%; hydroxyl 1.20 eq./100 g. Found (H_2O-free basis): C, 58.0%; H, 6.28%; N, 16.3%; hydroxyl, 1.26 eq./100 g.

Similarly, solutions of polyacrolein cyanohydrin were prepared in organic solvents such as dioxane and methanol.

Preparation of γ-Ethoxypropylimine of Polyacrolein. A 5-g. portion of 1.5 IV polyacrolein was added to 52 g. of γ-ethoxypropylamine. The reaction became pasty immediately and was diluted with 50 ml. dioxane after 30 min. Most of the polymer dissolved overnight (25°C.). After 3 days, the clear solution was diluted with 250 ml. dioxane and precipitated by addition to 1500 ml. H_2O to give, after drying, 8.0 g. white powder. The infrared spectrum of the product had a strong 6.0 μ C=N band.

Anal. Calcd. for $(C_8H_{15}NO)_x$: C, 68.1%; H, 10.7%; N, 9.9%; O, 11.3%. Found: C, 67.2%; H, 10.0%; N, 8.9%; O, 13.9%.

Preparation of Morpholine Reaction Product of Polyacrolein. A 10-g. portion of 1.5 IV polyacrolein was suspended in 100 g. of morpholine and the mixture warmed at 100°C. for 4 hr., during which time a light yellow solution formed. Precipitation in water gave a powder which on vacuum drying weighed 10 g. The product had a very weak carbonyl band at 5.81 μ, a water band at 6.15 μ, and a strong hydroxyl band at 2.95 μ.

Anal. Calcd. for $(C_{10}H_{17}NO_3)_x$: C, 60.3%; H, 8.6%; N, 7.05%. Found: C, 61.8%; H, 9.2%; N, 7.03%.

Reaction of Polyacrolein with LiOH (Cannizzaro Reaction). To 3.5 liters of 1*N* LiOH maintained at 5°C. under nitrogen, was added, portionwise, 407 g. of hydrated 1.5 IV polyacrolein containing 1.16 mole aldehyde. The solution of the polymer was rapid at 5°C. The reaction was completed by stirring at room temperature. After standing for 72 hr., the solution was cooled to 5°C. and titrated to pH 3 with 735 ml. 5*N* H_2SO_4 to precipitate the product (63 g.; 86%). NaOH and KOH worked equally well.

Anal. Calcd. for $(C_9H_{14}O_4)_x$:* C, 58.2%; H, 7.6%; acidity, 0.53 eq./100 g. Found: C, 59.8%; H, 7.6%; acidity, 0.45 eq./100 g.

Reaction of Polyacrolein with NaOH and CH_2O. To 2 liters 1*N* NaOH held at 5°C. under nitrogen was added, with stirring, 415 g. of wet 1.6 IV polyacrolein (corresponding to 1.0 mole dry polymer as C_3H_4O). The polymer was pretreated by blending it with 400 ml. H_2O and 42 ml. (0.5

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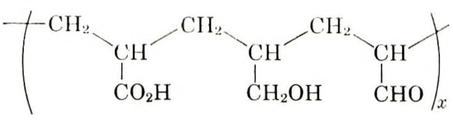

$$\left(-CH_2-\underset{CO_2H}{\underset{|}{CH}}-CH_2-\underset{CH_2OH}{\underset{|}{CH}}-CH_2-\underset{CHO}{\underset{|}{CH}}-\right)_x$$

mole) of 37% formalin in a Waring Blendor. The mixture was stirred overnight at room temperature. After standing for 3 days, the solution was titrated with 400 ml. 5*N* H_2SO_4 (final pH 2.5) to precipitate the product which was washed with H_2O and dried at 25°C./1 mm. to give 58 g. (86%) of a hard, white polyhydroxy acid.

ANAL. Calcd. for ($C_{13}H_{22}O_6$.2% H_2O):* C, 55.5%; H, 8.1%; H_2O, 2.0%; carbonyl, 0.37 eq./100 g.; acidity, 0.37 eq./100 g., hydroxyl 1.1 eq./100 g. Found: C, 56.1%; H, 7.6%; H_2O, 2.0%; carbonyl, 0.33 eq./100 g.; acidity, 0.39 eq./100 g.; hydroxyl, 1.4 eq./100 g.

References

1. Redtenbacher, J., *Ann.*, **47,** 113 (1843).
2. Schulz, R. C., *Kuntstoffe*, **47,** 303 (1957).
3. Schulz, R. C., *Makromol. Chem.*, **17,** 62 (1955).
4. Schulz, R. C., and W. Kern, *Makromol. Chem.*, 18/19, 4 (1956) and subsequent papers.
5. Ryder, E. E., Jr., and P. Pezzaglia, *J. Polymer Sci.*, **A3,** 3459 (1965).
6. Bell, E. R., V. A. Campanile, and E. Bergman, U. S. Pat. 3,105,801, to Shell Oil Co.
7. Brit. Pat. 797,459, to Degussa.
8. Schulz, R., J. Kovacs, and W. Kern, *Makromol. Chem.*, **67,** 187 (1963).

Résumé

La polyacroléine de poids moléculaire élevé réagit facilement avec une quantité de réactifs de l'aldéhyde pour former des dérivés solubles. Les réactions ont lieu à une vitesse mesurable à température de chambre lorsqu'elles sont catalysées d'une façon convenable par un acide ou une base. Un léger chauffage est parfois nécessaire pour atteindre des vitesses de réactions convenables. Les réactions de la polyacroléine sont divisées d'une façon commode en deux types comprenant (*a*) la fonction aldéhyque seule ou (*b*) l'hydrogène actif en α. La première classe comprend les réactions aved >CN $Na_2S_2O_4$, les amines primaires et secondaries, les alcools, les thiols et les bases en solution agueuse. Le second type de réaction comprend les addition au carbanion en α et les oxydations impliquant une scission de chaîne. Suivant le réactif employé et les conditions expérimentales, la réaction de la polyacroléine fournit des dérivés à chaine ouverte ou une structure tétrahydropyranique disubstituée en 2,6, laquelle est présente en grande quantité dans la polyacroléine hydratée. (Voyez résumé en anglais.) Le disproportionnement, catalysé par les bases, de la polyacroléine fournit un acide polyméthylal-polycarboxylique en passant par une réaction de Cannizzaro interne. En présence de formaldéhyde, des groupements -méthyloliques sont introduits au cours du disproportionnement.

Zusammenfassung

Hochmolekulares Polyacrolein reagiert leicht mit einer Vilelzahl von Aldehydreagentien unter Bildung löslicher Derivate. Bei geeigneter Katalyse durch Säuren oder Basen verlaufen die Raktionen bei Raumtemperatur mit messbarer Geschwindigkeit. Zur Erreichung brauchbarer Reaktionsgeschwindigkeiten bedarf es gelegentlich einer

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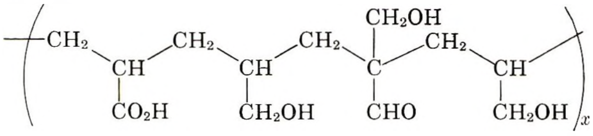

schwachen Erwärmung. Die Polyacroleinreaktionen werden zweckmässig in solche (*a*) unter Beteiligung der Aldehydfunktion allein oder (*b*) des aktiven α-Wasserstoffs eingeteilt. Zur ersten Klasse gehören Reaktionen mit HCN, $NaHSO_3$, (SO_2), $Na_2S_2O_4$, primären und sekundären Aminen, Alkoholen, Thiolen und wässriger Base. Reaktionen vom zweiten Typ sind Addition an das α-Carbanion und Oxydationen unter Kettenspaltung. Je nach dem verwendeten Reagens und den angewendeten Bedingungen liefert die Reaktion von Polyacrolein offene Kettenderivate oder die 2,6-disubstituierte Tetrahydropyranstruktur, welche in hydratisiertem Polyacrolein in grossem Ausmass vorhanden ist (siehe englische Zusammenfassung). Basenkatalysierte Disporportionierung von Polyacrolein liefert über eine innere Cannizzaro-Reaktion eine Polymethylolpolycarbonsäure. In Gegenwart von Formaldehyd werden während der Disproportionierung α-Methylolgruppen eingeführt.

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Thermoplastic Properties of Polyacrolein and Its Acetals*

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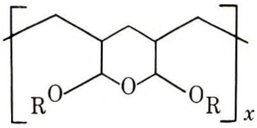
Synopsis

Free-radical polyacrolein is an essentially pure head-to-tail vinyl polymer which results in its being a poly- 1,5-dicarbonyl compound. The proximity of these carbonyl groups results in a partial cyclization (laddering) in the polymer or in its derivatives, which in turn has about the same effect on modulus as adding methyl groups to the backbone chain of a polyacrylate or pendant phenyl groups to the backbone chain of polyethylene. Above a viscosity-average molecular weight of about 200,000, respectable high polymer properties are attained, comparable to those of poly(methyl methacrylate) or polystyrene with higher heat deflection temperatures. Although thermal properties are sufficient to withstand boiling water, actual water and solvent resistances are marginal to poor.

Introduction

Polyacrolein can be prepared, by radical catalysis, as an essentially pure head-to-tail vinyl polymer, modified at least in part to a ladder polymer and by some crosslinking.[1,2] Since such a structure can also arise by successive Diels-Alder or Michael-type reactions, its intrinsic physical properties have a rather general importance in the polyacrolein complex.

Polyacrolein can be converted to a variety of aldehyde derivatives.[2-4] Requirements are mildly acidic catalyst, swelling solvent, and an excess of the aldehyde reagent. Among the derivatives are the acetals (I) in which a portion of the ladder structure is preserved, and a sulfurous acid derivative (II)



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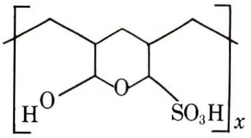

II

which reverts in part at least to the original polymer structure on evaporation to dryness.

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Physical State

It is known[5] that the poly(alkyl acrylates) are in the elastomeric state at ambient temperature. In the absence of other influences, it would be expected that polyacrolein would also be an elastomer. However the restriction in free rotation imposed by cyclization of both polyacrolein and of its acetals should tend to increase the glass temperature of these materials. Preliminary physical measurements showed that this was the case, and indeed that polyacrolein and a few of its acetals are organic glasses at room temperature.

Free-radical polyacrolein is obtained as a finely divided, noncrystalline, white powder with a very large surface area. It is always more or less hydrated or solvated by polar solvents, if these have been present during or after polymerization. Since the material is crosslinked, it can be dissolved only by reaction, and it softens only very lightly under the influence of heat and pressure. However at 150°C. and 4000–5000 psi, flow is sufficient to permit compression molding to clear, homogeneous specimens for physical testing.[6] Provided adsorbed monomer has been removed by washing, no acrolein is evolved on molding. Irreversible crosslinking sets in during this process, since the specimens are not remoldable.

Fundamental information about the polymer itself is obtained by inference from properties of the solubilized derivatives. Since these derivatives are not crosslinked, they are soluble; therefore solution properties can be determined. Being thermoplastic, they are of course remoldable.

Molecular weights of solubilized materials can be determined[7] from the expression

$$[\eta] = 2.05 \times 10^{-4} M^{0.70}$$

In spot checks the same intrinsic viscosity values have been found for acetals as for sulfur dioxide adducts. The values for aqueous sulfur dioxide solutions remain constant indefinitely in the absence of air. It seems reasonable, therefore, that the molecular weight of the solubilized polymer represents the molecular weight of the elements of the crosslinked network of polyacrolein.

Figure 1 shows the relationship of tensile strength to molecular weight for the compression-molded methyl acetal of polyacrolein, and for reconstituted polyacrolein obtained by evaporation of aqueous sulfur dioxide solutions.

Flexural strengths (data not plotted) of both compression-molded polyacrolein and of its methyl acetal are in the range 8000–9000 psi at intrinsic viscosities above 1.0 dl./g. It is clear from this and from Figure 1 that all three materials are physically similar, and that physical strength is typical of that of an organic glass once a minimum viscosity-average molecular weight of about 200,000 is attained.

This is confirmed in Figure 2, where the dependence of Izod impact strength on molecular weight again shows no distinction between polyacrolein and its acetals.

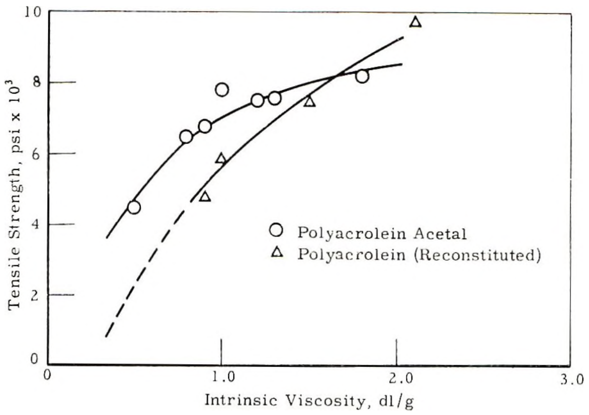

Fig. 1. Tensile strength vs. molecular weight.

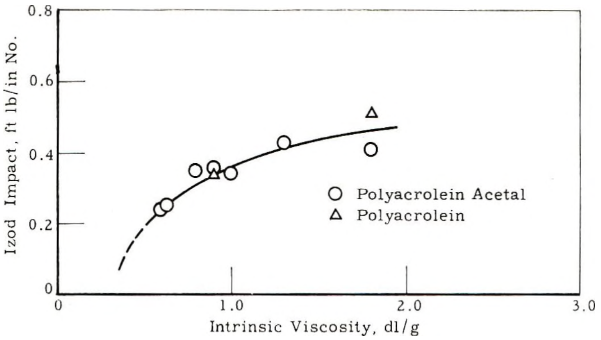

Fig. 2. Load impact vs. molecular weight.

Flexural strength, tensile and flexural moduli, and elongations at break are also very similar to the corresponding values for the commercial organic glasses.

Heat deflection temperatures for polyacrolein range from 95 to 115°C., depending on the original solvent from which the polymer precipitated. Polyacrolein adsorbs up to 25–30% of its weight of aliphatic alcohols or glycols. This alcohol is not lost on compression molding, even at 175–

TABLE I
Heat Deflection Temperatures for Polyacrolein Acetals

Acetal	Heat deflection temperature, °C.
Methyl	101–111
Ethyl	78–92
Allyl	80
Cyclohexyl	127
2-Methyl-2,4-pentanediol	65

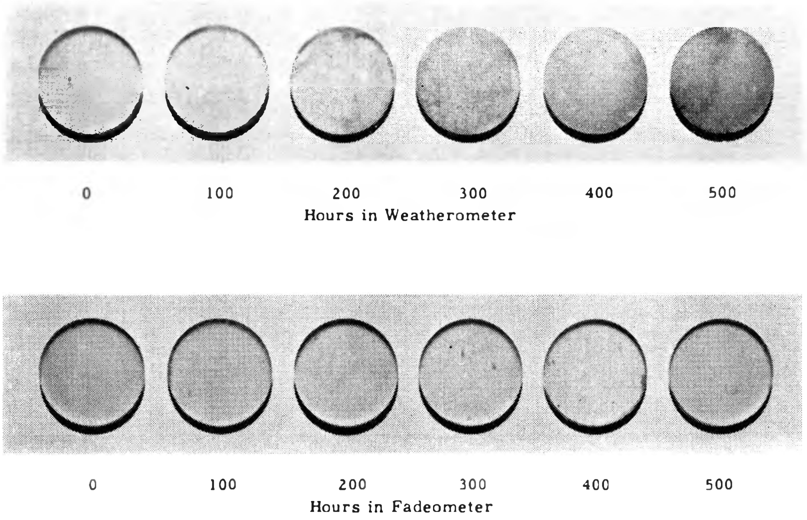

Fig. 3. Exposure data for polyacrolein.

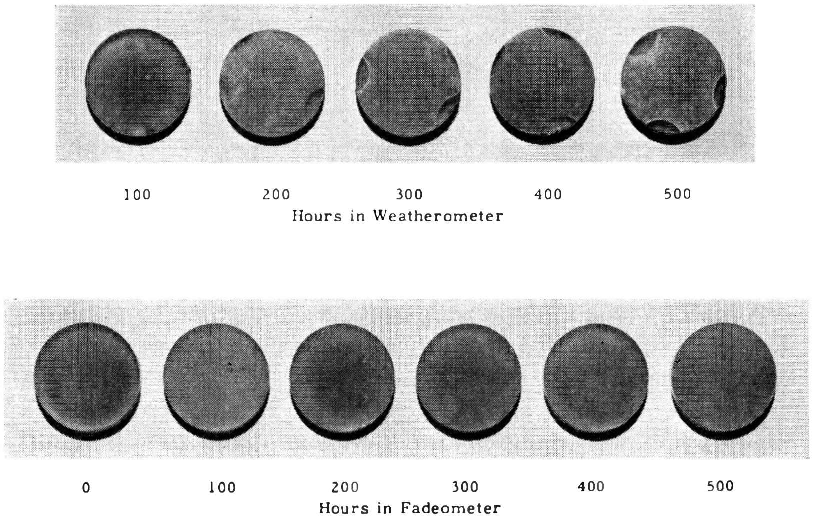

Fig. 4. Exposure data for polyacrolein acetal.

TABLE II
Solvent Uptake (1 Month)

	Solvent uptake, %						
Derivative	H_2O	Acetone	Benzene	Ethanol	Heptane	10% H_2SO_4	10% NaOH
Polyacrolein	+6.0	+3.6	−0.2	+1.5	—	+4.9	Disintegrates
Methyl acetal	+2.4	Soluble	Soluble	Swelled	—	+1.7	+2.0
Ethyl acetal	+0.96	Soluble	Soluble	Swelled	+34.4	+0.9	+0.8

TABLE III
Physical Properties

Polymer	Tensile strength × 10^{-3}, psi	Flexural strength, × 10^{-3}, psi	Izod impact, ft.-lb./in. notch	Heat deflection, temperature, °C.	Water absorption (24 hr.), %	Color	Trans-parency	Acid resistance	Alkali resistance
Polystyrene, general purpose	5–9	8–14	0.25–0.40	82–88	0.03–0.04	Excel.	Excel.	Excel.	Excel.
Poly(methyl methacrylate)	7–9	12–17	0.4 –0.5	80–98	0.3 –0.4	Excel.	Excel.	Excel.	Good
Polyacrolein methyl acetal	7–9	9.1	0.22–0.36	102–124	0.65–0.73	Fair	Fair	Good	Good
Polyacrolein ethyl acetal	7–9	8.5	0.22–0.39	78–92	0.43	Good	Fair	Good	Good
Polyacrolein	6–10	7.9	0.35–0.51	91–132	0.45	Good	Fair	Good	Poor

200°C., and the heat deflection temperature of the specimen is progressively lowered by these adsorbed alcohols.

On the other hand, heat deflection temperatures for the thermoplastic acetals are generally set by the structure of the alcohol used. Table I summarizes the available data. Butyl, benzyl, lauryl, and β-chloroethyl alcohols gave acetals softening at or near room temperature. Of the alcohols which gave acetals with heat deflections in the area of interest (>100°C.), cyclohexanol had the disadvantage of being quite sluggish and of therefore reacting incompletely to yield dark, turbid, still slightly crosslinked derivatives. By contrast, the methyl and ethyl acetals were quite easily prepared, were nearly clear and colorless, and were easily molded and otherwise amenable to thermoplastic processing. They were therefore selected for further testing (solvent resistance, Fadeometer, Weatherometer). Results are summarized in Table II, along with typical results for a compression-molded polyacrolein.

Noteworthy is the surprisingly good resistance of both polyacrolein and its acetals to aqueous acid. Only in alkali resistance (Cannizzaro reaction?) is polyacrolein markedly inferior to its acetals. The poor water resistances were confirmed in short-term boiling tests, which caused severe surface etching. Furthermore, Fadeometer and Weatherometer tests have shown the following: (*1*) polyacrolein moldings are affected in as little as 100 hr. in the Weatherometer and quite badly degraded in 500 hr.; (*2*) they are unaffected in the Fadeometer; (*3*) acetal moldings are slowly but progressively etched in the Weatherometer: at 100 hr. the effect is detectable, at 200 hr. it is evident, and at 500 hr. it is obvious, but the bulk of the specimens are unaffected; (*4*) acetal moldings are not affected in the Fadeometer. The good ultraviolet and high-temperature resistance are also confirmed by long storage in sunlight and on repeated molding at 160–170°C.

Figures 3 and 4 show the Weatherometer and Fadeometer tests for polyacrolein and its methyl acetal, respectively.

Physical data for polyacrolein and its acetals are summarized in Table III, along with typical data for poly(methyl methacrylate) and polystyrene.[8]

References

1. Schulz, R. C., and W. Kern, *Makromol. Chem.*, **18, 19,** 4 (1956).
2. Hunter, L., and J. W. Forbes, *J. Polymer Sci.*, **A3,** 3471 (1965).
3. Schulz, R. C., *Kunststoffe*, **48,** 257 (1957).
4. Bergman, E., W. T. Tsatsos, and R. F. Fischer, *J. Polymer Sci.*, **A3,** 3485 (1965).
5. Schildknecht, C. E., *Vinyl and Related Polymers*, Wiley, New York, 1952, pp. 246, 247.
6. Schilling, H., *Kolloid-Z.*, **175,** 110 (1961).
7. Schulz, R. C., E. Muller, and W. Kern, *Makromol. Chem.*, **30,** 39 (1959).
8. Schildknecht, C. E., *Vinyl and Related Polymers*, Wiley, New York, 1952, pp. 44, 215.

Résumé

La polyacroléine obtenue par polymérisation radicalaire est un polymère vinylique essentiellement tête à queue, parce qu'il est un composé poly-(1,5-dicarbonylique). La proximité de ces groupements carbonyles conduit à une cyclisation partielle (formation d'échelles) du polymère ou de ses dérivés, lequel à son tour a environ le même effet sur le module que les groupements méthyles ajoutés à la chaîne principale d'un polyacrylate ou que les groupements phényles attachés à la chaîne principale du polyéthylène. Au dessus d'un poids moléculaire moyen viscosimétrique d'environ 200.000 les propriétés d'un haut polymère sont atteintes, comparables à celles du polyméthacrylate de méthyle ou du polystyrène, avec des températures de dispersion calorifique plus élevées. Bien que les propriétes thermiques lui permettent de résister à l'eau bouillante, les résistances actuelles à l'eau et aux solvants sont faibles.

Zusammenfassung

Radikalisches Polyacrolein ist im wesentlichen ein reines Kopf-Schwanz-Vinylpolymeres, nämlich eine Poly(1,5-dicarbonyl)-Verbindung. Die Nachbarschaft dieser Carbonylgruppen führt zu einer teilweisen Zyklisierung (Leiterbildung) im Polymeren oder seinen Derivaten, welche ihrerseits etwa den gleichen Einfluss auf den Modul besitzen, wie die Addition von Methylgruppen an die Hauptkette eines Polyacrylats oder von Phenylgruppen an die Hauptkette von Polyäthylen. Oberhalb eines Viskositätsmittel-Molekulargewichts von etwa 200.000 werden beachtliche Polymereigenschaften erreicht, durchaus denjenigen von Poly(methylmethacrylat) oder Polystyrol vergleichbar, mit höheren Hitzeverformungstemperaturen. Obgleich die thermischen Eigenschaften für eine Beständigkeit gegen die Temperatur des siedenden Wassers ausreicht, ist die tatsächliche Wasser- und Lösungsmittelbeständigkeit eher schlecht.

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cis–trans Isomerization in Polyisoprenes. Part VII. Double Bond Movement During the Isomerization of Natural Rubber and Related Olefins

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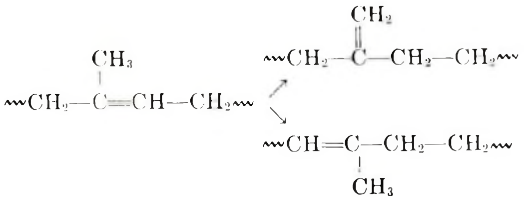
Synopsis

When *trans*-3-methylpent-2-ene or *trans*-3-methylhex-3-ene is treated with butadiene sulfone, thiolbenzoic acid, and dibenzoyl disulfide under anaerobic conditions, the olefin undergoes only *cis–trans* isomerization. However, similar reactions in the presence of oxygen or peroxides also cause changes in the position of the double bond. The latter structural modification is probably caused by acidic compounds formed by oxidation of the isomerization reagents. With natural rubber the nonrubber substances prevent movement of the double bond, and *cis–trans* isomerization is the sole change, even when the reaction with sulfur dioxide is carried out under aerobic conditions.

Previous work has shown that the treatment of squalene, natural rubber, gutta-percha, and the *cis*- and *trans*- forms of 3-methylpent-2-ene with sulfur dioxide, thiolbenzoic acid, dibenzoyl disulfide, and related materials caused *cis–trans*-isomerization.[1–6] The results with natural rubber were particularly interesting because examination of the vulcanizates made from a series of isomerized rubbers showed that isomerization markedly influenced important physical properties such as rate of crystallization[1–3,5,6] tensile strength,[6,7] tear strength, cut growth, and resistance to abrasion.[7,8] However from the above studies it was difficult to decide if the observed isomerization resulted from or was accompanied by movement of the double bond. The infrared spectra of the polymers obtained after treating natural rubber and gutta-percha with the isomerizing reagents were consistent with *cis–trans* changes and movement of type (a) could be definitely excluded, but it was not possible to exclude movement of type (b).[5] A similar conclusion can be drawn from the spectra of polyisoprenes isomerized with selenium,[9] and Shipman and Golub have stated that bond movement of type (b) does not occur during the vulcanization of *cis*-polyisoprene-3-d_1 by sulfur.[10]



$$\sim CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2\sim \;\begin{cases} \nearrow \; \sim CH_2-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_2-CH_2\sim & \text{(a)} \\ \searrow \; \sim CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2\sim & \text{(b)} \end{cases}$$

TABLE I
Isomerization of 2-Methylpent-1-ene and 2-Methylpent-2-ene by Butadiene Sulfone at 140°C.[a]

Olefin[b]	Reaction time, hr.	Constitution of product, wt.-%: 2-Methylpent-1-ene	Constitution of product, wt.-%: 2-Methylpent-2-ene
2-Methylpent-1-ene	0.0	98.1	0.6
	0.5	39.7	60.3
	1.0	21.9	78.1
	3.0	18.7	81.3
	24.0	19.6	80.4
	1.0[c]	98.1	0.6
2-Methylpent-2-ene	0.0	0.0	99.5
	68.0	22.0	77.5

[a] 3 wt.-% butadiene sulfone used in all these experiments.

[b] The olefin was not degassed and hence traces of oxygen were present in these experiments.

[c] No oxygen, hydroperoxides, or peroxides present, i.e., anaerobic conditions.

However, the autoxidation characteristics of highly isomerized natural rubber in solution at 65°C. were almost identical with those of normal natural rubber.[11] This suggests the absence of structural changes of either type (a) or (b) because the introduction of the former structure would lead to crosslinking on oxidation and the latter to a considerably enhanced rate of oxidation, since a 1,4-diene such as 2,6-dimethylhepta-2,5-diene oxidizes about 60 times faster than the corresponding 1,5-diene.[12]

On the other hand, although type (b) changes cannot be detected with *cis*- and *trans*-3-methylpent-2-ene ($MeCH{=}CMeCH_2Me$) because movement of the double bond from carbon atoms 2 and 3 to carbon atoms 3 and 4 yields the same olefin, the infrared spectrum of the olefin mixture obtained after treatment of the geometric isomers with sulfur dioxide, apart from showing *cis*- and *trans*- changes, indicated the presence of a small amount of $CH_2{=}CRR'$ groups.[13] These were subsequently shown by gas–liquid chromatographic analysis to be due to 2-ethylbut-1-ene, and therefore a positional change of type (a) had occurred.

This paper is concerned with the occurrence of double bond movement during the course of geometric isomerization in the systems mentioned above and with the definition of reaction conditions whereby *cis–trans* isomerization can be obtained with and without movement of the double bond.

The simplest trialkylethylene capable of distinguishing between *cis–trans* isomerization and double bond movement is either 3-methylhex-2-ene or 3-methylhex-3-ene. A sample of *trans*-3-methylhex-3-ene was prepared[14] and attempts were made to carry out the investigation with this olefin. An important observation concerned the effect of oxygen and certain oxygenated compounds. In their absence (i.e., anaerobic conditions), a mixture of the *cis* and *trans* isomers only was obtained when *trans*-3-meth-

TABLE II
Isomerization of a Mixture of 2-Methylpent-1-ene and *trans*-3-Methylpent-2-ene at 140°C. in the Presence of Various Additives[a]

			Constitution of product, wt.-%				
Isomerization reagent (3 wt.-%)	Additive (3 wt.-%)	Reaction time, hr.	2-Methylpent-1-ene	2-Methylpent-2-ene	*trans*-3-Methylpent-2-ene	*cis*-3-Methylpent-2-ene	2-Ethylbut-1-ene
Butadiene sulfone	No addition[b]	5	43.9	0.0	41.3	14.8	0.0
Butadiene sulfone	Dicumyl peroxide	5	6.7	31.7	38.4	21.0	2.2
Butadiene sulfone	*tert*-Butyl hydroperoxide	5	7.2	31.8	36.9	21.7	2.4
Dibenzoyl disulfide	No addition[b]	86	40.8	0.0	44.2	15.0	0.0
Dibenzoyl disulfide	*tert*-Butyl hydroperoxide	76	33.9	10.7	34.8	19.5	1.1
Thiolbenzoic acid	No addition[b]	86	40.2	0.0	39.4	20.3	0.0
Camphor sulfonic acid	No addition[b]	5	6.9	25.3	41.3	23.8	2.7

[a] The original composition of the mixture was 2-methylpent-1-ene 40.3% and *trans*-3-methyl pent-2-ene 59.9%, but since it was transferred for use by vacuum distillation it gradually became richer in the latter component; only trace amounts of 2-methylpent-2-ene and *cis*-3-methylpent-2-ene were present.

[b] No oxygen, hydroperoxide, or peroxides present i.e. anaerobic conditions.

ylhex-3-ene was heated with butadiene sulfone at 140°C. However, in the presence of oxygen or oxidation products (i.e., aerobic conditions), a complex mixture was obtained which indicated substantial positional changes; unfortunately this mixture could not be quantitatively analyzed with the analytical techniques and reference compounds available.

With 2-methylpent-1-ene and 2-methylpent-2-ene there are no geometric isomers, and with these olefins the effect of oxygen and oxidation products was completely clear. In their absence the olefins could be recovered unchanged after treatment with butadiene sulfone in the usual way, but when they were present a rapid conversion to an equilibrium mixture consisting of about 80% 2-methylpent-2-ene and 20% 2-methylpent-1-ene took place (Table I).

With a mixture of 2-methylpent-1-ene and *trans*-3-methylhex-3-ene, treatment with butadiene sulfone under anaerobic conditions gave the *cis* and *trans* forms of the 3-methylhex-3-ene, and no 2-methylpent-2-ene was formed. A similar experiment under aerobic conditions gave a complex mixture of 3-methylhexene isomers and a large amount of 2-methyl-pent-2-ene. These results show that 2-methylpent-1-ene can be used as a sensitive

TABLE III

Isomerization of a Mixture[a] of 2-Methylpent-1-ene and *trans*-3-Methylpent-2-ene Heated for 5 Hr. at 140°C. in the Presence of Natural Rubber or Serum Solids

		Constitution of product, wt.-%				
Isomerization reagent (3 wt.-%)	Additive (3 wt.-%)	2-Methylpent-1-ene	2-Methylpent-2-ene	*trans*-3-Methylpent-2-ene	*cis*-3-Methylpent-2-ene	2-Ethylbut-1-ene
Butadiene sulfone	Natural rubber[b]	38.0	0.0	50.7	11.3	0.0
Butadiene sulfone	Serum solids and dicumyl peroxide	34.3	0.0	47.9	17.8	0.0
Camphor sulfonic acid	Serum solids	27.8	~0.4	70.6	1.2	<0.1

[a] See Table II for the original composition of the olefin mixture.

[b] 48.5 wt.-% of natural rubber was used; after this treatment it was found to contain 15% of the *trans*-form.

indicator of bond movement when it is mixed with a more complex olefin which is capable of undergoing both geometric and positional isomerization. In view of the analytical difficulties associated with the 3-methylhex-3-ene system, further experiments were carried out with a mixture of 2-methylpent-1-ene and *trans*-3-methylpent-2-ene. It was found that treatment of this mixture with butadiene sulfone or dibenzoyl disulfide always led to the formation of *cis*-3-methylpent-2-ene. Olefins resulting from bond movement, i.e., 2-methylpent-2-ene and 2-ethylbut-1-ene, were formed only under aerobic conditions (Table II). Other workers concerned with the reactions of sulfur dioxide with various olefins have reported confusing results with regard to double bond movement and *cis–trans* isomerization.[15] Clearly it has now been established that the controlling factor concerning positional changes is the presence of oxygen, hydroperoxides, and peroxides. If any of these are present, bond movement occurs, but in their absence *cis–trans* isomerization can take place without other structural changes (Table II). Since the movement of double bonds in the presence of acids (e.g., sulfonic acids) is well known,[16] it is suggested that acids formed by reaction of the isomerizing reagent with peroxidized olefin are responsible for the positional changes observed. In agreement with this it was found that camphor sulfonic acid had a very similar effect on the above olefin mixture (Table II), causing both movement of the double bond and *cis–trans* isomerization.

When a mixture of natural rubber and 2-methylpent-1-ene and *trans*-3-methylpent-2-ene was treated with butadiene sulfone in the usual way no double bond movement was detectable in the olefins as judged by the formation of 2-methylpent-2-ene or 2-ethylbut-1-ene (Table III). The formation of *cis*-3-methylpent-2-ene can therefore be taken as an indication of *cis–trans* isomerization occurring in the system without positional isomerism, and hence the changes observed in the infrared spectrum of the rubber—identical to those observed previously[5]—can only be ascribed to *cis–trans* isomerization. Since the natural rubber used was not specially purified and therefore some diperoxide–hydroperoxide groups would be present,[17] double bond movement might have been expected. However, it was found that if serum solids,[18] which contain many of the nonrubber ingredients present in natural rubber, were added to the mixture of 2-methylpent-1-ene and *trans*-3-methylpent-2-ene, then on treatment with butadiene sulfone in the presence of dicumyl peroxide only *cis–trans* isomerization occurred (Table III). Also when the olefin mixture was treated with camphor sulfonic acid, very little double bond movement or *cis–trans* isomerization occurred if serum solids were present (Table III).

Clearly the "acid" effect is suppressed by the serum solids. It is therefore concluded that when natural rubber is isomerized by treating dry rubber with sulfur dioxide conversion of the *cis* double bonds to the *trans* form occurs without any changes in the position of the double bonds.

EXPERIMENTAL

Materials

A mixture of 2-methylpent-1-ene and 2-methylpent-2-ene was prepared by the dehydration of 2-methyl-pentan-2-ol with *p*-toluenesulfonic acid by Dr. A. A. Watson in these laboratories. The isomers were separated by careful fractionation of the mixture through a column (165 × 1.5 cm. i.d.) packed with Dixon gauze rings. By gas liquid chromatography the purities of the Δ^1 and Δ^2-olefins were 98.1 and 99.5%, respectively.

trans-3-Methylpent-2-ene was obtained as previously described and had physical constants identical with those previously reported.[5] Natural rubber was RSS1, yellow circle smoked sheet; it was used without further purification.

trans-3-Methylhex-3-ene was prepared from *trans*-2-methylpent-2-enyl mesitoate and methyl magnesium iodide[14] and purified by preparative gas liquid chromatography to give a product containing only 2.6% impurity.

Butadiene sulfone, dibenzoyl disulfide, and thiolbenzoic acid were obtained and purified as previously described.[5] The acid was further purified by crystallization from *n*-heptane at −16°C., followed by distillation *in vacuo*. *tert*-Butyl hydroperoxide was redistilled to greater than 99% purity (gas-liquid chromatography).

Dicumyl peroxide was purified as previously described;[19] after this treatment its infrared spectrum showed the absence of carbonyl and hydroxyl groups.

Serum solids prepared by freeze-drying the serum from centrifuged latex were stored under nitrogen at −10°C.; they were obtained from the Rubber Research Institute of Malaya.[18]

Methods

All olefins were chromatographed through alumina under nitrogen immediately before use. Reactions under anaerobic conditions were carried out by degassing the chromatographed olefin on a vacuum line, followed by transfer of the olefin by vacuum distillation into the tube containing the isomerization catalyst. The tube was then sealed under vacuum, leaving the minimum free volume, and subsequently heated in an oil bath at 140°C.

Reactions under aerobic conditions were carried out as follows: (*1*) the olefin was sealed *in vacuo* with the isomerization catalyst, the olefin was not degassed, and therefore traces of oxygen were present in the reaction mixture; or (*2*) the olefin was sealed *in vacuo* in the presence of either dicumyl peroxide or *tert*-butyl hydroperoxide as well as the isomerization catalysts.

In the experiment with natural rubber the olefin mixture was recovered by vacuum distillation.

Analysis of Isomerized Materials

All the products obtained from the methyl pentenes after treatment with the various isomerizing reagents were analyzed at room temperature by gas-liquid chromatography by use of a 15 ft. × 4 mm. squalane on brickdust column. The components were identified by comparison of the found retention indices[20] with those of authentic materials. Samples containing methylhexenes were analyzed on a similar column at 75°C.

The *cis–trans* ratio for the isomerized natural rubber was calculated from the absorption at 1145, 1125, and 1090 cm.$^{-1}$ which was obtained with a Hilger H.800 double-beam spectrometer.[5]

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References

1. Cunneen, J. I., and F. W. Shipley, *J. Polymer Sci.*, **36**, 77 (1959).
2. Cunneen, J. I., W. P. Fletcher, F. W. Shipley, and R. I. Wood, *Trans. Inst. Rubber Ind.*, **34**, 260 (1959).
3. Cunneen, J. I., and W. F. Watson, *J. Polymer Sci.*, **38**, 521 (1959).
4. Cunneen, J. I., and W. F. Watson, *J. Polymer Sci.*, **38**, 533 (1959).
5. Cunneen, J. I., G. M. C. Higgins, and W. F. Watson, *J. Polymer Sci.*, **40**, 1 (1959).
6. Cunneen, J. I., *Rubber Chem. Technol.*, **33**, 445 (1960).
7. Cunneen, J. I., P. McL. Swift, and W. F. Watson, *Trans. Inst. Rubber Ind.*, **36**, 17 (1960).
8. Elliott, D. J., *Trans. Inst. Rubber 2nd*, in press.
9. Golub, M. A., *J. Polymer Sci.*, **36**, 523 (1959).
10. Shipman, J. J., and M. A. Golub, *J. Polymer Sci.*, **58**, 1063 (1962).
11. Bell, C. L. M., unpublished work.
12. Hargrave, K. R., and A. L. Morris, *Trans. Faraday Soc.*, **52**, 89 (1956).
13. Cunneen, J. I., and G. M. C. Higgins, *The Chemistry and Physics of Rubber-like Substances*, Maclaren, London, 1963, p. 25.
14. Saville, B., G. M. C. Higgins, and M. B. Evans, *J. Chem. Soc.*, **1965**, 702.

15. Boelhouwer, C., and H. I. Waterman, *Chem. Weekblad*, **55**, 465 (1959) and references therein.
16. Whitmore, F. C., *Ind. Eng. Chem.*, **26**, 94 (1934).
17. Bolland, J. L., and H. Hughes, *J. Chem. Soc.*, **1949**, 492.
18. Archer, B. L., and B. C. Sekhar, *Biochem. J.*, **61**, 503 (1955).
19. Moore, C. G., and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).
20. Kovats, E., *Helv. Chim. Acta*, **41**, 1915 (1958).

Résume

Quand on fait réagir du *trans*-3-méthylpent-2-ène ou du *trans*-3-méthylhex-3-ène avec de la butadiène-sulfone, de l'acide thiolbenzoique et du disulfure de benzoyle en absence d'air, l'oléfine subit uniquement l'isomérisation *cis–trans*. Cependant, des réactions similaires en présence d'oxygène ou des peroxydes montrent, en plus des changements de position de la double soudure. Cette dernière modification est probablement provoquée par des composés acides qui sont formés par oxydation des réactifs d'isomérisation. Dans le caoutchouc naturel, les substances non-caoutchouteuses empêchent le mouvement de la double soudure, et l'isomérisation *cis–trans* est le seul changement, même si la réaction est faite avec de l'anhydride sulfureux en présence d'air.

Zusammenfassung

Bei der Behandlung von *trans*-3-Methylhex-3-en oder *trans*-3-Methylpent-2-en mit Butadiensulphon, Thiobenzoesäureund Dibenzoyldisulphid unter anaeroben Bedingungen erleidet das Olefin nur eine *cis–trans*-Isomerisierung. In Gegenwart von Sauerstoff oder Peroxyden verursachen aber ähnliche Reaktionen zusätzlich eine Verschiebung der Doppelbindung. Letztere Strukturänderung wird wahrscheinlich durch saure, durch die Oxydation von Isomerisierungsreagentien gebildete Verbindungen verursacht. Bei Naturkautschuk verhindern die Nicht-Kautschuksubstanzen eine Verschiebung der Doppelbindung und die *cis–trans*-Isomerisierung bleibt die einzige Änderung, selbst wenn die Reaktion mit Schwefeldioxyd unter aeroben Bedingungen ausgeführt wird.

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Benzaldehyde Polymerization and Copolymerization Studies

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Synopsis

In attempts to homopolymerize benzaldehyde with various ionic and coordination catalysts, or by γ-radiation, only the ionic catalyst BF_3 etherate formed a polymeric product. This product was identified as polybenzyl with a degree of polymerization (DP) of 133. Mixtures of benzaldehyde and styrene did not copolymerize under γ-irradiation, but yielded only polystyrene. With a BF_3 etherate catalyst, however, mixtures of styrene and benzaldehyde were found to have copolymerized through the carbonyl group of the latter, and a 50:50 styrene–benzaldehyde monomer mixture yielded an 80:20 styrene–benzaldehyde copolymer with a DP of 139.

INTRODUCTION

The knowledge of the polymerization behavior of aliphatic aldehydes has developed fairly systematically, based on the early fundamental investigations of Hermann Staudinger. The more recent discoveries of stereospecificity and of stereospecific catalysts have renewed and intensified the interest in the polymerization of these compounds.[1]

There was, however, no similar development in the field of aromatic aldehydes. The reason for this lies probably in the fact that they do not possess as strong a tendency to polymerize as formaldehyde, nor to condense through the presence of an α hydrogen as acetaldehyde or its higher homologues. Furthermore, protonic acids, Lewis acids, metal alkyls, or alkoxides, which easily polymerize or condense aliphatic aldehydes, cause aromatic aldehydes to form addition products, or cause rearrangement or reduction reactions.

Benzaldehyde also has some tendency to form polymeric products. Formation of insoluble but poorly identified condensates have been reported when using $VOCl_3$,[2] $FeCl_3$, and $SbCl_5$,[3], or mixed ethylaluminum bromides[4] as catalysts. Recently, copolymerization of styrene with benzaldehyde by BF_3 was claimed,[5] but no structural proof could be found.

EXPERIMENTAL RESULTS

One part of the present study deals with attempts to polymerize benzaldehyde with various ionic and coordination catalysts, and by γ-irradiation. Only BF_3 etherate was found to form a polymeric product, identified as polybenzyl.

The other part of the study deals with the copolymerization of benzaldehyde and styrene. With BF_3 etherate, copolymerization through the carbonyl group was shown by the infrared spectra to have taken place. No copolymerization was, however, observed with γ-radiation, and only polystyrene was obtained in poor yields.

In these experiments, the monomers were subjected to the various catalysts either in solution (5% by weight in benzene or methylene chloride), or in bulk. In the solution experiments, the reactions were carried out for 90 min. at 0 or 25°C., in three-necked, round-bottomed flasks equipped with Lew-type stirrer, thermowell, condenser, and self-sealing rubber cap. After charging with solvent and monomer, the flask was purged with dry nitrogen, and thus maintained throughout the reaction. The catalysts were measured through the rubber cap with a hypodermic syringe.

The bulk experiments were carried out in glass containers, purged and filled with dry argon, and sealed after the addition of the monomer catalyst (1% by weight of the monomers); followed by heating in an oven at 150°C. for 15 hr.

In the radiation experiments, the undiluted or dissolved (5% by weight in benzene or methylene chloride) monomers were sealed under argon in constricted-stem, Kimble No. 12011 Neutraglas ampules, and exposed for 24 hr. to a Co^{60} source (4100 r/min.).

Polymerization was suspected whenever an increase in solution viscosity was noted and a precipitate was obtained upon addition of methanol.

Homopolymerization of Benzaldehyde

Neither irradiation with γ-rays from a Co^{60} source, nor treatment with $AlCl_3$, $TiCl_4$, $SnCl_4$, $VOCl_3$, silica gel, *n*-butyllithium, tetrabutyl titanate, diisobutylaluminum hydride (DIBAH), DIBAH–$TiCl_4$, or DIBAH–$VOCl_3$ gave any indication of polymer formation under the above described reaction conditions. Only in the experiments where benzaldehyde was heated with BF_3 etherate in the absence of a solvent at 150°C. was an increase in viscosity noted. On precipitation with methanol and reprecipitation from benzene, a light-brown powder was obtained in low yield (1.4% after repeated reprecipitation).

This product was soluble in acetone, benzene (with fluorescence), and methyl ethyl ketone; slightly soluble in ether; and insoluble in *n*-hexane. While softening and melting points were rather low (79 and 88°C., respectively), the product showed a remarkable resistance toward decomposition when heated in a test tube in an open flame. Molding under compression at 90°C. yielded a glossy, brittle disk.

The brown powder was dissolved in benzene and passed through activated alumina to remove polar impurities. The material that came through (97% of the sample) was used for elemental and spectrographic analyses.

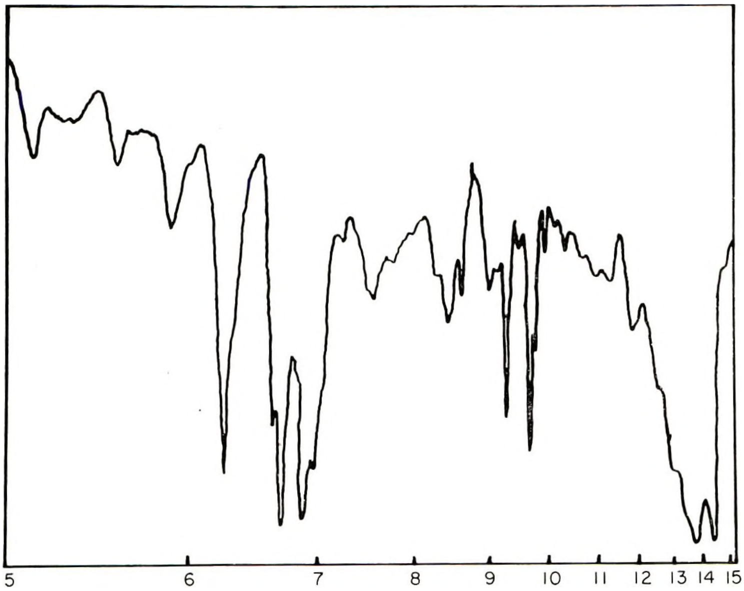
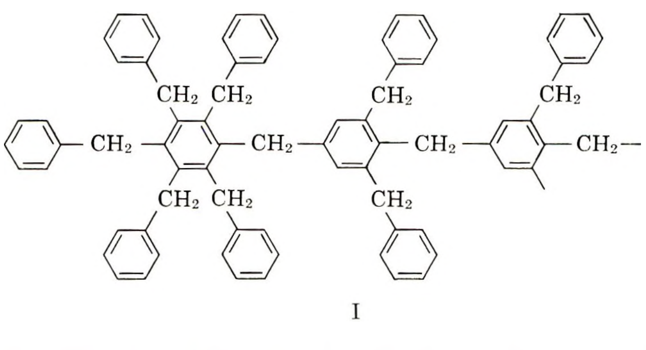


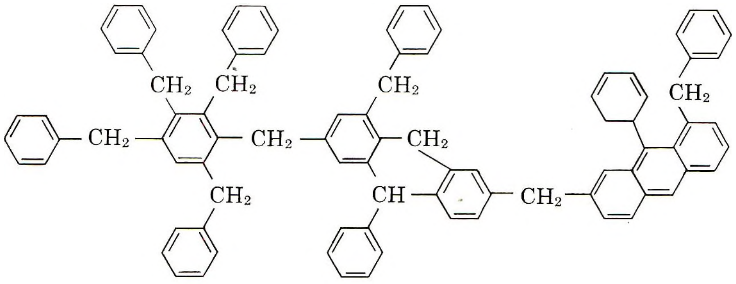
Fig. 1. Infrared spectrum from 5 to 15 μ of the polymeric product from benzaldehyde with BF_3 etherate.

The infrared spectrum (Fig. 1) of the product did not, however, show the C-O linkages expected if the benzaldehyde had polymerized through the carbonyl group, but resembled closely that given by several researchers[6–8] for polybenzyl. Because of the lack of similarity to a disubstituted benzene ring in the 5–6 μ and 12–15 μ ranges,[9] the spectrum is not consistent with the linear methylene-*p*-phenylene structure proposed by Shriner.[10] There are, however, very strong similarities to monosubstituted benzene compounds such as diphenylmethane and toluene, so that the structure (I) proposed by Haas[6] appears more probable.



I

Further condensation of the rings to make polynuclear aromatic regions in the macromolecule would account for the fluorescence observed in hydrocarbon solvents. Chromatography through alumina showed 97% of the material to be relatively nonpolar and fluorescent. The fluorescent substance could be different from the polymeric material and still elute from the alumina with the polymeric material by coincidence. However, the mechanism for forming polynuclear aromatics, presumably a Friedel-Crafts type reaction, might work as easily on the polymer as on smaller molecules. Formation of a stable diphenylmethylcarbonium ion to alkylate an adjacent ring, followed by dehydrogenation of the triphenylmethyls, would provide polynuclear aromatic regions in the macromolecule (II).



II

Elemental analysis of the product confirmed it to be polybenzyl: C, 93.0%, H, 6.7% (calculated for C_7H_6:C, 93.3%, H, 6.7%). No boron or fluorine was detected in the polymer by emission spectroscopy.

The intrinsic viscosity determined in toluene at 30°C. (0.050 dl./g.) indicated a polymer of low molecular weight. Ebulliometric determinations of the molecular weight in carbon tetrachloride as well as in benzene gave a value of 12,000 corresponding to a degree of polymerization (DP) of 133.

Copolymerization of Benzaldehyde with Styrene

By Catalysis with BF_3 Etherate. Mixtures of styrene and benzaldehyde were dissolved in methylene chloride and allowed to react at 0°C. with BF_3 etherate (1% by weight of monomers) for 90 min. After repeated precipitation from benzene into methanol, polymers with the properties shown in Table I were obtained.

TABLE I

BF_3-Catalyzed Copolymerization of Styrene and Benzaldehyde

Styrene/ benzaldehyde (weight ratio)	Yield, % of monomer	Softening point, °C.[a]	Bulk density, g./cc.[b]	[η], dl./g.
100/0	95	103	0.245	0.195
75/25	6	99	n.d.	0.060
50/50	25	89	0.141	0.042
25/75	3	87	n.d.	0.044
10/90	0	—	—	—

[a] Softening points were determined by a modified Vicat test.

[b] Bulk densities are those of the reprecipitated powders.

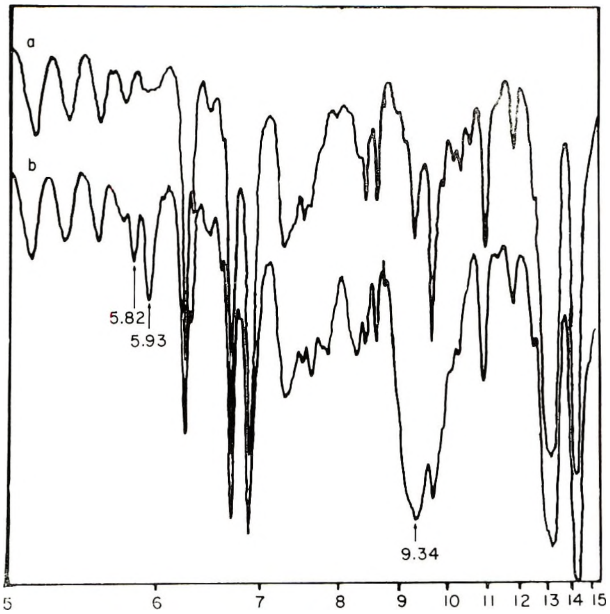
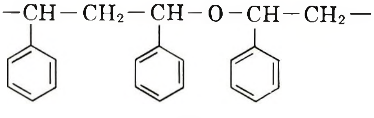


Fig. 2. Infrared spectrum from 5 to 15 μ of: (*a*) styrene without benzaldehyde; (*b*) styrene with 75% benzaldehyde.

A comparison of the infrared spectra (Fig. 2) indicates that copolymerization had indeed taken place between the styrene and benzaldehyde. The main difference from polystyrene is the strong O—C band at 9.34 μ in the copolymer which is presumably from ether linkages. A C=O band at 5.93 μ is nearly constant for the copolymers, but another at 5.82 μ increases with the higher ratio of benzaldehyde to styrene in the initial mixture of the monomers. Reprecipitation of the copolymer from benzene into methanol failed to diminish the strong band at 9.34 μ. Thus, copolymerization through the carbonyl group of the benzaldehyde to give an ether resulted in a copolymer isosteric with polystyrene (III), but which may not have a definite repeating unit.



III

No boron or fluorine was detected in the copolymer by emission spectroscopy. Elemental analysis of the 50:50 copolymer (C, 90.6%; H, 7.3%; O, 2.1%) indicated it to consist of approximately 80% styrene and 20% benzaldehyde. The ebullioscopic molecular weight in carbon tetrachloride or in benzene was 14,600, corresponding to a DP of 139.

By γ-Radiation. Mixtures of styrene and benzaldehyde, in the absence of a solvent or catalyst, were exposed to γ-radiation from a Co^{60} source, and

TABLE II
Exposure of Styrene–Benzaldehyde Mixtures to γ-Radiation

Styrene/ benzaldehyde (weight ratio)	Yield, % of monomer	Softening point, °C.[a]	Bulk density, g./cc.[b]	[η], dl./g.
100/0	9	112	0.047	0.440
75/25	19	108	0.115	0.325
50/50	16	107	0.185	0.226
25/75	9	102	0.195	0.139
0/100	0	—	—	—

[a] Softening points were determined by a modified Vicat test.
[b] Bulk densities are those of the reprecipitated powders.

repeatedly precipitated from benzene into methanol. Polymers with the properties shown in Table II were obtained.

Inspection of the infrared spectra of the products described in Table II showed that no copolymerization had taken place between the benzaldehyde and styrene, and that only polystyrene was obtained on irradiation of the mixtures. The x-ray diagrams of the polystyrenes obtained in the presence of benzaldehyde showed no increase in stereoregularity over that of polystyrene obtained by γ-irradiation of pure styrene.

References

1. Furukawa, J., and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Polymer Review Series, Vol. 3, Interscience, New York, 1963.
2. Brown, F. E., and J. E. Snyder, *J. Am. Chem. Soc.*, **47**, 2674 (1925).
3. Kovacic, P., and A. K. Sparks, *J. Org. Chem.*, **26**, 2541 (1961).
4. Groizeleau, L., *Compt. Rend.*, **242**, 1491 (1956).
5. Durgaryan, A. A., and A. O. Agunyan, *Vysokomolekul. Soedin.*, **5**, 1755 (1963).
6. Haas, H. C., D. I. Livingston, and M. Saunders, *J. Polymer Sci.*, **15**, 503 (1955).
7. Anderson, H. C., NOLTR 62-59, October 1962.
8. Conley, R. T., *Proc. Battelle Symp. Thermal Stability Polymers*, Columbus, Ohio, 1963.
9. Jones, R. N., and C. Sandorfy, in *Technique of Organic Chemistry*, A. Weissberger, Ed., Vol. IX, Interscience, New York, 1956, p. 247.
10. Shriner, R. L., and L. Berger, *J. Org. Chem.*, **6**, 305 (1941).

Résumé

Les essais d'homopolymérisation du benzaldéhyde par divers catalyseurs ioniques et de coordination ou par irradiation γ, ont montré que seul le catalyseur BF_3 éther forme un produit polymérique. Le produit identifié est du polybenzyle de DP égal à 133. Des mélanges de benzaldéhyde et de styrène ne copolymérisent pas sous l'irradiation gamma mais fournissent seulement du polystyrène. Avec le catalyseur éthérate de BF_3 cependant, des mélanges styrène–benzaldéhyde ont copolymérisé par l'intermédiaire du groupement carbonyle de ce dernier et un mélange des monomères styrène–benzaldéhyde à 50:50 fournit un copolymère styrène-benzaldéhyde a 80:20 ayant un DP de 139.

Zusammenfassung

Bei Versuchen, Benzaldehyd mit verschiedenen ionischen oder koordinativen Katalysatoren oder durch γ-Strahlung zu homopolymerisieren, lieferte nur der ionische Katalysator BF_3 Atherat ein polymeres Produkt. Dieses Produkt wurde als Polybenzyl mit einem DP von 133 identifiziert. Benzaldehyd- und Styrolmischungen lieferten unter γ-Bestrahlung keine Copolymeren sondern nur Polystyrol. Mit einem BF_3 Ätheratkatalysator trat jedoch in Styrolbenzaldehydmischungen Copolymeriation über die Carbonylgruppe des Aldehyds ein, und eine Monomermischung Styrol-Benzaldehyd von 50:50 liefert ein Styrolbenzaldehydcopolymeres von 80:20 mit einem DP von 139.

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Kinetics of Polyacrylamide Adsorption on Calcium Phosphate

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Synopsis

An extension of Langmuir's rate equation is obtained for polymeric adsorption when the initial concentrations of polymers differ significantly from the final or equilibrium concentrations. It is assumed that the equation developed has a general applicability for polymer adsorption whenever the experimentally determined equilibrium adsorption data can be represented by Langmuir's isotherm. Adsorption of high molecular weight polyacrylamides from aqueous solutions upon calcium phosphate is described at low concentration of the polymer. The rate of adsorption obeys a Langmuirian type equation.

In a previous investigation[1] Langmuir's rate equation has been applied for the rates of polymer adsorption upon solids with the assumption that the initial concentration of a polymer solution is constant during the adsorption process. Frequently, this assumption is well founded. However, it has been reported[2,3] that the final polymer concentration following the adsorption process is only a small fraction of the initial polymer concentration. Therefore, in this work it was attempted to obtain an extension of Langmuir's rate equation for the case when the initial polymer concentration changes significantly during the adsorption process. Furthermore, some experiments were carried out to test the applicability of the equation developed.

Langmuir's rate equation can be stated

$$d\theta/dt = k_1C(1 - \theta) - k_2\theta \tag{1}$$

where θ is the fraction of surface coverage, k_1 and k_2 are the rate constants for adsorption and desorption, respectively, and C is the polymer concentration.

The basic assumption we make is that the decrease in polymer concentration is proportional to the surface coverage. Consequently, C in eq. (1) may be substituted for $(C_0 - \alpha\theta)$, where C'_0 is the initial polymer concentration and α is a constant. Thus we obtain

$$d\theta/dt = k_1(C'_0 - \alpha\theta)\ (1 - \theta) - k_2\theta \tag{2}$$

Upon rearranging eq. (2) it can be written

$$d\theta/dt = k_1\ [\alpha\theta^2 - \theta(C'_0 + \alpha + b) + C'_0] \tag{3}$$

where $b = k_2/k_1$.

Integration gives

$$k_1 t = \frac{1}{(C_0 - \alpha + b)} \ln\{[(C_0 + b) - \alpha\theta]/[(C_0 + b)(1 - \theta)]\} \qquad (4)$$

From theoretical considerations it is believed that eq. (4) has a general applicability whenever the experimentally determined equilibrium adsorption data can be represented by Langmuir's isotherm. The experimental evaluation of this equation needs a large amount of data with various polymers and adsorbents which is beyond the scope of this present communication. Only the results of a few experiments with PAM adsorption on calcium phosphate are given here, since for this system Langmuirian adsorption has been indicated[4] from related experimental data.

Aqueous solutions of polyacrylamide (PAM) of various molecular weights[5] and calcium phosphate adsorbent (analytical grade, further purified[5]) were used to measure the rates of adsorption. Polymer solutions containing 10% (w/v) calcium phosphate were agitated at a constant rate. An ultraviolet spectrophotometric method was employed to measure the amount of adsorbed polymer.[6]

Figure 1 shows the adsorbed amounts of PAM of 1.0×10^6, 3.0×10^6, and 6.0×10^6 average molecular weights as a function of time. The initial concentrations were 0.100% PAM solutions containing 10% (w/v) adsorbent. Equilibrium adsorption data are shown in Table I.

TABLE I
Amounts of PAM Adsorbed at Equilibrium

Average molecular weight $\times 10^{-6}$	Initial concentration C_0, mole/l. $\times 10^8$	Final concentration C_{eq}, mole/l. $\times 10^8$	Max adsorption a_{eq}, mole/l./100 g. solid $\times 10^8$
1.0	100	7.5	92.5
3.0	33.3	2.6	30.7
6.0	16.7	1.4	15.3

To evaluate the applicability of eq. (4) we may take the surface coverage at time t, $\theta = a/a_{eq}$, where a is the adsorbed amount at time t and a_{eq} is the adsorbed amount in equilibrium. (This fractional surface coverage may be considered as the ratio of the sites occupied at time t to that at $t = \infty$.) Then, a plot of log $[(C_0 + b)a_{eq} - \alpha a]/[(C_0 + b)(a_{eq} - a)]$ versus t gives a straight line.

It has already been reported[1] for low polymer concentrations that the rate constant of desorption is much smaller than the rate constant for adsorption. Considering $k_2 \ll k_1$, b can be neglected, thus a further simplification can be made. Although this assumption is plausible for the strongly

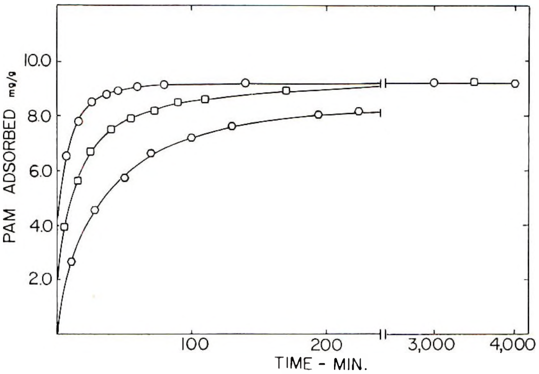

Fig. 1. Amount of PAM adsorbed vs. time: (O) PAM of 1.0 × 10^6 average molecular weight; (□) PAM of 3.0 × 10^6 average molecular weight; (⬡) PAM of 6.0 × 10^6 average molecular weight; initial concentrations 0. 100%; solid content 10.0% (w/v).

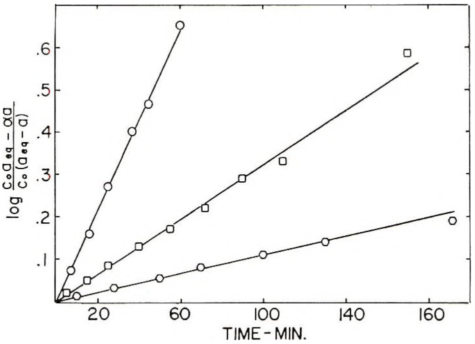

Fig. 2. Plot of log $[C_0 a_{eq} - \alpha a]/[C_0(a_{eq} - a)]$ vs. time for PAM of various molecular weights: (O) 1.0 × 10^6; (□) 3.0 × 10^6; (⬡) 6.0 × 10^6.

adsorbing PAM on calcium phosphate, calculation from additional data[5] confirms it. Figure 2 represents the corresponding plot of log $[C_0 a_{eq} - \alpha a]/[C_0(a_{eq} - a)]$ versus t. The value for the constant is taken as that of a_{eq}, since by definition $\alpha = (C_0 - C)/\theta$, and upon substitution of $C_0 - C = a$ and $\theta = a/a_{eq}$ we obtain $\alpha = a_{eq}$.

The slopes of the straight lines for PAM of various molecular weights and the corresponding rate constants are given in Table II.

TABLE II
Rate Constants k_1 for PAM

Average molecular weight × 10^{-6}	Slope, sec.$^{-1}$ × 10^5	k_1, sec.$^{-1}$-mole^{-1} × 10^{-3}
1.0	17.8	5.46
3.0	5.37	4.76
6.0	1.88	3.09

The values of k_1 indicate how the rate of adsorption of PAM decreases with increasing molecular weight.

Although recent theories of polymer adsorption do not indicate Langmuirian adsorption, much of the reported experimental data can be represented satisfactorily by Langmuir type isotherms. Consequently, the applicability of eq. (4), although it needs more experimental data to test, seems to be of interest to report.

References

1. Peterson, C., and T. K. Kwei, *J. Phys. Chem.*, **65,** 1330 (1961).
2. Jenckel, E., and B. Rumbach, *Z. Electrochem.*, **55,** 612 (1951).
3. Ruehrwein, R. A., and D. W. Ward, *Soil Sci.*, **73,** 485 (1952).
4. La Mer, V. K., and R. H. Smellie, Jr., *J. Colloid Sci.*, **13,** 589 (1958).
5. Jankovics, L., Ph.D. Dissertation, Columbia Univ., 1961.
6. Jankovics, L., *J. Polymer Sci.*, **B2,** 47 (1964).

Résumé

On a étendu l'équation de vitesse de Langmuir au cas de l'absorption des polymères lorsque les concentrations initiales de ceux-ci diffèrent sensiblement de leurs concentrations finales on de leurs concentrations à l'équilibre. On émet l'hypothèse que l'équation développée ici est d'application générale pour l'adsorption des polymères lorsque les données expérimentales de l'adsorption à l'équilibre peuvent être représentées par un isotherme de Langmuir. On décrit l'adsorption sur du phosphate de calcium de polyacrylamides de poids moléculaire élevé en solution aqueuse pour de faibles concentrations en polymère. La vitesse d'adsorption obéit à une équation du type Langmuir.

Zusammenfassung

Eine Erweiterung der Langmuir-Geschwindigkeitsgleichung wird für die Polymeradsorption erhalten, wenn sich die Anfangskonzentration des Polymeren wesentlich von der End- oder Gleichgewichtskonzentration unterscheidet. Es wird angenommen, dass die abgeleitete Gleichung für die Polymeradsorption allgemein anwendbar ist, solange die experimentell bestimmeten Adsorptionsgleichgewichtsdaten durch eine Langmuir-Isotherme dargestellt werden können. Die Adsorption hochmolekularer Polyacrylamide aus wässriger Lösung an Kalziumphosphat wird bei niedriger Polymerkonzentration beschrieben. Die Adsorptionsgeschwindigkeit gehorcht einer Gleichung vom Langmuir-Typ.

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Excluded Volume Effects in Swollen Polymeric Networks

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Synopsis

Information on the parameters of polymeric networks obtained by crosslinking in solution can be provided by deswelling measurements in polymer solutions of different concentration. However, under these conditions, the existing theories describing the swelling behavior are conflicting and no definite conclusion on the network properties seems as yet justifiable. Moreover, excluded volume and chain connectivity effects are not accounted for in either of the theories. Thirdly, the effect of the presence of crosslinks and the number of connected polymer segments in the network on the value of the Huggins' interaction parameter to be used in the expressions for the free energy of mixing is not clear. Nevertheless, the available experimental data have shown some preference for Hermans' theory over Flory's theory, whereas James and Guth's expression must be rejected altogether. A dependence of the degree of swelling q_0, at which the partial molar free energy of elasticity equals zero, on solvent power of the swelling agent has been previously observed and has been further investigated in this study. To this end, methyl methacrylate was copolymerized with small amounts of divinylbenzene in dilute benzene solutions yielding six samples with different crosslink densities and q_0 values. A large dependence of q_0 on the osmotic second virial coefficient in four solvents was observed. The applicability of current theories for polymer-solvent interaction upon intramolecular chain dimensions to the chains in the networks has been investigated. Flory's expression for volume expansion of polymer chains falls short, but two other relations for the same initial effect show that the second virial coefficient dependence of q_0 may be attributed to volume exclusion, similarly as in free chains. The validity of these relations, however, is expected to hold only for a rather limited range of the network parameters.

INTRODUCTION

There exists now a variety of thermodynamic treatments that describe the swelling pattern of crosslinked polymer networks. None of these is rigorous in the sense that excluded volume and chain connectivity effects are accounted for. Nevertheless, three different groups of workers have arrived at expressions which differ only in a term expressing the volume dependent part of the entropy of crosslinking.

According to Hermans,[1] the entropy of elasticity, i.e., the entropy change as a result of the new chain end distribution when the degree of

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(isotropic) swelling changes from q_0 to q, is

$$S_{\mathrm{el}} = kG \ln q/q_0 - 3/2kG[(q/q_0)^{2/3} - 1] \tag{1a}$$

whereas Flory and Wall[2] found

$$S_{\mathrm{el}} = (2/f)kG \ln q/q_0 - 3/2kG[(q/q_0)^{2/3} - 1] \tag{1b}$$

and James and Guth[3] obtained the relationship:

$$S_{\mathrm{el}} = -3/2kG[(q/q_0)^{2/3} - 1] \tag{1c}$$

Here, G stands for the number of chains between crosslinks and f is the functionality of the crosslinks, i.e., the number of chain ends that form a crosslink. The reasoning leading to the expressions (1) has been critically reviewed in full detail by Hermans[4] and need not be repeated here.

In an attempt to discriminate experimentally between the three theories, Rijke and Prins[5] and also Mukherji and Prins[6] crosslinked cellulose acetate in solution and studied the swelling behavior at degrees of swelling not too far removed from the state of "normal" coiling, q_0. To this end the samples were equilibrated with solutions of the same polymer of different concentrations in various solvents. The equilibrium requires that the chemical potential of the solvent in the gel phase equals that in the solution phase. Using the well-known Flory-Huggins expression for the entropy of mixing the polymer with the solvent, differentiation with respect to the number of solvent moles, multiplication by $(-T)$ and addition of the van Laar heat of dilution term then yields for the equilibrium the eqs. (2):

Hermans:

$$\Delta/\phi_{\mathrm{g}}^{1/3} = (1/p)q_0^{-2/3} - (1/p)\phi_{\mathrm{g}}^{2/3} \tag{2a}$$

Flory and Wall:

$$\Delta/\phi_{\mathrm{g}}^{1/3} = (1/p)q_0^{-2/3} - (2/fp)\phi_{\mathrm{g}}^{2/3} \tag{2b}$$

James and Guth:

$$\Delta/\phi_{\mathrm{g}}^{1/3} = (1/p)q_0^{-2/3} \tag{2c}$$

where $\Delta = \ln(1 - \phi_{\mathrm{s}}) + (1 - 1/x)\phi_{\mathrm{s}} + \chi_{\mathrm{s}}\phi_{\mathrm{s}}^2 - \ln(1 - \phi_{\mathrm{g}}) - \phi_{\mathrm{g}} - \chi_{\mathrm{g}}\,\phi_{\mathrm{g}}^2$. Here, ϕ_{s} is the volume fraction of the polymer in the solution phase, and $\phi_{\mathrm{g}}(= q^{-1})$ that in the gel phase. x and p stand for the number of lattice sites occupied by a solute molecule and chain between crosslinks, respectively. χ_{s} and χ_{g} are the Huggins' interaction parameters in the solution and gel phase.

By using these expressions, the values for p and q_0 follow from the slope and the intercept of the experimental plots of $\Delta/\phi_{\mathrm{g}}^{1/3}$ against $\phi_{\mathrm{g}}^{2/3}$. Values for x and χ were collected separately from osmometric studies on the solution phase.

It is seen that the theory of Flory and Wall predicts a chain length between crosslinks and a value for q_0 which differ from the theory of Hermans by a factor $2/f$ and $(2/f)^{-3/2}$, respectively. A firm decision on experimental grounds between the two theories can therefore only be made when the chain lengths in the networks have been accurately determined by some independent method.

The few available experimental data[5] show some preference for eq. (1a), but do not unequivocally provide full evidence for its correctness. On the other hand, the large discrepancy between the data obtained from swelling and chemical analyses as found by Mukherji and Prins[6] have led these workers to introduce a network parameter which accounts for the non-Gaussian distribution of the chains at the unrestrained state due to volume exclusion, i.e. the impossibility of the chains to cut through each other. However, the results do show that eq. (2c) must be rejected. According to this equation $\Delta/\phi_g^{1/3}$ should be independent of $\phi_g^{2/3}$ and always positive, and this is not found by the experiments.

The values found for q_0 according to the theory of Hermans are close to q^*, the degree of swelling of the polymer solution prior to crosslinking, whereas those according to Flory and Wall are consequently a factor $2^{3/2}$ larger (if $f = 4$). This implies, according to Flory and Wall, that the unconstrained mean-square end-to-end distance of the chains $\langle r^2\rangle_0$ changes by a factor of two as soon as the crosslinks are introduced. Although this is not inconceivable, the concept appears to be of rather artificial nature particularly since the relative change in $\langle r^2\rangle_0$ would be independent of crosslink density.

The experimental values of q_0 obtained for different solvents appeared to decrease with decreasing solvent power and seem to indicate that the degree of swelling at which the network is relaxed is dependent on the particular polymer–solvent interaction rather than on the concentration of the solution used at the time of crosslinking. This is true regardless of whether Hermans' or Flory and Wall's theory is used. The equilibrium volume of the network, according to the theoretical expressions, is therefore established relative to its state of normal coiling under the specific swelling circumstances, i.e., relative to the particular temperature, solvent, etc.

An attempt to interpret the observed dependence of q_0 on the solvent power has been made by comparison with similar interaction between segments of freely dispersed polymer molecules and solvent.[5] However, a statistical treatment of volume exclusion for polymer chains in a network does not exist, and the expressions for free chains must be expected to be of dubious value when applied to networks on the following grounds.

(*a*) The distribution of end-to-end distances of the chains in the network at q_0 on perturbation by preferential polymer–solvent interaction differs from the one for free chains in that certain configurations are excluded due to the condition that the chain ends are connected in *f*-functional crosslinks. In fact, this is equally true in the absence of any volume exclusion effects, for this accounts for the coherence of the chains in the network. It has been argued,[4] however, that the factor by which the number of accessible configurations is reduced is independent of the volume, and therefore not reflected in q_0, if the fully extended lengths of the chains between the crosslinks are large compared to the linear distances between these crosslinks, i.e., when the number of polymer segments between crosslinks is very large.

(*b*) The way in which the molecular expansion factor α is related to the number of connected segments in the network is not clear. Intuitively one would expect that, when more and more segments are connected together in the course of the crosslinking process, α would approach to its limiting value as predicted by the theories. This is, however, not found by the experiments. No relation between α and the total number of connected segments in either the primary molecules or the crosslinked sample has been observed. The few available data rather indicate that the molecular weight of the chains between crosslinks is to be related to the observed value of α, although it should be realized that this is by no means obvious.

(*c*) The introduction of excluded volume effects for the interpretation of solvent influence on q_0 values necessarily implies the application of volume exclusion in the terms for the free energy of mixing. This means that there is no certainty about the exact value of χ_g to be used in the expressions which lead to the observed q_0 values. According to Flory's treatment[7] of the molecular weight dependence of the second virial coefficient,

$$A_2 = \text{const.}\ (1/2 - \chi)[1 - \text{const.}\ (1/2 - \chi)M^{1/2} + \ldots]$$

from which it is seen that the molecular weight dependence enters in the form of a correction factor for the term $(1/2 - \chi)$. This effect may be small, therefore, whereas the observed χ dependence of q_0 is quite large.

(*d*) The effect of the polymer concentration in the relaxed network on the value of α is as yet undefined. Fixman[8] has shown for freely dispersed molecules, that α may depend very strongly on concentration and would at very high concentration approach unity, but again, this concept does not necessarily apply to chains in a network. The latter are unable to diffuse freely through the system due to their fixed position and any interaction of the segments with like segments is necessarily restricted to those of neighboring chains and likewise reflected in the concentration dependence of α. Although the concentration effect may become particularly effective in the neighborhood of the crosslinks, it is to be expected to become negligible for sufficiently large values of q_0.

In view of the above, it was decided to study the solvent power dependence of q_0 somewhat further. To eliminate the influence of uncertain factors in the interpretation of the swelling behavior as much as possible, a range of networks was prepared by copolymerization of methyl methacrylate with small amounts of divinylbenzene in dilute benzene solutions. The networks thus obtained showed high degrees of swelling with high q_0 values in four solvents—chloroform, benzene, toluene, and acetone—with values of χ ranging between 0.40 and 0.50. Information on the chain lengths between crosslinks and the values of q_0 was obtained by studying the swelling equilibrium in dilute solutions of poly(methyl methacrylate) and evaluating the data according to earlier applied procedures. χ values and the primary molecular weight of the network building polymer were collected from osmometric investigation in the four solvents. The observed dependence of q_0 on the solvent power has been interpreted in terms of current expressions for volume exclusion due to polymer–solvent interaction in free chains.

EXPERIMENTAL

Preparation of the Poly(methyl Methacrylate) Networks

Methyl methacrylate and divinylbenzene were copolymerized in benzene solution in various ratios at two concentrations with 0.1 wt.-% benzoyl peroxide as an initiator. Benzene was chosen as a solvent because of its low chain transfer constant with methyl methacrylate radicals.[9] The monomers were shaken with 5% alkali solution to remove the inhibitor and subsequently washed with distilled water. Drying over anhydrous magnesium sulfate was followed by careful distillation under nitrogen just before use. Divinylbenzene was distilled at reduced pressure. High-grade benzene was further purified according to the usual procedures and freshly distilled under nitrogen.

In a dry box under nitrogen atmosphere, the benzoyl peroxide was first dissolved in the methyl methacrylate. To the solutions to be diluted with benzene to 10 and 20% monomer content (by volume), 0.0, 3.3, 4.7, 6.0, and 0.0, 1.0, 1.7, and 3.0% divinylbenzene by volume methyl methacrylate was added, respectively. Previously, a larger range of monomer concentrations and divinylbenzene contents have been tried, but these did not provide the networks suitable for this investigation. The solutions were placed in thick-walled Pyrex tubes, stop-corked, frozen in liquid air, and subsequently sealed under vacuum. The tubes were heated in an oven at 80°C. for a period of 72 hr., after which the temperature was slowly lowered to room temperature to avoid vapor bubbles in the networks. No syneresis was observed. The samples were cut into the desired pieces and extracted in a Soxhlet to remove all unreacted material. The samples containing no divinylbenzene were slowly poured into a large excess of methyl alcohol and stirred to dissolve unconverted monomer. After 1 hr., the precipitate was filtered, washed with more methyl alcohol, and redissolved in benzene. This procedure was repeated three times.

For several reasons no attempt has been made to determine the number of crosslinks formed during the network formation. Also no estimate was made of the amount of unreacted material in the networks after the crosslinking.

Determination of the Degree of Swelling

The equilibrium degrees of swelling of the samples in two pure solvents were determined by equilibrating cylindrical rods, about 5 cm. long and

2 cm. wide, of gel in the swelling agents. The rods were removed at intervals, the excess solvent was removed by blotting them with filter paper, and the rods were weighed in closed bottles until the weights did not differ more than 0.5%. The dry weights were obtained by drying the samples in a vacuum oven at 60°C. till constant weight, q values were then calculated by assuming that the volumes of the polymer and the solvent are additive.

The degrees of swelling in the two other solvents and those in the polymer solutions were satisfactorily determined by measuring the change in one of the dimensions of the samples.[6] To this end the samples were cut into pieces approximately 2 × 10 × 30 mm. Two very small particles of chromic oxide were fixed in the samples near the two ends and their distance L_1 at equilibrium measured under a travelling microscope with an accuracy of 0.03%. The degree of swelling q_1 follows then from

$$q_1 = q(L_1/L)^3$$

where q is the degree of swelling of the samples as measured in the relevant solvent by the blotting method and L is the distance between the marks in this solvent.

A period of at least 48 hr. was allowed to reach equilibrium, after which no change in L was observed. The results were completely reproducible, i.e., replacing the samples in previous solvents or solutions yielded always the original value of L.

All swelling experiments were carried out at a constant temperature of 25 ± 0.1°C.

Characterization of the Polymer Material

In order to dispose of the thermodynamic information required for the interpretation of the swelling behavior, viscometric and osmometric measurements on the noncrosslinked samples were made as well as on the poly(methyl methacrylate) used for the deswelling solutions.

The intrinsic viscosities of samples 10-00 and 20-00 in the four solvents were measured in an Ubbelohde viscometer at 25 ± 0.1°C. The measured time of flow of the pure solvents exceeded 120 sec. Kinetic energy corrections were applied. The values for the samples appeared to be essentially the same for each solvent, so that only the data for sample 20-00 are listed in Table I. From these data it was estimated which commercially available poly(methyl methacrylate) grade would be the most suitable polymer for the deswelling solutions. The sample designated PMMA 2010* was chosen because of its number-average molecular weight and molecular weight distribution which would provide for an appropriate reduction of the chemical potential of the solvent at not too high polymer concentrations without the likely occurrence of permeation of solute into the gel phase. Viscometric data are also listed in Table I.

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* The sample, Lucite 2010, was kindly provided through the courtesy of E. I. Du Pont de Nemours, Geneva Office, Switzerland.

TABLE I
Viscometric and Osmometric Data of Samples
20-00 and PMMA 2010 at 25°C.

Sample	Solvent	$[\eta]$, dl./g.	Huggins' k'	$\bar{M}_n \times 10^{-3}$	$A_2 \times 10^4$, cm.^{3}-mole/g.^{2}	χ
20-00	Chloroform	1.488	0.31	150.5	8.26	0.405
	Benzene	1.033	0.35	152.0	4.74	0.440
	Toluene	0.785	0.39	—	2.80[a]	0.457[a]
	Acetone	0.610	0.59	153.8	1.48	0.484
PMMA 2010	Chloroform	0.469	0.43	48.7	11.38	0.370
	Benzene	0.363	0.39	46.4	6.90	0.412
	Toluene	0.296	0.46	45.8	4.29	0.435
	Acetone	0.260	0.00	52.6	2.90	0.470

[a] Obtained by interpolation from the plot in Fig. 1.

Osmotic pressures over a concentration range of 0.5–2.5 g. polymer/100 ml. solution were measured according to the usual procedures by using modified Zimm-Meyerson osmometers equipped with cellophane membranes (Ultracella filter, Allerfeinst, Membran Filter Gesellschaft, Göttingen, Germany). Straight lines were obtained when the reduced osmotic pressures were plotted against concentration up to the highest concentrations measured for both samples in all solvents. The values for the number-average molecular weight, second virial coefficient, and Huggins' interaction parameter χ are listed in Table I. The highest concentrations of the polymer solutions applied in the deswelling experiments were about twice as high as those investigated osmometrically. In the calculations of

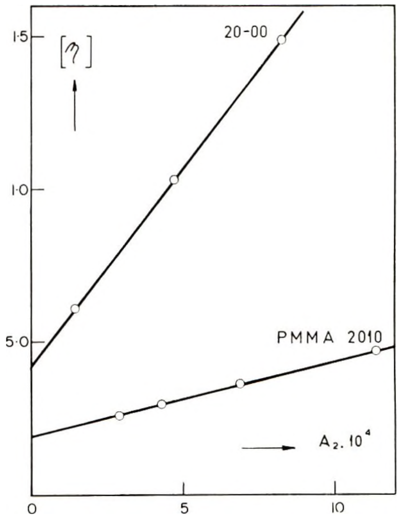

Fig. 1. Intrinsic viscosity of network building polymer (20-00) and deswelling solute (PMMA 2010) in four solvents plotted against osmotic second virial coefficient.

the solvent activity, it was assumed, however, that the linearity of the π/c versus c graphs is maintained up to the concentrations used, i.e., that the relative partial molar free energy of mixing is expressed by

$$RT[\ln(1-\phi_s)+(1-1/x)\phi_s+\chi_s\phi_s^2]$$

over this range of concentration.

Figure 1 shows the plots of the intrinsic viscosities of samples 20-00 and PMMA 2010 in the four solvents versus the respective second virial coefficients as measured by osmometry. Similar linear relationships have been observed for a wide variety of other polymer–solvent systems up to remarkably large values of A_2.[10,11] They have been successfully used to calculate intrinsic viscosities under Θ conditions and unperturbed chain dimensions following a semiempirical relation suggested by Krigbaum:[11,12]

$$[\eta] = [\eta]_\Theta + 4.4 \times 10^{-3}A_2M + \ldots \qquad (3)$$

which has recently enjoyed some more theoretical support.[13] It can be shown that the molecular weight appearing in the second term should be the weight-average when the polymer is heterogeneous.[10] Thus, from the slopes of the lines in Figure 1, a rough estimate of the M_w values for these samples can be made according to eq. (3). By using these values in the well-known Flory-Fox equation

$$[\eta]_\Theta = KM^{0.5}$$

values for K then follow from the intercepts of the lines which equal $[\eta]_\Theta$. The results are listed in Table II. The K values for both samples are in good agreement and compare favorably with literature values.[7,14] The ratio $(\langle r_0^2\rangle/M)^{1/2}$ of the unperturbed root-mean-square chain displacement to the square root of the molecular weight may be obtained from the expression[12]

TABLE II

Values of K and $(\langle r_0^2\rangle/M)^{1/2}$ for Samples 20-00 and PMMA 2010 from Figure 1 at 25°C.

Sample	Intercept $[\eta]_\Theta$	Slope	$\bar{M}_W \times 10^{-3}$ from slope	$K \times 10^4$		$(\langle r_0^2\rangle/M)^{1/2} \times 10^{11}$	
				Calc.	Lit.[7,14]	Calc.	Lit.[7,14]
20-00	0.418	1294.6	294.2	7.7	6.5	665	680[a]
PMMA 2010	0.190	246.3	56.0	8.0	7.0 ± 2.0		640 ± 60

[a] At 30°C.

$$(\langle r_0^2\rangle/M)^{1/2} = (K/\Phi)^{1/3}$$

where Φ is the Flory viscosity constant. There appears to be some question about the appropriate value of Φ to be used, but this does not seriously affect the value of $(\langle r_0^2\rangle/M)^{1/2}$ due to the one-third power of K/Φ. The average value of 665×10^{-11} is well in line with other literature data.

RESULTS AND DISCUSSION

The equilibrium degrees of swelling of the six samples in pure acetone and toluene have been determined by the blotting method. Those in benzene and chloroform have been derived from the degrees of swelling in toluene using the travelling microscope method. Deswelling measurements in the PMMA 2010 solutions of various concentrations were performed under similar conditions and calculated as indicated in the previous section. The data were plotted according to eq. (2) on the basis of χ_g values as found for the sample 20-00. The results are collected in Table III and shown graphically for one of the samples in Figures 2 and 3.

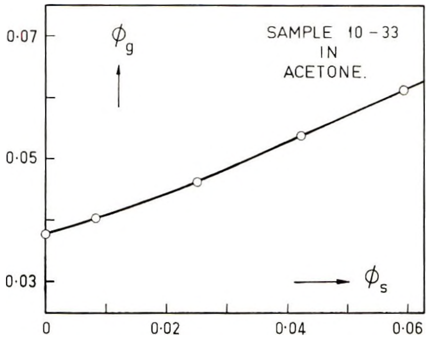

Fig. 2. Deswelling of sample 10-33 in acetone solutions of PMMA 2010 at 25°C.

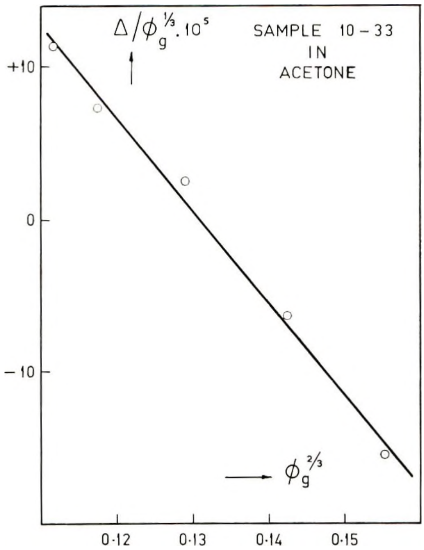

Fig. 3. Plot of $\Delta/\phi_g^{1/3}$ versus $\phi_g^{2/3}$ for sample 10-33 from deswelling in acetone solutions of PMMA 2010 at 25°C.

TABLE III
Degrees of Swelling, Molecular Weight of the Chains between Crosslinks, and Relaxed Degrees of Swelling of the Networks in Four Solvents at 25°C.

Sample[a]	Solvent	χ_g	q	p	$M_c \times 10^{-3}$[b]	q_0[b]
10-33	Chloroform	0.405	58.4	140.1	11.47	40.5
	Benzene	0.440	37.9	141.7	12.60	29.9
	Toluene	0.457	29.5	117.8	12.53	24.9
	Acetone	0.484	26.8	166.0	12.25	21.1
10-47	Chloroform	0.405	43.4	114.4	9.61	29.0
	Benzene	0.440	30.6	91.6	8.68	22.6
	Toluene	0.457	24.1	87.2	9.69	18.4
	Acetone	0.484	21.2	139.3	10.59	15.9
10-60	Chloroform	0.405	38.5	103.1	8.76	26.3
	Benzene	0.440	28.3	98.6	9.23	19.9
	Toluene	0.457	—	—	—	—
	Acetone	0.484	20.0	109.6	8.60	14.8
20-10	Chloroform	0.405	35.72	137.0	11.23	22.67
	Benzene	0.440	25.63	119.8	10.93	17.16
	Toluene	0.457	18.82	103.1	11.20	14.00
	Acetone	0.484	—	—	—	—
20-17	Chloroform	0.405	25.00	109.8	9.27	14.10
	Benzene	0.440	18.21	96.5	9.06	10.77
20-30	Chloroform	0.405	19.90	111.0	9.36	10.25
	Benzene	0.440	13.99	80.9	7.75	7.92

[a] The first number in the sample code refers to the concentration of methyl methacrylate in the polymerizing solution, the second number to the tenfold percentage of divinylbenzene (by volume methyl methacrylate) added.

[b] According to Hermans' theory.

Similar plots were obtained for all samples in all solutions. From the slopes and the intercepts of the lines, such as the one shown in Figure 3, values for p and q_0 were collected, and from the former values for M_c, the molecular weight of the chain between crosslinks, were calculated according to

$$M_c = pV_1/\bar{v}$$

where V_1 is the molar volume of the solvent and $\bar{v}$ the (partial) specific volume of the polymer. The values for M_c in Table III have been corrected for network imperfections, i.e., parts of the primary molecules that do not contribute to the elasticity of the system, by multiplication with a factor $(1 - 2M_c/M)$ as suggested by Flory.[7] M is here the molecular weight of the primary molecule. In doing so, it is tacitly assumed that the formation of the "primary" molecules in the networks during the polymerization process occurs independently of the presence of the divinylbenzene, i.e., the divinylbenzene merely links the poly(methyl methacrylate) chains together and does not have any effect upon termination, chain transfer, etc. This concept seems reasonable, since the divinylbenzene was always present in very small amounts.

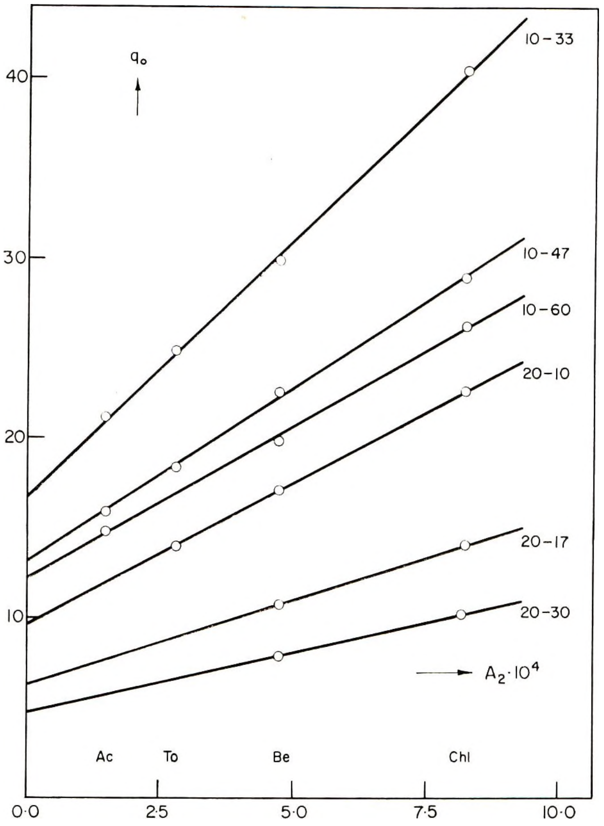

Fig. 4. Second virial coefficient dependence of q_0.

It is seen from Table III that the molecular weights of the chains between the crosslinks are essentially constant for each sample as found in the different solvents, as, of course, it should be. They appear to decrease with increasing divinylbenzene content and indicate that the swelling behavior of the networks in this range of polymer concentration follows the theoretical predictions expressed by either eq. (2a) or (2b), but not by eq. (2c). However, for networks with a degree of swelling in the pure solvents less than about 12.0, considerable scatter was found when the results were plotted according to Figure 3, which rendered the evaluation of p and q_0 unreliable. For this reason, the data for samples 20-17 and 20-30 in toluene and acetone have been omitted. A similar scatter was observed when the degree of swelling exceeded 60. At these high q values, as well as for $q < 12.0$, the terms in the expressions describing the swelling of networks must, however, be expected to have lost their validity for several reasons.

The values of q_0 for the samples in the various solvents show a large dependence on solvent power, particularly when M_c is large. This effect is the most pronounced for the samples prepared in the 10% monomer

TABLE IV
Comparison of Experimental Results with Theory [Eqs. (6) and (7)]

		q_0 vs. A_2		$\log (\alpha^2 - 1)/A_2$ vs. $\log M_c$ [eq. (6)]					$\log (\alpha^3 - 1)/A_2$ vs. $\log M_c$ [eq. (7)]				
				Slope		Const. from intercept			Slope		Const. from intercept		
Sample	$M_c \times 10^3$ (av.)	Slope $\times 10^4$	Intercept q_0°	Exptl.	Theory	Hermans	Flory	Theory	Exptl.	Theory	Hermans	Flory	Theory
10-33	12.25	2.85	16.77	0.57	0.50	4.54	6.72	4.97	0.57	0.50	7.70	11.47	7.45
10-47	9.61	1.94	13.44										
10-60	8.84	1.70	12.13										
20-10	11.12	1.57	9.69										
10-17	9.16	0.95	6.29										
20-30	8.56	0.66	4.79										

concentration. When the q_0 values are plotted against the second virial coefficient, straight lines are obtained, as shown in Figure 4. A similar result has been obtained for a cellulose acetate network crosslinked by oxalyl chloride.[5] Extrapolation of the lines to $A_2 = 0$ yields values for q_0 in an "ideal" solvent, i.e., under Flory θ conditions. Under these circumstances, the excluded volume vanishes and the resulting molecular configuration of the chains in the network would be characteristic for the polymer under consideration if it were unaffected by network restrictions.

It is feasible to write

$$q_0/q_0^\circ = (\langle r^2\rangle_0)^{3/2}/(\langle r_0^2\rangle)^{3/2} = \alpha^3 \tag{4}$$

where q_0° is the degree of swelling of the relaxed network in the absence of volume exclusion ($A_2 = 0$) and α is the molecular expansion factor.

It is seen from the data in Table IV that the value of q_0° increases with molecular weight between crosslinks within each of the series of networks, as do the slopes of the lines in Figure 4. The largest values of q_0° and the slopes in the q_0 versus A_2 plots are found for the networks prepared from the solution with the lower monomer concentration. It appears, therefore, that the degree of swelling, and therefore the molecular configuration of the chains in the networks, is in the absence of volume exclusion not only related to the length of the chains—as is the case for free chains, which follow then Gaussian statistics—but also in an as yet unforeseen way to the conditions prevailing during the network preparation. These conditions are determinative for the topology of the network and control the swelling behavior throughout all further experiments. They become, for instance, of particular importance in the extreme limit of crosslink density[15] and are conveniently referred to as the "memory" of the network.

In the following treatment of volume exclusion for chains in the network, it will be assumed that the perturbation of the unstretched network can be followed by the changes in q_0 for each sample. This change is then related to the molecular expansion factor α of the chains between crosslinks as indicated by eq. (4).

In view of the objections that can be raised to the application of the existing expressions for volume exclusion to chains in a network, it is considered appropriate to test the experimental data only to a number of current expressions which have enjoyed previous success in correlating experimental results. The various refinements and improvements of more recent data will be referred to only when necessary.

The well-known expression of Flory for volume expansion of polymeric chains may be written

$$\alpha^5 - \alpha^3 = C_F A_2 M^{1/2} \tag{5}$$

where C_F is a constant specific for the polymer under consideration, which equals

$$C_F = (9/2\pi)^{3/2} N_A^{-1}(\langle r_0^2\rangle/M)^{-3/2} \tag{5a}$$

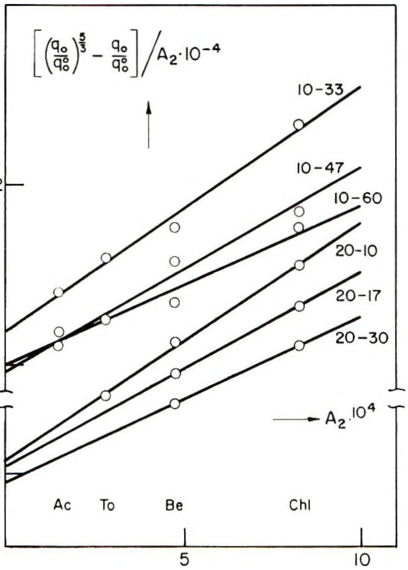

Fig. 5. Dependence of $(\alpha^5 - \alpha^3)/A_2$ on second virial coefficient $[\alpha = (q_0/q_0^\circ)^{1/3}]$.

where N_A is Avogadro's number. Thus, values of $(\alpha^5 - \alpha^3)/A_2$ should, according to eq. (5), be virtually constant for each network, the constant being proportional to $M_c^{1/2}$. This is, however, not found by the experiments. Plots of $\alpha^5 - \alpha^3$ versus A_2 show upward curvatures, and $(\alpha^5 - \alpha^3)/A_2$ decreases more or less linearly with decreasing A_2 values for all samples with the largest slopes found for the samples with the largest M_c values (see Fig. 5).

When χ is near 0.50, eq. (5) may, of course, be expanded to

$$\alpha^2 - 1 = C_F A_2 M^{1/2} + \dots \tag{5'}$$

which differs only slightly from another expression for the initial effect of polymer–solvent interaction upon the intramolecular chain dimensions, derived by no less than five different groups of workers.[16]

This expression is

$$\alpha^2 = 1 + 4/3z + \dots \tag{6}$$

where z is the parameter commonly encountered in perturbation theories of the expansion factor and is given, expressed in Flory's symbolism, to a first approximation, by

$$z = 2(3/2\pi)^{3/2} N_A^{-1}(\langle r_0^2\rangle/M)^{-3/2} A_2 M^{1/2} \tag{6a}$$

The difference between eq. (6) and eq. (5′) resides only in the value of the numerical factor, and for this reason Stockmayer[16] has suggested a change in the magnitude of the constant C_F, which is supported by experimental evidence.

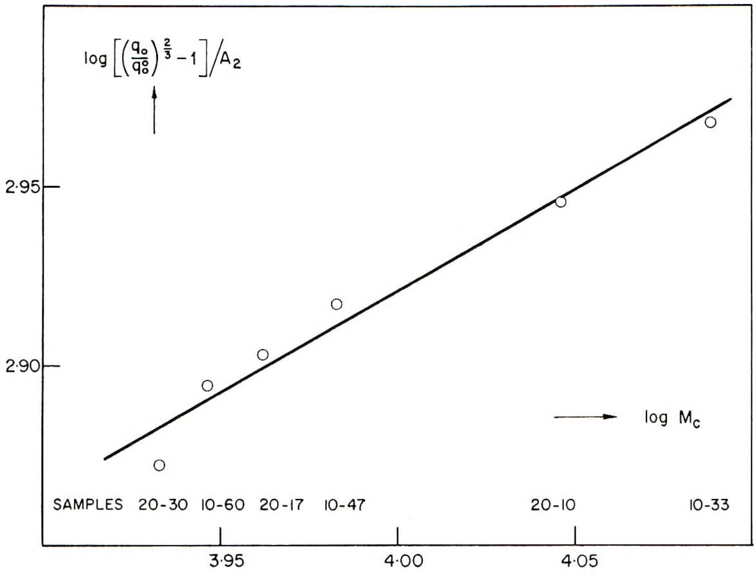

Fig. 6. Plot of log $(\alpha^2 - 1)/A_2$ vs. log M_c according to eq. (6).

When the data are applied to eq. (6) by plotting $\alpha^2 - 1$ versus A_2, straight lines are obtained for all samples with slopes proportional to M_c and intercepts equal to zero or nearly so. Plotting log $(\alpha^2 - 1)/A_2$ against log M_c should then, according to eqs. (6) and (6a), yield a straight line with a slope of 0.5 and an intercept equal to log C_F', where $C_F' = 0.51C_F$. The results are shown in Figure 6 and Table IV. It is seen that the experimental points do lie on a straight line, with the largest scatter caused by the points made up by the samples 20-17 and 20-30. The dependence of q_0 on the second virial coefficient for these samples has been derived from investigation of only two solvents, and the values for log $(\alpha^2 - 1)/A_2$ are therefore likely to be subject to a relatively larger error. However, as can be seen from Figure 6, these points do not alter the outcome critically. The slope of the line equals 0.57, which is in good agreement with theory. The value of 4.54 found for C_F' from the intercept is well in line with the value of 4.97 as predicted by eqs. (6) and (6a), when the experimental value of 665×10^{-11} for $(\langle r_0^2 \rangle / M)^{1/2}$ is used in eq. (6a).

More recently, Stockmayer and Fixman[13] have drawn attention to a simple closed expression

$$\alpha^3 = 1 + 2z \qquad (7)$$

which is numerically very close to a more complicated relation obtained by Kurata, Stockmayer, and Roig[17] in an attempt to improve on Flory's eq. (5). None of these equations is rigorous, but their agreement with each other and with the diamond lattice calculations of Wall and Erpenbeck[18] may be regarded as a support for their validity. Also, eq. (7) has provided more theoretical support for Krigbaum's semiempirical eq. (3), correlating

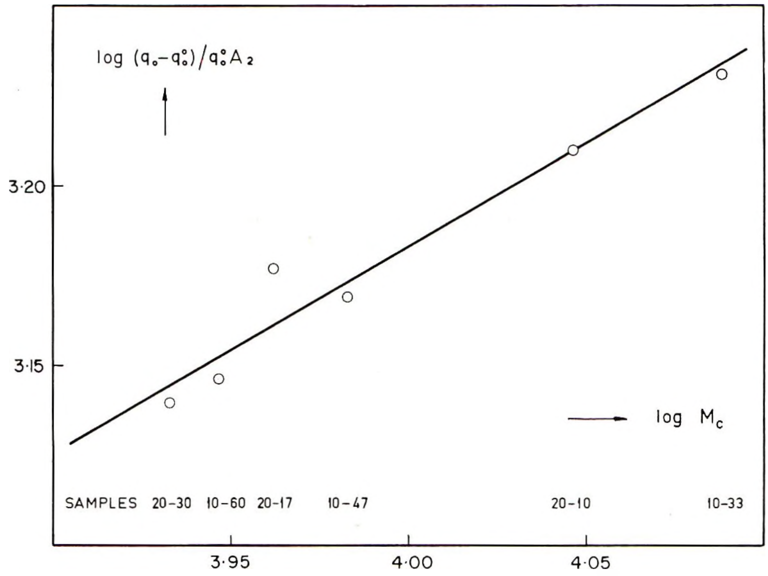

Fig. 7. Plot of log $(\alpha^3 - 1)/A_2$ vs. log M_c according to eq. (7).

intrinsic viscosities with second virial coefficients, which has been well established by a large body of experimental results.

Figure 7 shows the results when the experimental data are plotted according to eq. (7). Here the logarithm of $(\alpha^3 - 1)/A_2$ (which equals the ratio of the slope to the intercept of the lines in Fig. 4) is given as a function of log M_c for all samples. A straight line similar to the one in Figure 6 is obtained with a slope of 0.57 and an intercept equal to the logarithm of 7.70, which compare well with the theoretical values of 0.50 and 7.45, respectively.

The above results have been obtained by using values for q_0 and M_c according to the theory of Hermans [eq. (1a)] throughout all calculations. However, the application of q_0 and M_c values according to Flory's treatment changes the numerical value of M_c by a factor 1/2 ($f = 4$), but does not affect the molecular expansion factor $\alpha = (q_0/q_0^\circ)^{1/3}$. The lines in Figures 6 and 7 will therefore be shifted only a distance (−log 1/2) to the left when Flory's values for M_c, are used, yielding similar lines with equal slopes but with intercepts increased by (−0.57 log 1/2). The results are summarized in Table IV, indicating that the values for q_0 and M_c according to Hermans give a somewhat better fit to eqs. (6) and (7) than those according to Flory for this series of networks.

CONCLUSION

The results obtained by the deswelling experiments have shown that the behavior of the solution-polymerized poly(methyl methacrylate) networks follows the same line as that of the cellulose acetate networks in former work[5,6] and thus add experimental evidence to the theoretical predictions as given by eq. (2).

In evaluating values for q_0 and M_c following the above procedure, certain assumptions concerning the network parameters must be made. Of these, the value for χ_g to be used in the expression for the free energy of mixing is the most speculative, particularly when long-range volume exclusion for the chains in the network is considered. However, this series of networks has been prepared and subsequently investigated under conditions which rule out certain ambiguous factors in the interpretation as much as possible. To this end the networks have been prepared from relatively diluted monomer solutions with low crosslink density and their behavior was studied in relatively poor solvents and solutions. Thus, high degrees of swelling with not too large q/q_0 values as well as a pronounced dependence of q_0 on χ were attained. The tentative conclusion that the dependence of q_0 on solvent power can be described by eqs. (4), (6), and (7) and thus follows a behavior as if the chains were freely dispersed must therefore be expected to hold only for a relatively small range of the network parameters. In the limit of large M_c values, eqs. (1) and (2) will lose their validity as shown by the observed smaller values of M_c on smaller amounts of divinylbenzene added together with unlikely high values of q_0. At still higher degree of swelling, considerable scatter was found in the plots of $\Delta/\phi_g^{1/3}$ versus $\phi_g^{2/3}$. Similarly, the validity of eq. (2) will break down when M_c is too low. This and the conditions to be met by q_0 and χ have been discussed elsewhere in more detail.

Although the network topology will impose restrictions to the molecular configuration of the chains also under conditions which may be regarded as the most similar to those of free chains, the analogy between the second virial coefficient dependence of q_0 (Fig. 4) and that of $[\eta]$ for the free chains (Fig. 1) is remarkable. [It is to be noted that log $[\eta] - [\eta]_\Theta/[\eta]_\Theta A_2$ plotted against log M yields a slope and intercept in agreement with eq. (7).] Here, also, the theory predicts an initial linear dependence of $[\eta]$ and $(\langle r^2\rangle_0)^{3/2}$ on A_2 and gives an adequate account of the experimental slopes, but the linearity observed at larger A_2 values is unexpected. At the present stage, this can only be ascribed to a fortuitous cancellation of various factors omitted.

References

1. Hermans, J. J., *Trans. Faraday Soc.*, **43,** 591 (1947).
2. Wall, F. T., and P. J. Flory, *J. Chem. Phys.*, **19,** 1435 (1951); P. J. Flory, *Trans. Faraday Soc.*, **56,** 722 (1960); P. J. Flory, *J. Am. Chem. Soc.*, **78,** 5222 (1956).
3. James, H. M., and E. Guth, *J. Chem. Phys.*, **21,** 1039 (1953).
4. Hermans, J. J., *J. Polymer Sci.*, **59,** 191 (1962).
5. Rijke, A. M., and W. Prins, *J. Polymer Sci.*, **59,** 171 (1962).
6. Mukherji, B., and W. Prins, *J. Polymer Sci.*, **A2,** 4367 (1964).
7. Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
8. Fixman, M., *Ann. N. Y. Acad. Sci.*, **89,** 657 (1961).

9. Basu, S., J. N. Sen, and S. R. Palit, *Proc. Roy. Soc. (London)*, **A202,** 485 (1950).
10. Krigbaum, W. R., *J. Polymer Sci.*, **18,** 315 (1955).
11. Boyes, A. G., and U. P. Strauss, *J. Polymer Sci.*, **22,** 463 (1956).
12. Krigbaum, W. R., *J. Polymer Sci.*, **28,** 213 (1958).
13. Stockmayer, W. H., and M. Fixman, *J. Polymer Sci.*, **C1,** 137 (1963).
14. Kurata, M., and W. H. Stockmayer, *Adv. Polymer Sci.*, **2,** 196 (1963).
15. Lloyd, W. G., and T. Alfrey, Jr., *J. Polymer Sci.*, **62,** 301 (1962).
16. Stockmayer, W. H., *J. Polymer Sci.*, **15,** 595 (1955).
17. Kurata, M., W. H. Stockmayer, and A. Roig, *J. Chem. Phys.*, **33,** 151 (1960).
18. Wall, F. T., and J. J. Erpenbeck, *J. Chem. Phys.*, **30,** 634 (1959).

Résumé

Des mesures de dégonflage en solution polymérique de différentes concentrations fournissent certains renseignements concernant les paramètres des réseaux polymériques obtenus par pontage en solution. Cependant, dans ce cas, les théories existantes qui décrivent le gonflement sont contradictoires et aucune conclusion nette sur les propriétés des reséaux ne semble apparaître jusqu'à présent. De plus, l'effet de volume et de connectivité des chaînes ne sont pris en considération dans aucune de ces théories. L'effet de la présence des pontages et aussi du nombre des segments polymériques connectés dans le reseau sur la valeur du paramètre d'interaction solvant–polymère d'Huggins utilisé dans les expressions pour l'energie libre du mélange n'est pas clair non plus. Néanmoins, les données expérimentales disponibles ont indiqué une certaine préférence pour la théorie d'Hermans sur celle de Flory, tandis que la théorie de James and Guth doit être complètement rejetée. Une dépendance du degré de gonflement q_0, dans lequel l'energie partielle molaire libre d'élasticité est nulle, de la capacité de solution des liquides gonflants a été observée auparavant. Elle a été examinée d'une façon plus approfondie dans la présente étude. A cet effet, du methyl methacrylate a été copolymérisé avec de petites quantités de divinylbenzène en solutions riche en benzène fournissant six échantillons à degré de pontage et valeurs de q_0 différents. Une grande dépendance de q_0 sur le second coëfficient virial dans quatre solvants a été observée. La possibilité d'appliquer les théories existantes à l'interaction solvant–polymère aux dimensions intramoléculaires a été examinée pour nos chaînes dans les réseaux. L'expression de Flory pour l'expansion des chaînes polymériques n'atteint pas notre but, mais deux autres relations, qui décrivent le même effet initial ont indiqué que la dépendance de q_0 du second coëfficient virial peut être attribué à l'effet de volume, comme on le rencontre dans le cas des chaînes libres. Il est vraisemblable cependant, que la validité de ces relations se limite aux faibles variations des valeurs des paramètres des réseaux.

Zusammenfassung

Angaben über Parameter von Polymerisaten mit Netzstruktur, die durch Vernetzung in Lösung erhalten wurden, können mit Hilfe von Entquellungsmessungen in Polymerlösungen verschiedener Konzentration bestimmt werden. Unter diesen Bedingungen müssen die bestehenden Theorien, die das Verhalten beim Quellungsvorgang beschreiben, jedoch noch als strittig betrachtet werden und sie lassen daher auch noch keine endgültigen Schlussfolgerungen über die Eigenschaften der Polymeren Netzstruktur zu. Volumenausschluss und Kettenbindungs-Effekte wurden bei beiden Theorien nicht berücksichtigt. Die Wirkung der vorhandenen Knotenpunkte und der Zahl der verbundenen Kettensegmente im Netzwerk auf den Wert des Hugginsschen Wechselwirkungsparameters der zur Bestimmung der Enthalpie der Misschung erforderlich ist, ist noch nicht geklärt. Die bereits vorhandenen experimentellen Werte haben jedoch gezeigt, dass der Theorie von Hermans gegenüber der von Flory den Vorzug gegeben werden kann. Die Theorie von James und Guth erwies sich als völlig ungeeignet. Eine Abhängigkeit des Quellungsgrades q_0, bei welchem die freie partielle Molarenergie der Elastizität gleich null ist, von dem Lösungsvermögen des Quellungsmittels wurde schon früher beobachtet und wurde jetzt näher in dieser Arbeit untersucht. Zu diesem Zwecke wurde Methylmethacrylat mit kleinen Mengen von Divinylbenzol in Form einer verdünnten Benzollösung kopolymerisiert, wobei Proben mit verschiedenem Vernetzungsgrad und q_0-Werte erhalten wurden. Eine weitgehende Abhängigkeit des q_0-Wertes von dem osmotischen zweiten Virialkoeffizienten wurde in vier Lösungsmitteln festgestellt. Die Anwendbarkeit der allgemein üblichen Theorien für die Wechselwirkungen zwischen Polymer und Lösungsmittel auf intramolekuläre Kettenausdehnung bezüglich der Ketten im Netzwerk wurde untersucht. Florys Ausdruck für Volumenausdehnung von Polymerketten hat sich als unzulänglich erwiesen. Zwei andere Beziehungen hinsichtlich der gleichen Aufangswirkung haben jedoch gezeigt, dass die zweite Virialkoeffizientabhängigkeit des q_0-Wertes auf den Volumenausschluss zurückgeführt werden kann, ähnlich wie im Falle der freien Ketten. Die Gültigkeit dieser Beziehungen wird jedoch nur für einen recht begrenzten Bereich der Netzwerkparameter angenommen.

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Crosslinking of Copolymers Containing *N,N*-Dimethylacrylamide

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Synopsis

Aqueous solutions of *N,N*-dimethylacrylamide–acrylic copolymers crosslink in the presence of peroxydisulfates at elevated temperature. It is shown that effectiveness of crosslinking depends on the amount of *N,N*-dimethylacrylamide present in the copolymer, being quite effective with as little as one unit of *N,N*-dimethylacrylamide in each eleven units of copolymer. Dilute solutions of these copolymers are slowly degraded initially by peroxydisulfate, and then begin to crosslink after a few minutes. Crosslinking is believed to proceed via sulfate- and hydroxyl-radical attack of *N*-methyl in the polymers to yield *N*-methylol derivatives capable of crosslinking with other reactive sites.

INTRODUCTION

Oxidative *N*-demethylation of *N,N*-dimethylamides by peroxydisulfate was recently reported.[1,2] These demethylations are thought to proceed via radical attack of *N*-methyl to yield *N*-methylol derivatives as intermediates. It was considered that this procedure might provide a method for crosslinking copolymers containing *N,N*-dimethylamido groups through *in situ* generation of methylol by peroxydisulfate. These methylol groups would in turn form crosslinks with other reactive side chains in the copolymer. A series of copolymers of various acrylics and *N,N*-dimethylacrylamide were prepared to test this hypothesis.

EXPERIMENTAL

Monomers and Reagents

The monomers used in this study were acrylamide (American Cyanamid Company), *N,N*-dimethylacrylamide (Borden Chemical Company), acrylic acid (Eastman Kodak Company), and ethyl acrylate (Borden Chemical Company). The last three monomers we redistilled prior to use. Baker Analyzed ammonium and potassium peroxydisulfate and silver nitrate were used. *N,N*-Dimethylacetamide (DMA) was Eastman White Label grade. *N,N,N′,N′*-tetramethylsuccinamide (TMS) (m.p. 80–82°C.) was prepared by reaction of succinyl chloride and dimethylamine in dry benzene.

Preparation of Copolymers

In a 250-ml. flask equipped with a nitrogen inlet tube, reflux condenser, thermometer, and magnetic stirrer were placed the monomers, ammonium peroxydisulfate, and water. Nitrogen was bubbled through the solution for 30 min., and the solutions were then heated at 60–70°C. with stirring for 30 min. to yield viscous, colorless solutions of copolymer. Ethyl acrylate–*N*,*N*-dimethylacrylamide copolymer was a white colloidal suspension in water. These polymers were isolated in near quantitative yields by precipitation from solution by addition of acetone or by removal of water at room temperature under vacuum. These copolymers were freely soluble in common polar and nonpolar organic solvents. The recipes and properties of polymers of these polymerizations are found in Table I.

TABLE I
Composition of Polymerization Runs and Copolymer Characteristics[a]

Comonomer(s)	Amt., g.	*N*,*N*-Dimethyl-acrylamide, g.	Water, ml.	N, %		η_{inh}[b]
				Calc.	Found	
Acrylamide	10.0	1.00	100	19.3	18.2[c]	3.25
"	10.0	0.50	100	19.5	19.4[c]	3.33
"	10.0	0.10	100	19.7	19.6[c]	3.71
"	10.0	None	100	19.7	19.6[c]	3.31
Acrylic acid	10.0	1.00	100	0.96	1.30	3.00
Acrylic acid acrylamide	10.0 1.00	1.00	110	2.56	2.56	—
Ethyl acrylate	10.00	1.00	300	1.30	1.20	—

[a] Ammonium peroxydisulfate catalyst (0.020 g.) was used in each polymerization.

[b] Inherent viscosity of 0.4% copolymer in water at 30°C.

[c] Analysis was made on the polymer solution. Precipitated and dried samples of these polymers gave consistently low nitrogen values.

Crosslinking of Copolymers

To 10.0 g. of 11% copolymer solutions containing a 10:1 ratio of comonomer to *N*,*N*-dimethylacrylamide (preparation described above) was added 0.23 g. (0.001 mole) of ammonium peroxydisulfate or 0.27 g. (0.001 mole) of potassium peroxydisulfate. Heating of these mixtures at 70°C. or higher gave water-insoluble polymers. These polymers were insoluble in even the most polar solvents.

Viscosity Studies of Crosslinking

The compositions of solutions used in these studies are listed in Table II. The solutions of 0.787–0.834 g. of polymer/100 ml. of water were heated to 70°C., and ammonium peroxydisulfate and any additional additive were mixed into the solution. A portion of the resulting mixture was transferred immediately to an Ostwald (size 100) viscometer and placed in a constant

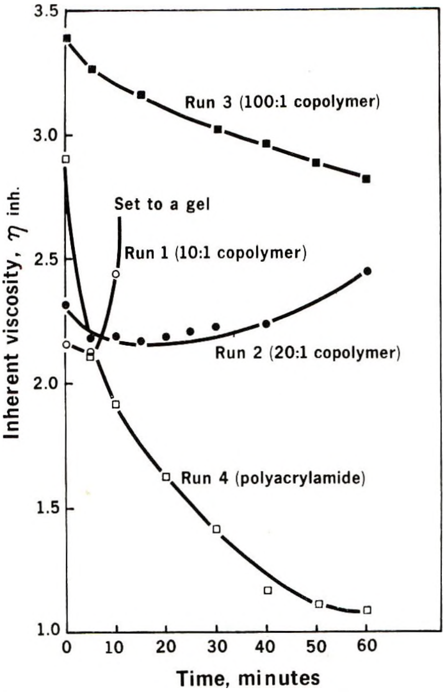


Fig. 1. Change in inherent viscosity of polymers in the presence of peroxydisulfate (70°C.).

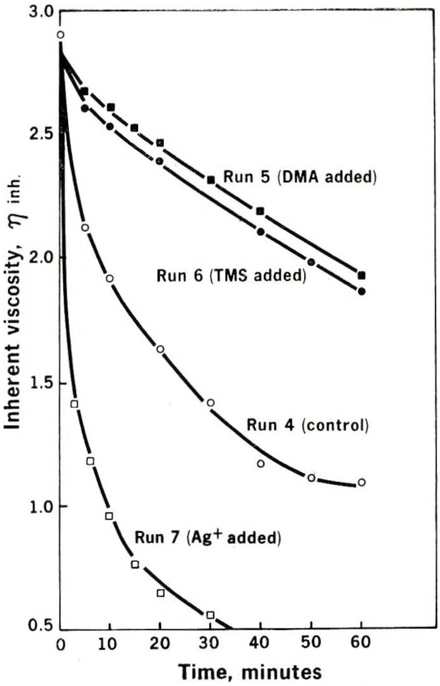


Fig. 2. Change in inherent viscosity of polyacrylamide in the presence of peroxydisulfate and other additives (70°C.).

TABLE II

Composition of Polyacrylamide and Acrylamide–*N*,*N*-Dimethylacrylamide Copolymer Solutions for Viscosity Studies[a]

Run	Ratio of acrylamide to *N*,*N*-dimethylacrylamide	Polymer concn., g./100 ml.	$(NH_4)_2S_2O_8$ concn., g./100 ml.	Additive	Additive concn., g./100 ml.
1	10:1	0.815	0.171	—	—
2	20:1	0.828	0.0911	—	—
3	100:1	0.787	0.0180	—	—
4	Polyacrylamide	0.834	0.175	—	—
5	"	"	"	DMA	0.0677
6	"	"	"	TMS	0.0660
7	"	"	"	$AgNO_3$	0.0200

[a] Viscosity determinations run at 70.0 ± 0.1°C.

temperature bath at 70.0 ± 0.1°C. The viscosity of the solution was followed over a period of 1 hr. (Figs. 1 and 2).

RESULTS AND DISCUSSION

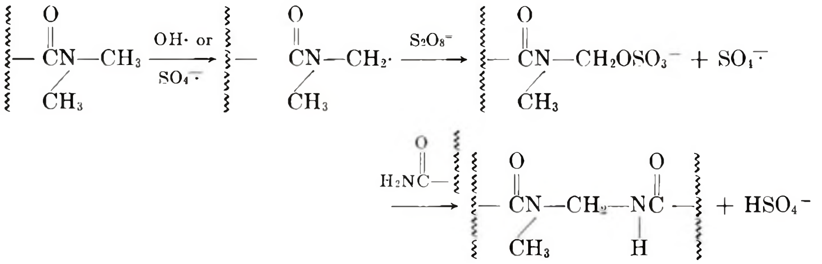
Aqueous solutions or suspensions of copolymers containing *N*,*N*-dimethylacrylamide (Table I) were crosslinked by reaction with peroxydisulfate at 70°C. or higher. Crosslinking in experiments using dilute solutions of acrylamide–*N*,*N*-dimethylacrylamide copolymers and polyacrylamide was followed by measuring the change of viscosity with time (Fig. 1 and 2). It will be noted that dilute solutions of polyacrylamide and 100:1 acrylamide–*N*,*N*-dimethylacrylamide copolymers degrade in the presence of peroxydisulfate at 70° C. (Fig. 1), whereas 10:1 and 20:1 acrylamide–*N*,*N*-dimethylacrylamide copolymers degrade initially and then begin to crosslink after a few minutes. The 10:1 copolymer is most effectively crosslinked at these dilutions; with *N*,*N*-dimethylacrylamide at less than 10 wt.-% crosslinking is less effective.

Peroxydisulfate is known to yield sulfate- and hydroxyl-free radicals on decomposition in aqueous solutions.[3] The measured changes in viscosity of the various copolymer solutions in the presence of peroxydisulfate suggest that these radicals attack either the polymer main chain causing degradation or *N*-methyl causing crosslinking. These are competitive reactions, and their relative importance is dependent on the composition of the copolymer, degradation becoming less significant as the *N*,*N*-dimethylamide content of the copolymer is increased.

Peroxydisulfate attack of dilute solutions of polyacrylamide was studied in the presence of other additives (Fig. 2). Addition of silver ion, known to accelerate homolytic decomposition of peroxydisulfate,[3] increased the rate of polyacrylamide degradation. Peroxydisulfate is observed[1,2] to demethylate oxidatively such *N*,*N*-dimethylamides as *N*,*N*-dimethylacetamide (DMA) and *N*,*N*,*N*′,*N*′-tetramethylsuccinamide (TMS) to yield formaldehyde, a crosslinking reagent for polyacrylamide.[4] However, when these amides were added to dilute solutions of polyacrylamide and peroxydisulfate at 70°C., only degradation of the polymer was found, although the rate of degradation was somewhat less. This shows that crosslinking of copolymers containing *N*,*N*-dimethylacrylamide is not due simply to generation of free formaldehyde from *N*,*N*-dimethylamido groups, but rather to generation of a reactive group from *N*,*N*-dimethylamido within the polymer.

The results of the viscosity studies and the effect of various additives are in harmony with the scheme of eqs. (1) and (2) for the crosslinking reaction:

$$S_2O_8^{=} \xrightarrow{\Delta} SO_4^{\overline{\cdot}} \xrightarrow{H_2O} OH\cdot + HSO_4^- \qquad (1)$$



(2)

This scheme is related, of course, to that previously suggested for the oxidative dealkylation of simple amides.[2] In accord with the original hypothesis, these results demonstrate the feasibility of crosslinking of copolymers containing *N*,*N*-dimethylamido groups by the *in situ* generation of a crosslinking group therefrom by reaction with peroxydisulfate at elevated temperatures.

Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

References

1. Needles, H. L., and R. E. Whitfield, paper presented at the 147th Meeting, American Chemical Society, Philadelphia, Pa., April. 1964; *Abstracts of Papers*, p. 50N.
2. Needles, H. L., and R. E. Whitfield, *J. Org. Chem.*, **29,** 3632 (1964).
3. House, D. A., *Chem. Revs.*, **62,** 185 (1962).
4. *Chemistry of Acrylamide*, American Cyanamid Co., New York, 1956, p. 19.

Résumé

Des copolymères *N*,*N* diméthylacrylamide-acide acrylique, en solution aqueuse, se pontent en présence de peroxydisulfate à température élevée. On démontre que l'efficacité du pontage dépend de la quantité de *N*,*N* diméthylacrylamide présent dans le copolymère, l'efficacité étant suffisante avec une unité de *N*,*N* diméthylacrylamide toutes les onzes unités de copolymère. Des solutions diluées de ces copolymères sont lentement dégradées initialement par le peroxydisulfate, et ensuite la pontage commence après quelques minutes. Il est probable que le pontage se fait via l'attaque du radical sulfate ou hydroxyle du groupement *N*-méthyl dans les polymères pour former des dérivés *N*-methylol, qui sont capables de se ponter avec d'autres sites réactionnels.

Zusammenfassung

Wässrige Lösungen von N,N-Dimethylacrylamid-Acrylkopolymeren vernetzen in Gegenwart von Peroxydisulfaten bei erhöhter Temperatur. Es wird gezeigt, dass die Vernetzungsausbeute von der Menge des im Kopolymeren vorhandenen N,N-Dimethylacrylamid abhängt, wobei eine gute Wirksamkeit schon mit nur einer N,N-Dimethylacrylamideinheit auf 11 Kopolymereinheiten auftritt, Verdünnte Lösungen dieser Kopolymeren werden anfangs durch Peroxydisulfat langsam abgebaut und beginnen dan nach einigen Minuten zu vernetzen. Es wird angenommen, dass die Vernetzung über einen Sulfat- und Hydroxylradikalangriff auf das N-Methyl im Polymeren unter Bildung von N-Methylolderivaten verläuft, welche einer Vernetzung mit anderen reaktionsfähigen Stellen fähig sind.

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Polymers from *ortho* Aromatic Tetraamines and Aromatic Dianhydrides

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Synopsis

Aromatic heteropolymers were synthesized from aromatic tetraamines and dianhydrides; some of the polymers had a ladder-type structure. The properties and thermal stability of the polymer were studied. The experimental conditions yielding the imidazolone structure were determined on model compounds. Polymers containing mixed aromatic units in the chain were prepared from pyromellitic anhydride or 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, and 3,3′-diaminobenzidine, 3,3′,4,4′-tetraaminodiphenyl ether, 1,4,5,8-tetraaminonaphthalene, or 1,2,4,5-tetraaminobenzene. The polycondensations were carried out in melt and in solution (in melted phenol, pyridine, dimethylacetamide, 116% polyphosphoric acid). The inherent viscosities of a number of polymers synthesized by melt condensation were in the range of approximately 0.2–0.7; the higher polymers were obtained by carrying out the polycondensations in solution in 116% polyphosphoric acid; in this case, the intrinsic viscosities ranged from 1.1 to 1.8. Most of the polymers do not melt at 350°C. and are soluble in the usual organic solvents, but the ladder-type structure polymers were soluble only in concentrated sulfuric acid.

For several years the thermal and oxidative stability of aromatic structures has been recognized, and a variety of polymers have been synthesized in which aromatic rings are linked together in chains or networks. In most cases, the connecting groups are less stable than the rings, and the stability of the polymer is determined largely by the nature of connecting groups. Among the more stable linking groups that have been used to make high polymers are imidazole rings and imide groups.

The synthesis of a variety of polybenzimidazoles has been previously reported by this laboratory;[1–4] the polymers were obtained by melt polycondensation of suitable aromatic tetraamines and polyesters of dicarboxylic acids. Also the synthesis of high molecular weight polyimides by polycondensation of pyromellitic anhydride and diamino compounds is well known.[5–12]

The present paper is concerned with the preparation and properties of a series of new polymers in which aromatic rings are linked by imidazolone groups to give linear polymers of high thermal stability. The polymers

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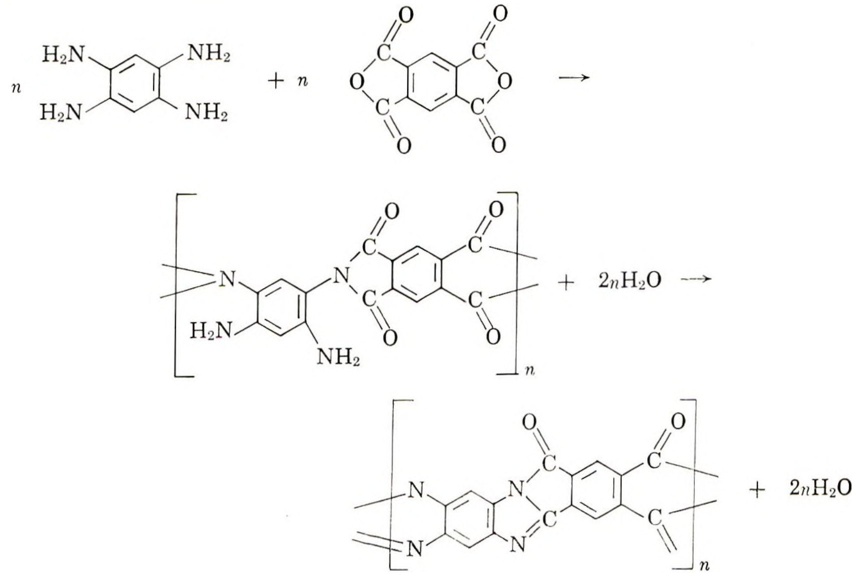
were obtained by polycondensation of aromatic dianhydrides with aromatic tetraamines containing amino groups in *ortho* position.



The dianhydrides used were pyromellitic and 3,3′,4,4′-benzophenone tetracarboxylic dianhydrides; the tetraamino compounds were 3,3′-diaminobenzidine, 3,3′,4,4′-tetraaminodiphenyl ether, 1,2,4,5-tetraaminobenzene, and 1,4,5,8-tetraaminonaphthalene. By polycondensation of the latter two amino compounds with pyromellitic anhydride, we were able to synthesize a high molecular weight, conjugated ladder-type polymer.

DISCUSSION

Model Compounds

Before attempting the synthesis of polymers, we investigated the condensation reaction with bifunctional compounds and determined the influence of the experimental conditions on the structure of the reaction products. Indeed the condensation of *o*-phenylenediamine with phthalic anhydride yields several reaction products; depending on the experimental conditions, they are 1,2-benzoylbenzimidazole (I), *o*-phenylene bibenzimidazole (II), and *N*,*N*′-diphthaloyl-*o*-phenylenediamine (III).

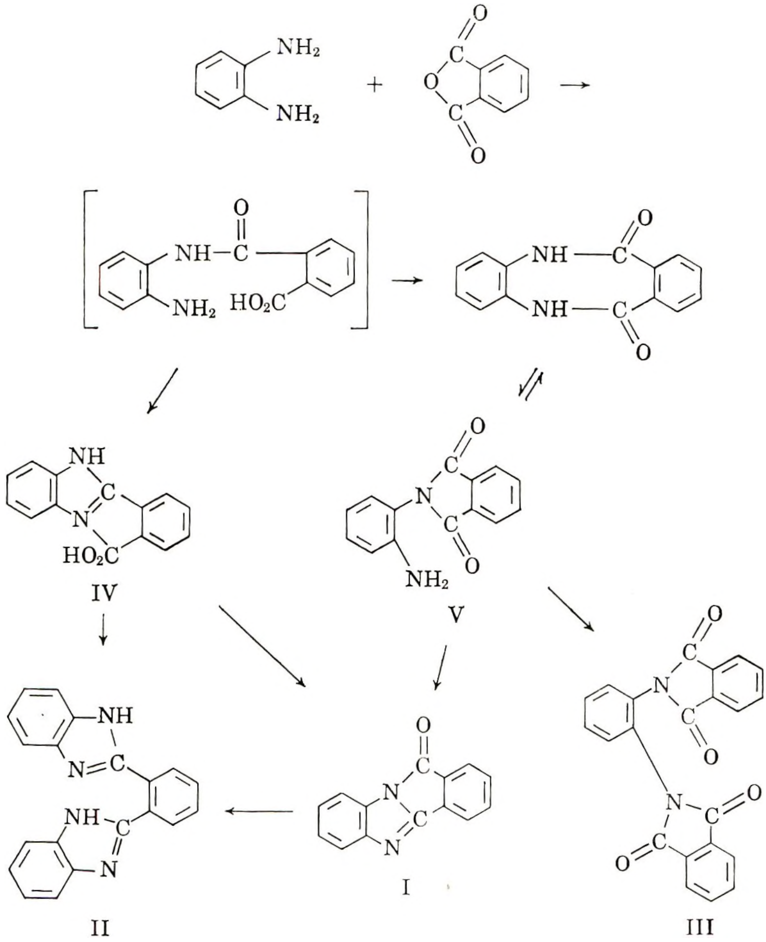
The compounds have been described by different workers,[13,14] and some alkoylimidazole derivatives have been used as fluorescing dyes for Dacron.[15]

Heating the components in alcoholic solution has been reported to give the *o*-substituted benzoic acid (IV);[16–20] direct heating of equimolecular amounts of *o*-phenylenediamine and phthalic anhydride to 140–150°C. gives 1,2-benzoylbenzimidazole (I);[21] *o*-phenylene bibenzimidazole (II) may be obtained by heating the components at higher temperature[2,21,22] or by reaction of 1,2-benzoylbenzimidazole with *o*-phenylenediamine.[23]

Finally, N,N'-diphthaloyl-*o*-phenylenediamine (III) is obtained by a similar reaction to that involved in the polyimide synthesis.

Bistrzycki and Lecco[21] proposed the formation of benzimidazole-*o*-benzoic acid (IV) as an intermediate compound during the synthesis of 1,2-benzoylbenzimidazole (I).

We attempted to get more information about the structure of the products formed during the condensation in carrying out the reaction in solution in dimethylsulfoxide and by following the transformation by means of nuclear magnetic resonance. Most of the NMR spectra showed the presence of a mixture of compounds. Apparently, more than one mechanism is involved in the reaction, and the formation of benzimidazole-*o*-benzoic acid (IV) and of N,N'-(*o*-aminophenyl)phthalimide (V) seems to be competitive. But we observed that it is possible to favor the formation of the compound IV or V by varying the experimental conditions.

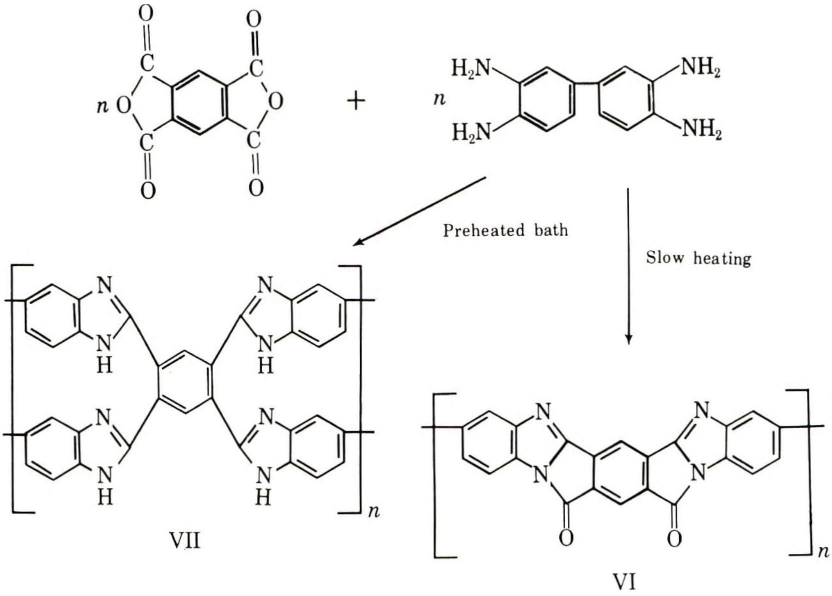


These observations were confirmed by a quantitative study of the melt condensation of *o*-phenylenediamine and phthalic anhydride; the results are recorded in Figure 1.

Depending on the heating rate and the starting anhydride/amine molar ratio, the reaction product is *o*-phenylenebibenzimidazole or 1,2-benzoylbenzimidazole. Slow heating (about 2°C./min.) and an anhydride/amine molar ratio equal to or greater than 1 give the highest yield of 1,2-benzoylbenzimidazole.

Polybenzimidazolimides

The investigation with model compounds showed that, when the polycondensation is carried out with tetrafunctional reagents, such as 3,3′-diaminobenzidine and pyromellitic anhydride, a slow and progressive heating is most suitable to get linear polymers (VI) and to avoid insolubility due to the formation of a tridimensional polymer (VII).



The highest molecular weight polymers, however, were obtained from an equimolecular ratio of starting material; indeed, an anhydride/amine molar ratio greater than 1 increases the polymer (VI) yield but decreases the molecular weight.

In melt, the polycondensations were initiated at temperatures around 105–110°C. but the ring closure by intramolecular condensation was performed only at higher temperature (140–150°C.). A list of the polymers which have been prepared is given in Table I.

It should be noted that the ladder-type polymers have usually a slightly lower inherent viscosity than the linear polymer. This is presumably due

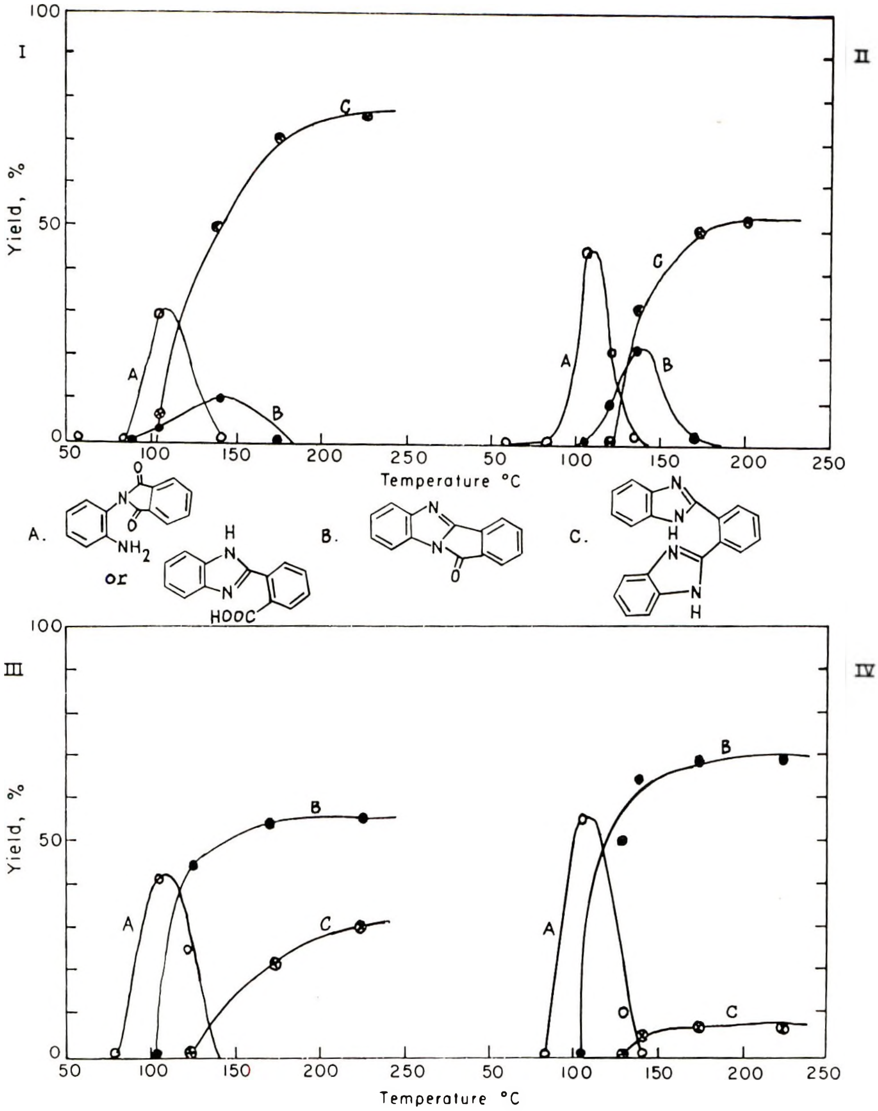
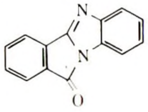
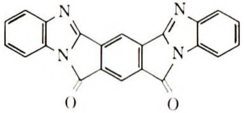
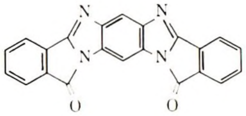
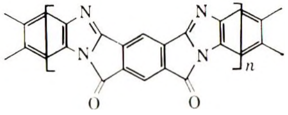


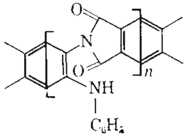
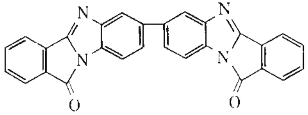
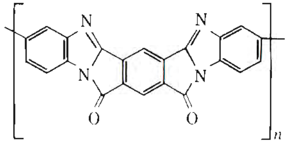
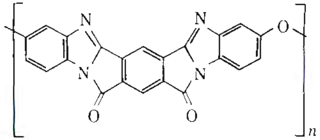
Fig. 1. Formation of model compounds: (*I*) molar ratio anhydride/amine = 0.5, preheated bath; (*II*) molar ratio anhydride/amine = 1, preheated bath; (*III*) molar ratio anhydride/amine = 1, slow heating (2°C./min.); (*IV*) molar ratio anhydride/amine = 2, slow heating (2°C./min.).

not only to the greater oxidizability of the starting amino compounds, but also to more rigidity of the chain because of the ladder structure.

The aromatic polybenzimidazolones are colored powders, not melting below 400°C. and soluble in dimethylformamide, dimethylacetamide, dimethyl sulfoxide and concentrated sulfuric acid, but the ladder-type polymers were mostly insoluble in the usual organic solvents.

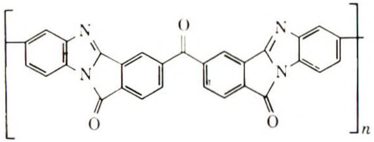
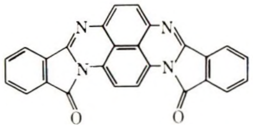
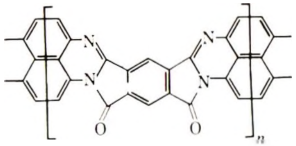
TABLE I
Data on Preparation, Structure, Inherent Viscosity, and Ultraviolet Absorption of Polybenzimidazolones and Some Model Compounds

Starting material	Exptl. conditions	Reaction temp., °C.^{a}	Compound or repeating unit	Viscosities	λ_{max}, mμ^b	$E^{1\%}_{1\text{ cm.}}$
Phthalic anhydride + *o*-phenylenediamine	Melt	140–150		—	350 315 263 244	560 485 950 1230
Pyromellitic anhydride + *o*-phenylenediamine	Melt	140–150		—	355 320 280	155 223 635
Phthalic anhydride + 1,2,4,5-tetraaminobenzene	Melt	140–150		—	354 322 280	210 237 641
Pyromellitic anhydride + 1,2,4,5-tetraaminobenzene + 1,2,4,5-tetraaminobenzene tetrahydrochloride	Melt PPA^d	220–300 220–220		0.24–0.30^c 1.10^e	330 (shoulder) 310 230	337 387 1700

Pyromellitic anhydride + 1,3-dianilino-4,6-diaminobenzene	Melt	220–300		0.27^{c}		
Phthalic anhydride + 3,3′-diaminobenzidine	Melt	230		—	310 (wide) 230	600 1570
Pyromellitic anhydride + 3,3′-diaminobenzidine	Melt	220–300		0.40–0.64^{c}	335	207
+ 3,3′-diaminobenzidine	In diglyme or DMAc	160		0.71–0.94^{f}	(shoulder) 320 (shoulder)	275
+ 3,3′-diaminobenzidine tetrahydrochloride	PPA^{d}	200–220		1.25–1.80^{g}	305 250 (shoulder) 335	290 535 1625
Pyromellitic anhydride + 3,3′,4,4′-tetraaminophenyl ether	Melt	175–320		0.38–0.44^{c}	365 (shoulder) 315	175 300
+ 3,3′,4,4′-tetraaminodiphenyl ether tetrahydrochloride	PPA^{d}	200–220		1.26^{e}	(wide) 275 (wide) 225	400 2460

(continued)

TABLE I (*continued*)

Starting material	Exptl. conditions	Reaction temp., °C.[a]	Compound or repeating unit	Viscosities	λ_{max}, $m\mu$[b]	$E^{1\%}_{1\text{ cm.}}$
3,3′,4,4′-benzophenone tetracarboxylic dianhydride + 3,3-diaminobenzidine	Melt	220–320		0.17–0.32[c]	372 (wide) 315 (wide) 255 235 215	200 850 1680 1870 2000
Phthalic anhydride + 1,4,5,8-tetraamino-naphthalene	In diglyme	230–300		—	320–15 (wide) 227	540 1700
Pyromellitic anhydride + 1,4,5,8-tetraaminonaphthalene	In diglyme	230–300		0.34–0.41[e]	370 (shoulder) 330 (shoulder) 320 300 235 219	130 367 410 418 1670 1780

[a] The reaction temperatures were reached by a slow and gradual heating (about 2°C./min.).

[b] The ultraviolet absorption spectra were measured on concentrated sulfuric acid solutions of the polymers.

[c] The reported values are inherent viscosities measured at 0.25% concentration in dimethyl sulfoxide.

[d] The starting concentration in polyphosphoric acid ranged from 0.6 to 3.0 wt.-%.

[e] The reported values are intrinsic viscosities measured in concentrated sulfuric acid.

[f] The reported values are inherent viscosities measured at 0.25% concentration in sulfuric acid.

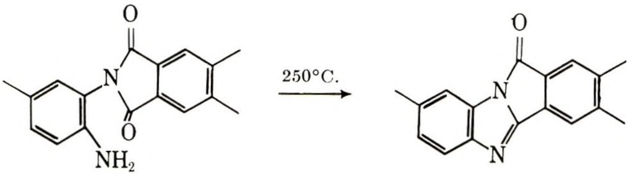
[g] The reported values are intrinsic viscosities measured in dimethyl sulfoxide.

A comparison of the infrared spectra of the new polymers and the model compounds are recorded in Figures 2–6.

Most of the elemental analyses of the polymers indicated material corresponding to the expected polybenzimidazolone structure. Only the polycondensation with pyromellitic anhydride and 1,3-dianilino-4,6-diaminobenzene failed to yield the expected structure; indeed, in this case the ring closure was not performed even at high temperature (320°C.), presumably because of the steric hindrance from the phenyl groups.

Sometimes, at high temperatures, the ring closure by intramolecular condensation involves intermolecular reaction and, consequently, insolubility of the polymer. To promote intramolecular cyclization, we tried to complete dehydration by heating uncyclized polymers at lower temperature in the presence of concentrated sulfuric acid or acetic anhydride, but all the attempts were unsuccessful.

Heating with sulfuric acid involves a partial sulfonation of the polymer, and, in the presence of acetic anhydride (pure or diluted in pyridine), we observed some acetylation instead of dehydration. In order to get some high molecular weight polymers, we carried out the polycondensation in solution (in melted phenol, pyridine, dimethyl sulfoxide, dimethylacetamide, and polyphosphoric acid). In such experimental conditions, we observed usually higher polymer yields and inherent viscosities, but most of the elemental analyses of the samples synthesized in solution showed an incomplete ring closure; the polyimidazalone structure was obtained by reheating the polyaminoimides above 250°C. under vacuum.



In the presence of polyphosphoric acid, we synthesized high molecular weight polymers, with intrinsic viscosities ranging from 1.1 to 1.8. Many of the polymers were still soluble in dimethyl sulfoxide or in concentrated sulfuric acid; it was possible to get some films by evaporation of the dimethylsulfoxide solutions. The polymers do not melt below 350°C. but they turn brown at about 230°C., apparently without decomposition, and then become insoluble in the usual organic solvents.

Besides the advantage of getting higher molecular weights, the experimental procedure is very much easier when the polycondensations are carried out in polyphosphoric acid; indeed, the stable tetrahydrochloride is the starting material, and the liberation of the tetraamino compound is carried out directly in polyphosphoric acid;[25] consequently, oxidation of the free amino compound is avoided.

The resistivity and dielectric constant of a sample of the polymer synthesized from 1,4,5,8-tetraaminonaphthalene and pyromellitic anhydride were typical of insulating organic polymers. The measured values at room temperature were 5×10^{10} ohm-cm. for the resistivity and 4 (1 Mcycle) for the dielectric constant.

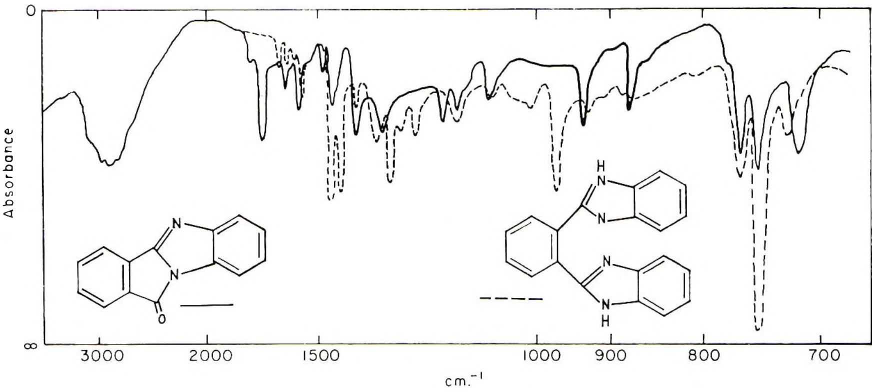


Fig. 2. Infrared spectra.

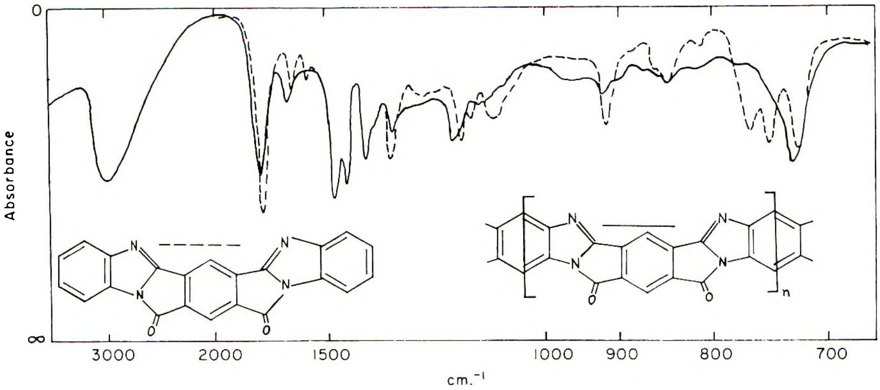


Fig. 3. Infrared spectra.

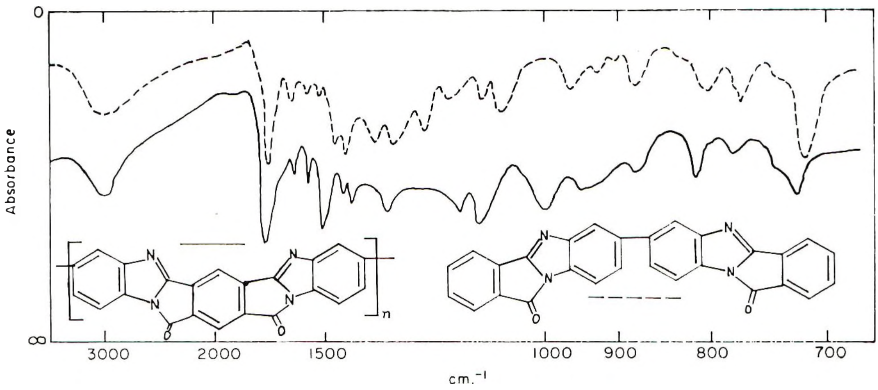


Fig. 4. Infrared spectra.

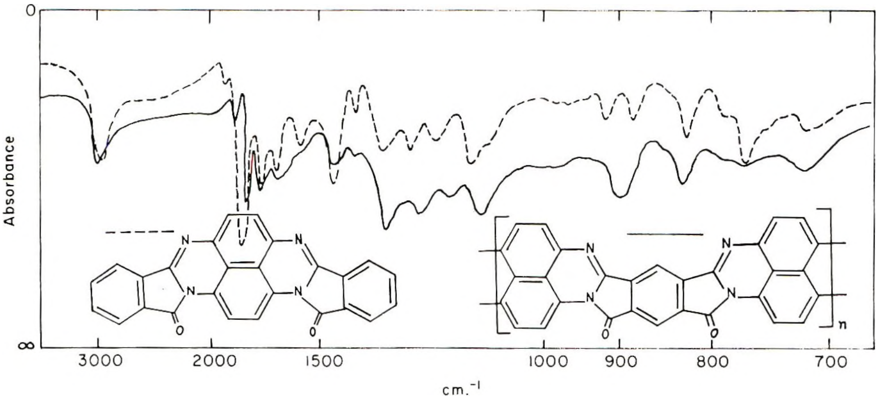


Fig. 5. Infrared spectra.

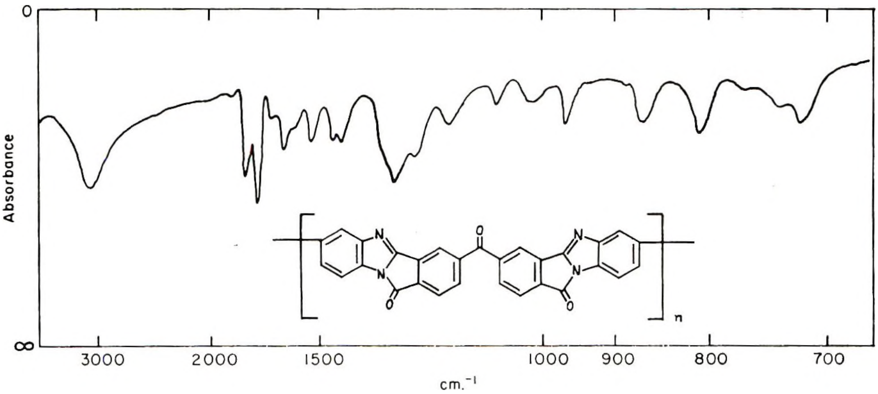


Fig. 6. Infrared spectrum.

Thermogravimetric analysis of these polymers show that most of them are stable to 450–500°C. under nitrogen. Some of the polymers prepared in polyphosphoric acid seemed to decompose at a little lower temperature, which may mean that they still were contaminated with polyphosphoric acid. In air the polymers tested oxidized rather rapidly at 350–400°C. (Figs. 7–9).

EXPERIMENTAL

Monomers

Phthalic Anhydride and Pyromellitic Anhydride. The phthalic anhydride used was a commercial grade (Eastman Organic Chemicals) recrystallized from benzene. The pyromellitic anhydride was a gift from Dr. B. W. Howk, Explosives Department, E. I. du Pont de Nemours and Co., and also was recrystallized from benzene.

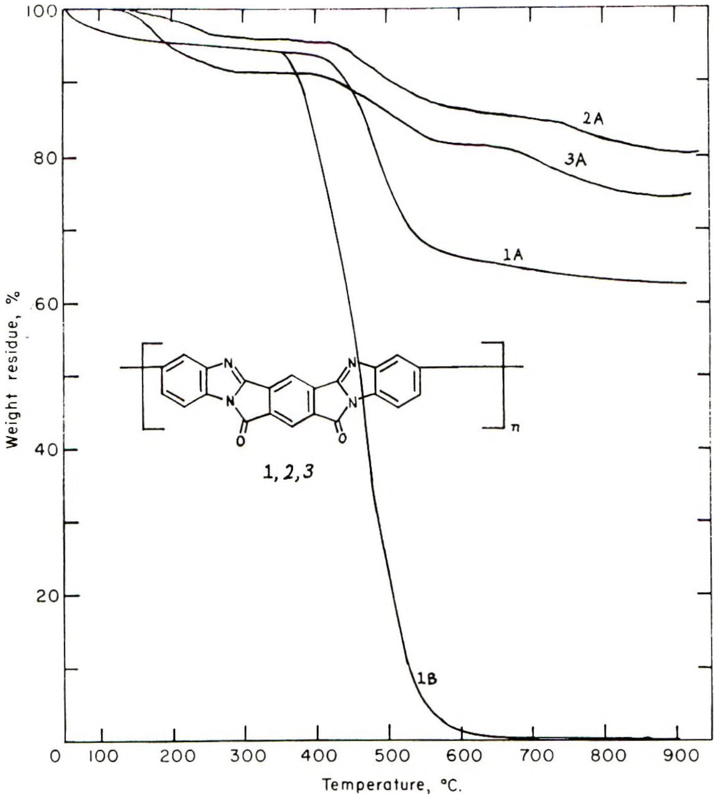


Fig. 7. Thermographic analysis ($\Delta T = 6$°C./min.) of: (*1A*) polymer synthesized by melt condensation under nitrogen; (*1B*) same polymer synthesized by melt condensation in air; (*2A*) same polymer synthesized in 116% polyphosphoric acid under nitrogen; (*3A*) same polymer synthesized in dimethylacetamide.

3,3′,4,4′-Benzophenone Tetracarboxylic Dianhydride. The 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (Gulf Research and Development Company) was used without further purification, m.p. 236°C.

***o*-Phenylenediamine.** The *o*-phenylenediamine (Eastman Organic Chemicals) was recrystallized several times from diethyl ether in the presence of decolorizing charcoal, m.p. 102°C.

3,3′-Diaminobenzidine. The 3,3′-diaminobenzidine was provided by Koppers Company, Inc.; the commercial product was recrystallized twice from boiling methanol, sublimed at 0.1 mm. Hg and collected under nitrogen, m.p. 179–180°C.

ANAL. Calcd. for $C_{12}H_{14}N_4$: C, 67.29%; H, 6.54%; N, 26.17%. Found: C, 67.46%; H, 6.63%; N, 26.22%.

1,4,5,8-Tetraaminonaphthalene. The 1,4,5,8-tetraaminonaphthalene was obtained by reduction of 1,4,5,8-tetranitronaphthalene in the presence of palladium catalyst on charcoal, with hydrogen under a pressure of 50 psi;

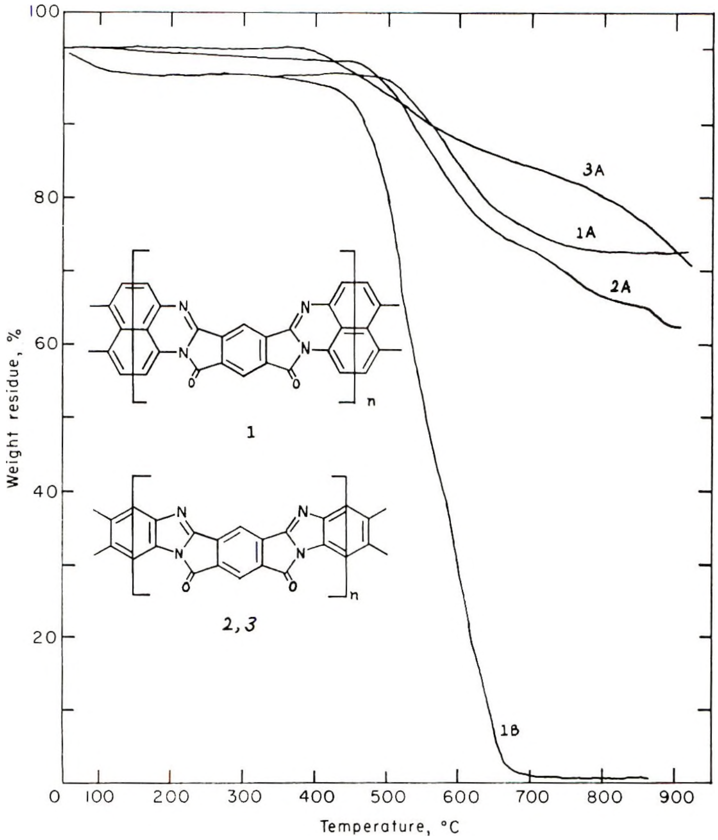


Fig. 8. Thermographic analysis ($\Delta T = 6°C./min.$) of (*1A*) polymer 1 synthesized by melt condensation under nitrogen; (*1B*) polymer synthesized by melt condensation in air (700 ml./min.); (*2A*) polymer synthesized by melt condensation under nitrogen; (*3A*) polymer synthesized in 116% polyphosphoric acid.

the unstable tetraamino compound was used in solution in diglyme (bis-2-methoxy ethyl ether, b.p. 160–163°C.).[26]

3,3′,4,4′-Tetraaminodiphenyl Ether. The 3,3′,4,4′-tetraaminodiphenyl ether was synthesized as previously described,[4] according to the following steps: treatment of 4,4′-diaminodiphenyl ether (oxydianiline, technical grade obtained from E. I. du Pont de Nemours and Company) with acetic anhydride to produce the 4,4′-diacetamidodiphenyl ether; nitration of the diacetyl derivative with acetyl nitrate, then hydrolysis with base to obtain 3,3′-dinitro-4,4′-diaminodiphenyl ether (m.p. 179–180°C.); and finally reduction of 3,3′-dinitro-4,4′-diaminodiphenyl ether with stannous chloride to give 3,3′,4,4′-tetraaminodiphenyl ether, m.p. 150–151°C.

ANAL. Calcd. for $C_{12}H_{14}N_4O$: C, 62.60%; H, 6.08%; N, 24.30%. Found: C, 62.58%; H, 6.08%; N, 24.08%.

1,2,4,5-Tetraaminobenzene. The 1,2,4,5-tetraaminobenzene tetrahydrochloride was prepared by modifying the procedure of Nietzki and

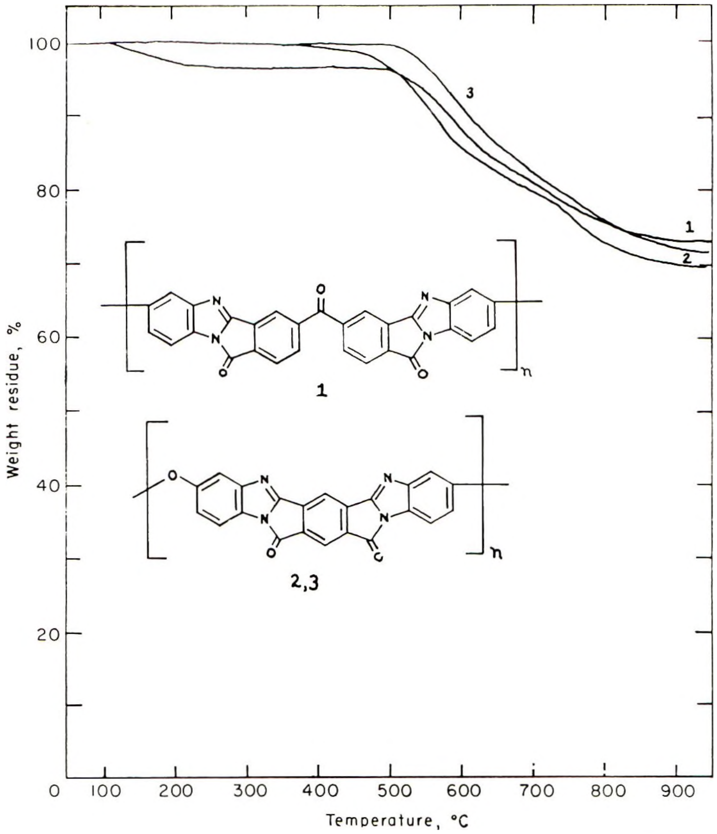


Fig. 9. Thermographic analysis ($\Delta T = 6$°C./min.) of (*1*) polymer 1 synthesized by melt condensation; (*2*) polymer synthesized by melt condensation; (*3*) polymer synthesized in 116% polyphosphoric acid.

Schedler[27] from *m*-dichlorobenzene by nitration, reaction with ammonia, and reduction. Since this amine is difficult to obtain, a more detailed description of its preparation is given in this part.

The amination was carried out under atmospheric pressure by heating dinitrodichlorobenzene with ammonium acetate at 150°C. in the presence of ammonia gas, following a procedure reported for the amination of monochlorodinitrobenzene;[28] but we obtained mostly the monoamino derivative by this procedure. In order to get a more complete reaction by avoiding the formation of a solid cake, we tried to run the amination in solutions in tetrahydrofuran, according to a procedure described for the amination of 1,5-difluoro-2,4-dinitrobenzene,[29] but the reaction temperature was too low in the case of the dichloro derivative and we recovered almost all of the starting material. The best results were obtained by carrying out the amination in the presence of a mixture of ammonium acetate and an inert, high-boiling solvent, such as nitrobenzene; the reaction was performed at 180°C. for 48 hr. in the presence of ammonia gas. By pouring the cooled reaction mixture into a controlled amount of methanol, it is possible to isolate pure dinitrodiaminobenzene (m.p. 309–310°C.) with 88% yield, from unreacted dinitrodichlorobenzene (2% yield, m.p. 102–103°C.) and from monoaminomonochlorodinitrobenzene (6% yield, m.p. 176–177°C.).

ANAL. Calcd. for $C_6H_6N_4O_4$: C, 36.40%; H, 3.00%; N, 28.30%; O, 32.30%. Found: C, 36.34%; H, 3.05%; N, 26.79%; O, 32.18%.

The reduction step of 1,5-dinitro-2,4-diaminobenzene was performed in concentrated hydrochloric acid in the presence of stannous chloride, but we observed that the tetraaminobenzene tetrahydrochloride contained some residual stannous salt, in spite of several recrystallizations. We tried to carry out the reduction in the presence of iron powder, but the yield was very low and again we observed the presence of some mineral salt in the tetrahydrochloride. Finally, the best results were obtained by catalytic reduction of dinitrodiaminobenzene in solution in diglyme at 50°C. in the presence of a palladium catalyst on charcoal with hydrogen under a pressure of 50 psi. Most of the tetraamino compound remains adsorbed on the palladium catalyst but can be recovered with 90% yield by pouring the reaction mixture under inert atmosphere into concentrated hydrochloric acid. The tetrahydrochloride was purified by dissolution in distilled water, filtration to separate carbon and palladium chloride, and precipitation in ice-cold concentrated hydrochloric acid.

ANAL. Calcd. for $C_6H_{14}N_4Cl_4$: C, 25.35%; H, 4.93%; N, 19.72%; Cl, 50.00%. Found: C, 25.31%; H, 5.07%; N, 19.05%; Cl, 48.36%.

The liberation of 1,2,4,5-tetraaminobenzene from the tetrahydrochloride was carried out by shaking under nitrogen a solution of the tetrahydrochloride in boiled oxygen-free water with an ice-cold 15% sodium hydroxide solution. The precipitate was filtered with suction under nitrogen, washed with ice-cold ethanol, and finally dried to constant weight at 50°C. at 0.1 mm. Hg pressure and sealed under nitrogen. The yield was about 70%, m.p. 274–276°C.

1,3-Dianilino-4,6-diaminobenzene. The diphenyl derivative was synthesized as reported in an earlier publication[2] from *m*-dichlorobenzene, by nitration, amination in the presence of aniline, and reduction with sodium sulfide nonahydrate. The overall yield was 25%, m.p. 210–211°C.

Model Compounds

1,2-Benzoylbenzimidazole and *o*-Phenylene Bibenzimidazole. Phthalic anhydride (1.85 g.) and *o*-phenylenediamine (1.35 g.) (molar ratio anhydride/amine = 1) were placed under nitrogen in a round-bottomed flask; the flask was progressively heated in a silicone oil bath to 140°C. (about 2°C./min.). The melt was then put under high vacuum and heating was continued for 1 hr. at 140°C. The cake was pulverized, dissolved in boiling acetic anhydride, and precipitated in water to give a yellow powder. The yield of 1,2-benzoylbenzimidazole was 44%, m.p. 211–212°C.

ANAL. Calcd. for $C_{14}H_8N_2O$: C, 76.36%; H, 3.64%; N, 12.73%; O, 7.27%. Found: C, 76.23%; H, 3.72%; N, 12.96%.

When the heating was stopped at 115°C., uncolored crystals soluble in hot alcohol were obtained with 32% yield. The compound is presumably the *N*(*o*-aminophenyl)phthalimide.

ANAL. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.60%; H, 4.20%; N, 11.76%; O, 13.44%. Found: C, 71.10%; H, 4.54%; N, 10.86%; O, 13.64%.

Finally, the flask containing the starting material was immersed in a preheated bath at 200°C. and when the melt was formed, the heating was continued for 2 hr. at 250°C. at 0.1 mm. Hg pressure. The reaction product was dissolved in dimethyl sulfoxide and precipitated in methanol to give a white powder, m.p. 445–450°C. The yield of *o*-phenylenebibenzimidazole was 49%.

ANAL. Calcd. for $C_{20}H_{14}N_4$: C, 77.42%; H, 4.51%; N, 18.07%. Found: C, 77.42%; H, 4.72%; N, 17.48%.

Further, we were able to isolate three different compounds from the same run; for example, 1.85 g. of phthalic anhydride and 2.70 g. of *o*-phenylenediamine (molar ratio anhydride/amine = 0.5) were gradually heated to 140°C. under nitrogen; when the melt was formed, high vacuum was applied to the flask. A partial sublimation was observed and heating of the residue was continued until 300°C. for 2 hr. The sublimate was poured into hot methanol; the soluble part was recrystallized to give about 1.5% yield of *N*(*o*-aminophenyl)phthalimide.

ANAL. Found: C, 69.83%; H, 4.75%; N, 10.72%.

The insoluble part in alcohol was recrystallized from boiling dimethyl sulfoxide to give 5% yield of 1,2-benzoylbenzimidazole.

ANAL. Found: C, 75.91%; H, 3.84%; N, 12.58%.

Finally, the residual cake was pulverized, dissolved in dimethylformamide and precipitated in a mixture of water–alcohol. The yield of *o*-phenylenebibenzimidazole was 44%.

ANAL. Found: C, 77.31%; H, 4.92%; N, 18.11%.

Pyromellitic Anhydride and *o*-Phenylenediamine. Pyromellitic anhydride (1.36 g.) *o*-phenylenediamine (1.35 g.) were gradually heated to 140°C. under nitrogen; when the melt was formed, heating was continued to 200°C. for 2 hr. under vacuum. The reaction product was purified by precipitation from a dimethyl sulfoxide solution. The yield was 62% of a yellow-green powder, softening at about 290°C. and not melting at 330°C.

The elemental analysis agrees with the expected 13*H*,15*H*-bisbenzimidazo[1,2-*a*:1′,2′-*a*′]benzo[1,2-*c*:5,4-*c*′]dipyrrole-13,15-dione structure.

ANAL. Calcd. for $C_{22}H_{10}N_4O_2$: C, 72.92%; H, 2.76%; N, 15.47%; O, 8.84%. Found: C, 72.60%; H, 3.11%; N, 14.70%, O, 9.59% (by difference).

Phthalic Anhydride and 1,2,4,5-Tetraaminobenzene. Phthalic anhydride (1.48 g.) and 0.69 g. of 1,2,4,5-tetraaminobenzene were gradually heated to 140°C. under nitrogen and then at 200°C. under high vacuum for 1 hr. The yellow-brown cake was dissolved in dimethyl sulfoxide and the solution precipitated in a mixture of water and alcohol; the yield was 51% of 12*H*,16*H*-diisoindolo[2,1-*a*:2′,1′-*a*′]benzo[1,2-*d*:5,4-*d*′]imidazole-12,-16-dione not melting at 300°C. The compound showed an isomer composition of the 13*H*,15*H*-bisbenzimidazo-[1,2-*a*:1′,2′-*a*′]benzo[1,2-c:5,-4-*c*′]dipyrrole-13,15-dione.

ANAL. Found: C, 73.07%; H, 3.24%; N, 15.11%; O, 8.66%.

Phthalic Anhydride and 3,3′-Diaminobenzidine. A 1.48-g. portion of phthalic anhydride and 2.14 g. of 3,3′-diaminobenzidine were gradually heated to 230°C. under nitrogen; the cake was reheated at 300°C. for 2 hr. under vacuum, and then dissolved in dimethyl sulfoxide and purified as previously reported. The yield of (7,7′-bi-11*H*-isoindolo[2,1-*a*]benzimidazole)-11,11′-dione was 73%; the compound does not melt at 300°C.

ANAL. Calcd. for $C_{28}H_{14}N_4O_2$: C, 76.72%; H, 3.20%; N, 12.78%; O, 7.30%. Found: C, 75.40%; H, 3.60%; N, 13.44%; O, 7.20%.

Phthalic Anhydride and 1,4,5,8-Tetraaminonaphthalene. To a solution of 0.94 g. of 1,4,5,8-tetraaminonaphthalene in 40 ml. of diglyme under nitrogen was added 1.48 g. phthalic anhydride. The reaction mixture was gradually heated to 180°C. and the solvent distilled; the residue was heated at 300°C. under vacuum for 2 hr. and then recrystallized from hot alcohol; the yield was 83% of isoindolo[2,1-*a*]isoindolo-[2′,1′:1,2]pyrimido-[4,5,6-*gh*]perimidine-13,18-dione not melting at 300°C.

ANAL. Calcd. for $C_{26}H_{12}N_4O_2$: C, 72.50%; H, 3.20%; N, 15.10%; O, 8.20%. Found: C, 73.06%; H, 3.83%; N, 13.03%; O, 10.86%.

Melt Polycondensations

General Procedure. The polymers were synthesized according to the experimental procedure previously described for polybenzimidazoles.[30] The apparatus was carefully purged with pure nitrogen by repeated evacuation and refilling. The flask containing the monomer components was then placed in a silicone oil bath and the bath was gradually heated to 220°C. (about 2°C./min.). When the melt was formed and the evolution of water observed, the flask was put under high vacuum and heating was continued at the particular temperature. The polymers were purified by dissolution in dimethyl sulfoxide, dimethylformamide, or concentrated sulfuric acid, and reprecipitation. The eventual insoluble part was separated by filtration or centrifugation.

Polymer from Pyromellitic Anhydride and 3,3′-Diaminobenzidine. A mixture of 1.30 g. of pyromellitic anhydride and 1.28 g. of 3,3′-diaminobenzidine was gradually heated under nitrogen to 220°C.; heating was continued for 2 hr. at 250°C. under high vacuum. The yield was 75% of soluble polymer, not melting at 350°C.; the inherent viscosity measured at 0.25% concentration in dimethyl sulfoxide at 30°C. was 0.45 and measured at 0.20% concentration in formic acid at the same temperature was 0.50. The composition agrees with a polymer of 13*H*,15*H*-bisbenzimidazo[1,2-*a*:1′,2′-*a*′]benzo[1,2-*c*:5,4-*c*′]dipyrrole-13,15-dione.

ANAL. Calcd. for $(C_{22}H_8N_4O_2)_n$: C, 73.33%; H, 2.22%; N, 15.55%; O, 8.88%. Found: C, 72.57%; H, 2.00%; N, 14.87%; O, 9.06%.

Polymer from Pyromellitic Anhydride and 3,3′,4,4′-Tetraaminodiphenyl Ether. A mixture of 1.64 g. of pyromellitic anhydride and 1.74 g. of 3,3′,4,4′-tetraaminodiphenyl ether was gradually heated under nitrogen to 220°C.; when the melt was formed, heating was continued at 320°C. under vacuum for 3 hr. The yield was 62% of soluble polymer not melting at 350°C. The inherent viscosity measured at 0.25% concentration in dimethyl sulfoxide was 0.44. The reaction product could be described as a polymer of 3,9-dihydroxy-13*H*,15*H*-bisbenzimidazole[1,2-*a*:1′,2′-*a*′]-benzo[1,2-*c*:5,4-*c*′]dipyrrole-13,15-dione.

ANAL. Calcd. for $(C_{22}H_8N_4O_3)_n$: C, 70.2%; H, 2.11%; N, 15.00%; O, 12.76%. Found: C, 70.31%; H, 2.04%; N, 14.91%; O, 12.24%.

From a mixture of 2.18 g. of pyromellitic anhydride and 1.15 g. of 3,3′,4,4′-tetraaminodiphenyl ether (molar ratio anhydride/amine = 2), the yield of soluble polymer was 85%; the inherent viscosity measured at 0.25% concentration in dimethyl sulfoxide was 0.38.

Polymer from 3,3′,4,4′-Benzophenonetetracarboxylic Dianhydride and 3,3′-Diaminobenzidine. A mixture of 0.85 g. of 3,3′-diaminobenzidine and 2.57 g. of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride was gradually heated at 220°C. under nitrogen, and then at 320°C. under high vacuum for 3 hr. The yield of soluble polymer was 55%; the inherent viscosity measured at 0.25% concentration in dimethyl sulfoxide was 0.17. The composition agrees with a polymer of 3,3′-carbonylbis[11*H*-isoindolo(2,1-*a*)benzimidazol-11-one].

ANAL. Calcd. for $(C_{29}H_{12}N_4O_3)_n$: C, 75.00%; H, 2.70%; N, 12.00%; O, 10.30%. Found: C, 74.82%; H, 2.94%; N, 11.77%; O, 10.40%.

Polymer from Pyromellitic Anhydride and 1,2,4,5-Tetraaminobenzene. A mixture of 0.58 g. of 1,2,4,5-tetraaminobenzene and 1.7 g. of pyromellitic anhydride was gradually heated at 220°C. under nitrogen and the melt was then reheated at 300°C. under high vacuum for 3 hr. The yield was 86% of ladder polymer mostly insoluble in the usual organic solvents; the inherent viscosity measured at 0.25% concentration in concentrated sulfuric acid was 0.30.

ANAL. Calcd. for $(C_{16}H_4N_4O_2)_n$: C, 67.60%; H, 1.40%; N, 19.72%; O, 11.27%. Found: C, 65.41%; H, 1.97%; N, 18.12%; O, 13.06%.

Polymer from Pyromellitic Anhydride and 1,3-Dianilino-4,6-diaminobenzene. A mixture of 0.86 g. of 1,3-dianilino-4,6-diaminobenzene and 1.75 g. of pyromellitic anhydride was gradually heated at 220°C. under nitrogen and then at 330°C. under vacuum for 2 hr. The yield was 65%

and the inherent viscosity measured at 0.25% concentration in dimethyl sulfoxide was 0.27. The elemental analysis showed the rings were not closed, and the polymer had a composition in agreement with the poly-1,3-dianilino-4,6-pyromellitimide structure.

ANAL. Calcd. for $(C_{20}H_{10}N_2O_2)_n$: C, 72.50%; H, 3.00%; N, 11.90%; O, 13.60%. Found: C, 73.71%; H, 3.32%; N, 12.12%; O, 11.30%.

Polymer from Pyromellitic Anhydride and 1,4,5,8-Tetraaminonaphthalene. A solution of 0.75 g. of 1,4,5,8-tetraaminonaphthalene in diglyme was added under nitrogen to 1.74 g. of pyromellitic anhydride and the solvent was evaporated. The residue was heated at 300°C. under vacuum for 2 hr. The yield was 60% and the inherent viscosity measured at 0.25% concentration in concentrated sulfuric acid was 0.41.

ANAL. Calcd. for $(C_{20}H_6N_4O_2)_n$: C, 71.85%; H, 1.80%; N, 16.75%; O, 9.58%. Found: C, 71.42%; H, 1.92%; N, 14.89%; O, 11.45%.

Polycondensations in Solution

Polycondensation in Melt Phenol

A mixture of 0.85 g. of 3,3′-diaminobenzidine, 0.87 g. of pyromellitic anhydride and 2 g. of phenol was heated under nitrogen at 180°C. for 2 hr. and then at 330°C. under high vacuum for 3 additional hr. The yield was 94% and the inherent viscosity measured at 0.25% concentration in concentrated sulfuric acid was 0.53, but the elemental analysis disagrees with the expected structure.

ANAL. Found: C, 56.16%; H, 3.31%; N, 10.61%; O, 25.11%.

Polycondensation in Pyridine

A solution of 0.85 g. of 3,3′-diaminobenzidine and 0.87 g. of pyromellitic anhydride in 50 ml. of pyridine was heated under nitrogen at reflux of pyridine (115°C.) for 70 hr. The gradual formation of a brown precipitate was observed. The cooled reaction mixture was filtered and the precipitate washed with diethyl ether. The yield was 90% and the inherent viscosity measured at 0.25% concentration in concentrated sulfuric acid was 0.65. The composition of the polymer showed a polyaminopyromellitimide structure.

ANAL. Calcd. for $(C_{22}H_{12}N_4O_4)_n$: C, 66.60%; H, 3.20%; N, 14.10%; O, 16.10%. Found: C, 66.49%; H, 3.50%; N, 14.21%; O, 15.97%.

The polyaminopyromellitimide was reheated at 300°C. under high vacuum for 2 hr. The inherent viscosity of the polymer at 0.25% concentration in concentrated sulfuric acid was 0.74 and then the composition agrees with the expected structure of the polymer of 13*H*,15*H*-bisbenzimidazo[1,2-*a*:1′,2′-*a*′]benzo[1,2-*c*:5,4-*c*′]dipyrrole-13,15-dione.

ANAL. Found: C, 72.44%; H, 3.08%; N, 14.39%; O, 8.98%.

Polycondensation in a Mixture of Diglyme and 10% Volume of Pyridine

The same reaction carried out at reflux (about 240°C.) of a mixture of 100 ml. diglyme and 10 ml. pyridine yielded 94% of polymer; the inherent viscosity measured at 0.25% concentration in concentrated sulfuric acid was 0.71.

Anal. Found: C, 71.05%; H, 3.20%; N, 14.54%; O, 11.63%.

Polycondensation in Dimethylacetamide.

A solution of 0.85 g. of 3,3′-diaminobenzidine and 0.87 g. of pyromellitic anhydride in 60 ml. dimethylacetamide was heated at 160°C. under nitrogen for 3 hr.; an abundant precipitate was formed after about 15 min. of heating, but the isolated polymer was still soluble in concentrated sulfuric acid; the inherent viscosity was 0.94.

Anal. Found: C, 66.78%; H, 4.04%; N, 16.46%; O, 13.02%.

The complete ring closure was obtained by reheating the polymer at 300°C. under vacuum.

Polycondensation in Polyphosphoric Acid

General Procedure. In a three-necked flask equipped with N_2 inlet and outlet, a stirrer, and an apparatus to introduce the reagents under inert atmosphere, the 116% polyphosphoric acid was heated at 200°C. for 2 hr. and then cooled under nitrogen; when the temperature was maintained at 140°C., the tetraamino tetrahydrochloride compound was gradually added under a thin stream of nitrogen, and hydrogen chloride was eliminated. When the tetraamino compound was completely dissolved and the evolution of hydrochloric acid ended, the dianhydride was added and the reaction mixture heated under nitrogen at 200°C. Usually, after 30 min. of heating, the reaction mixture became very viscous and the formation of a rubbery solid was observed.

The concentrations of starting materials in polyphosphoric acid ranged from 0.6 to 3.0% by weight. The polymer was isolated by pouring the hot reaction mixture into water; the solution was centrifuged and the precipitate washed thoroughly with water; the solid was then dipped in dilute ammonium carbonate solution overnight. We preferred the treatment with ammonium carbonate rather than the reported procedure[25] with sodium bicarbonate solution because we observed that the polymers treated with the sodium salt contained a great amount of inorganic residue.

Finally the polymer was washed again with water and methanol and then dried at 50°C. and 0.1 mm. Hg pressure.

Polymer from Pyromellitic Anhydride and 3,3′-Diaminobenzidine Tetrahydrochloride. A 1.55-g. portion of 3,3′-diaminobenzidine tetrahydrochloride was heated at 140°C. in solution in 120 g. of 116% polyphosphoric acid. Then 0.95 g. of pyromellitic anhydride was added under nitrogen, and heating was continued at 200°C. for 2 hr. The yield of the polymer of 13*H*,15*H*-bisbenzimidazo[1,2-*a*:1′,2′-*a*′]benzo[1,2-*c*:5,4-*c*′]dipyrrole-13,-15-dione was 82% and the intrinsic viscosity measured in dimethyl sulfoxide was 1.25.

ANAL. Found: C, 72.07%; H, 2.79%; N, 15.33%; O, 9.61%.

The same reaction performed at 200°C. for 40 hr. yielded 98% of polymer, mostly insoluble in the usual organic solvents.

Polymer from Pyromellitic Anhydride and 3,3′,4,4′-Tetraaminodiphenyl Ether Tetrahydrochloride. 3,3′,4,4′-tetraaminodiphenyl ether tetrahydrochloride (2.25 g.) was dissolved at 140°C. in 120 g. of 116% polyphosphoric acid; 1.31 g. of pyromellitic anhydride was added under nitrogen to the solution and heating was continued at 200°C. for 3 hr. The yield of the polymer of 3,9-dihydroxy-13*H*,15*H*-bisbenzimidazo[1,2-*a*:1′,2′-*a*′]benzo-[1,2-*c*:5,4-*c*′]-dipyrrole-13,15-dione was 90%, and the intrinsic viscosity measured in concentrated sulfuric acid was 1.26.

ANAL. Found: C, 69.65%; H, 2.65%; N, 14.84%; O, 11.75%.

Polymer from Pyromellitic Anhydride and 1,2,4,5-Tetraaminobenzene Tetrahydrochloride. A 0.85-g. portion of 1,2,4,5-tetraaminobenzene tetrahydrochloride was dissolved in 120 g. of 116% polyphosphoric acid; 0.65 g. of pyromellitic anhydride was added under nitrogen to the solution and the reaction mixture was heated at 200°C. for 2 hr. The yield of ladder-type polymer was 86%, and the intrinsic viscosity measured in concentrated sulfuric acid was 1.10.

ANAL. Found: C, 66.93%; H, 1.52%; N, 19.23%; O, 11.54%.

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References

1. Vogel, H., and C. S. Marvel, *J. Polymer Sci.*, **50**, 511 (1961).
2. Vogel, H., and C. S. Marvel, *J. Polymer Sci.*, **A1**, 1531 (1963).
3. Plummer, L., and C. S. Marvel, *J. Polymer Sci.*, **A2**, 2559 (1964).
4. Foster, R. T., and C. S. Marvel, *J. Polymer Sci.*, **A3**, 417 (1965).
5. E. I. du Pont de Nemours and Co., U. S. Pat. 2,710,853 (June 14, 1955); Brit. Pat. 762,152 (November 12, 1956).
6. E. I. du Pont de Nemours and Co., Australian Pat. Appl. 58,424 (1960).
7. E. I. du Pont de Nemours and Co., Brit. Pat. 903,271-2 (August 15, 1962).

8. Amborski, L. E., *Ind. Eng. Chem. Prod. Res. Develop.*, **2,** 189 (1963).

9. Amborski, L. E., paper presented at 144th Meeting, American Chemical Society, Los Angeles, April 1963; *Polymer Preprints*, **4,** No. 1, 175 (1963).

10. Bower, G. M., and L. W. Frost, paper presented at 144th Meeting, American Chemical Society, Los Angeles, April 1963; *Polymer Preprint* , **4,** No. 1, 357 (1963).

11. Bower, G. M., and L. W. Frost, *J. Polymer Sci.*, **A1,** 3135 (1963).

12. Nishizaki, S., and A. Fukami, *Kogyo Kagaku Zasshi*, **66,** 382 (1963).

13. Hofmann, K., *Imidazole and Its Derivatives, I*, Interscience, New York (1953).

14. Arient, J., and J. Marhan, *Collection Czechoslov. Chem. Communs.*, **25,** 124 (1960); *ibid.*, **26,** 98 (1961).

15. Compagnie Francaise des Matieres Colorantes, Fr. Pat. 1,090,115 (March 28, 1955).

16. Anderlini, F., *Gazz. Chim. Ital.*, **24,** 145 (1894).

17. Meyer, R., and J. Maier, *Ann.*, **327,** 41 (1903).

18. Thiele, J., and K. G. Falk, *Ann.*, **347,** 116 (1906).

19. Fischer, O., and O. Jonas, *Ber.*, **27,** 2780 (1894).

20. Chakravarti, G. C., *Quart. J. Indian Chem. Soc.*, **1,** 19 (1924).

21. Bistrzycki, A., and A. Lecco, *Helv. Chim. Acta*, **4,** 425 (1921).

22. Walther, R., and T. Von Pulawski, *J. Prakt. Chem.*, **59,** 249 (1899).

23. Lieb, H., *Monatsh. Chem.*, **39,** 873 (1918).

24. Porai-Koshits, B. A., and M. M. Antoshul'skaya, *Zh. Obshch. Khim.*, **13,** 339 (1943).

25. Iwakura, Y., K. Uno, and Y. Imai, *J. Polymer Sci.*, **A2,** 2605 (1964).

26. Dawans, F., B. Reichel, and C. S. Marvel, *J. Polymer Sci.*, **A2,** 5005 (1964).

27. Nietzki, R., and A. Schedler, *Ber.*, **30,** 1666 (1893).

28. *Organic Syntheses*, Coll. Vol. II, Wiley, New York, 1961, p. 221.

29. Knobloch, U., and H. N. Niedrich, *Ber.*, **91,** 2562 (1958).

30. Cabaness, R., and F. E. Neumann, *Macromolecular Synthesis*, in press.

Résumé

Des hétéropolymères aromatiques ont été synthétisés à partir de tétraamines aromatiques et de dianhydrides; certains polymères ont une structure du type "échelle." Les propriétés et la stabilité thermique de ces polymères ont été déterminées à l'aide de composés modèles. Des polymères ayant diverses unités aromatiques dans la chaine ont été préparés à partir d'anhydride pyromellitique, de dianhydride 3,3′,4,4′-benzophenonetetracarboxylique et 3,3′-diaminobenzidine, éther 3,3′,4,4′-tetraamino-diphénylique, naphthalène-1,4,5,8-tetraaminé et benzène 1,2,4,5-tetraaminé. Les polycondensations ont été effectuées à l'état fondu et en solution (dans le phénol fondu, la pyridine, le diméthylformamide et l'acide polyphosphorique 116%). Les viscosités inhérentes d'un certain nombre de polymères synthétisés par condensation à l'état fondu, étaient comprises environ entre 0.2 et 0.7; les polymères à poids moléculaires les plus élevés ont été obtenus par polycondensation en solution dans l'acide polyphosphorique 116%; dans ce cas, les viscosités intrinsèques étaient comprises entre 1.1 et 1.8. La plupart des polymères ne fondent pas à 350°C. et sont solubles dans les solvants organiques ordinaries, toutefois les polymères du type "échelle" n'étaient solubles que dans l'acide sulfurique concentré.

Zusammenfassung

Aromatische Heteropolymere wurden aus aromatischen Tetraminen und Dianhydriden synthetisiert; einige der Polymeren besassen eine "Leiter"-Struktur. Eigenschaften und thermische Stabilität des Polymeren wurden untersucht. An Modellverbindungen wurden die Versuchsbedingungen emittelt, welche die Imidazolstruktur liefern. Polymere mit gemischten aromatischen Einheiten in der Kette wurden aus Pyromellitsäureanhydrid, 3,3′,4,4′-Benzophenontetracarbonsäuredianhydrid und 3,3′-Diaminobenzidin,

3,3′,4,4′-Tetraaminodiphenyläther, 1,4,5,8-Tetraaminonaphthalin und 1,2,4,5-Tetraaminobenzol dargestellt. Die Polykondensation wurde in der Schmelze und in Lösung (in geschmolzenem Phenol, Pyridin, Dimethylacetamin, 116% Polyphosphorsäure) ausgeführt. Die Viskositätszahlen einiger durch Schmelzkondensation synthetisierter Polymerer lagen im Bereich von etwa 0,2 bis 0,7; höhere Polymere wurden durch Ausführung der Polykondensation in 116% iger Polyphosphorsäurelösuug erhalten; in diesem Falle lag die Viskositätszahl im Bereich von 1,1 bis 1,8. Die meisten Polymeren schmelzen bei 350°C. nicht und sind in den üblichen organischen Lösungsmitteln löslich; die Polymeren mit "Leiter"-Struktur waren jedoch nur in konzentrierter Schwefelsäure löslich.

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Glass Temperatures of Some Acrylic Polymers

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Synopsis

Dilatometrically determined glass transition temperatures and thermal expansion coefficients of 47 different polymers, most of them acrylics, are reported. The experimental values are discussed in terms of the effect of side-chain flexibility, bulkiness, and polarity on the glass transition temperature and are compared with the isofree-volume theory of the glass transition temperature, as recently set forth by Simha and Boyer. Possible reasons for the poor agreement with this theoretical treatment are discussed. The effect of equilibrium time at each temperature during a dilatometric run was determined for one sample, polystyrene, which was measured both in the usual way and with long equilibrium times (over a week) at each temperature, yielding glass temperatures of 97 and 89°C. for the usual and for the long equilibrium times, respectively.

INTRODUCTION

There have recently been a number of publications on the nature of the glass transition and on the possibility of predicting the glass transition temperature of a polymer from various other types of data on the polymer. Simha and Boyer,[1] Bueche,[2] and Kanig[3] have worked on free volume theories of the glass transition, while Gibbs and DiMarzio[4] have used a thermodynamic treatment in which the glass temperature turned out to be a second-order transition.

In the treatment of Simha and Boyer,[1] the prediction is made that

$$(\alpha_L - \alpha_G)T_g = K \tag{1}$$

where α_L and α_G are the volume expansion coefficients of the polymer in the rubbery state and in the glassy state, respectively, T_g is the glass transition temperature in degrees Kelvin, and K is a constant which was empirically found to be equal to 0.113. In an empirical treatment of the glass temperature by Hayes,[5] on the other hand, T_g is related to the molar cohesive energy density of the polymer and to the rotation of the atoms and side chains in the polymer. Only the treatment of Simha and Boyer[1] allows direct comparison of glass temperature data of homopolymers with theory.

The investigation of the applicability of any of these theoretical treatments has been hampered by lack of enough of the necessary experimental

TABLE I
Synthesis of Polymers for Glass Temperature Measurements

	Polymerization conditions				
No.	T, °C.	M, wt.-%	Solvent	Conversion, %	Comments on monomer purity and characterization
1	50	25	Benzene	7	Twice distilled
2	44.1	43	Methyl propionate	30	b.p. 53°C./95 mm.
3	60	48	Benzene	27	GLC (1 peak); 23–30 min. induction
4	60	50	Toluene	33	GLC and IR (>99% pure); b.p. 64.7–65.3°C./35 mm.
5	60	48	Toluene	46	IR (pure); b.p. 58–58.5°C./32 mm.
6	60	50	Benzene	43	Monomer-Polymer Corp.; alkali-washed and distilled; b.p. 75°C./1 mm); kinetically pure
7	60	20	DMF	78	Celanese Corp.; alkali-washed and distilled
8	60	55	Benzene	33	n_D^{20} = 1.4952; Br_2 No. = 8.07 (8.13 calc'd.); 5 min. induction
9	60	50	Toluene	32	n_D^{20} = 1.5206; Br_2 No. = 12.18 (12.32 calc'd.); Sap. No. = 346.4 (346.0 calc'd.); kinetically pure.
10	60	50	Toluene	19	n_D^{20} = 1.5210; Br_2 No. = 12.63 (13.5 calc'd.); Sap. No. = 382.5 (379 calc'd.); Acid No. = 0
11	60	40	DMF	71	Br_2 No. = 10.48 (10.68 calc'd.)
12	60	20	Acetone	64	m.p. 68.5–69.0°C.; Br_2 No. = 11.6 (11.5 calc'd.)
13	60	50	Acetone	75	Same as No. 12
14	65	14	Benzene	50	IR (good)
15	64.5–65	32	Benzene	60	IR (good)
16	64–66	20	Benzene	70	m.p. 81°C.; % Cl = 55.38 (55.33 calc'd.); sp. gr. = 1.01 (23°C.).
17	60	33	Acetone	68	n_D^{20} = 1.5302; Sap. No. = 304 (314.4 calc'd.); Acid No. negative
18	60	45	Benzene	—	n_D^{20} = 1.5589; % N_2 = 7.2 (7.3 calc'd.); Acid No. = 0.9; b.p. 110–114°C./1.1 mm.
19	60	—	Bulk	60	n_D^{20} = 1.5271; Br_2 No. = 9.7 (9.7 calc'd.); Acid No. = 0.57
20	60	50	Benzene	>50	n_D^{20} = 1.5297; Br_2 No. = 9.81 (9.7 calc'd.)
21	60	16	Benzene	76	m.p. 82.0–82.5°C.; Br_2 No. = 9.8 (9.7 calc'd.)
22	60	—	Bulk	22	n_D^{20} = 1.5190; Br_2 No. = 9.5 (9.1 calc'd.); Acid No. negative
23	60	59	Benzene	30	n_D^{20} = 1.5178; Br_2 No. = 9.27 (9.1 calc'd.); Acid No. = 0.6
24	60	40	Acetone	74	m.p. 45–46°C.; Br_2 No. = 9.4 (9.1 calc'd.)
25	60	44	Benzene	5	n_D^{20} = 1.5138; Br_2 No. = 8.8 (8.1 calc'd.)
26	44.1	22	Methyl propionate	20	Distilled; GLC (2 very small extra peaks); Slight accelerating impurity.

TABLE I (*continued*)

	Polymerization conditions				
No.	T, °C.	M, wt.-%	Solvent	Conversion, %	Comments on monomer purity and characterization
27	60	—	Bulk	8	Sap. No. (94–100% pure); Br_2 No. 98–99% pure); sp. gr. = 0.879–0.882 (25°C.)
28	60	—	Bulk	6	GLC (1 peak); kinetically pure
29	44.1	—	Bulk	9	Prepolymerized (44.1°C.); b.p. 24°C./3 mm.
30	60	33	Chloroform	—	Monomer-Polymer Corp.; twice distilled; b.p. 94–95°C./2.5 mm.; n_D^{20} = 1.5084
31	60	36	Acetone	33	Celanese Corp.; alkali-washed; distilled
32	60	—	Bulk	9	b.p. 97°C./11 mm.; prepolymerized; slight accelerating impurity
33	60	62	Acetonitrile	30	n_D^{25} = 1.4902; b.p. 116–118.5°C./0.1 mm.; slight induction period
34	−20	—	Bulk	—	Distilled; polymerized in freezer
35	44.1	61	Benzene	—	b.p. 53°C./14 mm.
36	60	—	Bulk	—	b.p. 65°C./5 mm.; n_D^{20} = 1.4750; % Br_2 = 41.4 (41.5 calc'd.); Sap No. = 580 (581 calc'd.)
37	60	—	Bulk	4	Distilled; GLC (cont'd. some methacrylic acid and ethylene glycol dimethacrylate).
38	60	—	Bulk	5	Monomer-Polymer Corp.; alkali-washed; distilled; b.p. 89°C./3 mm.; GLC (1 peak); kinetically pure
39	—	—	Bulk	High	n_D^{20} = 1.5146; Sap. No. = 353 (346 calc'd.); Acid No. = 0
40	60	25	Benzene	34	Br_2 No. = 10.67 (10.68 calc'd.); % N_2 = 7.40 (7.48 calc'd.); slightly retarded rate
41	60	28	Acetone	27	Sharp m.p.
42	60	42	Acetone	53	m.p. 60–61°C.
43	60	70	Benzene[a]	66	m.p. 35.5–36.5°C.
44	60	—	Bulk	62	—
45	50	—	Emulsion	50	Br_2 No. = 15.63 (15.60 calc'd.); Sap. No. = 439 (437 calc'd.); Acid No. = 0
46	−20	—	Bulk	High	Contained inhibitor; polymerized in freezer
47	−20	—	Bulk	—	Monomer-Polymer Corp.; polymerized in freezer
48	60	28	Methanol	—	b.p. 79–82°C./17 mm.; n_D^{20} = 1.4740; Br_2 No. (97% pure); GLC and IR (high purity)
49	90	—	Bulk	88	—
50	—	—	—	—	—
51	60	—	Bulk	11	—

[a] Acetone got into solution when ampule containing monomer cracked; final solution contained 66 wt.-% acetone.

TABLE II
Glass Temperature Data

No.	Polymer of	T_g, °C.	$\alpha_G \times 10^4$	$\alpha_L \times 10^4$	Dilatometric data range, °C. From	To	$\bar{M}_n \times 10^{-3}$
	Acrylates						
1	Isopropyl	−8	2.4	6.6	−30	40	—
2	Isopropyl	−5	2.8	6.9	−35	80	121
3	*sec*-Butyl	−17	2.9	6.5	−35	90	250
4	3-Pentyl	−6	3.4	6.1	−40	100	114
5	Neopentyl	22	2.1 ± 0.3	6.8	−35	90	97.7
6	2-Phenylethyl	−3	1.6	5.2	−30	130	570
7	2-Cyanoethyl	4	1.5	4.3	−30	100	59.8
8	3-Chloro-2,2-bis(chloromethyl)propyl	46	1.5	3.9	−30	160	1020
9	Benzyl	6	1.5	4.1	−40	100	256
10	Phenyl	55	1.6	5.1	0	140	300
11	*p*-Cyanobenzyl	44	1.4	4.7	−30	170	92.8
12	*p*-Cyanophenyl	94	1.4	4.6	0	170	71
13	*p*-Cyanophenyl	90	1.4	4.6	−30	170	277
14	*o*-Chlorophenyl	53	1.4	4.2	−20	150	—
15	2,4-Dichlorophenyl	60	1.1	3.7	−20	170	115
16[a]	Pentachlorophenyl	145	0.94	1.9	−30	200	—
	Rerun	147	0.85	3.0	−30	200	—
17	*p*-Methoxyphenyl	48	1.7	4.7	−35	150	310
18	*m*-Dimethylaminophenyl	47	1.6	5.0	−35	130	46.6
19	*o*-Carbomethoxyphenyl	46	1.5	4.5	−30	110	—
20	*m*-Carbomethoxyphenyl	38	1.3	4.5	−35	130	184
21[b]	*p*-Carbomethoxyphenyl	67	1.8	3.7	−20	140	—
22	*o*-Carboethoxyphenyl	30	1.8	4.7	−30	150	246
23	*m*-Carboethoxyphenyl	24	1.7	4.9	−35	130	700
24[c]	*p*-Carboethoxyphenyl	37	1.8	4.4	−35	165	197
25	*p*-Carbobutoxyphenyl	13	2.9	5.5	−35	130	688
	Methacrylates						
26	Isopropyl	78	2.1	6.7	−35	160	153
27	Isobutyl	48	2.6	6.0	0	130	912
	Rerun	48	2.3	6.4	−30	130	912
28	*sec*-Butyl	60 ± 2	3.5	6.6	5	150	160
29	*tert*-Butyl	107	2.8	7.2	30	150	250
30	2-Phenylethyl	26	1.8	5.1	−30	130	—

data in the literature. Part of the purpose of this paper is to provide a number of such data on well-characterized homopolymer samples. The data which will be discussed below were obtained over a number of years, originally to elucidate the relative effects of side-chain bulkiness and polarity on the glass transition temperatures of polyacrylates and polymethacrylates.

EXPERIMENTAL

Monomers

Although some of the monomers were commercial products which had to be purified in various ways, most of the monomers used in this work were

TABLE II (*continued*)

No.	Polymer of	T_g, °C.	$\alpha_G \times 10^4$	$\alpha_L \times 10^4$	Dilatometric data range, °C.		$\bar{M}_n \times 10^{-3}$
					From	To	
31	2-Cyanoethyl	91	1.0	3.1	30	190	985
32	*tert*-Butylaminoethyl	33	2.0	5.7	−30	110	—
33	2-Ethylsulfinylethyl	25	1.5	4.6	−30	110	54
34	Dimethylaminoethyl	19	2.7	6.0	−30	170	—
35	Dimethylaminoethyl	17	3.7	5.8	−30	100	242
36	2-Bromoethyl	52	0.99	3.2	−30	150	431
37	2-Hydroxyethyl	55	1.02	2.6	−30	140	—
38	Benzyl	54	1.7	5.0	0	170	400
39	Phenyl	110	1.6	5.3	30	160	816
40	*p*-Cyanophenyl	155	1.1	4.1	30	200	848
41	*p*-Carbomethoxyphenyl	106 ± 3	1.7	4.6 ± 0.3	−25	180	129
42	*p*-Cyanomethylphenyl	128 ± 3	1.8	4.8	30	195	700
	Miscellaneous polymers						
43	*p*-Carbomethoxystyrene	131	2.2	5.4	30	180	146
44[d]	*p*-Cyanostyrene	120	2.2	4.6	30	160	—
	Rerun	120	2.1	4.1	30	160	—
45	Ethyl α-ethylacrylate	27	1.5	5.7	−30	80	40
46	Dimethyl methylene-malonate	66	0.8	3.3	−30	160	—
47	*N*,*N*-Dimethylacrylamide	89	1.6	4.6	30	170	77
48	*N*,*N*-Dimethylacrylamide	110	1.7	4.6	−30	140	64
49	Dimethyl-2-methylene-5-methyl adipate	34	2.0	5.6	−30	140	123
50	Dimethyl-2-methylene-5-methyl adipate	28	1.9	6.0	−40	120	100 ± 20
51	Styrene	97	2.2	5.8	30	160	159
	Rerun (1 week equilibrium times)	89	1.9	6.0	160	30	159

[a] First run: a slight second transition was observed at 35 ± 10°C.; below this temperature range, $\alpha_G = 0.69 \times 10^{-4}$. No second transition was observed in the rerun.

[b] X-ray diffraction pattern indicated crystallinity. Curvature of the volume–temperature plot from 140 to 190°C. may indicate m.p. >190°C.

[c] Dilatometric m.p. = 151°C.; $\alpha_L = 6.00 \times 10^{-4}$ above m.p.

[d] This sample was insoluble in all solvents and was therefore considered to be cross-linked.

synthesized by individuals at the Rohm & Haas Company. For the purpose of this paper, the methods of monomer synthesis are much less relevant than the final purity of each monomer. For this reason, the comments on monomer purity and characterization in Table I do not include synthesis data. In the case of monomers prepared at the Rohm & Haas Company, either in commercial quantities or in the laboratory, Table I includes most of the available purification and characterization data. The sources of all monomers which did not originate at Rohm & Haas are stated.

The numbers assigned to the monomers in Table I are identified in Table II. All the monomers were polymerized by free-radical methods, except for a few that polymerized thermally while they were being stored in a freezer. The initiator was azobisisobutyronitrile in all cases, except the sample prepared by emulsion polymerization. The polymerization conditions given in Table I are those which may turn out to be important in an evaluation of the glass temperature data. The polymerization temperature may affect tacticity, while the type and amount of solvent present during the polymerization and the percent conversion of monomer to polymer may affect the incorporation of impurities, the molecular weight distribution, and the degree of branching of the resulting polymer. The comments on monomer purity and characterization in Table I include different sorts and amounts of information for each monomer for various reasons. Unfamiliar monomers were usually, but not always, characterized more extensively than familiar ones. Also, monomers that were known to contain impurities were often treated more extensively than those which were more pure. The sorts of information given in the table include distillation data, boiling points with pressure given in millimeters of mercury, melting points, gas chromatography data (GLC), comments about the infrared spectra (IR), refractive indices, bromine number (Br_2 No.) in centigrams of bromine per gram of monomer, saponification number (Sap. No.) and acid number (Acid No.) in milligrams of KOH per gram of monomer, and some comment on the kinetics of the polymerization where these were observed. A monomer which polymerized with no induction period and without retardation or acceleration was considered kinetically pure.

Number-Average Molecular Weights

These were obtained in the modified Schulz-Wagner osmometers discussed by Fox and co-workers.[6]

Dilatometric Measurements

Mercury was used as the containing liquid in the dilatometers in all cases. Samples weighing 0.5–1.0 g. were measured with the use of capillaries of 1–2 mm. diameter.

Each sample was degassed under vacuum at that temperature at which the polymer just started to flow, i.e., at which any sharp edges in the polymer film became blurred, usually at least 30°C. above the glass transition temperature, before mercury was added to the dilatometer. Each sample was then equilibrated at the same temperature in the presence of the mercury before any measurements were made. Measurements were started at low temperatures and ended at high temperature in almost all cases. Measurements were made at 5–10°C. intervals; a sample was held at any single temperature until the volume of sample plus mercury had remained constant for at least ten minutes. The only exception to these rules was polystyrene (No. 51, rerun, in Table II). In this case, measurements were started at the highest temperature, and each temperature was held until the volume of sample plus mercury had remained constant for at least one week.

RESULTS

Table II identifies all the polymers which were measured. It also shows the experimentally determined glass transition temperature for each sample, the volume expansion coefficient below and above the glass temperature, the temperature intervals in which dilatometric data were obtained, and the number-average molecular weights of most of the samples. In a few cases, the same polymer is identified by two numbers in Table II; this indicates that two entirely different samples which were prepared differently (see Table I) were measured. In those cases in which the same sample was measured several times, the second measurement is identified as a rerun.

We have identified the temperature interval in which dilatometric data were obtained in order to show the interval in which no other transitions were observed. For those few cases in which the volume–temperature plots did not consist of two essentially straight lines which intersected at the glass temperature, a note has been made at the end of the table. Most of the glass temperatures could be determined to within ±1°C.; where this was impossible, the limits of error are given.

Number-average molecular weights were obtained in most cases because of the well-known molecular weight dependence of T_g. We used 40,000 as the absolute lower limit of tolerable $\bar{M}_n$; most of the number-average molecular weights cited were, however, above 70,000. These limiting values were decided upon after consideration of the following literature data. Fox and Flory,[7] working with polystyrene fractions, found that T_g stops increasing at a value of $\bar{M}_n$ between 2.2×10^4 and 8.5×10^4, while Ueberreiter and Kanig,[8] working with fractions of the same polymer, found that the limiting T_g was reached at $\bar{M}_n = 4.1 \times 10^4$. They also found that the glass temperatures of mixtures of these fractions depended only on the $\bar{M}_n$ of the mixtures, i.e., not on the molecular weight distributions. In the case of poly(methyl methacrylate), Beevers and White[9] found that the limiting T_g was reached when $\bar{M}_n$ was between 3.8×10^4 and 7.2×10^4. For polyacrylonitrile, they[10] found the limiting T_g between $\bar{M}_n = 1.8 \times 10^4$ and 6.6×10^4.

DISCUSSION

A fairly extensive literature search revealed previously published glass transition temperature data for only five of the polymers shown in Table II. Only transition temperatures obtained by dilatometry or by refractive index–temperature measurements were considered strictly comparable to our data in Table II. Transition temperatures obtained by other methods, such as dynamic mechanical measurements, dielectric measurements, and differential thermal analysis were not considered comparable because of

TABLE III
Glass Temperature Data from the Literature

	No. (Table II)	T_g, °C.	
Polymer of		Dilatometric	Refractometric
Acrylates			
Methyl	—	8[11]	0[12]
Ethyl	—	−24[11]	−23,[12] −29[12]
n-Propyl	—	—	−44,[12] −51.5[12]
Isopropyl	1, 2	−3 to −6[11]	—
n-Butyl	—	—	−70[12]
sec-Butyl	3	−22[11]	—
tert-Butyl	—	43[11]	—
Methacrylates			
Methyl	—	104,[11] 105[13]	72[14]
Ethyl	—	66,[11] 65[13]	47[14]
n-Propyl	—	35[13]	33[14]
Isopropyl	26	81[11]	—
n-Butyl	—	19,[11] 20,[13] 8[15]	17,[14] 27[16]
Isobutyl	27	53[11]	—
Miscellaneous			
Styrene	51	100,[7] 88,[17] 83,[18] 92[19]	91[19]
p-Carbomethoxystyrene	43	133[20]	—

differences in the time scale of the measurements and possible difficulties in interpretation. Table III shows the comparable literature data for the simplest polyacrylates and polymethacrylates as well as those for the five polymers mentioned above.

The literature data, where available, agree quite well with the data in the present work. To be honest, however, it is necessary to note that one of us (J. A. Shetter) is the author of reference 11, with which a number of the comparisons are made.

Other workers have tested the equilibrium time dependence of the glass transition temperature of polystyrene. Alfrey, Goldfinger, and Mark[18] found a glass transition of 75°C. using a cooling rate of 0.2°C./min.; when they used longer equilibrium times at each temperature, the glass transition was observed at 83°C. Later, Millane and McLaren[21] and Spencer and Boyer[22] published data which they said indicated that the glass transition temperature disappeared when very long equilibrium times were used. Both sets of data can be questioned. Millane and McLaren do not mention the length of their long equilibrium times; furthermore, their data seem to show a lower density for the "equilibrium" sample than for the sample which was run more quickly. This is the exact opposite of any reasonable theoretical predictions and of the experimental data in the present work and in the work of Alfrey et al.[18] and of Kovacs.[23] The data of Spencer and Boyer, on the other hand, are quite scattered and do indicate a glass transition in the usual range, even at their long equilibrium times (24 hr.), which are much shorter than the equilibrium times used in the present work (1 week). Since we found a change of only 8°C. in the observed glass transition temperature when the equilibrium time was changed from 10 min. to 1 week, we feel that a glass transition temperature would be observed in polystyrene no matter what equilibrium times, within the humanly observable range, are used.

The data in Tables II and III can be used to make some general remarks about the variation of glass transition temperatures in different polymer series as the side-chain bulkiness, flexibility, and polarity varies. For example, polymers of ethyl acrylate, ethyl methacrylate, and ethyl α-ethylacrylate, with glass temperatures of -24, 66, and 27°C., respectively, form an interesting series. In the series, the substituent directly on one of the polymer backbone carbons changes from —H to —CH_3 to —CH_2CH_3. The polymer with the —CH_3 substituent has the highest glass temperature, while the —C_2H_5 group introduces the most bulk but also the most flexible group directly next to the polymer backbone. Of the three groups, the —CH_3 group is the only one that introduces bulk without flexibility directly next to the polymer backbone. The same sort of behavior can be observed in many other polymer series.

The glass transition temperatures of homologous series such as the poly(n-alkyl acrylates) and the poly(n-alkyl methacrylates) generally decrease as the length of the side chain increases. The longer side chain, in each case, has both greater bulk and greater flexibility.

The data in Table II indicate that a similar decrease in glass temperature occurs when a bulky group such as a phenyl group is moved farther away from the polymer backbone. The glass temperatures in the series poly(phenyl acrylate), poly(benzyl acrylate), poly(2-phenylethyl acrylate) are 55, 6, and -3°C. In the same methacrylate series the glass temperatures are 110, 54, and 26°C. In both series, the decrease in the glass transition temperature is greater going from the phenyl to the benzyl ester than it is going from the benzyl to the 2-phenylethyl ester, i.e., the bulky phenyl group appears to have the greatest effect on the glass transition temperature when it is closest to the polymer backbone.

Qualitatively, glass temperatures of isomers increase as the bulkiness of side chains increases, or, alternatively, as the flexibility of the side chains decreases. This is easiest to see in the butyl methacrylate series, in which the glass temperatures increase from 19 to 48 to 60 to 107°C. going from the n-butyl to the isobutyl to the *sec*-butyl to the *tert*-butyl isomer.

These discussions of side-chain bulkiness near the polymer backbone and of side-chain flexibility all imply that the glass transition temperature of a polymer depends mostly on intrachain interactions of some sort. There is a strong implication that the glass temperature is most affected by the ease with which the polymer backbone and the side-chains can move. However, there are data in Table II that indicate that other factors also influence glass temperatures.

Two sets of substituted polyphenyl acrylates, which differ only in the position of the substituent were measured. The *ortho*-, *meta*-, and *para*-substituted carbomethoxyphenyl acrylate polymers with glass temperatures of 46, 38, and 67°C., respectively, and the *ortho*-, *meta*-, and *para*-substituted carboethoxyphenyl acrylate polymers with glass temperatures of 30, 24, and 37°C., respectively, show the same trend. The polymer with the *ortho*-substituted side chain has the bulkiest group near the backbone, and the glass temperatures of the *ortho*-substituted polymers are higher than those of the *meta*-substituted polymers, as expected. In both cases, however, the *para*-substituted polymers have the highest glass transition temperatures, even though the *para*-substituted side chains have the least bulk near the polymer backbones. The substituents in the *para*-position, however, are in the best location for interference with the motion of neighboring molecules. There is strong possibility that interchain interactions have affected the glass transition in these cases. If these strong interchain interactions really exist, they could affect the dimensions of these polymers in bulk, making them different from the unperturbed values in solution. The change of the polymer dimensions with temperature in bulk polymer would be quite different from that of the unperturbed dimensions in solution.

Interchain interactions are also implied by all the data on cyano-substituted polyacrylates and polymethacrylates. All the substituted 2-ethyl methacrylate polymers have glass temperatures lower than that of poly(ethyl methacrylate) except poly(2-cyanoethyl methacrylate). Some of the other substituents are much bulkier than the —CN group; therefore, it seems likely that the large dipole moment of the —CN is the cause of the interactions which affect the glass temperature. Unusually high glass temperatures were also found for poly(*p*-cyanophenyl acrylate), poly(*p*-cyanobenzyl acrylate), poly(*p*-cyanophenyl methacrylate), and poly(*p*-cyanomethylphenyl methacrylate). Poly(2-hydroxyethyl methacrylate), on the other hand, in which one might expect contributions from hydrogen bonding, had a glass transition temperature of 55°C., lower than that of poly(ethyl methacrylate).

In most cases in which a polymer sample was run more than once, or in which different preparations of the same polymer were run, the results, as shown in Table II, agreed very nicely. In the case of the two samples of poly(*N*,*N*-dimethylacrylamide), samples 47 and 48, however, the samples had glass temperatures which were 21°C. apart. There are two possible explanations for this: (*1*) the 80°C. difference in polymerization temperature (see Table I) which may have affected polymer tacticity, or (*2*) the great difference in monomer purity. The monomer used to prepare sample 48 was very pure, while that used to prepare sample 47 was of unknown, therefore, possibly, low purity.

Enough data are given in Table II to allow comparison with the Simha-Boyer[1] free volume treatment of the glass transition temperature, i.e., eq. (1). Figure 1 shows plots of $(\alpha_L - \alpha_G)$ versus T_g of all our samples. The curve drawn on the figure is eq. (1), 0.113 being used as the value of K. It can be seen that the data of the polyacrylates fall mostly below this curve, while the data of the polymethacrylates and the miscellaneous poly-

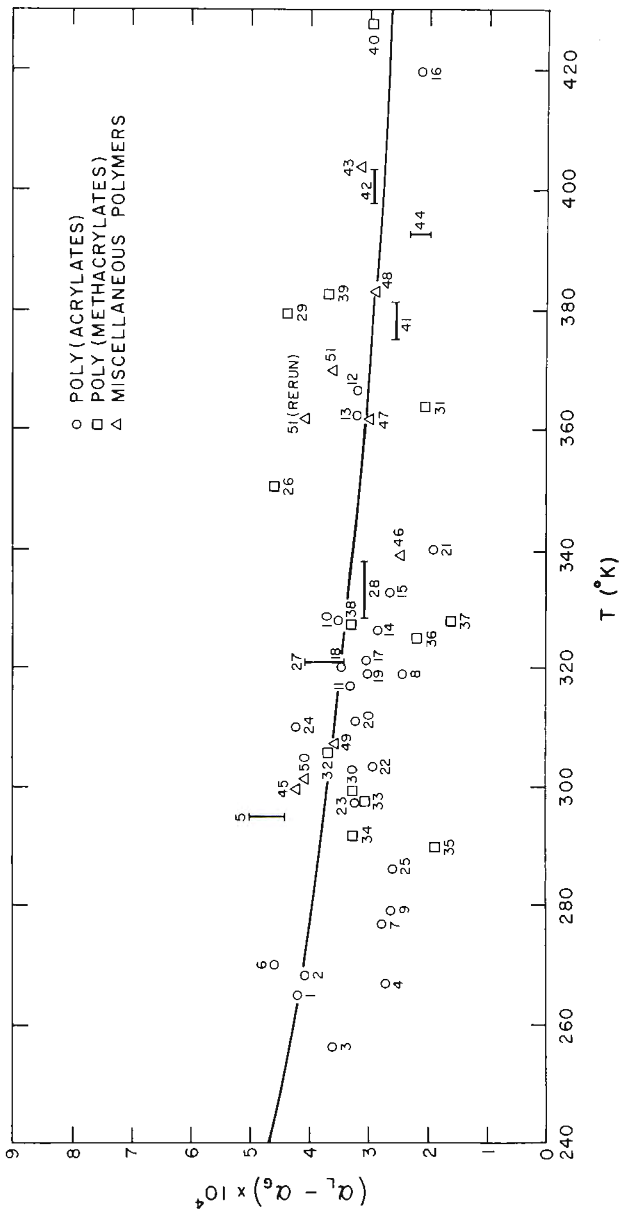
○ POLY (ACRYLATES)
□ POLY (METHACRYLATES)
△ MISCELLANEOUS POLYMERS
51 (RERUN)
$(\alpha_L - \alpha_G) \times 10^4$
T (°K)
0
1
2
3
4
5
6
7
8
9
240
260
280
300
320
340
360
380
400
420

Figure 1.

mers fall above, as well as below the curve. According to Simha and Boyer,[1] deviations below the line indicate the existence of transitions below the glass temperature. In the cases cited by Simha and Boyer, the poly(*n*-alkyl methacrylates), these low temperature transitions created some free volume below the glass transition temperature, thus raising α_G above the usual values. In the case of our polymers, however, α_G of most of the samples whose data fall below the theoretical curve is well below 2×10^{-4}. We can find no special criteria for the samples that fall either above or below the curve.

There are two major possible reasons for the disagreement of our data with the theoretical treatment of Simha and Boyer.[1] One ever-present possibility concerns the data, which may, for one reason or another, not be in a form in which they can be compared with the theory. First, there is the problem of the equilibrium time dependence of both the glass transition temperature and the values of the volume expansion coefficients. There is not enough experimental evidence at hand for us to say very much about this problem, except to note that both of our values for polystyrene fall above the curve in Figure 1, the data from the longer equilibrium times falling farther from the curve. Then, data from two samples of the same polymer may or may not fall in exactly the same relationship to the line. The two samples of poly(isopropyl acrylate), poly(*p*-cyanophenyl acrylate), and poly-*N*,*N*-dimethylacrylamide, that were run all fall directly on the curve. Although both samples of poly(dimethylaminoethyl methacrylate) fall below the curve, one falls very much lower than the other, and, in the case of poly(dimethyl-2-methylene-5-adipate), one sample falls on the curve and one falls slightly above. Furthermore, when a single sample was run twice for the same equilibrium time, although the glass temperature was reproducible, the volume expansion coefficients varied somewhat. The data on the reruns of the three samples which were run twice (see Table II), may or may not be closer to the curve than the original run, depending on the sample. These data merely indicate that the polymer volume expansion coefficients depend somewhat on sample history, not necessarily in the same manner for all polymers. We make these remarks in order to show how much caution must be exercised when making a comparison of values of polymer volume expansion coefficients with theory. Glass transition temperatures, although dependent on equilibrium times, seem to be less dependent on sample history.

The second possible reason for the discrepancy between theory and experiment concerns inadequacies in the isofree-volume treatment of glass transition temperatures. Simha and Boyer explained the fact that the data for hevea rubber fell below their curve by suggesting that hevea needs less free volume than other polymers at T_g. Continuing this argument, Figure 1 indicates that a number of different polymers need less free volume at T_g, but that some polymers need more.

Our results indicate that the isofree-volume approach to the glass transition temperature is at best a first approximation to the true state of affairs.

Some other type of theoretical treatment, which takes into account the effect of equilibrium times on both glass temperature and expansion coefficients, the greater effect of sample history on expansion coefficients than on glass temperatures, and the possibility of intermolecular interactions, will probably have to be devised.

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References

1. Simha, R., and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).
2. Bueche, F., *J. Chem. Phys.*, **36**, 2940 (1962).
3. Kanig, G., *Kolloid-Z.*, **190**, 1 (1963).
4. Gibbs, J. H., and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
5. Hayes, R. A., *J. Appl. Polymer Sci.*, **5**, 318 (1961).
6. Fox, T. G, J. B. Kinsinger, H. F. Mason, and E. M. Schuele, *Polymer*, **3**, 71 (1962).
7. Fox, T. G, and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).
8. Ueberreiter, K., and G. Kanig, *J. Colloid Sci.*, **7**, 569 (1962).
9. Beevers, R. B., and E. F. White, *Trans. Faraday Soc.*, **56**, 744 (1960).
10. Beevers, R. B., and E. F. White, *Trans. Faraday Soc.*, **56**, 1529 (1960).
11. Shetter, J. A., *J. Polymer Sci.*, **B1**, 209 (1963).
12. Wiley, R. H., and G. M. Brauer, *J. Polymer Sci.*, **3**, 647 (1948).
13. Rogers, S. S., and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
14. Wiley, R. H., and G. M. Brauer, *J. Polymer Sci.*, **3**, 455 (1948).
15. Bueche, F., *J. Appl. Phys.*, **26**, 738 (1955).
16. Yin, T. P., and J. D. Ferry, *J. Colloid Sci.*, **16**, 166 (1961).
17. Kolb, H. J., and E. F. Izard, *J. Appl. Phys.*, **20**, 564 (1946).
18. Alfrey, T., G. Goldfinger, and H. Mark, *J. Appl. Phys.*, **14**, 700 (1943).
19. Illers, K., *Z. Elektrochem.*, **65**, 679 (1961).
20. Kolesnikov, G. S., and T. A. Soboleva, *Izv. Akad. Nauk SSSR*, **7**, 760 (1958).
21. Millane, J. J., and S. M. McLaren, *J. Appl. Chem.*, **2**, 554 (1952).
22. Spencer, R. S., and R. F. Boyer, *J. Appl. Phys.*, **17**, 398 (1946).
23. Kovacs, A. J., *J. Polymer Sci.*, **30**, 131 (1958).

Résumé

On donne les températures de transition vitreuse déterminées par dilatométrie et les coefficients de dilatation thermique de quarante différents polymères, dont la plupart sont des polymères acryliques. On discute les résultats expérimentaux du point de vue de l'influence de la flexibilité de la chaîne latérale, de l'encombrement stérique et de la polarité sur la température de transition vitreuse et on les compare avec la théorie du volume libre égal à la température de transition vitreuse, proposée récemment par Simha et Boyer. On discute les raisons probables du mauvais accord avec cette théorie. L'influence du temps d'équilibre pour chaque température pendant les mesures dilatométriques à été determinée pour un seul échantillon, le polystyrène. Les mesures ont été effectuées de facon habituelle et pendant de longues durées d'équilibre à chaque température (plus d'une semaine), ce qui donne des températures de transition vitreuse de 97° et 89°C pour les durées d'équilibre ordinaires et longues respectivement.

Zusammenfassung

Dilatometrisch bestimmte Glasumwandlungstemperaturen und thermische Ausdehnungskoeffizienten von 47 verschiedenen Polymeren, die meisten davon Acrylpolymere, werden mitgeteilt. Die experimentellen Werte werden in Bezug auf den Einfluss der Seitenkettenfexibilität, -raumerfüllung und -polari-tät auf die Glasumwandlungstemperatur diskutiert und mit der Iso-freien- Volumstheorie der Glasumwandlungstemperatur, wie sie kürzlich von Simha und Boyere ntwickelt wurde, verglichen. Mögliche Gründe für die schlechte Übereinstimmung mit dieser theoretischen Behandlung werden diskutiert. Der Einfluss der Gleichgewichtsdauer bei jeder Temperatur während einer dilatometrischen Messung wurde an einer Probe, Polystyrol, bestimmt, welche sowohl in der gewöhnlichen Weise als auch mit langer (eine Woche) Gleichgewichtsdauer bei jeder Temperatur gemessen wurde, und dabei Glastemperaturen von 97° bzw. 89°C für die übliche bzw. die längere Gleichgewichtsdauer lieferte.

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Divinyl Copolymerization Initiated by High Intensity, Low Energy Electrons

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Synopsis

Solutions of unsaturated esters in styrene were copolymerized by 0.04 M.e.v. electrons at dose rates of 0.44–85.8 Mrad/min. Disappearance of each monomer and gel fractions were measured as a function of dose rate. Rates noted under these conditions of high linear energy transfer exhibited linear dependence on intensity, followed by a region independent of intensity. The data suggest that polymerization occurs in discrete volume elements, and that chain growth is initiated by hot radicals. For 65% ester solutions, the polymerization rate of the bulk sample, $d\alpha_t/dt$, is given by $d\alpha_t/dt = \{(k_p{}^{*2}/k_t)[M_2{}^\circ]\}V$, where $k_p{}^*$ is an activated propagation rate constant tenfold greater than that for more conventional polymerizations, k_t is the termination rate constant, $[M_2{}^\circ]$ is the starting ester concentration, and V, proportional to the radiation intensity, is the volume fraction of the sample occupied by the reacting elements. The volume of the element in which polymerization is occurring, estimated from experimental data and using reasonable values for the life of a growing radical, is 3×10^9 A.^{3}, a value consistent with what is known of electron impact processes in liquids.

This paper summarizes the effects of 0.04 M.e.v. electrons over a 200-fold range in dose rates (upwards of 0.4 Mrad/min.) on the kinetics of and product structure resulting from the copolymerization of styrene with the polyvinyl ester [$\sim$OC—CH = CH—COO—CH$_2$—CH(CH$_3$)—OOC—C$_6$H$_5$—COO—CH$_2$—CH(CH$_3$)—O$\sim$]$_n$. Rates of disappearance of each monomer, gel fractions, and equilibrium weight swelling ratios of the gel were measured.

The results obtained under the present rather unusual conditions of inordinately high initiating radical concentrations and high linear energy transfer (i.e., where a greater fraction of the energy of the incident electron is lost at each collision compared with commonly used 1 M.e.v. electrons) suggest that polymerization occurs in discrete volume elements swept out by the impinging particles, and that chain growth is initiated within these elements by "hot" or energetic radicals. Qualitative kinetic data (mainly that rates are directly proportional to intensity) indicative only of thermal reactions in volume elements are reported for 1 M.e.v.-polymerized tetraethylene glycol dimethacrylate[1] and vinyl stearate.[2,3] In general, however, such behavior is in contrast to most radical polymerizations induced by 1 M.e.v. photons or particles. Thus, for styrene and methyl methacrylate so polymerized,[4] both reaction rate and product molecular weight depend on the (radiation intensity)$^{0.5}$ up to about 1000 rad/min., while at somewhat higher dose rates, the dependence on intensity decreases; from these homogeneous kinetics, it is concluded that under the conditions studied, the distribution of ionized and excited molecules produced about the track of the incident radiation was random.

EXPERIMENTAL

Monomers

Starting ester, synthesized from reagent grade maleic anhydride, phthalic anhydride, and propylene glycol, was characterized as reported:[5] M_n, 890; double bond concentration, 1.5 per molecule. Styrene was redistilled *in vacuo* before use. The molar ratio of styrene to ester unsaturation in the polymerizing mixture was 3.

Irradiations

About 0.02 cc. of degassed solutions containing 65% ester in redistilled styrene was transferred, in a nitrogen atmosphere, to a Perkin-Elmer attenuated total reflectance cell, fitted with a silver chloride hemicylinder prism. The liquid was contained with 0.0018 in. aluminum foil, which is transparent to the 0.3 M.e.v. incident electrons used (from a High Voltage Engineering ICT-powered accelerator). Radiation polymerization was effected in the cell, through a 0.5 cm.^{2} window cut in the metal backing plate. Since infrared analyses, and therefore the kinetics, describe the layer of the film farthest from the electron beam, blue cellophane dosimetry was measured in this region. Incident electrons striking the upper surface of the assembly are attenuated to an estimated[4] 0.040 M.e.v. by the time their effects are "seen" by the infrared; the penetration both of the 0.04 M.e.v. electrons[5] and the infrared beam is about 2×10^5 A. Rates ranged from 0.44 Mrad/min. to 85.8 Mrad/min. A dose of 1 Mrad corresponds to the absorption of 63×10^{18} e.v./g. of polymer.

The sealed cell then was driven through an aluminum tunnel, in the top of which was a slit; exposures of 0.01–100 sec. were obtainable with this shutter arrangement. All runs were 25 ± 1°C.

Kinetics and Gel Fractions

Infrared analyses of ester (6.10 μ) and styrene peaks (6.15 μ) were performed immediately after exposure. A Perkin-Elmer Model 237 grating spectrophotometer was used, in conjunction with a Leeds and Northrup Speedomax H recorder to permit fivefold scale expansion of the appropriate portion of the transmission range. The average absorbance of the 6.35 μ reference peak of the ester spectrum obtained from at least three runs of the starting mixture was taken as an internal standard. Three or more sets of spectra were obtained at a given dose rate and exposure, and monomer disappearance measured from those sets in which the absorbance of the reference 6.35 μ peak was within 6% of the "standard" value. Sufficient material for gel fraction measurements was obtained by irradiating degassed 0.005 in. films of ester–styrene solutions in an aluminum cell fitted with a 0.005 in. Teflon spacer and a 0.0018 in. aluminum window to contain the sample; irradiations were carried out in the shutter assembly described for kinetic runs.

Details of gel fraction determinations, experimental evidence for the absence of a dark or "post-irradiation" reaction, and for the absence of soluble copolymer (from which it is concluded that copolymer entering the gel phase is of short chain lengths) are published.[5] Equilibrium weight swelling ratios of the gel fraction were measured in benzene.

Precision

Reproducibility of infrared-derived measurements of ester concentrations is estimated to be ±10%; of styrene concentrations, ±5%. Gel fractions are reproducible to ±5%; dosimetry to ±10%.

Table I summarizes the experimentally measured parameters upon which the discussion is based.

RESULTS AND DISCUSSION

Copolymerization of the divinyl system has been effected by low intensity γ-rays (8.3×10^{-3} Mrad/min.), and a reasonable picture of the reaction reported.[5] It is assumed this description also obtains for the electron-initiated reaction: Radicals initiate network copolymerization independently at each ester double bond; gelation occurs at about 1% unsaturation conversion, at which stage the system is comprised of a gel, highly swollen with the mixture of monomers, in which are incorporated pendant vinyl groups; growing copolymer radicals attain only short chain lengths before adding to gel, as propagation and gel formation continue. Chain termination is bimolecular, but cannot occur between two gel radicals because of their large size. While polymerization occurs in highly viscous or even rigid media, diffusion control of the propagation and assumed termination reactions is not noted, probably because of the high diffusivity of the short primary chains formed (kinetic chain length of 15).

Gel Composition

In the present electron-induced polymerization, the rates at which styrene and ester unsaturation, separately, disappear are given in Figure 1, from which it is seen that each component enters the gel at a constant rate and at a ratio of styrene to ester unsaturation of 3.6 over the entire electron dose rate range studied. Such linearity is not predicted from monomer reactivities estimated from the more dilute ester solutions,[5] which predicts a ratio of about 1.5 at these conversions. Molecular models indicate that both configurations are attainable, but the one with only a

TABLE I
Copolymerization of 65% Ester–Styrene Solutions Initiated by 0.04 M.e.v. Electrons at 25°C.

	Infrared absorbance			Rate of conversion, min.$^{-1}$		
Time t, min.	Ester unsat. (610 μ)	Styrene, (615 μ)	Dose rate, Mrad/min.	Styrene $d\alpha_1/dt$	Ester $d\alpha_2/dt$	Overall $d\alpha/dt$
0.00	0.043	0.101	0.44	0.202	0.180	0.197
0.68	0.041	0.081				
1.61	0.023	0.069				
2.51	0.025	0.050				
3.40	0.018	0.012				
0.00	0.043	0.119	1.32	0.216	0.201	0.213
0.22	0.038	0.117				
0.66	0.037	0.103				
1.09	0.033	0.089				
1.52	0.022	0.063				
1.96	0.017	0.024				
0.00	0.042	0.088	4.32	0.970	0.516	0.872
0.07	0.038	0.081				
0.15	0.039	0.078				
0.22	0.039	0.065				
0.29	0.037	0.062				
0.37	0.034	0.061				
0.44	0.035	0.054				
0.52	0.031	0.044				
0.66	0.017	0.017				
0.00	0.041	0.110	10.74	1.33	1.82	1.43
0.04	0.037	0.109				
0.11	0.033	0.093				
0.18	0.030	0.085				
0.25	0.022	0.071				
0.00	0.034	0.114	21.48	2.69	2.99	2.75
0.02	0.034	0.108				
0.04	0.027	0.101				
0.06	0.030	0.095				
0.07	0.024	0.092				
0.09	0.022	0.087				

single styrene unit between ester molecules is sterically hindered. Since the glass transition temperature of the gel[1] is about 100°C., the observed ratio may result from the fact that the rapid electron-initiated reaction (several seconds or less required for polymerization) occurs in the glass where limited segmental mobility prohibits sufficient relaxation for incorporation of fewer than 3.6 styrene molecules between chains. The equilibrium weight swelling ratio in benzene of the gel fraction, 2–3, is independent of conversion and radiation intensity over the entire range studied; this observation is in accord with a "sterically controlled" copolymerization.

TABLE I (*continued*)

	Infrared absorbance			Rate of conversion, min.$^{-1}$		
Time t, min.	Ester unsat. (610 μ)	Styrene, (615 μ)	Dose rate, Mrad/min.	Styrene $d\alpha_1/dt$	Ester $d\alpha_2/dt$	Overall $d\alpha/dt$
0.13	0.025	0.074				
0.17	0.019	0.066				
0.20	0.013	0.052				
0.24	0.009	0.027				
0.00	0.044	0.106	32.16	2.65	2.87	2.70
0.01	0.037	0.097				
0.02	0.035	0.096				
0.03	0.031	0.095				
0.05	0.031	0.089				
0.07	0.030	0.085				
0.11	0.027	0.077				
0.14	0.024	0.065				
0.18	0.021	0.045				
0.21	0.014	0.027				
0.00	0.038	0.084	42.90	2.31	2.71	2.40
0.01	0.035	0.079				
0.02	0.036	0.074				
0.04	0.033	0.066				
0.05	0.027	0.068				
0.09	0.028	0.068				
0.12	0.024	0.060				
0.20	0.019	0.044				
0.27	0.011	0.018				
0.00	0.044	0.117	85.80	2.27	2.93	2.41
0.04	0.038	0.108				
0.07	0.031	0.098				
0.11	0.030	0.085				
0.15	0.023	0.082				
0.18	0.026	0.067				
0.22	0.015	0.062				
0.26	0.012	0.036				

Rates

The rate at which overall unsaturation disappears, to a first approximation is linearly dependent on intensity (actually proportional to $I^{0.85}$) over the range of about 1–20 Mrad/min., then becomes intensity-independent up to 100 Mrad/min. (Fig. 2). It is postulated that polymerization, which occurs in about 0.1 sec., takes place in discrete "volume elements" swept out by the 0.04 M.e.v. electron; as intensity increases, overlap of these elements and interaction of radical species of neighboring elements result in a rate decrease.

The dose rate dependence reflects the fact that radicals within a track are produced simultaneously, and polymerization is rapid enough so that reaction among reactive fragments within a volume element occurs before a neighboring track is formed. The point at which overlap of the reacting

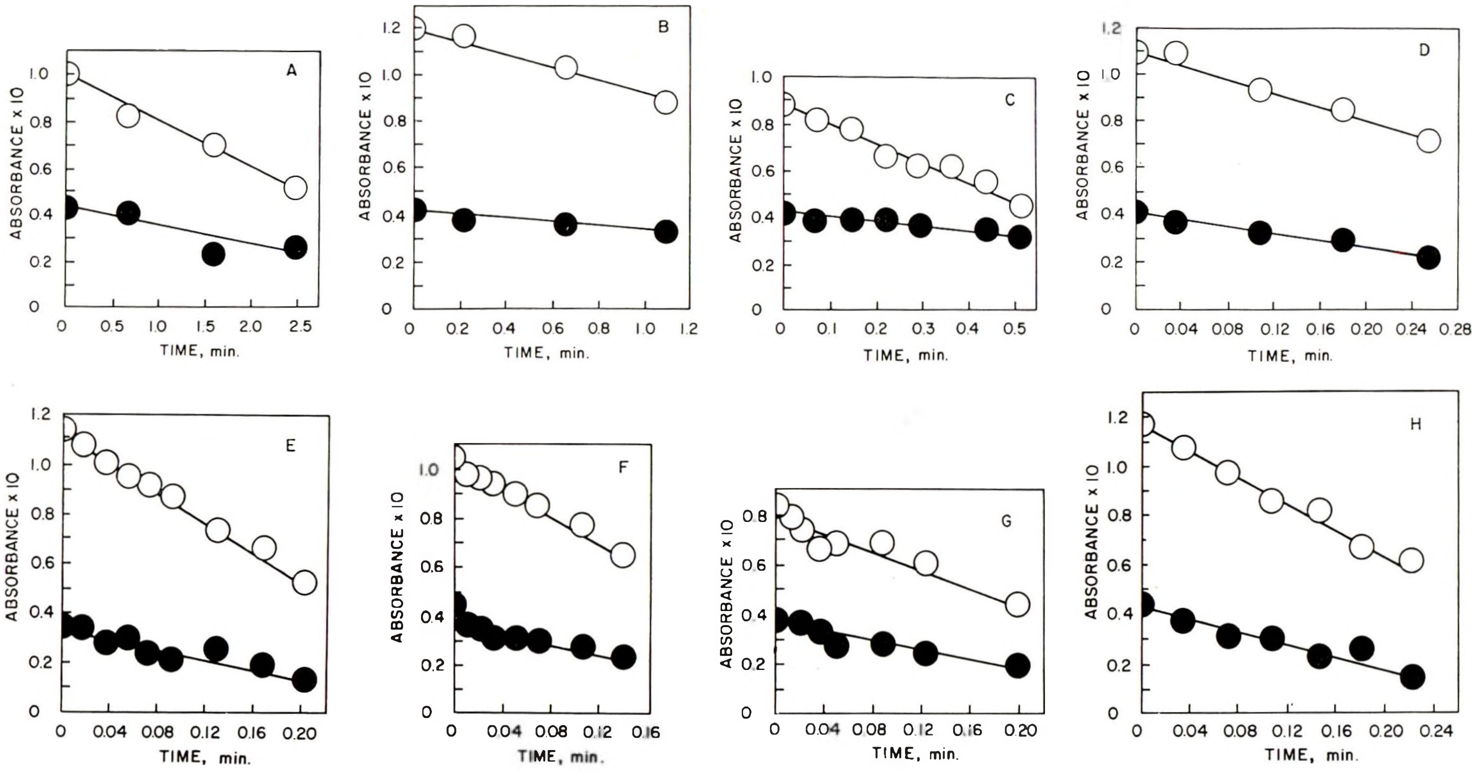

Fig. 1. Polymerization rates from infrared absorbances for (●) ester unsaturation and (○) styrene at various dose rates: (*A*) 0.44 Mrad/min.; (*B*) 1.32 Mrad/min.; (*C*) 4.32 Mrad/min.; (*D*) 10.74 Mrad/min.; (*E*) 21.48 Mrad/min.; (*F*) 32.16 Mrad/min.; (*G*) 42.90 Mrad/min.; (*H*) 85.80 Mrad/min.

elements, or saturation, is noted (Fig. 2) appears to mark the onset of a steady state, but it is predicted that after the polymerizing regions have overlapped appreciably, new damaging effects, such as chain crosslinking or degradation will become evident.

From these rate–intensity data, and with the help of several seemingly reasonable assumptions about electron radiation effects in liquids, the reaction rates within the volume elements and their size are estimated, as described below.

Polymerization rates within this volume element are 100-fold more rapid than predicted from the published γ-ray kinetics[5] or, indeed, by any conventional scheme using reasonable values for the kinetic constants. Thus, use of a high initiation rate constant is precluded by the energetics of the system, since G (initiating radical) of over 100 would be required; the hundredfold decrease demanded in the termination rate constant appears unreasonable; and the energy of the electron is dissipated so rapidly (to room temperature in about 10^{-11} sec.) within the proposed volume elements, that high average propagation rate constants due to local heating cannot be evoked. It is most convenient to assume that chain initiation occurs by an energetic radical before it loses its excess energy, i.e., a hot radical. For such initially formed hot radicals, the rate constant for the propagation reaction, k_p (activated), is given by the pre-exponential factor only; e.g., for styrene,[7] k_p (activated) $= 1.3 \times 10^9$ l./mole min., rather than the value of about 6×10^3 reported for the "normal" reaction. Furthermore, since uniquely low chain lengths are noted for this copolymerization, dissipation of the excess energy after a single initiation step (and a hot radical would not be expected to maintain its energy for times greater than a single collision) still would be reflected in the overall kinetics. Interaction of radiation-produced highly energetic species with neutral hydrocarbon molecules of low molecular weight is indicated for some liquid phase radiolyses: Bond

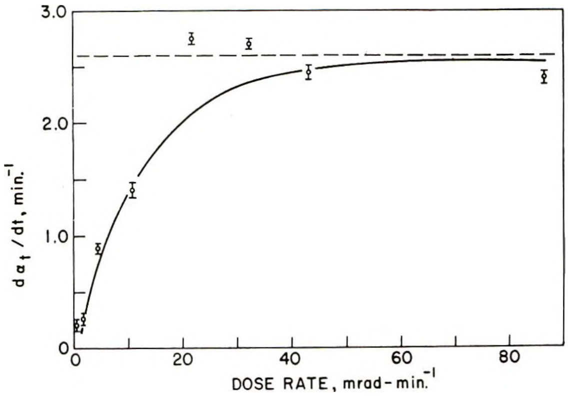

Fig. 2. Symbols (O) indicate measured dependence of overall polymerization rate on radiation intensity; (——) plot of eq. (3); (--) rate when the volume elements overlap.

formation leading to dimers via attack of radicals with energies much in excess of thermal energies has been postulated.[8–11]

If an "activated" propagation rate constant k_p^* is taken, the rate within each proposed polymerizing element can be described, assuming the kinetics reported for the γ-initiated copolymerization of this divinyl system. When the measured overall polymerization rate becomes independent of intensity (Fig. 2), the volume elements within which polymerization is occurring are at the point of overlap, so now the reaction most closely approaches a homogeneous process; consequently, it appears reasonable to use the bulk data to derive information about rates within the discrete volume elements: Thus, the concentration of radicals in the sol and gel phases, separately, in the element is approximated by[5]

$$d[\mathrm{S}\cdot]/dt = k_iI(1-g) - k_t\,[\mathrm{S}\cdot]\,(2[\mathrm{S}\cdot] + [\mathrm{G}\cdot]) - k_p^*\,[\mathrm{S}\cdot][M_2] = 0$$

and

$$d[\mathrm{G}\cdot]/dt = k_iI(g) - k_t\,[\mathrm{S}\cdot][\mathrm{G}\cdot] + k_p^*\,[\mathrm{S}\cdot][M_2] = 0$$

where [S.] is the concentration of soluble radicals at time t (in mole/l.); k_i is the initiation rate constant (in mole/l.-Mrad); I is the electron dose rate (in. Mrad/min.); $k_iI = k_1$ of the previous paper;[5] g is the gel fraction; $(1-g)$ is the sol fraction $= S$; k_t is the termination rate constant (in l./mole-min.); [G.] is the concentration of radicals in the gel phase (in mole/l.); k_p^* is the hot propagation rate constant (in l./mole-min.); $[M_2]$ is the overall concentration of ester double bonds at time t (in mole/l.). The rate at which overall unsaturation disappears within the volume element then is given by

$$\frac{d\alpha}{dt} = \frac{k_p^{*2}}{2k_t}\left\{\frac{[M_2](1-\alpha)}{(1-2g)} + \sqrt{\left[\frac{[M_2](1-\alpha)}{(1-2g)}\right]^2 + \frac{2k_iIk_t(1-\alpha)^2}{k_p^{*2}(1-2g)}}\right\} \qquad (1)$$

where α is the fraction of initial unsaturation that has reacted.

Experimental data preclude use of the conventional copolymerization composition scheme to obtain the required relation between $[\mathrm{M}_2]$ and α. This information, however, can be measured from Figure 2: $[\mathrm{M}_2] = [\mathrm{M}_2^0] - (\alpha/4.6)([\mathrm{M}_1^0] + [\mathrm{M}_2^0])$ and $[\mathrm{M}_1] = [\mathrm{M}_1^0] - (3.6\alpha/4.6)([\mathrm{M}_1^0] + [\mathrm{M}_2^0])$, where $[\mathrm{M}_1^0]$ and $[\mathrm{M}_2^0]$ are the initial molar concentration of styrene and ester, respectively. For the starting concentrations used $[\mathrm{M}_1^0] = 3.36$ mole/l.; $[\mathrm{M}_2^0] = 0.93$ mole/l.), and from gel fraction–conversion measurements (Fig. 3), the relation between the two parameters can be approximated by $(1-2g) = (1-\alpha)^2$. Since $2k_iI\,k_t/k_p^{*2}[\mathrm{M}_2^0]^2 \cong 1/\mathrm{DP}^2 \ll 1$ for any DP equal to or greater than 5, where DP is the degree of polymerization of the copolymer, eq. (1) becomes

$$d\alpha/dt = (k_p^{*2}/k_t)\,[\mathrm{M}_2^0]$$

The value of k_p^{*2}/k_t must be 2.8 l./mole-min., corresponding to a value of k_p^* one order of magnitude greater then that for the conventional polymerization.

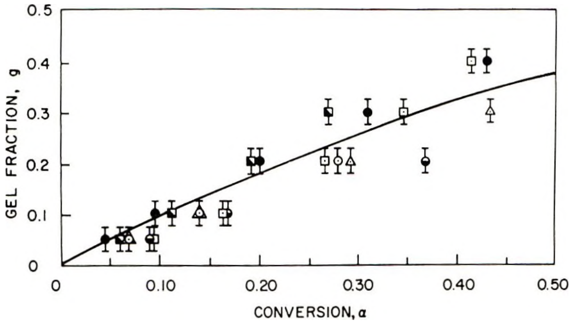

Fig. 3. Dependence of gel fraction on conversion at various dose rates: (◪) 4.32 Mrad/min.; (□) 10.74 Mrad/min.; (◒) 21.48 Mrad/min.; (△) 32.16 Mrad/min.; (○) 42.90 Mrad/min.; (●) 85.80 Mrad/min.

Now the volume of the reacting elements can be estimated. The polymerization rate of the bulk sample, $d\alpha_t/dt$, is given by

$$d\alpha_t/dt = (k_p{}^{*2}/k_t)[\mathrm{M}_2{}^0]V \tag{2}$$

where V is the volume fraction of the sample occupied by the reacting elements. Since the number of reacting volume elements n, is assumed an exponential function of the radiation intensity

$$dn/dI = C[1 - (nv_s/v_t)]$$

where v_s and v_t are the volume of the element and the sample, respectively, and nv_s/v_t is the volume fraction V of the sample occupied by the volume elements in which polymerization is occurring; upon rearranging and integrating there is obtained $V = 1 - e^{-(v_s/v_t)CI}$. Consequently eq. (3) becomes

$$d\alpha_t/dt = \{(k_p{}^{*2}/k_t)[\mathrm{M}_2{}^0]\}[1 - e^{-(v_s/v_t)CI}] \tag{3}$$

From experimentally measured rates, intensities, and monomer concentrations, and using the value of $k_p{}^{*2}/k_t$ of 2.8 l./mole-min. the term $(v_s/v_t)\ C$ was evaluated to be 7.5×10^{-2} min./Mrad. Saturation (when $V = 1$) occurs when $d\alpha_t/dt = 2.6$ min.$^{-1}$; therefore if the lifetime of a growing chain in the gel is 1.6×10^{-3} min. (an arbitrary, but reasonable, value taken only to illustrate the proposed mechanism), the volume of the reacting element is found to be 2.9×10^9 A^3. Equation (3) so evaluated is plotted in Figure 2. Assuming the electron deposits all its energy in the organic film, at the lowest dose rate (0.44 Mrad/min.) it is calculated that there is found 1 electron/sec./30 "potential" volume elements.

The results of this empirical scheme are not inconsistent with a simple model of radiation damage, admitting that electron impact processes in liquids are understood only qualitatively: Consider the interaction of a 0.04 M.e.v. electron with an organic absorber. The track range[12a] of such a low energy electron in a material of unit density is about 2.0×10^5 A., with total path length[12b] of 2.8×10^5 A. The volume swept out by this electron, an unknown quantity, is assumed for present purposes, to be a cylinder 2.0×10^5 A. long of 68 A. radius; on using this arbitrarily chosen, but likely, value for the radius, the calculated volume is 3.0×10^9 A^3.

It is recognized that important considerations were neglected in this simplified treatment: inhomogeneity of the 0.04 M.e.v. beam and radical yields from the more energetic knock out electrons, unequal spacing of the collisions, the varying chemical structure of the chain initiating species, and diffusion effects. Further, since the "adjustable" figures chosen for the radical lifetime and radius of the swept-out cylinder afford exceptionally wide latitude in model fitting, agreement of the model (i.e., that polymerization occurs in high-energy-density volume elements) with experiment is taken to indicate the reasonableness rather than the correctness of the approach.

It is a pleasure to acknowledge the valuable discussions of this work with Dr. Serge Gratch and Dr. Martin Goldstein.

References

1. Chapiro, A., *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962, pp. 162–166, 177–179.
2. Ballantine, D., Report of Fission Products Utilization Group, Brookhaven National Laboratory, November 1954.
3. Collinson, E., and A. Swallow, *Chem. Revs.*, **56,** 488 (1956).
4. Burlant, W., and A. Adicoff, *J. Polymer Sci.*, **27,** 269 (1958).
5. Burlant, W., and J. Hinsch, *J. Polymer Sci.*, **A2,** 2135 (1964).
6. Barrett, R., and M. Gordon, *The Physical Properties of Polymers*, Soc. Chem. Ind. Monograph No. 5, Macmillan, New York, 1959, p. 183.
7. Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953, p. 158.
8. Ausloos, P., and C. Trumbore, *J. Am. Chem. Soc.*, **81,** 3866 (1959).
9. Dewhurst, H., *J. Phys. Chem.*, **62,** 15 (1958).
10. Gevantman, L., and R. Williams, *J. Phys. Chem.*, **56,** 569 (1952).
11. Miller, J., and R. Dodson, *J. Chem. Phys.*, **18,** 865 (1950).
12. Evans, R., *The Atomic Nucleus*, McGraw-Hill, New York, 1955; (a) p. 621 et seq.; (b) p. 611 et seq.

Résumé

On a copolymérisé des solutions d'esters insaturés dans le styrène par des électrons de 0,04 Mev à des vitesses de dose allant de 0,44 à 85,8 Mrad/min. La disparition de chaque monomère et les fractions de gel sont mesurées en fonction des vitesses de dose. Les vitesses observées sous ces conditions de transfert linéaire d'énergie élevée révéla une dépendance linéaire etre l'énergie et l'intensité suivie d'une région d'indépendance vis-à-vis de l'inntensité. Ces résultats suggèrent que la polymérisation a lieu dans des volumes élémentaires discrets et que la croissance de chaîne est initiée par des radicaux "chauds." Pour une solution d'ester à 65% la vitesse de polymérisation de l'échantillon en bloc, $d\alpha_t/dt$, est donnée par $d\alpha_t/dt = \{k_p{}^{*2}/k_t\}M_2{}^0\ V$, où $k_p{}^*$ est une constante de vitesse de propagation dix fois plus grande que celle observée dans les polymérisations conventionnelles, k_t est la constante de vitesse de terminaison, $M_2{}^0$ est la concentration de départ en ester et V, proportionnel à l'intensité d'irradiation, est la fraction de volume de l'échantillon occupé par les éléments réactifs réagissants. Le volume de l'élément dans lequel a lieu la polymérisation, estimé au départ de résultats expérimentaux et en utilisant des valeurs raisonnables pour la vie d'un radical en croissance, est de 3.10^9 Å^3, valeur qui est en accord avec ce qui est connu quant au processus d'impact électronique dans les liquides.

Zusammenfassung

Lösungen ungesättigter Ester in Styrol wurden durch 0,04-MeV-Elektronen bei Dosisleistungen von 0,44 Mrad/min bis 85 Mrad/min copolymerisiert. Der Umsatz eines jeden Monomeren sowie die Gelfraktion wurden als Funktion der Dosisleistung gemessen. Die unter diesen Bedingungen hoher linearer Energieübertragung festgestellten Geschwindigkeiten zeigten lineare Abhängigkeit von der Intensität, gefolgt von einem intensitätsunabhängigem Bereich. Die Daten zeigen, dass die Polymerisation in diskreten Volumselementen verläuft und dass das Kettenwachstum durch heisse Radikale initiiert wird. Für 65%ige Esterlösungen ist die Polymerisationsgeschwindigkeit der Gesamtprobe $d\alpha_t/dt$ durch $d\alpha_t/dt = \{(k_p{}^{*2}/k_t)\mathrm{M}_2{}^0\}\ V$ gegeben, wo $k_p{}^*$ eine Geschwindigkeitskonstante für das aktivierte Wachstum, zehnmal grösser als diejenige bei konventioneller Polymerisation, k_t die Abbruchsgeschwindigkeitskonstante, $\mathrm{M}_2{}^0$ die Anfangskonzentration des Esters und V der zur Strahlungsintensität proportionale, durch die reagierenden Elemente besetzte Volumsbruchteil der Probe ist. Das Volumen des Elements, in welchem die Polymerisation verläuft, ergibt such aus den experimentellen Daten unter Annahme eines plausiblen Werts für die Lebensdauer eines wichsenden Radikals zu 3.10^9 Å^3; dieser Wert entspricht durchaus den bei Elektronenstossprozessen in Flüssigkeiten auftretenden Verhältnissesn.

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Phase Separation, Viscosity, and Thermodynamic Parameters for Poly-2-methyl-5-vinylpyridine–Diluent Systems

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Synopsis

Liquid–liquid phase separation has been investigated for several poly-2-methyl-5-vinylpyridine fractions in eleven solvents. The plots of precipitation temperatures against polymer volume fractions are shown for a few systems. The agreement between two curves calculated according to Flory and the experimental ones is only qualitative, and the calculated critical concentrations are much smaller than the experimental ones. Plots of reciprocal critical precipitation temperature against reciprocal square root molecular weight of the polymer are straight lines. From the intercepts and slopes the values of the thermodynamic paramerers Θ and ψ were calculated. Intrinsic viscosities were determined for a fraction of 990,000 molecular weight in five solvents at various temperatures. Theta measurements yielded for Flory's constant K the value 8.4×10^{-4}, which can be assumed to be constant with the temperature and the solvent. Moreover the parameter Θ and ψ were calculated according to Flory and Fox, Kurata, Stockmayer, and Roig, and Kurata and Stockmayer. The viscometric ψ are different from each other and all much smaller than the ones from phase separation. An attempt is made to compare the above theories by utilizing intrinsic viscosity results on fractions of various molecular weights in n-propyl acetate and methyl isobutyl ketone. The results show nearly the same behavior for all the three theories.

Introduction

The study of phase separation uses the direct equilibrium method to determine the thermodynamic parameters of mixing. For liquid–liquid phase separation for a high molecular weight polymer–diluent binary system, the dependence of both critical concentration and critical temperature from the molecular weight are predicted, according to Flory,[1] by eqs. (1) and (2)

$$v_c = (V/M\bar{v})^{1/2} \tag{1}$$

$$1/T_c = (1/\Theta)\{1 + [(V/\bar{v})^{1/2}/\psi]/M^{1/2}\} \tag{2}$$

where v_c is the critical concentration of the polymer expressed as volume fraction, V is the molar volume of the solvent, $\bar{v}$ is the specific volume of the polymer, M is the molecular weight of the polymer, T_c is the critical temperature, Θ is the well known "ideal" temperature, and ψ is the thermodynamic parameter which characterizes the entropy of dilution of the polymer with the solvent. Experimental measurements over a number of polymers have confirmed the linearity between $1/T_c$ and $1/M^{1/2}$, and the values of Θ so obtained are confirmed by other types of measurements. Furthermore the shape of the phase separation curves is well predicted, but the theoretical values of v_c are much smaller than the experimental ones.[2,3] Several years ago Tompa[4,5] showed that this discrepancy could be avoided by assuming the free energy interaction parameter ${}^1\chi$ to be dependent in a simple way on the concentration, an assumption widely accepted in subsequent developments[6-8] and supported by a great number of experimental results. According to Flory and Fox[1] it is possible to obtain the thermodynamic parameters of mixing for polymer–diluent systems also by simple calculations from viscosity data, i.e., even from measurements of an essentially nonequilibrium property. Intercept and slope of a plot $(K_T/K_0)(\alpha^5 - \alpha^3)/M^{1/2}$ versus $1/T$ according to eq. (3)

$$\alpha^5 - \alpha^3 = 2C_M\psi(1 - \Theta/T)M^{1/2} \tag{3}$$

may yield, in fact, the values of ψ and Θ. In eq. (3) α is the linear expansion factor of the macromolecule and C_M may be considered to vary with the temperature inversely as the well known Flory constant K does. Stockmayer[9] later suggested on theoretical grounds that, for temperatures which are not far from Θ, C_M should be replaced by the value $0.4913C_M$. Kurata, Yamakawa, and Utiyama[10,11] and Ptitsyn and Eizner[12] showed that, due to the non-Gaussian character of polymer chains with excluded volume, the empirically well established Flory and Fox equation,

$$[\eta]/[\eta]_\theta = \alpha^3 \tag{4}$$

where $[\eta]$ is the intrinsic viscosity of the polymer, should be replaced by:

$$[\eta]/[\eta]_\theta = \alpha^{2.43} \tag{5}$$

Recently Kurata, Stockmayer, and Roig[13,14] proposed that eq. (3), obtained by hypothesizing a spherical distribution of the segments around the center of mass of the polymer molecule should be replaced by eq. (6):

$$\alpha^3 - \alpha = Cg(\alpha)z \tag{6}$$

where

$$g(\alpha) = 8\alpha^3/(3\alpha^2 + 1)^{3/2} \tag{7}$$

and C is a numerical constant. This equation derives from considerations based on an equivalent ellipsoid model, and, by expressing[9] the excluded volume parameter[15] z in terms of Flory theory, becomes:

$$(1 - \alpha^{-2})(\alpha^2 + 1/3)^{3/2} = (2^5/3^3)(134/105)C_M\psi(1 - \Theta/T)M^{1/2} \tag{8}$$

Very recently, Kurata and Stockmayer,[16] emphasizing that the hydrodynamic radius of polymer chains increases less rapidly than the statistical radius, as the excluded volume increases, proposed that the ratio $[\eta]/[\eta]_\theta$ defined the cube of a new empirical parameter α_η; this should replace

α in eq. (6) in which only the numerical value of the constant should be changed. This new equation, in terms of Flory, reads:

$$(1 - \alpha_\eta^{-2})(\alpha_\eta^2 + 1/3)^{3/2} = (2^5/3^3)1.10C_M\psi(1 - \Theta/_T)M^{1/2} \qquad (9)$$

Parameters Θ and ψ can be obtained from eqs. (8) and (9) in analogous manner as from equation (3).

In the present work experimental data of phase separation and viscosity for several poly-2-methyl-5-vinylpyridine–diluent systems are given. The values of the thermodynamic parameters obtained from both types of measurements are also reported, as calculated through the application of the above mentioned theories.

Experimental

The preparation, fractionation, and drying of poly-2-methyl-5-vinyl pyridine (poly-MVP) were performed as previously described.[16] Fractions of approximately 5–6% of the whole, seldom 10% were used. Their molecular weight was calculated from the intrinsic viscosity in methyl ethyl ketone by the use of the equation:

$$[\eta] = 1.9 \times 10^{-4}M^{0.64}$$

which was obtained from intrinsic viscosity and light scattering measurements over fractions.[16]

The solvents were all of high purity; nevertheless the esters were washed with sodium bicarbonate solutions. All the solvents were rectified prior to use. The selection of the solvents for the study of the phase separation was made with the criterion that their refractive index differed at least 5% from that of the polymer. Because of this refractive index requirement, a number of solvents (benzene, toluene, xylene, anisole, benzoates, etc.) with which poly-MVP forms mixtures which are likely to undergo phase separation at convenient temperatures, could not be studied. The water content of the solvents, as determined according to the K. Fischer method, was in every case ca. 0.02%. Esters and chloroform did not contain free acid. Chloroform contained 0.5% ethanol. The measurement of the phase separation was effected visually in glass ampules which were similar to those employed by Shultz and Flory;[2] they were equipped with a glass stirrer and a side arm which was connected to a bulb containing the drying agent (Anhydrone).

Accurately weighed quantities of polymer, not less than 40 mg. were placed in the ampules, then the desired solvent amount was added, care being taken to avoid clump formation by repeated additions, accompanied by vigorous stirring.

After being allowed to stand a few hours at a temperature which was 20–30°C. higher than the one which was previewed for phase separation, the mixtures were thoroughly stirred; the ampules were then allowed to cool in a bath. When the temperature was a few degrees higher than the precipitation temperature, the rate of cooling was reduced to less than 0.05°C./min.

The temperature at which slight opalescence began to appear was generally determined to within about ±0.2°C.; a greater error affected the measurements at high polymer concentrations. The temperature was read on a thermometer which was immersed in the well stirred cooling bath. The exact mixture composition was determined immediately after the temperature was read by accurately weighing the glass ampules. The expression in term of volume fraction was calculated by making use of the solvent densities taken from the literature. The density of the polymer is 1.12 g./ml. at 25°C. This constant value was used in calculating the volume fractions, and the assumption was made of no volume change on mixing.

Each mixture was used for only one determination; in other terms it was neither concentrated nor diluted. As a matter of fact if the ampules were opened even for a few seconds, the precipitation temperature was observed to become higher, even by a few degrees, possibly owing to the great tendency for moisture absorption of the polymer. On the other hand, excellent reproducibility was obtained if the ampule was not opened and if the mixture was allowed to cool as above after being heated a few degrees

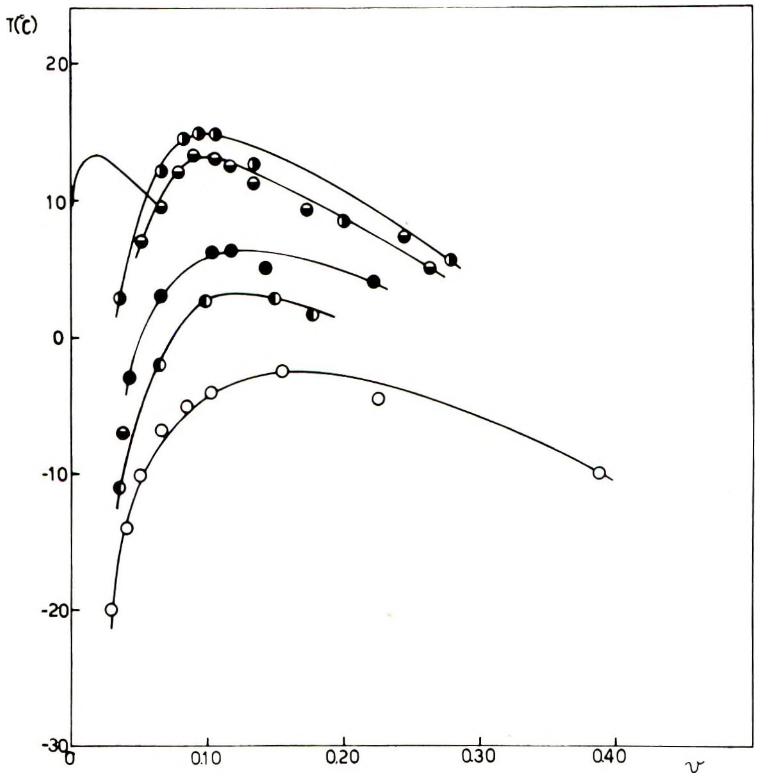

Fig. 1. Precipitation temperatures T for poly-MVP fractions in n-butyl acetate plotted against polymer volume fractions v: (○) $M = 50{,}000$; (◐) $M = 73{,}000$; (●) $M = 165{,}000$; (◒) $M = 420{,}000$; (◑) $M = 600{,}000$. For the fraction with $M = 420{,}000$ the theoretical curve according to Flory is also shown.

above the precipitation temperature. Mixtures having different compositions were always separately prepared in different ampules.

Viscosity measurements were carried out in Bischoff suspended-level dilution viscometers, in a water bath, which was thermostated to ±0.05°C.; the solvent flow time varied from 100 to 150 sec. for volumes of 0.4–0.5 ml. To obtain the intrinsic viscosity, the time was measured at four concentrations in the range 0.2–0.8 g./dl.

Results and Discussion

The results of measurements of phase separation for several poly-MVP–solvent pairs are given in Table I. In Figures 1 and 2 precipitation temperature is plotted versus the volume fraction of the polymer. Two theoretical curves calculated according to Flory are also shown for comparison. The agreement is only qualitative. In particular, the calculated v_c values are much smaller than the experimental values. In Figure 3 a plot of $1/T_c$ against $1/M^{1/2}$ for several systems is given. The experimental points lie with good approximation on straight lines according to

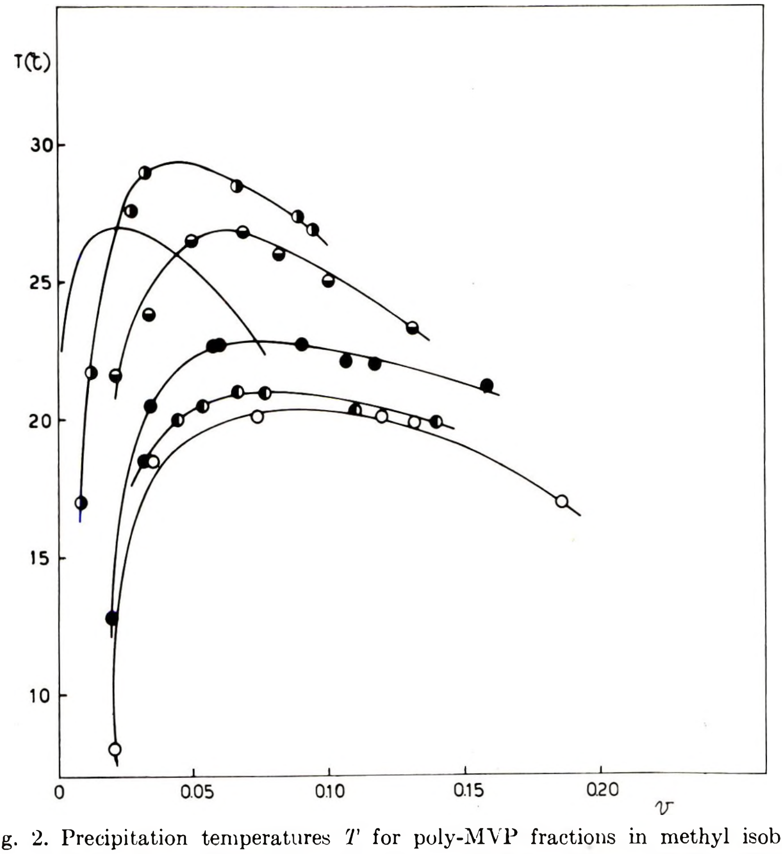

Fig. 2. Precipitation temperatures T for poly-MVP fractions in methyl isobutyl ketone plotted against polymer volume fractions v: (○) M = 90,000; (◐) M = 102,000; (●) M = 145,000; (⊖) M = 263,000; (◑) M = 320,000. For the fraction with M = 263,000 the theoretical curve according to Flory is also shown.

eq. (2). The values of Θ and ψ obtained from intercepts and slopes are listed in Table II. It can be seen that almost all our polymer–solvent pairs belong to the second group, as indicated by Shultz and Flory,[3] that is, most of them have a heat of dilution which is slightly positive, while the deviation from the normal entropy of dilution is small and positive. The most striking exceptions seem to be represented by *n*-propyl propionate and *n*-amyl acetate (which are, by the way, the most symmetrical and the least symmetrical among the above esters).

In the case of ethyl butyrate, owing to uncertainties in the extrapolation, we can only state that the Θ temperature lies in a range of about 10°C. around the value listed in Table II; for the same reason the value of ψ was not calculated.

TABLE I

Critical Miscibility Temperatures for Various Poly-MVP–Diluent Systems

Diluent	$M \times 10^{-3}$	T_c, °C.	Diluent	$M \times 10^{-3}$	T_c, °C.
Propionitrile	56	−16.9	*n*-Amyl acetate	30	38.2
	100	−13.2		66	42.8
	193	−11.5		126	43.2
	284	−10.8		165	43.8
	370	−8.8		233	44.6
	442	−7.8		483	45.5
			Isobutyl acetate	56	32.1
n-Propyl acetate	56	3.3		87	33.5
	152	9.5		170	39.2
	336	12.3		320	41.9
	370	12.7			
	440	13.4	Tetrahydronaphthalene	100	40.6
	690	14.7		123	41.6
				165	43.1
				233	43.8
n-Butyl acetate	50	−2.4		275	44.1
	73	3.4		335	44.5
	165	6.4			
	420	13.4	Isoamyl acetate	87	33.4
	600	14.8		152	36.0
				193	39.4
Ethyl propionate	56	14.0		275	41.6
	123	18.8		320	45.4
	276	19.4			
	335	20.4	*n*-Propyl propionate	87	30.3
	400	21.2		113	32.2
				181	39.0
				412	44.3
Methyl isobutyl ketone	90	20.3			
	102	21.0	Ethyl *n*-Butyrate	30	42.5
	145	22.7		145	42.8
	263	26.8		197	43.3
	320	29.3		222	45.0
				263	45.9

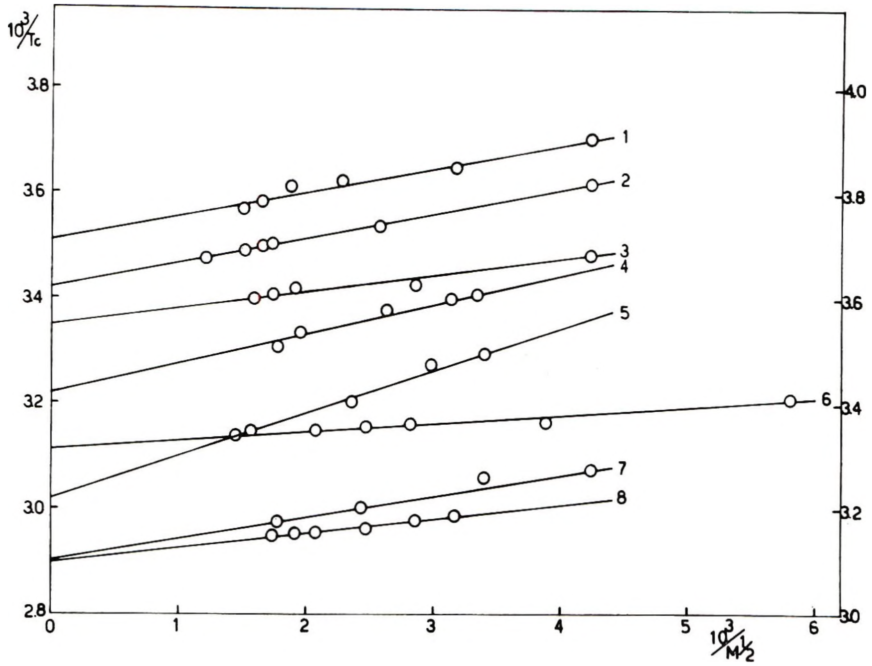

Fig. 3. Reciprocal critical precipitation temperatures $1/T_c$ plotted against reciprocal square root molecular weights of the polymer for various poly-MVP–diluent systems: (*1*) propionitrile; (*2*) *n*-propyl acetate; (*3*) ethyl propionate; (*4*) methyl isobutyl ketone; (*5*) *n*-propyl propionate; (*6*) *n*-amyl acetate; (*7*) isobutyl acetate; (*8*) tetrahydronaphthalene. Left-hand ordinate for curves *2, 3, 4, 5,* and *6;* right-hand ordinate for curves *1, 7,* and *8.*

In Table III the results of intrinsic viscosity measurements carried out in various solvents at various temperatures are given. We were able to carry out measurements of intrinsic viscosity even at temperatures lower than Θ, since inspection of the critical miscibility plots showed the concentration of the solution used to be in the one-phase region. Values of K calculated through the use of the equation

$$K = [\eta]_\theta/M^{1/2}$$

are also listed in Table III. These values are practically independent not only of the solvent, but also of the temperature, at least in the range considered. The average value 8.4×10^{-4} is in excellent agreement with the one found from the intercepts of log-log plots of $[\eta]_\theta$ versus M for *n*-butyl acetate, methyl isobutyl ketone, and *n*-amyl acetate.[16]

The values of $(\alpha^5 - \alpha^3)/M^{1/2}$, with α calculated from eq. (4) for each case, are plotted against $1/T$ in Figure 4, for a polymer fraction with 990,000 molecular weight in different solvents. The experimental points

TABLE II

Thermodynamic Parameters from Phase Separation and Viscosity Measurements

Solvent	From eq. (2)			From eqs. (3) and (4)			From eqs. (5) and (8)		From eq. (9)	
	Θ, °C.	ψ[a]	Group (ref. 4)	Θ, °C.	ψ[a]	ψ with the factor 0.4913 in eq. (3)	Θ, °C.	ψ[a]	Θ, °C.	ψ[a]
n-Propyl acetate	19.3	0.83	2	19.2	0.023	0.048	19.2	0.052	19.4	0.12
n-Butyl acetate	21.8	0.63	2	21.7	0.020	0.040	21.7	0.043	21.8	0.10
Methyl isobutyl ketone	37.4	0.68	2	38.6	0.024	0.049	38.7	0.055	38.9	0.13
n-Amyl acetate	48.2	2.4	1	48.4	0.027	0.054	48.6	0.062	48.4	0.14
n-Propyl propionate	58.0	0.45	3	57.8	0.021	0.042	58.0	0.052	58.1	0.11
Propionitrile	−3.6	0.73	2							
Ethyl propionate	25.4	1.2	1–2							
Isobutyl acetate	49.0	0.95	2							
Tetrahydronaphthalene	49.5	1.4	1							
Isoamyl acetate	53.2	0.68	2							
Ethyl *n*-butyrate	50	—	—							

[a] Reference temperature: 25°C.

TABLE III
Viscometric Data for Poly-MVP Fractions in Various Solvents

Solvent	T, °C.	$M \times 10^{-3}$	$[\eta]$, dl./g.	$K = [\eta]_\theta / M^{-1/2} \times 10^4$
n-Propyl acetate (K average $= 8.4 \times 10^{-4}$)	19.3	990	0.825	8.3
	30.0	990	0.875	—
	40.0	990	0.905	—
	48.2	990	0.943	—
	48.2	158	0.353	—
	48.2	340	0.535	—
	48.2	510	0.660	—
	48.2	690	0.775	—
	19.3	158	0.335	8.4
	19.3	340	0.495	8.5
	19.3	510	0.600	8.4
	19.3	690	0.695	8.4
n-Amyl acetate	48.2	990	0.800	8.0
	60.0	990	0.838	—
	70.0	990	0.875	—
n-Propyl propionate	48.2	990	0.838	—
	58.0	990	0.875	8.8
	68.0	990	0.911	—
Methyl isobutyl ketone (K average $= 8.3 \times 10^{-4}$).	25.0	990	0.768	—
	37.4	990	0.837	8.4
	48.2	990	0.876	—
	60.0	990	0.920	—
	70.0	104	0.271	—
	70.0	170	0.380	—
	70.0	340	0.548	—
	70.0	690	0.794	—
	37.4	104	0.254	7.9
	37.4	170	0.348	8.4
	37.4	340	0.500	8.6
	37.4	690	0.702	8.4
n-Butyl acetate	21.8	990	0.840	8.3
	35.2	990	0.880	—
	48.2	990	0.918	—
	65.0	990	0.965	—

lie satisfactorily on straight lines in agreement with eq. (3). From the intercepts and the slopes, the values of ψ and Θ were calculated both with and without the use of the factor 0.4913. The results are listed in Table II. Plots of $(1 - \alpha^{-2})(\alpha^2 + 1/3)^{3/2}/M^{1/2}$ versus $1/T$ and $(1 - \alpha_\eta^{-2})(\alpha_\eta^2 + 1/3)^{3/2}/M^{1/2}$ versus $1/T$ according to eqs. (8) and (9), respectively, are also straight lines. From the abscissa intercepts, values of Θ are calculated which are, of course, in excellent agreement with those from phase separation. On the contrary, the ψ values are quite different from those calculated according to eq. (3) and from each other. All these values are shown in Table II. It can be seen that the ψ values from phase separation are much larger than all values obtained from viscosity measure-

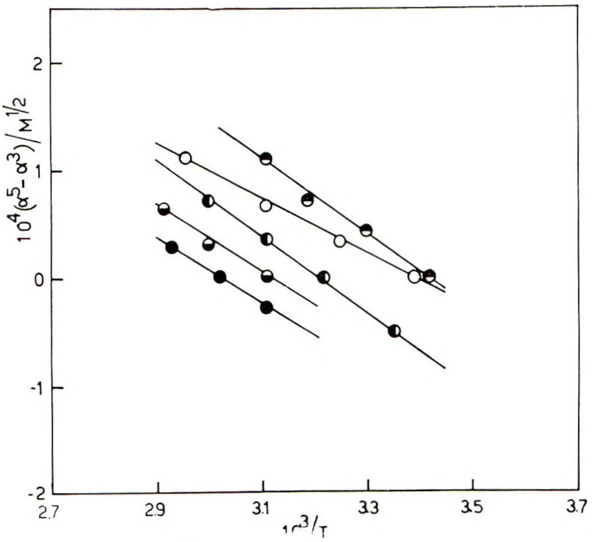

Fig. 4. Plot of $(\alpha^5 - \alpha^3)/M^{1/2}$ against reciprocal temperature $1/T$ for a poly-MVP fraction with $M = 990{,}000$ in various solvents: (●) *n*-propyl proponate; (◒) *n*-amyl acetate; (◐) methyl isobutyl ketone; (○) *n*-butyl acetate; (◓) *n*-propyl acetate.

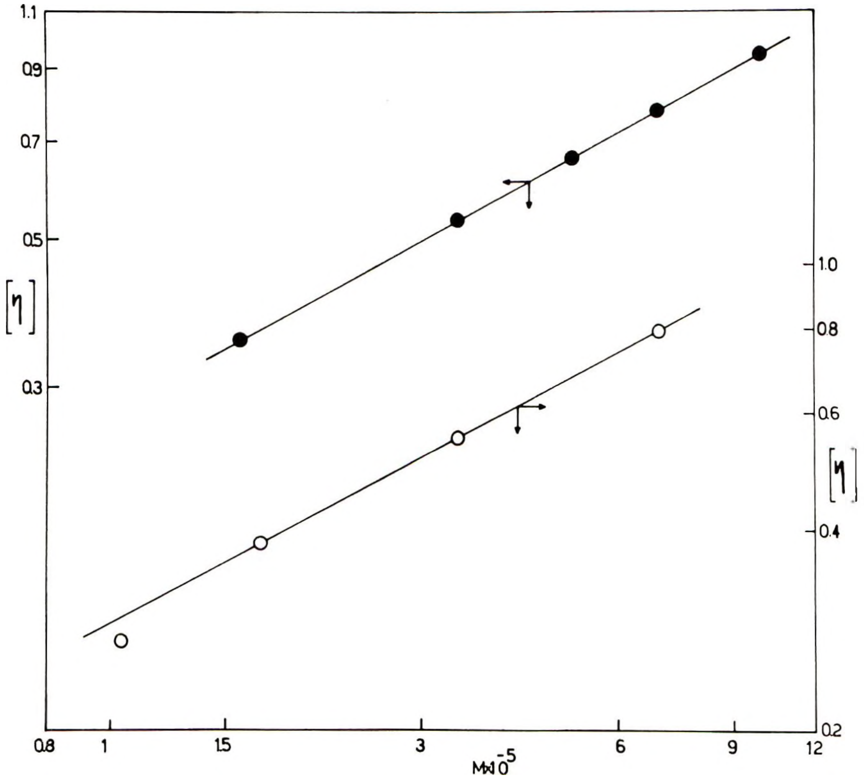

Fig. 5. Plot of intrinsic viscosity against molecular weight for poly-MVP fractions (●) in *n*-propyl acetate at 48.2°C.; and (○) in methyl isobutyl ketone at 70.0°C.

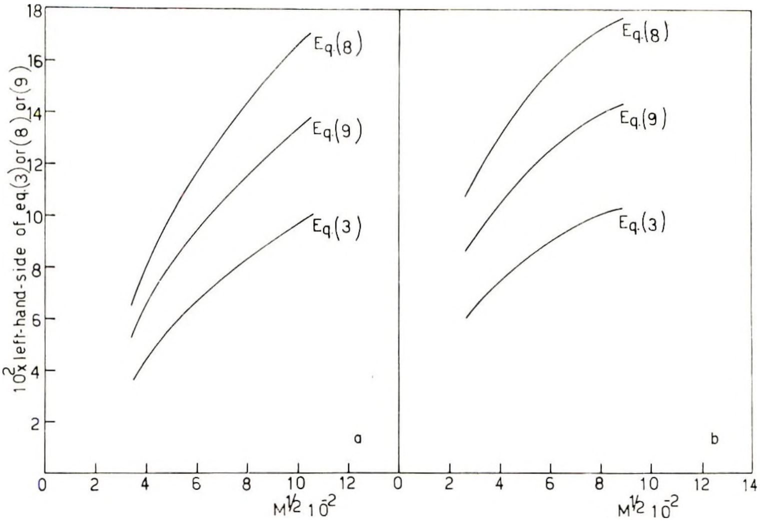

Fig. 6. Plots of left-hand-side of eqs. (3), (8), and (9) against square root polymer molecular weight: (*a*) poly-MVP–*n*-propyl acetate at 48.2°C.; (*b*) poly-MVP–methyl isobutyl ketone at 70.0°C.

ments. Such disagreement though not so high as in the present work, was previously found between values of ψ from phase separation and viscosity.[17–19] It must be remembered that even though both types of measurements were carried out at temperatures not very far from Θ, where theory should apply, the former measurements are performed at rather high concentrations and the latter in dilute solutions. However, for several systems the thermodynamic parameters from phase separation were found[3] entirely consistent with the corresponding parameters for systems of small molecules of similar structure. The abnormally low entropies of mixing calculated from the viscosity data seem to indicate a high degree of order in poly-MVP solutions, possibly as a consequence of their polar character.

It can be seen from Table II that the ψ values obtained by the three different viscometric equations are quite different. We tried to compare the above theories in another way, namely, by plotting the functions of α or α_η expressed in eqs. (3), (8), and (9) versus $M^{1/2}$. We carried out viscosity measurements on a few fractions in *n*-propyl acetate and methyl isobutyl ketone at 48.2 and 70°C., respectively and at the respective theta temperatures (Table III). Figure 5 shows the intrinsic viscosities plotted versus the molecular weights on log-log paper.

Plots of the left-hand sides of eqs. (3), (8), and (9) versus $M^{1/2}$ are drawn in Figure 6. The calculations were carried out for a number of "ideal" points lying on the straight lines of Figure 5, assuming for K the value 8.4×10^{-4}. Straight lines passing through the origin should be obtained. This is not the case. Plots quite similar are obtained with all three equations. These plots show a slight curvature, and, at least for n-propyl acetate, extrapolation to low molecular weights yields, a positive intercept on the abscissa. Similar results were also obtained by Okada and co-workers[20] for polystyrene–solvent pairs. However, our range of ordinate values is much narrower than the one usually found in similar plots in the literature.[1,20] This is a consequence of the low value of the expansion factor experimentally obtained, which arises in turn from the very low temperature dependence of the intrinsic viscosity in our systems. It is, in fact, rather unusual that intrinsic viscosities carried out about 30°C. above the theta temperature are only 5–15% higher than the respective theta values, depending on the molecular weight. Similar results, as far as low α values are concerned were obtained by us from intrinsic viscosity measurements at room temperature in a number of solvents (ethyl acetate, toluene, cyclohexanone, dimethylformamide, n-butylamine, 2-methyl-5-ethylpyridine) with an unfractionated poly-MVP of 400,000 molecular weight. The only exception was chloroform. However, the results of intrinsic viscosity carried out at 17°C. for fractions with molecular weight ranging from 70,000 to 700,000, and fitting the equation $[\eta] = 10.8 \times 10^{-5} M^{0.75}$, yielded, according to Kurata and Stockmayer,[14] a K value of 12.6×10^{-4} which is considerably higher than the value (8.4×10^{-4}) found from theta measurements. Similar results were also found for methanol[16] possibly due to association or ionization.

We wish to acknowledge the assistance of Dr. A. Mula, who carried out the fractionation of the polymer.

References

1. Flory, P. J., *Principles of Polymer Chemistry,* Cornell University Press, Ithaca New York, 1953.
2. Shultz, A. R., and P. J. Flory, *J. Am. Chem. Soc.*, **74,** 4760 (1952).
3. Shultz, A. R., and P. J. Flory, *J. Am. Chem. Soc.*, **75,** 3888 (1953).
4. Tompa, H., *Compt. Rend. 2nd Reunion Soc. Chim. Phys., Paris,* 1952.
5. Tompa, H., *Polymer Solutions,* Butterworths, London, 1956.
6. Orofino, T. A., and P. J. Flory, *J. Chem. Phys.*, **26,** 1067 (1957).
7. Maron, S. H., *J. Polymer Sci.*, **38,** 329 (1959).
8. Maron, S. H., and N. Nakajima, *J. Polymer Sci.*, **54,** 587 (1961).
9. Stockmayer, W. H., *J. Polymer Sci.*, **15,** 595 (1955).
10. Kurata, M., and H. Yamakawa, *J. Chem. Phys.*, **29,** 311 (1958).
11. Kurata, M., H. Yamakawa, and H. Utiyama, *Makromol. Chem.*, **34,** 139 (1959).
12. Ptitsyn, O. B., and Yu. E. Eĭzner, *Zh. Fiz. Khim.*, **32,** 2464 (1958).
13. Kurata, M., W. H. Stockmayer, and A. Roig, *J. Chem. Phys.*, **33,** 151 (1960).
14. Kurata, M., and W. H. Stockmayer, *Fortschr. Hochpolymer-Forsch.*, **3,** 196 (1963).
15. Zimm, B. H., W. H. Stockmayer, and M. Fixman, *J. Chem. Phys.*, **21,** 1716 (1953).
16. Garbuglio, C., L. Crescentini, A. Mula, and G. B. Gechele, *Madromol. Chem.*, in press.
17. Krigbaum, W. R., *J. Am. Chem. Soc.*, **76,** 3758 (1954).
18. Fox, T. G, *Polymer,* **3,** 111 (1962).
19. Wagner, H. L., and P. J. Flory, *J. Am. Chem. Soc.*, **74,** 195 (1952).
20. Okada, R., Y. Toyoshima, and H. Fujita, *Makromol. Chem.*, **59,** 137 (1963).

Résumé

On a étudié la séparation en phase liquide-liquide de plusieurs fractions de poly(2-méthyl-5 vinylpiridine) dans onze solvants. Le rapport entre les températures de précipitations et les fractions de volume de polymère est présenté sous forme de graphique pour quelques systèmes. L'accord entre les deux courbes calculées selon Flory et celle déterminée expérimentalement n'est que qualitatif, et les concentrations critiques calculées sont beaucoup plus petites que celles déterminées expérimentalement. La relation entre l'inverse de la température critique de précipitation et l'inverse de la racine carrée du poids moléculaire du polymère est linéaire. A partir des valeurs d'interception et des tangentes, les valeurs des paramètres thermodynamiques Θ et ψ ont été calculées. Les viscosités intrinsèques ont été déterminées pour une fraction de poids moléculaire de 990 000 dans cinq solvants et différentes températures. Les valeurs expérimentales de théta donnent pour la constante de Flory K la valeur de $8{,}4.10^{-4}$, valeur qui peut être considérée comme demeurant constante avec la température et la nature du solvant. En plus, les paramètres Θ et ψ ont été calculées selon Flory et Fox, Kurata, Stockmayer et Roig, et Kurata et Stockmayer. Les valeurs de ψ déterminées par viscosimétrie sont différenres des autres et sont beaucoup plus petites que celles obtenues par séparation de phases. On a essayé de comparer les théories ci-dessus en utilisant les résultats des viscosités intrinsèques des fractions de différents poids moléculaires dans l'acétate de *n*-propyle et la méthylisobutylcétone. Les résultats sont sensiblement les mêmes dans les trois théories.

Zusammenfassung

Die Trennung in zwei flüssige Phasen wurde an einigen Poly-(2-methyl-5-vinylpyridin)-Fraktionen in 11 Lösungsmitteln untersucht. Diagramme für die Fällungstemperatur gegen den Volumsbruch des Polymeren werden für einige Systeme mitgeteilt. Die Ubereinstimmung zwischen der nach Flory berechneten Kurve und der experimentell erhaltenen ist nur qualitativ, wobei die berechneten kritischen Konzentrationen viel kleiner sind, als die experimentellen. Die Auf tragung der reziproken kritischen Fällungstemperatur gegen die reziproke Wurzel aus dem Molekulargewicht des Polymeren liefert gerade Linien. Aus dem Ordinatenabschnitt und der Neigung wurden die Werte der thermodynamischen Parameter Θ und ψ berechnet. Viskositätszahlen wurden an einer Fraktion mit dem Molekulargewicht 990.000 in 5 Lösungsmitteln bei verschiedenen Temperaturen bestimmt. Theta-Messungen liefern für die Flory-Konstante K den Wert $8{,}4.10^{-4}$, welcher als konstant in Bezug auf Temperatur und Lösungsmittel angenommen werden kann. Ausserdem wurden die Parameter Θ und ψ nach Flory und Fox, Kurata, Stockmayer und Roig, sowie Kurata und Stockmayer berechnet. Die viskosimetrischen Werte von ψ sind untereinander verschieden und alle bedeutend kleiner als die aus dem Zwei-Phasengleichgewicht erhaltenen. Es wird versucht, einen Vergleich der obigen Theorien durch Benützung von Viskositätszahlergebnissen an Fraktionen mit verschiedenem Molekulargewicht in *n*-Propylacetat und Methylisobutylketon durchzuführen. Die Ergebnisse zeigen für alle 3 Theorien nahezu das gleich Verhalten.

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Interaction between Alkaline Earth Metal Cations and Poly(methacrylic Acid) in Dilute Solutions.
I. Viscometric and Conductometric Titrations

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Synopsis

The viscometric and conductometric behavior of poly(methacrylic acid) in dilute aqueous solutions over the whole range of neutralization with barium, strontium, and calcium hydroxides were studied. The results show minima in reduced viscosity and specific conductance near degrees of neutralization of 0.2 and 1.0. These minima do not appear with neutralization with monovalent bases and are more closely related to the higher degree of association of polyanions with divalent counterions than with monovalent ions. From the fractional charge of polyanions we may conclude that about 90% of the divalent counterions are associated with polyanions in almost the whole range of neutralization. The results show the specific influence of strontium cations on the behavior of PMA solutions.

The effects of alkaline earth metal counterions on the properties of polyelectrolytes have been studied mainly in solutions to which salts were added. Under such conditions the decrease of reduced viscosities was greater than in solutions of monovalent ions with the same ionic strength.[1-5] This has been ascribed to more effective shielding of polyion charge by bivalent ions or to the contracting effects of chelation. Similarly, the decrease in the second virial coefficient of the solutions[5,6] has been discussed in terms of the association of counterions with polyions. In more concentrated solutions, precipitation of polyelectrolytes has been observed.[7-10]

Some authors report interaction between divalent counterions and polyions in salt-free solutions.[11,12] In these cases the polyacid was neutralized with divalent hydroxides, and a decrease in viscosity was also noted. At sufficiently high concentrations of the polyacid, precipitation may also occur. This is related to the ion association and the formation of salt bridges.[13] Interaction between strontium counterion and poly(acrylic acid) has been studied by an electrolytic method at such concentrations that neutralization without precipitation was possible only below 25 degrees of neutralization.[14]

Previous studies showed that the behavior of poly(methacrylic acid) neutralized with barium, strontium or calcium hydroxides is quite different than that seen with neutralization with monovalent hydroxides.[15,16]

The present paper deals with poly(methacrylic acid) neutralized with Ba, Sr, and Ca hydroxides over the whole range of neutralization. Viscometric and conductometric measurements were performed in dilute solutions to avoid precipitation of polysalts.

Experimental

Methacrylic acid was obtained by hydrolysis of pure methyl methacrylate by ethanolic potassium hydroxide.[7] The crude acid was purified by distillation *in vacuo* and subsequent crystallization. The obtained product showed a refractive index n_D^{20} = 1.4312; b.p. 160°C./760 mm. The polymerizations of methacrylic acid were carried out in aqueous solutions with different amounts of hydrogen peroxide as initiator. In this way three samples of poly(methacrylic acid) (PMA) were obtained. These were dissolved in water and purified by electrodialysis against redistilled water. The average molecular weights determined by viscosity measurements[17] were: PMA-I, 33,000; PMA-II, 195,000; PMA-III, 826,000. Viscometric measurements were carried out in a Ubbelohde viscometer modified in order to allow successive dilutions in the bottom bulb of the viscometer. This viscometer had the following characteristics: capillary radius, 0.0218 cm.; capillary length, 13.5 cm.; efflux volume, 2.98 ml., volume of bottom bulb, 250 ml.; efflux time for water, 281.5 sec.; velocity gradient for water, 867.8 sec.$^{-1}$. The Hagenbach correction was negligible. All measurements were carried out at 25.05 ± 0.01°C. in a nitrogen atmosphere to avoid carbon dioxide contamination. The viscometer described above was also modified to permit conductometric measurements of the same solutions. For this purpose bright platinum electrodes were sealed into the bottom bulb. The cell constant, 0.0999 cm.$^{-1}$, was determined by measuring the specific conductance of a KCl solution.[18] All conductance measurements were performed with a simple conductivity bridge at 1000 cycle/sec. The accuracy was to ±1%. All PMA solutions were prepared with carbon dioxide-free water (specific conductance $5-10 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$). PMA concentrations were determined by conductometric titrations with standard $Ba(OH)_2$.[15] The 0.01*M* PMA solutions of different degrees of neutralization were prepared by dilution from a more concentrated stock which was stored in a refrigerator. More dilute solutions were obtained by dilution in the viscometer. Dilute solutions were thoroughly stirred by bubbling of nitrogen. All reagents were analytical grades from Polskie Odczynniki Chemiczne, Gliwice, Poland, except $Sr(OH)_2.8H_2O$, which was laboratory reagent from BDH. Concentrations of solutions are expressed in base moles per liter and reduced viscosities in deciliters per gram.

Results and Discussion

Figures 1 and 2 show the changes of the reduced viscosities of PMA-II and PMA-III neutralized with barium, strontium, and calcium hydroxides at various concentrations. The curves shown in these figures have a small

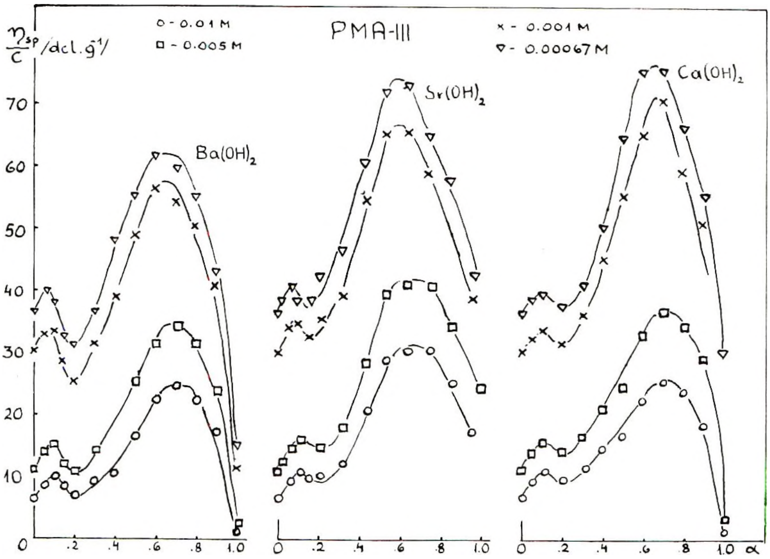

Fig. 1. Dependence of reduced viscosity η_{sp}/c of poly(methacrylic acid) (PMA-III) at various concentrations on the degree of neutralization, α, with the barium, strontium, and calcium hydroxides.

maximum near a degree of neutralization $\alpha = 0.1$, a minimum near $\alpha = 0.2$, and a second maximum near $\alpha = 0.7$. The changes observed with PMA-I have the same features; they were shown in a previous paper.[16] We see that these characteristics are independent of the molecular weight of PMA, the concentration of the solutions, or the kind of hydroxide, but the value of reduced viscosity is dependent on the base used. The changes of the reduced viscosities are mainly related to the shape of the molecules in the solution.[17] When PMA is neutralized with alkali metal hydroxides the size of the molecules gradually increases to a degree of neutralization near 0.6. The same results were observed when PMA was neutralized with quaternary ammonium bases.[19] The present experiments indicate that the behavior of PMA neutralized with the alkaline earth metal hydroxides is quite different. At a low degree of neutralization up to $\alpha = 0.1$ the size of the molecules increases, then it decreases up to a minimum at $\alpha = 0.2$, and then it increases again up to $\alpha = 0.7$. The changes of the size are about tenfold smaller than those observed with monovalent bases (Cf. ref. 16, Figs. 1 and 2). This difference may be related to the association of divalent counterions with polyanions. It depresses the net charge of polyanions and then their sizes.

The changes of the size of poly(methacrylic acid) molecules up to $\alpha = 0.2$ are quite similar to changes observed by Katchalsky and Zwick[20] with the swollen volume of crosslinked PMA neutralized with $Ba(OH)_2$. This may mean that in this range of neutralization the behavior of the molecules of PMA is independent of whether they are free in solution or crosslinked in the gel.

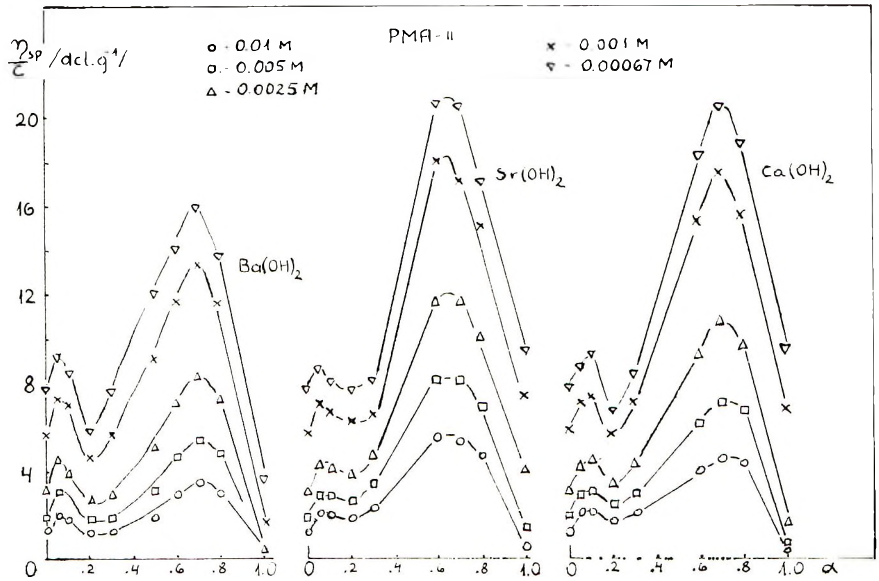

Fig. 2. Dependence of η_{sp}/c of PMA-II solutions at various concentrations on degree of neutralization with the barium, strontium, and calcium hydroxides.

The reduced viscosity of polyelectrolyte solutions was related to concentration by Fuoss.[21] His empirical relation was also successfully applied for the solution of PMA neutralized with NaOH.[22] The application of this relation in the present paper gave negative values of intrinsic viscosities of PMA neutralized with $Me(OH)_2$ (Me = Ba, Sr, or Ca). Similarly, Terayama[4] found that intrinsic viscosities of aqueous solutions of potassium cellulose sulfate in the presence of $BaCl_2$ become negative.

It was found that intrinsic viscosities may be obtained by the use of a relation similar to that proposed by Markowitz and Kimball[23] for poly(acrylic acid) (PAA) in the presence of salt and by Schaefgen[24] for polyamides in formic and sulfuric acids:

$$z = \eta_{sp}/c = A/(1 + Bc) + D \tag{1}$$

where c is the concentration in grams per deciliter and A, B, and D are characteristic constants.

From this relation we see that for $c = 0$ the reduced viscosity becomes equal to $A + D$. That may be regarded as the intrinsic viscosity.

For three different concentrations we obtain three different equations of this kind with three unknown constants. The solution of those equations gives the A, B, and D constants. They may also be found in the manner described by Fuoss.[25] From eq. (1) we may write

$$1/y = (1/A) + (Bc/A) \tag{2}$$

where $y = z - D$.

By the method of trial and error a proper value for D may be chosen for which a plot of $1/y$ versus c becomes linear; the A and B constants may then be determined from the slope and intercept. Both methods give the same values for A, B, and D. Some results of the determinations are shown in Table I. Figure 3 shows plots of $1/y$ versus c and z versus c.

TABLE I

Results of Viscosity Measurements of PMA-I Neutralized with $Me(OH)_2$

Hydroxide	α	A	B	D	A+D
$Ba(OH)_2$	0.05	2.26	243.0	0.34	2.60
	0.2	1.68	125.6	0.16	1.84
	0.3	3.00	234.0	0.17	3.17
	0.4	3.39	234.0	0.18	3.57
	0.5	5.63	220.0	0.17	5.80
	0.6	5.49	110.0	0.22	5.71
	0.7	5.02	95.3	0.40	5.42
	0.8	4.80	87.4	0.30	5.10
$Sr(OH)_2$	0.5	6.33	125.3	0.55	6.88
	0.6	6.42	84.7	0.65	7.07
	0.7	5.48	77.3	0.65	6.13
$Ca(OH)_2$	0.6	5.67	124.7	0.40	6.07
	0.7	5.92	102.5	0.45	6.37
	0.8	5.13	97.5	0.45	5.58

Figures 4 and 5 show the changes of the specific conductance $\varkappa$ of PMA neutralized with $Me(OH)_2$ at various concentrations. We see a pronounced minimum near $\alpha = 0.2$ and a maximum near $\alpha = 0.7$. This phenomenon does not appear when PMA is neutralized with alkali metal or quaternary ammonium bases.[19] In those cases the specific conductance passes through a small minimum near $\alpha = 0.05$ and then gradually increases with α.

Figures 6 and 7 present the equivalent conductances Λ of PMA for $\alpha = 0.1$ and 0.7 as a function of c (in equivalents of counterions per liter). The Λ–c plots exhibit a dependence of conductance on the molecular weight of PMA and a kind of a base used. We see that the lower the molecular weight of PMA, the higher the values of conductances and that for the samples of PMA of higher molecular weight (PMA-II and PMA-III) the conductances have nearly the same values. A similar dependence of conductance of PMA neutralized with alkali metal bases on molecular weight was found by Eisenberg.[26] In Figures 4–7 we find that, in spite of the limiting conductance of the counterions when PMA is neutralized with $Sr(OH)_2$, the conductance is higher than with $Ba(OH)_2$ or $Ca(OH)_2$. This is in accordance with the higher values of the reduced viscosities of these solutions.

In Figures 5–7 we may compare the conductance of PMA neutralized with NaOH and $Me(OH)_2$. For $\alpha = 0.1$ the conductances obtained with NaOH are about twice as high as those obtained with $Me(OH)_2$, but for $\alpha =$

0.7 they are about fourfold higher. The slight changes of conductance of PMA neutralized with $Me(OH)_2$ and viscometric results indicate that the number of free divalent counterions is lower than that of sodium ions.

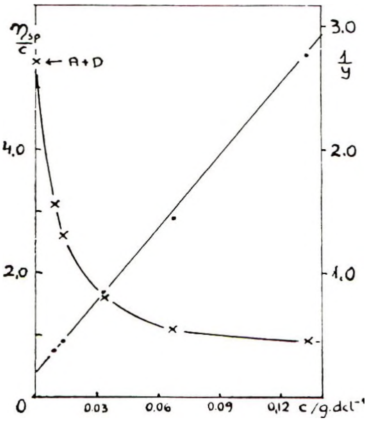

Fig. 3. Dependence of η_{sp}/c (left ordinate scale) on concentration c and $1/y$ (right ordinate scale) on c for PMA-I neutralized with $Ba(OH)_2$ at $\alpha = 0.7$ (Cf. Table I).

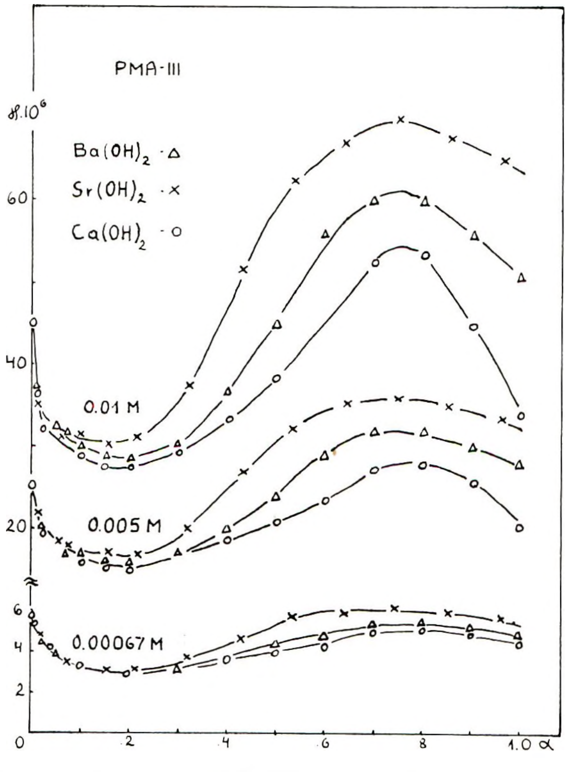

Fig. 4. Specific conductance $\varkappa$ of PMA-III at various concentrations vs. degree of neutralization with the barium, strontium, and calcium hydroxides.

That means that a large fraction of the barium, strontium, and calcium counterions have to be firmly bound up with the polyanions. The behavior of PMA is undoubtedly related to this association.

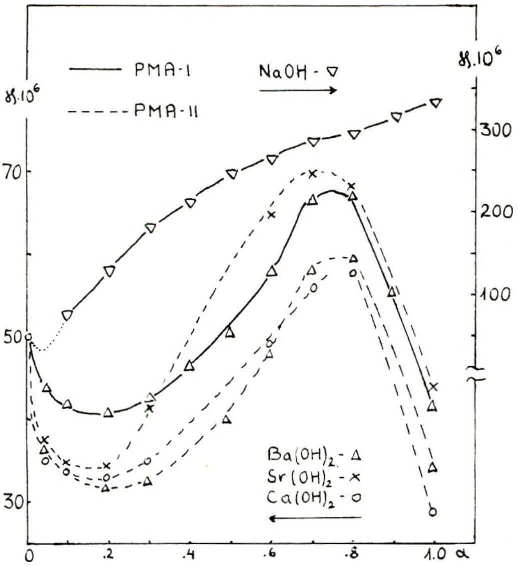

Fig. 5. Specific conductance of PMA-I and PMA-II at 0.01M solutions vs. degree of neutralization with the barium, strontium, and calcium hydroxides (left ordinate scale) and with sodium hydroxide (right ordinate scale).

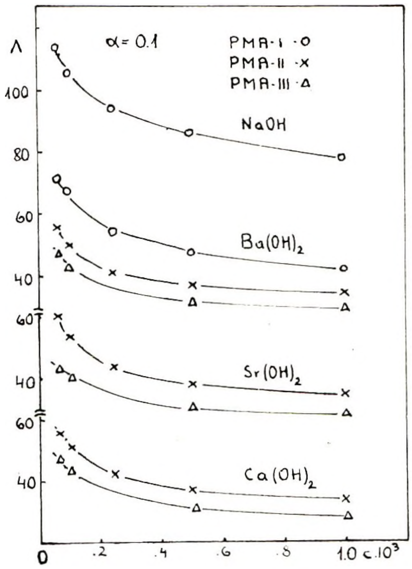

Fig. 6. Equivalent conductance Λ of PMA-I, PMA-II, and PMA-III at $\alpha = 0.1$ with the sodium, barium, strontium, and calcium hydroxides vs. concentration c (in equivalents of counterions per liter).

Gregor, Gold, and Frederick[19] defined the equivalent conductance of polysalts Λ_p in terms of its fractional charge Z

$$\Lambda_p = Z(\lambda_+{}^0 + \lambda_-{}^0) \tag{3}$$

where $\lambda_+{}^0$ and $\lambda_-{}^0$ are the limiting conductance of the counterion and polyanion, respectively. Then combining the viscometric and conductometric measurements they calculated Z from the expression

$$AZ^2/(\eta_{sp})^{1/3} + Z\lambda_+{}^0 - \Lambda_p = 0 \tag{4}$$

using experimental data for η_{sp} and Λ_p.

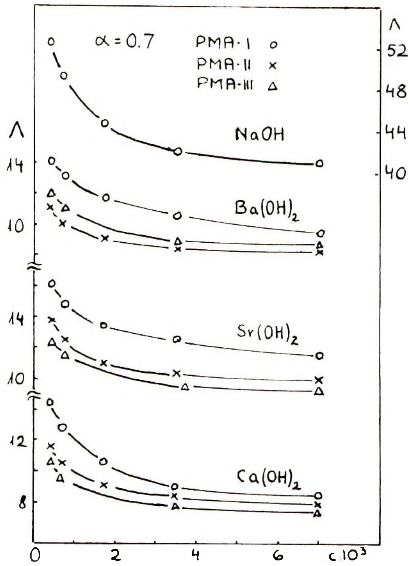

Fig. 7. Equivalent conductance of PMA-I, PMA-II, and PMA-III at degree of neutralization $\alpha = 0.7$ with the barium, strontium, and calcium hydroxides (left ordinate scale) and with sodium hydroxide (right ordinate scale) vs. concentration c (in equivalents of counterions per liter).

Because of smaller changes of the sizes of molecules of PMA neutralized with $Me(OH)_2$ than those observed with MeOH, the application of eq. (4) in the present paper seems to be still more appropriate. The fractional charge was therefore calculated according to Gregor et al. The value of A was evaluated by setting $Z = \alpha$ at low values of degree of neutralization of PMA-I with NaOH. As the value of A is assumed constant in the whole range of neutralization with NaOH we may assume that it will be suitable for the calculation of Z with neutralization of PMA with $Me/OH)_2$.

Figure 8 shows that the fractional charge of polymethacrylate ions in $0.01M$ PMA neutralized with $Me(OH)_2$ changes from 0.04 to 0.11. In Figure 8*a* the curve obtained at $0.01M$ PMA-I neutralized with $Ba(OH)_2$ may be compared with that obtained with NaOH. The latter is almost

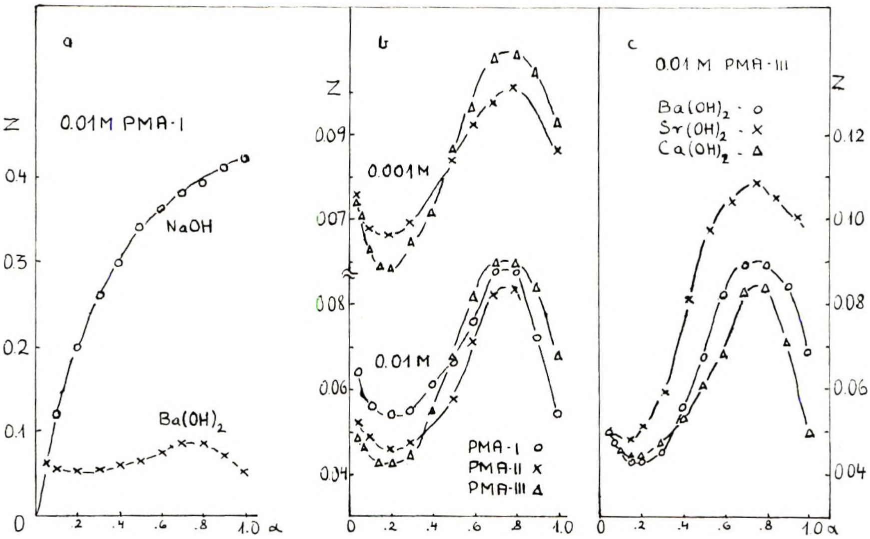

Fig. 8. Fractional charge Z of PMA vs. degree of neutralization for (*a*) $0.01M$ PMA-I neutralized with the barium and sodium hydroxides; (*b*) $0.01M$ and $0.001M$ PMA-I, PMA-II, and PMA-III neutralized with barium hydroxide; (*c*) $0.01M$ PMA-III neutralized with the barium, strontium, and calcium hydroxides.

identical with that of Gregor. The lower values of Z obtained with $Me(OH)_2$ are related to the enhanced association of divalent counterions. Figure 8*c* shows that, for given sample of PMA, Z is the highest with $Sr(OH)_2$ and the lowest with $Ca(OH)_2$. In all cases we observe the minimum of Z near $\alpha = 0.2$. Figure 8*b* shows that this minimum is the larger the higher molecular weight of PMA. Figure 8*b* shows the values of Z at $0.01M$ and $0.001M$ PMA neutralized with $Ba(OH)_2$. The increase of Z with dilution is in line with Wall's results with PAA and NaOH[27] as well as with PAA and $Sr(OH)_2$.[14] The results presented here may be especially compared with the results of the latter. Wall and Eittel studied more concentrated solutions (0.02–$0.1M$), so they were able to perform measurements only up to $\alpha = 0.25$ because of gel formation. Values obtained for PMA-II and $Sr(OH)_2$ are quite similar to those presented by Wall and Eittel for PAA ($M = 215{,}000$) in the same range of α. The charge fraction at $0.0736M$ PAA and 25°C. increases gradually from 0.0443 to 0.0701 at $\alpha = 0.05$ and 0.25, respectively. The fractional charge of PMA is higher, and a minimum was observed. This difference may be attributed to the characteristics of PMA and to the lower concentration of PMA solutions.

From the low numerical values of Z we may conclude that in almost the whole range of α about 90% of divalent counterions are associated with polyanions.

The differences in the behavior of PMA neutralized with NaOH and $Me(OH)_2$ we observed occurred in the range of α (0.2) in which other peculiar changes have been noted. Recently Leyte and Mandel[28] described the potentiometric behavior of PMA in terms of a conformational transition. The transition region they observed was also near $\alpha = 0.2$. The peculiar changes observed by the other investigators during viscometric, diffusion, and potentiometric measurements were also cited there.

The potentiometric behavior of PMA neutralized with $Me(OH)_2$ will be discussed in a later paper.

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References

1. Flory, P. J., and J. E. Osterheld, *J. Phys. Chem.*, **58,** 653 (1954).
2. Schneider, N. S., and P. Doty, *J. Phys. Chem.*, **58,** 762 (1954).
3. Inagaki, H., H. Sakurai, and T. Oda, *Bull. Inst. Chem. Res., Kyoto Univ.*, **33,** 257 (1955).
4. Terayama, H., *J. Polymer Sci.*, **15,** 575 (1955).
5. Buchner, P., R. E. Cooper, and A. Wassermann, *J. Chem. Soc.*, **1961,** 3974.
6. Inagaki, H., S. Hotta, and M. Hirami, *Makromol. Chem.*, **23,** 1 (1957).
7. Katchalsky, A., and P. Spitnik, *J. Polymer Sci.*, **2,** 432 (1947).
8. Michaeli, J., *J. Polymer Sci.*, **48,** 291 (1960).
9. Imai, N., *J. Phys. Soc. Japan*, **16,** 746 (1961).
10. Ikegami, A., and N. Imai, *J. Polymer Sci.*, **56,** 133 (1962).
11. Kagawa, I., and K. Katsuura, *J. Polymer Sci.*, **7,** 89 (1951).
12. Kargin, V., S. Mirlina, V. Kabanov, and G. Micheleva, *Vysokomolekul Soedin.*, **3,** 139 (1961).
13. Wall, F. T., and J. W. Drenan, *J. Polymer Sci.*, **7,** 83 (1951).
14. Wall, F. T., and M. J. Eittel, *J. Am. Chem. Soc.*, **79,** 1550, 1556 (1957).
15. Wojtczak, Z., *Chem. Anal.*, **6,** 587 (1961).
16. Wojtczak, Z., *J. Polymer Sci.*, **B2,** 661 (1964).
17. Katchalsky, A., and H. Eisenberg, *J. Polymer Sci.*, **6,** 145 (1951).
18. Jones, G., and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55,** 1780 (1933).
19. Gregor, H. P., D. H. Gold, and M. Frederick, *J. Polymer Sci.*, **23,** 467 (1957).
20. Katchalsky, A., and M. Zwick, *J. Polymer Sci.*, **16,** 221 (1955).
21. Fuoss, R. M., *J. Polymer Sci.*, **3,** 603 (1948).
22. Oth, A., and P. Doty, *J. Phys. Chem.*, **56,** 43 (1952).
23. Markowitz, H., and G. E. Kimball, *J. Colloid Sci.*, **5,** 115 (1950).
24. Schaefgen, J. R., and C. F. Trivisonno, *J. Am. Chem. Soc.*, **74,** 2715 (1952).
25. Fuoss, R. M., and G. J. Cathers, *J. Polymer Sci.*, **4,** 97 (1949).
26. Eisenberg, H., *J. Polymer Sci.*, **30,** 47 (1958).
27. Huizenga, J. R., P. F. Griegier, and F. T. Wall, *J. Am. Chem. Soc.*, **72,** 2636 (1950).
28. Leyte, J. C., and M. Mandel, *J. Polymer Sci.*, **A2,** 1879 (1964).

Résumé

On a étudié le comportement viscosimétrique et conductimétrique de l'acide polyméthacrylique en solutions aqueuses diluées dans tout le domaine de neutralisation avec les hydroxydes de baryum, de strontium, et de calcium. Les résultats montrent un minimum de viscosité réduite et de conductivité pour un degré de neutralisation situé aux environs de 0,2 et de 1,0. Ces minima n'apparaissent pas avec les bases monovalentes et se rapportent à un degré plus élevé d'association des polymères avec les contre-ions divalents qu'avec les ions monovalents. D'après la charge fractionnelle des polyanions, nous pouvons conclure que environ 90% de contre-ions divalents est associé avec les polyanions dans à peu près tout le domaine de neutralisation. Les résultats montrent l'influence spécifique des cations strontium sur le comportement de solutions de PMA.

Zusammenfassung

Das viskosimetrische und konduktometrische Verhalten von Polymethacrylsäure wurde in verdünnter wässriger Lösung im ganzen Neutralisationsbereich mit Barium, Strontium und Kalziumhydroxyd untersucht. Die Ergebnisse zeigen ein Minimum für die reduzierte Viskosität und die Leitfähigkeit in der Nähe des Neutralisationsgrades 0,2 und 1,0. Die Minima treten nicht mit enwertigen Basen auf und stehen zu dem höheren Assoziaitionsgrad der Polyänionen mit zweiwertigen Gegenionen in Vergleich zu den einwertigen Ionen in Beziehung. Aus dem Ladungsbrüchteil der Polyanionen kann man schliessen, dass etwa 90% der zweiwertigen Gegenionen fast im gesamten Neutraliationsbereich mit Polyanionen assoziiert sind. Die Ergebnisse zeigen einen spezifischen Einfluss von Strontiumkationen auf das Verhalten von PMA-Lösungen.

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Thioureas and Isothiuronium Salts. Polymeric Derivatives

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Synopsis

A series of derivatives of *N*-(*p*-vinylphenyl)thiourea were found to be capable of free radical polymerization. *N*-(*p*-Vinylphenyl)-*N'*-methylthiourea was copolymerized with *p*-aminostyrene, *p*-*N*,*N*-dimethylaminostyrene, and *N*-vinyl-phthalimide. *S*,*N*-Dimethyl-*N*-(*p*-vinylphenyl) isothiuronium iodide was also polymerized in a similar fashion. *p*-Vinylphenyl isothiocyanate was found to undergo polymerization with difficulty. The latter polymer was reacted with dimethylamine to yield the polymeric thiourea.

INTRODUCTION

A great majority of the polymeric thioureas reported in the literature are those whose backbones are composed of thiourea linkages. These have been prepared principally by two methods: (*a*) by the reaction of organic diamines with carbon disulfide and (*b*) by the reaction of diamines with diisothiocyanates. Examples of the former type are the plastic polymeric thioureas formed from carbon disulfide and diamines having greater than three carbon atoms.[1] Examples of the latter type are the polymers prepared by the condensation of polymethylene diisothiocyanates with polymethylene diamines.[2] An example of the polythiourea in which the thiourea linkage is present as a side chain is that prepared by the reaction of polyvinylamine with phenyl isothiocyanate.[3]

Polymeric isothiuronium salts, in which either the main chain or the side chain is composed of isothiuronium units, have also been prepared. Linear polymeric isothiuronium salts have been synthesized by the reaction of a primary dihalide with a thiourea.[4] Examples of polymeric isothiuronium salts in which the functional group is present on the side chain are those of Izard and Morgan,[5] Nakamura,[6] Okawara et al.,[7] and Arcus and Salomons.[8]

Polymeric isothiuronium salts have found use in the preparation of ion-exchange resins. Such a resin has been prepared by treating a poly(vinyl alcohol) solution with thiourea in an acid medium. Subsequent reaction with formaldehyde yielded a water-insoluble anion-exchange resin.[9] Similar resins have been prepared by the treatment of chloromethylated polystyrene and copolymers of styrene and divinylbenzene, with thiourea.[10,11] Parrish,[12] using a similar procedure, hydrolyzed the polyisothiuronium salt formed as an intermediate to yield a polythiol resin.

A study[13] of the polymerizability of *N*-vinyl derivatives of ureas and carbamates has produced interesting results. *N*-Vinylurea, a white crystalline solid, was prepared by the action of anhydrous ammonia on vinyl isocyanate. It was found that unsubstituted and *N*′-alkyl-substituted-*N*-vinylureas polymerized with relative ease by free radical means. However, the polymerizability of the unsubstituted compound was found to be low. A cryoscopic molecular weight determination of the polymer in urethane gave a molecular weight of 700–1100. This conforms to a structure of an oligomer having a degree of polymerization of ca. 10. The *N*-vinylcarbamates synthesized were also found to be capable of polymerization.

Surprisingly, it was found that aryl substitution of an amido hydrogen on the urea or carbamate in question completely hindered the polymerization. Alkyl groups had no noticeable effect in this fashion. For example, *N*-vinyl-*N*′-ethylurea was found capable of undergoing polymerization, whereas the corresponding phenyl derivative did not polymerize.

A second complicating factor was found to be the presence of a thiono sulfur group. The *N*-vinylthioureas are colorless, crystalline substances, whereas the *N*-vinylthionocarbamates are colorless, viscous, distillable liquids. Interestingly, both were found to be incapable of polymerization.[13] An examination of the infrared spectra of these compounds indicated the presence of a vinyl group. It is of further interest that *N*-vinylcarbamates as well as *N*-vinylthiocarbamates were found to be capable of undergoing polymerization. However, all thiono compounds prepared did not show this property.

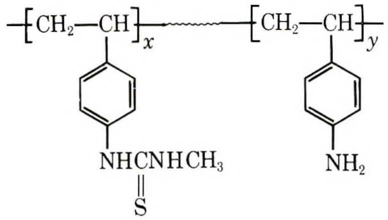
RESULTS AND DISCUSSION

Two methods by which it would be expected that polymeric derivatives of *p*-vinylphenylthiourea would be capable of preparation are by either the reaction of poly(*p*-vinylphenyl isothiocyanate) with an amine or the polymerization of the monomeric thiourea. An example of the former method is afforded in the urea series by Manecke and Singer.[14] They reacted poly-*p*-aminostyrene with phosgene to obtain the polymeric isocyanate. The isocyanate, upon reaction with di-*n*-butylamine afforded the polymeric urea.

An example of the latter procedure is the work of Hankins and Melamed,[15] who reported the preparation and polymerization of a number of acrylamide derivatives of *N*-aminoalkylthioureas. The polymerizations were carried out in *N*,*N*-dimethylformamide as the solvent with the use of a free-radical initiator. However, the analyses of the polymers were not completely satisfactory.

It was decided to attempt to apply the second procedure to the synthesized thioureas in order to obtain polymers thereof. *N*-(*p*-Vinylphenyl)-*N*′-methylthiourea was dissolved in *N*,*N*-dimethylformamide along with α,α'-azobisisobutyronitrile as a polymerization initiator. The solution, sealed under vacuum in a polymerization tube, was heated at 65°C. for a period of 16 hr. The polymer was precipitated from the solution in a 75% yield by dropwise addition to methanol. An intrinsic viscosity of the compound gave a value of 0.19. However, an infrared spectrum of the compound showed an unexpected peak at 1650 cm.$^{-1}$. This was attributed to the dimethylamide group from solvent chain transfer.

Under similar conditions the thiourea was copolymerized with *p*-aminostyrene, *p*-*N*,*N*-dimethylaminostyrene, and *N*-vinylphthalimide. All reactants were present in a 1:1 molar ratio. In the first two instances the solution turned deep blue during the course of the polymerization. This color did not appear in the copolymerization of the thiourea with *N*-vinylphthalimide. The copolymers with *p*-aminostyrene, *p*-*N*,*N*-dimethylaminostyrene, and *N*-vinylphthalimide (structures I, II, and III, respectively) gave intrinsic viscosities of 0.17, 0.12, and 0.13, respectively. The values for y/x shown in the structures were 1.6, 0.8, and 0.7, respectively.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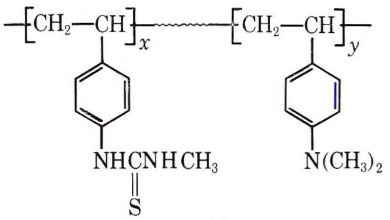
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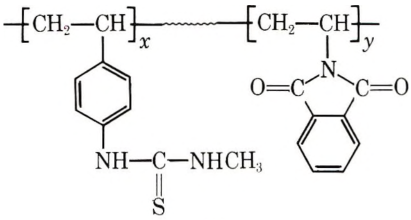
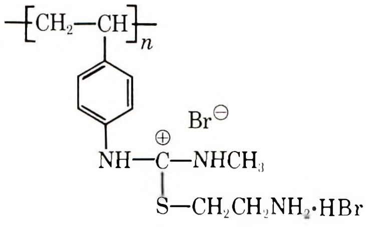

III

Since all polymers prepared in *N*,*N*-dimethylformamide exhibited absorption at 1650 cm.$^{-1}$, it was desirable to find a solvent capable of dissolving the monomers but giving a negligible amount of solvent chain transfer. Ethanol and benzene were poor solvents, but dimethyl sulfoxide satisfied both requirements. Thus an infrared spectrum of poly[*N*(*p*-vinylphenyl)-*N'*-methylthiourea] formed in dimethyl sulfoxide solution showed the same absorbances as that from *N*,*N'*-dimethylformamide except for peaks attributable to solvent chain transfer. In addition, the conversion yield was 80% with an intrinsic viscosity of 0.36 and a polymer melt temperature[16] of ca. 150°C.

With dimethyl sulfoxide as the solvent, the two other monomeric thioureas were polymerized. Poly *N*-(*p*-vinylphenyl)thiourea was isolated in a 78% yield. It had a polymer melt temperature of ca. 185°C. The intrinsic viscosity could not be determined, since the polymer was difficultly soluble in common organic solvents. Poly[*N*-(*p*-vinylphenyl)-*N′*,*N′*-dimethylthiourea] was isolated in a 73% yield. It had an intrinsic viscosity of 0.27 and a polymer melt temperature of greater than 300°C.

N-(*p*-Vinylphenyl)-*N′*,*S*-dimethylisothiuronium iodide was polymerized in *N*,*N*-dimethylformamide under conditions similar to those used for the thiourea. Once again, an infrared absorption spectrum of the polymer indicated solvent chain transfer. The polymer was isolated as a hygroscopic yellow solid in a yield of 86%. An intrinsic viscosity determination in a solution of potassium iodide in *N*,*N*-dimethylformamide yielded a value of 0.19. Attempts to polymerize the two other isothiuronium salts in dimethyl sulfoxide failed.

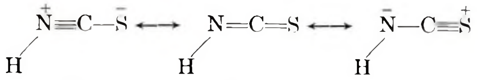
Poly[*N*-(*p*-vinylphenyl)-*N′*-methylthiourea] was reacted with β-bromoethylamine hydrobromide to give poly[*S*-2-aminoethyl-*N*-(*p*-vinylphenyl)-*N′*-methylisothiuronium bromide hydrobromide] (IV) in 42.9% yield.



IV

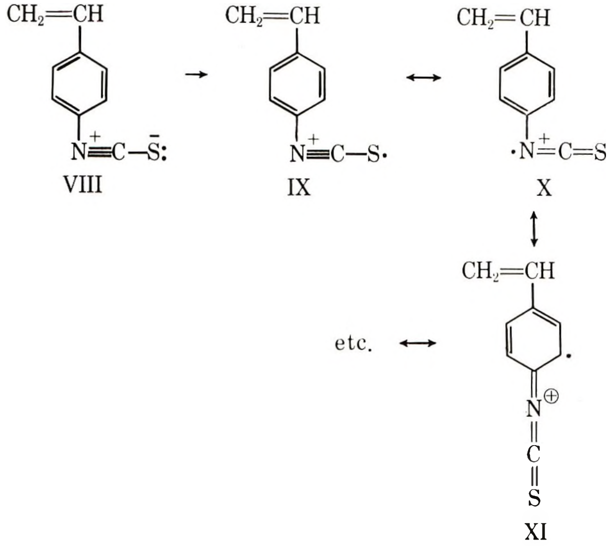
It was desired to prepare and study the properties of poly(*p*-vinylphenyl isothiocyanate). The monomer was dissolved in benzene and subjected to free-radical polymerization conditions. However, very surprisingly, only a very viscous oil was formed. The polymer was dissolved in *N*,*N*-dimethylformamide and precipitated from methanol to give a low molecular weight polymer in a yield of 31%. An infrared spectrum indicated the presence of the isothiocyanate linkage in the polymer by exhibiting a very strong absorption at 2110 cm.$^{-1}$. An intrinsic viscosity of 0.08 indicated the material to be an oligomer. The polymer was added to anhydrous dimethylamine and allowed to react in a heterogeneous phase. An analysis of the product demonstrated the conversion of the isothiocyanate to the thiourea to be nearly quantitative. An infrared spectrum of the polymer indicated the same results.

In attempting to understand the possible reasons for the low polymerizability of the monomer, the structure of the isothiocyanate linkage must be examined. Recent investigations[17,18] on free isothiocyanic acid have established that this species is a resonance hybrid represented by structures V–VII. Structure VII makes the least contribution to the actual structure.



V VI VII

It is not unreasonable to assume that extensive chain transfer takes place through the sulfur atom, making formation of a high polymer very unlikely. In addition, if such a free radical were formed it would be stabilized by resonance in the aromatic system, as shown in VIII–XI.



EXPERIMENTAL

All monomers were prepared as described in a previous paper.[19] All analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of the Homopolymers

Poly-[*N*-(*p*-vinylphenyl)-*N*′-methylthiourea]. *N*-(*p*-vinylphenyl)-*N*′-methylthiourea (1.0 g.) was dissolved in 4.5 g. of dimethyl sulfoxide which had been purified by distillation under reduced pressure. α,α'-Azobisisobutyronitrile (8.9 mg., 0.89 wt.-%) was added to the solution. Oxygen was removed from the system by alternately freezing the solution in a Dry Ice–acetone mixture, evacuating the tube, and liquifying the contents under nitrogen. After repeating this procedure several times the tube was evacuated, while its contents were frozen, and sealed.

The solution was heated at 65°C. for 16.5 hr., after which the tube was cooled and opened. The polymer was precipitated by dropwise addition of the solution to ten times its volume of methanol. Dissolution of the polymer in a small quantity of dimethyl sulfoxide followed by a second precipitation of the polymer yielded 0.80 g. (80% conversion), after drying in vacuo.

The polymer was soluble in *N,N*-dimethylformamide and in dimethyl sulfoxide. It was insoluble in benzene and ethanol.

ANAL. Calcd. for $C_{10}H_{12}N_2S$: C, 62.46%; H, 6.29%; N, 14.57%; S, 16.68%. Found: C, 62.28%; H, 6.55%; N, 14.70%; S, 16.68%.

The polymer melt temperature[16] was found to be ca. 150°C. An intrinsic viscosity determination taken in *N*,*N*-dimethylformamide at 25.0°C. gave a value of 0.36.

Poly[*N*-(*p*-Vinylphenyl)thiourea]. *N*-(*p*-Vinylphenyl)thiourea (0.90 g., 0.005 mole) and α,α'-azobisisobutyronitrile (8.8 mg., 0.96 wt.-%) were dissolved in dimethyl sulfoxide (4.6 g.). The procedure for polymerization was essentially the same as that used in polymerization of *N*-(*p*-vinylphenyl)-N′-methylthiourea. The yield of polymer isolated was 0.70 g. (77.8% conversion).

The polymer was soluble in dimethyl sulfoxide but only partially soluble in *N*,*N*-dimethylformamide. It was insoluble in benzene and ethanol.

ANAL. Calcd. for $C_9H_{10}N_2S$: N, 15.72%; S, 17.99%. Found: N, 15.71%; S, 17.19%.

The polymer melt temperature was found to be ca. 185°C. The intrinsic viscosity was not determined due to solubility difficulties.

Poly[*N*-(*p*-Vinylphenyl)-*N*′,*N*′-dimethylthiourea]. *N*-(*p*-Vinylphenyl)-*N*,*N*-dimethylthiourea (1.1 g., 0.005 mole) and α,α'-azobisisobutyronitrile (8.6 mg., 0.78 wt.-%) were dissolved in dimethyl sulfoxide (4.7 g.). The procedure for polymerization was essentially the same as that used for the other polymerizations described above. The yield of polymer isolated was 0.80 g. (72.8% conversion).

The polymer was soluble in dimethyl sulfoxide and in *N*,*N*-dimethylformamide. It was insoluble in benzene and ethanol.

ANAL. Calcd. for $C_{11}H_{14}N_2S$: N, 13.58; S, 15.54%. Found: N, 13.38%; S, 15.73%.

The polymer melt temperature was found to be greater than 300°C. An intrinsic viscosity determination in *N*,*N*-dimethylformamide at 25.0°C. gave a value of 0.27.

Copolymers of *N*-(*p*-Vinylphenyl)-*N*′-methylthiourea

p-Aminostyrene was prepared and purified as described in a previous paper.[19]

p-Dimethylaminostyrene* was purified by a vacuum distillation, b.p. 103–104°C./4 mm.; $n_D^{22.5}$ 1.6006 (lit.:[20] b.p. 90–91°C./2.5–3 mm.; n_D^{20} 1.6010).

N-Vinylphthalimide (Monomer-Polymer Laboratory) was recrystallized from methanol to give a m.p. of 86–87°C.(lit.:[21] m.p. 86°C.).

α,α'-Azobisisobutyronitrile (Eastman Organic Chemicals) was recrystallized from ether to a m.p. of 105°C. (lit.:[22] m.p. 106°C.).

N,*N*-Dimethylformamide (Matheson, Coleman and Bell) was purified by a vacuum distillation. The middle fraction was used.

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* Sample received by the courtesy of Prof. Herbert Morawetz, Polytechnic Institute of Brooklyn.

Copolymer with *p*-Aminostyrene. *N*-(*p*-vinylphenyl)-*N*′-methylthiourea (1.92 g., 0.01 mole), *p*-aminostyrene (1.19 g., 0.01 mole), and α,α'-azobisisobutyronitrile (50.5 mg., 1.5 mole-%) were dissolved in 12.0 g. of *N*,*N*-dimethylformamide. The solution was added to a polymerization tube and sealed, *in vacuo*, after being deoxygenated. The deoxygenation was carried out by repeatedly flushing the solution with nitrogen and evacuating the tube. The sealed tube was heated at 65°C. for 16.5 hr. During the course of the polymerization the solution turned a deep blue color. Following this period the solution was added dropwise to 300 ml. of methanol. A white powder was isolated in a yield of 1.80 g. (57.9% conversion). The copolymer was purified by dissolution in *N*,*N*-dimethylformamide and reprecipitation from methanol. An infrared spectrum indicated the absence of vinyl groups. The polymer, when filtered, began turning yellow and had to be dried in a vacuum desiccator. The dry substance had a pink tinge. A peak at 1600 and at 1650 cm.$^{-1}$ in the infrared indicated the presence of an amino group and solvent chain transfer, respectively.

An elemental analysis for sulfur (8.25%) indicated the ratio of *p*-aminostyrene to the thiourea to be 1.6 units. The intrinsic viscosity at 25.0°C. in *N*,*N*-dimethylformamide was 0.17.

Copolymer with *p*-Dimethylaminostyrene. *N*-(*p*-Vinylphenyl)-*N*′-methylthiourea (1.92 g., 0.1 mole), *p*-dimethylaminostyrene (1.47 g., 0.01 mole), and α,α'-azobisisobutyronitrile (48.4 mg., 1.5 mole-%) were dissolved in 12.5 g. of *N*,*N*-dimethylformamide. The solution was deoxygenated and heated as in the copolymerization with *p*-aminostyrene. During the course of the polymerization a deep blue color developed in the polymerization tube. The solution did not yield a satisfactory precipitate from methanol, isopropanol, benzene, dioxane, or chloroform. The polymer apparently was soluble in these solvents to varying degrees. Precipitation was effected from 300 ml. of ether, yielding a yellow polymer in a yield of 1.30 g. (38.3% conversion). Unreacted monomer was separated from the polymer by extraction with refluxing methanol. The compound appeared to be very hygroscopic. However, after drying in a vacuum desiccator the material could be kept in air. An infrared spectrum indicated the absence of vinyl groups and the presence of an amide group from solvent chain transfer.

An elemental analysis for sulfur (10.32%) indicated the ratio of monomer units of *p*-dimethylaminostyrene to the thiourea to be 0.8. An intrinsic viscosity determination at 25.0°C. in *N*,*N*-dimethylformamide gave a value of 0.12.

Copolymer with *N*-Vinylphthalimide. *N*-(*p*-Vinylphenyl)-*N*′-methylthiourea (1.92 g., 0.01 mole), *N*-vinylphthalimide (1.73 g., 0.01 mole), and α,α'-azobisisobutyronitrile (45.9 mg., 1.4 mole-%) were dissolved in 12.5 g. of *N*,*N*-dimethylformamide. The polymerization was carried out as in the previous procedures. Precipitation of the polymer from 300 ml. of methanol gave a light yellow substance in a yield of 1.95 g. (53.4% conversion). It was purified by dissolution in *N*,*N*-dimethylformamide and reprecipitation from methanol. A peak at 1680 cm.$^{-1}$ indicated the amide linkage. Solvent chain transfer was once again indicated by a peak at 1650 cm.$^{-1}$.

An elemental analysis for sulfur (10.48%) indicated the ratio of *N*-vinylphthalimide to the thiourea to be 0.7 units. The intrinsic viscosity 25.0°C. in *N*,*N*-dimethylformamide was 0.13.

Other Polymers

Poly[*N*-(*p*-Vinylphenyl)-*N'*,*S*-dimethylisothiuronium Iodide]. *N*-(*p*-Vinylphenyl)-*N'*,*S*-dimethylisothiuronium iodide (1.68 g., 0.005 mole) was dissolved in *N*,*N*-dimethylformamide. α,α'-Azobisisobutyronitrile (19.3 mg., 2.4 mole-%) was added to a polymerization tube, deoxygenated as described in a previous procedure, and sealed. The tube was heated for 16.5 hr. at 65°C. The yellow polymer was isolated by precipitation from acetone, in a yield of 1.45 g. (86.3% conversion). It was found to be extremely hygroscopic. However, if the wet polymer was put into a vacuum desiccator and a high vacuum applied immediately, the compound thus dried appeared to be stable in air. An infrared spectrum indicated solvent chain transfer by absorption at 1650 cm.$^{-1}$. A polymer structure was also indicated by the disappearance of the vinyl group absorption in the infrared.

ANAL. Calcd. for $C_{11}H_{15}IN_2S$: C, 39.53%; H, 4.52%; N, 8.38%; S, 9.59%; Found: C, 39.42%; H, 4.80%; N, 8.46%; S, 9.44%.

An intrinsic viscosity determination in a 0.5% solution of potassium iodide in *N*,*N*-dimethylformamide at 25.0°C. gave a value of 0.19.

Poly[*S*-(2-Aminoethyl)-*N*-(*p*-vinylphenyl)-*N'*-methylisothiuronium Bromide Hydrobromide]. Poly[(*N*-*p*-vinylphenyl)-*N'*-methylthiourea] (0.85 g., 0.04 mole), and β-bromoethylamine hydrobromide (1.30 g., 0.06 mole) were reacted in *N*,*N*-dimethylformamide for 3 hr. at 100°C. During the course of the reaction two layers developed in the solution. After the reaction was completed, the solution was transferred into a semipermeable membrane and dialyzed for two days in distilled water. At the end of this time a test for bromide anion in the water proved negative. The polymer, a white solid, was isolated by freeze drying the aqueous solution from the membrane; yield 0.75 g. An analysis for Br (17.27%) indicated the desired conversion had taken place to a degree of 49.2%.

Poly(*p*-vinylphenyl Isothiocyanate). *p*-Vinylphenyl isothiocyanate (4.80 g., 0.026 mole) and α,α'-azobisisobutyronitrile (31.1 mg., 0.73 mole-%) were dissolved in benzene. The solution was deoxygenated as described in a previous procedure and sealed in a polymerization tube. The tube was heated at 65°C. for 30 hr. At the end of this time a viscous orange oil had settled out of the solution. The polymer was isolated by dissolving the oil in *N*,*N*-dimethylformamide and precipitating the polymer from methanol, 1.5 g. (31.2% conversion). Repetition of this process yielded an analytical sample.

ANAL. Calcd. for C_9H_7NS: N, 8.69%; S, 19.89%. Found: N, 8.67%; S, 20.11%.

An intrinsic viscosity determination in *N*,*N*-dimethylformamide at 25.0°C. yielded a value of 0.08. An infrared absorption spectrum indicated the isothiocyanate linkage by a very strong absorption at 2110 cm.$^{-1}$.

Reaction of Poly(*p*-vinylphenyl Isothiocyanate) with Dimethylamine. Poly(*p*-vinylphenyl isothiocyanate) (1.19 g., 0.01 mole) was added to a large excess of anhydrous, liquid dimethylamine. The mixture was stirred at room temperature for 7 hr. A Dry Ice condenser equipped with a drying tube prevented the amine from evaporating and prevented moisture from condensing inside the reaction flask. The yield of polymer isolated was 0.56 g. An analysis indicated nearly a quantitative conversion of the isothiocyanate to the thiourea.

ANAL. Calcd. for $C_{11}H_{14}N_2S$: N, 13.58%. Found: N, 13.25%.

An infrared spectrum of the polymer showed just very weak absorption in the isothiocyanate region (2110 cm.$^{-1}$).

The authors wish to thank Messrs. Harold Edelstein and Donald Sussman for taking the infrared spectra. Support from the Office of the Surgeon General of the United States Army under Contract No. DA-49-193-MD-2032 is also gratefully acknowledged.

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References

1. Courtaulds, Ltd., Brit. Pat. 524,795 (1940).
2. Hoshino, J., Y. Iwakura, and S. Komatsu, *Kobunshi Kagaku*, **2,** 320 (1945).
3. Blomquist, A. T., W. J. Tapp, and John R. Johnson, *J. Am. Chem. Soc.*, **67,** 1519 (1945).
4. Hunt, M., U. S. Pat. 2,347,827 (1944).
5. Izard, E. F., and P. W. Morgan, *Ind. Eng. Chem.*, **41,** 617 (1949).
6. Nakamura, Y., *Kogyo Kagaku Zasshi*, **58,** 269 (1955).
7. Okawara, M., T. Nagakawa, and E. Imoto, *Kogyo Kagaku Zasshi*, **60,** 73 (1957).
8. Arcus, C. L., and N. S. Salomons, *J. Chem. Soc.*, **1963,** 1175.
9. Cerny, J., and O. Wichterle, Brit. Pat. 796,457 (1958).
10. Cerny, J., and O. Wichterle, *J. Polymer Sci.*, **30,** 50 (1958).
11. Cerny, J., and O. Wichterle, Ger. Pat. 1,043,633 (1958).
12. Parrish, J. R., *Chem. Ind. (London)*, **1956,** 137.
13. Welzel, G., Ph.D. Thesis, Albert-Ludwigs Universitat zu Freiberg i. Br. (Germany), 1960; *Makromol. Chem.*, **31,** 230 (1959).
14. Manecke, G., and S. Singer, *Makromol. Chem.*, **37,** 119 (1960).
15. Hankins, E. M., and S. Melamed, U. S. Pat. 2,727,016 (1955).
16. Sorenson, W. R., and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 49.
17. Beard, C. I., and B. P. Bailey, *J. Chem. Phys.*, **15,** 762 (1947).
18. Jones, L. H., and R. M. Badger, *J. Chem. Phys.*, **18,** 1511 (1950).
19. Overberger, C. G., and H. A. Friedman, *J. Org. Chem.*, **30,** 1926 (1965).
20. Marvel, C. S., C. G. Overberger, R. E. Allen, and J. H. Saunders, *J. Am. Chem. Soc.*, **68,** 736 (1946).
21. Bachstez, M., *Ber.*, **46,** 3087 (1913).
22. Thiele, J., and K. Heuser, *Ann.*, **290,** 1 (1896).

Résumé

On a trouvé que toute une série de dérivés de la *N*(*p*-vinylphényl) thiourée pouvaient polymériser radicalairement. On a copolymérisé la *N*-(*p*-vinylphényl)-*N*-méthyl-thiourée avec le *p*-aminostyrène, le *p*-*N*,*N*-diméthylaminostyrène et la *N*-vinylphthalimide. L'iodure de *N*-diméthyl-*N*-(*p*-vinylphényl)isothiourée a été polymérisé de la même façon. D'autre part on a trouvé que le *p*-vinylphénylisothiocyanate ne polymérisait que difficilement. On a fait réagir ce dernier polymère avec la diméthylamine pour donner la thiourée polymérique.

Zusammenfassung

Eine Reihe von *N*-(*p*-Vinylphenyl)thioharnstoffderivaten konnte radikalisch zur Polymerisation gebracht werden. *N*-(*p*-Vinylphenyl)-*N*-methylthioharnstoff wurde mit *p*-Aminostyrol, *p*-*N*,*N*-Dimethylaminostyrol und *N*-Vinylphthalimid kopolymerisiert. *S*,*N*-Dimethyl-*N*-(*p*-vinylphenyl)isothiuroniumjodid wurde ebenfalls in ähnlicher Weise polymerisiert. *p*-Vinyl-phenylisothiocyanat konnte nur schwierig zur Polymerisation gebracht werden. Das Polymere reagiert mit Dimethylamin unter Bildung des polymeren Thioharnstoffs.

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High Energy Electron Irradiation of Trihydroperfluoroalkyl Acrylate Monomers: Statistical Evaluation of Factor Interdependency

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Synopsis

A 2,2,2,2-factorial design was used for the irradiation-induced polymerization of 1,1,3-trihydroperfluoropropyl and 1,1,7-trihydroperfluoroheptyl acrylates with a 2-M.e.v. electron accelerator in order to more critically determine the effect of variables. From the data obtained, it is concluded that: (*1*) degassing, flame-out, and time-lapse are significant, dependent main effects for both monomers, and atmosphere is a significant, dependent main effect for the heptyl ester, (*2*) the atmosphere and flame-out, degassing and time-lapse, and flame-out and time-lapse interactions are independently significant for the propyl ester, whereas for the heptyl ester the atmosphere and flame-out is independently significant, but degassing and flame-out, degassing and time-lapse, and flame-out and time-lapse are dependently significant, (*3*) the degassing, flame-out and time-lapse interaction is independently significant for the heptyl ester, and (*4*) experimental variables may be significantly interdependent.

Introduction

Experiments were designed to determine the effects of atmosphere, degassing, flame-out, and post-irradiation time-lapse on the irradiation-induced polymerization, with high energy electrons, of trihydroperfluoroalkyl acrylates.* The data were subjected to analyses by use of a factorial design. The results show that each of these four factors has a significant effect on the per cent polymerization per unit of radiation energy and that there are interdependencies of certain variables.

Previous studies in this laboratory have shown that the irradiation-induced polymerization of vinyl monomers is dependent, in general, on experimental variables[1] and that the specific effect of any variable is a function of the monomer system and other variables.

The rate of absorption of radiation energy and its effective utilization in polymerization thus become functions of the experimental variables. These factors determine the relative concentration of the initiating centers

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* The trihydroperfluoroalkyl acrylates were courteously supplied by E. I. du Pont de Nemours and Co., Wilmington, Delaware.

and the competition between initiation, propagation, termination, and radiolysis.

The efficiency of the reaction (per cent and type of polymer per unit of radiation energy) increases in general with a decrease in dose rate, with an increase in temperature, and with a decrease in oxygen[2] and moisture content of the system.[3] Predrying of the monomer with calcium hydride or another appropriate reagent, vacuum distillation of the monomer just prior to preparation of the samples, flame-out of the reaction tubes under vacuum before introduction of the monomer, and degassing of the monomer in the reaction tubes all serve to minimize the undesirable effects of moisture and oxygen.

Experimental Design

In this statistical study, samples of 1,1,3-trihydroperfluoropropyl and 1,1,7-trihydroperfluoroheptyl acrylates ($H_2C{=}CH{-}CO_2{-}CH_2{-}(CF_2)_n{-}CF_2H$, where $n = 1$ for the propyl and $n = 5$ for the heptyl ester) were irradiated under 16 combinations of four two-level variables (factorial design Tables I and II):[4-8] (*1*) a 1-day lapse versus a 30-day post-irradiation time-lapse before processing of the samples; (*2*) in an evacuated system versus in the presence of air; (*3*) with two degassings (DG) of the monomer in the reaction tubes versus no degassing; and (*4*) with three flame-outs (FO) of the reaction tubes prior to the introduction of the monomer versus no flame-outs.

TABLE I

Experimental Design and Data for 1,1,3-Trihydroperfluoropropyl Acrylate[a]

No.	Atmosphere	DG	FO	Conversion to polymer, %	
				1 day time-lapse	30 day time-lapse
1	Air	0	0	0.02, 0.04, 0.03	2.84,[b] 2.42, 3.30
2	"	0	3	0.05, 0.05, 0.04	2.91, 2.70, 3.21
3	"	2	0	0.05, 0.05, 0.04	0.02, 0.04, 0.02
4	"	2	3	0.06, 0.04, 0.04	1.55, 1.35, 1.55
5	Vacuum	0	0	0.04, 0.16, 0.02	0.01, 0.14,[b] 0.02
6	"	0	3	2.50, 2.45,[b] 2.39	3.29, 3.00, 3.58
7	"	2	0	0.02, 0.01, 0.01	0.02, 0.04, 0.03
8	"	2	3	0.02, 0.01, 1.24?	1.62, 1.61, 1.80

[a] Dose: one exposure at 3000 rad per pass at 25°C. with a conveyer speed of 93 in./min.

[b] Missing observation, average of other two.

There were three replications for each of the 16 combinations of variables. The polymer formation was determined by direct weighing of the nonvolatile portion of each sample, which was obtained by heating a methyl ethyl ketone solution of the reaction mixture on a hot plate at 65°C. to form a film of the polymer and then at 85°C. in a vacuum oven for 4 hr. to remove traces of occluded monomer and diluent.

TABLE II
Experimental Design and Data for 1,1,7-Trihydroperfluoroheptyl Acrylate[a]

No.	Atmosphere	DG	FO	Conversion to polymer, % 1 day time-lapse	Conversion to polymer, % 30 day time-lapse
1	Air	0	0	0.02, 0.01, 0.01	0.01, 0.01, 0.01
2	"	0	3	0.09, 0.08, 0.03	16.3, 14.9, 10.6[b]
3	"	2	0	0.10,[b] 0.05, 0.04	0.04, 0.04, 0.03
4	"	2	3	0.04, 0.04, 0.04	4.90, 4.20, 4.40
5	Vacuum	0	0	0.01, 0.02, 0.06	0.01, 0.01, 0.01
6	"	0	3	6.66, 6.11, 9.14[b]	19.0, 21.0, 20.6
7	"	2	0	0.05, 0.04, 0.06	0.05, 0.03, 0.04
8	"	2	3	3.45, 3.03, 3.62	9.3,[b] 12.85, 11.85

[a] Dose: one exposure at 3000 rads per pass at 25°C. with a conveyer speed of 93 in./min.

[b] Appear to diverge too much from mean.

This procedure is direct and simple provided that: (*1*) only about 20% or less of the monomer is polymerized, (*2*) glass reaction tubes are used so that complete removal of the polymer by the solvent can be observed by inspection with transmitted light, (*3*) the solvent and excess monomer is removed on a hot plate at about 65°C. to leave a dry film of the polymer in the aluminum weighing tray, and (*4*) the resulting product is then heated in a vacuum oven at about 85°C. for 4 hr.

The experimental design permitted testing for: the average effect of each variable and the interaction of each pair of variables, each combination of three, and each combination of four variables, thus providing the optimum data for the 16 combinations. The design also permitted analyses: to estimate the experimental error, to determine which effects are statistically significant, and to evaluate the quantitative risk of accepting a false effect (type 1 error).*

Procedure

The monomer was vacuum-distilled, dried in an argon atmosphere at about 5°C. over anhydrous potassium carbonate or another suitable drying reagent, and siphoned as needed into a 250 ml. glass-stoppered graduate, which was connected in turn to an automatic-leveling buret, through which a slow stream of argon flowed. The buret was filled from the graduate by use of slight argon pressure.

Sixteen 1 × 8 in. borosilicate test tubes, equipped with 12/30 ground-glass male joints with a constriction in the tubing for convenience in sealing, were placed on the vacuum manifold and flamed out (if required by the experimental design) three times at 5 μ and filled with argon to minimize diffusion of moisture and oxygen into the tubes. A 5-ml. portion of the

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* A type 1 error results from asserting that a real difference exists when there is no significant difierence in the results.[7b]

freshly vacuum-distilled and dried monomer was then transferred from the buret to each of the test tubes, which were replaced on the manifold.

Dewar flasks of liquid nitrogen were slowly raised by lab jacks to freeze the monomer. The manifold stopcocks were opened, and the tubes evacuated to about 100 μ with an auxiliary pump; then the manifold was opened to the regular vacuum system, and the pressure reduced to 5 μ. The stopcocks to the tubes were then closed, the Dewar flasks lowered, and the monomer allowed to melt if degassing was desired (samples which were not degassed were sealed after freezing). The monomer was refrozen, the stopcocks opened, the system evacuated as before to 5 μ, and the tubes sealed (if only one degassing was programmed) and stored at −20°C. until all of the samples were ready for irradiation.

These tubes were passed under the beam in a horizontal position in order to obtain complete penetration of the samples and were irradiated at room temperature with 2 M.e.v. electrons, which have sufficient energy to penetrate about a 1 cm. layer of water whereas the thickness of the monomer layer was only about 0.2 cm. As a consequence of in-scattering and back-scattering, there were about 50% more ionization paths (as determined by the use of MSC 300 blue cellophane film) within than without a 1-in. Pyrex tube of the type used in these studies.[1] The conveyer speed was 93 in./min. The samples received one pass under the scanning beam, at a beam current of 2.87 μa., to give a delivered dose of 3000 rad.

Half of the samples with otherwise comparable variables were processed the next day after irradiation, whereas the other half was allowed to stand in the dark at room temperature for 30 days before processing in order to evaluate the post-irradiation effect on polymer formation from these monomers (Tables I and II).[9]

Experimental Results

The data for conversion to polymer as a function of the four two-level variables are given in Tables I and II. Inasmuch as all samples received 3000 rads, the efficiency of irradiation (or the amount of polymer obtained per unit of radiation energy) is proportional to the per cent polymerization.

A significant post-irradiation effect is apparent from the data for both 1,1,3-trihydroperfluoropropyl and 1,1,7-trihydroperfluoroheptyl acrylates (Tables I and II). The effect is more pronounced, however, for the samples from the tubes which were flamed-out three times at 5 μ to remove most of the adsorbed moisture and oxygen. These data also indicate that the degassing of the freshly distilled monomers does not appear to contribute to polymer formation under the conditions employed. More than traces, however, of oxygen in the system does have an inhibitory effect.

Statistical Evaluation of Data

The analyses of variance for the polymerization of 1,1,3-trihydroperfluoropropyl acrylate are given in Table III, which lists only significant variables and combinations. It is observed that the variance ratio for degassing is 22.7, for flame-out is 49.7, and for time-lapse is 48.3, as compared in each case with an F statistic at the 1% level of only 7.5. It is apparent, that flame-out and time-lapse are the most important single variables, and degassing the least. This may be concluded from the data of Table I, but it is doubtful if the three first-order interactions are obvious: atmosphere and flame-out (11.2 vs. 7.5), degassing and time lapse (8.2 vs. 7.5), and flame-out and time-lapse (16.2 vs. 7.5).

TABLE III

1,1,3-Trihydroperfluoropropyl Acrylate, Significant Variables[a]

No.	Source and combinations	Degrees of freedom	Mean squares	Variance ratio
1	Degassing (DG)	1	7.4[b]	22.7
2	Flame-out (FO)	1	16.2[b]	49.7
3	Time-lapse (T)	1	15.7[b]	48.3
4	Atmosphere, flame-out	1	3.6[c]	11.2
5	Degassing, time-lapse	1	2.7[c]	8.2
6	Flame-out, time-lapse	1	5.3[c]	16.2
7	Residual	1	0.17	
8	Error (within)	32	0.33	

[a] The F statistic at the 1% level = 7.50.

[b] Dependently significant variables.

[c] Independently significant variables.

The highest conversion for the atmosphere and flame-out interdependency was obtained by use of three flame-outs and an evacuated system (5μ), whereas the least polymer was formed in an evacuated system with no flame-out of the reaction tubes (Table I). For the degassing and time-lapse interdependency, the most polymer was formed with no degassing and a 30-day time lapse, whereas the least was with no degassing and a 1-day time lapse (Table I). For the flame-out and time-lapse interdependency, the best conversion was by use of three flame-outs and a 30-day time lapse, and the least from no flame-out and a 1-day time lapse (Table I).

The statistically significant variables of the 16 combinations used for the irradiation-induced polymerization of 1,1,7-trihydroperfluoroheptyl acrylate are given in Table IV. There are four dependently significant variables: atmosphere (103.5 vs. 7.5), degassing (90.4 vs. 7.5), flame-out (672.2 vs. 7.5), and time-lapse (281.0 vs. 7.5). There are also four first-order interdependent reactions: atmosphere and flame-out (103.4 vs. 7.5), degassing and flame-out (92.5 vs. 7.5), degassing and time-lapse (38.0 vs. 7.5), and flame-out and time-lapse (282.9 vs. 7.5). There is, moreover, one second-order interdependent reaction: degassing, flame-out, and time-lapse with a variance ratio of 37.9, whereas the F statistic has a value of only 7.5.

The effect of the variables on the polymerization of these two monomers appears to be somewhat similar except for the amount of polymer formation. Tentatively it is assumed that this results from increased activation of the vinyl group by the 1,1,7-trihydroperfluoroheptyl substituent over the corresponding propyl group.

Data for the atmosphere and flame-out interaction are given in Table II. It is observed that very little polymerization occurred, in either air or in an evacuated system at 5 μ with no flame-out of the reaction tubes, but with three flame-outs about twice as much polymer was obtained in an evacuated system as in the presence of air.

TABLE IV

1,1,7-Trihydroperfluoroheptyl Acrylate, Significant Variables[a]

No.	Source and combinations	Degrees of freedom	Mean squares	Variance ratio
1	Atmosphere (A)	1	105.6[b]	103.5
2	Degassing (DG)	1	92.2[b]	90.4
3	Flame-out (FO)	1	685.7[b]	672.2
4	Time-lapse (T)	1	286.6[b]	281.0
5	Atmosphere, flame-out	1	105.5[c]	103.4
6	Degassing, flame-out	1	94.3[b]	92.5
7	Degassing, time-lapse	1	38.7[b]	38.0
8	Flame-out, time-lapse	1	288.6[b]	282.9
9	DG, FO, T	1	38.7[c]	37.9
10	Residual	1	3.8	
11	Error (Within)	32	1.02	

[a] The F statistic at the 1% level = 7.50.

[b] Dependently significant variables.

[c] Independently significant variables.

All four of the factors evaluated have an effect on the per cent polymerization of 1,1,3-trihydroperfluoropropyl and 1,1,7-trihydroperfluoroheptyl acrylates, but the real effects of these variables become apparent only by the combined evaluation of both single factors and combinations of the experimental variables.

Discussion of Experimental Design

Consider a four-factor experiment in which factor A is tested at c levels, $1,2,\ldots i,\ldots c$: factor B at d levels, $1,2,\ldots j,\ldots d$: factor C at e levels, $1,2,\ldots k,\ldots e$: factor D at f levels, $1,2,\ldots l,\ldots f$: and each treatment is tested n times, $1,2,\ldots q,\ldots,n$.

When the treatment combination $A_iB_jC_kD_l$ is tested for the qth time, the response is Y_{ijklq}; if the treatment were tested a large number of times the mean response would shift toward the true value of $E(Y_{ijklq}) = \mu_{ijkl}$. The response Y_{ijkl} differs from μ_{ijkl} because of experimental error, which has a standard deviation of σ.

The mathematical model used in the analysis of a factorial experiment postulates that: $\mu_{ijkl} = \mu + A_i + B_j + C_k + D_l + E_{ij} + F_{ik} + G_{il} + H_{jk} + I_{jl} + J_{kl} + K_{ijk} + L_{ijl} + M_{jkl} + N_{ijkl}$. The true response, μ_{ijkl}, is built up, accordingly, from the overall mean μ plus a contribution characteristic of the ith level of A, plus a contribution characteristic of the jth level of B, . . ., plus the term E_{ij}, etc.

If the effect of changing the level of A were always the same, irrespective of the level of B or C or D, and vice versa, the term E_{ij}, F_{ik}, . . . N_{ijkl} would be zero. If, however, the effect of changing the level of A varies as the level of B changes (but not as the levels of C and D) then the value of E_{ij} is not zero. The value of E_{ij} becomes, consequently, a measure of the lack of independence of factors A and B or of their interaction or interdependency.

Inasmuch as μ is the mean of μ_{ijkl} and the same number of trials is made for each treatment, the results may be equated as: $\Sigma A_i = \Sigma B_j = \Sigma C_k = \Sigma D_l = \Sigma\Sigma F_{ij} = \ldots = 0$.

The expectation of a sum or difference of quantities whether independent or not is the sum or difference of the individual expectations, or $E(Y_{ijkl}) = \mu_{ijkl}$, where E is the mathematical expectation. It can be shown, moreover, that: $E(\bar{y}) = \mu$, $E(\bar{y}_j - \bar{y}) = B_j$, $E(\bar{y}_i - \bar{y}) = A_i$, and $E(\bar{y}_{ij} - \bar{y}_i - \bar{y}_j + \bar{y}) = E_{ij}$, where $\bar{y}$ is the average of all results, y_i is the average of all results at the ith level of A, $\bar{y}_j$ is the average for the jth level of B, and $\bar{y}_{ij}$ is the mean value of all results with the treatment A_iB_j, and so on.

Since the variation arising from changes in the levels of factors is systematic and not random, there is no universe or standard variance of which the mean squares are estimates. The mean squares vary between replications only because of random variations in the experimental error. In the systematic design of a factorial experiment, each mean-square expectation contains only one term other than σ^2.

Summary

From the data presented, it may be concluded that: (*1*) degassing, flame-out, and time-lapse are significant, dependent main effects for both monomers, and atmosphere is a significant, dependent main effect for 1,1,7-trihydroperfluoroheptyl acrylate; (*2*) the atmosphere and flame-out, degassing and time-lapse, and flame-out and time-lapse interactions are independently significant for 1,1,3-trihydroperfluoropropyl acrylate, whereas for 1,1,7-trihydroperfluoroheptyl acrylate the atmosphere and flame-out is independently significant, but degassing and flame-out, degassing and time-lapse, and flame-out and time-lapse are dependently significant; (*3*) the degassing, flame-out, and time-lapse interaction is independently significant for 1,1,7-trihydroperfluoroheptyl acrylate; and (*4*) experimental variables may be significantly interdependent.

It is believed that studies in this laboratory present the first demonstration of the interdependency of experimental variables for the irradiation-induced polymerization of vinyl monomers.

References

1. Degering, E. F., C. Merritt, Jr., M. Bazinet, and G. J. Caldarella, *Ind. Eng. Chem. Prod. Res. Devel.*, **2**, No. 2, 114 (June 1963).

2. Degering, E. F., G. J. Caldarella, F. E. Evans, and S. Grib, Radiation Chemistry Laboratory Series, Research Report No. 5, January 1961.

3. Degering, E. F., F. E. Evans, and S. Grib, Radiation Chemistry Laboratory Series, Research Report No. 7, March 1961.

4. Davies, O. L., *Design and Analysis of Industrial Experiments*, Hafner, New York, 1960, pp. 247–493.

5. Youden, W. S., *Statistical Methods for Chemists*, Wiley, New York, 1951.

6. Fraser, D. A. S., *Statistics: An Introduction*, J. Wiley, New York, 1958, pp. 140–141.

7. Davies, O. L., *Statistical Method in Research and Production*, Hafner, New York, 1957, (a) p. 108; (b) p. 255.

8. Stevens, W. L., *Biometrika*, **35**, 346 (1948).

9. Degering, E. F., G. J. Caldarella, and M. Mancini, *ASTM Spec. Tech. Publ.* No. **276**, 244 (1959).

Résumé

Une factorielle 2,2,2,2 a été employée pour la polymérisation induite par irradiation des acrylates de 1,1,3-trihydroperfluoropropyle et de 1,1,7-trihydroperfluoroheptyle au moyen d'un accélérateur d'électrons de 2 Mev, afin de déterminer d'une façon plus critique l'influence des variables. Des résultats obtenus on peut conclure: (*1*) que le dégazage, l'extinction et l'intervalle de temps sont importants, ont des influences notables pour les deux monomères et que l'atmosphère à une influence importante pour l'ester heptilyque, (*2*) que l'atmosphère et l'extinction, le gégazage et l'intervalle de temps, de même que les interactions extinction et intervalle de temps sont indépendamment significatives pour l'ester propylique, tandis que pour l'ester heptylique l'atmosphère et l'extinction ont une importance indépendante, mais le dégazage et l'extinction, le dégazage et l'intervalle de temps, et l'extinction et l'intervalle de temps sont reliés entre eux, (*3*) que le dégazage et l'interaction extinction-intervalle de temps sont indépendamment significatifs pour l'ester heptylique et (*4*) que les variations expérimentales peuvent être interdépendantes de façon significative.

Zusammenfassung

Ein 2,2,2,2-Faktorenschema wurde bei der strahlungsinduzierten Polymerisation von 1,1,3-Trihydroperfluorpropyl- und 1,1,7-Trihydroperfluorheptylacrylaten im 2-MeV-Elektronenbeschleuniger zu einer kritischeren Bestimmung des Einflusses der Variablen benützt. Aus den erhaltenen Ergebnissen wird geschlossen, dass: (*1*) Entgasung, Ausheizung und Zeitintervall für beide Monomeren signifikante abhängige Hauptgrössen und die Atmosphäre eine signifikante abhängige Hauptgrösse für den Heptylester ist, (*2*) Atmosphären-Ausheizungs-, Entgasung-Zeitintervall- sowie Ausheizung-Zeitintervall-Wechselwirkung für den Propylester unabhängig signifikant sind, während für den Heptylester die Atmosphäre und die Ausheizung unabhängig signifikant, jedoch Entgasung und Ausheizung, Entgasung und Zeitintervall sowie Ausheizung und Zeitintervall abhängig signifikant sind, (*3*) die Entgasungs-, Ausheizungs- und Zeitintervallwechselwirkung für den Heptylester unabhängig signifikant ist und (*4*) die Versuchsvariablen in signifikanter Weise voneinander abhängig sein können.

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Gel Permeation Chromatograms: Approximate Relation of Line Shape to Polymer Polydispersity

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Synopsis

Characteristics of gel permeation chromatograms are investigated for three molecular distribution functions assuming a linear relation between elution volume and the logarithm of solute molecular weight. The average molecular weight, $\bar{M}_{\text{gpc}}$, determined by the peak position of a chromatogram lies between the $\bar{M}_w$ and $\bar{M}_n$ for a polydisperse polymer.

Gel permeation chromatography is a method of obtaining molecular size distributions of polymers.[1,2] A sample in dilute solution is allowed to permeate through a column (or columns) of tightly packed highly crosslinked polymer beads (e.g., styrene–divinylbenzene copolymers) of controlled porosities. Under a constant total flow rate the permeation rate of molecular species of different sizes in the polymer differ. The smaller molecules, having greater accessible volumes in the polymer gel-packed column permeate more slowly than larger molecules, having more limited accessible volumes in the column. Polymer concentration in the effluent from the column is continuously monitored by a differential refractometer. Volume increments of effluent are recorded by collecting a small predetermined volume of solution and then pulsing a recorder each time this volume is collected. The resulting recorder trace of the differential refractive index as ordinate versus elution volume, V, as abscissa is the gel permeation chromatogram.

Experiments with polymer fractions of known molecular weights have revealed an empirical relation[1]

$$\log M = A - BV_M \tag{1}$$

between the polymer molecular weight M and the elution volume V_M corresponding to its passage through a given column. A and B are constants determined by the polymer type, solvent, and the particular gel column used. Although deviations from the linearity suggested by eq. (1) do occur, and "cut-offs" are noted for extremely high molecular weight polymers, it is possible to approximate eq. (1) for very broad molecular weight ranges by appropriate choice of columns and conditions. The applicability of eq. (1) throughout the whole range of polydisperse polymer molecular sizes is assumed in the following treatment.

By eq. (1) the chromatogram abscissa can be expressed in terms of log M and the ordinates in terms of $W_{\log M}$, the weight fraction of polymer with logarithm of molecular weight log M. The normalized integral distribution is then

$$\int_{-\infty}^{\infty} W_{\log M} d(\log M) = 1 \tag{2}$$

One ordinarily considers the distribution in terms of W_M, the weight fraction of polymer having molecular weight M, for which the integral distribution is

$$\int_0^{\infty} W_M dM = 1 \tag{3}$$

From the equivalence

$$\int_{-\infty}^{\infty} W_{\log M} d(\log M) = \int_0^{\infty} W_M dM \tag{4}$$

it is apparent that

$$W_{\log M} = MW_M \tag{5}$$

The proportionality of the ordinate of a chromatogram trace to MW_M rather than to W_M reflects the compression of the volume increment $\Delta V = -(\Delta \log M)/B = -\Delta M/BM$ by the factor $1/M$ relative to the ΔM increment. The gel permeation chromatogram can now be interpreted as a plot of MW_M versus log M, or in terms of the degree of polymerization x as a plot of xW_x versus log x.

To compare experimentally obtained chromatograms with possible theoretical line shapes, three molecular distribution functions are here considered. These are the logarithmic normal distribution,[3,4]

$$W_x = \frac{e^{-\sigma^2/2}}{\sigma\sqrt{2\pi}} \cdot \frac{1}{x_0} \cdot e^{-[\ln(x/x_0)]^2/2\sigma^2} \tag{6}$$

the Schulz-Zimm distribution,[5,6]

$$W_x = \frac{\lambda^{\alpha+1}}{\Gamma(\alpha+1)} x^{\alpha} e^{-\lambda x} \tag{7}$$

and a modified Stockmayer distribution,[7–9]

$$W_x = (2/\gamma x)e^{-(1+\gamma)x/\bar{y}_n} I_2(2\gamma^{1/2}x/\bar{y}_n) \tag{8}$$

where $I_2(2\gamma^{1/2}x/\bar{y}_n)$ is an imaginary Bessel function of the first kind.

The relations of the weight-average and number-average chain lengths, $\bar{x}_w$ and $\bar{x}_n$, to the distribution parameters for the three distribution functions are given in rows 1 and 2 of Table I. The distribution functions may be

TABLE I
Distribution Functions

	Log-normal	Schulz-Zimm	Modified Stockmayer
$\bar{x}_w$	$x_0 e^{3\sigma^2/2}$	$(\alpha + 1)/\lambda$	$2\bar{y}_n/(1 - \gamma)$
$\bar{x}_n$	$x_0 e^{\sigma^2/2}$	α/λ	$\bar{y}_n/[1 - (\gamma/3)]$
x_m	$x_0 e^{\sigma^2}$	$(\alpha + 1)/\lambda$	[a]
$\bar{x}_w/\bar{x}_n$	e^{σ^2}	$(\alpha + 1)/\alpha$	$2[1 - (\gamma/3)]/(1 - \gamma)$
$x_m/\bar{x}_n$	$(\bar{x}_w/\bar{x}_n)^{1/2}$	$\bar{x}_w/\bar{x}_n$	[a]
$x_m/\bar{x}_w$	$(\bar{x}_w/\bar{x}_n)^{-1/2}$	1	[a]
Width at half-height $\Delta \ln x_{1/2}$	$2(\ln 4)^{1/2} [\ln (\bar{x}_w/\bar{x}_n)]^{1/2}$	[b]	—
Distance between inflection points $\Delta \ln x_i$	$2[\ln (\bar{x}_w/\bar{x}_n)]^{1/2}$		—

[a] x_m and $x_m/\bar{x}_n$ are evaluated in the Appendix as functions of γ. $x_m/\bar{x}_n$ lies between 2.0 and 1.5 for $0 \leq \gamma \leq 1$.

[b] $\Delta \ln x_{1/2}$ appears in the transcendental equation: $\Delta \ln x_{1/2} = \Delta x_{1/2}\bar{x}_w^{-1}$.

[c] $\ln \left\{ \frac{3\left(\frac{\bar{x}_w}{\bar{x}_n}\right) - 1 + \sqrt{\left(5\frac{\bar{x}_w}{\bar{x}_n} - 1\right)\left(\frac{\bar{x}_w}{\bar{x}_n} - 1\right)}}{3\left(\frac{\bar{x}_w}{\bar{x}_n}\right) - 1 - \sqrt{\left(5\frac{\bar{x}_w}{\bar{x}_n} - 1\right)\left(\frac{\bar{x}_w}{\bar{x}_n} - 1\right)}} \right\}$

restated in terms of the breadth-controlling parameters, σ, α, and γ, and the number-average chain lengths:

$$W_x = (\sigma\sqrt{2\pi}\,\bar{x}_n)^{-1} \exp\left\{ - \left[\ln(x/\bar{x}_n) + \frac{\sigma^2}{2}\right]/2\sigma^2 \right\} \tag{6a}$$

$$W_x = (\alpha/\bar{x}_n)^{\alpha+1}\, x^{\alpha} \exp(-\alpha x/\bar{x}_n)/\Gamma(\alpha + 1) \tag{7a}$$

$$W_x = (2/\gamma x) \exp\left\{ - \left(\frac{3 + 3\gamma}{3 - \gamma}\right)\left(\frac{x}{\bar{x}_n}\right)\right\} I_2 \left[\left(\frac{6\gamma^{1/2}}{3 - \gamma}\right)\frac{x}{\bar{x}_n}\right] \tag{8a}$$

Figure 1 represents theoretical gel permeation chromatograms as xW_x versus $\log(x/\bar{x}_n)$ for the above distribution functions at $\bar{x}_w/\bar{x}_n$ ratios 2, 3, and 10. The maxima of the curves (cf. Table I and Appendix) correspond to $x_m/\bar{x}_n$ values having x_m, the value of x at the maxima, equal to $(\bar{x}_n\bar{x}_w)^{1/2}$, $\bar{x}_w$, and $R\bar{x}_n$ for the logarithmic-normal, Schulz-Zimm, and modified Stockmayer distributions, respectively. The factor R (Appendix and Figure 2) varies slowly from 2 to 1.5 as $\bar{x}_w/\bar{x}_n$ increases from 2 to ∞, i.e., as γ increases from 0 to 1. It is thus seen that the average molecular weight $\bar{M}_{\text{gpc}}$ obtained from the position of the maximum in a gel permeation chromatogram lies between the weight-average and number-average molecular weight according to the present treatment. It coincides with the weight-average molecular weight if the distribution is adequately represented by eq. (7), but it lies far below $\bar{M}_w$ for broad distributions corresponding to eq. (8).

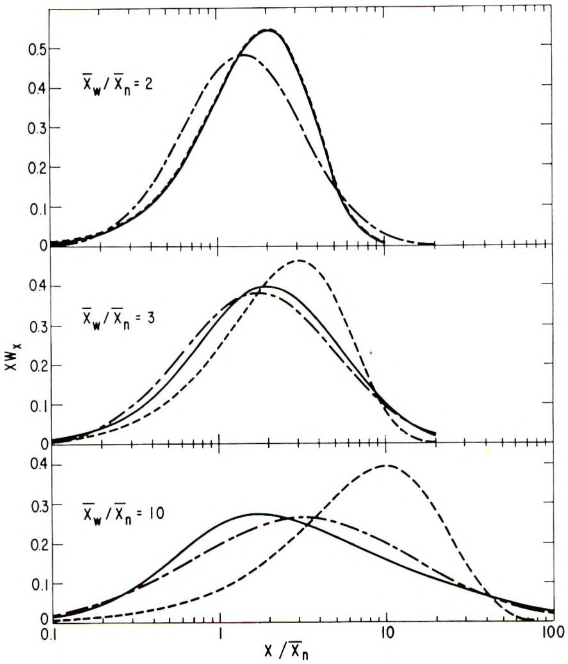

Fig. 1. Theoretical gel permeation chromatograms for three values of $\bar{x}_w/\bar{x}_n$ according to (—-) logarithmic normal, (- - -) Schulz-Zimm, and (——) modified Stockmayer distribution function formulations.

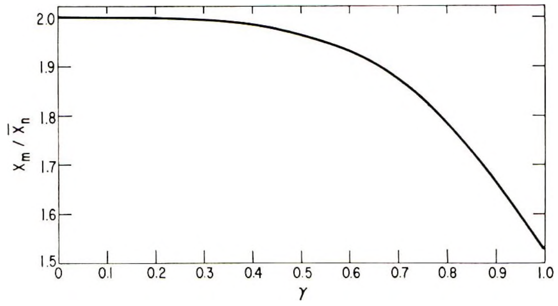

Fig. 2. Plot of $x_m/\bar{x}_n$ vs. γ, based on eq. (A-4), for the modified Stockmayer distribution function.

The width of the chromatograms at half-height, herein designated as $\Delta \ln x_{1/2}$, is explicitly given by $2(\ln 4)^{1/2}[\ln(\bar{x}_w/\bar{x}_n)]^{1/2}$ for the logarithmic-normal distribution. For the Schulz-Zimm distribution it must be evaluated from the transcendental equation $\Delta \ln x_{1/2} = \bar{x}_w^{-1} \Delta x_{1/2}$, where $\Delta x_{1/2}$ is defined as the difference in x values at half-height on the chromatograms. $\Delta \ln x_{1/2}$ can be stated in no simple functional form for the modified Stockmayer distribution. Within the limitations of the present treatment it is apparent that there is no unique relationship of $\Delta \ln x_{1/2}$ to $\bar{x}_w/\bar{x}_n$ for arbitrary molecular weight distributions. $\Delta \ln x_{1/2}$ therefore cannot be used for quantitative determination of $\bar{x}_w/\bar{x}_n$ for a polydisperse polymer.

The difference in $\ln x$ on the theoretical chromatograms, $\Delta \ln x_i$, between the upper and lower inflection points is stated for the logarithmic-normal and Schulz-Zimm distributions in the last row of Table I. Since these inflections are difficult to determine experimentally with any appreciable precision, their utility is limited.

The theoretical gel permeation chromatograms considered here have been based upon the assumption that a linear relation exists between the elution volumes and the logarithm of solute molecular weights. The elution volumes should be more directly related to some function of the solute molecular volumes or cross sections, since the accessible volume within the packed column should reflect some reciprocal correspondence to solute size. For homologous, flexible linear polymer molecules the essential proportionality of molecular "size" to some simple power of the number of units in the chains appears to provide linearity in terms of $B \log x$. Random, trifunctional branching which leads to the modified Stockmayer distribution would cause "sharpening" of the chromatograms due to progressively increasing size depression by the greater branching of the higher molecular weight components. The position of the maximum would be shifted by only a slight reduction in R, however, because the extent of branching in molecules in the region of $2\bar{x}_n$ remains fairly slight.

APPENDIX

The value of x ($x = x_m$) at the maximum of the gel permeation chromatogram is obtained from the relation

$$\frac{d(xW_x)}{d(\ln x)} = x\,\frac{d(xW_x)}{dx} = 0 \qquad \text{(A-1)}$$

The modified Stockmayer distribution function contains a Bessel function $I_n(ax)$ which is differentiated according to

$$\frac{d}{dx} I_n(ax) = aI_{n-1}(ax) - \frac{n}{x} I_n(ax) \qquad \text{(A-2)}$$

The use of eqs. (8a) and (A-2) in evaluating eq. (A-1) yields

$$\frac{2\gamma^{1/2}}{1-(\gamma/3)}\frac{x_m}{\bar{x}_n}\,\frac{I_1\left[\dfrac{2\gamma^{1/2}}{1-(\gamma/3)}\dfrac{x_m}{\bar{x}_n}\right]}{I_2\left[\dfrac{2\gamma^{1/2}}{1-(\gamma/3)}\dfrac{\bar{x}_m}{x_n}\right]} = \frac{1+\gamma}{1-(\gamma/3)}\frac{x_m}{\bar{x}_n} + 2 \qquad \text{(A-3)}$$

The term on the left side of eq. (A-3) has been tabulated[10] and is given the symbol τ_2. Thus,

$$\tau_2\left(\frac{2\gamma^{1/2}}{1-(\gamma/3)}\frac{x_m}{\bar{x}_n}\right) = \frac{1+\gamma}{1-(\gamma/3)}\frac{x_m}{\bar{x}_n} + 2 \qquad \text{(A-4)}$$

Figure 2 shows a plot of $x_m/\bar{x}_n$ versus γ obtained by evaluating eq. (A-4).

References

1. Moore, J. C., *J. Polymer Sci.*, **A2,** 835 (1964).
2. Determann, H., G. Lüben, and T. Wieland, *Makromol. Chem.*, **73,** 168 (1964).
3. Lansing, W. D., and E. O. Kraemer, *J. Am. Chem. Soc.*, **57,** 1369 (1935).
4. Wesslau, H., *Makromol. Chem.*, **20,** 111 (1956).
5. Schulz, G. V., *Z. Physik. Chem.*, **B43,** 25 (1939).
6. Zimm, B. H., *J. Chem. Phys.*, **16,** 1099 (1948).
7. Stockmayer, W. H., *J. Chem. Phys.*, **11,** 45 (1943); *ibid.*, **12,** 125 (1944).
8. Shultz, A. R., *J. Polymer Sci.*, in press.
9. Shultz, A. R., and H. L. Berger, *J. Polymer Sci.*, in press.
10. Onoe, M., *Tablets of Modified Quotients of Bessel Functions of the First Kind for Real and Imaginary Arguments*, Columbia University Press, New York, 1958.

Résumé

On a étudié les charactéristiques des chromatogrammes d'imprégnation de gel, de trois fonctions de distribution moléculaire en supposant une relation linéaire entre le volume d'élution et le logarithme du poids moléculaire du soluté. Le poids moléculaire moyen $\bar{M}_{gpc}$ déterminé au moyen de la position des pics sur un chromatogramme se situe entre $\bar{M}_w$ et $\bar{M}_n$ pour un polymère polydispersé.

Zusammenfassung

Die Charakteristika von Gelpermeationschromatogrammen werden für drei Molekulargewichtsverteilungsfunktionen unter Annahme einer linearen Beziehung zwischen Eluierungsvolumen und Logarithmus des Molekulargewichts des gelösten Polymeren untersucht. Für ein polydisperses Polymeres liegt das aus der Lage des Maximums eines Chromatogramms bestimmte mittlere Molekulargewicht, $\bar{M}_{gpc}$ zwischen $\bar{M}_w$ und $\bar{M}_n$.

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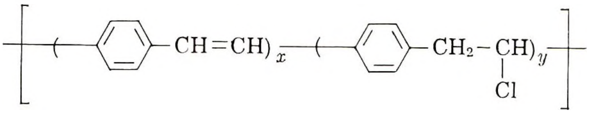
NOTES

Xylylidene–Chloroxylylene Copolymers

The reaction of α,α'-dichloro-p-xylene with sodium amide in liquid ammonia has been reported to produce random xylylidene–xylylene copolymers (I) in which both $x + y$ and x/y equals about 10.[1] These polymers were considered to possess aminomethyl endgroups.



I

A concurrent study of this polymerization method has indicated that a variety of polymers of Type I for which $x + y$ is 7–85 and x/y is 1–25 are possible. In addition, evidence has been obtained that the Type I polymers contain oxygen, and that nitrogen-containing groups other than primary amine are probably formed during the polymerizations.

Type I polymers presumably form by the 3-step mechanism proposed by Kharasch[2] for the conversion of benzyl halides to *trans*-stilbene by sodium amide in liquid ammonia. This mechanism involves (*1*) the α-ionization of dihalide II to produce carbanion III (step A); (*2*) the self-condensation of III, or alkylation of III by II, to produce polymeric halide IV (step B); and (*3*) the dehydrohalogenation (β-elimination) of IV to produce polymer VI (step C). Branched forms of VI are possible if alkylations of transient carbanion V occur prior to the β-elimination.

Table I presents typical data showing the effect of several polymerization parameters on the structure of Type I polymers.

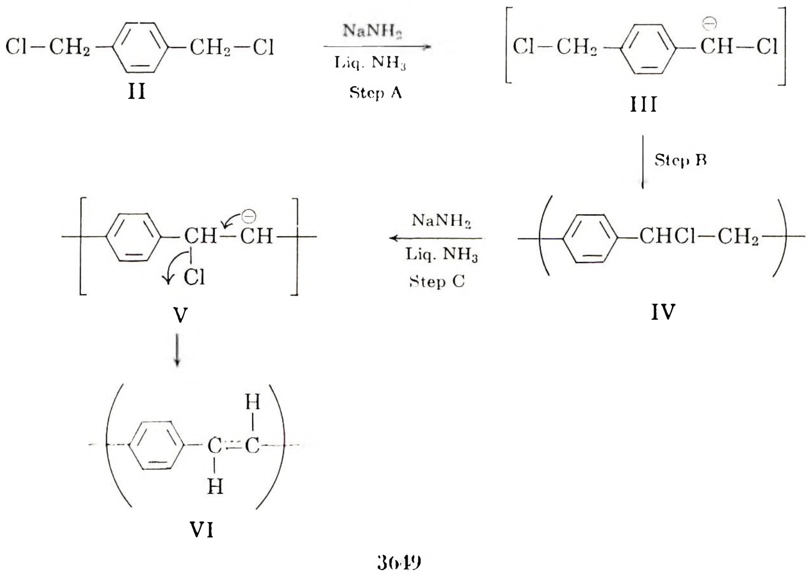


TABLE I
Alkali Metal Amide Polymerizations of α,α'-Dichloro-*p*-Xylene

Expt. no.	Metal	Mole ratio, metal/monomer	Polymerization temp., °C.	Conversion, %[a]	Elemental analyses[b]						$x + y$[d]	x/y[e]
					C	H	N	Cl	O	Ash[c]		
1	Na	2.1/1[f]	−35	103	88.9	6.3	1.7	1.5	1.9	0	15	25
2	K	2.1/1[f]	−35	103	85.4	6.3	1.3	3.2	—	0.99	18	10
3	Li	2.1/1[f]	−35	104	87.2	5.7	1.1	3.3	2.1	0	25	10
4	K	0.5/1[g]	−35	1	60.1	4.6	0.6	10.1	—	20.9	40	2
5	K	1/1[g]	−35	18	74.2	5.6	0.4	12.0	—	4.8	60	1–2
6	K	1.1/1[g]	−35	39	76.8	4.9	0.5	11.9	—	2.7	65	1–2
7	K	1/1[g]	−35	47	78.8	6.1	3.3	9.1	—	0.55	7	2–3
8	K	1/1[g]	−35	80	81.8	5.5	2.8	3.5	—	1.1	8	9–10[f]
9	K	1/1[f]	−78 to −35	47	78.9	5.9	0.6	11.2	—	1.2	40	1–2
10	Li	1/1[f]	−78 to −35	75	71.5	5.3	0.3	21.5	—	1.0	85	<1

[a] Based on $+C_6H_4—CH=CH+_n$ with endgroups disregarded.

[b] By Clark Microanalytical Laboratories, Urbana, Illinois.

[c] Contains principally iron, and arises from catalyst for amide preparation.

[d] Based on N-content, and assuming a Type I structure, amine endgroups, and an arbitrary repeating unit weight of 110.

[e] Based on chlorine content, $+C_6H_4—CH=CH+$ and $+C_6H_4CHCl—CH_2+$ repeating units, and disregarding endgroups.

[f] Regular addition procedure.

[g] Reverse addition procedure.

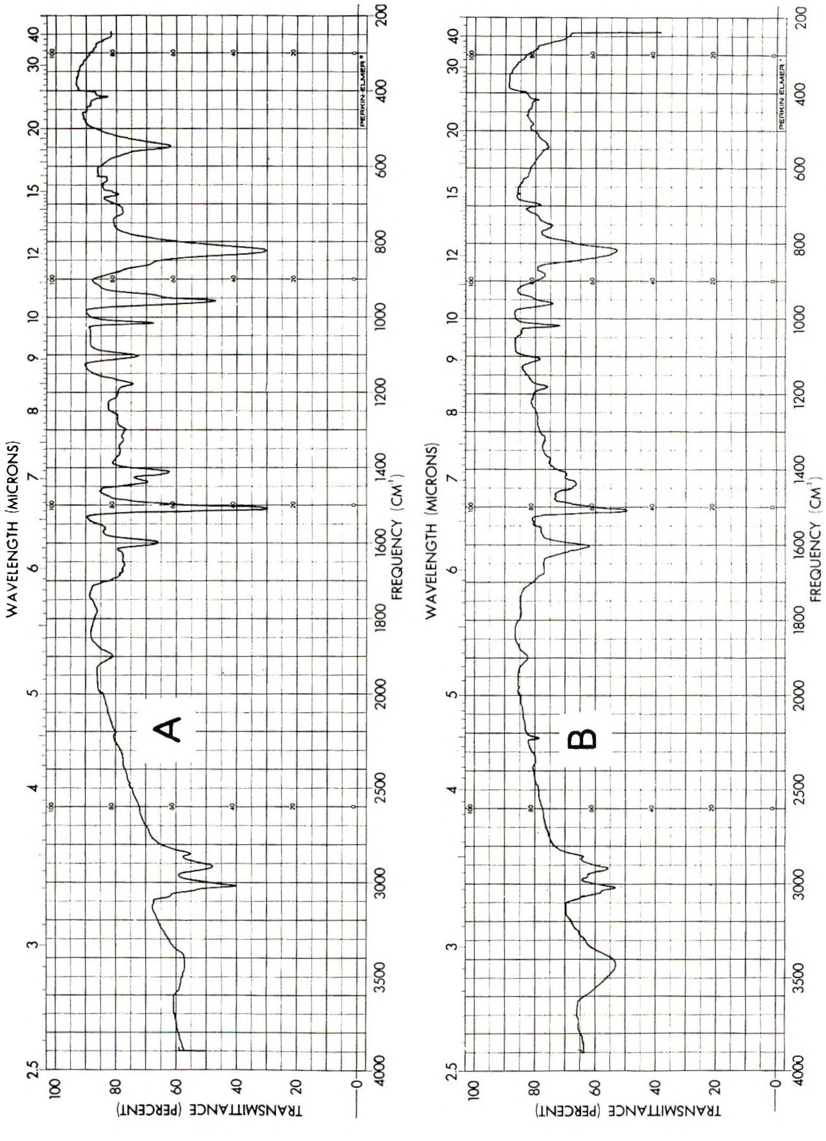


Fig. 1. Infrared absorption spectra (in KBr pellets) of (*A*) expt. 3 xylylidene–xylylene copolymer and (*B*) the same polymer after heating to 530°C. under vacuum.

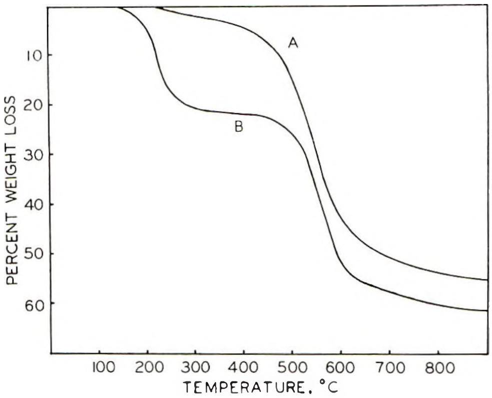


Fig. 2. Thermogravimetric analysis curves (heated at 10°C./min. under vacuum) of (*A*) expt. 3 xylylidene-xylylene copolymer having 3.3% chlorine content and (*B*) expt. 10 polymer having 21.5% chlorine content.

Alkali metal amide suspensions were formed by adding ferric chloride catalyst to solutions of the metals in liquid ammonia. Two polymerization procedures were used: (*1*) direct addition in which II in tetrahydrofuran was added quickly to the amide suspensions at −35°C.; and (*2*) reverse addition, in which the amides were added to II dispersed in ammonia-tetrahydrofuran mixtures. The reaction mixtures were stirred several hours, then neutralized by ammonium chloride, and evaporated to dryness. The yellow, fluorescent residues were washed with water, aqueous acid and base, acetone, and methanol, and then vacuum dried.

The reactions converting dihalide II to polymer VI call for 2 equivalents of amide ion. Experiments 1–3, Table I, indicate that 2.1 equivalents of potassium, sodium, or lithium amides provide essentially complete conversions of II to polymer. As expected, the products are highly unsaturated, having x/y values of 10–25.

If step C in the polymerization scheme is significantly slower than steps A and B, the reverse addition of one equivalent or less of amide II should limit the amount of dehydrohalogenation (step C) occurring, and permit higher molecular weight, and possibly more tractable polymers or predominantly structure IV. Experiments 4–6, Table I, show that reverse additions of potassium amide may indeed produce polymers having $x + y$ values of 40–65, and x/y values of about 2. The still appreciable degrees of unsaturation and low conversions indicate, however, that step C does compete with steps A and B for the available amide. Similar results were obtained (Expt. 7 and 8) using either the direct or reverse addition of one equivalent of potassium amide to II. In these cases, reduced conversions (47–80%), low $x + y$ values (7–8), and x/y values of 2–10 were obtained.

Reduced reaction temperatures have been observed to hinder the dehydrohalogenation step C, but not steps A and B. The polymerization of II by one equivalent of potassium amide at −35°C. (Expt. 7, Table I) produced a polymer with an $x + y$ value of 7 and an x/y value of 2–3. Upon repeating this reaction at −78°C. (then warming quickly to −35°C.), a product having an $x + y$ value of 40 and an x/y value of 1–2 was obtained (Expt. 9). A more pronounced effect was observed upon using one equivalent of lithium amide at −78°C. (Expt. 10), in which case a product was obtained having an $x + y$ value of 85 and an x/y value of <1.

The infrared spectrum of a typical xylylidine-chloroxylylene copolymer (Fig. 1*A*) shows absorption at 960 cm.$^{-1}$ characteristic of transethylenic groups. A strong absorption at 860 cm.$^{-1}$ indicates *p*-disubstituted benzene groups. The presence of *trans*-substituted olefins and high conjugation from *p*-phenylene repeat units expected in the polymer structure make the interpretation of complex absorptions in the 1600–1700 cm.$^{-1}$ region very difficult. While the high degree of conjugation would increase the normal 1640–1620 cm.$^{-1}$ —C=C— frequency, symmetry considerations following the *trans*-substitution would suggest a very weak absorption, if any. The relatively high frequency of most of this complex band pattern, together with elemental analysis showing both nitrogen and oxygen present, suggest the presence of an amide carbonyl group. This assignment is strongly corroborated by the spectrum of this polymer after heating to 530°C. in vacuum (Fig. 1*B*), which shows a decrease in this 1600–1700 cm.$^{-1}$ complex, with a concomitant appearance of a sharp absorption at 2225 cm.$^{-1}$ which can only be assigned to a C≡N stretching frequency.

Elemental analyses (Table I) indicate that Type I polymers do contain oxygen. However, the variable oxygen:nitrogen ratios suggest a variety of end (as well as nonterminal) groups may be formed. Amine groups may be formed by the aminolysis of chloromethyl groups.[2] The possible conversion of amines to imines by amide ion in liquid ammonia,[3] followed by hydrolysis (during polymer work-up), provides a potential route to amide and carboxylic acid groups.

Thermogravimetric analyses (Fig. 2) of the various polymer samples indicated that thermally-induced dehydrochlorination begins at about 150°C. The curves plateau upon completion of dehydrochlorination, and the resulting highly unsaturated polymers (Type V) remain stable to about 400°C., at which temperature the major decomposition begins. In general, unsaturated structures of Type VI underwent 45–55% weight losses upon being heated from 400 to 900°C.

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References

1. Hoeg, D. F., D. I. Lusk, and E. P. Goldberg, *Polymer Letters*, **2,** 697 (1964).
2. Kharasch, M. S., W. Nudenberg, and E. K. Fields, *J. Am. Chem. Soc.*, **66,** 1276 (1944).
3. Hauser, C. R., W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78,** 1653 (1956).

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Copolymer Composition in Condensation Copolymerization

Few studies on the copolymer composition in condensation copolymerization have been made, compared with the numerous investigations on addition copolymerization. In the melt condensation copolymerization at high temperature, nearly random copolymer may be formed, independent of the feed composition and the difference of the reactivity of functional groups, because of the exchange reaction between polymers. However, in the case of interfacial poly-condensation[1,2] and low temperature solution polycondensation,[3] the average composition and the block-like structure of the copolymer may depend upon the feed composition and the difference of the reactivity of functional groups. A simple explanation about the copolymer composition in condensation copolymerization is given in this paper.

As a rough approximation, the principle of equal reactivity of functional groups is assumed, namely, that the reactivity of a functional group is independent of the size of the molecule to which it is attached.[4] Then, condensation copolymerization reaction of F_1—functional group with F_2— and F_3— functional groups can be simply expressed by eqs. (1) and (2).

$$\sim\!F_1 + F_2\!\sim \underset{k_{12d}}{\overset{k_{12}}{\rightleftharpoons}} \sim\!F_1 - F_2\!\sim + E_2 \tag{1}$$

$$\sim\!F_1 + F_3\!\sim \underset{k_{13d}}{\overset{k_{13}}{\rightleftharpoons}} \sim\!F_1 - F_3\!\sim + E_3 \tag{2}$$

where F_1, F_2, and F_3 are F_1—, F_2—, and F_3— functional groups, respectively, and E_2 and E_3 are low molecular weight compounds formed by condensation reaction, of such compounds as water, alcohol, and sodium chloride. Some examples are shown in Table I.

TABLE I

Some Examples of Condensation Copolymerization

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
F_1	acid chloride	alcohol	phenol	alcohol	alcohol	phenol
F_2	divalent phenol	ester	acid chloride	acid	acid	acid chloride
F_3	amine	ester	acid chloride	acid	ester	acid
E_2	HCl	alcohol	HCl	water	water	HCl
E_3	HCl	alcohol	HCl	water	alcohol	water

In Table I, combinations such as those listed in Nos. 5 and 6 are possible in principle However, the reactivity of F_2 and F_3 toward F_1 is so different that such a combination is almost meaningless.

If E_2 and E_3 are expelled immediately from the reaction region, which is usual in practice,

$$-d[F_2]/dt = k_{12}\,[\mathrm{Cat}]^{n1}[F_1]^{n2}([F_2] + [F_3])^{n3}[F_2]^{n4} \tag{3}$$

$$-d[F_3]/dt = k_{13}[\mathrm{Cat}]^{n1}[F_1]^{n2}([F_2] + [F_3])^{n3}[F_3]^{n5} \tag{4}$$

Then,

$$d[F_2]/d[F_3] = (k_{12}/k_{13})([F_2]^{n4}/[F_3]^{n5}) = r_{23}([F_2]^{n4}/[F_3]^{n5}) \tag{5}$$

Equation (5) corresponds to the copolymer composition equation for addition copolymerization.

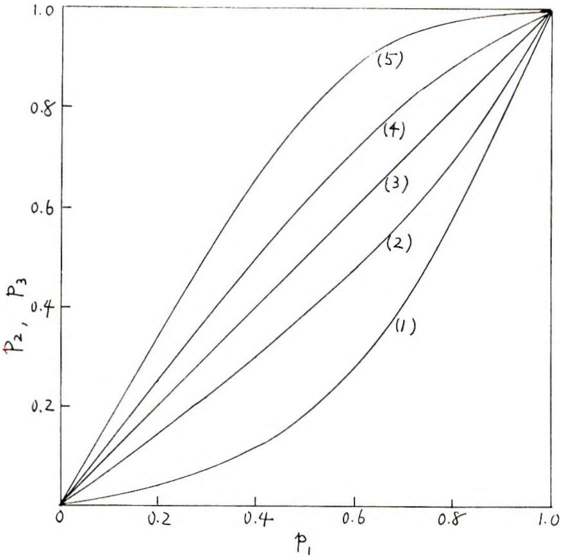

Fig. 1. Correlation of p_2, p_3, and p_1 for various values of r_{23}, for $\gamma = 1$ and $\alpha = 0.5$. Values of r_{23} for p_2 are: (*1*) 0.1; (*2*) 0.5; (*3*) 1; (*4*) 2; (*5*) 10. Values of r_{23} for p_3 are: (*1*) 10; (*2*) 2; (*3*) 1; (*4*) 0.5; (*5*) 0.1.

In the absence of added strong acid as catalyst, the polyester-forming reaction between glycols and dibasic acid is third order. In this case, $n_1 = 0$ and $n_2 = n_3 = n_4 = n_5 = 1$. Then, eq. (5) reduces to eq. (5a).

$$\mathrm{d}[\mathrm{F}_2]/d[\mathrm{F}_3] = r_{23}\frac{[\mathrm{F}_2]}{[\mathrm{F}_3]} \tag{5a}$$

In the presence of added strong acid as catalyst, the polyester-forming reaction is second order. In this case, $n_3 = 0$ and $n_2 = n_4 = n_5 = 1$ and eq. (5) again reduces to eq. (5a). The order of the polymer-forming reaction between carboxyl–amine and acid chloride–amine is not generally known at present. But, the second-order reaction is reported in the case of interfacial polycondensation between acid chloride–amine and acid chloride–phenol.[6] It is clear that eq. (5) reduces to eq. (5a), except $n_4 \neq 1$ and $n_5 \neq 1$. This exceptional case has not been reported in the literature. We will use eq. (5a) hereafter. As is clear from the above argument, this treatment is more general than the ordinary second order treatment in addition copolymerization.

Now, we introduce the "extent of reaction," which is defined by eqs. (6–8).

$$p_1 = ([\mathrm{F}_1]_0 - [\mathrm{F}_1])/[\mathrm{F}_1]_0 \tag{6}$$

$$p_2 = ([\mathrm{F}_2]_0 - [\mathrm{F}_2])/[\mathrm{F}_2]_0 \tag{7}$$

$$p_3 = ([\mathrm{F}_3]_0 - [\mathrm{F}_3])/[\mathrm{F}_3]_0 \tag{8}$$

Integrating eq. (5a), expressing $[\mathrm{F}_2]$ and $[\mathrm{F}_3]$ by p_1, p_2, and p_3, we obtain eq. (9).

$$(1 - p_2) = \left(\frac{p_2[\mathrm{F}_2]_0 - p_1[\mathrm{F}_1]_0 + [\mathrm{F}_3]_0}{[\mathrm{F}_3]_0}\right)^{r_{23}} \tag{9}$$

Parameters α, β, and γ, are introduced as follows.

$$[\mathrm{F}_3]_0 = (\alpha/1 - \alpha)[\mathrm{F}_2]_0 = \beta[\mathrm{F}_2]_0 \tag{10}$$

$$[\mathrm{F}_1]_0 = ([\mathrm{F}_2]_0 + [\mathrm{F}_3]_0)\gamma = (1 + \beta)\gamma[\mathrm{F}_2]_0 \tag{11}$$

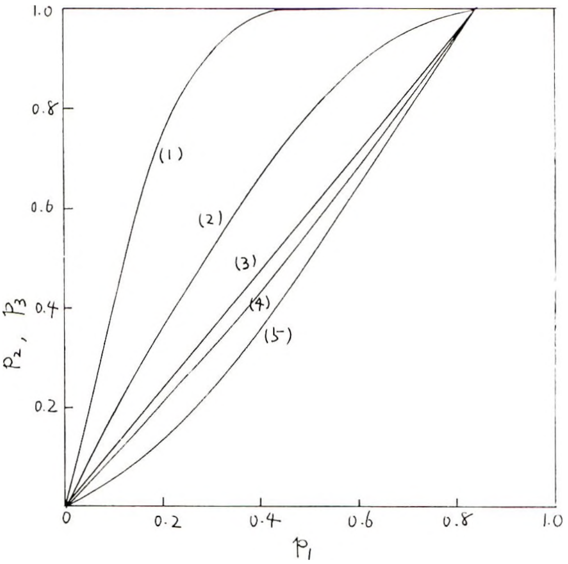

Fig. 2. Correlation of p_2, p_3, and p_1 for r_{23} of 10, 2, and 1 for $\gamma = 1.2$ and $\alpha = 0.8$. Values of r_{23} for p_2 are: (*1*) 10; (*2*) 2; (*3*) 1. Values of r_{23} for p_3 are: (*3*) 1; (*4*) 2; (*5*) 10.

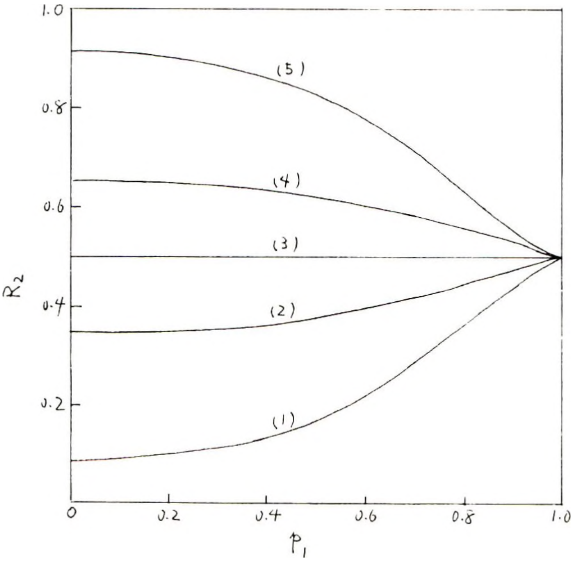

Fig. 3. Correlation of R_2 and p_1 at values of r_{23} = (*1*) 0.1; (*2*) 0.5; (*3*) 1; (*4*) 2; (*5*) 10 for $\gamma = 1$ and $\alpha = 0.5$.

α is the initial molar fraction of F_3 to the sum of F_2— and F_3— concentration and γ is the ratio of F_1— concentration to the sum of F_2— and F_3— concentration in the feed.

From eqs. (9), (10), and (11), we can obtain eq. (12).

$$(1 - p_2)\beta^{\gamma_{23}} = [\beta + p_2 - (1 + \beta)\gamma p_1]^{\gamma_{23}} \tag{12}$$

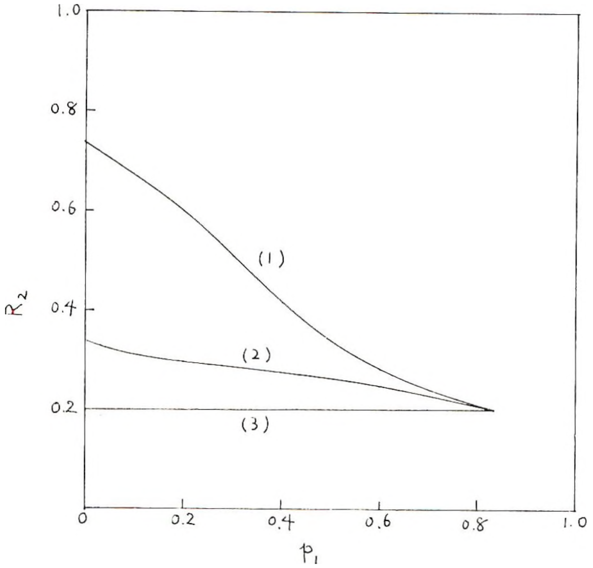

Fig. 4. Correlation of R_2 and p_1 at values of r_{23} = (*1*) 10; (*2*) 2; and (*3*) 1, for $\gamma = 1.2$ and $\alpha = 0.8$.

Equation (13) is also easily obtained.

$$p_3\beta = (1 + \beta)\gamma p_1 - p_2 \tag{13}$$

Now, p_2 and p_3 can be calculated as a function of p_1, using eq. (12) and (13). For one example, Figure 1 shows the relation between p_2, p_3, and p_1 at values of r_{23} = 0.1, 0.5, 1, 2, and 10, for $\gamma = 1$, and $\alpha = 0.5$. Another example is shown in Figure 2 for the case of $\gamma = 1.2$ and $\alpha = 0.8$.

Moreover, if R_2 and R_3 are defined as F_2— and F_3— fraction of the total F_2— and F_3— groups reacted till the extent of reaction of p_1, the following equations are easily derived

$$R_2 = p_2/(p_2 + \beta p_3) \tag{14}$$

$$R_3 = 1 - R_2 = \beta p_3/(p_2 + \beta p_3) \tag{15}$$

R_2 and R_3 are functions of p_2 and p_3, which are functions of p_1 and r_{23}, according to eqs. (12) and (13), for given β and γ. As a result,

$$R_2 = f(p_1,r_{23}) \tag{16}$$

$$R_3 = 1 - R_2 = g(p_1,r_{23}) \tag{17}$$

Equations (16) and (17) correspond to the integral composition equation for addition copolymerization. As one example, Figure 3 shows the correlation of R_2 and p_1 at values of r_{23} = 0.1, 0.5, 1, 2, and 10 for $\gamma = 1$ and $\alpha = 0.5$. Another example is shown in Figure 4 for the case of $\gamma = 1.2$ and $\alpha = 0.8$.

The above treatment can be applied to the homogeneous condensation reaction. The local concentration in the reaction phase must be considered in the heterogeneous reaction. Whether the reaction is diffusion-controlled or not is unimportant, like the case of addition copolymerization. Satisfactory experimental data which can be analyzed by this treatment has not yet been determined. However, the references cited discuss something about the monomer reactivity in condensation copolymerization of the following: copolyurea and copolyamide-urethane,[6] copoly(hydroxy-benzoate),[7] copoly(ethyleneterephthalate-phthalate),[8] copoly(1,4-cyclohexane-dimethyleneterephthalate-succinate),[9] and copolyether amide from isophthaloyl chloride, *p,p'* dihydroxy-diphenyl-2,2-propane, and hexamethylene diamine.[10]

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References

1. Wittbecker, E. L., and P. W. Morgan, *J. Polymer Sci.*, **40**, 289 (1959).
2. Morgan, P. W., *SPE J.*, **15**, 485 (1959).
3. Morgan, P. W., and S. L. Kwolek, *J. Polymer Sci.*, **A2**, 181 (1964).
4. Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953, pp. 70, 102.
5. Hodnett, E. M., and D. A. Holms, *J. Polymer Sci.*, **58**, 1415 (1962).
6. Lyman, D. J., and S. L. Jung, *J. Polymer Sci.*, **40**, 407 (1959).
7. Gilkey, R., and J. R. Caldwell, *J. Applied Polymer Sci.*, **2**, 198 (1959).
8. Tyuzyo, K., Y. Harada, and J. Suzuki, *Polymer Chem. Japan*, **21**, 225 (1964) (in Japanese).
9. Eastman Kodak Co., U. S. Pat. 3117950.
10. Korshak, V. V., *Polymer Sci. (USSR)*, **4**, 886 (1963).

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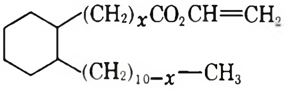
*Polymerization of Vinyl Esters of Cyclic Acids**

INTRODUCTION

Continuing our efforts to find a comonomer which can be polymerized with vinyl chloride to give a permanently plasticized copolymer,[1] the vinyl esters of some cyclic C_{18} and C_{20} acids have been studied. In earlier work[2] the vinyl ester of a cyclized linolenic acid which had been partially hydrogenated and partially dehydrogenated to yield a mixture of cyclohexane (I) and benzene (II) derivatives had been studied and showed some promise. We have now been able to obtain the hydrogenated product (I) free of the aromatic derivative and it is coded 5668-71-1 in this report. The vinyl ester used contained 34% of cyclic acid and the remainder was open chain C_{16} and C_{18} acids.



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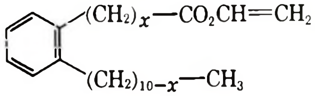

II

We have also made vinyl chloride copolymers with the vinyl ester of the pure cyclic acid (I) coded 5668-76-1; the vinyl ester of a C_{20} acid obtained by hydrogenating the ethylene addition product of tung oil acids (coded 5668-71-1); and the vinyl ester of a mixture of acids which contain 51% cyclic C_{20}, 38% stearic acid, and 15% palmitic acid. All of these esters were prepared at the Northern Regional Laboratory under the supervision of Dr. J. C. Cowan.[3]

EXPERIMENTAL

Vinyl Ester Monomers

These were prepared by Dr. John Friedrich who reported the following properties:

Sample 5668-71-1 contained 38% of cyclic C_{18} acid; b.p. of ester 130–165°C./50 microns; acid value 1; iodine value 82; n_{D}^{30} 1.4541.

Sample 5668-76-1 was the vinyl ester of reduced cyclic ester of C_{18} acid (I).

Sample 5668-77-1 was the vinyl ester of the cyclic acid obtained by addition of ethylene to tung oil acid; iodine value 82; acid value 1.

Sample 5668-73-1 was the mixed vinyl esters of hydrogenated C_{20} cyclic acid (51%), stearic acid (38%), and palmitic acid (11%); b.p. 120–130°C./50 microns, acid value 2, iodine value 84; n_{D}^{30} 1.4533.

Homopolymerization

The homopolymerizations were carried out in a tube with stopcock.[4] The tube containing 1.0 g. of vinyl ester and 0.020 g. azobisisobutyronitrile was flushed with nitrogen and evacuated to 1 mm. pressure. After heating the tube in a Fisher Isotemp oven at 65°C. for 20 hr., the polymers were dissolved in tetrahydrofuran and reprecipitated in methanol. The polymers were soft, tacky materials until the residual solvent was removed. Some properties of these homopolymers are described in Table I.

* This is a partial report of work done under contract with four Utilization Research and Development Divisions, Agricultural Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.

TABLE I
Solution Homopolymerization of the Vinyl Esters of Cyclic Acids[a]

Vinyl ester	Conversion, %	Softening range, °C.	Calc. C, %	Calc. H, %	Found C, %	Found H, %	η_{inh}[b]
5668-71-1	55	<25	76.85	11.8	76.25	12.3	0.160
5668-73-1	48	<25	77.10	11.1	76.75	11.5	0.172
5668-76-1	52	<25	77.70	10.4	77.50	10.8	0.163
5668-77-1	45	<25	77.70	10.4	77.65	10.5	0.158

[a] 1.0 g. of vinyl ester, 0.01 g. of azobisisobutyronitrile, and 5 ml. of benzene heated to 60°C. for 24 hr.

[b] Inherent viscosity of a 0.2% tetrahydrofuran solution measured at 30°C. in a No. 50 Cannon-Fenske viscometer.

Copolymerization of the Vinyl Esters with Vinyl Chloride

Evaluation samples of copolymers of vinyl chloride and 25 and 30 wt.-% vinyl ester were prepared. Their physical properties are listed in Table II. Each sample is a composite of 10–20 individual polymerization batches consisting of a total of 10 g. of monomers, 0.6 g. of ORR soap, 4 ml. of 2.5% potassium persulfate and 45 ml. of deoxygenated water in a glass tube (Ace Glass T 1506). After tumbling for 72 hr. at 60°C., the emulsion was coagulated by pouring into a saturated salt solution. The copolymer was filtered, washed 2 times with water, dissolved in tetrahydrofuran, and precipitated into water. After 13 reprecipitations into water and two into methanol, the copolymer was dried under reduced pressure to remove residual solvent and water. Table II contains the data for these copolymers.

TABLE II
Emulsion Copolymerization of Vinyl Chloride with Vinyl Esters of Cyclic Acids at 60°C. for 72 Hour

Vinyl ester (sample number)[a]	% Vinyl ester in starting charge[b]	Conversion[c] %	Analysis C, %	Analysis H, %	Analysis Cl, %	η_{inh}[d]	Ester content,[e] %
5668-71-1							
107	25	65	49.51	7.08	40.36	0.85	29
108	30	58	55.35	7.83	32.18	1.14	43.5
5668-73-1							
75	25	69	45.22	5.97	46.77	0.59	17.8
65	30	55	45.72	6.28	47.01	0.98	17.2
5668-76-1							
106	25	75	48.46	6.62	42.20	0.435	25.9
102	30	68	51.88	7.31	37.76	0.97	33.6
5668-77-1							
105	25	64	47.10	6.33	43.95	0.84	22.7
101	30	57	45.85	6.18	46.78	0.96	17.5

[a] Each polymer sample is a composite of many individual polymerization batches.

[b] Each polymerization batch contained 10 g. of monomer in the ratio shown.

[c] Average conversion of all batches after 2 reprecipitations into water.

[d] Inherent viscosity of a 0.2% tetrahydrofuran solution measured at 30°C. in a No. 50 Cannon-Fenske viscometer.

[e] Weight-% of ester in copolymer calculated on basis of chlorine analysis.

Evaluation

The polymers described in Table II have been sent to Mr. G. R. Riser of the Eastern Laboratory for evaluation. None of the polymers showed evidence of internal plasticization due to the incorporated cyclic ester.

References

1. Marvel, C. S., J. H. Griffith, J. L. Comp., J. C. Cowan, and J. L. O'Donnell, *J. Polymer Sci.*, **A2,** 2559 (1964).

2. Marvel, C. S., J. C. Hill, J. C. Cowan, J. P. Friedrich, and J. L. O'Donnell, *J. Polymer Sci.*, **A2,** 2523 (1964).

3. Friedrich, J. P., E. W. Bell, and R. E. Beal, *J. Am. Oil Chemists' Soc.*, **39,** 420 (1962); J. P. Friedrich, and R. E. Beal, *J. Am. Oil Chemists' Soc.*, **39,** 528 (1962); J. P. Friedrich, J. C. Palmer, E. W. Bell, and J. C. Cowan, *J. Am. Oil Chemists' Soc.*, **40,** 584 (1963).

4. Marvel, C. S., J. H. Griffith, J. L. Comp, T. H. Applewhite, and L. A. Goldblatt, *J. Polymer Sci.*, **A3,** 2991 (1965).

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On the Relevance of Intrinsic Viscosity to the Concentration Dependence of the Toms Effect

The turbulent-flow friction reduction due to very low concentrations (as low as one part per million for 20% reduction) of high molecular weight polymers in solution may be called the Toms effect.[1,2] In order to investigate the dependence of the effect upon macromolecular parameters, pipe-flow tests of a series of 5 poly(ethylene oxides) of molecular weights from 200,000 to 8 million in aqueous solution were made[2] at Reynolds numbers around 10^5. Perhaps the most significant finding was an apparent correlation between the concentration dependence of flow rate and the intrinsic viscosities. However, the relevance of intrinsic viscosity has been questioned by Metzner and Park.[3]

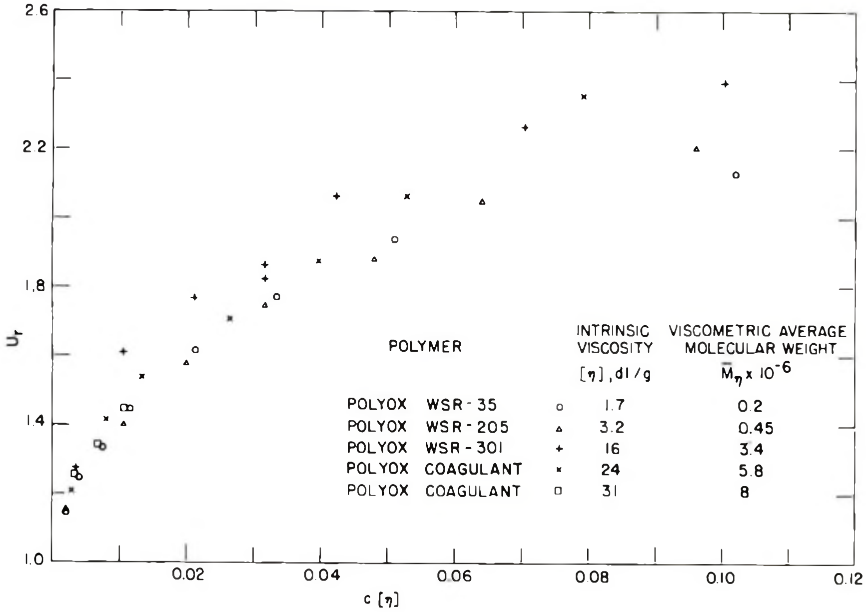

Fig. 1. Flow ratios for aqueous solutions of 5 poly(ethylene oxides) compared to pure solvent, for wall friction = 1000 dyne/cm.^{2}.

A better way of seeing this seeming correlation than those used previously is given in Figure 1, which is a replot of the data for flow-rate ratio U_r versus the dimensionless concentration $c[\eta]$ instead of versus c. $[\eta]$ is intrinsic viscosity for zero shear rate, in units of dl./g. if concentration c is in units of g./dl. U_r is the ratio of flow rates of solution to solvent for particular fixed pressure drop per unit length over the second half of the pipe, from about 400–800 diameters downstream of the inlet. The reference water mean flow speed is 620 cm./sec. through the 1.02-cm.-diameter pipe.

Since the range of $[\eta]$ is 1.7–31 dl./g., while the maximum spread of the data in Figure 1 corresponds to a factor of about 2 in $c[\eta]$, a major collapse toward a single curve has been obtained by weighting the concentration scale by $[\eta]$. Note that while there is no evidence of a dependence on $[\eta]$ for $c[\eta] < 0.05$, there appears to be one when $c[\eta]$ has reached 0.1, i.e., as the curves level out and the flow rate becomes relatively insensitive to concentration. It is conceivable that this loss of concentration dependence corresponds to general molecular entanglement.[2]

The above remarks are offered as background for evaluation of the argument by Metzner and Park[3] which is based on a comparison of the friction reduction effectiveness versus relative intrinsic viscosities of four nonhomologous polymers at a few, apparently very high concentrations relative to $c[\eta] \leq 0.1$. This writer would respectfully submit that their comparison has little bearing on the question, because they have not investigated the dependence upon concentration. Since this dependence is a key—at least practical—aspect of the Toms effect, it would be regrettable if misdirected argument should obscure the issue.

It would seem desirable to obtain U_r versus $c[\eta]$, for $c[\eta] \rightarrow 0$, for nonhomologous polymers in a given solvent, and for a given polymer in various solvents. Other work[4,5] has shown that a wide class of linear, very soluble, high polymers are effective additives in water and has indicated a rough ordering by molecular weight in relative effectiveness for very low concentrations. Thus it would appear reasonable to anticipate that for such a class of effective polymers in a given solvent the dependence upon $c[\eta]$ may be similar to that in Figure 1. Of course, when comparing nonhomologous polymers, it is natural to expect effects of the same parameters which control the variation of intrinsic viscosity with shear rate.[6]

References

1. Toms, B. A., *Proc. Int'l. Congr. Rheology, 1948*, North, Amsterdam, 1949, p. 135.
2. Fabula, A. G., *Proc. Int'l. Congr. Rheology, 4, 1963*. Interscience, New York, 1965.
3. Metzner, A. B. and Park, M. G., *J. Fluid Mech.*, **20**, 291–304 (1964).
4. Fabula, A. G., Hoyt, J. W., and Crawford, H. R., *Bull. Am. Phys. Soc.*, **8**, 430 (1963).
5. Hoyt, J. W., and Fabula, A. G., *Proc. Hydrodynamics Symposium, 5*, Bergen, Norway, 1964, to be published.
6. Lohmander, U., *Makromol. Chem.*, **72**, 159 (1964).

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Dilute Solution Properties of High Molecular Weight Poly(isobutyl Methacrylate). I. Viscosity

Earlier papers from this laboratory have reported the dilute solution properties of a series of alkyl methacrylates. In this paper we have considered several methods for the correction of shear in the determination of intrinsic viscosity. Also considered are a few methods for the determination of intrinsic viscosity and Huggins constant.

Initial investigations have shown that the solution viscosities of this polymer were shear dependent. Corrections for this shear dependence were applied by using a five-bulb capillary viscometer. The data were treated by a conventional double plot method, a triple plot method, and by including a higher concentration term. Intrinsic viscosities

TABLE I

Intrinsic Viscosities of Poly(isobutyl Methacrylate) Fractions

Fraction	$[\eta]$ in MEK at 25°C.	$[\eta]$ in acetone at 25°C.	$[\eta]$ in acetone at 25°C., uncorrected
F-3B	7.36	7.94	5.25
F-2B	6.30	5.78	4.65
F-4B1	5.95	6.80	4.85
F-5B1	5.60	5.26	4.35
F-6B1	4.34	4.48	3.50
F-6B	3.70	4.03	—
F-4B11	3.15	3.40	2.90
F-2A	3.10	2.60	2.42
F-6B11	2.30	2.43	2.00
F-7B	1.67	—	—
F-2	1.35	1.38	1.20
Original	4.50	4.17	3.35

TABLE II

Viscosity Data of Poly(isobutyl Methacrylate) Fractions in Methyl Ethyl Ketone

Temp.,				Uncorrected k_1 values				
°C.	Fraction	$[\eta]$	k_1	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
44	F-4B1	7.04	0.197	0.213	0.208	0.203	0.193	0.162
	F-5B1	6.41	0.173	0.160	0.153	0.138	0.120	0.111
	Original	4.70	0.095	0.210	0.153	0.148	0.143	0.100
	F-2A	3.10	0.073	—	—	—	—	—
30	F-4B1	6.10	0.226	0.342	0.322	0.310	0.300	0.285
	F-5B1	6.00	0.222	0.289	0.264	0.253	0.233	0.230
	Original	4.55	0.106	0.282	0.280	0.263	0.258	0.250
	F-2A	3.00	0.080	—	—	—	—	—
25	F-4B1	5.95	0.340					
	F-5B1	5.60	0.270					
	Original	4.50	0.148					
	F-2A	3.10	0.250					
20	F-4B1	5.60	0.424	0.470	0.450	0.415	0.395	0.389
	F-5B1	5.50	0.350	0.339	0.324	0.304	0.288	0.274
	Original	4.26	0.292	0.426	0.378	0.347	0.334	0.313
	F-2A	2.70	0.466	—	—	—	—	—

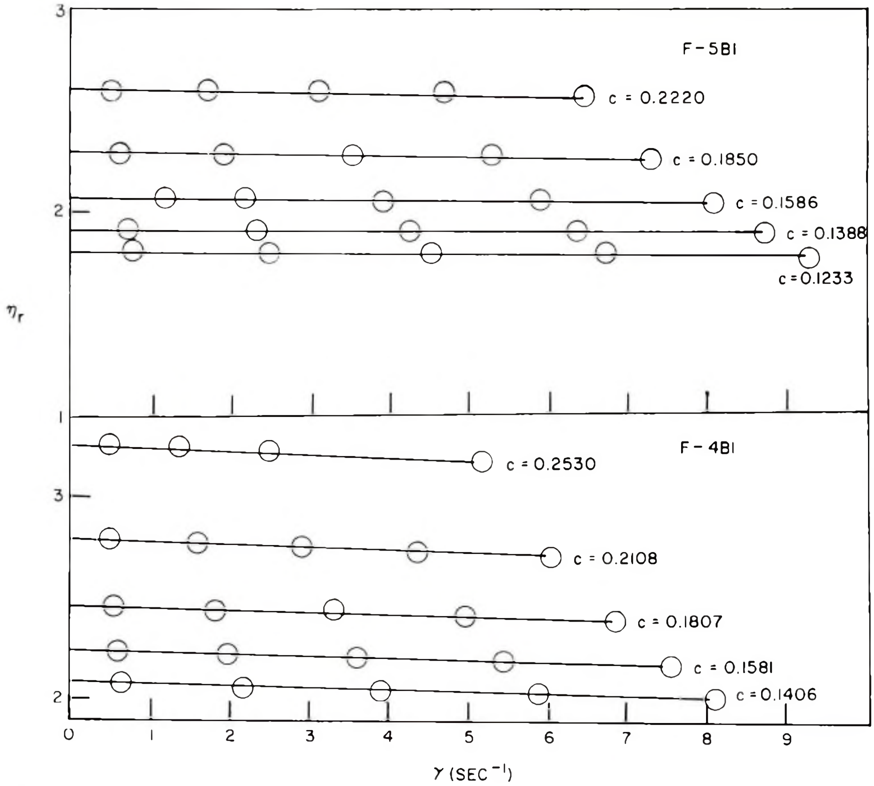

Fig. 1. Shear rate dependence of relative viscosity for poly(isobutyl methacrylate) fractions F-4B1 and F-5B1 in MEK at 25°C.

obtained from the different treatments agreed well. A few samples of this material were run at different temperatures, and the k_1 values were studied.

The polymer furnished by Edgewood Arsenal, Edgewood, Maryland, was a high molecular weight, linear poly(isobutyl methacrylate) #937. The fractionation was carried out using acetone as the solvent and methanol as the nonsolvent. A three-stage fractionation was used, the polymer being successively precipitated from 3, 2, and 0.3% solutions. A five-bulb Ubbelohde type viscometer[1] was used. Solutions were prepared, filtered, and diluted in the conventional manner. Flow times for each bulb were measured in duplicate.

The usual equation for the kinematic viscosity is

$$\nu = \frac{\pi R^4 \bar{h} g}{8VL} \times t \frac{-mV}{8\pi L} \cdot \frac{1}{t} = At - B\frac{1}{t}$$

The constants A and B are determined in the conventional manner, and then ν is determined for the temperature in question. The rate of shear is then determined by the equation

$$\gamma = \frac{R\bar{h}g}{3L\nu\eta_r} = \frac{k}{\eta_r}$$

The apparent relative viscosities for each concentration at several rates of shear are determined and plotted. Extrapolation to zero shear rate gives the values used in the subsequent evaluation of intrinsic viscosity and Huggins constant.

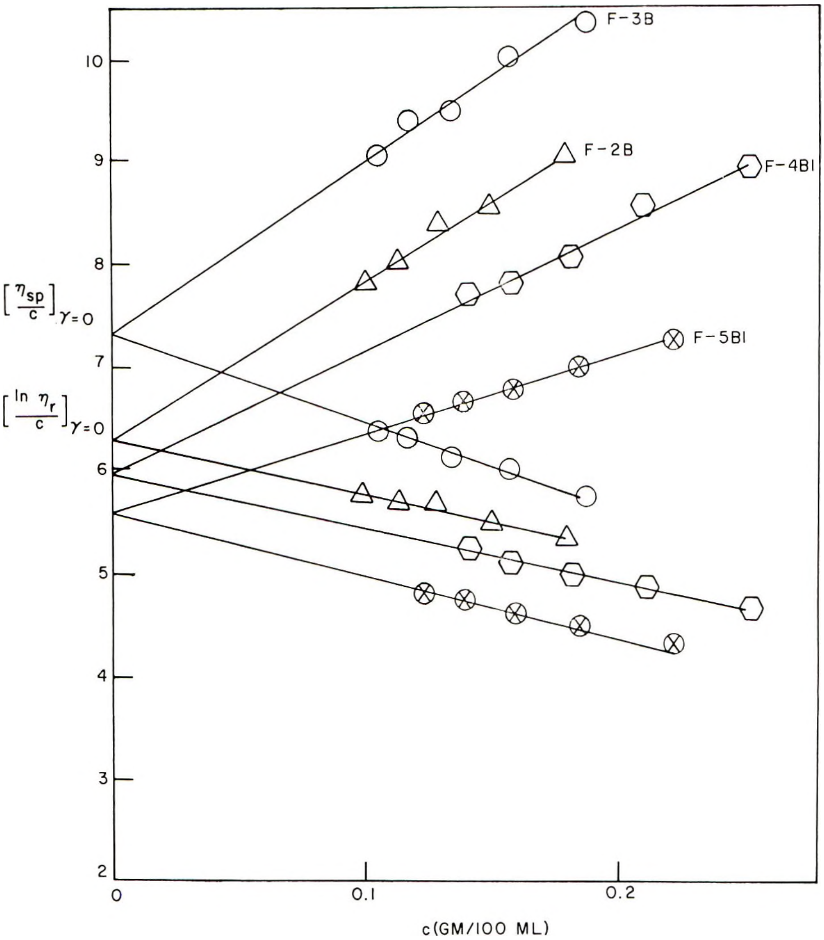

Fig. 2. η_{sp}/c and ln η_r/c vs. c for some poly(isobutyl methacrylate) fractions in methyl ethyl ketone at 25°C.

In methyl ethyl ketone at 25°C. the six highest molecular weight samples showed a marked shear dependence. In acetone at 25°C. there was a shear correction for all samples except F-3. Table I also lists the uncorrected intrinsic viscosities in acetone all run with the same Ubbelohde viscometer for comparison purposes.

Next we studied the effect of temperature on the intrinsic viscosity of several fractions of the polymer, and the effect of temperature and shear rate on the Huggins constant was also studied. Samples F-4B1, F-5B1, Original, and F-2A were run in methyl ethyl ketone at 20, 30, and 44°C. This work was then combined with the original work at 25°C. The original work at 25°C. was run in a different shear viscometer and so the k_1 values for each bulb could not be compared with the k_1 values obtained with a different viscometer. The corrected intrinsic viscosities have been duplicated in both viscometers.

The intrinsic viscosity increases with increasing temperature. It seems that the polymer is considerably more entangled at the lower temperatures, and spreads out as the temperature increases, giving more resistance to flow and thereby increasing the [η] value. The Huggins constant, probably decreases with increasing temperature for the above reason.

From the uncorrected data from plots of $\eta/_{sp}c$ versus concentration for each of the five bulbs, it was found that the k_1 values increase with increasing shear. As the shear stress is increased, the flexible coil becomes more asymmetrical through deformation and under tension becomes more rigid.[9] It follows that the k_1 should increase with shear stress.

The plots of η_{sp}/c versus concentration for F-2A are almost horizontal hence the k_1 values are very low and erratic, and we have neglected using them.

Under the influence of the temperature gradient, the k_1 values decrease with increasing temperature for the uncorrected data from each bulb in the same manner as the corrected k_1 values (Table II).

Fraction F-2A has essentially the same intrinsic viscosity as the temperature increases from 20–44°C. Using a regular Ubbelohde viscometer there is a slight increase in the intrinsic viscosity. This is probably due to a balance of forces acting on the solvent and polymer due to the temperature gradient. We have compiled this data[12] along with some light-scattering data.

References

1. Cragg, L. H., and H. van Oene, *Can. J. Chem.*, **39,** 203 (1961).
2. Flory, P. J., and T. G Fox, Jr., *J. Am. Chem. Soc.*, **73,** 1904 (1951).
3. Craig, A. W., and D. A. Henderson, *J. Polymer Sci.*, **19,** 215 (1956).
4. Peterlin, A., and M. Copick, *Bull. Sci., Conseil Acad. RPF Yugoslavie*, **3,** 41 (1956).
5. Ubbelohde, L., *J. Inst. Petrol. Technologist*, **23,** 427 (1937).
6. Holtzer, A. M., H. Benoit, and P. Doty, *J. Phys. Chem.*, **58,** 624 (1954).
7. Schurz, J., and E. H. Immergut, *J. Polymer Sci.*, **9,** 279 (1952).
8. Kobayashi, H., *J. Polymer Sci.*, **B1,** 299 (1963).
9. Heller, W., *J. Colloid Sci.*, **9,** 547 (1954).
10. van Oene, H., and L. H. Cragg, *J. Polymer Sci.*, **57,** 209 (1962).
11. Huggins, M. L., *J. Am. Chem. Soc.*, **64,** 2716 (1942).
12. Valles, R. J., *J. Polymer Sci.*, in press.

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Styrene Polymerizations with tert-*Butyl Hydroperoxide and Metal Acetylacetonates*

Introduction

In an effort to assay the initiator efficiencies in styrene polymerization of the system *tert*-butyl hydroperoxide–metal acetylacetonate for a number of different metals, it was noted that polymerization was not much enhanced beyond that which would have occurred in the absence of the metal chelate (Table I). That the chelating agent does not merely render the metal inactive is evident from enhanced hydroperoxide decomposition rates in the presence of at least certain of the metal acetylacetonates (Table II).[1] Oxygen absorption in the system olefin–*tert*-butyl hydroperoxide–metal acetylacetonate is promoted by those metals which also enhance peroxide decomposition.

The difficulty in using styrene as a free radical trap for describing the mode of polymerization initiation by hydroperoxides has been amply implied.[2,3,4,5,6,7] Our results corroberate the general finding that hydroperoxide polymerization efficiency is low. The main kinetic complexities attributed to the system have been radical induced decomposition of the hydroperoxide and nonradical interactions between hydroperoxide and olefin or solvent. Another complexity which probably interferes with the straightforward kinetic analysis possible for other polymerization initiators, such as benzoyl peroxide or azobisisobutyronitrile, arises from any hydroperoxide decomposition that leads to the production of molecular oxygen. Since hydroperoxides are known to decompose to oxygen, both neat and in inert solvents[6,8,9] as well as in the presence of metal salts[1,9,10] and nonpolymerizable olefins,[2] it seems reasonable to expect at least a portion

TABLE I
Bulk Polymerization of Styrene with *tert*-Butyl Hydroperoxide[a]–Metal Acetylacetonate at 50°C. *in Vacuo*

Metal	$(\Delta \text{ Styrene}/\Delta t) \times 10^6$, mole/l./sec.[g]
Cu(II)[b]	4.8
Co(III)[b]	3.3
Cr(III)[c]	3.1
Fe(III)[c]	2.6
V(III)[b]	2.4
Mn(II)[d]	2.3
Zn(II)[b]	2.2
Fe(II)[b]	2.1
Ni(II)[b]	2.0
VO(II)[c]	2.0
TiO(II)[b]	2.0
Zr(IV)[b]	1.9
Al(III)[b]	1.8
Co(II)[c]	1.7
—[e]	2.0
—[f]	0.74

[a] 1×10^{-3} molar.
[b] 1×10^{-4} molar.
[c] 2×10^{-4} molar.
[d] 8×10^{-4} molar.
[e] No chelate.
[f] No chelate, no hydroperoxide.
[g] Measured at 9.4×10^{-5} sec.

of the hydroperoxide decomposition that occurs in polymerizing systems to go by a path that yields molecular oxygen. Molecular oxygen would undoubtedly be copolymerized with the styrene,[7,11] tending to lower the polymerization rate and the molecular weight of polymer produced in the same way that a weak inhibitor might.[12] Any O—O linkages found by infrared analysis would be greater in number than predicted on the basis of chain transfer reactions of the kind proposed by Walling and Chang.[3] Indeed these workers found more O—O bonds by titrimetric methods than could be accounted for by chain transfer. The absence of molecular oxygen in the system has also been noted,[6] but the possibility that oxygen has been produced and immediately copolymerized seems to have escaped consideration. Tobolsky and Matlack[4] have demonstrated olefin–cumene hydroperoxide and solvent–hydroperoxide interactions in styrene and methyl methacrylate polymerization by means of kinetic analysis and infrared spectra. Benzyl alcohol, dimethyl aniline, and pyridine enhance polymerization rates; benzene, carbon tetrachloride, and cyclohexane do not. Any oxygen produced by hydroperoxide decomposition would have contributed to the solvent effects observed in the measured polymerization rates. Competition between solvent and monomer for molecular oxygen would tend to increase the polymerization rate.

TABLE II
Decomposition of *tert*-Butyl Hydroperoxide[a] by Metal Acetylacetonates[b] at 25°C. in 2,4,4-Trimethyl-1-Pentene *in Vacuo*.[1]

Metal	(Δ Peroxide/Δt) × 10^6 mole/l./sec.[9]
Cu(II)	1.9
Co(III)	1.4
Cr(III)	3.1
Fe(III)	—[d]
V(III)	1.3
Mn(II)	2.0
Zn(II)	—[d]
Ni(II)	—[d]
VO(II)	1.5
TiO(II)	—[d]
Zr(IV)	—[d]
Al(III)	—[d]
Co(II)	2.8
—[c]	—[d]

[a] 2.0 molar.
[b] 4 × 10^{-4} molar.
[c] No chelate.
[d] Negligible decomposition at 6.1 × 10^5 sec.

A detailed consideration of Tables I and II leads to the conclusion that Al(III), Zr(IV), TiO(II), Ni(II), and Zn(II) have little or no effect on *tert*-butyl hydroperoxide as polymerization initiators, that small quantities of Cu(II), Co(III), Cr(III), and Fe(III) promote *tert*-butyl hydroperoxide polymerization initiation, and that V(III), Mn(II), VO(II), Fe(II), and Co(II) enhance *tert*-butyl hydroperoxide decomposition but do not promote polymerization initiation. Higher concentrations of metal acetylacetonates than those cited in Table I actually lowered the rate of polymerization even for those acetylacetonates which enhance the rate. It is therefore likely that an optimal concentration range exists for metal acetylacetonate–hydroperoxide initiation of polymerization. At least one possible source for the lowered efficiency at increased metal acetylacetonate concentrations is the production of oxygen.

It should be noted that no obvious correlation exists between results cited here and another study in which metal acetylacetonates were used to catalyze hydroperoxide epoxidation of nonpolymerizable hydrocarbon olefins.[1] A different order of efficiency is to be expected from this initiator system in chain autoxidations.[7]

Experimental

Styrene was fractionally distilled at reduced pressure; metal acetylacetonates (The MacKenzie Chemical Corp.) were recrystallized from acetone; *tert*-butyl hydroperoxide (Lucidol Division, Wallace and Tiernan Corp.) was purified by the technique of Walling and Zavitsas.[13]

Polymerizations were carried out in sealed evacuated Carius tubes of 5-ml. capacity in a thermostated oil bath at 50 ± 0.02°C. Polymer samples were isolated by precipitation with methanol and determined gravimetrically. Metal acetylacetonates had no appreciable effect on the thermal polymerization rate of styrene. Both thermal rates and *tert*-butyl hydroperoxide initiated rates agreed well with literature values[3,4,9] after appropriate temperature extrapolations. Hydroperoxide disappearance was measured iodometrically.[3]

References

1. Indictor, N., and W. Brill, *J. Org. Chem.*, **30**, 2074 (1965).
2. Brill, W., and N. Indictor, *J. Org. Chem.*, **29**, 710 (1964).
3. Walling, C., and Y. Chang, *J. Am. Chem. Soc.*, **76**, 4878 (1954).
4. Tobolsky, A. V., and L. Matlack, *J. Polymer Sci.*, **55**, 49 (1961).
5. Tobolsky, A. V., and B. Baysal, *J. Polymer Sci.*, **8**, 529 (1952).
6. Walling, C., and L. Heaton, *J. Am. Chem. Soc.*, **87**, 38, 48 (1965).
7. Hiatt, R., C. Gould, and F. Mayo, *J. Org. Chem.*, **29**, 3461 (1964).
8. Stannett, V., and R. Mesrobian, *J. Am. Chem. Soc.*, **72**, 4125 (1950).
9. Walling, C., *Free Radicals in Solution*, Wiley, New York, 1957.
10. (a) Richardson, W., *J. Am. Chem. Soc.*, **87**, 247, 1096 (1965); (b) Berger, H., and A. Bickel, *Trans. Faraday Soc.*, **57**, 1325 (1961); (c) Dean, M., and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1958).
11. Mayo, F., *J. Am. Chem. Soc.*, **80**, 2465 (1958).
12. Lloyd, W., and C. Lange, *J. Am. Chem. Soc.*, **86**, 1491 (1964).
13. Walling, C., and A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963).

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Polymerization of Isoprene on the Surface of α-Titanium Trichloride

The polymerization of olefins and diolefins catalyzed by Ziegler-type catalysts is believed to occur at the surface of $TiCl_3$[1] which is covered by active centers and adsorbed monomer molecules. Although there is no uniform view on the mechanism of these reactions as well as on the role of any particular component,[2] the reactivity of $TiCl_3$ alone has been found practically negligible.[3-5] The present communication reports the results of an examination of isoprene adsorption on purple $TiCl_3$.

Experimental

Adsorption measurements were performed at 20°C., using a common volumetric apparatus. Samples of $TiCl_3$ were prepared by reduction of $TiCl_4$ with hydrogen, followed by efficient grinding in heptane suspension under nitrogen. Thereafter the suspension was transferred into ampoules connected with a vacuum line, *n*-heptane was evaporated, and the solid was then evacuated for 48 hr. at an elevated temperature. Isoprene of an analytical grade was dried by refluxing over sodium suspension and vacuum distilled into the apparatus. At various time intervals the measurement of the isoprene adsorption was interrupted, the sample was evacuated and the argon surface area was determined at −196°C. by the BET method. Two sets of samples differing in specific surface areas, i.e., 59 m.^{2}/g. and 110 m.^{2}/g., were investigated.

Results and Discussion

Adsorption of isoprene was investigated within a pressure range of 10–200 mm. Hg. A set of typical kinetic absorption curves on a sample with a specific surface area of 110 m.^{2}/g. at successively increased initial monomer pressure is shown in Figure 1 in a semilogarithmic plot. The sorption was fully irreversible, and associated with a sharp decrease of the free surface area estimated from the argon adsorption (Fig. 2). Simultaneously, $TiCl_3$ crystals became coated with polymeric film. In no case was the true adsorption equilibrium reached even after 30 hr.

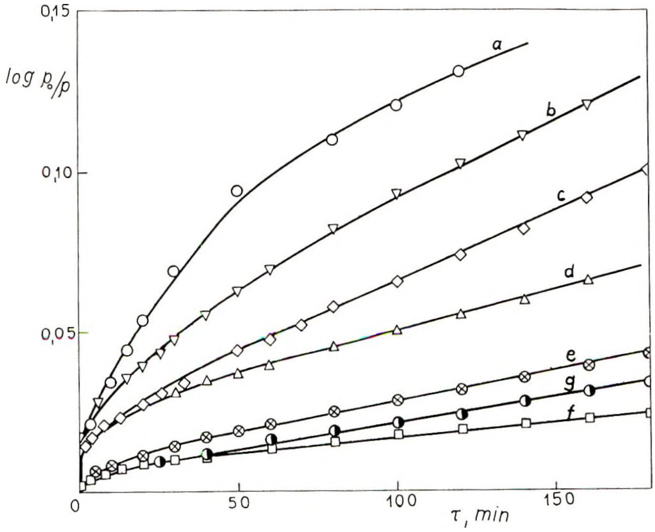

Fig. 1. Kinetic adsorption curves of isoprene on α-$TiCl_3$ (specific surface area 110 m.^{2}/g.) at 20°C. (Curves a–f) initial pressures 20, 35, 45, 58, 72, 90, and 120 mm. Hg.

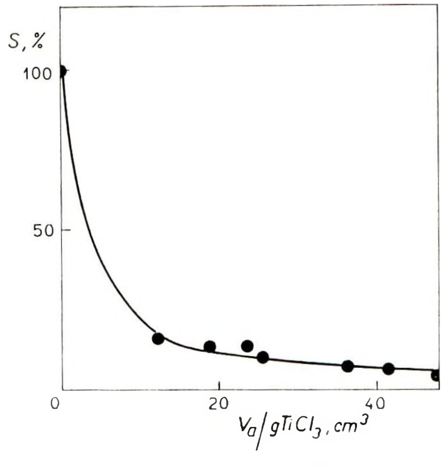

Fig. 2. The dependence of the free surface area S on the total amount of isoprene adsorbed. S expressed in %, adsorbed amount V_a expressed in ml. of gaseous isoprene at 0°C. and 760 mm. Hg.

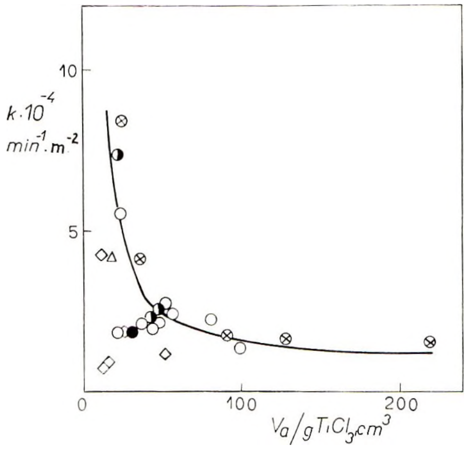

Fig. 3. Variation of the values of K (slopes of the linear parts of kinetic adsorption curves) with an increase of the total adsorbed amount V_a. (◇, ●) samples of specific surface area 59 m.^{2}/g.; (O, ⊗, △, ◑) samples of specific surface area 110 m.^{2}/g.

From Figure 1 it is seen that the sorption process has two stages, the first relatively fast corresponding to the proper adsorption and the latter, which can be described by a first-order reaction plot, being connected with the polymerization. After long adsorption periods, however, marked deviations from the first-order dependence occur due to the diminution of the surface area with the increase of the total amount adsorbed.

The kinetic picture of the polymerization process is rather complicated because neither the number of active sites nor the free surface available for the monomer adsorption remain constant. Figure 3 represents the changes of the slopes k (apparent polymerization rate constants), calculated from linear parts of different kinetic adsorption curves obtained with $TiCl_3$ samples of two different specific surface areas, as a function of the degree of coverage of the surface. Each value of k has been related to the surface area corresponding to the actual adsorbed amount of isoprene according to a calibration

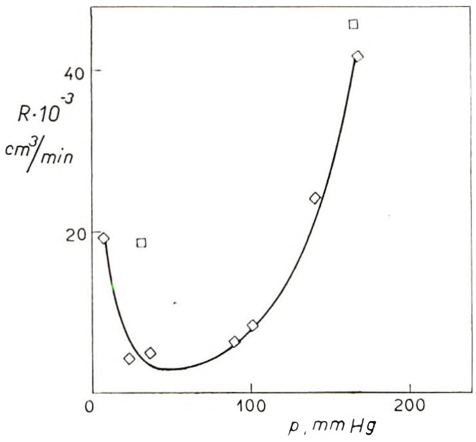

Fig. 4. The dependence of the polymerization rate on pressure related to the free surface area as estimated from argon adsorption measurements. Reaction rate R expressed in ml. of isoprene at 0°C. and 760 mm. Hg adsorbed per min. The total adsorbed amount increases gradually with pressure.

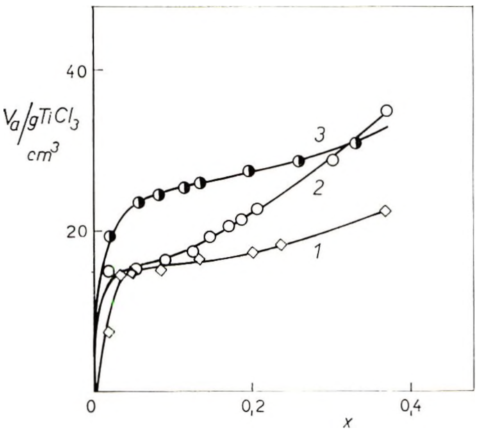

Fig. 5. Adsorption isotherms of isoprene on α-TiCl$_3$ at 20°C., calculated from kinetic adsorption curves by subtracting the amount which corresponds to polymerization, x, the relative pressure; (◇) specific surface area 59 m.^{2}/g.; (○, ◐) specific surface area 110 m.^{2}/g. Curves 1 and 2: adsorbed amount after 1 hr.; curve 3: adsorbed amount after 8 hr. of sorption.

curve, the initial part of which is the curve in Figure 2. The argon surface area becomes practically independent of the total amount of adsorbed isoprene when this latter exceeds the value 50 ml./g. TiCl$_3$. The diminution of the apparent polymerization rate constant with the increasing amount of the sorbate is quite understandable because it involves the concentration of active centers, deactivation of which is brought about by build-up of polymer and starts even at the very beginning of the sorption.

The constancy of k values at higher adsorbed amounts corresponding to the almost complete coverage of the surface by polymer, suggests that either holes are present in the polymer layer through which the diffusion of the monomer to the surface continues almost unhindered, or that active sites are located on the surface of the polymeric coating.

Because the overall polymerization rate is a function of the surface area and of the monomer pressure and, as it is not possible to change the pressure without changing simultaneously the surface area, the dependence of the polymerization rate on monomer pressure has a minimum, as is shown in Figure 4. When raising successively the initial monomer pressure, the surface area decreases due to the formation of a polymer layer and the resulting effect is a decrease of the polymerization rate. When the surface area has reached its limiting minimum value (Fig. 2), a further increase of the monomer pressure causes the increase of the reaction rate according to normal kinetic laws. It is interesting to note that the number of active sites remained unchanged even when the polymerization had been interrupted, the sample evacuated, and cooled down to −196°C. for surface area measurements. Afterwards, when the original pressure had been restored, the polymerization continued at an essentially unchanged rate.

From the total amount of monomer adsorbed on a given surface, adsorption isotherms were calculated by extrapolation of the linear portions of kinetic curves to zero time, presuming that the pressure difference given by this point and the known value of the initial pressure, represents a pressure drop due to a pure adsorption process (Fig. 5). Such adsorption isotherms however, are of illustrative character, because the quality of the surface, i.e., area and sorption activity, changes when the sorption proceeds.

In some cases infrared spectra of polymers formed during adsorption were examined. From the ratio of extinctions of adsorption bands at 1383 and 1465 cm.$^{-1}$ ($\log E_{1465}/E_{1383} = 1.275$) and from the character of the spectrum below 1200 cm.$^{-1}$,[4] it can be concluded that the polymer is completely cyclic. As shown recently[5,6] cyclic polymers may be formed in cationic polymerization. Thus, the surface of $TiCl_3$, contains centers of a cationic nature on which either monomer or the organometallic compound are adsorbed as recently depicted in detail.[7] Highly reactive monomers, such as isoprene, undergo thereon polymerization by a free carbonium ion mechanism.

References

1. Gaylord, N. G., and H. F. Mark, *Linear and Stereoregular Polymers*, Interscience, New York, 1959, and references given therein.
2. Saltman, W. M., *J. Polymer Sci.*, **46**, 375 (1960).
3. Yamazaki, N., T. Suminoe, and S. Kambara, *Makromol. Chem.*, **65**, 157 (1963).
4. Kössler, I., J. Vodehnal, and M. Štolka, *J. Polymer Sci.*, **A3**, 2081 (1965).
5. Kössler, I., M. Štolka, and K. Mach, *J. Polymer Sci.*, **C4**, 977 (1963).
6. Matyska, B., K. Mach, and J. Vodehnal, *Collection Czech. Chem. Commun.*, in press.
7. Cossee, P., *Trans. Faraday Soc.*, **58**, 1226 (1962).

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Growth of Polyethylene from Ethylene Vapor on Solid Surfaces

Recently, Lyda[1] reported the observation of polyethylene forming on large $TiCl_3$ surfaces of solid cocatalysts prepared from aluminum alkyls in the absence of solvents.

During our investigation of new low-pressure polymerization catalysts for preparing polyethylene, we prepared a series of solid, organometal-free, heterogeneous catalysts from representative metal–metal halides of Group II–VI of the periodic table. The catalyst was dispersed in hydrocarbons at moderate pressures and temperatures for polymerizing ethylene. A cursory examination of these systems was made to determine whether polymer growth would occur on the catalyst surface in the absence of solvent.[2]

In order to determine the activity of the catalyst in the absence of solvent, a catalyst was prepared by heating finely divided titanium (10 g.) in an atmosphere of $TiCl_4$ at 450°C. for 5 hr. and the catalyst was transferred to a stainless steel bomb in a dry box and sealed. The bomb was then flushed and filled with ethylene at 450 psi, and heated to 50°C. for 19 hr. (Pressure drops are indicated in Table I.) Upon cooling, the bomb was vented and the catalyst, bound with polyethylene, was removed. When extracted with boiling xylene, 2.1 g. of polyethylene, melting at 129°C., was obtained. Catalyst particles were embedded in the polymer where polymer growth had occurred about the nuclei of catalyst particles.

TABLE I

Time, hr.	T, °C.	Pressure, psi
0	50	450
1.0	50	300[a]
1.5	50	445[a]
19.0	50	150

[a] Repressured to 500 psi.

In another experiment, 2.0 g. of titanium trichloride and 0.5 g. of aluminum metal (20 mesh) were ballmilled in the dry state for 8 days. Approximately 0.5 g. of the pyrophoric catalyst was transferred in a dry box to a stainless steel bomb and pressured with ethylene as shown in Table II. Upon cooling and venting, 0.2 g. of solid polyethylene was obtained.

TABLE II

Time, hr.	T, °C.	Pressure, psi
0	32	500
0.5	98	540
1.0	100	550
19.0	150	530

In still another experiment, 10 g. of aluminum metal (20 mesh) was heated to 500°C. for 5 hr. while titanium tetrachloride vapor was passed over the metal. On cooling, 1.5 g. of catalyst was transferred to the bomb as described above. The bomb was pressured with ethylene as shown in Table III. On cooling and venting, 11.2 g. of solid polyethylene was obtained.

TABLE III

Time, hr.	T, °C.	Pressure, psi
0	25	200[a]
12	50	720[a]
36	50	470[a]
37	50	1080[b]
37.25	65	1080

[a] Repressured to 1100 psi.
[b] Raised temperature to 65°C.

These experiments clearly indicate that growth of solid polyethylene occurred directly from the gas phase on solid catalyst surfaces in the absence of aluminum alkyls or solvents. Under these conditions, the gas was above its critical pressure ruling out the possibility that the ethylene had liquefied.

References

1. Lyda, T. B., and H. F. Rase, *J. Polymer Sci.*, **A3**, 2400 (1965).
2. Miranda, T. J., Ph.D. Thesis, University of Notre Dame (1959).

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BOOK REVIEWS

Configurational Statistics of Polymeric Chains: High Polymers, Vol. XVII, M. V. VOLKENSTEIN, Interscience, New York, 1963. 562 pp., $20.00

The reviewer of this book, groping for a set of adjectives to convey its scope, its spirit, and its success, finally rejected them all; they can collectively be replaced by one adjective: scientific. Volkenstein's is a scientific book in the fullest sense, in that it will create new knowledge. It ranges widely over the equilibrium configurations (but not the kinetic or relaxational properties) of straight-chain, branched, natural, and synthetic polymers, and relates, never uncritically, the classical mathematical theories which have been formulated by such men as Markov and Debye, Frenkel and Kirkwood, and many others. The Russian book was written in 1958, and the author has in part brought up to date the literature cited until 1962 for this English edition. Some parts of the book, like that on the hereditary code, may have begun to date a little, but most of it will not seriously be out of date for many years to come. For as long as men think about macromolecules, they will turn to this authoritative account of the statistics of model chains and of real chains, and to the chapters on optical properties and on rubber elasticity.

The author infuses his personality into this work, not least through his distinguished contributions concerning rotational isomerism in long chains of atoms. But he does not attempt the Herculean task of unifying this vast subject within a single mathematical framework, of turning it into any kind of teaching text. Volkenstein is primarily a critical exposition of the best available theories in the terms that commended themselves to their original creators. Thus Stockmayer and Zimm's famous treatment of branched molecules is admirably summarized; and to have, within the same covers, Chandrasekhar's derivation of random-flight distributions is most convenient.

Actually, neither Chandrasekhar nor the other creators of theories covered by Volkenstein's book have used the full power of relevant statistical theories. In particular, systematic use has never been made of (*a*) the properties of characteristic functions, (*b*) the central limit theorem of probability theory, or (*c*) the theory of generalized functions (Schwartz, Lighthill). Another famous Soviet scientist, (A.I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, Dover, New York, 1949), has shown how much the presentation of the parent subject of statistical mechanics can be compressed and illuminated by using (*a*) and (*b*) systematically. Thereby he has pointed the way in which Volkenstein's book could even be improved further. Let us consider as an example the Chandrasekhar theory just mentioned. It has recently been improved by S. Dvořák [*Collection Czech. Chem. Commun.*, **28,** 251 (1963)] who obtains the Gaussian and Langevin distributions in a clearer and simpler way. But even here a third of the work is concerned with the derivation of Markov's equation for the end-to-end vector distribution $W_z(h)$ in terms of the distribution $W(\xi)$ of the z individual vectors composing the random flight:

$$W_z(h) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} \exp i\lambda h \left[\int_{-\infty}^{\infty} W(\xi)\exp - i\lambda\xi d\xi\right]^z d\lambda$$

Yet, this equation can be written down immediately from the theorem, generally attributed to Borel, which has been known to statistical users of characteristic functions since the last century. Namely, the distribution of the sum of z random variables is the inverse Fourier transform of the product of the Fourier transforms of the z individual distributions. (It is on this that Khinchin, *loc. cit.*, bases his own proof of the central limit theorem.)

This is not to detract from the book under review. Indeed, Volkenstein's book is the only literature reference that Dvořák thought it appropriate to cite! It is a book every polymer scientist will be proud to own, and no doubt, through its very excellence, it will in turn stimulate further improvements, based on more systematic use of mathematical power.

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Inorganic Polymers, D. N. HUNTER, Wiley, New York, 1963. ii + 100 pp. $7.25.

The stated purpose of this book is to give a concise account, both theoretical and practical, of modern ideas concerning inorganic polymers. In compiling this volume the author has paid particular attention to the Russian literature, much of which is not as well-known as it should be to the English-speaking world. Chapter I deals with homopolymers of boron, carbon, silicon, germanium, tin, nitrogen, oxygen, sulfur, selenium, and tellurium. Heteropolymers of hydrogen, carbon, and nitrogen with metals and, metalloids are the subject of Chapter II. Other chapters cover heteropolymers of oxygen and organic derivatives of inorganic polymers. The final chapter deals with applications of inorganic polymers.

ERRATA

Intrinsic Viscosity–Molecular Weight Relationship for Polyethylene

(a article in *J. Polymer Sci.*, **36**, 91, 1959)

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On page 96 line 12 from the top of the page should read:

$$q \cong \frac{\bar{M}_z^{3/2}\bar{M}_n}{(\overline{M^{3/2}})_n\bar{M}_w}$$

where $(\overline{M^{3/2}})_n$ denotes the number-average of the $^3/_2$ power of the molecular weight being equal to $M_0^{3/2} \exp(-3\beta^2/16)$.

On the same page line 14 should read:

$$q \cong (\bar{M}_w/\bar{M}_n)^{13/8}$$

[see Newman, et al., *J. Polymer Sci.*, **14**, 451 (1954)]

The explicit function of q can be obtained directly by substituting $\epsilon = 0$ into eq. (16b) and making use of the relationship $\bar{M}_w/\bar{M}_n = \exp(\beta^2/2)$.