Computer Program for Calculations and Automatic Data Plotting in Binary Copolymerization

G. E. MOLAU, *Plastics Department Research, The Dow Chemical Company, Midland, Michigan*

Synopsis

The copolymer composition equation as well as the composition-drift equation recently published by Meyer and Lowry have been transformed into a weight fraction–weight conversion form. The resulting weight-notation equations contain the original mole-notation equations as a special case. Based on the weight-notation equations, a computer program has been written which allows calculations and automatic data plotting of composition and composition-drift data in binary copolymer systems in either weight or mole notation.

Based on the general Alfrey-Price Q–e scheme,[1] Seiner[2] and Friedman[3] have presented programs for the treatment of copolymerization problems on digital computers. Recently, Meyer and Lowry[4] have published a new equation which describes the changes in the composition of a binary monomer mixture occurring in the course of a copolymerization. The composition-drift equation of Meyer and Lowry is an analytical solution to the Skeist equation[5] which describes the drift in composition of the monomer mixture for the general case.

For binary systems, rapid calculations of the copolymer composition as a function of the composition of the monomer mixture and of the drifts in monomer and in copolymer composition with increasing conversion can be made by combined use of the Meyer-Lowry equation and of the copolymer composition equation[6,7] in one computer program. The program which is written in ALGOL 60 (extended for the Burrough's B-5500 computer) provides for numerical output in the form of data tables as well as for graphical output in the form of diagrams. The diagrams are produced on a CALCOMP plotter. The plotter is directed by a Scientific Data Systems computer which receives its information from magnetic tape created by the described program on the B-5500 computer.

The input parameters to the program consist of either r_1, r_2 values or Q, e values plus any number of initial monomer compositions to be studied. One column in the printed data table and one curve in the composition-drift diagrams is produced for each initial monomer composition.

The data can be processed, printed, and plotted in either mole fraction–mole conversion notation or in weight fraction–weight conversion

notation.   This flexibility is achieved by transforming the Meyer-Lowry equation and the copolymer composition equation, which were originally published[4,6,7] in mole notation, into a weight notation.   As will be seen, the resulting weight equations contain the original mole equations as the special case for equal molecular weights of the monomers.

The copolymer composition equation[6,7] can be written in the form

$$\frac{Y_1}{Y_2} = \frac{X_1}{X_2}\left[\frac{r_1(X_1/X_2) + 1}{r_2 + (X_1/X_2)}\right] \tag{1}$$

where X_1 and X_2 are the mole fractions of the monomers in the monomer mixture, Y_1 and Y_2 are the mole fractions of the monomers in the copolymer, and r_1 and r_2 are the reactivity ratios.   The mole fractions are related to the weight fractions by the equations

$$X_1/X_2 = (1/\alpha)\,(F_1/F_2) \tag{2a}$$

$$Y_1/Y_2 = (1/\alpha)\,(P_1/P_2) \tag{2b}$$

where $\alpha = M_1/M_2$ is the ratio of the molecular weights of the monomers and F and P denote the weight fractions of the monomers in the monomer mixture and in the copolymer, respectively.   Combination of eqs. (1), (2a), and (2b) yields after rearrangement

$$\frac{P_1}{P_2} = \frac{F_1}{F_2}\left[\frac{r_1\,(F_1/F_2) + \alpha}{\alpha r_2 + (F_1/F_2)}\right] \tag{3}$$

Elimination of F_2 and P_2 from eq. (3) with the relations $F_2 = 1 - F_1$ and

$$P_1 = (P_1/P_2)/[1 + (P_1/P_2)] \tag{4}$$

gives the final form of the composition equation in weight notation:

$$P_1 = \frac{(r_1 - \alpha)\,F_1^2 + \alpha F_1}{[(r_1-1) + \alpha(r_2-1)]\,F_1^2 + [1 + \alpha(1-2r_2)]\,F_1 + \alpha r_2} \tag{5}$$

The corresponding equation in mole notation is obtained from eq. (1) by using the relation (4) with Y instead of P:

$$Y_1 = \frac{(r_1 - 1)\,X_1^2 + X_1}{[(r_1 - 1) + (r_2 - 1)]\,X_1^2 + 2\,(1 - r_2)\,X_1 + r_2} \tag{6}$$

Comparison of eqs. (5) and (6) reveals that eq. (6) constitutes the special case of eq. (5) for equal molecular weights of the monomers ($\alpha = 1$), taking into account that, in this case, the weight fractions become identical with the mole fractions.

The Meyer-Lowry equation[4] can be written in the form

$$\frac{N}{N^0} = \left(\frac{X_1}{X_1^0}\right)^A\left(\frac{1 - X_1}{1 - X_1^0}\right)^B\left(\frac{E_M - X_1}{E_M - X_1^0}\right)^D \tag{7}$$

where N is the total number of moles of monomer at any conversion, adn the superscript zero denotes the mole fractions at zero conversion.   The

constants A, B, D, and E_M have the values: $A = r_2/(1 - r_2)$; $B = r_1/(1 - r_1)$; $D = (r_1 r_2 - 1)/(1 - r_1)(1 - r_2)$; and $E_M = (1 - r_2)/[(1 - r_1) + (1 - r_2)]$. Transformation of eq. (7) into weight notation leads to a product of powers of the mole ratio $N/N°$ and the corresponding weight ratio $G/G°$. This product can be simplified considering the definitions of the constants A, B, and D, which lead to the relation $1 + A + B + D = 0$. Further simplification of the weight notation form of eq. (7) is achieved by defining a new constant E_W:

$$E_W = \frac{\alpha E_M}{1 - (1 - \alpha)E_M} = \frac{\alpha(1 - r_2)}{(1 - r_1) + \alpha(1 - r_2)} \qquad (8)$$

The final transformed form of eq. (7) is obtained with introduction of the weight conversion, $C_W = 1 - (G/G°)$:

$$C_W = 1 - \left(\frac{F_1}{F_1^0}\right)^A \left(\frac{1 - F_1}{1 - F_1^0}\right)^B \left(\frac{E_W - F_1}{E_W - F_1^0}\right)^D \qquad (9)$$

Introducing the mole conversion, $C_M = 1 - (N/N°)$, eq. (7) can be written as:

$$C_M = 1 - \left(\frac{X_1}{X_1^0}\right)^A \left(\frac{1 - X_1}{1 - X_1^0}\right)^B \left(\frac{E_W - X_1}{E_W - X_1^0}\right)^D \qquad (10)$$

Again, eq. (9) contains eq. (10) as the special case for equal molecular weights of the monomers, since for $M_1 = M_2$ one finds $\alpha = 1$; $E_W = E_M$; $C_W = C_M$; and $F_1 = X_1$.

Meyer[4] has shown that the constant E_M is equal to the mole fraction of the crossover point in the case that $r_1 < 1$ and $r_2 < 1$. Examination of eqs. (5) and (8) reveals that, analogously, E_W represents the weight fraction of the crossover point in the case of $r_1 < 1$ and $r_2 < 1$.

The computer program is based on eqs. (5) and (9), since these equations are more general than eqs. (6) and (10). If calculations and output in weight notation are desired, the molecular weights of the monomers are supplied as input parameters. In this case, the captions in the graphs and the column headings in the data tables will contain F_1, $F_1°$, P_1, C_W, and E_M. If calculations and output in mole notation are desired, the values $M_1 = 1$ and $M_2 = 1$ are supplied instead of the true molecular weights. This type of input causes processing and output in mole notation. In this case, the captions and headings will contain X_1, $X_1°$, Y_1, C_M, and E_M.

In order to prevent divisions by zero, the computer program must contain instructions for the cases $r_2 = 0$, $r_1 = 1$, or $r_2 = 1$. In the case of $r_2 = 0$, the order of the monomers is reversed and the initial feed compositions, $F_1°$, or $X_1°$, are replaced by $1 - F_1°$ or $1 - X_1°$, respectively, and a message is printed out stating that these rearrangements have been carried out. In the cases of $r_1 = 1$ or $r_2 = 1$, a reactivity ratio having the value one is replaced by a value slightly different from one. The differences are kept so small that they are unnoticeable in the output tables and graphs.
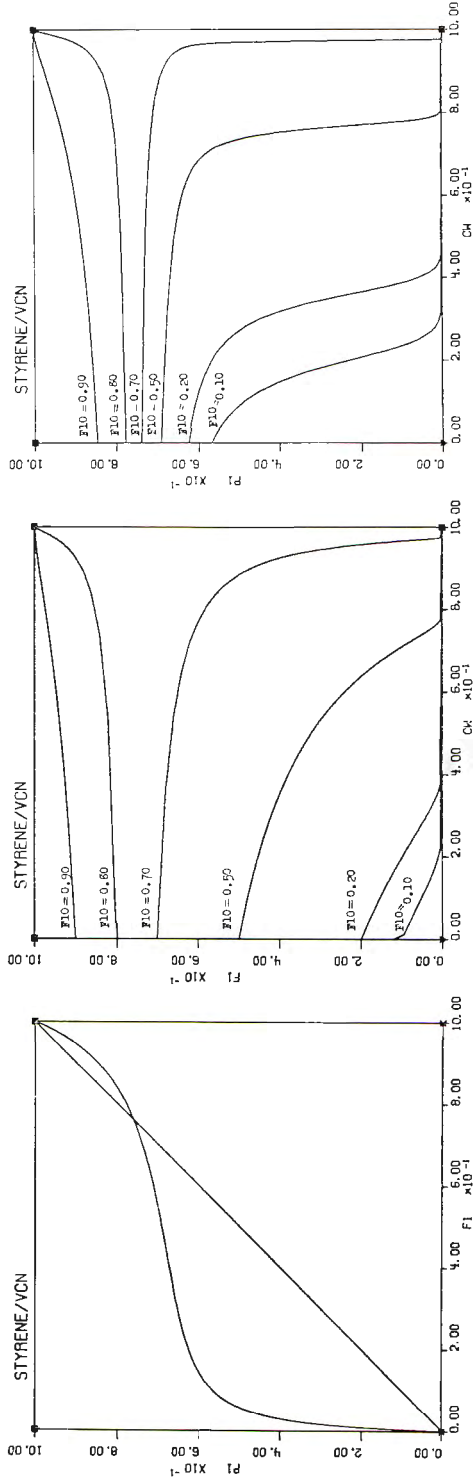
G. E. MOLAU

Fig. 1. Copolymerization of styrene (M_1) and acrylonitrile: $r_1 = 0.40$; $r_2 = 0.03$. Output in weight fraction–weight conversion.

As the first step in the calculations, a one-dimensional array of numbers is generated in the computer which contains values for F_1 or X_1, respectively, ranging from zero to one. This array is filled by dividing the interval $0 < F_1 < 1$ in several subintervals and filling each subinterval with as many numbers as are needed to give smooth curves in the diagrams. The number of subintervals and the number of points in each subinterval can be varied according to needs. The reason for this variable point density distribution can best be explained with the aid of an example for the graphical output.

Figure 1 is a photographic reproduction of a CALCOMP plotter chart showing graphs in weight notation for the system styrene–acrylonitrile ($r_1 = 0.40$; $r_2 = 0.03$), styrene being monomer 1. The original graphs are 5×5 in. in size and contain 97 data points per curve. The first graph (Fig. 1a), which is a direct plot of eq. (5), shows the copolymer composition P_1 as a function of the monomer composition F_1. The second graph (Fig. 1b), which is an inverse plot of eq. (9), shows the changes of the monomer composition F_1 with conversion C_W, for six initial monomer compositions $F_1°$. The third graph (Fig. 1c), which is produced by plotting of the combined P_1 and C_W arrays, shows the changes of the copolymer composition P_1 with conversion C_W for the same six initial monomer compositions, $F_1°$. Since eq. (9) is given in an implicit form and since P_1 and C_W are not related by one single equation, the only independent variable in the system is F_1. As a consequence of the steepness of most composition curves in the ranges $0 < F_1 < 0.1$ and $0.9 < F_1 < 1$, small intervals of F_1 lead to large intervals of P_1 and C_W in these ranges. Too large intervals of P_1 and C_W result in a degeneration of the curves into straight lines in the lower parts of the second and particularly of the third graph. This degeneration is caused by a lack of data points in these areas. Since the CALCOMP plotter is a digital instrument, which merely connects points, straight lines are drawn from the last calculated data point to the last point of the diagrams at $C_W = 1$. Without the artifice of a variable point density distribution, 10,000 data points instead of 97 points would be necessary to obtain the curves shown in Figure 1 free of degeneration.

As the second step in the calculations, a second one-dimensional array of numbers containing the P_1 or Y_1 values, respectively, is filled by inserting the F_1 or X_1 values into eq. (5). As the third step, a two-dimensional array of C_W or C_M values, respectively, is built up by either inserting the F_1 or X_1 values into eq. (9) or using programed instructions for the regions of F_1 or X_1 values in which the C_W or C_M values calculated with eq. (9) have no physical meaning. These instructions must cover three different cases: *case 1.* If $r_1 > 1$ and $r_2 < 1$, C_W is replaced by zero for all $F_1 \geqq F_1°$; *case 2.* if $r_1 < 1$ and $r_2 > 1$, C_W is replaced by zero for all $F_1 \leqq F_1°$; *case 3.* If $r_1 < 1$ and $r_2 < 1$, a crossover point is found at $F_1 = E_W$. For all initial compositions, $F_1° < E_W$, case 3 is identical with case 1, and for all $F_1° > E_W$, case 3 is identical with case 2. At the crossover point, $F_1° = E_W$, the monomer and the copolymer composition are, of course independent of

conversion. Without these editing instructions, which include the directions of composition drifts into the program, each curve in the composition–conversion diagraphs would be drawn with two branches, but only one of these branches represents the real copolymerization behavior of the system.

References

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Résumé

L'équation de composition de copolymérisation aussi bien que l'équation de variation de composition récemment publiées par Meyer et Lowry ont été transformées sous forme d'une conversion en fraction pondérale. Les équations pondérales en résultant contiennent les équations primitives de notations molaires comme un cas particulier. Sur la base de ces équations avec notations pondérales un programme peut être écrit qui permet le calcul et l'enrégistrement automatique de variation de composition dans un système de copolymérisation binaire soit en poids soit en moles.

Zusammenfassung

Die Gleichung für die Zusammensetzung von Copolymeren sowie die kürzlich von Meyer und Lowry veröffentlichte Gleichung für die Änderung der Zusammensetzung mit steigendem Umsatz wurden auf eine Form mit Gewichtsbruchteilen und Gewichtsumsatz gebracht. Die Gleichungen mit den Gewichtsgrössen enthalten die Gleichungen mit Molgrössen als Spezialfälle. Auf Basis der Gewichtsgleichung wurde ein Programm für Rechenautomaten beschrieben, das sowohl die Berechnung als auch die automatische graphische Darstellung der Zusammensetzung und der Zusammensetzungsänderung in binären Copolymersystemen in Gewichts- und Molgrössen erlaubt.

Head-to-Head Units in Poly(propylene Oxide) by Ozonation

CHARLES C. PRICE, ROBERT SPECTOR, and ANTHONY L. TUMOLO, *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
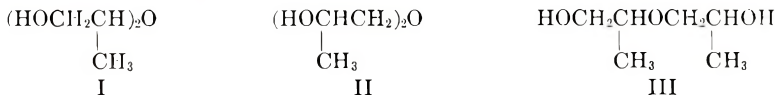
Synopsis

By extensive ozonation and lithium aluminum hydride reduction, poly(propylene oxide) can be converted to material containing dipropylene glycol. Since the diprimary, disecondary, and primary-secondary isomers are readily separable by vapor-phase chromatography, it has been possible to show that some (but not all) noncrystalline PPO samples contain many head-to-head, tail-to-tail monomer units. Correlation of the fraction of head-to-head units with the optical rotation of noncrystalline fractions from optically active monomer, indicates that there is one asymmetric center inverted for every unit inserted head-to-head. The earlier suggestion that the noncrystalline fraction was due to atactic stereochemistry is thus shown to be generally incorrect in favor of an explanation due to positional isomerization.

DISCUSSION

Some years ago we speculated[1] that the origin of noncrystalline fractions of high molecular weight poly(propylene oxide) (PPO) from optically active monomer with stereoselective coordination catalysts was partial racemization of the asymmetric center through carbonium intermediates producing partially atactic polymer. A number of recent reports have cast some doubt on this interpretation, especially the work by Vandenberg[2] showing that the polymerization of *cis*- and *trans*-2-butene oxide proceeds solely with inversion of configuration at one asymmetric center with no evidence for a "racemization" process, either by coordination or cationic-type catalysts.

The ozone degradation of polyethers[3] has been extended so as to produce dimeric degradation products. It turns out that the three structurally isomeric dipropylene glycols, diprimary (I), disecondary (II), and primary-secondary (III), previously reported by Sexton and Britton[4] can be readily separated by vapor-phase chromatography. In fact, for isomer I, even the two stereoisomeric forms were readily separable (see Fig. 1). Only III had been expected for normal head-to-tail monomer units in poly(propylene oxide).

$$(HOCH_2CH)_2O \qquad (HOCHCH_2)_2O \qquad HOCH_2CHOCH_2CHOH$$
$$\quad | \qquad\qquad\qquad | \qquad\qquad\qquad\quad | \qquad\quad |$$
$$\quad CH_3 \qquad\qquad\quad CH_3 \qquad\qquad\quad CH_3 \quad\; CH_3$$
$$\qquad I \qquad\qquad\qquad\quad II \qquad\qquad\qquad\qquad III$$

Indeed, for isotactic poly(propylene oxide), for liquid atactic PPO prepared by base catalysis and for one sample of high molecular weight rubbery PPO (supplied by General Tire and Rubber Company and prepared by a special proprietary catalyst), III was almost the exclusive dimeric product obtained (see Table I).
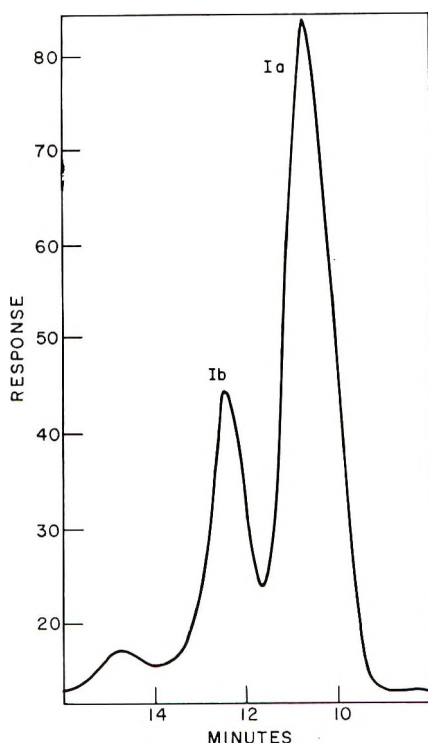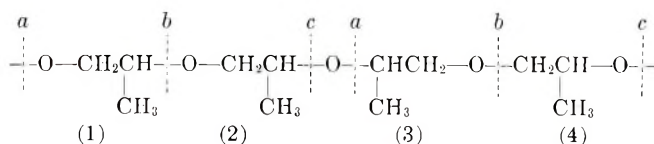

Fig. 1. Vapor-phase chromatogram of diprimary glycol (I); column (1), temperature 160°C., helium flow 100 ml./min., 2 μl.

For the noncrystalline fractions from several other stereoselective coordination catalysts, substantial amounts of dimer were isomers I and II. The presence of these two isomers must have arisen from head-to-head and tail-to-tail units in the polymer chain.

$$a \qquad\qquad b \qquad\qquad c \quad a \qquad\qquad b \qquad\qquad c$$
$$-O-CH_2CH--O-CH_2CH--O-CHCH_2-O-CH_2CH-O-$$
$$CH_3 \qquad\quad CH_3 \qquad\quad CH_3 \qquad\qquad CH_3$$
$$(1) \qquad\qquad (2) \qquad\qquad (3) \qquad\qquad (4)$$

The insertion of a single unit, (3) in the chain, in the inverse structural sense would provide the opportunity for producing the various diglycol isomers observed. Ozone cleavage at *aa* would produce III; cleavage at *bb* would produce I, at *cc*, II.

TABLE I

Diglycols from Ozonation of Poly(propylene Oxide)

PPO	III, % [a]	I and II, %	$[\alpha]_D^{20}$ [b]	I and II (calcd.), [c] %
Al(i-PrO)$_3$·ZnCl$_2$ (isotactic)[e]	>95	<5	−25°	—
Commercial (General Tire)	>95	<5	—	—
KOH	∼90	∼10	∼ −20°	10
AlEt$_3$·H$_2$O[d]	76	24	−18°	14
FeCl$_3$(PO)$_4$[d]	71	29	−10°	30
Et$_2$Zn·H$_2$O[d]	67	33	−5°	40

[a] By vapor-phase chromatographic analysis.

[b] Data of Chu and Price.[5]

[c] Data of Price and Tumolo.[3]

[d] Amorphous fractions.

[e] Calculated from $[\alpha]_D^{20}$ assuming an inversion of configuration for every head-to-head unit.

It should be pointed out that the cleavage procedure we employed cannot necessarily give information on the stereochemistry of adjacent units in the chain, as can the butyllithium procedure used by Vandenberg.[2] The ozonation produces ester, ketone, aldehyde, and carbonyl groups, all reduced back to alcohol by lithium aluminum hydride. It is highly likely that many secondary alcohols were ketones before reduction, and thus would have lost their original configuration.

In Table I, we have correlated the results of the structural isomerism in various samples of PPO with optical data obtained earlier for similar polymer samples made from optically pure monomer.[8] The data are very well interrelated if one assumes that whenever a monomer unit was inserted inverse to the normal opening at the primary carbon, it not only produced head-to-head and tail-to-tail sequences, but must have opened the epoxide ring at the asymmetric center with inversion of configuration.

These data are thus in full accord with those of Vandenberg on *cis*- and *trans*-2-butene oxides[2] and of Price and Spector[6] on *cis*- and *trans*-1,2-dideuteroethylene oxide which indicate that every step in epoxide polymerization by cationic, anionic, or coordination catalysts proceeds with inversion of configuration at the carbon atom where ring opening occurs.

The data in Table I indicate only the ratio of diglycol isomers. These ratios would be accurate indications of the composition of head-to-head units in the polymer only if the ozone degradation is entirely random and if the various diglycol isomers are equally resistant to further ozone degradation. We have no reason to believe this is not so but no evidence to support it.

It is of interest to note that Natta et al.[7] have recently presented an interpretation of infrared spectra of noncrystalline polypropylene suggesting that at least a part of the imperfections are due to head-to-head sequences.

EXPERIMENTAL

Vapor-Phase Chromatography

Separation by vapor-phase chromatography utilized Beckman Model GC-2 (1 and 2), a Burrell (3) and Resco (4) instruments with helium carrier gas and four columns: (1) an F & M Scientific Corp. 9 ft. by $1/4$ in. packed with 20% di-(2-ethylhexyl) sebacate on 30–60 mesh caustic washed Chromosorb W, (2) a 10 ft. by $5/8$ in. column packed with 33 g. of di(2-ethylhexyl)sebacate on 137 g. of 30–60 mesh caustic-washed Chromosorb W, (3) an 8-ft. long column packed with 10% Carbowax 250 (a Union Carbide polyethylene glycol) on Chromosorb P (non acid washed), and (4) a modified Resco instrument and a 6 ft. by $1/8$ in. column packed with Carbowax 20 M terephthalic acid-terminated (20%) on Chromosorb Z.

Peak areas were measured by a planimeter or cut out and weighed. Internal standards were used to estimate yields.

Spectra

Infrared spectra were determined on carbon tetrachloride solutions with a Perkin-Elmer Infracord spectrophotometer, Model 137, and nuclear magnetic resonance spectra on a Varian Associates Model 4700-D HR 60 spectrometer and a Hewlett-Packard 200-CD wide-range audiooscillator calibrated against a 521-C frequency counter.

Dipropylene Glycols

Diprimary (I). The diprimary alcohol was prepared by a procedure similar to the method of Sexton and Britton.[4] A solution of 10.9 g. (5.0 mmole) of diethyl dilactate in 50 ml. of dry ether was slowly added to a cooled, stirred solution of excess lithium aluminum hydride (4 g., 10.2 mmole) in 200 ml. of ether. After 30 min., ethyl acetate was slowly added until there was no apparent reaction. Excess water was added and the solution filtered. The precipitate was continuously extracted with ether in a Soxhlet extractor for 6 hr. The ether extracts were combined, dried over anhydrous magnesium sulfate and concentrated by evaporation on a rotary evaporator under vacuum. The crude product, 6.6 g. (98%), was fractionated by vapor-phase chromatography (Fig. 1) by using column 1 at 160°C. with a helium flow or 100 ml./min. and a vaporizer temperature of 300°C. Two dipropylene glycol fractions were obtained in approximately a 2:1 ratio. The elution times were 10.7 and 12.5 min., respectively. The virtually identical infrared spectra of the two fractions are given in Figure 2.

Disecondary (II) and Primary-Secondary (III). Commercial dipropylene glycol (Matheson, Coleman and Bell, Practical grade) was separated by using the vapor-phase chromatography technique described in the preceding experiment. The elution times of the disecondary alcohol and the primary-secondary alcohol were 8.3 and 9.5 min., respectively, as
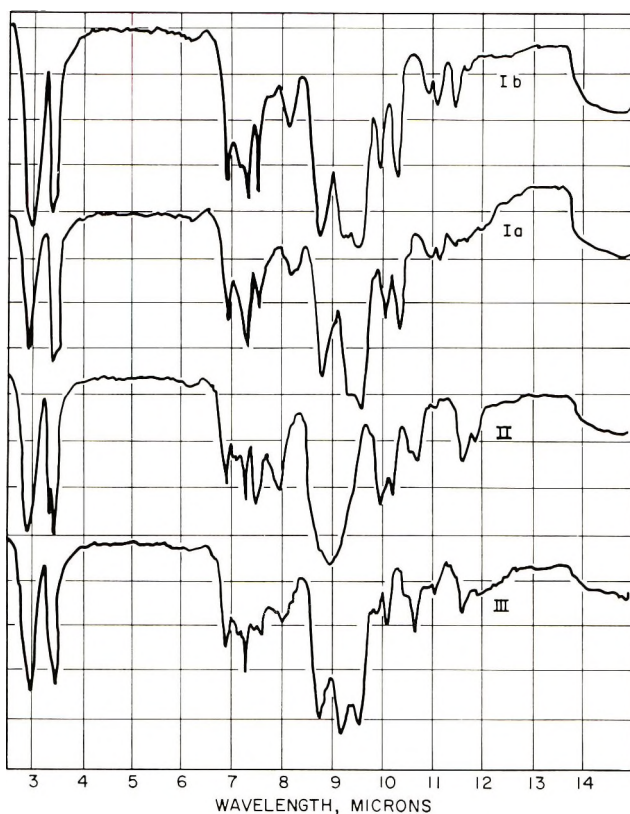
Fig. 2. Infrared spectra of dipropylene glycol isomers.

shown in Figure 3. The relative areas show about 45% II, 50% III, and perhaps 5% I which was not clearly separated from the III. It was necessary to use very small quantities (less than 5 μl.) for satisfactory separation. After repetitive collections sufficient material was obtained for the infrared spectra shown in Figure 2.

The identity of the three diglycol isomers was further confirmed by NMR spectra (neat). I had a doublet at 8.79 τ ($J = 15$) (6H), a singlet (4H) over a broad multiplet (2H) centered at 6.23 τ, and a singlet at 4.65 τ (OH). II had a doublet at 8.85 τ ($J = 15$) (6H), a doublet at 6.64 τ ($J = 15$) (4H), a sextuplet at 6.05 τ ($J = 15$) (2H), and a singlet at 5.01 τ (OH). III had a broadened doublet at 8.91 τ (6H), a broad doublet (4H) over a multiplet (1H) at 6.51 τ, a multiplet at 6.09 τ (1H), and a singlet at 4.97 τ (OH).

Polymerizations of Propylene Oxide

Diethylzinc–Water Catalyst. Propylene oxide (20 g., 0.34 mole) which had previously been dried and distilled over calcium hydride was placed in a polymerization tube which had been flushed out several times with

dry nitrogen and covered with a serum cap, and 3.55 ml. (3.41 mmole) of a solution of diethylzinc in heptane was then added together with 61.4 μl. water. The tube was then sealed and allowed to stand at steam bath temperature for 2 days and at room temperature for 12 days. The tube was opened and the contents dissolved in 200 ml. of acetone, containing 2 ml. of water and 0.5 g. of 2,6-di-*tert*-butyl-*p*-cresol. The acetone solution was then chilled to −20°C. in order to precipitate the crystalline (isotactic) polymer. The amorphous (atactic) fraction was obtained by removal of the acetone using a rotary evaporator. The yield of crystalline polymer
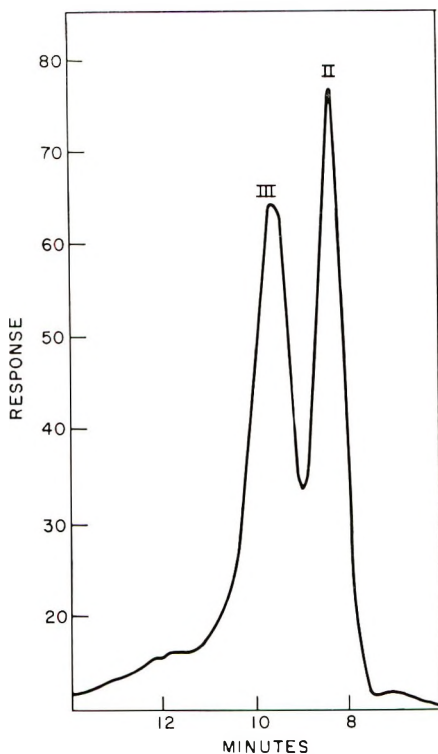

Fig. 3. Vapor-phase chromatogram of commercial dipropylene glycol; column (1), temperature 160°C., helium flow 100 ml./min., 1.5 μl.

was 3.7 g., and of atactic polymer, 13.8 g. (69%) of a very viscous oil, [η] = 2.53 in benzene at 25.0°C.

Triethylaluminum–Water. Dry monomer (25 g., 0.43 mole), 2.5 ml. (3.63 mmole) of a 1.45M solution of triethylaluminum in heptane (Hercules Powder Co.) and 54 μl. (2.97 mmole) of water were added to a polymerization tube which was prepared and sealed and polymerization was carried on as in the previous experiment. The work-up of the crude polymer was carried out in a similar manner. The yield of crystalline polymer was 3.0 g., and the yield of atactic polymer was 15.3 g. of a pale yellow material which was too viscous to flow, [η] = 0.61 in benzene.

Ferric Chloride–Propylene Oxide Catalyst. The catalyst was prepared according to directions supplied to us by Pruitt;[3] 1 g. of this was used with 25 ml. of dry monomer. After sealing, the tube was placed in an iron pipe on a steam bath for 24 hr. The crude polymer was worked up by dissolving it in 250 ml. of hot acetone containing 0.5 g. of 2,6-di-*tert*-butyl-*p*-cresol. The color of the solution changed from dark brown to yellow when 5 ml. of concentrated hydrochloric acid was added to hydrolyze the unreacted catalyst. The isotactic and atactic fractions were recovered as previously described. After washing with water the yield of atactic polymer was 17.3 g. of a brown, viscous oil, $[\eta] = 0.260$ in benzene. The yield of crystalline polymer was 2.7 g.

Potassium Hydroxide Catalyst. The directions of St. Pierre and Price[9] were used. Dry propylene oxide (50 g.) and dry powdered potassium hydroxide (4.2 g.) were placed in a 250-ml., three-necked round-bottomed flask equipped with a mechanical stirrer and water-cooled condenser. The reaction was allowed to continue for 3 days at room temperature. The reaction mixture was then dissolved in 50 ml. of anhydrous ether and shaken with an acid ion exchange resin until the solution showed an acid reaction to litmus. The ether was then removed using a rotary evaporator, leaving 31 g. of light yellow oil; $[\eta] = 0.105$ in benzene.

Ozone Degradation

Ozone degradation of 7.3 g. of isotactic polypropylene oxide (m.p. 68.5°C., mol. wt. 215,000)[3] in 110 ml. of methylene chloride was carried out by treating with ozonized oxygen from a Welsbach model T-23 ozonator at the rate of 87.4 mg./min. After 3.48 g. had been passed through, 2.90 g. was found to have been absorbed, i.e., 1 mole of O_3 for each 2.1 moles of ether linkages.

The solution was concentrated to about 75 ml. with a rotary vacuum evaporator at room temperature. The reaction mixture at room temperature was then slowly added during a period of about 1 hr. to a large excess of lithium aluminum hydride (10 g., 264 mmole) in 350 ml. of ether. The mixture was allowed to react overnight and the excess lithium aluminum hydride destroyed by slowly adding ethyl acetate. The metal alkoxides were decomposed by slowly adding 50 ml. of water. The solution was filtered and the ether solution concentrated on a rotary evaporator. The precipitate was continuously extracted with ether for 5.5 hr. in a Soxhlet extractor. The ether extracts were combined with the bulk of the product and evaporated on a rotary evaporator. The crude product, containing a large amount of solvent, weighed 12.5 g. The product was analyzed by vapor-phase chromatography by use of the preparatory size column (2) to avoid repetitive collections. The temperature was 150°C. and the helium flow rate was 300 ml./min. The elution time of the single dipropylene glycol fraction was 31.8 min. Decyl alcohol was used as an internal standard. The yield, based on area ratios, was 2.8 g., i.e., 35% of theory

based on one mole of dipropylene glycol per mole of ozone reacted.   The
infrared spectrum of the dipropylene glycol fraction is given in Figure 4.

By a similar procedure, 7.5 g. of a solid rubbery amorphous polymer
($[\eta]$ 4.7 at 60°C. in isopropanol) in 500 ml. of methylene chloride was treated
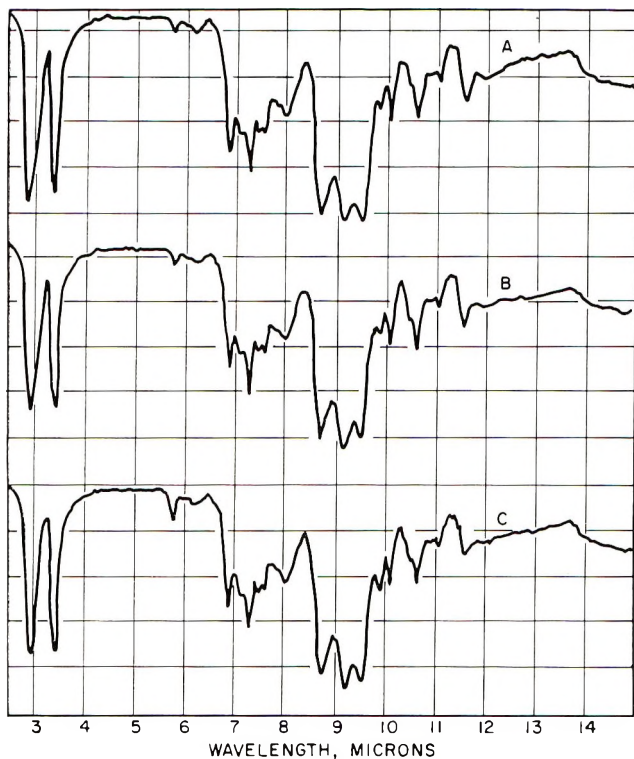

Fig. 4. Infrared spectra of dipropylene glycols from degraded poly(propylene oxides):
(A) amorphous, cyanide catalyst; (B) liquid, base catalyst; (C) crystalline, Al(i-PrO)$_3$·
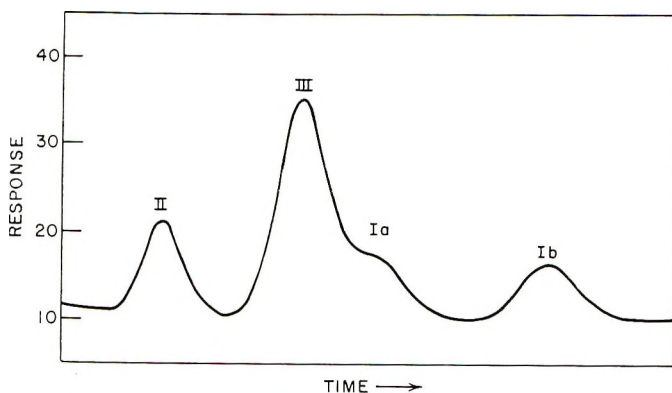ZnCl$_2$ catalyst.

Fig. 5. Vapor-phase chromatogram of dipropylene glycol from amorphous poly(propylene
glycol), ZnEt$_2$·H$_2$O catalyst.

with 3.11 g. (64.7 mmole) of ozone. It absorbed 2.78 g. (58.0 mmole), i.e., 1 mole of ozone for each 2.2 moles or ether linkages. Isolated as before, the weight of crude product was 6.6 g. Analysis by vapor-phase chromatography showed a single dipropylene glycol peak, elution time 31.2 min., yield 1.3 g., i.e., 17% of theory based on one mole per mole of ozone reacted. The infrared spectrum of the dipropylene glycol fraction is given in Figure 4.

A solution of 7.5 g. of commercial polypropylene oxide (mol. wt. 2025) in 500 ml. of methylene chloride was treated with 2.37 g. (49.5 mmole) of ozone. It absorbed 2.15 g. (43.7 mmole), i.e., 1 mole of ozone for each 3.0 moles ether linkages. The crude product, 7.3 g., on analysis by the vapor-phase chromatography gave a single diglycol peak, elution time 31.3 min., yield 0.7 g., i.e., 12% of theory based on one mole per mole of ozone reacted. The infrared spectrum of the dipropylene glycol fraction is given in Figure 4.

When various other amorphous polymers prepared as above were similarly ozonized, the diglycol fraction showed substantial amounts of I and II, in addition to III. A typical example is illustrated in Figure 5. All the diglycol data are summarized in Table I.

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Résumé

Par ozonisation prolongée et réduction subséquente à l'hydrure de lithium aluminium le PPO peut être transformé en un matériau contenant du dipropylène-glycol. On peut aisément séparer par chromatographie en phase vapeur, les isomères diprimaires, disecondaires et primaires-secondaires; c'est ainsi qu'il est possible de montrer que certains, mais non tous les échantillons de PPO non-cristallins, contiennent certains arrangements tête-à-tête en queue-à-queue des monomères. La corrélation entre la fraction tête-à-tête en queue-à-queue des monomères. La corrélation entre la fraction tête-à-tête avec la rotation optique des fractions non-cristallines au départ de monomères optiquement actifs, indique qu'il y a un centre d'asymétrie, inverti pour chaque unité insérée en tête-à-tête. La suggestion antérieure, que la fraction non-cristalline serait due à la stéréochimie atactique, est ainsi montrée incorrecte de façon générale en faveur d'une explication due à une isomérisation de position.

Zusammenfassung

Durch weitgehende Ozonisierung und Reduktion mit Lithium-aluminiumhydrid kann PPO in ein Material, das Dipropylenglykol enthält, umgewandelt werden. Da die diprimären, disekundären und primär-sekundären Isomeren gaschromatographisch leicht getrennt werden können, war es möglich in einigen (aber nicht in allen) nicht-kristallinen PPO-Proben viele Kopf–Kopf und Schwanz–Schwanz-Monomerbausteine nachzuweisen. Die Korrelation zwischen dem Bruchteil an Kopf–Kopf-Bausteinen und der optischen Drehung der nichtkristallinen Fraktionen aus optisch aktivem Mono-meren zeigt, dass ein Asymmetriezentrum für jede vorhandene Kopf–Kopf-Einheit invertiert ist. Die früher vorgeschlagene Erklärung, dass nämlich der nicht-kristalline Bruchteil auf eine ataktische Struktur zurückzuführen ist, erweist sich daher als im allgemeinen unrichtig gegenüber der Erklärung durch Stellungsiomerie.

Ionic Polymerization of *p*-Vinylbenzyl Methyl Ether

ROBERT O. SYMCOX and JOHN D. COTMAN, JR.,* *Central Research Department, Monsanto Company, St. Louis, Missouri 63166*

Synopsis

Ionic polymerizations of vinylbenzyl methyl ether initiated by either carbanions or Lewis acids has been found to lead to crosslinked polymers. By comparative studies of strong carbanionic bases and Lewis acids with benzyl ethers, it has been possible to define details of mechanisms which in conjunction with cationic or anionic propagation lead to crosslinks. The α-hydrogens of benzyl ethers have been found to be sufficiently acidic to terminate anionic polymerization of styrene and displacement of alkoxide anion from the benzyl ether linkage by nucleophilic polymer anions is proposed as a mechanism leading to branching and eventual crosslinking in anionic polymerization of vinylbenzyl methyl ether. Cationic polymerization of vinylbenzyl methyl ether is quite complex. In addition to propagation, chain transfer, and spontaneous termination of cation chain carriers, there is evidence for complex formation between Lewis acid initiator and the benzyl ether substituent. A slow decomposition of ether–Lewis acid complexes produces benzylcarbonium ions which alkylate aromatic rings of polymer and thereby crosslink the polymer. Benzyl ether has been found to be an effective chain terminator for cationic styrene polymerization.

Free-radical polymerization of *p*-vinylbenzyl methyl ether has been found to follow a normal mechanism involving initiation, propagation, and bimolecular free-radical termination.[1] The benzyl ether substituent was observed to be reactive to free radicals from the initiator and particularly susceptible to hydrogen abstraction by methyl or acetyl free radicals generated by photolysis of biacetyl. In case of free-radical initiation, the side reaction involving the substituent which resulted in the extreme in crosslinking was kinetically significant with peroxides only at high conversion. Crosslinking occurred at all conversions for the photoinitiator biacetyl. In peroxide initiation, crosslinking could be avoided by polymerization in benzene which competed effectively with benzyl hydrogens of the substituent for initiator radicals. Attempts at ionic polymerization of this monomer have indicated that initiation by either anionic or cationic species does not lead to linear poly(vinylbenzyl methyl ether) but to crosslinked products due to involvement of the functional benzyl ether grouping with chain carriers and initiator. The reactivity of the benzyl ether grouping toward carbonium ions or carbanions is so great that benzyl-type ethers interfere with ionic polymerization of styrene. Some of the observations and details of mechanism that have been elaborated are presented below.

* To whom all correspondence should be addressed.

EXPERIMENTAL

Materials

p-Vinylbenzyl methyl ether or the mixed *ortho* (25%) and *para* isomers (75%) were prepared by the method of Abramo and Chapin.[2] Purification was effected by distillation at reduced pressure from calcium hydride, b.p. 52°C./1–2 mm. Styrene was freed of inhibitor, dried over calcium hydride, and distilled under nitrogen at reduced pressure. Initiators for cationic polymerization were analytical grade and, except for aluminum chloride, were used without additional purification. Aluminum chloride was mixed with powdered aluminum and sublimed in a stream of nitrogen. The sublimed product was evacuated for several hours to remove adsorbed hydrogen chloride. Solvents were dried over suitable reagents and fractionally distilled in a nitrogen atmosphere. Dimethoxyethane was dried over sodium and fractionally distilled from disodium benzophenone ketyl under nitrogen immediately before use. Tetrahydrofuran was purified in an analogous fashion. Naphthalene, tetraphenylethylene, biphenyl, and triphenylmethyl chloride were purified by repeated crystallization and vacuum dried before reaction to form anionic initiators. Sodium biphenyl and sodium naphthalene in dimethoxyethane or disodium tetraphenylethylene in tetrahydrofuran were prepared immediately before use by reaction of excess sodium and hydrocarbon in purified solvent under nitrogen with cooling. Molarities were determined by hydrolysis of aliquots and titration with standard acid. Sodium triphenyl methide in ether was prepared by reaction of triphenylmethyl chloride with 1% sodium amalgam.

Polymerization Procedures

Anionic initiation of vinylbenzyl methyl ethers was carried out in a round-bottomed three-necked vessel equipped with connections to a vacuum line, a tapered seat for a monomer vial with break seal, and a neck with a self-sealing rubber septum. Stirring was provided by a Teflon-covered magnetic bar. Before a run the reactor was heated in an oven to 120°C. and cooled with a stream of dry nitrogen passing through. Monomer was introduced from the vial, the reactor evacuated, and solvent distilled in under vacuum. After degassing, the reactor was brought to 1 atm. with nitrogen, immersed in a bath at the desired temperature, and initiator introduced through the septum by means of a hypodermic syringe. Polymer formed was isolated by pouring into methanol, filtering, and drying in vacuum.

In preliminary cationic polymerization runs, 10% solutions of monomer in solvent in tubes were flushed with nitrogen and initiator added as a solution or suspension in the same solvent. For more detailed study, reactions were carried out in a cylindrical reactor described elsewhere[3] equipped with a thermocouple to measure temperature rise. The solution of monomer in solvent was degassed on a vacuum line, sealed off under vacuum, and immersed in a bath at the desired temperature. Initiator

solution was introduced through a rubber septum by means of a hypodermic syringe. Reactions were usually instantaneous and resulted in a temperature rise. Polymers were isolated by precipitation into a large excess of methanol 10% in hydrochloric acid. After methanol washing and filtration, polymers were vacuum-dried. Intrinsic viscosities in chloroform were measured at 25°C. in an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Anionic Initiation

Addition of sodium triphenyl methide in ether or sodium biphenyl or sodium naphthalene in dimethoxyethane to solutions of mixed *o*- and *p*-vinylbenzyl methyl ethers 0.027*M* in dimethoxyethane at 25°C. resulted in immediate discharge of initiator color with precipitation of a small amount of red-brown insoluble solid. Lowering of the temperature to −78°C. before addition of initiator resulted in identical observations. Incremental addition of initiator at −78°C. was found to result in progressively more insoluble red-brown polymer, and approximately quantitative yield of polymer was obtained by addition of 0.015 mole of disodium tetraphenylethylene in tetrahydrofuran to 0.027 mole monomer in dimethoxyethane. Polymer formed at once, and the deep color of the disodium adduct discharged slowly. After 15 hr. the reaction mixture was poured into methanol and polymer isolated. This polymer was found to be insoluble in acetone, dimethoxyethane, methyl ethyl ketone, toluene, or cyclohexanone. Infrared spectra on Nujol mulls revealed a polymer structure similar to free-radical initiated poly(*p*-vinylbenzyl methyl ether) but of lower benzyl ether content and containing some hydroxyl groups.

Polymerization of a mixture of equal volumes of styrene and benzyl methyl ether in dimethoxyethane (∼0.1*M* in styrene) at −78°C. by addition of sodium naphthalene in dimethoxyethane resulted in a transient red coloration of the styryl anion which soon disappeared, accompanied by colored precipitate formation. Incremental addition of initiator was followed after each addition by the same transient styryl anion. Polymer yields were found to be <5%. These results clearly indicated that the benzyl ether groups were reacting to destroy styryl anions.

Benzyl methyl ether was found to react with sodium naphthalene in dimethoxyethane, or metallic sodium. In a study of the reaction of benzyl methyl ether with sodium a number of products were isolated. For example, reaction of 12.2 g. of benzyl methyl ether (0.082 mole) with 2.0 g. of sodium wire (0.087 g.-atom) was observed to be quite exothermic. A transient green color appeared in the liquid phase, which faded to yellow as red solids formed on the surface of the sodium. Over a period of time increased amounts of red-brown solid separated from the solution as reaction progressed. After 8 hr. the gas phase was analyzed and a methane yield of 1% determined. Distillation on the vacuum line removed toluene (37%) and benzyl methyl ether (14%), leaving behind the dark

colored solid. (Yields are based on benzyl methyl ether charged.) Addition of 4.0 ml. of D_2O hydrolyzed the solid product and by distillation on the line methanol-OD (36%) and a small amount of deuterated benzyl methyl ether (<5%) were separated. Work up of the residue yielded α-phenylethanol-OD (~28%), a trace of dibenzyl (0.1%), and a polymeric residue (16%).

In a similar run 0.1 mole of benzyl methyl ether was reacted with 0.10 g.-atom of sodium at 50°C. for 8 hr. and after removal of methane (3%), benzyl methyl ether, and toluene, the solid residue reacted with oxygen for 4 days. By aqueous extraction followed by acidification 0.6 g. (5%) of benzoic acid was isolated. The benzoic acid was a product of oxidation of the anion C_6H_5—$\overset{(-)}{C}H$—OCH_3. Reaction of 0.076 mole benzyl methyl ether with 0.041 mole of butyllithium in pentane at −78°C. formed a deep red anion which reacted exothermically on warming to room temperature. On product workup, 3.45 g. of benzyl methyl ether (31.4%), 3.10 g. of α-phenylethanol (28.9%), and poorly defined polymer (9%) were isolated.

From the results of reactions of benzyl methyl ether with sodium and with butyllithium it was possible to define in some detail reasons for observations on polymerization attempts with mixed vinylbenzyl methyl ethers, and to account for the inhibiting effect of benzyl methyl ether on anionic polymerization of styrene. Schörigin[4] and more recently Moore[5] have observed that reaction of benzyl ethers with metallic sodium resulted in cleavage of ether in part to form toluene and rearrangement in part to α-alkyl benzyl alcohol. Wittig[6] has demonstrated that benzyl ethers react with strong bases such as lithium alkyls to form anions which rearrange to α-alkyl benzyl alcohols. Anion exchange by reaction of a styryl anion on benzyl methyl ether, as shown in eq. (1):
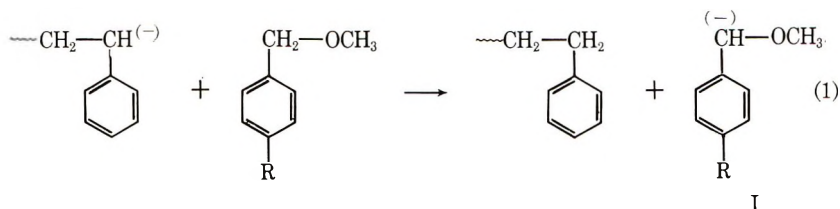

would explain the inhibition of styrene polymerization by benzyl methyl ether if the α-methoxybenzyl anion (I) is too unreactive to add to styrene. The anion-exchange reaction is effectively a termination of polymerization.

This type of reaction could also intervene in anionic polymerization of vinylbenzyl methyl ether and would result in very low polymer yield per initiator molecule consumed. However, the anion exchange reaction would not result in crosslinked polymer but rather in polymer of low DP. In our reactions of benzyl methyl ether with either sodium or butyllithium there have been isolated in each reaction polymeric fractions corresponding to anion displacement reactions on the benzyl ether group. The major

products of reaction, except for polymer, are consistent with the series of reactions of eqs. (2) and (3):
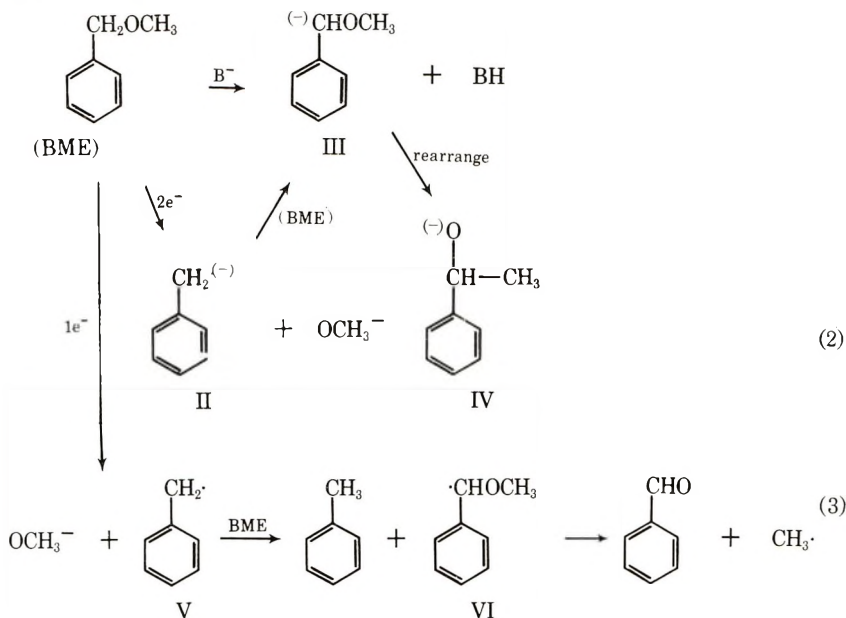
In the mechanism sequence proposed, the α-methoxybenzyl anion (III) is formed either by hydrogen abstraction from benzyl methyl ether (BME) by a strong base B⁻ or by reaction of the benzyl anion formed by cleavage of benzyl methyl ether involving two sodium atoms designated (2e⁻). In the latter case, BH is toluene, which is a major reaction product. Rearrangement of III to IV is the well-described Wittig rearrangement. The alternative (1e⁻) route is postulated to account for traces of methane (1–3%) isolated but is not considered a major reaction path. The reactions above represent the Shörigin-Wittig chemistry. Both the results with benzyl methyl ether and anionic polymerization of vinylbenzyl methyl ether indicate in addition nucleophilic displacement reactions such as that shown in eq. (4).
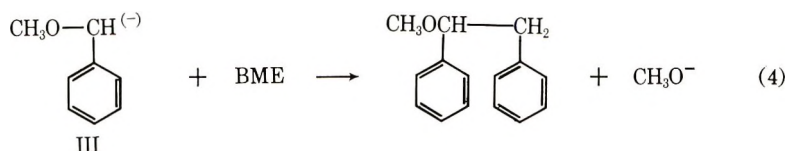
This additional detail of mechanism requires a greater yield of methanol than toluene for a sodium cleavage of benzyl methyl ether. To determine if this was so, 24.5 g. (0.171 mole) of benzyl methyl ether was reacted with excess sodium (0.20 g.-atom) and after hydrolysis of the solid phase, methanol yield determined not by distillation but by quantitative conversion to methyl nitrite[7,8] under conditions which did not

hydrolyze benzyl ethers ($NaNO_2$ in water + acetic acid). The volatile nitrite was swept from solution by nitrogen, freed of acids by passing over solid sodium nitrite then over solid sodium bicarbonate, and finally reacted with acidified potassium iodide. Nitrous acid released by hydrolysis converted iodide to iodine which was titrated with standard thiosulfate. The methanol yield was 60%. Analysis of the other products of reaction by vapor-phase chromatography gave: toluene, 47%; α-phenylethanol, 26%; polymeric oils, ~17%. (The yield of polymeric oil is indefinite because of a deficiency of —OCH_3.) Assuming that deviation of (methanol yield)/(toluene yield) > 1.0 is due to reaction (4), we were able to account for 93% of reacted benzyl methyl ether. The remaining few per cent may have been C_6H_5—$\overset{(-)}{CH}$—OCH_3 which we did not determine in the solid reaction phase.

In summary, the evidence for nucleophilic displacement of —OCH_3 from benzyl ether groupings by either α-methoxybenzyl anions or benzyl type anions to form dimeric products is sufficient for reaction (4) to be considered as a route to crosslinked polymer. If, after limited anionic propagation, the polymeric anion (VII) terminates by hydrogen abstraction from a polymer benzyl ether group [eq. (1′)]

VII   VIII
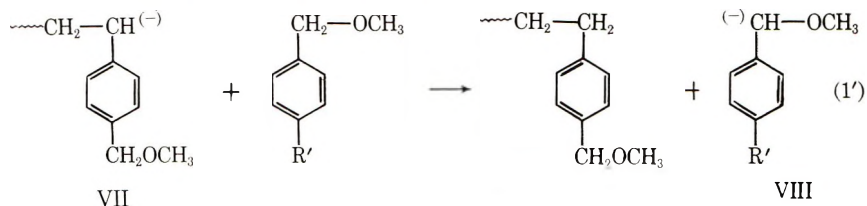
to form an α-methoxybenzyl anion on polymer (VIII), where R′ is a polymer chain, VIII may rearrange to an alcohol or displace —OCH_3 from another polymer benzyl ether group to form a polymer branch. The addition of increments of strong base (initiator) leads to an appreciable concentration of VIII units in polymer already formed, and crosslinking may be a consequence of type (4) reactions of the substantial number of anions on the polymer functional groups.

Cationic Initiation

Preliminary screening tests on the reactivity of mixed vinylbenzyl methyl ethers with a variety of initiators of carbonium ion polymerization were carried out in a number of solvents at 25°C., unless otherwise indicated. Results of these experiments are summarized in Table I. The plus sign (+) indicates that for a particular solvent–catalyst combination polymerization took place. The absence of polymer formation is designated by a minus (−). From these results it appeared that strong Lewis acids and sulfuric acid were effective initiators for polymerization of vinylbenzyl methyl ether, whereas less electrophilic or very insoluble metal salts (Al_2F_6) were ineffective as initiators. In systems where polymerization

occurred, reaction was rapid and quite exothermic. Polymers complexed with catalyst were quite deeply colored, but the color usually discharged on quenching with acidified methanol. Except for sulfuric acid initiation, polymers prepared were usually of low molecular weight at high initial monomer (M_0) to catalyst (I_0) ratios and molecular weights increased progressively as M_0/I_0 was lowered. For example, in a polymerization of vinylbenzyl methyl ether in nitrobenzene at 20°C. with Al_2Cl_6 as initiator, for $M_0/I_0 = 61.2$, the polymer isolated was a viscous oil of very low molecular weight. For $M_0/I_0 = 3.0$, polymer isolated was solid and had an intrinsic viscosity in toluene of 0.10. When sulfuric acid was used as initiator, polymers formed were always crosslinked.

TABLE I

Cationic Polymerization of Vinylbenzyl Methyl Ether at 25°C.

| Initiator	Polymer formation							
	Bulk	Hexane	Toluene	Ethyl-ene dichlo-ride	Nitro-benzene	Nitro-ethane	Ethyl ether	Liquid sulfur dioxide ($-10°$ C.)
$SbCl_5$			+		+			
$BF_3 \cdot Et_2O$	+	−	−	+	+	+		−
$SnCl_4$	+	+	+	+	+	+		+
Al_2Cl_6	+	+	+	+	+	+		+
H_2SO_4	+	+	+	+	+	+		+
$ZnCl_2$	−	−	−	−	−	−	−	−
$HgCl_2$	−	−	−	−	−	−	−	−
Al_2F_6[a]			−	−			−	
Al_2F_6[b]			−	−			−	
$(C_6H_5)_3CCl-$ HgCl_2	−		−				−	

[a] Prepared by $Al_2Cl_6 + CH_3CH_2F \xrightarrow{CH_3Cl} Al_2F_6$.

[b] Prepared by $Al_2Cl_6 + BF_3 \xrightarrow{CH_3Cl} Al_2F_6$.

The abnormal dependence of molecular weight of polymer formed on M_0/I_0 indicated that reactions other than cationic vinyl polymerization were taking place, and a sequence of experiments was carried out which established the involvement of the benzyl ether function in polymerization and crosslinking. Poly(p-vinylbenzyl methyl ether) of $[\eta] = 0.50$, prepared by free-radical initiation, was dissolved in chloroform and stannic chloride added dropwise. On each addition of stannic chloride, polymer precipitated from solution. The precipitated polymer on standing in contact with the Lewis acid in solution slowly became red in color. Polymer recovered by alcohol wash was no longer soluble in chloroform and was crosslinked. Infrared spectra of mulls of crosslinked polymer in Nujol were quite similar to those of the original soluble polymer. Similar results were obtained by addition of sulfuric acid.

The fact that there was a slow reaction of the benzyl ether function with a Lewis acid was also confirmed by experiments with benzyl methyl ether. Equimolar stannic chloride and benzyl methyl ether reacted when mixed at 25°C. Considerable hydrogen chloride was evolved over a period of time, the reaction mixture became quite viscous, and a deep red color developed. The red color was discharged on addition of methanol which precipitated the polymer as a cream-colored solid. Similar products were formed at a much more rapid rate when benzyl chloride in methylene chloride reacted with catalytic quantities of stannic chloride.

Other workers[9-11] have found that benzyl ethers are cleaved by Lewis acids to form benzyl carbonium ions, and our results suggest conversion of vinylbenzyl methyl ether into crosslinked polymer by alkylation of polymer by electrophilic benzyl carbonium ions produced by Lewis acid cleavage of benzyl ether groups on polymer in addition to cationic propagation:
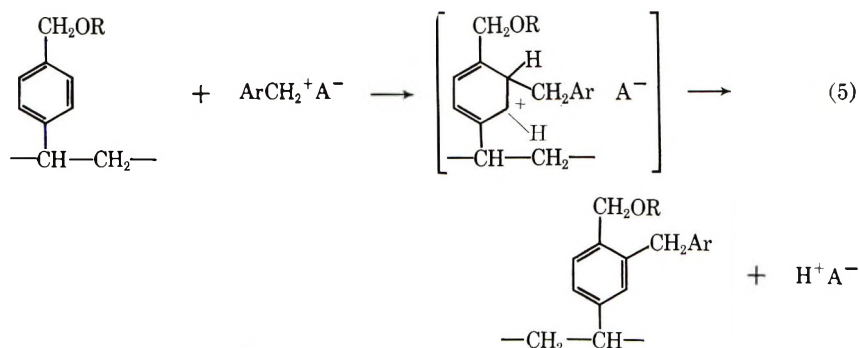
$$\text{where Ar is } -CH_2-\overset{|}{CH}-C_6H_4.$$

Additional confirmatory evidence that substituent groups on polymer were reactive was afforded by an experiment in which vinylbenzyl methyl ether in nitrobenzene (6 g./20 ml.) was polymerized at 20°C. by incremental addition of $0.45M$ aluminum chloride in nitrobenzene. The temperature rise after each addition of initiator to cumulative M_0/I_0 ratios indicated are summarized in Table II. Even at the high final ratio of initiator to monomer, conversion to polymer was incomplete. A total of 4.5 g. of polymer was isolated, of which 0.5 g. was crosslinked. The polymer yield was essentially equal to the content of the *para* isomer. The intrinsic viscosity of soluble polymer was approximately 0.1. The observation of crosslinking before conversion of monomer to high polymer was complete suggests a substantial competition of functional groups on polymer with residual monomer for added increments of initiator. However, analysis of soluble polymer (C, 81.4%; H, 7.82%) corresponds to an elemental composition $C_{10.1}H_{11.5}O$, which is sufficiently close to the theoretical ($C_{10}H_{12}O$) for vinylbenzyl methyl ether to conclude that the fraction of ether groups cleaved to generate benzyl carbonium ions was small.

TABLE II

Cationic Polymerization of Vinylbenzyl Methyl Ether in Nitrobenzene, AlCl$_3$ Initiator

Cumulative M_0/I_0	Temperature increase, °C.
60	12
20	2
5	6
2.6	5
2.0	4

In the absence of evidence for substantial loss of methoxyl by formation of benzyl carbonium ions we arrive at the conclusion that the exotherms observed on incremental addition of initiator subsequent to initial polymerization are due in part to polymerization and in part to formation of strongly solvated ether complexes of aluminum chloride by exchange of ether for nitrobenzene of the nitrobenzene complex. Dilke et al.[12] have found that the heat of solution of aluminum chloride in nitrobenzene is −7.9 kcal./mole while formation of the slightly more stable complex with anisole is exothermic to −8.2 kcal./mole. Whereas establishment of equilibrium:

$$C_6H_5NO_2 \cdot AlCl_3 + R\ddot{O}Ar \rightleftharpoons C_6H_5NO_2 + \underset{Ar}{\overset{R}{\diagdown}}O: AlCl_3 \qquad (6)$$
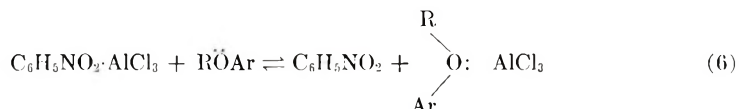
would be only slightly exothermic, transfer of AlCl$_3$ from nitrobenzene to the aliphatic benzyl methyl ether should be considerably more exothermic because of greater electron pair availability on oxygen of a benzyl ether than for anisole. The increase in color as more initiator was added is probably due to formation of complexes such as
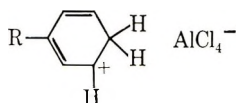
involving aluminum chloride, aromatic nuclei, and traces of free HCl.

The failure to polymerize a fraction of monomer exactly equal to the percentage of the *ortho* isomer in the monomer mix may be due to steric interference of cationic polymerization of the *ortho* isomer which has been reported by Pepper[13] for 2- or 6-substituted styrenes.

Haas et al.[14] and Kockelbergh and Smets[15] have reported that cationic graft polymerization takes place in the monomer–polymer combinations styrene–poly-*p*-methoxystyrene and isobutylene–polychloromethylstyrene. Haas et al. have postulated that grafting in the system styrene–poly-*p*-methoxystyrene involves an alkylation mechanism similar to our route to branching and eventual crosslinking. Overberger and Endres[16] have also postulated electrophilic substitution of aromatic nuclei as a mechanism of chain transfer in cationic styrene polymerization.

The very low molecular weight of poly(vinylbenzyl methyl ether) formed by cationic initiation with catalytic quantities of aluminum chloride we ascribe to very rapid chain transfer and termination mechanisms. The initial exothermal reaction indicated in Table II corresponds to substantial monomer conversion to low molecular weight polymer. Other polymers isolated at this M_0/I_0 were oils. It was also found that polymerization of styrene in the presence of a benzyl ether produced lower molecular weight polystyrene. Results of comparative polymerizations of styrene in the presence and absence of benzyl ether are summarized in Table III.

TABLE III
Cationic Polymerization of Styrene in Nitrobenzene at 25°C.

	1	2
Styrene, mole/l.	2.94	2.43
$(C_6H_5CH_2)_2O$, mole/l.	0.00	0.879
$AlCl_3$, mole/l.	0.037	0.031
Polymer yield, %	73	48.5
$[\eta]$ of polymer	0.114	0.095

Both yield and $[\eta]$ were lower in the presence of benzyl ether. Pepper and his co-workers[17-20] have examined in some detail the nature of transfer and termination mechanisms in cationic polymerization of styrene initiated by sulfuric acid and report that ethers are effective chain terminators for what is essentially a "dead end" cationic polymerization. The low polymer yield of styrene polymerization in the presence of 0.36 times its concentration of benzyl ether indicates that a benzyl ether is also an effective hydrogen-ion acceptor from a polystyryl counterion pair, and to a degree this effect probably pertains for polymerization of vinylbenzyl methyl ether. In the presence of vinylbenzyl methyl ether rapid reinitiation by a process such as (7):

$$[CH_3O - CH_2Ar]AlCl_4^- + M \rightarrow M^+AlCl_4^- + CH_3OCH_2Ar \qquad (7)$$
$$H^+$$
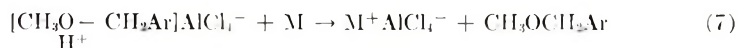
could result in high conversions to polymer of relatively low molecular weight. To the extent that protonated ether does not reinitiate polymerization, hydrogen transfer to ether becomes a termination reaction.

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Résumé

Les polymérisations anioniques de l'éther vinylbenzyl-méthylique initiées soit par des carbanions ou par des acides de Lewis fournissent des polymères pontés. Par des études comparatives de fortes bases carbanioniques et des acides de Lewis avec des éthers benzyliques, il a été possible de déterminer les détails du mécanisme qui, outre la propagation cationique ou anionique, fournit des ponts intermoléculaires. Ce sont les hydrogènes en α des éthers benzyliques, qui sont suffisamment acides pour terminer la polymérisation anionique du styrène; c'est le déplacement de l'anion alcoxyde au départ du lien éther benzylique par l'anion nucléophile polymérique qui est responsable du mécanisme amenant la ramification et éventuellement le pontage en cours de polymérisation anionique de l'éther vinylbenzyl-méthylique.

Zusammenfassung

Die durch Carbanionen oder Lewis-Säuren gestartete ionische Polymerisation von Vinylbenzylmethläther führt zu vernetzten Polymeren. Durch vergleichende Untersuchungen starker Carbanionbasen und Lewis-Säuren mit Benzyläthern konnten Einzelheiten des bei kationischem und anionischem Wachstum zur Vernetzung führenden Mechanismus aufgeklärt werden. α-Wasserstoffe von Benzyläthern sind genügend sauer, um die anionische Polymerisation von Styrol abzubrechen und als Verzweigungs- und eventuell Vernetzungsmechanismus bei der anionischen Polymerisation von Vinylbenzylmethyläther wird eine Verdrängung des Alkoxydanions aus der Benzylätherbindung durch nukleophile Polymeranionen vorgeschlagen.

Polymerization of 1,3-Butadiene on Cobalt and Nickel Halides

W. S. ANDERSON, *Shell Development Company, Emeryville, California 94608*

Synopsis

Butadiene polymerizes to *cis*-1,4 polymer on irregularly stacked, halogen-deficient crystals of cobalt(II) or nickel(II) halides. Halogen is removed from the halides by heating the salts under high vacuum or by photolyzing them in the presence of butadiene. Intrinsic viscosity and solubility of the polymer reach a steady state during polymerization. Cobalt chloride produces polymer of higher intrinsic viscosity than nickel chloride, but polymerization on nickel chloride is faster. Catalytic activity is attributed to the presence of $\leq 0.1\%$ of nickel and cobalt monohalides in the catalyst.

INTRODUCTION

Low oxidation-state transition metal halides are known to be catalysts for the polymerization of monoolefins. Titanium(II) chloride, for example, is reported to polymerize ethylene[1] and propylene[2] in the absence of other catalyst components. Equally simple compositions which will polymerize dienes in stereoregular fashion have not been reported. This paper describes the heterogeneous stereoregular polymerization of 1,3-butadiene on defective nickel(II) and cobalt(II) halides.

RESULTS

Butadiene polymerizes on solid anhydrous cobalt(II) and nickel(II) chlorides to a polymer in which 90% (CoCl₂ catalyst) and 95% (NiCl₂ catalyst) of the monomer linkages are of the *cis*-1,4 type.[3] The structure of the polymer is concluded from infrared absorption spectra, which display a strong *cis*-olefin C-H bending mode at 13.7 μ and relatively weak bands at 11.0 μ (vinyl) and 10.3 μ (*trans* olefin). These polymers thus differ sharply in structure from ordinary free radical- or cation-initiated polybutadienes. Only about half of the polybutadiene prepared on nickel(II) chloride or cobalt(II) chloride is soluble in benzene, the remainder being gelled (see Table I). Gelled polymer is 5–10% higher in *trans* content and correspondingly lower in *cis* content, but otherwise displays no infrared absorptions not found in the soluble polymer. There is no visible change in the cobalt chloride or nickel chloride during polymerization, except that it becomes covered with gelled polymer. Polymer prepared on nickel chloride

TABLE I
Polymerization of Butadiene on Nickel(II) Chloride, 25°C.[a]

Conversion, %	Intrinsic viscosity, dl./g.[b]	Solubility in benzene, %
16	0.88, 0.97	46, 46
17	1.05	43
24	0.86, 0.94	45, 47
33	0.90	50
34	1.03	47
85[c]	0.73	48

[a] 10.0 ml. butadiene, 0.10 g. NiCl$_2$, sealed Pyrex ampules, 25°C., illuminated with a General Electric BH-6 lamp 40 cm. from ampules.

[b] Toluene, 25°C.

[c] Illuminated with a BH-6 lamp for 16 hr., then with a fluorescent lamp for 200 hr.

does contain 0.01–0.05% of bound chlorine, however. No dimers or trimers could be detected by extraction and distillation of the polymer prepared on NiCl$_2$.

The intrinsic viscosities of the soluble polymers produced by nickel chloride are consistently lower than those prepared on cobalt chloride. Cobalt chloride produces polymers of intrinsic viscosity 1–2 dl./g. (toluene, 25°C.), whereas nickel chloride under the same conditions (Table I) produces polymers of intrinsic viscosity 0.7–1.0 dl./g. From Table I it is evident that the intrinsic viscosity of the soluble product does not increase with conversion.

In darkness, the polymerization on cobalt or nickel chloride alone is very slow. Light from an incandescent lamp, fluorescent tube, or high pressure mercury arc may be used to accelerate it, however. Illumination of one side of a static bed of nickel or cobalt chloride in butadiene causes the illuminated catalyst particles to become covered with polymer before any polymer appears on the unilluminated particles. Polymerization on illuminated nickel(II) chloride is about five times faster than polymerization on illuminated cobalt(II) chloride, which, in turn, is faster than polymerization on iron(II) chloride. Figure 1 shows the course of polymerization of butadiene on nickel(II) chloride in rocked, sealed ampules illuminated with a high-pressure mercury arc. As the figure shows, butadiene can be stored over NiCl$_2$ for many hours with only slight polymerization; after long storage in the dark, exposure to light accelerates polymerization sharply. An increase in bath temperature when added to exposure to light increases polymerization rate still further, as shown in Figure 1, but produces polymer of slightly lower intrinsic viscosity (Table II) and of 92% cis-1,4, 6% trans-1,4 and 2% vinyl content. The cis-1,4 content is thus measurably lower at the higher polymerization temperature. Irradiation of butadiene alone under the conditions represented in Figure 1 does not initiate polymerization. Similarly, irradiation of nickel(II) chloride at 25°C. in evacuated sealed tubes prior to contact with butadiene does not produce a measurable acceleration. After exposure of the buta-
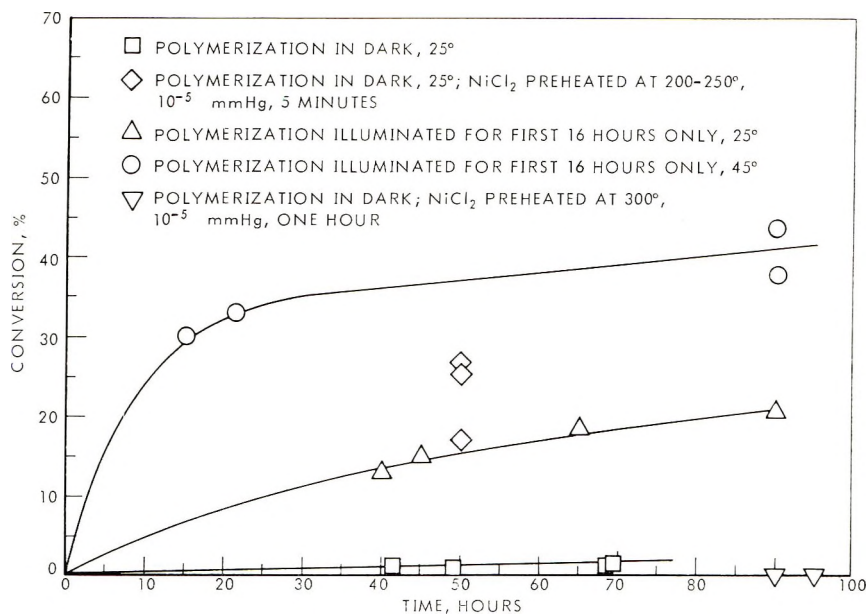
Fig. 1. Polymerization of butadiene on nickel chloride with 10 ml. butadiene, and 0.10 g. nickel chloride in sealed Pyrex ampules 40 cm. from BH-6 arc. Each point represents a different polymerization.

diene–nickel chloride mixture to light, polymerization proceeds in darkness until monomer is exhausted and a vacuum develops in the reaction vessel. Polymerization resumes if butadiene is readmitted two years after the exhaustion of the initial monomer supply. Electron bombardment (3 M.e.v.) of butadiene mixed with nickel or cobalt chloride is not as effective as illumination of these mixtures because high-energy radiation is absorbed by the monomer.[4]

TABLE II
Polymerization of Butadiene on Nickel(II) Chloride, 45°C.[a]

Conversion, %	Intrinsic viscosity, dl./g.	Solubility, %
30	0.67	51
33	0.64	48
39	0.62	51
47	0.78	50

[a] Same illumination and concentrations as in Table I.

If nickel chloride is heated at 200–250°C. and evacuated to 10^{-5} mm. it darkens in color due to the loss of chlorine.[5-11] The preheated, rapidly cooled material is an active catalyst in the absence of light, giving a dark polymerization rate at least equal to that obtainable on unheated, il- luminated nickel chloride. Table III shows the structure of some polymers

obtained on preheated nickel chloride. It is best that the catalyst not be heated until metallic nickel appears; heating nickel chloride at 300°C. for 1 hr. at 10^{-5} mm. renders the sample ferromagnetic and catalytically inactive. Cobalt chloride is also dehalogenated and activated by preheating in vacuum, although the change in catalyst color is not as apparent as in the nickel example on account of the initially darker color of the cobalt salt and the stronger metal-to-halogen bond.

The gradual decrease in polymerization rate shown in Figure 1 is attributed to the coverage of the catalyst with gelled polymer. Crosslinking sets in at low conversions, as is apparent from Table I, and polymer solubility remains constant at 40–50% from conversions of 15% to at least 85%; i.e., there is no sharp gel point. If the polymerization is allowed to continue for several weeks, however, all of the product is gelled. Soluble polymer mixed with fresh nickel chloride and exposed in vacuum to light from a high-pressure mercury arc is also gelled. This suggests that soluble and insoluble polymer are not produced by two independent polymerization

TABLE III
Polymerization of Butadiene on Preheated Nickel(II) Chloride[a]

Polymerization temperature, °C.	cis, %	trans, %	Vinyl, %
0	96	3	1
25	95	3.5	1.5
45	92	6	2
65	92	5	3
85	92	5	3

[a] Preheated at 10^{-5} mm. Hg and 200–250°C. on a manifold connected to a trap cooled in liquid nitrogen. Concentrations as in Table I. Gel content of polymer is 50 ± 10%; microstructures refer to the soluble portion.

reactions and that the crosslinking is a second step. The constancy of the sol fraction (Table II) suggests that the crosslink density does not change with conversion and that therefore the constant intrinsic viscosity of the soluble portion represents constant molecular weight. In an attempt at eliminating the crosslinking during polymerization, anthracene was added to the charge. Anthracene is a known butadiene radical acceptor and retards crosslinking in the radiation-induced polymerization of ethylene,[12,13] but saturating the monomer with anthracene does not eliminate the crosslinking process in the butadiene–nickel chloride system. Butadiene containing 0.3% carbon dioxide as an inhibitor for anionic reactions also polymerized with crosslinking. No means for eliminating crosslinking was found.

Among cobalt halides, catalytic activity falls in the order $Co(CN)_2 \sim CoCl_2 > CoBr_2 > CoI_2$. Under identical polymerization conditions (bulk polymerization for 2 weeks in sealed tubes at 25°C. on catalysts preheated 5 min. at 400°C. on a manifold at 10^{-5} mm.), cobalt iodide gives <1% yield

of polymer, cobalt bromide gives approximately 50% conversion, and cobalt cyanide and chloride give nearly complete conversion to polymer.

In contrast to the dry halides, a number of cobalt and nickel derivatives failed to convert butadiene to high polymer at detectable rates under the conditions of our experiments (25°C., bulk monomer, sealed tubes, fluorescent light). These include cobalt or nickel metal prepared by heating the formates under high vacuum, cobalt or nickel oxide preheated in high vacuum or in air at 200–400°C. (or not preheated), nickel(II) chloride hexahydrate, and aqueous nickel(II) chloride or aqueous cobalt(II) chloride. The dichlorides of platinum, palladium, copper, manganese, and zinc were also inactive. Copper(II) chloride was partially reduced by butadiene to white crystals of copper(I) chloride.

Supported catalysts can be more effective than unsupported types. Nickel chloride on silica–alumina, for example, gave a polymerization rate several times higher than pure nickel chloride. Cobalt chloride on carbon black was effective, but the polymerization in this case could not be promoted by light, possibly because the support was opaque. Nickel chloride or cobalt chloride films vacuum-sublimed onto the walls of Pyrex ampules were very inefficient catalysts; polymerization on such films required several days to reach detectable conversion.

Defective nickel chloride at 25°C. proved rather specific for polymerization of butadiene. 1-Hexene and 1,5-hexadiene did not yield high polymer. Isoprene required weeks for significant conversion, and the product was not as high in cis-1,4 structure as polybutadiene prepared on the same catalyst. Styrene was polymerized on this catalyst to a low molecular weight, noncrystallizable polymer; the polymerization rate was greater than in the absence of nickel chloride, however. The high specificity for butadiene is reminiscent of the behavior of the more practical $CoCl_2$-based polybutadiene catalysts. Thus the cis-polybutadiene catalyst $CoCl_2$ + $AlCl_3$ + AlR_3 + C_6H_6 does not convert monolefins to high polymer and polymerizes isoprene relatively slowly to a product lean in cis-1,4 structure.

EXPERIMENTAL

Materials

Butadiene was Phillips pure grade material found by gas chromatography to be 99.8% pure. Anhydrous nickel(II) chloride and cobalt(II) chloride were prepared from reagent grade hexahydrates by pumping at 1 mm. Hg at 100–150°C. for 5–10 hr., grinding in a mortar to pass a 50-mesh screen, and redrying. Water was collected in a trap cooled in Dry Ice. The resulting $NiCl_2$ dissolved rapidly and completely in water, which suggested that very little hydrolysis of the chloride occurs during dehydration. Ferromagnetic nickel content (Faraday method) was <0.0001%. Cobalt chloride is partially hydrolyzed during dehydration; the dehydrated product is not completely water soluble. Elemental analyses indicated that the extent

of hydrolysis was small, however.   Calculated for $CoCl_2$:   Co, 45.4%; Cl, 54.6%. Found: Co, 44.8%; Cl, 53.8%.

The halides were weighed into ampules and redried by pumping at 10^{-4} to 10^{-5} mm. Hg for 1–2 hr. on a manifold equipped with a liquid nitrogen trap and mercury diffusion pump.

Polymerization Technique

All polymerizations were conducted in sealed Pyrex ampules.   On a high vacuum manifold, outgassed butadiene was distilled from a bulb at $-78°C$. into ampules containing the dried catalyst.   The monomer was then outgassed again.   The ampules were sealed with a torch and attached to a rocking platform immersed in a constant temperature water bath.   When polymerizations were to be conducted in darkness, the ampules were wrapped in aluminum foil.   Lamps were placed above the bath.   Conversions were determined by opening the ampules, evaporating the monomer in stream of nitrogen, and weighing the residue.   Polymer solubility was determined by gently rocking the dried sample in benzene for 24 hr., then determining the concentration of polymer in solution by evaporation. Infrared spectra were obtained by evaporating a benzene solution of polymer on a sodium chloride plate and recording the spectrum of the resulting film on a Beckman IR-4 instrument.   Polymer composition was calculated by using the absorptivities of Hampton.[14]

CONCLUSIONS

The transition metal ions in perfect layer-lattice halides are well protected from monomer by the close-packed halide ions.   However, neutron diffraction patterns[15] show that crystals of $CoCl_2$ have many stacking faults when prepared by dehydration of the hydrate.   Similarly, $FeCl_2$ prepared by slow dehydration has a random stacking sequence until sublimed; sublimation produces the close-packed cubic structure.[16]   Grinding also probably contributes to the concentration of stacking faults, especially to translations between the halogen layers.[17]   The low density of stacking faults (and, therefore, of steps and edges) in sublimed $NiCl_2$ and $CoCl_2$ accounts for the relative inactivity of sublimed samples as catalysts.

The mere presence of stacking faults in $NiCl_2$ is not enough to make it a polymerization catalyst.   Some dehalogenation is required.   This can be accomplished by heating the salt to 200°C., where it loses 0.1 mole-% chlorine,[5,6] or by photolyzing it in the presence of butadiene thus transferring halogen to butadiene, or, as is well known, by adding a chemical reducing agent such as a metal alkyl.   However, complete removal of halogen from the nickel chloride does not yield a polymerization catalyst; initiation and termination of polymerization are bifunctional on atomic nickel, and therefore reaction stops at the cyclic oligomer stage.[18,19] Furthermore, samples of nickel chloride heated until they become strongly ferromagnetic (free nickel) are not polymerization catalysts.   Finally,
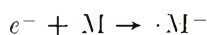
nickel is known to react with nickel chloride at high temperature to produce nickel monochloride;[20] the species responsible for the initiation of butadiene polymerization is probably nickel monochloride. The single halogen atom, it is assumed, would block the cyclization step but still allow nickel to bond covalently to butadiene.

Since $Co(CN)_2$ decomposes when heated to yield CoCN whereas $Ni(CN)_2$ decomposes directly to the elements,[25] it was predicted that preheated $Co(CN)_2$ would be a better catalyst than heated $Ni(CN)_2$. In fact no polymer was obtained on preheated $Ni(CN)_2$, whereas preheated $Co(CN)_2$, as indicated above, is highly effective.
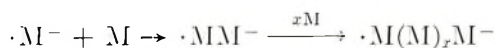
As temperature falls below 1200°C., nickel monochloride disproportionates extensively into metal plus dichloride.[21] There are two conclusive pieces of evidence that aluminum chloride stabilizes the monochloride against this disproportionation: (1) $AlCl_3$ increases the solubility of nickel metal in $NiCl_2$;[22] and (2) polarography of $NiCl_2$ (or $CoCl_2$) in $AlCl_3$–NaCl shows two distinct waves;[23] in NaCl–KCl only one wave is seen.[24] Therefore, a probable role of aluminum halide and aluminum alkyl halide in the more practical cobalt and nickel halide-based recipes for *cis*-polymerization of butadiene is simply to stabilize the catalyst; *cis*-polymerization can clearly be accomplished with a catalyst containing transition metal halide alone.

One school of heterogeneous catalysis on semiconductors treats reactions in terms of electron transfers to and from the substrate.[26] Thus, for a polymerization on a subvalent transition metal halide one might write three steps:
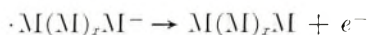
Initiation:

$$e^- + M \rightarrow \cdot M^-$$

Propagation:

$$\cdot M^- + M \rightarrow \cdot MM^- \xrightarrow{xM} \cdot M(M)_x M^-$$

Chain transfer:

$$\cdot M(M)_x M^- \rightarrow M(M)_x M + e^-$$

Termination:

None

Such an electronic shuttle would account for the catalytic steady state, for the failure of the catalyst to be consumed by the polymerization and for the need of a subvalent metal ion with high reduction potential. Theoretical molecular weight distributions can also be calculated for this model. This scheme fails to provide any really useful predictions, however; it fails to interpret or predict relative reactivity of monomers, penultimate effects or polymer microstructure. In the author's opinion, the model fails because it does not consider that electron transfer occurs in two direc-

tions in all three steps of polymerization. Thus all treatments of Ziegler-type polymerizations using such concepts as carbonium ions, carbanions, hydride ions, and radicals have little predictive value. A really useful theory of such polymerizations will probably treat the steps of polymerization as concerted processes.

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Résumé

Le butadiène polymérise en un polymère *cis*-1,4 sur des cristaux irrégulièrement empilés et déficients en halogène de chlorure de cobalt(II) ou de nickel(II). L'halogène était éliminé au départ de ces halogénures par chauffage des sels sous vide élevé ou par photolyse en présence de butadiène. La viscosité intrinsèque et la solubilité du polymère atteignait un état stationnaire au cours de la polymérisation. Le chlorure de cobalt produit un polymère de viscosité intrinsèque plus élevée que le chlorure de nickel,

mais la polymérisation sur le chlorure de nickel est plus rapide. L'activité catalytique est attribuée a la présence de $\leq 0.1\%$ de monohalogénures de nickel et de cobalt au sein du catalyseur.

Zusammenfassung

Butadiene polymerisiert an unregelmässig gestapelten Kristallen von Kobalt-(II)- oder Nickel-(II)-halogeniden mit Halogenfehlstellen zum *cis*-1,4-Polymeren. Halogen wird aus den Halogeniden durch Erhitzen der Salze im Hochvakuum oder durch Photolyse in Gegenwart von Butadiene entfernt. Viskositätszahl und Löslichkeit des Polymeren erreichen während der Polymerisation einen stationären Wert. Kobaltchlorid erzeugt Polymere mit höherer Viskositätszahl als Nickelchlorid, die Polymerisation an Nickelchlorid verläuft aber rascher. Die katalytische Aktivität wird auf die Anwesenheit von $\leq 0,1\%$ Nickel- und Kobaltmonohalogeniden im Katalysator zurückgeführt.

Graft Copolymerizations of Gaseous Vinyl Chloride and Vinylidene Chloride on Preirradiated Polypropylene

KIYOSHI HAYAKAWA and KAORU KAWASE, *Government Industrial Research Institute, Nagoya; Hirate-machi, Kita-ku, Nagoya, Japan*

Synopsis

The graft copolymerizations onto the preirradiated polypropylene fibers of gaseous vinyl chloride and also of gaseous vinylidene chloride were carried out. The fibers were preirradiated with γ-rays from a ^{60}Co source at $-78°$C. in air to a total dose of 8×10^6 rad, and were thus presumed to contain peroxide radicals which were active in grafting at ordinary temperature. The volume decrease of monomers at constant pressures due to the sorption and the grafting reaction was followed automatically at temperatures ranging from -10 to $80°$C. The net monomer consumption through the grafting process was estimated by subtracting the volume change due to the sorption from the total volume change of monomers. In general, the extent of grafting was lower at the higher grafting temperature and the decrease of the grafting activity of fibers was also accelerated. The grafting was found to increase almost linearly with the logarithm of the reaction time and the logarithm of the radiation dose to the fibers. The extent of grafting was also proportional to the vapor pressure of monomer at a given reaction temperature and was supposed to be controlled by the amount of the monomer adsorbed. Raising the irradiation temperature higher than $0°$C. brought about a marked decrease in the activity of preirradiated polypropylene. The grafting activity was successfully retained by the polymer for at least a fortnight at $-78°$C.

INTRODUCTION

In the majority of the works hitherto carried out on the radiation graft copolymerizations, the polymers destined to be the backbone were usually dipped into liquid monomers or the monomer solution on reaction, or alternatively the polymers preliminarily swollen in the liquid monomer were irradiated to obtain the graft copolymers.[1-3]

Only recently that the use of monomer vapor in graft copolymerization has attracted the attentions of many research workers; this tends to avoid the problem of homopolymer formation which inevitably occurs in liquid monomer with the radiation grafting and thus depresses the efficiency of the monomer utilization considerably. Also a higher degree of grafting is sometimes attainable by the grafting method with monomer vapor than by using liquid monomer directly.[4-6] Moreover, the fact that there is substantially no homopolymer formation minimizes the after-treatments required, which is a major point in favor of the vapor-phase method from the industrial point of view.

In the several graft copolymerizations by gaseous monomers previously reported, the direct radiation grafting technique was used predominantly and a preirradiation technique seemed to be rarely adopted. As we earlier noticed the remarkable after-effect in the direct radiation grafting of gaseous vinyl chloride and also of vinylidene chloride on the polypropylene fibers,[7] we have tried to study in further detail the preirradiation grafting with the same combination of the polymer and monomers to elucidate the reaction kinetics, because this has not previously been reported.

The preirradiation method applied to the polypropylene fibers in this experiment belongs to the so-called low-temperature preirradiation method. Matsuda and his collaborators[8] have found that when polypropylene, cellulose, and other polymers were irradiated by γ-rays at Dry Ice temperature in the presence of air, a considerable amount of peroxide radicals was produced and trapped in the polymers, and these were able to initiate very efficient graft copolymerization without raising the reaction temperature. Consequently the homopolymer formation due to the heating and to the hydroxyl radicals from the cleavage of hydroperoxides has purposely been depressed. The radicals are also known to be stable for a long time at Dry Ice temperature.

Apart from the argument on the nature of the radicals concerned, the above method seemed to be especially suitable for vapor-phase grafting, for the lower temperatures usually favor this kind of grafting reaction. In order to reduce fluctuations in the data which frequently cause ambiguity in the graft copolymerization, an automatic recording apparatus has been devised to follow the volume change of the monomer vapor, thus making the kinetic discussion easier. The correlation between the grafting and the sorption of monomers was also investigated.

EXPERIMENTAL

Materials

The polypropylene used in this experiment was the fibrous form (5 den.) supplied by Toa Spinning Co. Ltd. and having a molecular weight of 45,000. The fibers were cut to lengths of about 6 cm., extracted with tetrahydrofuran for 8 hr. with a Soxhlet extractor, dried in air at room temperature, and stored in a desiccator over silica gel.

Vinyl chloride was supplied by Toa Synthetic Co. Ltd., and dried with anhydrous calcium chloride in the system which was attached to an automatic recording apparatus (shown in Fig. 1). After condensing vinyl chloride gas into the bottom of the monomer reservoir, a small part of it was pumped out at −78°C., and then the monomer was allowed to evaporate again and stored in the monomer reservoir at atmospheric pressure.

Vinylidene chloride was obtained from Tokyo Kasei Industrial Co. Ltd. and treated in the same way as vinyl chloride; it was stored in a monomer reservoir at a pressure of about 300 mm. mercury.
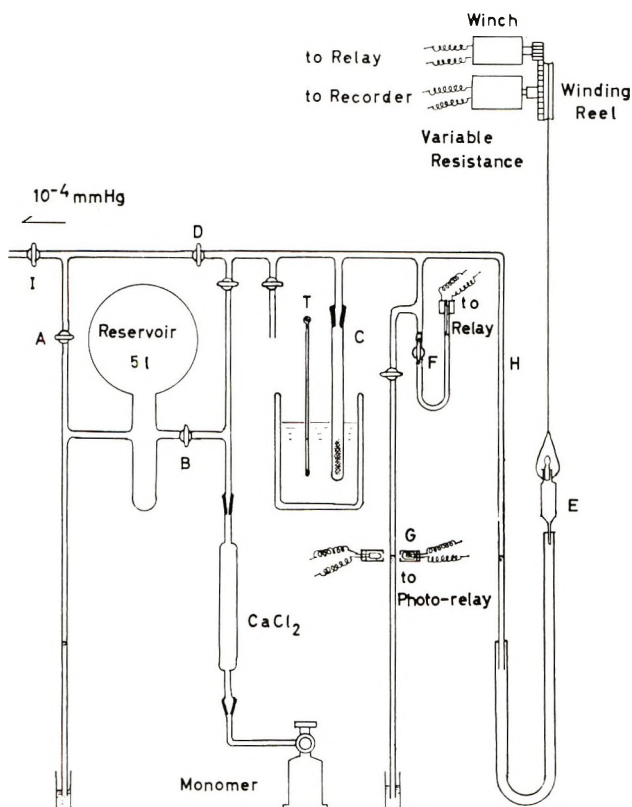
Fig. 1. Automatic recording apparatus.

Irradiation of Polypropylene Fibers

The irradiation of polypropylene was carried out by γ-rays from a 3000-c. ^{60}Co irradiation facility at a dose rate of 3.3×10^4 rad/hr. In the ordinary procedure about 1 g. of polypropylene fibers for the vinyl chloride experiments, and 0.2 g. for the vinylidene chloride experiments, were put into a 20-mm. diameter glass tube fitted with an interchangeable tapered ground joint and tightly closed off with a glass stopper and the use of lubricating grease.

The glass tubes containing fibers were set into a Dewar flask containing a Dry Ice–methanol mixture in the standard procedure, and the irradiation was carried out for about 24 hr. to a total dose of 8×10^5 rad in all the experiments except as otherwise noted.

Automatic Recording Apparatus

Figure 1 shows a diagram of the automatic recording apparatus for measuring the volume change of monomer at a constant pressure. The monomer vapor was stored in a reservoir which had previously been evacuated by a mercury diffusion pump with a liquid nitrogen trap as was

mentioned above. The glass-stoppered tube containing the irradiated fibers was then attached to the connection C, and pumped for 10 min. through the tap D, with the tap F closed. The sample was kept at −78°C. during the pumping to reserve the produced radicals. After that the Dewar flask in which the sample had been kept at the irradiation temperature was replaced by a thermostated bath regulated to the grafting temperature without introducing air, and the evacuation was continued for 5 min. more. The tap I was closed, and the monomer in the reservoir was introduced to the sample tube through stopcocks A and D as fast as possible until a defined pressure was reached. The reaction system was then isolated from the monomer reservoir system by closing stopcock D. The whole volume of the reaction system, including the sample tube, was about 120 ml.

As soon as the monomer vapor is introduced to the reaction tube, both sorption and grafting of monomer on fibers set in and the decrease in volume of monomer brings about a decrease in internal pressure in the system. The apparatus is provided with two kinds of the pressure change detector. One of the detectors, which is used for experiments at atmospheric pressure, is an ordinary contact relay utilizing the platinum wire and mercury. The tap F is opened as soon as enough monomer is introduced to bring the system to atmospheric pressure. As the monomer in the reaction system is consumed by any type of reaction, the decrease in the internal pressure breaks the contact of the platinum wire with mercury. The connected relay sets in motion the synchronous motor which changes the position of the mercury reservoir to restore the initial internal pressure again by decreasing the inner volume. The motor stops as the wire again makes contact with the mercury. The axis of the winding reel controlling the mercury reservoir is connected directly to a variable resistance and the change in the electric resistance along with the wound-up height is recorded by an autobalancing type recorder, Yokogawa Type ER-32. The recorder graduation increase is strictly proportional to the volume decrease in the glass tube under a constant pressure.

For measurements at reduced pressure the contact-type relay was replaced by the one using photocell G, but it was slightly inferior to the contact relay in sensitivity to pressure changes.

The whole apparatus was set in the shaded corner of the laboratory to avoid as much as possible changes of the room temperature during the experiment. Usually the fluctuation of monomer volume with room temperature change was negligible, compared with the rapid consumption of monomer, except in grafting at a high temperature. However, it did not seem desirable to continue the grafting longer, because the decreased rate at the later stages of reaction made the error caused by the variation of room temperature considerable. The grafting reaction was carried out for 3 hr. in an ordinary experiment.

After a given time of reaction, the tap F attached to the relay was closed and the fibers were pumped vigorously to remove all the unreacted monomers. After 15 min. evacuation air was introduced and the weight of the

fibers was determined gravimetrically. The results were expressed by the weight increase $(P - P_0)$ divided by the original weight P_0 of polypropylene fibers. The percentage of grafting was

$$\text{Percentage of grafting} = 100 \ (P - P_0)/P_0$$

No special treatment was adopted for the elimination of occluded homopolymer in each experiment. The occluded homopolymer constituted less than 6% of the amount grafted in the ordinary case as determined by extraction with hot tetrahydrofuran for 12 hr., and even this value was suspected to be an overestimate owing to a possible contamination with the grafted copolymer caused by the severe extraction. It would be hard to suppose that a considerable amount of the monomer polymerized itself in the matrix of polypropylene fibers without irradiation. Formation of polymer on the wall of the glass tube could not be observed.

Analysis of the Volume Change Curve

Figure 2 shows a typical plot of volume change of vinyl chloride with grafting time for 1 g. of polypropylene fibers. The ordinate is in arbitrary units of recorder graduations, which may be converted to the absorbed volume or absorbed weight of monomer by a suitable calibration. Hence the corresponding value on the right-hand ordinate in Figure 2 represents the percentage of the assumed weight increase calculated from the overall volume change. (It is not a real weight increase, because it results from both sorption and grafting reaction.)

The upper curve, is that for the preirradiated fibers, receiving 8×10^5 rad at a dose rate of 3.3×10^4 rad/hr. at $-78°C$. The lower curve is for
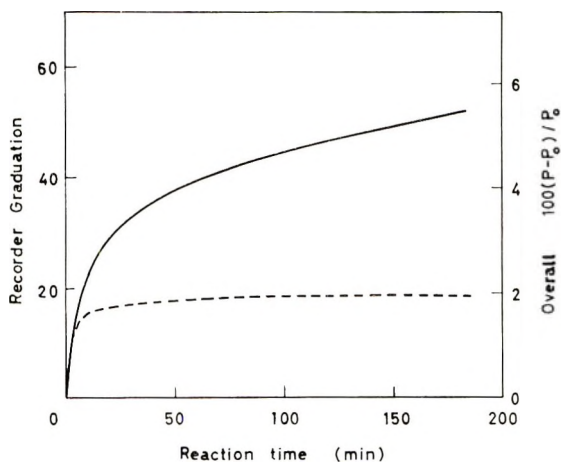

Fig. 2. Absorption of vinyl chloride by fibers of polypropylene and irradiated polypropylene; (———) polypropylene receiving total dose 8×10^6 rad, irradiated at a dose rate of 3.3×10^4 rad/hr. at $-78°C.$; (- - -) unirradiated polypropylene. Vinyl chloride, 760 mm. Hg, reaction temperature, 25°C.

the unirradiated fibers. In both cases, the quantity of monomer vapor consumed increased with the reaction time, but it could be seen that the limiting value of the absorbed amount was reached rapidly (within an hour) in the unirradiated polymer. This is considered to be due to the simple adsorption, because the original weight can be easily recovered by evacuation in a short time (about 10 min. pumping), and no weight increase is observed as a result. For the irradiated polymer, on the other hand, the curve showed no sign of the saturation, especially at a low grafting temperature, although the rate of the consumption decreased gradually with time, and a net increase of weight was observed even after intense evacuation. The increase in weight, however, was definitely lower than the $(P - P_0)/P_0$ value calculated from the actual volume change. It is obvious that a real grafting reaction occurred in parallel with the sorption by the polymer. That is to say, it would be impossible to arrive at any conclusion on the grafting reaction from the overall volume change curve of monomer without eliminating such an overlapping process. In this work the estimation of the net grafting reaction from obtained curves was made by subtracting the corresponding amount of the monomer consumed by the unirradiated fibers from that for the irradiated fibers (in other words, subtracting the lower curve from the upper curve in Fig. 2).

The consumption of monomer vapor by the unirradiated polymer seems to be due to simple (perhaps physical) adsorption. It would not be proper to ignore the diffusion or dissolution of monomer into the polymer matrix, although the assumption that the effects of these processes would be small in this combination of polymer and monomers may be permissible. However, we have no additional results to go more deeply into this problem at present, and so we include these phenomena under the term equilibrium sorption or adsorption.

Furthermore, it is doubtful whether the irradiated polymer in which the grafting reaction is proceeding exhibits the same adsorption behavior as the unirradiated one does. But, (1) in almost all the runs, the final grafted amount of monomer thus calculated was well in accordance with the grafted amount measured gravimetrically; (2) the grafted amount was less than 5% of the polymer in many cases, especially when vinyl chloride was used as the monomer vapor; (3) the polymer inactivated by a long storage at a room temperature showed almost the same behavior toward the gas as the unirradiated one did. From the above observation, we should be able to presume that the irradiated polymer shows behavior toward the monomer vapor similar to that of unirradiated polymer as far as the sorption process is concerned.

RESULTS AND DISCUSSION

Effect of the Grafting Temperature and the Reaction Kinetics

Figure 3 shows results for the grafting of vinyl chloride (760 mm. Hg) to preirradiated polypropylene at various temperatures. The irradiation
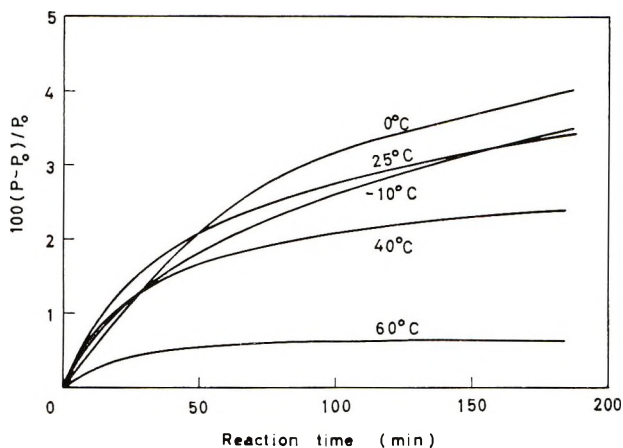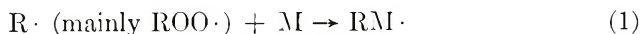
Fig. 3. Grafting of vinyl chloride at various temperatures. Vinyl chloride, 760 mm. Hg, polypropylene irradiated to a total dose of 8×10^5 rad at a dose rate of 3.3×10^4 rad/hr. at $-78°C$.

of the polymer was carried out according to the standard procedure. The elevation of the grafting temperature brings about the depression of the extent of grafting and also the activity of polymer for grafting is lost more rapidly at the higher temperature. At lower reaction temperatures the limiting value of percentage of grafting is not attained in a day or more, although the reaction rate becomes progressively slower. Vinylidene chloride was grafted more easily than vinyl chloride, even at lower pressures, but the overall aspect of the reaction seemed to be similar in both monomer–polymer combinations.

In order to interpret the observed results, the assumption was made that this reaction is due exclusively to propagation steps involving long-lived polymer chains. These were assumed to arise in the immobilized system owing to the reduced rate of recombination of radicals. The kinetic scheme shown in eqs. (1)–(4) may be applied from this view to the present system.
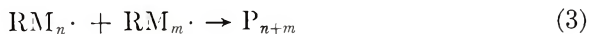
Initiation:

$$R \cdot \text{ (mainly } ROO \cdot \text{)} + M \rightarrow RM \cdot \tag{1}$$

Propagation:

$$RM_n \cdot + M \rightarrow RM_{n+1} \cdot \tag{2}$$

Termination:

$$RM_n \cdot + RM_m \cdot \rightarrow P_{n+m} \tag{3}$$

$$RM_n \cdot + R \cdot \rightarrow P_n \tag{4}$$

In this scheme, $R \cdot$ comprises mainly the polymer peroxide radical produced and trapped by the irradiation in the presence of air, but other types of radical are not excluded. (There is some disagreement on the nature of

the trapped radicals which are active for grafting.)   Some of them will be destroyed by the recombination with each other before reaction with polymer radicals or monomer [eq. (5)]

$$R \cdot + R \cdot \rightarrow X \tag{5}$$

$RM_n \cdot$ in eqs. (2)–(4) represents the propagating radical, and P_{n+m} and P_n are considered to be the grafted branches.   The termination would occur by other mechanisms, but in this scheme the mutual termination process was assumed for simplicity.

If it can be assumed that the various radicals including propagating ones have the same activity toward each other (that is, the same k_t can be assigned for the mutual recombination of the different radicals) or toward monomer, the number of free radicals and growing chains will decrease with time owing to the chain termination or the recombination in accordance with eq. (6):

$$d[RM_n \cdot + R \cdot]/dt = -k_t[RM_n \cdot + R \cdot]^2 \tag{6}$$

where k_t is the rate constant of the radical recombination.   Integrating this equation leads to

$$[RM_n \cdot + R \cdot] = [R \cdot]_0/(1 + k_t[R \cdot]_0 t) \tag{7}$$

Here $[R \cdot]_0$ is the initial concentration of polymer radicals at time $t = 0$. The rate of grafting is given by eq. (8):

$$R_g = k_p[RM_n \cdot + R \cdot] [M] \tag{8}$$

To simplify the equation, it is postulated that the concentration of monomer in the reaction site does not change widely with time except at the beginning of the reaction, owing to the rapid supply of the monomer to the fibers from the outer atmosphere.   As is shown in Figure 2, the rate of sorption of monomer considerably exceeded the rate of grafting.   For instance, the initial rate of adsorption was about $0.5\%/min$. at $25°C$., whereas that of grafting was the order of $0.1\%/min$. at the same temperature.   From the above assumption the monomer converted to the grafted branch during the time t is given by;

$$G = \int_0^t \{k_p[R \cdot]_0[M]/(1 + k_t[R \cdot]_0 t)\} dt$$

$$= k_p k_t^{-1}[M] \ln (1 + k_t[R \cdot]_0 t) \tag{9}$$

There are no data available to estimate the magnitude of $k_t[R \cdot]_0$ as far as the gas-phase graft copolymerization is concerned.   But assuming $G_R. = 1$ for polypropylene (though this may be an underestimation; see ref. 1, p. 606), 10^6 rad will give rise to a radical concentration of $[R \cdot] = 10^{-3}$ mole/1., when all the produced radicals are effectively accumulated. Therefore it seems to be possible to ignore 1 compared with $k_t[R \cdot]_0 t$ at
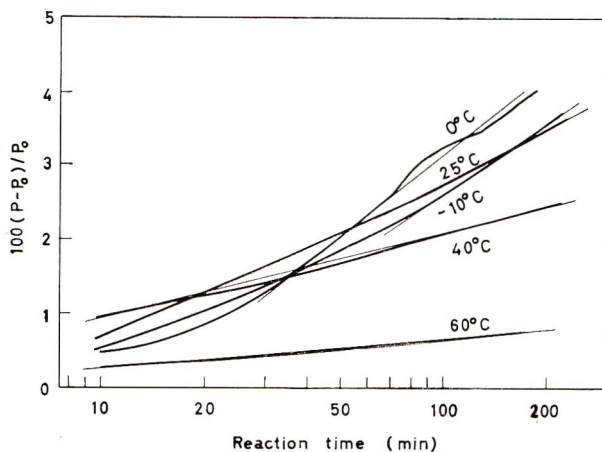
Fig. 4. Grafting of vinyl chloride at various temperatures plotted against the logarithm of the reaction time (from Fig. 3). Conditions as in Fig. 3.
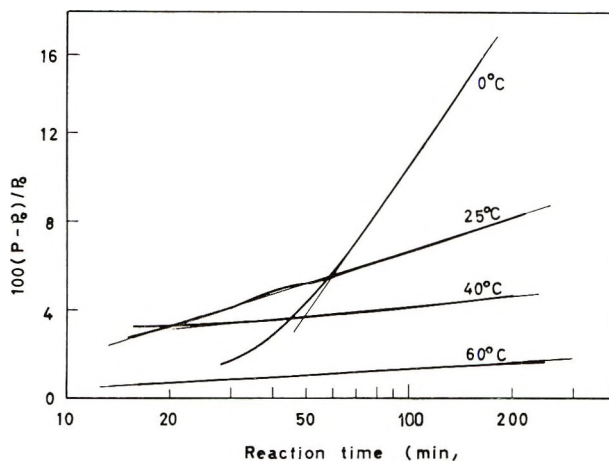

Fig. 5. Grafting of vinylidene chloride at various temperatures plotted against the logarithm of the reaction time. Vinylidene chloride, 200 mm. Hg; polypropylene irradiated to a total dose of 8×10^5 rad at a rate of 3.3×10^4 rad/hr. at $-78°C$.

sufficiently large t, even though k_t will not be allowed to have the ordinary order of values. From the above simplification eq. (10) is obtained;

$$G = k_p k_t^{-1}[M] \ln (k_t[R \cdot]_0 t) \qquad (10)$$

This final equation shows that the amount grafted should be directly proportional to [M] and also to log t for sufficiently large values of t.

In Figure 4 the percentages of grafting are plotted against the logarithm of time. The increase in amount of grafting is almost linear with the logarithm of the reaction time for a fairly long period in the later stage, in accordance with the above discussion. The deviation from the linear relationship in the initial stage is probably due to incomplete sorption of
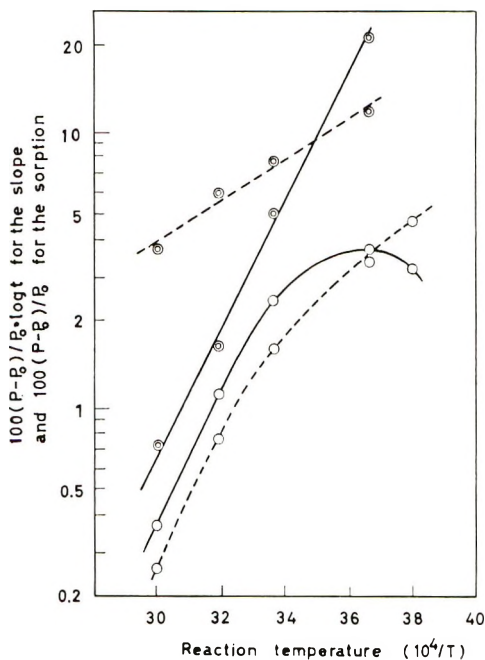
Fig. 6. Effect of Grafting temperature on the slope of the percentage grafting vs. log t plots and the equilibrium sorption on the unirradiated polymer: (———) slope of the percentage grafting vs. log t; (- - -) equilibrium sorption on the unirradiated polymer; (O) vinyl chloride at 760 mm. Hg; (⊚) vinylidene chloride at 200 mm. Hg.

monomer, because the duration of the deviation roughly coincides with that required to reach the equilibrium sorption when the monomer is introduced to the unirradiated polypropylene. The duration of deviation increased with decreasing grafting temperature. These results also suggest that the concentration of the monomer [M] should be able to be treated as a value which does not change so widely in the later stage at each temperature.

The same type of plot for vinylidene chloride grafting is shown in Figure 5, and they seem to resemble those for vinyl chloride grafting in overall appearance. But at $-10°C$. the vapor pressure of vinylidene chloride was lower than 200 mm. Hg. Therefore the experiment was restricted to a narrower temperature range.

If eq. (10) is acceptable, it follows that the slope of these straight lines in Figures 4 and 5 should be given by $k_p[M]/k_t$. Figure 6 shows the Arrhenius plot of the slope of the grafting percentage versus log t curve obtained from Figures 4 and 5. The equilibrium sorption of monomer on the unirradiated polypropylene at a constant pressure is also shown in the same figure for purposes of comparison. It is seen from Figure 6 that the rate of grafting has some intimate relationship with the sorption of monomer, especially in vinyl chloride experiment; both seem to be parallel over a wide range of reaction temperature. We have no satisfactory explanation,

however, at present as to why the rate of grafting at $-10°C.$ became slightly lower. Presumably, however, it is caused by the insufficient sorption of vinyl chloride, for it took a fairly long time to reach the equilibrium sorption at this temperature, as was already mentioned above.

In another case vinyl chloride was introduced to the irradiated and unirradiated polymer at various vapor pressures. The extent of grafting after 3 hr. reaction is shown in Figure 7, together with the sorption on the unirradiated polypropylene at various pressures of vinyl chloride. It
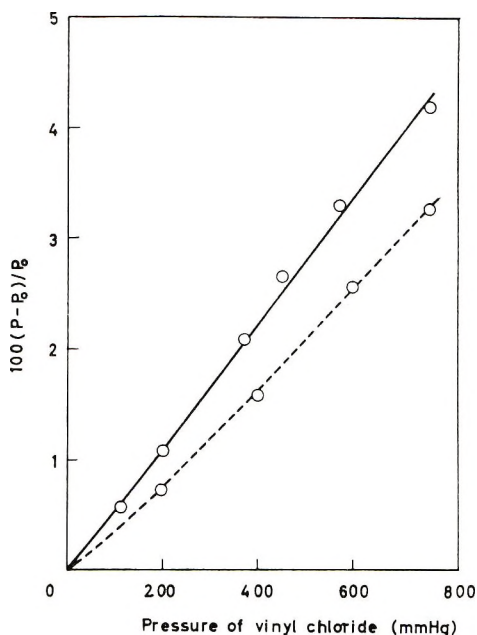

Fig. 7. Effect of the vapor pressure of vinyl chloride on the grafting and sorption: (——) percentage of grafting at 3 hr. reaction; (- - -) sorption isotherm for vinyl chloride on the unirradiated polymer. Reaction temperature, $0°C.$

was deduced from Figure 7 that (*1*) the equilibrium sorption was proportional to the pressure of monomer at a given temperature and (*2*) the amount of grafting also increased linearly with the increasing pressure of monomer and was parallel with the sorption.

From Figures 6 and 7, it would be natural to conclude that the rate of grafting is directly proportional to the equilibrium sorption, and [M] in eq. (9) or (10) should correspond to the amount adsorbed.

If it is assumed that [M] is determined by the adsorbed amount and is also temperature-dependent by the form of the Arrhenius relationship, $[M] = A_M e^{-E_M/RT}$ as well as $k_p = A_p e^{-E_p/RT}$ and $k_t = A_t e^{-E_t/RT}$, it is possible to calculate $E_t - E_p$ from Figure 6 and eq. (10) by simple subtraction. Thus, $E_t - E_p = 0$ for vinyl chloride and $E_t - E_p = 7.8$ kcal./mole for vinylidene chloride were obtained.
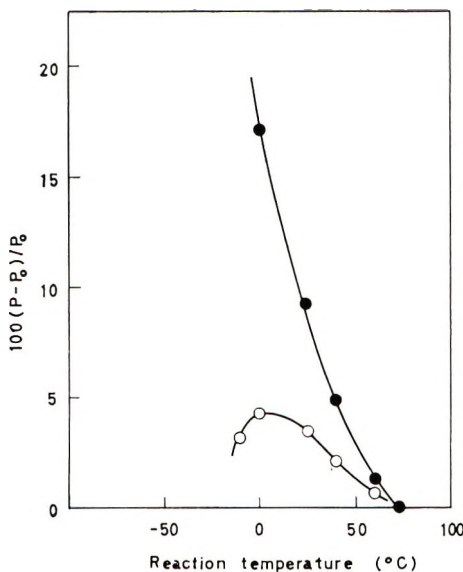
Fig. 8. Effect of grafting temperature on the percentage of grafting at 3 hr. reaction:
(O) vinyl chloride at 760 mm. Hg; (●) vinylidene chloride at 200 mm. Hg.

There is no reported value directly applicable to check the obtained results and accordingly, the validity of the assumption made to explain the phenomena. By speculation, however, if we presume that k_t is largely affected in each case by the rate constant of mutual termination of growing chains, it will have some meaning to compare those with the values reported on the polymerizations by the conventional means. In the liquid-phase polymerization of both monomers initiated by photochemical means, Burnett et al.[9,10] reported that there was no difference between E_p and E_t for vinyl chloride ($E_t - E_p = 0.5$ kcal./mole), but $E_t - E_p = 15$ kcal./mole for vinylidene chloride. These figures seem to be not so far from our results.

On the whole, the amount of grafting was profoundly affected by the grafting temperature, as is seen in Figure 8, which shows the change with grafting temperature of the extent of grafting at 3 hr. reaction for both monomers (from Figs. 4 and 5). Above 80°C. the grafting could not be achieved. The contribution to the initiation of the grafting of the radicals arising from the cleavage of hydroperoxides which were produced by irradiation seemed to be negligibly small if at all present.

Effect of Irradiation Dose of Polypropylene

Figure 9 shows the results of the 3 hr. grafting of vinyl chloride on the polypropylene irradiated to various doses at −78°C. in air. A previous electron spin resonance study showed that the concentration of trapped radicals in polypropylene increases linearly with increasing dose under these conditions.[8] If the mutual recombination mechanism allowing the ac-
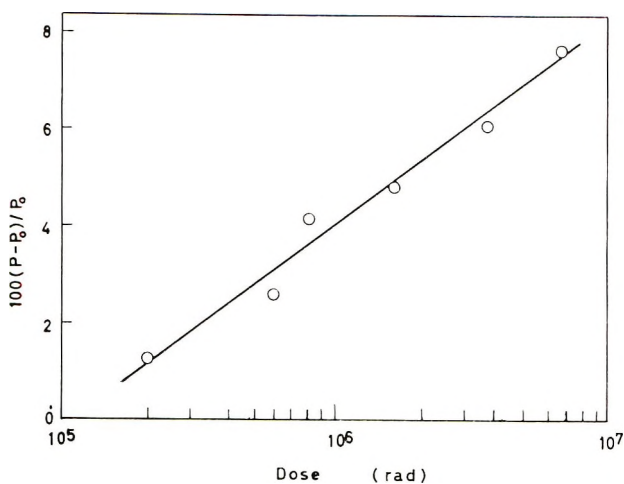
Fig. 9. Effect of irradiation dose on the percentage of grafting of vinyl chloride. Vinyl chloride, 760 mm. Hg; reaction time, 3 hr.; reaction temperature, 0°C.; irradiation temperature, −78°C.

cumulation of the trapped radicals is postulated, the relation between the grafting and the dose could be given by eq. (10), in which the concentration of initial radicals $[R \cdot]_0$ is replaced by cD, where D is dose given to the fibers and c is a constant. The results are rather scattered in Figure 9, but the linear relationship of the extent of grafting to the logarithmic dose was almost satisfactory, in accord with the above discussion.

Effect of Irradiation Temperature of Polypropylene

Apart from the standard irradiation procedure, the polymer was given the same dose of γ-radiation from ^{60}Co at various irradiation temperatures. It is seen in Figure 10 for vinyl chloride that the extent of grafting changed remarkably around 0°C. The fact that the second transition temperature of polypropylene lies in this region should be responsible for at least a part of the results.

Another aspect was that the yield of grafting for the polymer irradiated at −78°C. was almost the same as that for the polymer irradiated at liquid nitrogen temperature. It is known that when polypropylene is irradiated at a low temperature, the radical species produced differs, depending on the irradiation temperature. The radical formed at −196°C. was an alkyl type irrespective of the presence of air, but at −78°C. peroxide radicals were produced under the same circumstances.[8] The activity of the radicals concerned did not seem to differ from each other, if the G value of radical formation was independent of the irradiation temperature and the radicals were effectively accumulated at these temperatures.

The same dose was also given to the fibers by 5.3 M.e.v. electrons from a linear accelerator at 0°C. (the absorbed dose was measured with a cobalt
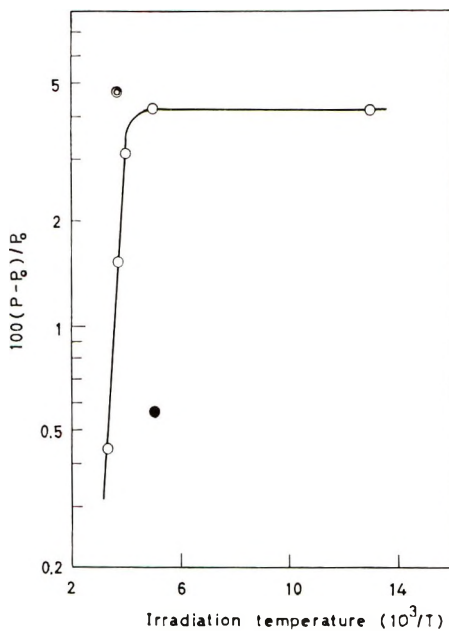
Fig. 10. Effect of the irradiation temperature of polypropylene fibers on the grafting: (◎) irradiated by 5.3 M.e.v. electrons from the linear accelerator; (●) grafting in the presence of 50 mm. Hg air; (○) irradiation dose 8×10^5 rad; vinyl chloride, 760 mm. Hg; grafting temperature, $0°C$.; grafting time, 3 hr.

glass dosimeter), and unusually high grafting was attained. The above results showed that at $0°C$. not all of the radicals formed by γ-ray irradiation seem to remain until the end of irradiation time, and there should be a definite dose rate dependency of grafting at this temperature.
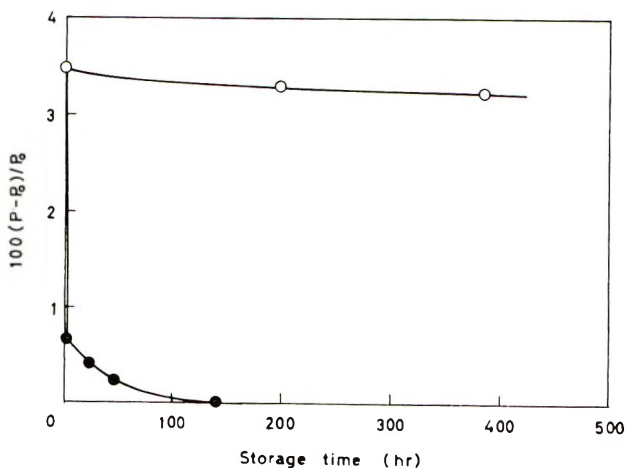

Fig. 11. Effect of storage in air of the irradiated polypropylene on grafting: (○) storage at $-78°C$.; (●) storage at $25°C$. Vinyl chloride, 760 mm. Hg; grafting time, 3 hr.: grafting temperature, $25°C$.

The introduction of 50 mm. Hg air (with 710 mm. Hg of vinyl chloride) depressed the grafting to almost zero as is also shown in Figure 10. The introduction of 5 mm. Hg of air depressed the grafting to about 40% of the normal value. These results may be attributable to retardation by the oxygen.

Effect of Storage of Irradiated Polypropylene

The polypropylene fibers irradiated by the ordinary procedure were stored at $-78°C.$ for a fortnight. The grafting ability tended to decrease very gradually with the storage time (as is shown in Fig. 11), which was in agreement with the results of liquid-phase graft copolymerization of styrene and acrylonitrile on the irradiated polypropylene.[8] The deactivation occurred very rapidly with storage in air at room temperature, and the fibers were rendered inactive in a few hours. The activity could, however, be kept unchanged for a fairly long time when the fibers were brought to the room temperature *in vacuo* after thorough degassing at Dry Ice temperature.

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Résumé

Les copolymérisations greffées de chlorure de vinyle gazeux et également de chlorure de vinylidène gazeux ont été effectuées sur des fibres de polypropylène préalablement irradiées. Les fibres ont été préirradiées avec des sources aux rayons-γ à base de Co^{60} à $-78°C$ dans l'air avec une dose totale de $8 × 10^5$ rads, et étaient donc supposées posséder des radicaux peroxydiques qui étaient actifs pour le greffage à la température ordinaire. La diminution de volume des monomères sous pressions constantes dues à la sorption et à la réaction de greffage était automatiquement suivie à des températures variant de -10 à $80°C.$ Et leur consommation nette au cours du processus de greffage a été évaluée en soustrayant la variation de volume due à la sorption de la variation totale de monomères. En général le degré d'avancement du greffage était plus faible aux températures de greffage plus élevées et la diminution de l'activité de greffage des fibres croissait plus fortement également. L'augmentation du taux de greffage a été trouvée être environ linéaire en fonction du logarithme de la durée de réaction et du logarithme de la dose donnée aux fibres. Le degré d'avancement du greffage est également proportionnel à la pression de vapeur du monomère pour une température de réaction

déterminée et était supposée contrôlée par la quantité de monomère absorbée. Une augmentation de la température d'irradiation plus haute que 0°C amenait à une remarquable diminution d'activité du polypropylène préirradié. L'activité de greffage du polymère était conservée avec succès au moins pour une nuit à −78°C.

Zusammenfassung

Die Propfcopolymerisation von gasförmigem Vinylchlorid und auch gasförmigem Vinylidenchlorid auf vorbestrahlte Polypropylenfasern wurde durchgeführt. Die Fasern wurden in Luft mit ^{60}Co-γ-Strahlen bei −78° mit einer Gesamtdosis von 8×10^5 rad vorbestrahlt und sollten daher Peroxyradikale enthalten, welche eine Aufpfropfung bei normaler Temperatur bewirken. Die durch Sorption und Propfreaktion bedingte Volumsabnahme bei konstantem Druck wurde bei Temperaturen im Bereich von −10 bis 80°C automatisch verfolgt. Der Nettoverbrauch durch den Aufpfropfprozess wurde durch Subtraktion der sorptionsbedingten Volumsänderung von der Gesamtvolumsänderung der Monomeren erhalten. Im allgemeinen war das Pfropfungsausmass bei der höheren Pfropftemperatur kleiner und auch die Pfropfwirksamkeit der Fasern nahm rascher ab. Die Aufpfropfung nahm fast linear mit dem Logarithmus der Reaktionsdauer und mit dem Logarithmus der Dosis zu. Das Pfropfungsausmass war bei einer gegebenen Reaktionstemperatur auch dem Dampfdruck eines Monomeren proportional und schien durch die absorbierte Monomermenge bestimmt zu sein. Eine Erhöhung der Bestrahlungstemperatur über 0°C führte zu einer merklichen Abnahme der Aktivität des vorbestrahlten Polypropylens. Die Pfropfungsaktivität des Polymeren konnte bei −78°C mindestens durch vierzehn Tage erhalten werden.

Emulsion Polymerization of Acrylonitrile.
Part I.   Role and Effect of Emulsifiers in the
Emulsion Polymerization of Acrylonitrile

ZENZI IZUMI, HIROSHI KIUCHI, and MASAMOTO WATANABE,
Central Research Laboratories, Toyo Rayon Company, Otsu, Japan

Synopsis

The role in and effects on the emulsion polymerization of acrylonitrile (AN) of three different groups of emulsifiers, i.e., low molecular emulsfiers, well-known water-soluble polymers, and new water-soluble polymers containing a sulfonate group have been investigated by a dilatometry and electron microscopy.   The major part of this paper concentrates on the study of the relation between the properties of the third group of emulsifiers and emulsion polymerization characteristics of AN such as rate, degree of polymerization, diameter and number of particles, and the degree of dispersion, by adding copolymers of AN and sodium *p*-styrenesulfonate (SSS) having various compositions. In the emulsion polymerization of AN, the hydrophobic portion of the emulsifier seems to act as a kind of nucleus around which polymer molecules precipitate and particle formation may occur, and the hydrophilic portion stabilizes the polymer particles thus formed.   As the number of particles and the degree of dispersion increases, the total surface of the particles increases, which may raise the overall rate of polymerization due mainly to an increased polymerization on the surface of the polymer particles.   The well-known emulsifiers may be classified by the properties and ratio of the nucleus portion and the stabilizing portion.   The unusual effect of emulsifiers on the degree of polymerization may be explained by a chain-transfer mechanism.

INTRODUCTION

Although the role and effect of emulsifiers in typical emulsion polymerization have been studied extensively,[1] little is known about the emulsion polymerization of water-soluble monomers.   In the emulsion polymerization of acrylonitrile (AN),[2] compared with typical emulsion polymerization, the emulsifier is usually effective at concentrations below the critical micellar concentration (CMC) and the degree of polymerization does not always increase with increasing concentration of emulsifier although the rate of polymerization increases.   It is the principal aim of this report to investigate the role and effect of emulsifiers in the emulsion polymerization of AN and to elucidate the several characteristics by systematic use of several emulsifiers.

In a previous report,[3] the authors found that there is a sharp rise in the rates of copolymerization of AN and sodium *p*-styrenesulfonate (SSS) in the transition from homogeneous to heterogeneous phase by the emulsion

copolymerization mechanism. Following this phenomenon, the rate of homopolymerization of AN was also found to be greatly enhanced by the addition of AN–SSS copolymer, and polymerization seems to occur in many particles, as is seen in the presence of anionic emulsifiers such as sodium lauryl sulfate. Emulsion polymerization of AN in the presence of AN–SSS copolymer has a great advantage in that the properties of emulsifiers for the polymerization of AN can be greatly changed by adding copolymers of different compositions. It is therefore possible merely by changing their compositions to investigate the relation between the properties of emulsifiers and such emulsion polymerization characteristics of AN as rate, degree of polymerization, diameter and number of particles, and the degree of dispersion. Therefore, we used mainly AN–SSS copolymers. In addition, as there have been few reports on the emulsion polymerization of AN in the presence of high molecular surface-active agents, several kinds of polymers containing the sulfonic acid group which have been found to have excellent properties as emulsifiers have been investigated. The well-known low molecular emulsifiers and water-soluble polymers were also investigated for comparison.

The effect of emulsifiers on the degree of polymerization in the emulsion polymerization of AN has been elucidated from the study of the solution polymerization of AN in dimethyl sulfoxide solution in the presence of various kinds of emulsifiers.

EXPERIMENTAL

Materials

Polymer grade AN (supplied by Nitto Chemical Co.) was dried with calcium chloride and then distilled twice under nitrogen. Ammonium persulfate (APS) (supplied by Wako Chemical Co.) was purified by recrystallization from water, and then the solution, of which the concentration was determined iodometrically, was stored in a refrigerator to minimize thermal decomposition. The AN–SSS, styrene (ST)–SSS, methyl acrylate (MEA)–SSS and AN–sodium allyl sulfonate (SAS) copolymers were prepared by the usual method, the conversion being kept under 10%. Sodium lauryl sulfate and sodium methylenebisnaphthalenesulfonate were purified by recrystallization from ethanol. Sodium dodecylbenzenesulfonate was dissolved in hot methanol, filtered, and then precipitated in water and washed with petroleum ether. Other reagents were used without further treatment.

Polymerization Technique

Rates of polymerization were obtained from the observed rates of volume contraction in a dilatometer described previously,[4] and all polymerization systems were evacuated under 10^{-4} mm. Hg pressure, the pH of the reaction mixtures being adjusted to 3 or 7 by addition of hydrochloric acid or sodium hydroxide, respectively.

The polymerization was stopped in a mixture of methanol and hydro-

chloric acid (1:1), washed with hot water, filtered in glass filters, and dried to constant weight in a vacuum oven kept at 50°C. under 1 mm. for about 50 hr.   The absolute purity of the recovered polymer was ascertained by infrared absorption.

The degrees of polymerization were calculated by Onyon's equation[5] for the relation between molecular weight and intrinsic viscosity in dimethylformamide at 25.0°C.

An electron microscope was used to observe the condition of reaction mixture and to estimate the particle size.   Samples withdrawn from the reaction mixture were cooled and diluted by as much as 50 times water to minimize further changes.   The samples were diluted further by as much as 1000 times water and were shadow-casted with chromium for the electron micrographs.   The surface average diameter of particle is calculated from micrometer measurements on 100 particles in the electron micrographs. The number of particles in the reaction mixture is calculated from the volume average diameter and the density of particles which was estimated at 1.01.

RESULTS

Low Molecular Emulsifiers

The effect of low molecular emulsifiers on the polymerization of AN in aqueous solution was investigated for comparison.   Results of some anionic emulsifiers are listed in Table I.   From Table I, it can be observed that there are two types of anionic emulsifiers.   Sodium dodecylbenzenesulfonate, sodium dialkylsulfosuccinate, and sodium lauryl sulfate act as accelerators for polymerization of AN, but the emulsion latex coagulates readily by addition of salt such as aluminum sulfate.   Sodium methylenebisnaphthalenesulfonate does not act as an accelerator for polymerization of AN, but the emulsion latex is very stable to salt.   For direct observation of the two kinds of polymerization, we examined them by electron microscopy.   Figure 1 shows the electron micrograph negative prints of the polymer particles at 20% conversion formed in the presence of (a) sodium lauryl sulfate, and (b) sodium methylenebisnaphthalenesulfonate.   From Figure 1, it may be seen that the polyacrylonitrile emulsion produced in the presence of sodium lauryl sulfate has a rather small diameter and coagulates a little, and that the emulsion produced in the presence of sodium methylenebisnaphthalenesulfonate has a rather large diameter and is dispersed in discrete particles.   The factors causing these differences will be discussed later.

Water-Soluble Polymers as Emulsifiers

The effect of well-known water-soluble polymers, poly(acrylic acid), polyacrylamide, poly(vinyl pyrrolidone), and poly(vinyl alcohol) on the polymerization of AN in aqueous solution is listed in Table II.   Poly-(acrylic acid) inhibits the coagulation of polymer particles slightly.   Poly-

TABLE I
Effect of Low Molecular Emulsifiers[a]

Emulsifier	Emulsifier concentration, g./l.	Rate of polymerization $R_p \times 10^5$, mole/l.-sec.	R_p/R_{p_0}[b]	Degree of polymerization (at 20% conversion)
None		2.08	1	7,200
Sodium	0.2	2.67	1.28	5,750
dodecyl-	0.5	4.16	2.00	3,300
benzene-	1.0	4.67	2.24	2,450
sulfonate	2.0	4.83	2.32	4,850
Sodium	0.1	2.08	1.0	—
dialkyl-	0.3	3.50	1.68	7,530
sulfosuccinate	0.5	4.16	2.0	—
	0.7	4.46	2.14	—
	1.0	4.17	2.0	5,660
	2.0	4.40	2.12	5,980
Sodium	0.05	2.08	1.0	7,170
lauryl	0.1	2.50	1.20	5,810
sulfate	0.2	4.69	2.25	5,780
	0.35	5.20	2.50	5,870
	0.5	5.55	2.67	5,000
	1.0	5.55	2.67	4,950
Sodium	0.5	1.88	0.904	2,490
methylenebis-	1.0	2.29	1.10	2,300
naphthalene-	2.0	2.50	1.20	2,060
sulfonate	3.0	1.89	0.908	1,680
	5.0	1.25	0.603	1,110

[a] Polymerization conditions: 0.5 mole/l. acrylonitrile, 0.01 mole/l. APS as initiator, 40°C., pH 3.0.

[b] R_{p_0} is the rate of polymerization of acrylonitrile without emulsifier.

TABLE II
Effect of Water-Soluble Polymers[a]

Water-soluble polymer	Concentration, g/l.	Rate of polymerization $R_p \times 10^5$, mole/l.-sec.	R_p/R_{p_0}	Degree of polymerization (at 20% conversion)
None		3.13	1	5,530
Poly(acrylic	0.3	2.80	0.9	5,530
acid)	1.0	2.82	0.9	5,470
Poly-	0.3	3.37	1.08	Insoluble
acrylamide	1.0	3.27	1.04	in DMF
Poly(vinyl	0.3	3.25	1.04	4,770
pyrrolidone)	1.0	4.06	1.30	3,170
	2.0	4.63	1.48	4,580
Poly(vinyl	0.3	3.40	1.08	Not
alcohol)	1.0	3.62	1.17	filterable
	2.0	4.63	1.48	

[a] Polymerization conditions: 0.5 mole/l. acrylonitrile, 0.01 mole/l. APS as initiator, 45°C., pH 3.0.
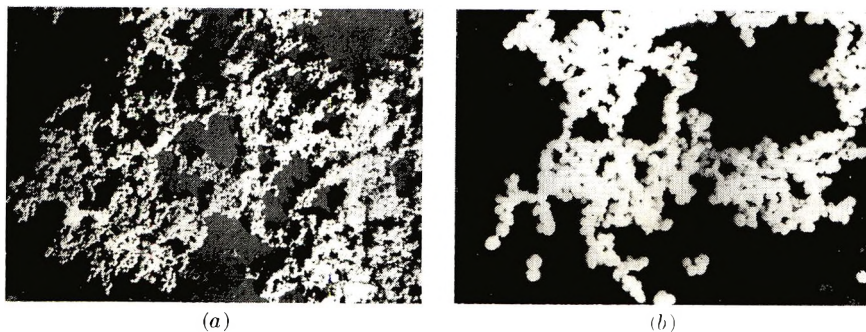
Fig. 1. Electron micrographs of polymer particles at 20% conversion formed in the presence of (a) sodium lauryl sulfate, and (b) sodium methylenebisnaphthalenesulfonate. Negative prints, 12,500×.

acrylamide shows the same effect with poly(acrylic acid), except that part of the polymer tends to be insoluble in dimethyl sulfoxide, which may be attributed to graft copolymerization. Both poly(vinyl pyrrolidone) and poly(vinyl alcohol) increase the rate of polymerization of AN. The emulsion latexes are rather stable; especially, poly(vinyl alcohol) resembles sodium methylenebisnaphthalenesulfonate in its action, being very stable to salt, and producing large, finely dispersed particles.

Water-Soluble Polymers Containing Sulfonate Group as Emulsifiers

Effect of Composition of Copolymer. The effect of composition of AN–SSS copolymer on the rate and degree of homopolymerization of AN in aqueous solution using APS as an initiator at pH 3 and pH 7 is shown in Figure 2. From Figure 2 and direct observation by an electron mi-
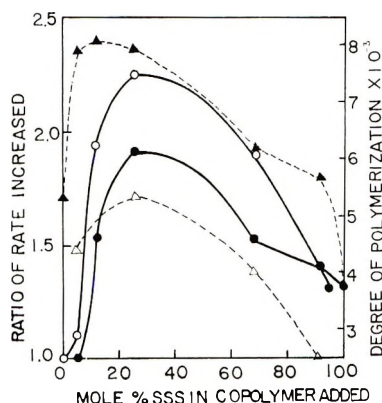

Fig. 2. Dependence of the rate and degree of polymerization of AN on the composition of AN–SSS copolymer added: (●) rate of polymerization at pH 3; (▲) degree of polymerization at pH 3; (O) rate of polymerization at pH 7; (△) degree of polymerization at pH 7. 0.5 mole/l. AN, 0.01 mole/l. APS as initiator, 0.3 g./l. copolymer as emulsifier at 45°C.

croscopy as shown later, the following results may be ascertained. The rate of polymerization of AN is greatly enhanced by addition of a small amount of AN–SSS copolymer; the effect is as large as that produced by the most effective low molecular anionic emulsifier. The effectiveness of AN–SSS copolymer on the rate of polymerization is greatly dependent on its composition, and reaches a maximum at 25 mole-% SSS in the copolymer. The degree of polymerization of AN increases as the rate of polymerization increases, but it tends to decrease with increasing content of SSS in the copolymer added. The stability of emulsion latex to coagulants tends to be higher as the content of SSS in the copolymer increases.
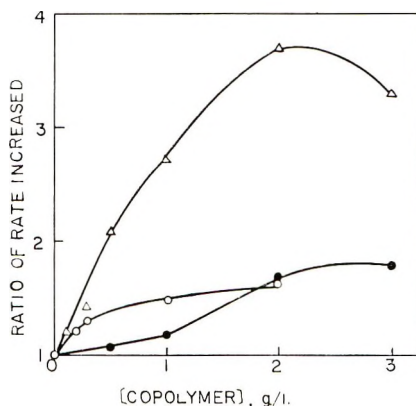

Fig. 3. Dependence of the rate of polymerization of acrylonitrile on the concentration of PSSS or AN–SSS copolymer added: (O) PSSS; (●) AN–SSS copolymer (7.3 mole-% SSS); (△) AN–SSS copolymer (19.8 mole-% SSS). 0.5 mole/l. AN, 0.01 mole/l. APS as initiator, 45°C., pH 3.

Effect of Concentration of Copolymer. The effect of concentration of sodium p-polystyrenesulfonate (PSSS) and two types of AN–SSS copolymers on the rate and degree of polymerization in aqueous solution using APS as an initiator is shown in Figure 3; from Figure 3, the following results may be ascertained. The relation between the rate of polymerization and the concentration of copolymer added depends upon the composition of the copolymer. The copolymer having a low AN content is effective at low concentration but the copolymer of high AN content is effective at rather high concentration. The critical concentration of copolymers, above which the rate decreases or remains constant, is rather high compared with typical low molecular emulsifiers. It is noticeable that the rate of polymerization of AN in aqueous solution is enhanced four times as much as that in the absence of emulsifier by the addition of 2.0 g./l. AN–SSS copolymer (19.5 mole-% SSS), which may be good evidence for our previous interpretation of the rate of copolymerization of AN and SSS.[3] The degree of polymerization increases with increasing concentration of low SSS content copolymer, but decreases with increasing concentration of high SSS content copolymer.

Copolymers of SSS and Other Vinyl Monomers

The effect of composition and concentration of SSS–styrene (ST) and SSS–methyl acrylate (MEA) on the rate and degree of polymerization of AN in the presence of APS as an initiator is shown in Table III.   These

TABLE III
Effect of SSS–Styrene Copolymer and SSS–Methyl Acrylate Copolymer[a]

Copolymer	Content of SSS in copolymer, mole-%	Concentration of copolymer, g./l.	Rate of polymerization $R_p \times 10^5$, mole/l.-sec.	R_p/R_{p_0}	Degree of polymerization (at 20% conversion)
SSS–	12.5	0.3	3.21	1.06	6,350
styrene	26.3	0.3	5.05	1.67	5,390
	26.3	1.0	5.05	1.67	—
SSS–	21.8	0.3	6.51	2.15	6,130
methyl	21.8	1.0	8.61	2.85	—
acrylate	58.2	0.3	3.59	1.19	—
	58.2	1.0	4.38	1.45	5,880

[a] Polymerization conditions: 0.5 mole/l. acrylonitrile, 0.01 mole/l. APS as initiator, 45°C., pH 3.0.

two new water-soluble polymers act as good emulsifiers for the polymerization of AN.

The copolymer of SSS and MEA corresponds to AN–SSS copolymer of higher SSS content.

Copolymer of AN and SAS

Effect of Composition of Copolymer.   The effect of composition of AN–SAS copolymer on the rate and degree of polymerization of AN in aqueous solution using APS as an initiator at pH 3 is shown in Table IV.   The

TABLE IV
Effect of AN–SAS (Sodium Allyl Sulfonate) Copolymer[a]

Content of SAS in copolymer, mole-%	Concentration of copolymer, g./l.	Rate of polymerization $R_p \times 10^5$, mole/l.-sec.	R_p/R_{p_0}	Degree of polymerization (at 20% conversion)
13.6	0.3	5.68	1.88	7,470
13.6	1.0	6.14	2.13	8,850
25.0	0.3	7.61	2.52	7,140
25.0	1.0	12.1	4.00	7,480
32.8	0.3	8.40	2.78	7,050
32.8	1.0	9.45	3.13	6,520
33.1	0.3	8.00	2.65	7,040
33.1	1.0	9.15	3.03	4,430

[a] Polymerization conditions: 0.5 mole/l. acrylonitrile, 0.01 mole/l. APS as initiator 45°C., pH 3.0.
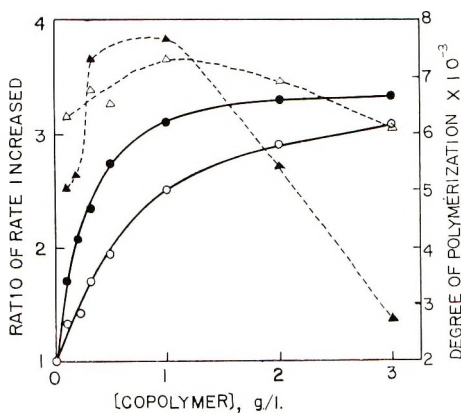
Fig. 4. Dependence of the rate and degree of polymerization of acrylonitrile on the concentration of AN–SAS copolymer added: (O) rate of polymerization and (△) degree of polymerization for AN–SAS copolymer (13.5 mole-% SAS); (●) rate of polymerization and (▲) degree of polymerization for AN–SAS copolymer (20.6 mole-% SAS). 0.5 mole/l. AN, 0.01 mole/l. APS as initiator, 45°C., pH 3.0.

effect of the copolymer as an emulsifying agent for the polymerization of AN resembles that of the copolymer of AN and SSS and is greater effect than any other known emulsifier.

Effect of Concentration of Copolymer. The effect of concentration of two kinds of copolymers on the rate and degree of polymerization is shown in Figure 4. The effects are similar to those of AN–SSS copolymer and need not be mentioned further.

DISCUSSION

To recapitulate the major experimental results reported above, the electron micrograph negative prints of the polymer particles at 20% conversion formed in the presence of various compositions of AN–SSS copolymer are shown in Figure 5. The average particle diameter and number of particles calculated from Figure 5, the degree of polymerization at 20% conversion, and initial rate of polymerization are all tabulated in Table V and Figure 6.

The effect of emulsifiers on the degree of polymerization was investigated in homogeneous polymerization in dimethyl sulfoxide solution. Experimental results are shown in Table VI, and it has been ascertained that emulsifiers act as chain transfer agents for the polymerization of AN.

Two important characteristics of emulsion polymerization of AN have been obtained in our laboratory, the details of which will be shown later:[6] the number of particles increases during polymerization, and the total amount of adsorbed monomer on or in the polymer particles is partly dependent upon the total surface of the polymer particles and is rather little compared with other vinyl monomers such as styrene[7] and vinyl acetate.[8]

TABLE V

Effect of Composition of AN–SSS Copolymer on the Emulsion Polymerization Characteristics of Acrylonitrile[a]

Electron micrograph no.[b]	Content of SSS in copolymer, mole-%	Rate of polymerization $R_p \times 10^5$, mole/l.-sec.	R_p/R_{p_0}	Number of polymer particles $n \times 10^{-13}$, cc.$^{-1}$[c]	Average particle diameter, $m\mu$[c]	Degree of polymerization[c]
6a	0	3.02	1	Impossible to estimate		5,370
6b	11.8	7.05	2.33	because of coagulation		11,000
6c	19.5	10.4	3.44	9.32	48.8	9,630
6d	48.1	7.15	2.36	2.67	71.7	7,850
6e	68.2	5.83	1.93	0.78	109	6,530
6f	91.5	4.84	1.60	0.24	162	5,250
6g	100.0	4.43	1.47	0.14	193	4,260

[a] Polymerization conditions: 0.5 mole/l. acrylonitrile, 0.01 mole/l. APS as initiator, 45°C., pH 3.0, copolymer concentration 1.0 g./l.

[b] Refers to Fig. 6.
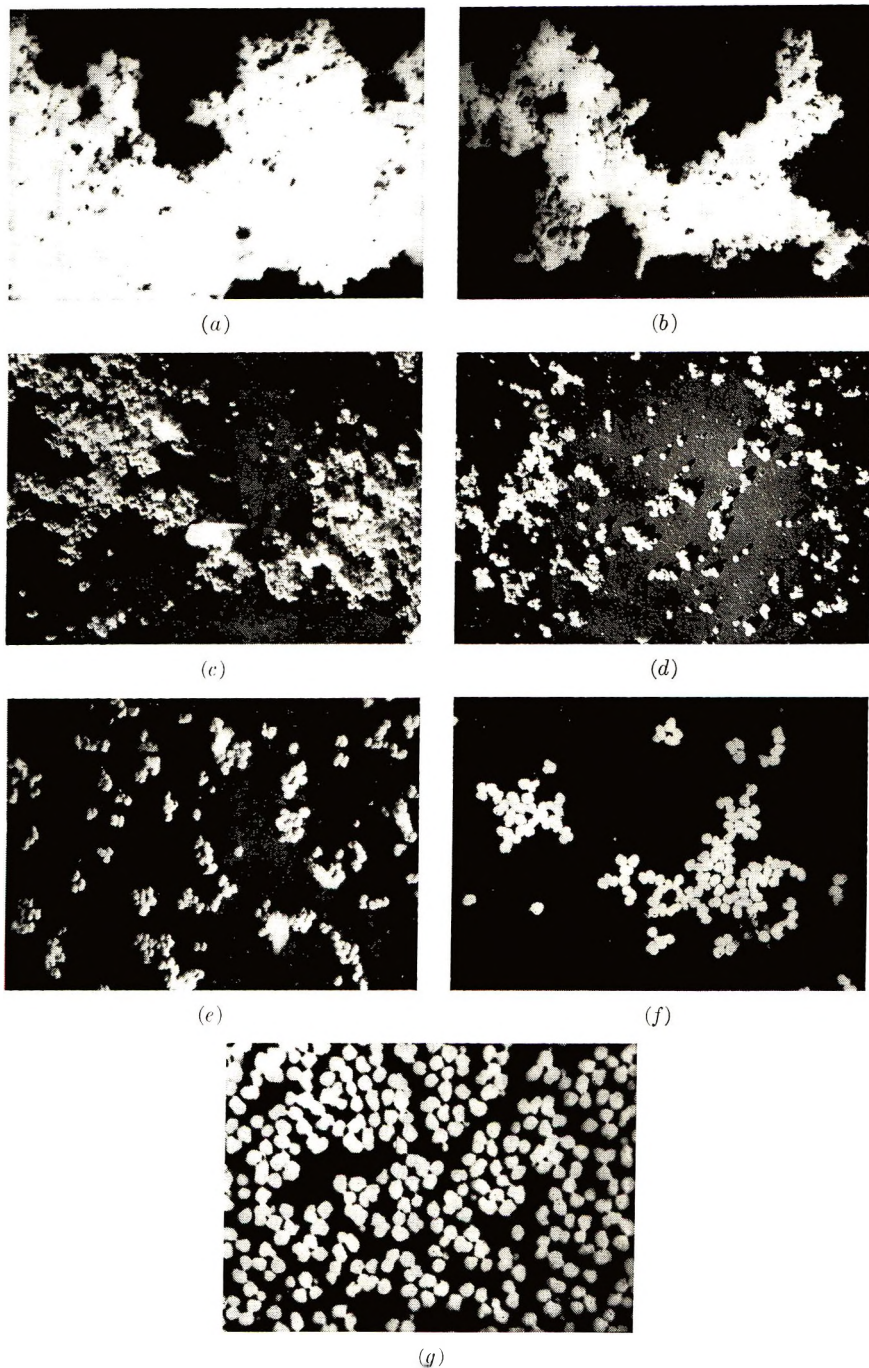
[c] At 20% conversion.

Fig. 5. Electron micrographs of polymer particles at 20% conversion formed in the presence of 1 g./l. AN–SSS copolymer with varying SSS contents: (*a*) 5 mole-%; (*b*) 11.8 mole-%; (*c*) 19.5 mole-%; (*d*) 48.1 mole-%; (*e*) 68.2 mole-%; (*f*) 91.5 mole-%; (*g*) 100 mole-% (PSSS). Negative prints, 12,500×.

In addition to these facts, we found that the copolymer composition curve of emulsion copolymerization of AN and MEA lies between that of suspension polymerization, in which the locus is restricted in the polymer particles, and solution polymerization, which shows that emulsion polymerization takes place both on or in the polymer particles and in the aqueous phase.[9]

From the experimental results shown above, it may be reasonable to consider that the emulsifier plays an important role in the particle formation and particle stabilization, which increases the rate of polymerization. Four cases may be considered in the behavior of polymer molecules formed
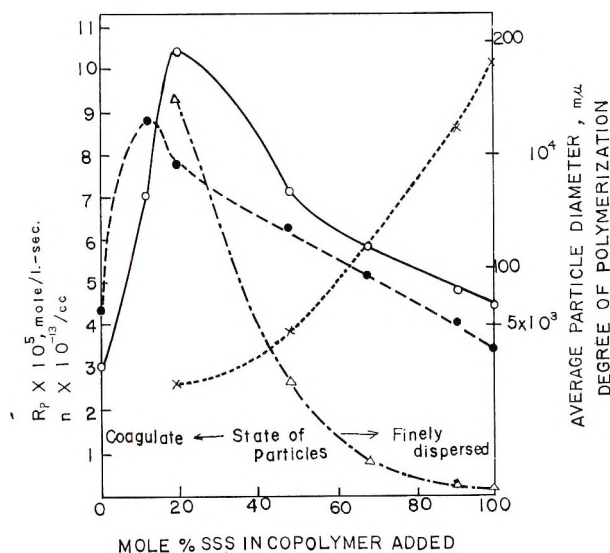

Fig. 6. Dependence of the emulsion polymerization characteristics of acrylonitrile on the composition of AN–SSS copolymer added: as emulsifier, 45°C., pH 3. (O) rate of polymerization; (●) degree of polymerization; (△) number of polymer particles; (×) average particle diameter. 0.5 mole/l. AN, 0.01 mole/l. APS as initiator, 1.0 g./l. copolymer.

in the aqueous phase; (1) polymer molecules might precipitate on some kind of nuclei and particle formation might occur, (2) polymer molecules might precipitate in a coarse form and might be stabilized by adsorbing emulsifier, (3) polymer molecules might be adsorbed on a polymer particle already present, (4) polymer molecules might precipitate in a coarse form and might be adsorbed on a polymer particle already present. Cases (3) and (4) might occur, as pointed out by Thomas[10] and Dainton.[11] However, cases (1) and (2) must be important in our experiment at the inception and during polymerization. In the emulsion polymerization of vinyl acetate under the CMC, Napper et al.[12] showed that case (2) prevails, that is, the polymer particle will adsorb the organic anion of the soap, leading to an increase in ζ potential and the attainment of the "critical" value at a

much smaller particle size. This explanation can not be accepted from the experimental results shown in Figure 6. In the emulsion polymerization of styrene under CMC, Van Der Hoff[13] suggested a similarity between the mechanism of particle formation and that of the precipitation of insoluble inorganic salts. This explanation cannot be applied to our case, as the dependence on the property of emulsifier and the new particle formation during polymerization can not be explained. The fact that the number of particles increases as the content of AN in AN–SSS copolymer increases indicates that the particle formation is caused by the portion of AN in copolymer (hydrophobic portion). As Thomas[10] pointed out, particle formation of polymer molecules in aqueous media may involve replacement of polymer molecules in aqueous media may involve replacement of polymer–water bonds with polymer–polymer bonds, and the AN portion

TABLE VI
Effect of Emulsifiers in the Solution Polymerization of Acrylonitrile
as Chain Transfer Agents[a]

Emulsifiers	Concentration of emulsifier, g./l.	Rate of polymerization $R_p \times 10^5$, mole/l.-sec.	Degree of polymerization (at 20% conversion)
None		1.04	2530
Sodium lauryl sulfate	0.5	1.04	2780
	1.0	1.04	2650
	5.0	0.94	2240
	10.0	1.00	2070
AN–SAS copolymer	0.5	0.94	2270
(SAS 20.6 mole-%)	1.0	0.91	2010
	5.0	0.91	1690
	10.0	0.90	1270
Sodium methylenebis-	1.0	1.02	2100
naphthalenesulfonate	5.0	0.92	260
	10.0	0.82	100

[a] Polymerization conditions: 2.0 mole/l. acrylonitrile in dimethyl sulfoxide solution, 0.02 mole/l. azobisisobutylonitrile as initiator, 45°C.

of copolymer dissolved in aqueous media may act as a kind of nucleus where polymer molecules precipitate and particle formation may occur, as the replacement of polymer–water bonds with polymer–solubilized hydrophobic molecule bonds may be easier than that with polymer–polymer bonds. In this case it may be reasonable to consider that the rate of formation of particles may increase as the ratio of hydrophobic portion in an emulsifier and the affinity with polymer molecules increase. For the stabilization of particles, the nucleus should have a negative charge and hydration properties; therefore, the degree of dispersion increases as the content of SSS in the copolymer increases. If only the free emulsifier molecules are available for particle formation, the concentration of the locus of new particle formation may be saturated at the CMC or the critical

concentration above which the emulsifier molecules affect each other. At low emulsifier concentration, the stabilization of polymer particles may be important for the increase of rate of polymerization, and the critical concentration may decrease with increasing negative charge on the emulsifier molecules. This may cause the variation of the effect of concentration with the composition of copolymers added as shown in Figures 3 and 4. In the emulsion polymerization of AN, polymerization proceeds concurrently on or in the polymer particles and in the aqueous phase.[6,9] As the number of particles and the degree of dispersion increases, the total surface of the particles increases, which may raise the ratio of polymerization on or in the polymer particles and the overall rate of polymerization as shown in Figure 6. The effect of emulsifier may be classified by the properties and balances of the hydrophobic portion and hydrophilic portion. Sodium dodecylbenzenesulfonate, sodium dialkylsulfosuccinate, and sodium lauryl sulfate may correspond to 10, 15, and 20 mole-% SSS content of copolymers, respectively. Sodium methylenebisnaphthalenesulfonate may correspond to PSSS, but it decreases the rate of polymerization with increasing concentration, probably due to degradative chain transfer.

The effect of emulsifier on the degree of polymerization may be determined by two factors. First, the degree of polymerization increases as the rate of polymerization increases, i.e., as the concentration of emulsifier increases to critical concentration. Second, the degree of polymerization decreases as the concentration of emulsifier increases by chain transfer, as is shown in Table VI. This may be the reason why the maximum points of the degree of polymerization and the rate of polymerization in Figure 6 are different. Perhaps, the copolymer of high SSS content may also reduce the rate of polymerization by degradative chain transfer.

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Résumé

On a étudié le rôle et les effets sur la polymérisation en émulsion de l'acrylonitrile (AN) de trois groupes différents d'émulsifiants, à savoir, les émulsifiants de bas poids moléculaires, les polymères hydrosolubles bien connus et des polymères nouveaux solubles dans l'eau contenant des groupes sulfoniques; les méthodes utilisées étaient la dilatométrie, la microscopie électronique. La partie principale de cet article est consacrée à l'étude de la relation entre les propriétés du troisième groupe d'émulsifiants et les caractéristiques de la polymérisation à l'émulsion de l'(AN) telles que la vitesse, le degré de polymérisation, le diamètre et le nombre desparticules, le degré de dispersion par addition de copolymères d'acrylonitrile et de sodium-p-styrènesulfonate (SSS) de différentes compositions. Dans la polymérisation en émulsion de AN, la partie hydrophobique de l'émulsifiant semble agir comme une sorte de noyaux autour duquel les molécules polymériques précipitent et autour desquels les particules peuvent se former, tandis que le portion hydrophile stabilise les particules polymériques ainsi formées. A mesure que le nombre de particules et que le degré de dispersion croit, la surface totale des particules croit également, ce qui peut augmenter la vitesse globale de polymérisation due principalement à une polymérisation accrue à la surface des particules polymériques. Les émulsifiants bien connus peuvent être classifiés suivant leurs propriétés et le rapport de leur partienoyaux à leur partie stabilisant. L'effet inhabituel des émulsifiants ur le degré de polymérisation peut être expliqué par un mécanisme de transfert de chaîne.

Zusammenfassung

Eine dilatometrische und elektronemikroskopische Untersuchung der Rolle und de Wirksamkeit von drei verschiedenen Emulgatorgruppen, nämlich niedermolekularer Emulgatoren, bekannter wasserlöslicher Polymerer und neuer wasserlöslicher Polymerer mit Sulfonatgruppen bei der Emulsionspolmerisation von Acrylnitril (AN) wurde durchgeführt. Der Hauptteil der vorliegenden Arbeit beschäftigt sich mit der Untersuchung der Beziehung zwischen den Eigenschaften der Emulgatoren der dritten Gruppe und den charakteristischen Grössen der Emulsionspolymerisation von AN, wie Geschwindigkeit, Polymerisationsgrad, Partikelzahl und -durchmesser sowie dem Dispersionsgrad bei Zusatz von Copolymeren von AN und Natrium-p-styrolsulfonat (SSS) mit verschiedener Zusammensetzung. Bei der Emulsionspolymerisation von AN scheint der hydrophobe Teil des Emulgators als eine Art Kern zu wirken, um welchen Polymermoleküle gefällt werden und Teilchenbildung auftreten kann; der hydrophile Teil stabilisiert die so gebildeten Polymerteilchen. Mit Ansteigen der Teilchenzahl und des Dispersionsgrades nimmt die Gesamtoberfläche der Teilchen zu, wodurch die Gesamtgeschwindigkeit der Polymerisation infolge der gesteilgerten Polymerisation an der Oberfläche der Polymerteilchen zunehmen kann. Die bekannten Emulgatoren können nach den Eigenschaften und dem Verhältnis von Kernteil zu stabilisierendem Teil klassifiziert werden. Der ungewöhnliche Einfluss von Emulgatoren auf den Polymerisationsgrad kann durch einen Kettenübertragungsmechanismus erklart werden.

Emulsion Polymerization of Acrylonitrile.
Part II.   Mechanism of Emulsion Polymerization of Acrylonitrile

ZENZI IZUMI, *Central Research Laboratories, Toyo Rayon Company, Otsu, Japan*

Synopsis

The mechanism of emulsion polymerization of acrylonitrile has been studied by measuring by dilatometry and electron microscopy the adsorption of monomer into polymer particles and polymerization characteristics such as rate, degree of polymerization, the growth of the particle during polymerization, and the degree of dispersion. In the emulsion polymerization of acrylonitrile, new particles are formed during polymerization at a rate which is proportional to the rate of polymerization and the ratio of unreacted monomer. The total amount of monomer adsorbed on or in the polymer particles is rather small, but the concentration on or in the polymer particles is sufficiently high and proportional to the monomer concentration in aqueous phase. The polymerization proceeds concurrently on or in the polymer particles and in aqueous phase, but the three loci may be continuous rather than discrete. A reaction scheme is introduced here which shows the coexistence of polymerizations on or in the polymer particles and in the aqueous phase.

INTRODUCTION

There have been several reports discussing the mechanism of heterogeneous polymerization of acrylonitrile (AN);[1-8] however, the question of polymerization on or in the particle versus polymerization in the true aqueous phase has not been resolved because of the lack of the quantitative information on the extent of adsorption of monomer by the polymer particles and on the growth of the polymer particles during polymerization. The polymer particles already present are considered to have a great effect on the mechanism of heterogeneous polymerization of AN. The addition of polymer increases the rate of polymerization,[9] and the separation of polymer by the action of a centrifugal field decreases the rate of polymerization.[6] As polyacrylonitrile (PAN) does not dissolve in its own monomer, the effect of polymer may be ascribed to the adsorption of monomer by the polymer. In this report the mechanism of emulsion polymerization of AN was investigated by measuring the adsorption of monomer by the polymer particles and by determining such polymerization characteristics of AN as rate and degree of polymerization, the growth of the particle during polymerization, and the degree of dispersion by dilatometry and electron microscopy.

EXPERIMENTAL

Materials

Polymer grade AN (supplied by Nitto Chemical Co.) was purified by the method of Bamford.[10] Ammonium persulfate (APS) (supplied by Wako Chemical Co.) was purified by recrystallization from water, and then the solution, of which the concentration was determined iodometrically, was stored in a refrigerator to minimize thermal decomposition. The AN–sodium p-styrenesulfonate (SSS) copolymers were prepared by the usual method, the conversion being kept under 10%. Sodium lauryl sulfate was purified by recrystallization from ethanol. Other reagents were of analytical grade and used without further treatment.

Procedure

Rates of polymerization were obtained from the observed rates of volume contraction in a dilatometer described previously,[11] and all polymerization systems were evacuated under 10^{-4} mm. Hg pressure, the pH of the reaction mixture being adjusted to 3 by addition of hydrochloric acid.

The polymerization was stopped in a mixture of methanol and hydrochloric acid (1:1), filtered in glass crucibles, and dried to constant weight in a vacuum oven kept to 50°C. under 1 mm. for about 50 hr.

The degrees of polymerization were calculated by using Onyon's equation[12] for the relation between intrinsic viscosity in dimethylformamide at 25.0°C. and molecular weight.

An electron microscope was used to observe the condition of the reaction mixture and to estimate the particle size. Samples withdrawn from the reaction mixture were cooled and diluted by as much as 50 times water to minimize further changes. The samples were diluted further by as much as 1000 times water and were shadow-cast with chromium for the electron micrographs. The average surface diameter of the particle was calculated from micrometer measurements on 100 particles in the electron micrographs. The number of particles in the reaction mixture was calculated from the volume-average diameter and the density of particles which was estimated at 1.01.

The amount of monomer adsorbed by the polymer particles was determined by the following procedure. After the polymerization was carried out to a certain conversion in a dilatometer, the dilatometer bulb was cooled with ice. Then the polymerization mixture was transferred to a tightly capped centrifuge tube and was centrifuged for 5 min. at 4000 rpm and divided into top and bottom portions. The AN concentration in the supernatant solution diluted by as much as 50 times water was estimated by ultraviolet absorption at 218 mμ standardized against solutions of known concentrations of acrylonitrile and $0.01 \times 1/50$ mole/l. APS, the decomposition of which was negligible,[13] as shown in Figure 1. The concentration of adsorbed AN which must be in the lower layer, is measured by difference. Sodium lauryl sulfate has no adsorption in the neighboring range, but the
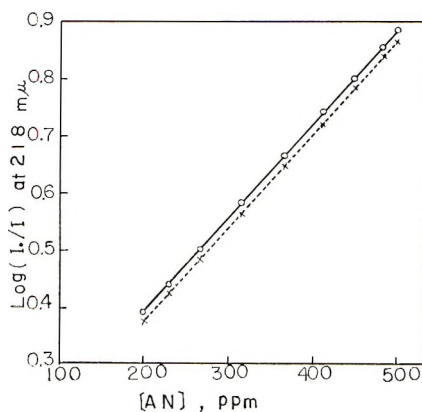
Fig. 1. The concentration of monomer in aqueous solution vs. optical density at 218 mμ: (×) without additives; (O) in the presence of 0.02 mole/l. APS.

AN–SSS copolymers have strong adsorption at 218 mμ. Therefore, the effect of emulsifier on the amount of monomer adsorbed on polymer particles was tested only in the former case.

RESULTS

Adsorption of Monomer

The amount of AN monomer adsorbed by the PAN particles during polymerization in four cases are shown in Table I. The obtained values are far less than that obtained by Nagao and Uchida,[14] but our obtained values may be more reasonable, compared with those systems (styrene[15] and vinyl acetate[16]) in which the polymers are soluble in their own monomers. From Table I, the following results may be ascertained. The amount of adsorbed monomer increases with increasing emulsifier concentration and parallels the rate of polymerization. The amount of adsorption increases four times while the monomer concentration increases two times; this means that the amount of adsorption varies with the square of the monomer concentration.

Number of Particles as a Function of Conversion

The data for the diameter and number of polymer particles as a function of conversion in the presence of 1 g./l. various kinds of emulsifier for several monomer concentrations are shown in Figure 2. From the above experiments, the following results may be ascertained. The number of polymer particles increases considerably during polymerization, which shows that many new particles are formed during the growth period. In the usual emulsion polymerizations, the number of polymer particles remains constant during the polymerization reaction. In the case of AN, Thomas[1] and Nagao[17] reported that no new particles were formed during the growth period, and Dainton discussed the mechanism of aqueous poly-

TABLE I
Amount of Monomer Adsorbed Onto the Polymer Particles[a]

Expt. no.	AN concn., mole/l.	Sodium lauryl sulfate concn., g./l.	Con-version, %	Total monomer (concn.), mole/l.	Amount of monomer adsorbed, mole/l.	Monomer concn. in aqueous phase, mole/l.
1	0.5	—	5.83	0.471	0.0221	0.449
			10.9	0.446	0.0179	0.428
			22.6	0.387	0.0183	0.369
			31.3	0.345	0.0149	0.380
			40.3	0.299	0.0164	0.283
			49.4	0.253	0.0154	0.238
2	0.5	0.5	6.18	0.469	0.0378	0.431
			7.38	0.463	0.0333	0.429
			12.7	0.437	0.0283	0.409
			22.4	0.388	0.0283	0.360
			24.1	0.380	0.0283	0.352
3	0.5	1.0	6.45	0.468	0.0462	0.422
			14.1	0.430	0.0443	0.386
			19.8	0.401	0.0443	0.357
			22.9	0.386	0.0499	0.336
			33.5	0.333	0.0481	0.285
			38.4	0.308	0.0588	0.249
4	1.0	—	6.12	0.939	0.0844	0.855
			12.0	0.880	0.0772	0.803
			16.0	0.840	0.0717	0.768
			23.1	0.796	0.0584	0.711
			25.7	0.743	0.0579	0.685
			30.8	0.692	0.0584	0.634
			36.4	0.636	0.0594	0.577

[a] Polymerization conditions: 0.01 mole/l. APS as initiator, 45.0°C., pH 3.0.

merization of AN on the basis of this theory. These results may be explained on the basis of adhesion of polymer particles during the polymerization reaction. The diameter of polymer particles is almost the same for different monomer concentrations at a finite conversion when the same emulsifier is used; that is, the number and total surface of polymer particles are proportional to the monomer concentration. From Figure 2, the relation between N and $1 - (1 - x)^2$ (where x is conversion) in the presence of 1.0 g./l. sodium lauryl sulfate is plotted in Figure 3. The experimental points are well represented by a straight line having a slope proportional to $[M_0]$. In this case, eq. (1) may be developed.

$$N = k[M_0][1 - (1 - x)^2] \qquad (1)$$

By differentiation

$$dN/dt = -2k[M]/[M_0](d[M]/dt) \qquad (2)$$

where k is a coefficient depending on polymerization condition such as emulsifier, initiator, and temperature. When each particle is sufficiently
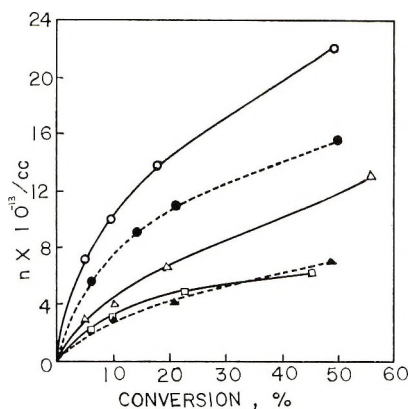
Fig. 2. Number of particles as a function of conversion in the presence of 0.01 mole/l. APS at 45.0°C., pH 3.0 at various monomer concentrations [Mo] with sodium lauryl sulfate (SLS), a copolymer of acrylonitrile with sodium p-styrenesulfonate containing 24 mole-% SSS [AN–SSS (24)], and a copolymer of acrylonitrile with sodium p-styrene-sulfonate containing 47 mole-% SSS [AN–SSS (47)] as emulsifiers: (O) [SLS] = 1.0 g./l., [Mo] = 1.0 mole/l.; (●) [AN–SSS (24)] = 1.0 g./l., [M_0] = 1.0 mole/l.; (△) [SLS] = 1.0 g./l., [M_0] = 0.5 mole/l., (▲) [AN–SSS (47)] = 1.0 g./l., [M_0] = 0.5 mole/l.; ([]) [SLS] = 1.0 g./l., [M_0] = 0.2 mole/l.
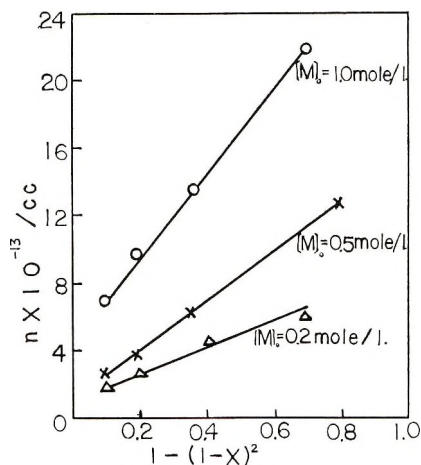
Fig. 3. Dependence of the number of particles n on the conversion x at various initial monomer concentrations [M_0].

dispersed, the total surface area of polymer particles may be calculated as:

$$S = (36\pi)^{1/3} k^{1/3} [M_0] x (2 - x)^{1/3} \tag{3}$$

$$= k' [M_0] x (2 - x)^{1/3}$$

The diameter of polymer particles also increases as polymerization proceeds, which shows that the polymerization occurs concurrently on and in the polymer particles already present and in the true aqueous phase.   The number

and the rate of formation of new particles depend on the emulsifier used, as discussed in detail in Part I.[18]

Effect of Monomer Concentration

The effect of monomer concentration on the rate and the degree of polymerization in the presence of 1.0 g./l. sodium lauryl sulfate is shown in Figure 4. The experimental points in Figure 4 are well represented by straight lines of slope 1.8, indicating about a second-power dependence of the rate and degree of polymerization on the monomer concentration. The relation between the number of particles and the monomer concentration is plotted in Figure 5 and the first-power dependence of the number of polymer particles on the monomer concentration at a finite conversion is clearly shown.
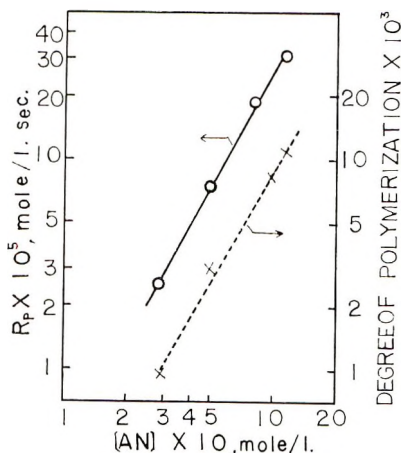
Fig. 4. Dependence of (O) the rate and (×) the degree of polymerization on the initial monomer concentration in the presence of 0.01 mole/l. APS at 45.0°C.
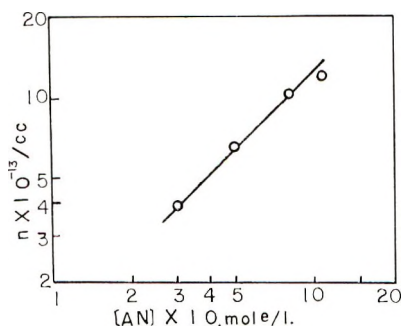
Fig. 5. Plot of number of particles vs. initial monomer concentration at 20% conversion in the presence of 0.01 mole/l. APS and 1.0 g./l. sodium lauryl sulfate at 45.0°C.

Effect of Initiator Concentration

Figure 6 shows the effect of initiator concentration on the rate of polymerization in three cases, without any additives, in the presence of 1.0 g./l.
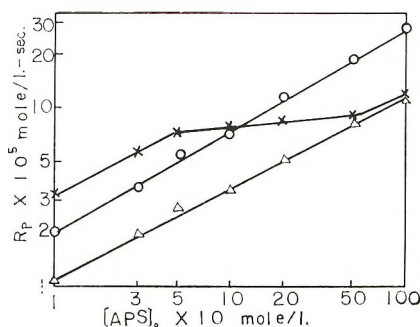
Fig. 6. Plots of initial rate of polymerization vs. initiator concentration: (△) without additives; (×) in the presence of 1.0 g./l. sodium lauryl sulfate; (○) in the presence of 1.0 g./l. AN–SSS (52:48) copolymer.
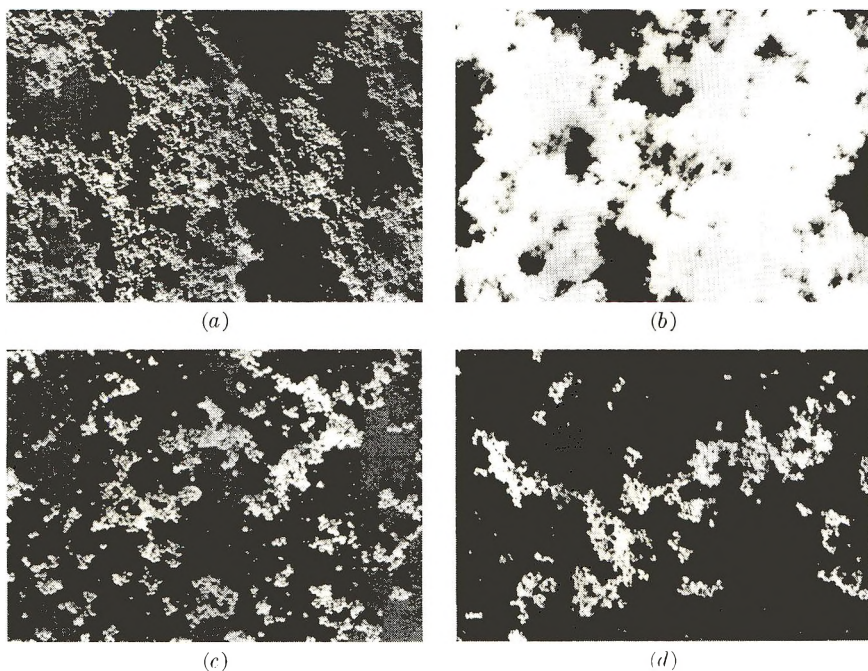

Fig. 7. Electron micrographs of the polymer particles formed in the presence of: (a) 0.005 mole/l. APS and 1.0 g./l. sodium lauryl sulfate; (b) 0.1 mole/l. APS and 1.0 g./l. sodium lauryl sulfate; (c) 0.01 mole/l. APS and 1.0 g./l. AN–SSS copolymer (52:48); (d) 0.1 mole/l. APS and 1.0 g./l. AN–SSS copolymer (52:48).

sodium lauryl sulfate and in the presence of 1.0 g./l. AN–SSS copolymer (52:48). Electron micrographs (negative prints) of the polymer particles are shown in Figure 7 for 20% conversion in the presence of (a) 0.005 mole/l. APS and 1.0 g./l. sodium lauryl sulfate, (b) 0.1 mole/l. APS and 1.0 g./l. sodium lauryl sulfate, (c) 0.01 mole/l. APS and 1.0 g./l. AN–SSS copolymer, and (d) 0.1 mole/l. APS and 1.0 g./l. AN–SSS copolymer. By comparing Figures 6 and 7, the physical effect on the kinetics of poly-

merization of AN can be easily understood. Without emulsifier, the phys-
ical condition does not change with the initiator concentration, and the
dependence of the rate on initiator concentration was 0.50 by chemical
effect. In the presence of 1.0 g./l. sodium lauryl sulfate, finely dispersed
polymer particles were formed below 0.005 mole/l. initiator concentration
as shown in Figure 7a. In this range, the rate was greatly increased and
its dependence on the initiator concentration was 0.50. Above 0.005
mole/l. initiator concentration, the polymer particles began to coagulate.
The rate increased only very slightly with increasing initiator concentration
and reached the same rate as that of the case in which the emulsifier was
absent. This effect may be explained on the basis of the coagulating
effect of APS, which perhaps decreases the total surface area available for
monomer adsorption. In the presence of 1.0 g./l. AN–SSS copolymer, the
physical condition did not change with initiator concentration, and finely
dispersed polymer particles were formed even at a high concentration of
APS, as shown in Figure 7d. In this case, the rate was greatly increased,
with the dependence of rate on initiator being approximately 0.50 in the
total range. The difference of coagulating effect of APS on the two kinds
of emulsifiers may be due to the different hydrophile–lipophile balances of
the emulsifiers.

Effect of Concentration of Emulsifier

The effect of concentration of emulsifier on polymerization characteristics
such as rate, degree of polymerization, and number of particles at 20% con-
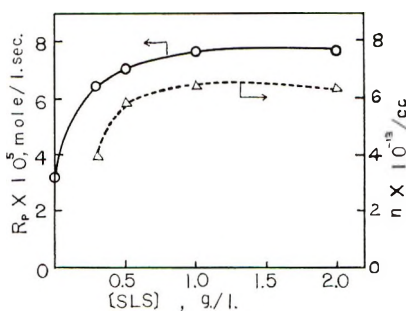version is shown in Figure 8. The rate dependence on emulsifier con-

Fig. 8. Plots of (O) initial rate of polymerization and (△) number of polymer particles
vs. sodium lauryl sulfate concentration in the presence of 0.01 mole/l. APS at 45°C.

centration is in accord with the number of polymer particles and the de-
gree of dispersion. The details of the role and effect of emulsifiers and
the fact that the number of polymer particles and the rate does not in-
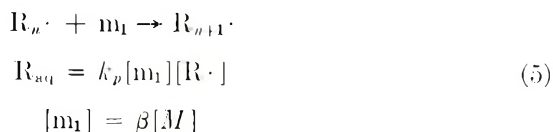crease with increasing emulsifier above a critical concentration have been
reported in part I.[18]

DISCUSSION

From the experimental results obtained above, the following reaction scheme may be introduced:
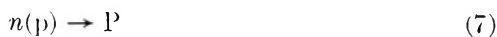
Initiation:

$$S_2O_8 = \rightarrow 2SO_4^-$$

$$R_i = 2k_d f[I] \tag{4}$$

Aqueous phase propagation:

$$R_n\cdot + m_1 \rightarrow R_{n+1}\cdot$$

$$R_{aq} = k_p[m_1][R\cdot] \tag{5}$$

$$[m_1] = \beta[M]$$

Aqueous phase termination:

$$2R_n\cdot \rightarrow (p)$$

$$R_t = kt[R\cdot]^2 \tag{6}$$

Particle formation:

$$n(p) \rightarrow P \tag{7}$$

Adsorption of monomer on polymer particle:

$$[m_2] = \alpha[m_1] = \gamma[M] \tag{8}$$

Absorption of monomer in polymer particle:

$$[m_3] = \delta[m_1] = \epsilon[M] \tag{9}$$
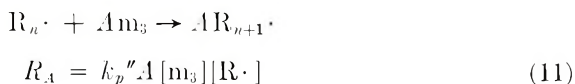
where $[M]$, $[m_1]$, $[m_2]$, and $[m_3]$ are total monomer concentration, monomer concentration in the aqueous phase, monomer concentration on the particles, and monomer concentration in the particles, respectively. α, β, γ, δ, and ϵ are constants which may depend on polymerization conditions, and (p) denotes an independent polymer molecule formed in an aqueous phase. In the absence of emulsifier, this molecule might be adsorbed on a particle already present. However, in the presence of sufficient emulsifier, the emulsifier molecule may act as a kind of nucleus where these polymer molecules precipitate, and new particle formation may occur. Assuming that the monomer and the radical are mobile between aqueous phase and in the polymer particles, and the radical concentration is the same in all loci of polymerization, then, the total rate of polymerization on polymer particles may be proportional to the concentration of adsorbed monomer on polymer particles $[m_2]$, total surface area of polymer particles S, and average radical concentration $[R\cdot]$. Furthermore, the total rate of polymerization in polymer particles may be proportional to the concentration of adsorbed monomer in polymer particles $[m_2]$, total amount of polymer particles A, and average radical concentration $[R\cdot]$. Then the following equations may be introduced:
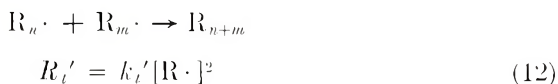
Propagation on particles:

$$R_m\cdot + Sm_2 \rightarrow SR_{n+1}\cdot$$

$$R_s = kp'S[m_2][R\cdot] \tag{10}$$
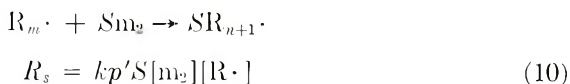
Propagation in particles:

$$R_n\cdot + Am_3 \rightarrow AR_{n+1}\cdot$$

$$R_A = k_p''A[m_3][R\cdot] \tag{11}$$

where A is as $[M_0]x$, and

Termination on particles:

$$R_n\cdot + R_m\cdot \rightarrow R_{n+m}$$

$$R_t' = k_t'[R\cdot]^2 \tag{12}$$

Termination in particles:

$$R_n\cdot + R_1\cdot \rightarrow R_{n+1}$$

$$R_t'' = k_t''[R\cdot]^2 \tag{13}$$

In the steady state, the radical concentration is constant.

$$2k_d f[1] = k_t[R\cdot]^2 + k_t'\mu[R\cdot]^2(S/V) + k_t''[R\cdot]^2 (A/V) \tag{14}$$

where V and μ are total volume of the reaction mixture and thickness of the adsorbed monomer, respectively. The second and third terms in eq. (14) may be negligible compared with the first term. Radical concentration may be expressed as in eq. (15).

$$[R\cdot] = (2k_d f/k_t)^{1/2} [I]^{1/2} \tag{15}$$

From eqs. (3), (5), (10), (11), and (15), the rate of polymerization in aqueous phase, on polymer particles, and in polymer particles may be shown as in eqs. (16), (17), and (18), respectively.

$$R_{aq} = k_p\beta(2k_d f/k_t)^{1/2} [I]^{1/2} [M] \tag{16}$$

$$R_s = k'k_p'\gamma(2k_d f/kt)^{1/2}[I]^{1/2}[M_0][M]x(2 - x)^{1/2} \tag{17}$$

$$R_A = k_p''\epsilon(2k_d f/k_t)^{1/2} [I]^{1/2} [M_0][M]x \tag{18}$$

The overall rate of polymerization is the sum of the rates in aqueous phase, on polymer particles and in polymer particles, and may be represented by:

$$R_p = R_{aq} + R_s + R_A$$

$$= k_p\beta\left(\frac{2k_d f}{k_t}\right)^{1/2} [I]^{1/2} [M] + k'k_p''\gamma\left(\frac{2k_d f}{k_t}\right)^{1/2} [I]^{1/2} [M_0][M]x(2 - x)^{1/2}$$

$$+ k_p''\epsilon\left(\frac{2k_d f}{k_t}\right)^{1/2} [I]^{1/2} [M_0][M]x \tag{19}$$

In addition, we found that the copolymer composition curve for emulsion copolymerization of AN and methyl acrylate lies between that of suspension polymerization, the locus of which is restricted in the polymer particles, and solution polymerization, which showed that emulsion polymerization takes place both on or in the polymer particles and in aqueous phase.

In other words, the mechanism of emulsion polymerization of AN may be described as follows. Polymerization may be initiated in the aqueous phase, and some polymer molecules formed may be deposited on emulsifier molecules with subsequent formation of particles. The rate of particle formation is proportional to the rate of polymerization and the ratio of unreacted monomer. A part of monomer molecules in aqueous phase is sorbed on and in those particles, the concentration of which is proportional to the monomer concentration in aqueous phase. The total amount of adsorbed monomer is rather small, but the concentration on or in polymer particles may be sufficiently high. The polymerization proceeds concurrently on and in polymer particles and in the aqueous phase, but the three loci may be continuous rather than discrete; therefore, radical concentration may be the same in all phases. The ratio of the polymerization in the three loci may depend on polymerization condition, such as the types and concentrations of emulsifiers, polymerization temperatures, and initiators. The dependence of overall polymerization with respect to initiators is a square-root dependence, if physical condition does not vary. The emulsifiers participate in particle formation and stabilization. If physical condition changes with initiator concentration and coagulation occurs above a certain initiator concentration, the rate decreases and does not follow the square root dependence on the initiator concentration. The rate of polymerization in aqueous phase is proportional to the first power of total monomer concentration and the rates on and in polymer particles are to the second power.

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Résumé

Le mécanisme de polymérisation à l'émulsion de l'acrylonitrile a été étudié en mesurant l'adsorption du monomère sur des particules polymériques et les caractéristiques de polymérisation telles que la vitesse, le degré de polymérisation, la croissance de la particule au cours de la polymérisation et le degré de dispersion utilisant un dilatomètre et un microscope électronique. Dans la polymérisation en émulsion de l'acrylonitrile, les nouvelles particules sont formées en cours de polymérisation à une vitesse qui est proportionnelle à la vitesse de polymérisation et au rapport du monomère non-réagi. La quantité totale de monomère absorbé aux particules polymériques est plutôt faible, mais la concentration dans les particules polymériques est suffisament élevée et proportionnelle à la concentration en monomères dans la phase aqueuse. La polymérisation se passe concurremment dans les particules polymériques et en phase aqueuse mais les trois endroits peuvent pêtre continus plutôt que séparés l'un de l'autre. Le schéma de réaction a été introduit; il montre la coexistence de polymérisations sur ou dans les particules polymériques et en phase aqueuse.

Zusammenfassung

Der Mechanismus der Emulsionspolymerisation von Acrylnitril wurde durch Messung der Adsorption von Monomerem durch Polymerteilchen und charakteristischer Polymerisationsgrössen, wie Geschwindigkeit, Polymerisationsgrad, Partikelwachstum während der Polymerisation und Dispersionsgrad mit Dilatometer und Elektronenmikroskop untersucht. Bei der Emulsionspolymerisation von Acrylnitril werden während der Polymerisation neue Teilchen mit einer der Polymerisationsgeschwindigkeit und dem Anteil an nicht umgesetzten Monomeren proportionalen Geschwindigkeit gebildet. Die Gesamtmenge des an oder in den Polymerteilchen adsorbierten Monomeren ist ziemlich klein, die Konzentration an oder in den Polymerteilchen aber genügend hoch und der Monomerkonzentration in der wässrigen Phase proportional. Die Polymerisation verläuft gleichzeitig an oder in den Polymerteilchen und in wässriger Phase, diese drei Orte sind aber kontinuierlich und nicht getrennt aufzufassen. Es wird hier ein Reaktionsschema eingeführt, das die Koexistenz der Polymerisation an oder in den Polymerteilchen und in wässriger Phase annimmt.

Photolysis of Poly(ethylene Terephthalate)

F. B. MARCOTTE,* D. CAMPBELL, J. A. CLEAVELAND,
and D. T. TURNER, *Camille Dreyfus Laboratory,
Research Triangle Institute, Durham, North Carolina*

Synopsis

The photolysis of poly(ethylene terephthalate) films was studied *in vacuo* with light of wavelengths 2537 and 3130 A. A very stable filter system which cuts out the 3025 A. line was developed to isolate 3130 A. from a mercury spectrum. Despite the fact that the penetration of 2537 A. light was limited to a depth of a ca. 10^3 A. whereas 3130 A. light was more uniformly absorbed it was possible to demonstrate that the quantum yields for CO and CO_2 formation were in agreement for the two wavelengths. Quantum yields for fractures and crosslinks were estimated by sol-gel analysis. An absorption maximum which develops near 13 μ after exposure of poly(ethylene terephthalate) to light or γ-rays was attributed to the formation of groups formed by elimination of CO and CO_2. ESR spectra for trapped radicals were tentatively assigned to the components p-C_6H_3· and ·O—CH_2—CH_2—. It is suggested that the former radicals combine to form crosslinks. Quantum yields ($\times$ 10^4) with 3130 A. light are: CO, 6; CO_2, 2; crosslinks, 5.5; trapped radicals, 1.5; With 2537 A. light, quantum yields are: CO, 6–9; CO_2, 2–3; the network formed was not characterized as to crosslinks and fractures; trapped radicals were observed to exist but not determined.

The present paper describes chemical changes which occur when poly-(ethylene terephthalate) is exposed *in vacuo* to monochromatic light of wavelengths 2537 and 3130 A.

Previously, the photolysis of poly(ethylene terephthalate) in air by light comprising wavelengths in the range 2800–3900 A. was followed by measurements of solution viscosity, and a quantum yield estimated for chain fractures of 5 $\times$ 10^{-4}.[1] It was claimed[2] that the most effective wavelength causing degradation was 3130 A. More pertinent studies of the photolysis of poly(ethylene terephthalate) *in vacuo* with monochromatic light of wavelength 2537 A. showed that the polymer turns an amber color, becomes brittle, evolves gas, and becomes partly insoluble in trifluoroacetic acid.[3–6] These latter results will be mentioned in more detail later.

EXPERIMENTAL

Materials

The poly(ethylene terephthalate) studied was Mylar C grade, which is a strong, biaxially oriented, transparent film of 50% crystallinity. It was

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* Present address: Summit Research Laboratories, Celanese Corporation, Summit, New Jersey.

made available in various uniform thicknesses by Dr. C. Heffelfinger of the DuPont Company, Circleville, Ohio. This polymer contains about 1% cyclic oligomers (mostly trimer) and a few parts per million of inorganic materials added during the condensation reaction as catalysts. The number-average molecular weight of the polymer molecules is about 18,000 and their distribution of sizes is approximately random. The endgroups are mostly —OH and —COOH.

Trifluoroacetic acid was of laboratory reagent grade.

Preparation of Thin Films

Thin continuous and transparent films were deposited on carefully cleaned quartz plates by slow evaporation of known volumes of a solution of poly(ethylene terephthalate) in trifluoroacetic acid (3 g./l.). These cast films were used solely for ultraviolet absorption measurements. They were found to be reasonably uniform.

Light Sources

A germicidal lamp was used which emits more than 90% of its light at 2537 A. (General Electric G15T8). No filters were necessary.

Also, a medium-pressure mercury arc was used as a source rich in 3130 A. light without serious line broadening (Hanovia 654A10, of effective length 10 cm., running at 3.2 amp. and 120 v.).

Filters for Hanovia Lamp

Removal of Infrared

The Hanovia lamp was surrounded by a coaxial, quartz annular cooling vessel through which tap water flowed. An air space of 1 cm. separated the surface of the lamp from the inner wall of the cooling vessel; the light path through the cooling water was 2 cm., sufficient to remove most of the infrared (Mylar is transparent to any effective infrared passed by water and quartz). The film temperature was estimated to be <40°C.

Removal of Wavelengths <3130 A.

Since Mylar does not absorb mercury lines longer than 3130 A. it was only necessary to filter out wavelengths ≤3025 A. The filter commonly employed to absorb 3025 A. and pass 3130 A. is aqueous potassium biphthalate.[7] It was found much too unstable toward photodegradation[8] to be of use in the extended exposures required in this work. Thin Mylar films may be useful as filters, but these have the disadvantage of eventually becoming opaque to short wavelength light. It was discovered that lead chloride in concentrated aqueous sodium chloride is reasonably stable and is a satisfactory filter. In early experiments, with the use of quartz windows on the filter cell, a thin gray film formed on the lamp-side window. This window was replaced with Pyrex to protect the solution from most of the ultraviolet of wavelength shorter than 2900 A. This arrangement proved satisfactory; such a filter cell was exposed to the Hanovia lamp

(about 4 cm. from the lamp) for 70 hr. with a diminution of only about 20% in transmission of 3130 A. retaining effective absorption of 3025 A. Light from the Hanovia lamp passed by this filter cell (1 cm. path) and absorbed by 6×10^{-4} cm. Mylar film was estimated to be about 96% 3130 A. with the remainder 3025 A.

In experiments in which it was desired to irradiate a large number of samples simultaneously to a high energy deposition, the above filter was replaced by a Pyrex filter of thickness 1 mm. At a distance of 4 cm. from the Hanovia lamp the intensity of 3130 A. at the surface of the samples was calculated to be 1.3×10^{-5} Einsteins/cm.^{2}-hr. 3025 A. light was incident at one order of magnitude less.

Actinometry

The intensity of light incident on Mylar was determined directly by uranyl oxalate actinometry. In the case of 3130 A. light, other effective wavelengths were removed with sodium chromate solution and Corning glass No. 9863.

Gas Formation and Analysis

Preparation of Samples

Samples of film were stored *in vacuo* for several weeks before being sealed in quartz tubes, which were sealed to a vacuum line, at a pressure $<1 \times 10^{-5}$ mm. Hg. If the pressure in the gas analysis apparatus was $<5 \times 10^{-5}$ mm. Hg after standing overnight the system was considered vacuum-tight and the polymer sufficiently outgassed to proceed.

Irradiation of Samples

2537 A. Films of size 20 cm. $\times$ 1 cm. $\times$ 2.5×10^{-3} cm. were exposed at a distance of 1 cm. from the germicidal lamp. The incident intensity of 2537 A. light was 4×10^{-5} Einsteins/cm.^{2}-hr.

3130 A. A film (4 cm. $\times$ 4 cm. $\times$ 6×10^{-4} cm.) was suspended from a fine glass rod threaded through slits at the top of the film and weighted with a similar rod at the bottom, so that the film approximated a plane; the center of the film was 8 cm. from the center of the Hanovia lamp, the latter being in a plane parallel to the film. The 3130 A. energy incident on the sample, via the special filter and the quartz tube housing the film system, was 4×10^{-6} Einsteins/cm.^{2}-hr.

To ensure constancy of intensity of absorbed light, an RCA 935 phototube was employed, with a continuous recorder, to monitor the 3130 A. light transmitted by the film. Filters were used to remove other wavelengths to which the phototube would respond. Air cooling of the Pyrex window of the lead chloride–sodium chloride filter cell was necessary to maintain the filter solution temperature between 27 and 30°C. (This filter solution is somewhat temperature-dependent: 1 cm. of the solution transmits 63% of 3130 A. light at 25°C., 55% at 30°C., and about 30% at 60°C.

In the range 27–30°C., transmission varies ±5% of the mean value.) During irradiation, the phototube readings varied no more than 6% from the mean value.

Gas Analysis

The quartz irradiation tube was connected to a McLeod gage; mercury cutoffs were used in place of greased stopcocks in those parts of the vacuum system which came into contact with the product gases. A U-tube trap in a Dry Ice bath was maintained between the quartz irradiation tube and the remainder of the gas collection system to eliminate mercury vapor and thus avoid possible complications due to absorption of resonance radiation in the vicinity of the film. During irradiation, liquid nitrogen baths were maintained on two traps in the gas collection system. The lamp was covered at intervals and the pressure of gases noncondensible at −196°C. measured. Subsequent removal of the liquid nitrogen baths followed by McLeod gauge readings to a constant value gave the increase in pressure corresponding to gaseous products condensible at −196°C. but not at −78°C. In this manner, the rate of formation of these two gaseous fractions was measured as a function of time. Products condensible at −78°C. were negligible.

In selected cases, the fractions mentioned above and sometimes the total gas volatile at 25°C. were analyzed in an AEI MS10 mass spectrometer.

Absorption Spectra

Ultraviolet absorption spectra were recorded by use of a Perkin-Elmer spectrophotometer (Model 202). A cast film of poly(ethylene terephthalate) of thickness 500 A. on a quartz plate was sealed *in vacuo* in a quartz tube and exposed to 2537 A. light of incident intensity 4×10^{-5} Einsteins/cm.²-hr. Changes in the spectrum as a function of irradiation time were determined by interruption of irradiation, removal of the quartz plate, and measurement of the spectrum. The quartz plate was then replaced, the system evacuated and irradiation resumed.

Infrared absorption spectra were recorded by using a Perkin-Elmer spectrophotometer (Model 137). The transmission of Mylar films (2.5 $\times 10^{-3}$ cm. thick) was examined after an exposure of 600 hr. *in vacuo* to 3130 A. light at an incident intensity of the order of magnitude 10^{-5} Einsteins/cm.²-hr. The surface zone of films exposed for 20 hr. *in vacuo* to 2537 A. light at an incident intensity of 4×10^{-5} Einsteins/cm.²-hr. was examined by using an ATR Wilks 20 reflection accessory to the Model 137.

Network Formation

Films of thickness 6×10^{-4} cm. was stored *in vacuo* for several months. Single strips of area 5×1 cm.² were sealed *in vacuo* in Pyrex tubes of internal diameter 1.2 cm. and of wall thickness 1 mm. These tubes were exposed at a distance of 4 cm. from the Hanovia lamp through a water-cooled quartz jacket. The nature and intensity of the incident light has been described above.

Solubility Analysis

The irradiated polymer (ca. 5 mg.) was cut into 7–10 pieces and weighed to 0.01 mg. in a filter funnel of gold foil (ca. 50 mg.), on a Cahn electrobalance. The gold filter funnel was carefully immersed in trifluoroacetic acid, whereupon the larger part of the polymer dissolved within 30 sec. The polymer was washed several times in acid over a period of 2 min. and finally coagulated and rinsed in isopropyl alcohol. The funnel and insoluble polymer were allowed to dry to constant weight at room temperature (usually within 30 min.) and the soluble fraction calculated.

Equilibrium Swelling Values

Equilibrium Swelling Values

Equilibrium swelling values were determined for the irradiated material insoluble in trifluoroacetic acid. This was washed free of excess acid by rapid immersion in two large volumes of water. The washed polymer was then extracted with distilled water (5 ml.) which was then titrated with $0.1N$ KOH from a microburet in the presence of pH indicator paper. The polymer was then reimmersed in acid and the whole procedure repeated to provide a check value. The polymer was dried and weighed on a micro balance and the volume of acid taken up by the polymer calculated.

Electron Spin Resonance

ESR at 3130 A.

Two films of size 5 cm. $\times$ 0.8 cm. $\times$ 2.5×10^{-3} cm. were degassed and sealed *in vacuo* in a composite Pyrex-Suprasil quartz tube. The two thicknesses of film were irradiated through Pyrex under conditions already described. After irradiation the films were flipped into the quartz section, which had been protected from light to avoid a spurious ESR signal, and examined over a range of orientations in the magnetic field of a Varian V.4502-10 ESR spectrometer at room temperature. The number of free radicals was estimated by numerical integration of a first derivative curve and by comparison with α,α'-diphenyl-β-picrylhydrazyl.

ESR at 2537 A.

Finely chopped Mylar film was exposed *in vacuo* to 2537 A. light through quartz. The quartz tube was rotated during irradiation to expose a large surface area of polymer. The irradiated polymer was shaken into the unirradiated end of the tube before examination.

Radiolysis Followed by Photolysis

Films were exposed *in vacuo* to γ-radiation from a ^{60}Co source at a dose rate of 10^{-2} Mrad/min. and then exposed to 3130 A. light and examined as described above.

RESULTS AND DISCUSSION

Ultraviolet Absorption

Absorption of Unirradiated Poly(ethylene Terephthalate)

The thinnest available Mylar film (6×10^{-4} cm.) transmits light of wavelength > 3200 A. but absorbs strongly near 3100 A. and is opaque to wavelengths $<$ ca. 3025 A. (Fig. 1). Examination of a much thinner cast film, ca. 500 A., reveals a strong absorption maximum near 2400 A. and a weaker one near 2900 A. (Fig. 2). Solutions of various phthalate esters, e.g., dimethyl phthalate, show similar absorption maxima, and it is concluded that the predominant chromophore in poly(ethylene terephthalate) in the range 2400–3200 A. is the group $-O-CO-C_6H_4-CO-O-$. This conclusion may appear trivial but is emphasized because in some other polymers photochemical changes are initiated by impurities and cannot be related directly to the photochemistry of the repeat unit in the polymer molecule.

Changes in Absorption on Exposure to 2537 A. Light

After 2 hr. irradiation (Fig. 2B) the maximum near 2400 A. decreases, while there is a general increase in absorption at wavelengths > 2600 A. After 20.7 hr., the spectrum became featureless and little further change was noticed after 67 hr.

Energy Deposition

There is a "skin" effect with light of wavelengths 2537 and 3025 A., but 3130 A. light is more uniformly absorbed.
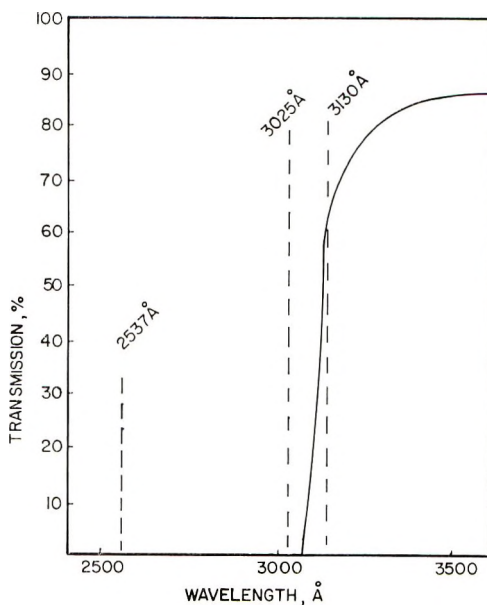

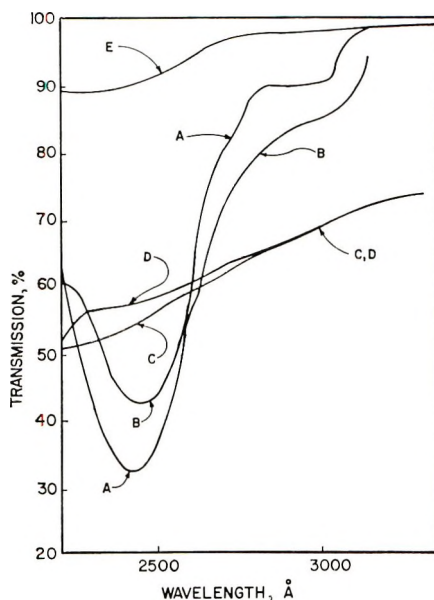Fig. 1. Transmission curve of 6×10^{-4} cm. Mylar film.

Fig. 2. Effect of 2537 A. irradiation on the transmission curve of a 500 A. poly(ethylene terephthalate) film (intensity 4.2×10^{-6} Einsteins/cm.²-hr.): (A) original cast film on quartz; (B) after 2 hr. irradiation; (C) after 20.7 hr. irradiation; (D) after 67 hr. irradiation; (E) quartz plate alone.

2537 A. From Figure 2 and a second set of similar data absorption coefficients k, (2537 A.) of 1.7×10^{-5} cm.$^{-1}$ and 1.0×10^{5} cm.$^{-1}$, respectively, were estimated for the initial film and one exposed to 2537 A. light for 20.7 hr. $[k = -l^{-1} \ln (II_0{}^{-1})]$. It may be estimated that 2537 A. light is reduced to 37% of its incident intensity after passing through a thickness of 600 A. of the poly(ethylene terephthalate) and that this same reduction occurs at 1000 A. depth in the highly irradiated film. Taking the latter depth, the average rate of energy deposition is ca. 4×10^{20} quanta/cc.-sec. This is an unusually high rate, each repeat unit in the polymer absorbing one quantum every 10 sec., on the average. This corresponds to an energy deposition of about 100 cal./sec.-cc., but as the thermal conductivity of Mylar is 3.6×10^{-4} cal./sec.-cm.² (°C./cm.),[9] this energy is readily transferred to the bulk of the polymer and the ambient temperature near the irradiated surface is not expected to increase by more than a few degrees.

3130 A. The absorption coefficient of poly(ethylene terephthalate) at 3130 A. is 7.7×10^2 cm.$^{-1}$ (Fig. 1). The absorbed energy distribution for 3130 A. in a 6×10^{-4} cm. film was calculated by considering the energy absorbed by each of ten successive layers into which one may imagine the film divided. If 100 units of energy flux are incident on the film surface, the average energy absorbed by a layer is 3.7 units. The mean deviation from the average is 0.4 (or 11%); the range is 3.0–4.5 units. In the gas phase, a rule of thumb is that the fraction of incident light which is ab-

sorbed should be one-half or less, and that mixing caused by convection and diffusion enables one to assume uniform energy absorption and concentrations of active species.[7]　In a solid polymer a quite different situation
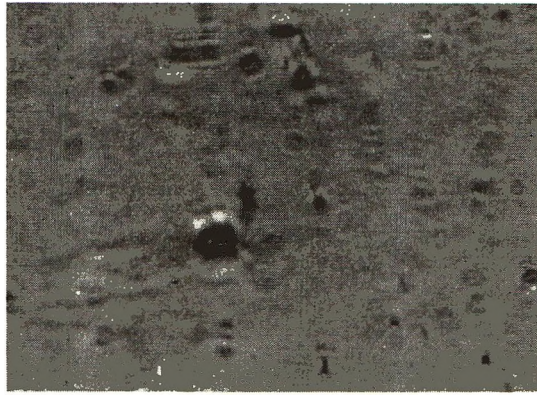
(A)

(B)

(C)

Fig. 3. Optical microfilms of Mylar (transmitted light) exposed to 2537 A. light for 200 hr. (A) unirradiated; (B) irradiated side up; (C) irradiated side down.　50×.

obtains; the movement of polymer molecules and large reactive species is severely restricted. Depending on the nature of potential reactions, very thin films may be rigorously required.

In the case of poly(ethylene terephthalate), the required degree of uniformity of energy absorption is not known for 3130 A. light. Since the quantum yields of gaseous products are quite low, 6×10^{-4} cm. Mylar appeared to be the lower limit in film thickness for production of adequate products in a reasonable time for measurement with sufficient accuracy.

Microscopic Examination of Films Exposed to 2537 A. Light

To the naked eye, 6×10^{-4} cm. Mylar film appears clear and uniform, but a magnification of 50 reveals irregularities (Fig. 3A). Prolonged exposure *in vacuo* to 2537 A. light results in the formation of distinctly different heterogeneities which sometimes have sharp and regular boundaries. As might be expected these are formed only near the irradiated surface of the film [Fig. 3, compare the front surface in (B) with the back surface in (C)]. Previously, heterogeneities have been observed in Mylar films and it appears that they are formed by crystallization of low molecular weight oligomers which may be removed by extraction.[11] Other experiments indicate that the predominant oligomer is a cyclic trimer.[10] However, the nature of the heterogeneities which appear following irradiation was not investigated further. Their appearance is adduced simply as evidence of changes confined to the irradiated side of the film.

Gas Evolution

2537 A. Light

The gas fractions volatile at -78 and $-196°C$. were identified by analysis in a mass spectrometer as CO_2 and CO (the latter fraction included a few per cent methane but we will refer to it subsequently as CO). Hydrogen was carefully sought but not found. Residual gas which was volatile *in vacuo* at $25°C$. was negligible. Previously it was reported from similar experiments that CO was the major gaseous product, along with some methane and a trace of hydrogen.[5] Thus, there is a serious discrepancy concerning the formation of CO_2. In the present experiments, confirmatory evidence for the formation of CO_2 was obtained by showing that the pressure–temperature relationship for the $-78°C$. fraction agreed with standard data for CO_2.

The rate of formation of both the -196 and $-78°C$. fractions decreased with increasing time of exposure of a 2.5×10^{-3} cm. film to 2537 A. light as shown in Figure 4A. Also, the ratio of these two fractions decreases with time (Fig. 4B), and this trend was confirmed directly by pumping off the total gas at half-hour intervals directly into a mass spectrometer.

The decreasing rate of gas formation is consistent with a "skin" effect. In a skin 1000 A. thick there are about 7×10^{-8} mole of repeat units/cm.[2] of film and, potentially, 14×10^{-8} mole of CO plus CO_2. This amount of

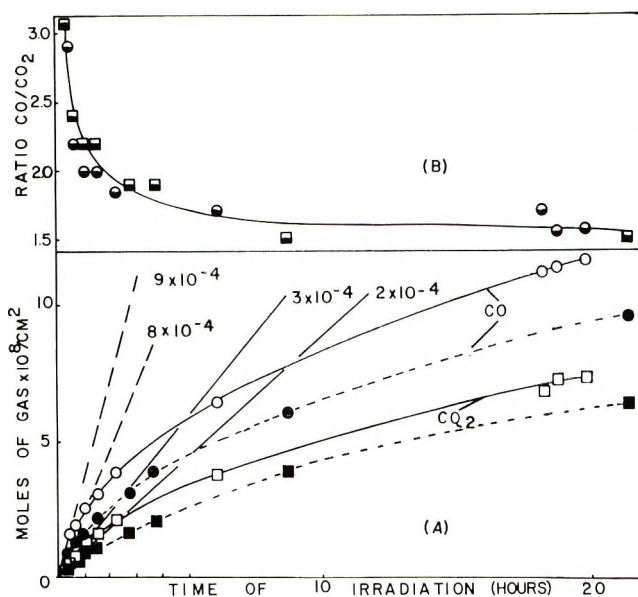Fig. 4. Gas formation on exposure of Mylar to 2537 A. light: (A) area of film = 16 cm.^{2}: (O) CO, (□) CO$_2$: area of film = 19 cm.^{2}: (●) CO, (■) CO$_2$: (B) (◐) area of film = 16 cm.^{2}, (◧) area of film = 19 cm.^{2}.

gas is evolved, on average, after 17 hr. exposure, at which time the rate of gas evolution has dropped to about one-tenth of its initial value. Thus gas is evolved at a decreasing rate from a "skin" which roughly correlates with the estimated penetration of the light. The change in the ratio of CO/CO$_2$ may be due to a difference in the photochemistry between the initial diester and an intermediate monoester; however, no experimental data on model compounds is available to check this suggestion.

Initial quantum yields for CO and CO$_2$ formation were estimated from the slopes shown in Figure 4A as (1) $\Phi_{CO} = 6 \times 10^{-4}$, $\Phi_{CO_2} = 2 \times 10^{-4}$ and (2) $\Phi_{CO} = 9 \times 10^{-4}$, $\Phi_{CO_2} = 3 \times 10^{-4}$. The ratio Φ_{CO}/Φ_{CO_2} is the same in each experiment, i.e., 3, and the absolute values are considered to be in reasonable agreement for this type of experiment. It will be seen that there is a subjective element in the choice of an initial slope for CO production in Figure 4A. An attempt was made to make a more objective estimate by plotting the logarithm of the apparent quantum yield at each dose against dose. In other work, this procedure allowed a linear extrapolation to zero dose with data on the photoisomerization of solid o-nitrobenzaldehydes[12] but failed with the present data even for the first three points. Presumably, this is because of the rapid change in mechanism evidenced by the rapid drop in the ratio of CO/CO$_2$.

3130 A. Light

The gaseous products formed by exposure of 6×10^{-4} cm. Mylar film to light of wavelength 3130 A. (cf. Fig. 5) were similar to those formed by exposure to light of wavelength 2537 A.

The dependence of gas evolution on the time of irradiation is shown for duplicate runs in Figure 6A. The rates of formation of both CO and CO_2 decrease and reach a constant value after about 2 hr. The reason for the high initial rate is not known. The eventual constant value is taken to be characteristic of the bulk of the polymer and used to evaluate quantum yields of $\Phi_{CO} = 6 \times 10^{-4}$ and $\Phi_{CO_2} = 2 \times 10^{-4}$.

In these experiments only about 0.3% of the CO and CO_2 potentially available (assuming 2 moles of gas per mole of repeat unit initially present) was obtained. As would be expected, the ratio CO/CO_2 remains approximately constant, between 2.0 and 3.0, at this low level of chemical reaction (Fig. 6B).

Network Formation

2537 A. Light

As reported previously, Mylar becomes partly insoluble in trifluoro-acetic acid after exposure to 2537 A. light. However, the analysis of such data to provide an estimate of the ratio of fractures to crosslinks, with its implicit assumption of uniform reaction throughout the 6×10^{-4} cm. film studied,[4] does not seem permissible, because of the limited penetration of 2537 A. light. In the present work attempts were made to overcome the problem by using thin films (several hundred Angstroms) to allow acceptably uniform energy deposition. In principle, the high extinction coefficient of the polymer near 2600 A., together with its constancy or irradiation, could be used to make a sensitive spectrophotometric analysis of the soluble fraction but, unfortunately, most of the solvents for poly(ethylene terephthalate) also absorb in this region. Concentrated sulfuric acid does
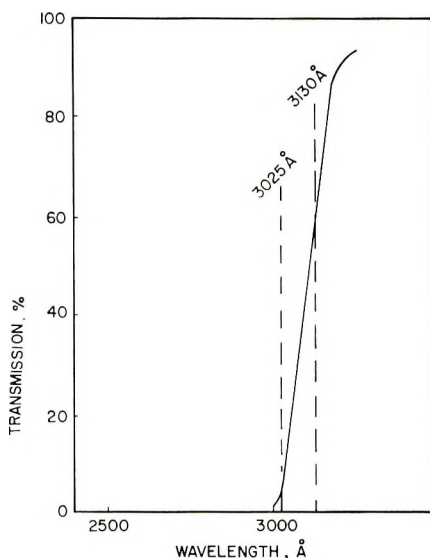

Fig. 5. Transmission curve for PbCl₂–NCl filter solution, path length, 1 cm.; filter composition; distilled water (100 ml.), PbCl₂ (0.5 g.), NaCl (30 g.).
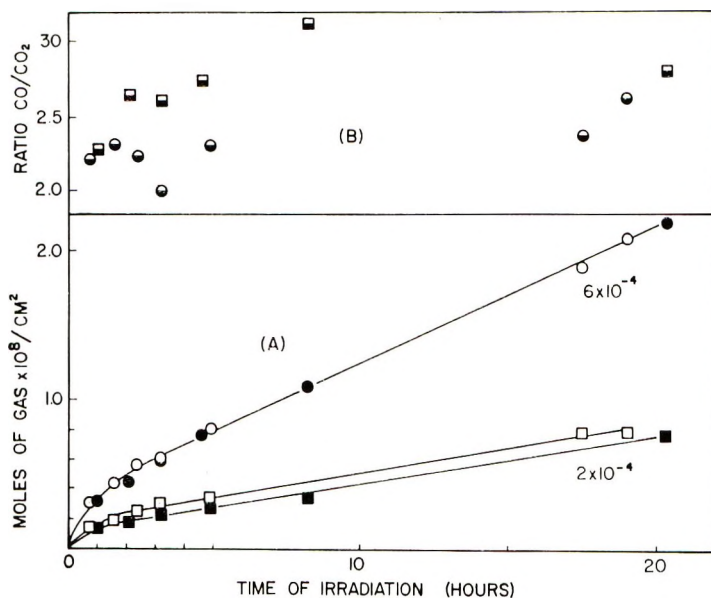
Fig. 6. Gas formation on exposure of Mylar to 3130 A. light: (A) area of films = 16 cm.², run 1: (O) CO; (□) CO_2; area of films = 16 cm.²; run 2: (●) CO; (■) CO_2; (B) ratio of CO/CO_2; (◐) run 1; (⊡) run 2.

not have this disadvantage but eventually had to be rejected because it was found to digest the insoluble fraction. This approach is mentioned because it is believed that it might prove successful with modification.

Predominantly 3130 A. Light

Films of 6×10^{-4} cm. thickness became increasingly yellow and brittle with increasing time of exposure to light from the Hanovia lamp, filtered through 1 mm. Pyrex. When sample tubes were opened after long exposures it was necessary to leak air in slowly in order to prevent the sample from being blown into fragments too small for convenient manipulation.

Swelling Values. When immersed in solvents for poly(ethylene terephthalate) such as o-chlorophenol at 90°C. or trifluoroacetic acid at room temperature, the irradiated polymer usually breaks up into what look to be brown needles ranging some 2–6 mm. in length. When the ends of these needles are examined under a microscope, while still in contact with solvent, they appear to be rolled-up sheetlets. It is difficult to judge qualitatively whether these fragments are swollen with solvent, while the usual quantitative test of comparing the weights of swollen and deswollen samples is unsatisfactory because the surface cannot be mopped dry of excess solvent without serious loss of any volatile acid which might be swollen in the polymer. The unconventional test finally devised depended on titration of any acid remaining in the sample after rinsing the surface rapidly with water as described in the experimental section. Pieces of insoluble reaction product on removal from trifluoroacetic acid gave titers

of 0.161 and 0.159 ml. of 0.1N KOH in consecutive cycles of immersion in trifluoroacetic acid rinsing, and equilibration for 5 min. in water. This reproducibility suggests that the washing procedure was adequate and that loss of acid by syneresis and evaporation was not serious. The sample of polymer weighed 0.35 mg. after drying to constant weight, giving an equilibrium swelling value of 1100%. This high value proves that a network is formed, as distinct from some insoluble chemical product. When the molecular weight between elastically effective crosslinks is estimated from the Flory-Huggins' equation[13] it is found to be many times greater than that of the initial molecules from which the network was formed. Presumably, a sequence of primary molecules are crosslinked together between ones which include two or more crosslinks and which serve to limit the expansion of the network. High swelling values, 800–2200%, have also been reported for networks formed by exposure of poly(ethylene terephthalate) to electrons.[14]

Sol–Gel Analysis. Preliminary experiments with a number of samples exposed separately for the maximum time studied indicated that most of the sol fraction had been removed after three minutes treatment with trifluoroacetic acid. Longer treatment with acid was avoided to minimize any polymer degradation and possible loss of small pieces of gel (Table I) In Figure 7.1, $1-s$, where s is the sol fraction, is plotted against time of exposure.

It has been shown theoretically that when fractures and tetrafunctional crosslinks are introduced at a uniform rate into linear polymer molecules with a random distribution of lengths the sol fraction s may be related to time t by eq. (1);[15] p and q are the probabilities that a repeat unit is fractured or crosslinked, respectively, in unit time, and $\bar{P}_n$ is the average number of repeat units per molecule at $t = 0$.

$$s + s^{1/2} = pq^{-1} + (q\bar{P}_n t)^{-1} \tag{1}$$

The polymer used in the present work does approximate to a random molecular weight distribution but the assumption, implicit in the derivation of eq. (1), of a uniform dose rate throughout the sample does not hold. Only 37% of the 3130 A. quanta are absorbed and, for present purposes,

TABLE I

Sol Fraction s After Successive Immersions in Trifluoroacetic Acid[a]

Sample	No. of immersions	s
1	1	0.66
	2	0.65
	3	0.69
2	1	0.56
	2	0.73
	3	0.74

[a] Time of exposure of poly(ethylene terephthalate) = 204.5 hr.; time of each immersion = 1 min.
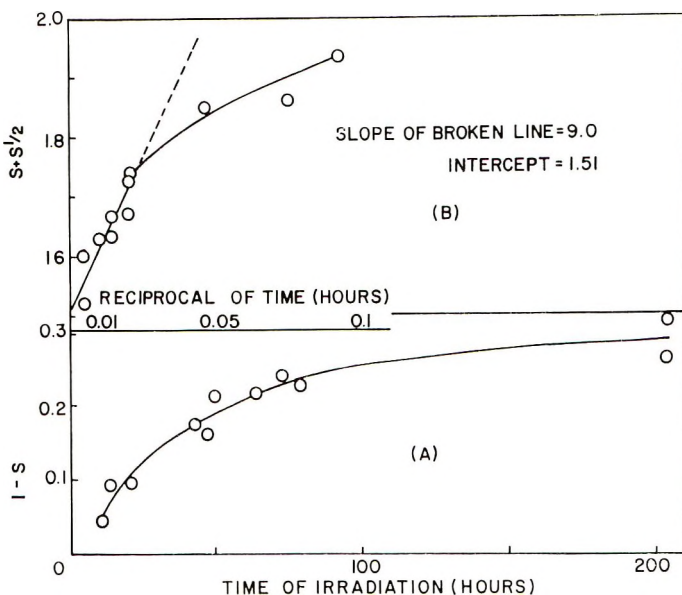
Fig. 7. Insolubilization of Mylar (6.3×10^{-4} cm.) on exposure to 3130 A. light: (A) insoluble fraction ($1 - s$) vs. time of irradiation; (B) data from (A) plotted in form $s + s^{1/2}$ vs. reciprocal of time of irradiation.

will be regarded as resulting in an approximately uniform energy deposition throughout the film. On the other hand, the 3025 A. quanta, incident at an intensity one order of magnitude lower, would be strongly absorbed near the surface ($k = 1.3 \times 10^4$ cm.$^{-1}$). This would result in an early formation of gel near the surface. However, as the gel front advances through the film with increasing exposure this effect will eventually become negligible because the gel fraction approaches an equilibrium value of about 30% (Fig. 7A). For this reason the gel fractions <0.1, after lower exposures, have been neglected in Figure 7B which was obtained by plotting the data in Figure 7A according to eq. (1).

The number of moles of units crosslinked/cm.^{2}-hr., ν_c, is given by eq. (2), in which l is the film thickness (6×10^{-4} cm.), ρ the density of the polymer (taken as constant throughout at 1.4), σ the slope in Figure 7B, and $\bar{M}_n$ the number-average molecular weight (18,000).

$$\nu_c = \rho l (\bar{M}_n \sigma)^{-1} \tag{2}$$

Division of ν_c by the number of Einsteins of 3130 A. quanta absorbed throughout 1 cm.^{2} of film per hour ($0.37 \times 1.3 \times 10^{-5}$) gives a quantum yield for crosslinked units of 11×10^{-4}. As there are two crosslinked units per crosslink the quantum yield for crosslinks, Φ_c is 5.5×10^{-4}. The quantum yield for fractures, given by $\Phi_c(pq^{-1})^{-1}$, is 16×10^{-4}. In order to obtain more accurate values it would be desirable to use pure monochromatic light and to decide whether it is necessary to make

corrections for the exponentially decreasing absorption of radiation along the lines suggested by Shultz.[16]

Infrared Absorption

Exposure of 6×10^{-4} cm. Mylar to 3130 A. light resulted in the formation of an absorption maximum near 12.9 μ (Fig. 8A). No other significant changes in infrared absorption were detected in the range 12.5–14.0 μ. A similar change was detected in a 6×10^{-4} cm. film exposed to 2537 A. light, but in this case the band was only detected by recourse to a reflectance technique which probes the surface zone (Fig. 8B). Previously, changes in infrared absorption in the region 12.7–13.3 μ have been reported after irradiation of poly(ethylene terephthalate) with both γ-rays[17] and electrons.[14] In the case of electron irradiation it was noted that a broad band appears with two peaks in the 775–755 cm.$^{-1}$ region (12.9–13.3 μ). Present results obtained by γ-irradiation confirm these observations (Fig. 8C) and indicate that the same type of damage is caused by a variety of radiations. In the case of electron irradiation this was attributed to the formation of polyphenyl systems which, additionally, together with changes of —O—CH₂—CH₂—O— group from the *trans* to *gauche* conformation, were supposed to be responsible for extensive changes observed at other wavelengths. As marked changes were not observed at other wavelengths in the present work an alternative interpretation, based on work by Miyake,[18] is preferred. This author assigned the absorption band at 14.1 μ in poly(ethylene terephthalate) to an out-of-plane O=C—O bending
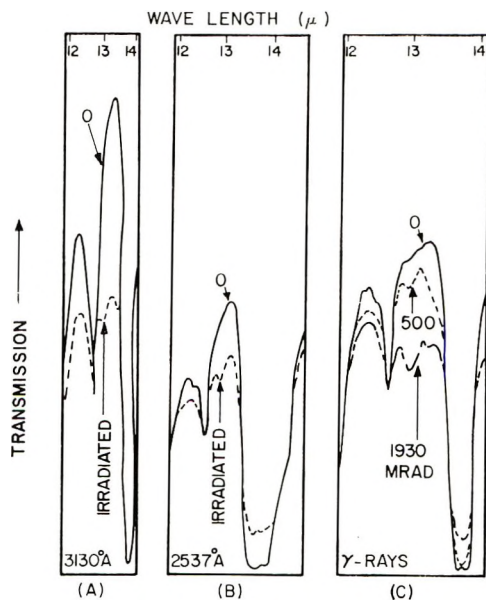

Fig. 8. Absorption of poly(ethylene terephthalate) near 13 μ after exposure to light or γ-rays.

mode and showed how, in a series of model compounds, the wavelength varied according to the *para* substituent of the benzene ring. For example, the band appears at 13.7 μ in p-CH$_3$—O—CO—C$_6$H$_4$—CO—O—CH$_3$ but at 13.3 μ in p-CH$_3$—C$_6$H$_4$—CO—O—CH$_3$. It is now suggested that the change observed on irradiation of poly(ethylene terephthalate) is due to the elimination of CO and/or CO$_2$ from one of the ester groups in a terephthalate di-ester. For example, a group such as p-O—CO—C$_6$H$_4$—O—CH$_2$— would appear to be a likely candidate responsible for either the 12.9 or 13.3 μ bands which are to be seen in Figures 8A and 8C. However, more detailed studies of model compounds would be necessary to justify detailed assignments of this kind.

Electron Spin Resonance

In preliminary experiments similar, but poorly resolved ESR spectra, were obtained from samples exposed to light of wavelengths 2537 and 3130 A. Subsequently, experiments were confined to strips of film which could be rotated in the magnetic field to provide information about anisotropy.[19] 3130 A. light was used to produce radicals throughout as large a thickness of material as possible although even with the more penetrating wavelength, the number of spins/gram was inconveniently small. The initial quantum yield for trapped radicals was 1.5×10^{-4} but this decreased with time of exposure, the concentration of trapped radicals beginning to level off after 5 hr. at about 8×10^{17} spins/g. (Fig. 9).

Typical examples of both first and second derivative spectra obtained at 25°C. are given in Figure 10. These were obtained with the magnetic field perpendicular to the plane of the films, but similar spectra were ob-
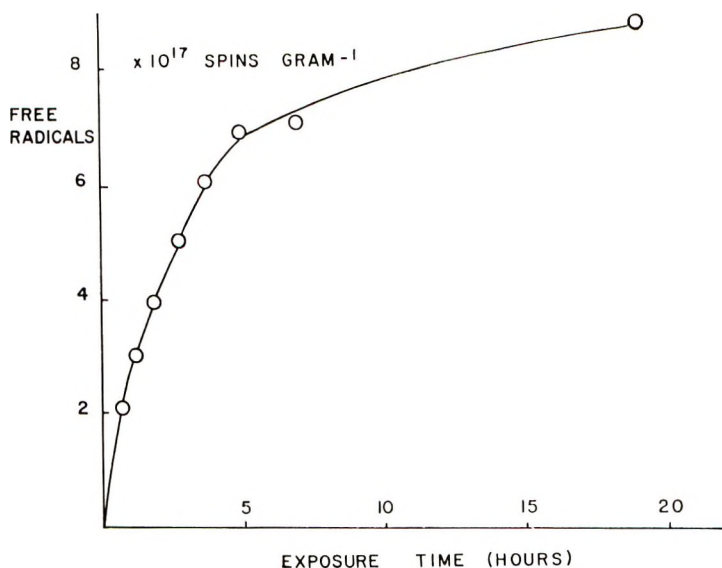

Fig. 9. Concentration of trapped radicals vs. time of exposure to 3130 A. light.

tained at all other orientations studied, i.e., no anisotropy was detected. Although the spectra are poorly resolved five lines are visible.

The present ESR spectra may be compared with those obtained previously by γ-irradiation of Mylar.[19,20] Two orientation-dependent com-

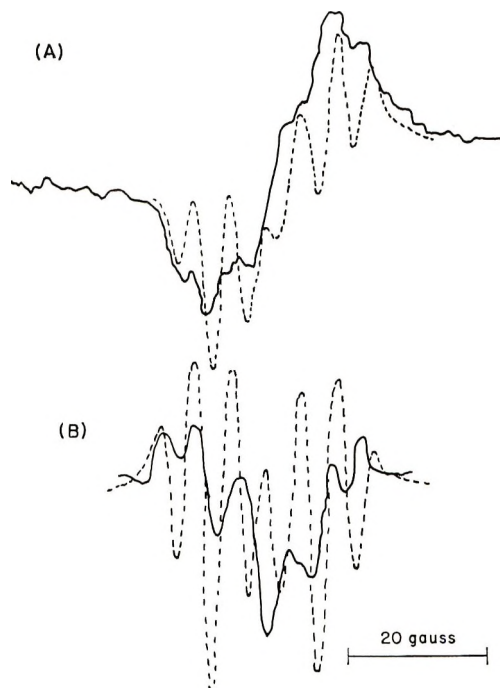Fig. 10. ESR Spectra of poly(ethylene terephthalate) after exposure to 3130 A. light: (A) first derivative; (B) second derivative; (−−) spectra obtained by γ–irradiation of poly(ethylene terephthalate) and previously assigned to p-C_6H_3.
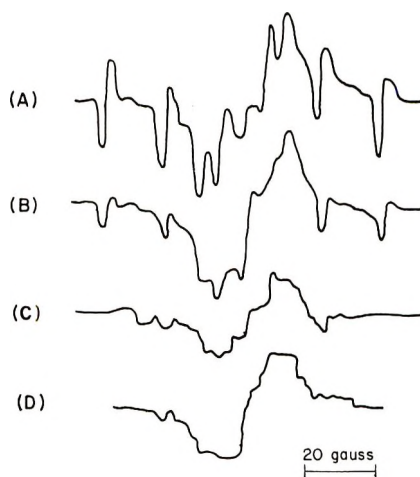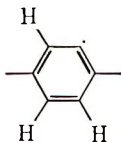

Fig. 11. ESR spectra of poly(ethylene terephthalate): (A) γ-irradiated; 30 Mrad followed by (B) 3130 A., 3 hr.; (C) 3130 A., 5.5 hr.; (D) 3130 A., 22 hr.

ponents were distinguished in spectra similar to that shown in Figure 11A and the predominant component assigned to the radical —O—ĊH—CH$_2$—O—. There is also a minor component, which persists on heating at 160°C., which has a smaller spread and comprises a pair of triplets 1:2:1:1:2:1. The latter spectrum was tentatively assigned to the radical p-C$_6$H$_3$·viz.

H

H   H

There is evidence that both these spectra arise from radicals trapped in crystalline regions. γ-Irradiation, additionally, results in radical trapping in a completely amorphous poly(ethylene terephthalate). However, in this case a poorly resolved spectrum is obtained not dissimilar from that observed in the present work (Fig. 10). From these observations we conclude that the radicals —O—ĊH—CH$_2$—O— and p-C$_6$H$_3$·· are not trapped in crystalline regions on exposure of Mylar to light. This is probably because C—H bonds are not fractured by light of wavelengths 2537 or 3130 A. as evidenced by the absence of hydrogen gas, which is formed by γ-irradiation. On the other hand, it has been observed that even if —O—ĊH—CH$_2$—O— radicals were formed they would be destroyed by light. This was shown by generating a population of trapped radicals, predominantly —O—ĊH—CH$_2$—O—, in Mylar by exposure to γ-rays and then subsequently exposing the sample, while still *in vacuo*, to 3130 A. light. The spectrum of the —O—ĊH—CH$_2$—O— radical decays, as shown in Figure 11 (B, C, and D).

With the above background, we offer a tentative interpretation of the spectra in Figure 10. The asymmetry of the spectra indicates that more than one free radical is present. The strong central line is assigned to a singlet while the four lines in the wings are suggested to be the four outer components of the 1:2:1:1:2:1 spectrum of the p-C$_6$H$_3$· radical (a spectrum previously assigned to this radical is included in Fig. 10 for comparison[19]). The two weak central lines are believed to be obscured by the singlet which is tentatively assigned to the radical ·O—CH$_2$—ĊH$_2$—.

Mechanism of Photolysis

The following observations need to be explained: (a) the main gaseous products are CO and CO$_2$; (b) groups of the kind p-O—CO—C$_6$H$_3$—X— are formed, in which X is not a —CO—O— group; (c) the polymer molecules are fractured and crosslinked; (d) the ESR spectra are consistent with formation of the following radicals: p-C$_6$H$_3$· and ·O—CH$_2$—CH$_2$—; (e) quantum yields are as shown in Table II.

It will be seen that the quantum yields for CO and CO$_2$ formation are similar for irradiation with light of wavelengths 2537 and 3130 A. Other changes are qualitatively similar, and it is believed that gross chemical

TABLE II
Quantum yield $\times 10^4$

λ, A.	CO	CO_2	Cross-links	Fractures	Trapped radicals
3130	6	2	5.5	16	1.5
2537	6–9	2–3	Network formed but not characterized		Observed but not determined

effects are closely similar even though in the case of 2537 A. light they occur in a much thinner layer.

The quantum yield for fractures, 16×10^{-4}, is about four times the value (4×10^{-4}) reported previously for poly(ethylene terephthalate) irradiated in air.[1] The latter value was estimated from measurements of solution viscosity which were converted to number-average molecular weights using relationships established for linear samples of poly(ethylene terephthalate). This procedure would be valid only if oxygen suppresses the formation of crosslinks. An indication that this might be the case is to be found in the report that air inhibits network formation on exposure of poly(ethylene terephthalate) to 2537 A. light.[4] However, definite conclusions about the role of oxygen in the photolysis of poly(ethylene terephthalate) and concerning the significance of the difference between Φ_F values in air and *in vacuo* must await further studies.

The following mechanism is consistent with the observations outlined at the beginning of this section.

The primary reactions leading to the formation of CO and CO_2 may be as shown in eq. (3):

$$\tag{3}$$
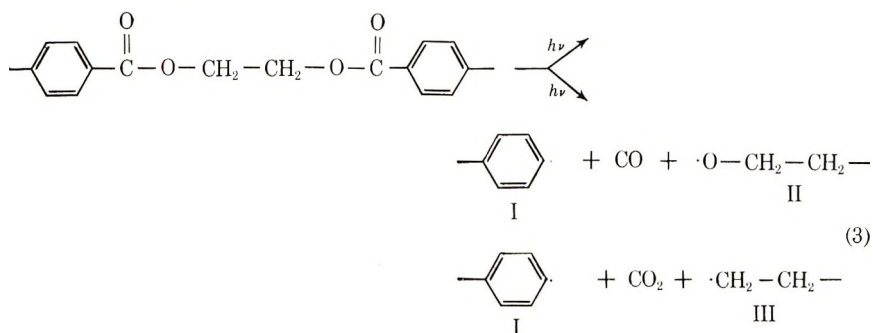
Radicals I, II, and III combine, disproportionate, or abstract hydrogen atoms from neighboring molecules. Combination would result in groups of the type p-O—O—CO—C_6H_4—X— . Disproportionation and hydrogen abstraction would consummate chain fracture. However, it would appear necessary to invoke additional fracture reactions because of the inequality $\Phi_F > \Phi_{CO} + \Phi_{CO_2}$. In the absence of more detailed analytical data it seems unprofitable to speculate on their nature.

An important consequence of hydrogen atom abstraction would be the

formation of free radicals which could account for crosslinking. On the basis of the ESR work we suggest that the crosslinking reaction (4) might be important:

$$2 \quad \longrightarrow \quad \tag{4}$$
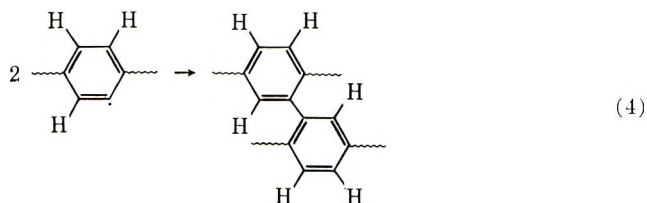
Finally, in a rigid medium such as poly(ethylene terephthalate), with glass transition and melting temperatures of about 80 and 250°C., respectively, it is to be expected that some of the more stable free radicals would be trapped at room temperature. The stability of the radical $p\text{-}C_6H_3\cdot$ has been mentioned previously while the other radical detected by ESR, $\cdot O-CH_2-CH_2-$, is expected to be less reactive than radicals of types I and III.

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Résumé

La photolyse de films de téréphthalate de polyéthylène a été étudiée sous vide à des longuerus d'ondes de 2537 Å et de 3130 Å. Un système filtrant très stable qui isole la ligne 3025 Å a été mis au point en vue d'isoler la raie 3130 Å du spectre de mercure. En dépit du fait que la pénétration de la lumière 2537 Å a été limitée à une profonduer d' environ 1000Å tandis que la ligne 3130 Å était plus uniformément absorbée, il était possible de démontrer que les rendements quantiques pour la formation de CO et CO_2 étaieht en accord avec les deux longeurs d'ondes. Les rendements quantiques pour les cassures et les pontages était estimés par analyses sol-gel; Un maximum d'absorption qui se développe aux environs de 13 μ après exposition du PET à la lumière ou aux rayons-γ a été attribué à la formation de groupes résultant de l'élimination de CO et de CO_2. Les spectres ESR des radicaux trappés ont été attribués à des composants —$\dot{C}_6H_3$— et ·O—CH_2—CH_2—. Les premiers radicaux sont suggérés se combiner entre eux pour former des ponts. Les rendements quantiques ($\times$ 10^4) sont donnés dans le résumé anglais.

Zusammenfassung

Die Photolyse von Polyäthylenterephthalatfilmen im Vakuum mit Licht der Wellenlänge 2537 Å und 3130 Å wurde untersucht. Ein sehr stabiles Filtersystem, das die Linie bei 3025 Å beseitigt, wurde zur Isolierung der Linie bei 3130 Å aus dem Quecksilberspektrum entwickelt. Ungeachtet der Tatsache, dass die Eindringtiefe des 2537 Å-Lichtes auf ca 10^3 Å begrenzt war, während das 3130 Å-Licht einheitlicher absorbiert wurde, war es möglich, zu zeigen, dass die Quantenausbeuten für die CO- und CO_2- Bildung für die beiden Wellenlängen übereinstimmten. Quantenausbeuten für Spaltung und Vernetzung wurden durch Sol-Gelanalyse bestimmt. Ein Absorptionsmaximum, das sich in der Nähe von 13 μ nach der Einwirkung von Licht oder γ-Strahlen auf PET entwickelt, wurde auf die bei der Eliminierung von CO und CO_2 gebildeten Gruppen zurückgeführt. ESR-Spektern eingeschlossener Radikale wurden vorläufig den Komponenten —$\dot{C}_6H_3$— und ·O—CH_2—CH_2— zugeordnet. Es wird angenommen, dass die ersteren Radikale unter Bildungen von Vernetzungen kombinieren. Bezüglich der Quantenausbeuten vgl. die englische Zusammenfassung.

Cyclo- and Cyclized Diene Polymers. XIII. γ-Ray-Initiated Polymerization of 1,3-Dienes

VÁCLAV ŠTĚPÁN, JOSEF VODEHNAL, and IVO KÖSSLER, *Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia*, and NORMAN G. GAYLORD, *Gaylord Associates Inc., Newark, New Jersey*

Synopsis

The γ-ray-initiated polymerization of butadiene, isoprene, and 2,3-dimethylbuta-diene-1,3 was carried out at temperatures of 20°C. and −78°C. Polymers of butadiene and isoprene with mixed linear and cyclic structure were proved to result from the polymerization at −78°C. A monocyclic structure was found for the 2,3-dimethylbuta-diene-1,3 polymers initiated either at −78°C. or in the thiourea canal complex at 20°C.

Introduction

Many investigators have studied the infrared spectra of polybuta-dienes[1-4] and polyisoprenes[5-9] prepared by exposure of the monomers to γ-radiation,[2,3,5-9] x-rays,[4] or electron beam[1] at temperatures of 20,[8] −40,[5] −78,[1,4,6,7] and −196°C.[2,3,7] The low-temperature radiation polymerization of many compounds is known to proceed by an ionic propagation mechanism.[10] Kinetic studies have shown that an ionic mechanism has to be considered in the polymerization of dienes at low temperatures, while at temperatures above 0°C. both radical and ionic mechanisms contribute to the polymerization.[2,5,7] The contribution of both mechanisms at various temperatures and dose rates has also been estimated.[7] The infrared spectrum of the 2,3-dimethylbutadiene-1,3 polymer prepared by irradiation of the thiourea canal complex[11] was found to be similar to the infrared spectrum of polymer prepared by $(i\text{-}C_4H_9)_3Al\text{-}TiCl_4$[12] and by $EtAlCl_2\text{-}TiCl_4$[13] catalyst systems. The objective of this work was to determine whether the polymers of 1,3-dienes initiated by γ-rays have a cyclic structure and to examine the influence of the thiourea canal complex of 2,3-dimethyl-butadiene-1,3 on the resulting polymer structure.

Experimental and Results

Butadiene (BD) was dried by distillation through a column packed with silica gel. The monomer used was 99% pure.

Isoprene (IP) was purified by fractional distillation and dried by refluxing with a sodium suspension.

TABLE I

γ-Ray-Initiated Polymerization of 1,3-Dienes

Diene[a]	20°C.			−78°C. to 0°C.			−78°C.		
	Dose rate, r./hr. × 10^5	Dose, r. × 10^5	Conversion, %	Dose rate, r./hr. × 10^5	Dose, r. × 10^5	Conversion, %	Dose rate, r./hr. × 10^5	Dose, r. × 10^5	Conversion, %
BD	5.6	37.32	6.4	2.55	5.68	1.2	2.42	15.73	4.1
IP	5.6	37.32	6.8	2.55	5.68	1.1	2.42	15.73	3.1
DMB	5.6	65.0	12.5	2.55	5.68	0.35	2.42	15.73	10.4
DMB in thiourea canal complex	3.63	1.0	76.2						

[a] BD = butadiene-1,3; IP = isoprene; DMB = 2-dimethylbutadiene-1,3.

2,3-Dimethylbutadiene-1,3 (DMB) was prepared by dehydration of pinacol according to Allen and Bell.[14] The product was purified by distillation and the purity checked by vapor-phase chromatography.

The pure monomers were outgassed by the freeze-thaw technique and distilled *in vacuo* into ampules (10 ml.), which were then sealed off and exposed to γ-radiation from a ^{60}Co source at temperatures of 20 to −78°C. The conditions of the radiation polymerization are shown in Table I. The products were isolated by evaporation of unreacted monomers. The resulting products of BD and IP were viscous oils in all cases, but powdery polymer of DMB was obtained from the polymerization at −78°C.

The radiation polymerization of DMB in the thiourea canal complex was accomplished according to the method of Brown.[11] DMB (1.20 ml.) was mixed with 1.88 g. finely ground, recrystallized thiourea containing 0.28 ml. of water. The mixture was introduced into the ampule which was then cooled, outgassed, and sealed off. After 8 days aging at 0°C. it was irradiated with a 1-Mrad dose of γ-radiation from the ^{60}Co source. The polymer formed was isolated in 76% yield by dissolving the complexing thiourea in ethyl alcohol and acetone; it was then washed with hot water and acetone and dried *in vacuo* at 45°C. The polymer melted at 235–250°C. and showed x-ray diffraction patterns indicating crystallinity.

The total content of double bonds in the products was determined by the addition of iodine monochloride.[15]

The products were analyzed by the use of infrared spectroscopy (Table II). The listed values can not, however, be considered absolute. The products from butadiene were analyzed by the KBr pellet technique, under the assumption that the methods of spectra evaluation for polymers can be used for this case. The content of *trans*-1,4 structure was determined by the use of band at 970 cm.$^{-1}$, the absorption coefficient of which was determined by the aid of stereoregular *trans*-1,4-polybutadiene. For

TABLE II
Analyses of Polymers

	Butadiene-1,3 (20 to −78°C.)	Isoprene			2,3-Dimethyl-butadiene-1,3	
		20°C.	0 to −78°C.	−78°C.	20°C.	0 to −78°C.
cis-1,4, %	0	17	0	0		
trans-1,4, %	∼50	68	60	58	a	b
1,2, %	∼13	6	6	5		
3,4, %	—	5	6	5		
C=C unsaturation, %	∼65	—	73	69	—	50

a Infrared spectrum similar to that of radical-initiated linear polymer.

b Infrared spectrum similar to that of cyclopolymer.

the 1,2 addition the band at 910 cm.$^{-1}$ and a low molecular weight standard were used. For unknown reasons, unusually high values for the content of the *trans*-1,4 form were obtained when the analysis was made with CS_2 solutions of the polymers, which corresponded neither to the total chemical $C=C$ unsaturation nor to the appearance of the spectrum in the 3000 cm.$^{-1}$ region. The infrared analysis of isoprene products in solution was accomplished by the usual method[16] used for polymers. The results for the products obtained at 0 to $-78°C$. and at $-78°C$. were correlated with the $C=C$ double bond content determined by the iodine chloride method. The infrared spectra of DMB polymers were not evaluated quantitatively.

Discussion

The radiation polymerization of BD and IP was proved to proceed by a cationic mechanism at low temperatures.[2,6,7,9] Since the cationic polymerization of 1,3-dienes was found to result in cyclic structures,[17,18] the same could be expected from γ-ray-initiated polymerizations at low temperatures. A monocyclic structure based on infrared and NMR analyses of polybutadiene initiated by x-rays has been suggested by Webb.[4] Geymer[10] found that a considerable part of the monomer units in the γ-ray-initiated polybutadiene was saturated.

The content of linear and cyclic forms in the polymer chains probably depends on the contribution of radical and cationic mechanisms to the polymerization. The radical mechanism is expected to predominate at higher temperatures, while at the lower temperatures mainly a cationic mechanism is presumed.[2,6,7] The results of experiments in this work were in agreement with the observations of the other authors.

The infrared analysis of the products from butadiene shows them not to be purely linear. The presence of cyclic structures is obvious from comparison of the infrared spectra at 3000 cm.$^{-1}$ of the radiation product and *cis*-1,4-, *trans*-1,4-, and cyclopolybutadiene (Fig. 1). The absorption coefficient of the band at 2920 cm.$^{-1}$ for the KBr pellet technique was found to be 1000 cm.^{2}/g. for *cis*-1,4-, 1200 cm.^{2}/g. for the *trans*-1,4-polybutadiene, and 2600 cm.^{2}/g. for the cyclopolybutadiene. The low value of 1130 cm.^{2}/g. for the radiation products is probably caused by the predominating monocyclic structure of the products. Whether a copolymer of linear with cyclic segments or a mixture of polymers was obtained was not resolved.

In all cases of the BD, IP, and DMB radiation polymerizations a considerable content of 1,2-addition units was found. In the case of BD and IP this was disclosed by the vinyl group band at 910 cm.$^{-1}$, in the DMB polymer by the isopropenyl band at 890 cm.$^{-1}$ This type of addition was very weak in the DMB polymer from polymerization in complex with thiourea.

About 17% *cis*-1,4-form was found in the γ-ray-initiated polyisoprene at 20°C. The content of the *cis* form decreased with a decrease of the polymerization temperature. The decrease of the $C=C$ unsaturation could not be ascribed to either crosslinking of the polymer (the material
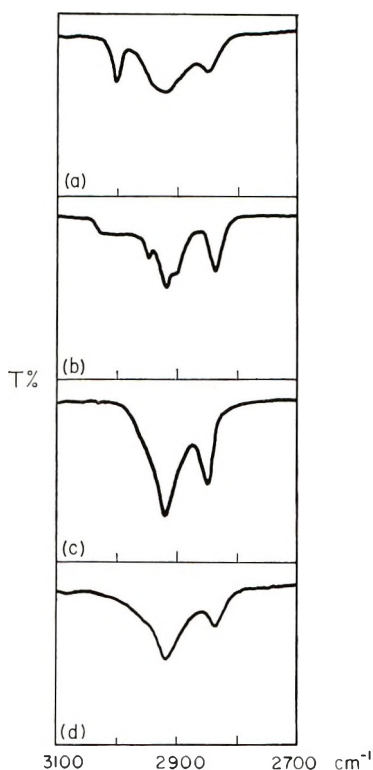
Fig. 1. Infrared spectra of (a) cis-1,4-, (b) trans-1,4-, (c) cyclo- and (d) radiation-initiated polybutadienes in the 3000 cm.$^{-1}$ region.

was easily soluble) or to oxidation, which should be seen in the infrared spectrum. It is caused by the formation of structures which is accompanied by a decrease of the original double-bond content, i.e., cyclic structures.

The DMB polymers obtained at temperatures below 0°C. had infrared spectra similar to those of the polymers prepared with the EtAlBr$_2$–TiCl$_4$ catalyst system.[13] The infrared spectrum of polymer initiated at 20°C. was analogous to the spectrum of the linear DMB polymer prepared by radical initiation at the temperature where the Diels-Alder formation of the DMB dimer was negligible.[13] The C=C unsaturation of the soluble part of the DMB polymer prepared in the temperature range from 0 to −78°C., determined by the addition of iodine chloride, showed the presence of a little more than one double bond in two monomer units, which is compatible with the monocyclic structure proposed for the cationic DMB cyclopolymer.[13] The polymer prepared at −78°C. was insoluble in benzene and carbon tetrachloride and formed gels in these solvents, showing that considerable crosslinking occurred during the polymerization.

The ability to form cyclic structures at −78°C. was found to be very high for DMB but was much lower and approximately the same for both BD and IP, where about 30% cyclic forms was found by the infrared analysis.

The radiation polymerization of DMB in thiourea canal complex, carried out according to Brown,[11] was found to proceed to about 80% conversion. In the bulk polymerizations of DMB where the samples were irradiated with much greater doses, the conversions did not exceed 13%. The lowest conversion for the DMB polymerization was observed in the range between 0 and −78°C., which may be explained if the rates of both radical and ionic polymerizations of DMB in this temperature range are presumed to be rather small. The increase of polymerization rate in the canal complex can be explained by the orientation of the monomer molecules in the complex. As was shown by Brown,[11] the DMB molecule belongs to the so-called "small flat molecules" which were assumed to overlap one another in the thiourea canal complex. The infrared spectrum of the DMB–thiourea canal polymer was similar to the spectrum of polymer prepared with the Ziegler catalyst for which a monocyclic structure was proposed.[13] The term "monocyclic" means a structure similar to that of the "monocyclic" structure of cyclized natural rubber with six-membered isolated (not fused) rings in the main chain:
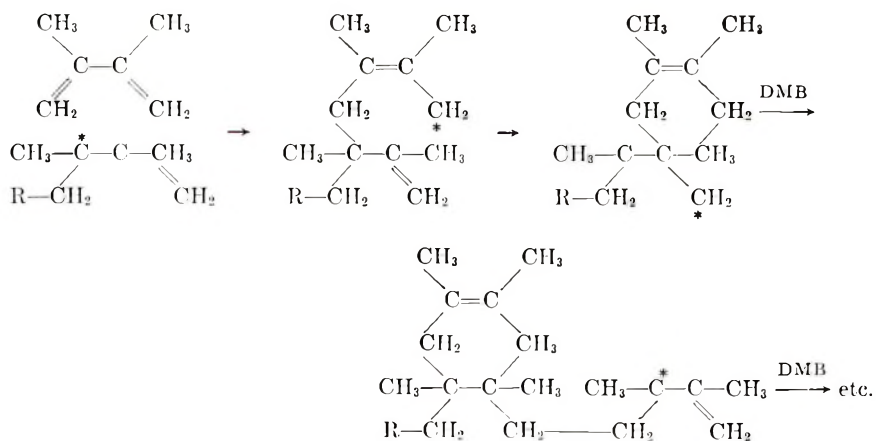
$$
\begin{array}{ccc}
\text{CH}_3 \quad \text{CH}_3 & \text{CH}_3 \quad \text{CH}_3 & \text{CH}_3 \quad \text{CH}_3 \\
\text{C}-\text{C} & \text{C}=\text{C} & \text{C}=\text{C} \\
\text{CH}_2 \quad \text{CH}_2 & \text{CH}_2 \quad \text{CH}_2 & \text{CH}_2 \quad \text{CH}_2 \\
\text{CH}_3-\overset{*}{\text{C}}-\text{C}-\text{CH}_3 & \text{CH}_3-\text{C}-\overset{*}{\text{C}}-\text{CH}_3 & \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\
\text{R}-\text{CH}_2 \quad \text{CH}_2 & \text{R}-\text{CH}_2 \quad \text{CH}_2 & \text{R}-\text{CH}_2 \quad \overset{*}{\text{CH}_2}
\end{array}
\xrightarrow{\text{DMB}}
$$

$$
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{C}=\text{C} \\
\text{CH}_2 \quad \text{CH}_3 \\
\text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \quad \text{CH}_3-\overset{*}{\text{C}}-\text{C}-\text{CH}_3 \xrightarrow{\text{DMB}} \text{etc.} \\
\text{R}-\text{CH}_2 \quad \text{CH}_2 ------ \text{CH}_2 \quad \text{CH}_2
\end{array}
$$

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Résumé

La polymérisation initiée aux rayons-γ du butadiène, de l'isoprène et du 2,3-diméthylbutadiène-1,3 a été effectuée à des températures de 20°C et −78°C. Les polymères de butadiène et d'isoprène avec structure mixte linéaire et cyclique ont été formés au cours de la polymérisation à −78°C. Une structure monocyclique est trouvée pour le 2,3-diméthylbutadiène-1,3 initié soit à −78°C, soit dans des complexes d'inclusion de thiourée à 20°C.

Zusammenfassung

Die γ-Strahlen-induzierte Polymerisation von Butadien, Isopren und 2,3-Dimethylbutadien-1,3 wurde bei Temperaturen von 20°C und −78°C durchgeführt. Bei der Polymerisation bei −78°C entstehen Butadien und Isopren polymere mit gemischter linearer und cyclischer Struktur. Bei den bei −78°C oder in Thioharnstoffeinschlusskomplexen bei 20°C gestarteten 2,3-Dimethylbutadien-1,3-polymeren wurde eine monocyclische Struktur festgestellt.

Mechanism of Stereoregular Polymerization of Butadiene by Homogeneous Ziegler-Natta Catalysts. I.   Effects of the Species of Transition Metals

KEI MATSUZAKI and TAMIO YASUKAWA, *Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo, Japan*

Synopsis

Butadiene was polymerized by catalysts of the type: metal acetylacetonate (metal: Ti to Ni in the periodic table)–triethylaluminum–aluminum halide, with various ratios of triethylaluminum to aluminum halide.   The minimum *cis* content was observed with vanadium catalyst in all cases, while the minimum polymer yields were observed with the iron and the manganese catalysts.   These transition metal effects are discussed in terms of the crystal field theory, and it is suggested that the electrostatic interaction between the nearly nonbonding electrons of transition metal atom and a butadiene molecule or a growing end of the polymeric chain plays an important role in the stereoregular polymerization of butadiene by homogeneous Ziegler-Natta catalysts.

INTRODUCTION

Ziegler-Natta catalysts give stereoregular polymers of many kinds of olefins, diolefins, etc.,[1,2] and some workers proposed reaction mechanisms of heterogeneous Ziegler-Natta catalysts to explain the stereospecific activities.[1]   As for the polymerization of butadiene by homogeneous Ziegler-Natta catalysts, remarkable effects of the species of transition metals and halogens were reported.[2]   However, up to now these effects do not seem to have been discussed sufficiently.   Moreover, the results already published were sometimes contradictory, perhaps due to the differences in experimental conditions to which the specific activities of the catalysts are fairly sensitive.   Therefore, it will be indispensable to compare the effects of transition metals and halogens under the same experimental conditions.

Recently, the ligand field theory has been quite successful in elucidating the properties and reactions of transition metal compounds.[3,4]   In the present work, the effects of transition metals and halogens on the stereoregular polymerization of butadiene will be discussed with the aid of the ligand field theory.

TABLE I
Yield and Microstructure of Polybutadiene
Obtained with $M(acac)_{2,3}$–Et_3Al–AlX_3 Catalyst[a]

Metal	Halogen	Et_3Al/ AlX_3	Microstructure			Yield, %	Property
			cis, %	1,2, %	trans, %		
Ti	Cl	2	52	16	32	80	Rubber
"	"	3	53	13	34	60	"
"	"	4	48	27	25	20	Oil
"	Br	1	64	12	24	50	Paste
"	"	2	59	11	30	50	"
"	"	3	42	27	31	30	"
"	I	1	72	5	23	90	Paste
"	"	2	74	12	14	90	Rubber
"	"	3	73	17	10	40	"
V	Cl	2	21	15	64	30	Plastic
"	"	3	22	18	60	5	"
"	Br	1	22	8	70	90	Plastic
"	"	2	21	13	66	20	"
"	"	3	8	17	75	20	"
"	I	1	16	15	69	80	Plastic
"	"	2	18	13	69	60	Jelly
"	"	3	13	35	52	20	"
"	Et_3Al solely		7	76	17	20	Oil
Cr	Cl	2	40	9	51	20	Paste
"	"	3	39	6	55	10	"
"	"	4	33	7	60	10	"
"	Br	1	44	9	47	50	Paste
"	"	2	38	11	51	50	"
"	I	1	35	19	46	80	Paste
"	"	2	26	18	56	60	"
"	"	3	41	17	42	10	"
"	Et_3Al solely		24	60	16	80	Jelly

(continued)

EXPERIMENTAL

Reagents

Acetylacetonates of the metals of the first transition series (Ti to Ni in the periodic table) were prepared by the usual methods.[5,6]

Butadiene was dried before use by passing through columns of potassium hydroxide and calcium hydride, liquefied by cooling to Dry Ice temperature, and thereafter dissolved in dry benzene.

Triethylaluminum (made by the Ethyl Corp., U.S.A.) was used without further purification.

Aluminum chloride and aluminum bromide were obtained from the Kanto Chemical Corp. (extra pure grade) and were used without further purification.

Aluminum iodide was prepared by the method described in the literature.[7]

TABLE 1 (continued)

Metal	Halo-gen	Et₃Al/AlX₃	Microstructure			Yield, %	Property
			cis, %	1,2, %	trans, %		
Mn[b]	Cl	2	49	20	31	5	Paste
"	Br	2	33	25	42	5	Paste
"	I	2	31	18	51	30	Paste
Fe	Cl	2	51	22	27	5	Paste
"	"	4	32	25	43	10	"
"	Br	1	42	9	49	50	Paste
"	"	2	40	19	41	40	"
"	"	3	21	29	50	20	Oil
"	I	1	33	17	50	50	Paste
"	"	2	32	28	40	30	"
"	"	3	31	28	41	10	"
Co	Cl	2	86	8	6	90	Rubber
"	"	3	84	9	7	70	"
"	"	4	63	27	10	10	Paste
"	Br	1	84	9	7	90	Gel
"	"	2	81	8	11	90	"
"	"	3	82	10	8	20	Plastic
"	I	1	59	29	12	90	Rubber
"	"	2	54	33	13	90	"
"	"	3	41	45	14	70	"
Ni[c]	Cl	2	91	2	7	90	Rubber
"	"	4	92	3	5	70	"
"	Br	1	80	3	17	90	Gel
"	"	2	82	2	6	90	Paste
"	I	1	81	10	9	90	Gel
"	"	2	84	6	10	90	Rubber

[a] Initial concentration of each component: M(acac)₂,₃, $1 \times 10^{-3}M$; total aluminum compounds, $1 \times 10^{-1}M$; butadiene, ca. $2M$.

[b] No polymers were obtained when Et₃Al/AlX₃ was above 3.

[c] No polymers were obtained when Et₃Al/AlBr₃ or AlI₃ was above 3.

Polymerization of Butadiene by Metal Acetylacetonate–Et₃Al–AlX₃.

Preparation of Et₃Al–AlX₃ Solutions.   To known amounts of aluminum halide, AlX₃ (X; Cl, Br or I), were added required amounts of triethylaluminum, Et₃Al ($1M$ benzene solution) to obtain various ratios of Et₃Al–AlX₃, and the resultant mixture solutions were gently warmed in a nitrogen stream.

Polymerization of Butadiene.   Known amounts of metal acetylacetonate, butadiene (ca. $2M$ benzene solution) and a mixture solution of Et₃Al–AlX₃ were introduced into 50-cc. reaction vessels in that order in a dry box flushed with dry nitrogen.

Initial concentrations of each compound were: metal acetylacetonate, $1 \times 10^{-3}M$; total aluminum compounds, $1 \times 10^{-1}M$; butadiene, ca. $2M$.

After 20 hr., the reaction was stopped by pouring the contents of reac-

tion vessels into methanol containing about 5% of hydrochloric acid; the polymers obtained were dried in an evacuated desiccator.

Infrared Analysis. Polymers were dissolved in carbon bisulfide for infrared analysis. The spectra of the samples were found by means of a Nihon-bunko double-beam spectrometer, Model 301, for the sodium chloride region and were analyzed by the method developed by Hampton.[8]

RESULTS

In Table I are shown the yield and microstructure of the polybutadiene obtained by the catalyst; metal acetylacetonate–Et_3Al–AlX_3 catalyst, where the metal may be Ti to Ni in the periodic table, and X may be Cl, Br, or I.

For most catalyst systems, the yields of polymer decreased when the ratio Et_3Al/AlX_3 was above 3.

The effects on the microstructure of the species of transition metals and halogens were prominently observed when the ratio Et_3Al/AlX_3 was 1 or 2, and minima in the *cis* content were observed for the vanadium catalysts with all species of aluminum halides.

Of the species of transition metals, iron and manganese are less effective to give high polymers.

With the titanium catalyst systems, the *cis* content of the polymers increased on the substitution of AlI_3 for $AlBr_3$ and $AlCl_3$, whereas for other transition metals the effects of halogens were in the reversed direction; i.e., the *cis* content increased in the order, iodide, bromide, chloride.

Generally speaking, the results obtained in the present work agree fairly well with those already published by other workers,[1,2] although somewhat different results have also been reported; for example, Natta et al.[9,10] obtained 1,2-polybutadiene by the systems, $Cr(acac)_3$–Et_3Al and $V(acac)_3$–Et_3Al in which the ratios Al/Cr or Al/V were less than in the present work, and Susa[11] obtained 1,2-polybutadiene instead of oligomers with the system $Co(acac)_3/Et_3Al$.[12] Recently, Takeuchi et al.[13] found that fairly large amounts of water (more than 50% relative to Et_3Al) must be added to the Et_3Al–Co compound system in order to produce 1,2-polybutadiene.

It is well known that Ziegler-Natta catalysts are fairly sensitive to experimental conditions, ratios of aluminum compounds to transition metals, and minor amounts of impurities. Hence, we can not attribute a universal validity to the present results concerning the effects of transition metals and halogens. However, since similar effects are observed with most homogeneous Ziegler-Natta catalysts under ordinary polymerization conditions, it would not be irrelevant to discuss these effects on the basis of the present results.

DISCUSSION

Properties of Active Species

Some conflicting explanations have been proposed[1] for the reaction mechanism of Ziegler-Natta catalyst, i.e., some workers considered that the

polymeric chain grows from the organoaluminum compound,[14] whereas other insisted that the catalytic active sites are on the transition metal atoms.[15,16]

As can be seen in Table I, remarkable transition metal effects are observed for butadiene polymerization, suggesting that the transition metals play important roles in the stereoregular polymerization of butadiene. Moreover, many organo-transition metal compounds have recently been synthesized which by themselves have catalytic activity to give oligomers of butadiene.[17,18]

Hence, we can consider that transition metals participate directly in the polymerization of butadiene.

In a previous paper[19] we reported that the acac⁻ ion in the system, Co-(acac)₃/Et₂AlCl, is transferred from the cobalt atom to form Al(acac)₃, while cobalt was supposed to form an organocobalt compound. Acetylacetonates of other transition metal ions (Cr, Mn, Fe, and Ni) also reacted with Et₂AlCl in the same way; i.e., the acac⁻ ion was transferred from transition metal ions.[20] Hence, active species in the present catalyst systems would have a structure similar to $Cp_2TiCl_2 \cdot AlEt_2$ which Natta et al.[21] reported for a homogeneous catalyst.

In reacting with organometallic compounds, most transition metal ions are reduced to nearly zero valence to form organo-transition metal compounds.[22] Although some titanium and vanadium compounds are reduced only partly to form $RTiCl_3$,[23] $RVCl_3$[24] and so on, the bond nature of these product compounds is primarily covalent.[20] Thus, according to the electroneutrality principle,[25] we may consider that net charges of the transition metal atoms are very close to zero. Discussing the mechanism of stereoregular polymerization by Ziegler-Natta catalysts, Furukawa[26] also considered that the transition metal atoms in active species are electrically nearly neutral.

Although the mechanism of stereoregular polymerization is far from settled, many workers postulate that the stereoregularity of polymers is determined by the conformation which the intermediate complex assumes in the transition state of the polymerization reaction.[1]

It would not be impertinent to postulate as follows: (*1*) active species of the present catalyst systems have a bridged complex structure similar to $R_2TiCl_2 \cdot AlEt_2$, and transition metal atoms in these complexes are electrically nearly neutral; (*2*) the transition metals participate directly in the polymerization reaction, and the stereoregularity of polybutadiene is determined by the conformation which a butadiene molecule or a growing end of polymeric chain assumes on coordinating with the catalyst metal atom in the transition state of the polymerization reaction.

Mechanism of Stereoregular Polymerization

As for the mechanism of *cis* polymerization of diolefins, Natta et al.[27] considered that the monomer coordinates with a transition metal atom in the *cis* conformation by the two double bonds, forming a π-complex. On
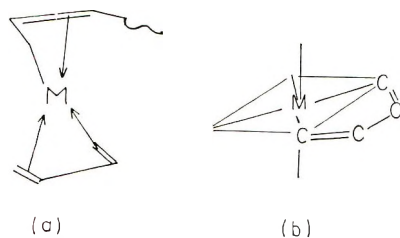
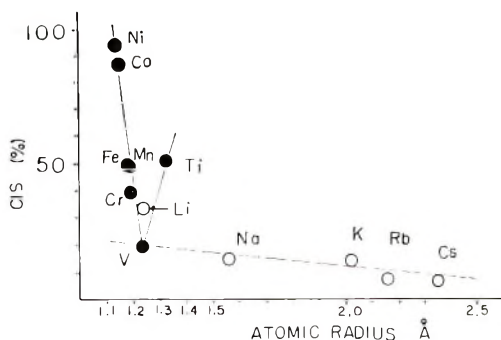Fig. 1. Schematic illustrations of the structure of intermediate complexes: (a) π type; (b) σ type.

Fig. 2. The *cis* contents of polybutadienes plotted against the atomic radii of catalyst metals: (●) M(acac)$_{2,3}$–Et$_3$Al–AlCl$_3$ catalysts, ratio of Et$_3$Al/AlCl$_3$ = 2 (Table I); (O) alkali metal catalysts, data of Binder.[28]

the other hand, Furukawa[26] thought that a butadiene molecule combines with a transition metal atom by σ bonds and that the *cis* content of polybutadiene increases when the atomic radius of the catalyst metal is appropriate for coordinating in the *cis* conformation (Fig. 1). In this respect, cobalt and nickel are more favorable than other metals.

In Figure 2 are plotted the *cis* contents of polybutadiene obtained by the catalysts, M(acac)$_{2,3}$–Et$_3$Al–AlX$_3$ against the atomic radii of the transition metals. The catalysts based on titanium, which has a larger atomic radius than vanadium, gave polymers of fairly high *cis* content in contrast with the polymers obtained by the vanadium catalysts. Figure 2 shows the published values of the *cis* content of polybutadienes obtained by alkali metal catalysts.[28] The influence of atomic radii is not so pronounced for alkali metal catalysts, in contrast with the remarkable variation of the microstructure of polymers obtained by various transition metal catalysts. Thus, we can conclude that steric effects such as the atomic radii of catalyst metals are not the sole factor determining the microstructure of polybutadiene.

Recently, Hoffman et al.[29] noticed that the highest occupied MO (HOMO) of butadiene is 1,4 antibonding while the lowest unoccupied MO (LUMO) is 1,4 bonding. Hence, either the removing electrons from HOMO (cation) or the adding them to LUMO (anion) should increase 1,4

bonding and thus stabilize the *cis* conformation relative to the *trans* conformation.   However, this effect would not be effective in the polymerization reaction since sodium and potassium catalysts which are more ionic than lithium catalyst[30] gave a polybutadiene of low *cis* content (Fig. 2).

Discussing the high *cis* content of polyisoprene obtained by lithium catalyst, Stearn et al.[31] noticed that the Li—C bond has a fairly covalent nature as a result of the large p character of the hybrid.   In the case of butadiene polymerization, too, the large contribution of the sp hybrid would be responsible for the fairly high *cis* content of polybutadiene obtained by lithium catalyst.

For transition metal catalysts, other effects are expected, since transition metals have d electrons, of which the contribution to chemical bonds is in many respects different from that of s and p electrons.   In catalytic reactions, the d electrons of transition metals play an important role. Close correlations were observed between the rate of catalytic reactions, such as hydrogenation, isotope exchange and decomposition, and the d character of catalyst metals and alloys.[32a,33]

According to the crystal field theory, the stabilization energy due to the electrostatic interaction between a transition metal ion and coordinated molecules shows a minimum for the d^5 ion as well as for the d^0 and d^{10} ions.[3,4]

Moreover, these ions have spherical electron distributions, and therefore the interaction of coordinated molecules with these ions would in many respects differ from the interaction with unsymmetrical ions.   Thus, in complexes in which the coordination bonds can well be discussed in terms of the crystal field theory, the spatial distribution of electrons of transition metal atoms would have a prominent effect on the properties of the coordinated molecules.   For example, Kern[34] observed that the frequency shift of the infrared bands of tetrahydrofuran on coordination with various metal ions of the first transition series showed a minimum for the Mn^{2+} ion, which has the d^5 structure.

Similar effects were also observed with some other ligands.[35]

In the present catalyst systems, according to the postulate that the transition metals are nearly neutral, vanadium has a spherical electron distribution.   Therefore, the butadiene molecules coordinating with a vanadium atom would retain the properties of the free state (where butadiene assumes the *trans* conformation) much more than those in other catalyst systems. It is noteworthy that sodium and potassium which also have nearly spherical electron distributions give a polybutadiene having the same order of *cis* content as the vanadium catalyst (Fig. 2).

On the other hand, for $Ni^0(d^{10})$ the contribution of the electronic structure $3d^9 4s$ would become prominent as in nickel metal, where the electronic structure is represented as $3d^{9.4} 4s^{0.6}$.[32b]   Consequently, the electron distribution in the nickel atom in the present catalyst system would be considerably deformed from spherical symmetry, resulting in a polybutadiene of high *cis* content.
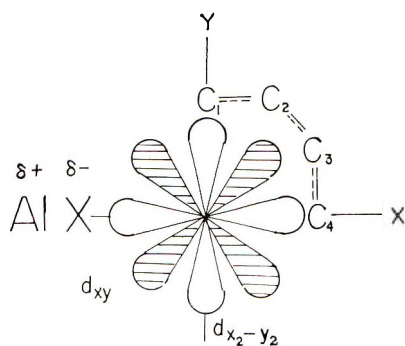
Fig. 3. Schematic illustration of the spatial distribution of d electrons in an intermediate complex.

For Fe^0 (d^8) and Mn^0 (d^7), the crystal field stabilization energies are so large that stable intermediates similar to $Bd \cdot Fe(CO)_3$[36] and $Bd \cdot Fe(CO)_4$[37] (where Bd denotes butadiene) would be formed, interrupting the catalytic activity. In fact, polymer yields with these catalysts were much lower than those with other metal catalysts (Table I).

We shall discuss further why the ions of unsymmetrical electron distribution are favorable for a butadiene molecule to coordinate in the *cis* conformation. Figure 3 shows a schematic illustration of the spatial distribution of d electrons in the intermediate complex (where σ-type bonds are supposed to be formed between the transition metal atom and the coordinated butadiene molecule). According to the crystal field theory, the energy level of the d_{xy} orbital is lower than that of the $d_{x^2-y^2}$ orbital and, consequently, the electron density is higher in the former orbital than in the latter one in most complexes other than those of the d^0, d^5, and d^{10} ions.[3,4]

For a free butadiene molecule, Parr and Mulliken[38] showed by the SCF LCAO calculation that the electronic energy is lower for the *cis* conformation than for the *trans* conformation by 0.85 e.v., whereas the electrostatic repulsion between two terminal carbon atoms is larger for the former than for the latter by 0.97 e.v.; consequently the *trans* conformation is more stable by ca. 0.1 e.v. On the other hand, for a butadiene molecule coordinated with an unsymmetrical ion, the repulsion between two terminal carbon atoms, C_1 and C_4 in Figure 3, would be reduced by the screening effect of the d_{xy} electrons which are interposed between them.

More general treatment of intermediate complexes of various forms (tetrahedral, π type, etc.) by the molecular orbital theory suggests that the nearly nonbonding electrons would exert screening effects similar to that of the d_{xy} electrons in the complex shown in Figure 3 to stabilize the *cis* conformation.

We may well conclude that, for the butadiene molecule coordinating with transition metal atoms other than V^0, the probability of assuming the *cis* conformation is increased by electrostatic interaction with $3d$ electrons, especially with nonbonding electrons.

CONCLUSION

The stereoregularity of polymers obtained by homogeneous Ziegler-Natta catalysts is determined principally by the interaction of catalyst metal atoms with monomers or the growing end of polymers chains, and the specificity of these interactions is closely related to the electronic structure of the metal atoms.

The interactions between catalyst metal atoms and monomers or growing ends of polymeric chains is not so strong, and the nature of the interactions is in accord with the crystal field theory.

It is interesting that a simple model based on the crystal field theory can, though only qualitatively, elucidate the effects of the species of transition metals on the stereoregular polymerization of butadiene by homogeneous Ziegler-Natta catalysts.

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Résumé

Le butadiène a été polymérisé avec les catalyseurs suivants: l'acétylacétonate métallique (métal: Ti jusque Ni dans le tableau périodique) triéthylaluminium, halogénure d'aluminium, dans différents rapports de triéthylaluminium à halogénure d'aluminium. La teneur minimum en structures cis a été observée avec un catalyseur vanadium dans tous les cas, tandis que le rendement minimum en polymère était observé avec des catalyseurs à base de fer et de manganèse. Les effets des métaux de transition ont été discutés sur la base de la théorie du champ cristallin et on en suggéré que l'interaction e'lectrostatique entre les électrons non-liés de l'atome métallique de transition et la molécule de butadiène ou l'extrémité croissante d'une chaîne polymérique joue un rôle important dans la polymérisation stéréorégulière du butadiène par des catalyseurs homogènes Ziegler-Natta.

Zusammenfassung

Butadien wurde mit folgenden Katalysatoren polymerisiert: Metallacetylacetonat (Metall: Ti bis Ni im periodischen System)/Triäthylaluminium/Aluminiumhalogenid, mit verschiedenem Triäthylaluminium-Aluminiumhalogenid-Verhältnis. Der geringste cis Gehalt wurde in allen Fällen mit Vanadinkatalysatoren gefunden, während die niedrigsten Polymerausbeuten mit Eisen und Mangankatalysatoren auftraten. Die Übergangsmetalleffekte wurden im Rahmen der Kristallfeldtheorie diskutiert und es wurde angedeutet, dass die elektrostatische Wechselwirkung zwischen den fast nicht-bindenden Elektronen des Übergangsmetallatoms und einem Butadienmolekül oder einem wachsenden Ende einer Polymerkette eine wichtige Rolle bei der stereospezifischen Polymerisation von Butadien mit homogenen Ziegler-Natta-Katalysatoren spielt.

Mechanism of Stereoregular Polymerization of Butadiene by Homogeneous Ziegler-Natta Catalysts. II. Effects of the Nature of Bases and Halogens

KEI MATSUZAKI and TAMIO YASUKAWA, *Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo, Japan*

Synopsis

The effects of the addition of various bases to metal acetylacetonate-diethylaluminum chloride catalyst systems were investigated. Generally speaking, the *cis* content of polybutadiene decreases as the basicity of bases in a homologous series increases. The effects were more prominent for the cobalt and the titanium catalysts than for the nickel and the vanadium catalysts. The effects of the species of halogens on the microstructure of polybutadiene were also discussed. In conclusion, the decrease of the *cis* content was ascribed to the decrease of the electron density of $d\pi$ orbitals of the transition metal atoms.

INTRODUCTION

It is well known that the stereospecific activities of Ziegler-Natta catalysts are affected not only by the species of transition metals but also by many other factors. For example, Cooper et al.[1] observed that the addition of bases to mixture of $RAlX_2/TiCl_3$ leads to high stereospecific catalysts for the polymerization of α-olefins and that both stereospecific and activity are influenced by the nature of the bases and halogens.

The effects of the addition of various bases to the $CoCl_2$–Et_2AlCl[2] and $TiCl_4$–Et_3Al[3] catalyst systems for butadiene polymerization were also reported. However, the nature of the active species in these systems has not been discussed sufficiently.

In Part I of the present paper,[4] we discussed the correlation between the stereospecific activities of homogeneous Ziegler-Natta catalysts and the electronic structure of the transition metals. In this paper we shall discuss the effects of the bases and halogens in terms of the electronic structure of the active species.

EXPERIMENTAL

Bases were dried with potassium hydroxide or calcium hydride before use. Known amounts of metal acetylacetonate (where the metal was Ti, V, Co, or Ni), base (1M benzene solution), butadiene (ca. 2M benzene solution), and diethylaluminum chloride were introduced, in that order,

into reaction vessels in an atmosphere of dry nitrogen. The initial concentration of each component was: metal acetylacetonate, $1 \times 10^{-3}M$ or $5 \times 10^{-3}M$; Et_2AlCl, $5 \times 10^{-2}M$; base, various amounts.

After 20 hr., reactions were stopped and the polymers obtained were analyzed by the infrared method. Details of experimental conditions were much the same as described in Part I.[4]

RESULTS

The microstructure of polybutadiene was affected not only by the addition of bases to the catalysts systems but also by the nature of the chelating reagents of the transition metal compounds.[5,6] For the present catalyst systems, the $acac^-$ ion is transferred from transition metal ions to form $Al(acac)_3$.[7] Hence, the effects of $Al(acac)_3$ were investigated. Figure 1 shows the decrease of the *cis* content on addition of increasing amounts of $Al(acac)_3$ to the $Co(acac)_3$–Et_2AlCl system.

Figure 2 shows the decrease of the *cis* content with the addition of increasing amounts of pyridine to the systems, $M(acac)_{2,3}$–Et_2AlCl. The effects on the microstructure of the addition of pyridine were not so marked for the vanadium and the nickel catalysts as for the cobalt and the titanium catalysts. Polymer yields decreased when the ratio of pyridine to Et_2-AlCl was above 0.4, and no polymers were obtained when the ratio was above 1.

The effects on the microstructure of the addition of various bases to the $Co(acac)_3$–Et_2AlCl system are shown in Table I for a Al/Co ratio of 50.

In Tables II and III are shown the effects on the microstructure of the addition of various bases to the titanium and the nickel catalysts for Al/Ti or Al/Ni ratios of 10.

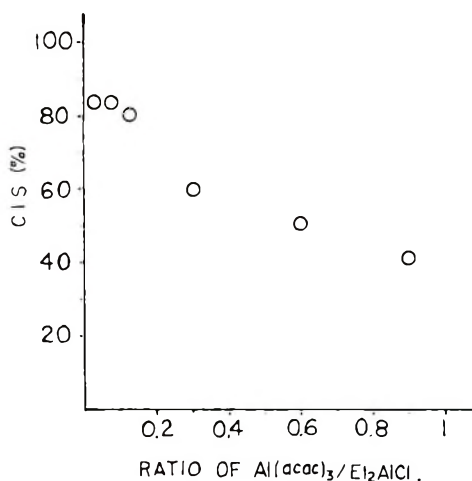Fig. 1. Decrease of the *cis* content on addition of various amounts of $Al(acac)_3$ to the $Co(acac)_3$–Et_2AlCl catalyst. Initial concentration: $Co(acac)_3$, $1 \times 10^{-3}M$; Et_2AlCl, $5 \times 10^{-2}M$.
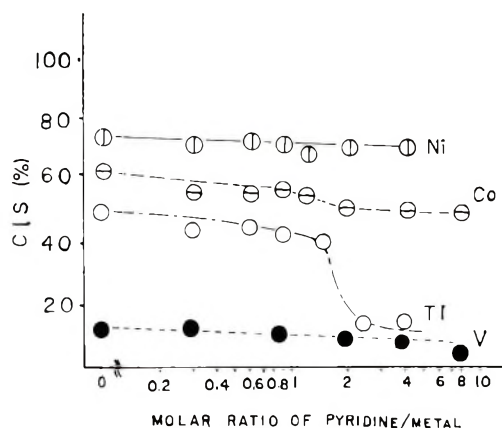
Fig. 2. Decrease of the *cis* content on addition of various amounts of pyridine to the $M(acac)_{2,3}$–Et_2AlCl catalyst, (where M is Ti, V, Co, or Ni). Initial concentration: M-$(acac)_{2,3}, 5 \times 10^{-3}M$; $Et_2AlCl, 5 \times 10^{-2}M$.

The microstructure and polymer yields are also dependent on the ratio of Et_2AlCl to $M(acac)_{2,3}$ and the effects of bases were more pronounced when the Al/Ti or Al/Ni ratio was 50, but the polymer yields were generally low.

TABLE I

Effects of the Addition of Various Bases to the $Co(acac)_3$–Et_2AlCl Catalyst[a]

| Base[b] | pK_a | Microstructure | | | Yield, % |
		cis, %	1,2, %	*trans*, %	
None	—	84	10	6	90
THF	<1	81	13	6	70
Thiophene	<1	74	21	5	90
TPA	<1	84	11	5	90
DMA	5.1	77	15	8	80
DEA	6.6	64	28	8	60
TEA	10.7	54	32	14	60
NMP	10.8	53	42	5	40
Quinoline	4.8	72	19	9	50
Pyridine	5.2	64	28	8	50
MQ	5.4	73	18	9	60
MP	5.9	57	31	12	70
DMP	6.8	52	32	16	50
TMP	9.6	59	29	13	40
BP	4.1	48	39	13	40
TPP	2.7	28	61	11	60

[a] Initial concentration of each component: $Co(acac)_3, 1 \times 10^{-3}M$; $Et_2AlCl, 5 \times 10^{-2}$ M; base, $2 \times 10^{-2}M$.

[b] THF, tetrahydrofuran; TPA, triphenylamine; DMA, dimethylaniline; DEA, diethylaniline; TEA, triethylamine; NMP, N-methylpiperidine; MQ, 2-methyl-quinoline; MP, 2-methylpyridine; DMP, 2,4-dimethylpyridine; TMP, 2,4,6-trimethyl-pyridine; BP, bipyridine; TPP, triphenylphosphine.

TABLE II

Effects of the Addition of Various Bases to the Ti(acac)₃–Et₂AlCl Catalyst[a]

| Base[b] | pK_a | Microstructure | | | Yield, % |
		cis, %	1,2, %	trans, %	
None	—	50	12	38	80
Thiophene	<1	48	3	49	90
DMA	5.1	40	12	48	80
TEA	10.7	17	34	49	60
NMP	10.8	17	18	65	20
Pyridine	5.2	15	23	62	40
MP	6.0	16	28	56	60
DMP	6.7	16	26	58	60
TMP	9.6	13	25	62	90

[a] Initial concentration of each component: Ti(acac)₃, $5 \times 10^{-3}M$; Et₂AlCl, $5 \times 10^{-2}M$; base, $2 \times 10^{-2}M$.

[b] See footnote b of Table I for abbreviations.

TABLE III

Effects of the Addition of Various Bases to the Ni(acac)₂–Et₂AlCl Catalyst[a]

| Base[b] | pK_a | Microstructure | | | Yield, % |
		cis, %	1,2, %	trans, %	
None	—	75	3	22	90
THF	<1	76	3	21	80
Thiophene	<1	73	2	25	90
DMA	5.1	72	2	26	80
TEA	10.7	73	2	25	80
NMP	10.8	76	3	21	90
Pyridine	5.2	71	4	25	90
MP	6.0	62	4	34	70
DMP	6.7	75	4	21	70
TMP	9.6	72	2	26	90
Bipyridine	4.1	67	2	31	90
TPP	2.7	49	11	40	90

[a] Initial concentration of each component: Ni(acac)₂, $5 \times 10^{-3}M$; Et₂AlCl, $5 \times 10^{-2}M$; base, $2 \times 10^{-2}M$.

[b] See footnote b of Table I for abbreviations.

The effects of various bases were quite marked for the titanium catalyst, and the *cis* content was reduced to less than 20% on addition of most bases. On the contrary, the effects of bases were not so pronounced for the nickel catalyst, and the decrease of the *cis* content was notable only with bipyridine and triphenylphosphine. It is interesting that, on addition of bases to the nickel catalyst, the *trans* content increased when the *cis* content decreased, whereas for the titanium and the cobalt catalysts an increase in the 1,2 content was observed. On the other hand, Cooper

et al.[2] obtained a bright blue complex on addition of $Et_2AlCl \cdot NEt_3$ to Co-Cl_2 and found that this complex produces high-*trans* 1,4-polybutadiene.

The effects of bases were ambiguous for the vanadium catalyst, i.e., the *cis* content was less than 10% and the ratio of the *trans* content to the 1,2 content was nearly invariable (ca. 5–6) for all the polymers obtained by vanadium catalysts containing various bases.

It is noteworthy that the effects of the species of halogens on the microstructure of polybutadiene obtained by the catalysts, $M(acac)_{2,3}-Et_3Al-AlX_3$, were also ambiguous for the nickel and the vanadium catalysts.[4]

The reproducibilities of polymer yields with other transition metal catalysts (Cr, Mn, and Fe) were not good, and therefore these results will not be cited here.

DISCUSSION

Effects of the Addition of Bases

The effects of the addition of bases to Ziegler-Natta catalysts are complicated, since bases form stable coordination compounds with organoaluminum compounds[8] and may reduce the concentration of effective organoaluminum compounds. In order to avoid this complication, Boor[9] investigated the effects of the addition of bases to the system, $Et_2Zn-Al_x-Ti_yCl_z$, and concluded that the bases coordinate with the exposed titanium sites.

For the present catalyst systems, we can consider that the bases coordinate directly with the transition metal atoms since many organo-transition metal compounds have been synthesized in which bases such as triphenylphosphine,[10] bipyridine,[11] and tetrahydrofuran[12] coordinate directly with transition metal atoms.

When bases coordinate with transition metal ions, the bases donate electrons to hybrid σ orbitals of the metal ions and, at the same time, some parts of the resultant large negative charges on metal atoms are back-donated to the antibonding orbitals of bases in order to keep the metal atoms nearly neutral.[13] Hence, the $d\pi$ electron density of the metals is expected to be much more reduced as a result of back-donation as the basicity of the coordinated bases becomes larger. In fact, Collins and Petit[14] found that this is the case with some organoiron compounds.

In Part I[4] we suggested that the nearly nonbonding $(d\pi)$ electrons play an important role in stabilizing the *cis* conformation of the butadiene coordinated to transition metal atoms. If this postulation is correct, the *cis* content of polybutadiene would decrease when some bases coordinate with the transition metal atom in active species and the effects would become more pronounced as the basicities increase.

As can be seen in Tables I and II, the effects of the addition of bases are marked with the cobalt and the titanium catalysts. Figure 3 shows the *cis* content of polybutadiene obtained by the $Co(acac)_3-Et_2AlCl-base$ system against the pK_a value of the added bases. The decrease of the *cis*

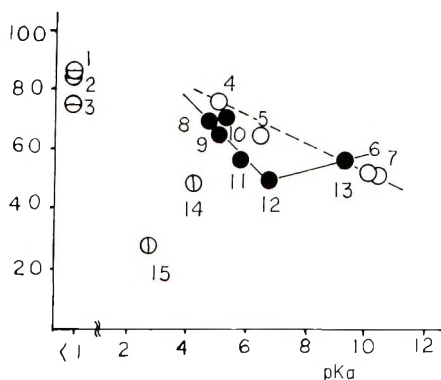Fig. 3. Plot of the *cis* content of polybutadiene obtained with the Co(acac)$_3$–Et$_2$AlCl–base catalyst system against the pK_a value of the base for (●) pyridine derivatives and (○) tertiary amines: (*1*) TPA; (*2*) THF; (*3*) thiophene; (*4*) DMA; (*5*) DEA; (*6*) TEA; (*7*) NMP; (*8*) quinoline; (*9*) pyridine; (*10*) MQ; (*11*) MP; (*12*) DMP; (*13*) TMP; (*14*) BP; (*15*) TPP.
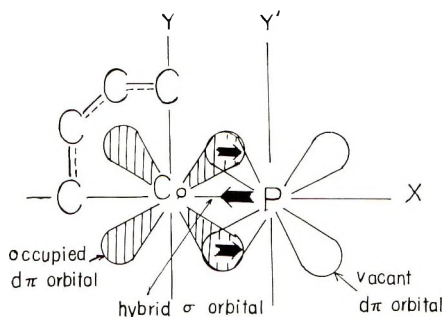

Fig. 4. Schematic illustration of the electron donor–acceptor interaction between a cobalt atom and a phosphine derivative.

content by the addition of pyridine derivatives as well as by the addition of tertiary amines became more marked as the basicities increased, with the exception of 2,4,6-trimethylpyridine, for which steric hindrance of two *o*-methyl groups is so large that the electron donor–acceptor interaction between the base and cobalt atom would be attenuated. The decrease of the *cis* content by the bases of similar basicities became more pronounced in the order: tertiary amines, pyridines, bipyridine, and triphenylphosphine. It is noteworthy that the energy level of the lowest unoccupied orbital becomes lower, and therefore the electron affinity increases in the order: tertiary amines, pyridines, and bipyridine.[15] Hence, the back-donation of $d\pi$ electrons of cobalt atom to the base would be facilitated and result in lower electron density of $d\pi$ orbitals in this order. Triphenylphosphine would be much more effective as a $d\pi$ electron acceptor than other bases, since the phosphorus atom has vacant d orbitals (Fig. 4). Studying the frequency shift of infrared absorption bands, Horrocks and Taylor[16] concluded that $d\pi$ electron-acceptor ability increases in the order ·

aliphatic amines, *o*-phenanthroline, triphenylphosphine, supporting our postulation.

An alternative explanation of the effects of bases would be that the co-ordinated bases interrupt the coordination of butadiene as a bidentate ligand by virtue of their steric hindrance. However, as for tertiary amines, the molecular dimension increases in the order, triethylamine, diethyl-aniline, triphenylamine, while the effects increase in the reversed order. Thus, we can conclude that the electron donor–acceptor interaction be-tween bases and metal atoms is responsible for the modification of specific activity of the present catalysts.

As can be seen in Table II, the decrease of the *cis* content and the increase of the 1,2 content were also observed for the titanium catalysts, and the effect was more drastic than for the cobalt catalyst.

On the contrary, the effects of bases were ambiguous, and an increase in *trans* content rather than in 1,2 content was observed for the vanadium and the nickel catalysts.

Effects of the Species of Halogen

As noted in Part I,[4] the microstructure of polybutadiene was also affected by the species of halogens in catalyst systems. Figure 5 shows the *cis* content of polybutadienes obtained by the $M(acac)_{2,3}$–Et_3Al–AlX_3 catalyst plotted against the electron affinity of halogens.

The *cis* content decreased when $AlCl_3$ was replaced by $AlBr_3$ or AlI_3 for most metals other than titanium.

In contrast to bases, halogen atoms withdraw the electrons of hybrid σ orbitals of transition metal atoms. Hence, the electron density of $d\pi$ or-bitals would increase by the back-donation from halogens and the increase of $d\pi$ electron density of the transition metal atom would become more pro-nounced as the electron affinity of halogen increases.
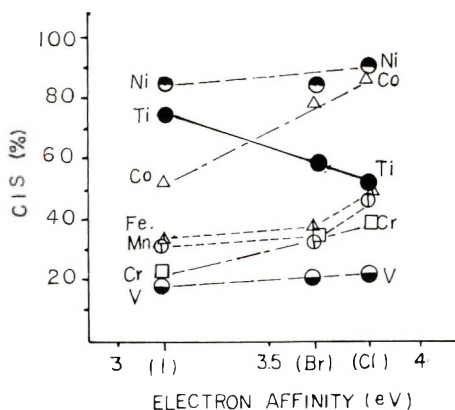

Fig. 5. Plot of the *cis* content of polybutadiene obtained with the $M(acac)_{2,3}$–Et_3-Al–AlX_3 catalyst against the electron affinities of halogens (from Table I of Part I;[4] the Et_3Al/AlX_3 ratio is 2).

Thus, we can ascribe the relatively high *cis* content of polybutadiene obtained with the catalysts based on $AlCl_3$ to the high electron density of $d\pi$ orbitals of transition metal atoms in these systems relative to that in the systems based on $AlBr_3$ or AlI_3.

On the other hand, for the titanium catalysts the effect of halogens is in the reversed order; namely, the *cis* content increased when AlI_3 was used instead of $AlBr_3$ or $AlCl_3$, although the *cis* content decreased on addition of bases in the same way as other metal catalysts. Beachell et al.[17] observed a similar reversed order of the apparent electron-withdrawing power of halogens in the study of the proton NMR spectra of derivatives of dichlorobiscyclopentadienyltitanium and ascribed it to the difference in the order of contribution of electron-releasing resonance of halogens.

The effects of the species of halogens were ambiguous for the nickel and the vanadium as in the cases of the addition of bases. The electronic structure of these atoms might be less affected by the coordination of bases or halogens than those of other metal atoms.

CONCLUSION

The results presented in this paper support the postulation that the electrostatic interaction between the nearly nonbonding electrons of transition metal atoms and a butadiene molecule or a growing end of polymeric chain plays an important role in the stereoregular polymerization of butadiene by homogeneous Ziegler-Natta catalysts.[4]

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Résumé

Les effets de l'addition de différentes bases au catalyseur, acétylacétonate métallique et chlorure de diéthylaluminium, ont été étudiés.   De façon générale la teneur en structure *cis* du polybutadiène décroît lorsque la basicité des bases d'une série homologue croît.   Les effets étaient plus importants pour le catalyseur à base de cobalt et de titane que pour le catalyseur à base de nickel et de vanadium.   Les effets de la nature des halogènes sur la microstructure du polybutadiène ont également été discutés.   En conclusion, la diminution de la teneur en structure *cis* est attribuée à la diminution de densité électronique des orbitales $d\pi$ des atomes métalliques de transiton.

Zusammenfassung

Der Einfluss des Zusatzes verschiedener Basen zum Katalysator, Metallacetylacetonat/Diäthylaluminiumchlorid, wurde untersucht.   Im grossen und ganzen nimmt der *cis*-Gehalt von Polybutadien mit steigender Baizität von Basen in homologen Reihen ab.   Der Effekt war bei Kobalt-und Titanakatalysatoren stärker ausgeprägt als bie Nickel- und Vanadinkatalysatoren.   Weiters wurden der Einfluss der Art des Halogens auf die Mikrostruktur von Polybutadien diskutiert.   Schliesslich wurde die Abnahme des *cis*-Gehaltes der Abnahme der Elektronendichte der $d\pi$-Orbitale der Übergangsmetallatome zugeschrieben.

High-Pressure Reactions.   II.   γ-Ray Polymerization of Acrylamide

M. PRINCE and J. HORNYAK, *Research Division, School of Engineering and Science, New York University, University Heights, New York, New York 10468*

Synopsis

The post-irradiation effect of high pressure on the γ-ray-initiated solid-state polymerization of acrylamide has been described. Polymer conversion was found to increase significantly with applied pressure. The molecular weight of polymer increases with pressure.

INTRODUCTION

A number of workers have reported that a variety of monomers can be polymerized in the solid state by exposure to γ-radiation.[1–11]   This monomer was chosen for study because it is typical of a class of vinyl monomers which exhibited solid-state polymerization.   There are only a few studies on the effect of pressure on reactions in the solid phase.   The vinyl polymerization studied is a true solid-phase reaction whose rate is essentially diffusion-controlled.   γ-Radiation was chosen as the initiator since it has no steric requirement and hence is independent of pressure.

The reaction was studied at γ-ray intensities of 0.224 and 0.482 Mrep./hr.   Irradiated acrylamide was pressurized to 500,000 psi.   Data were obtained which showed that the effects of pressure were (1) to increase polymer conversion and (2) to increase the molecular weight of the polymer formed.

EXPERIMENTAL

Acrylamide

The acrylamide used was the highest purity grade obtainable from the Fisher Scientific Company.   It was recrystallized twice from acetone and then vacuum-sublimed.   The melting point was 84°C.

Preparation and Irradiation of Samples

Precompressed pellets of acrylamide weighing approximately 0.5 g. were placed into Pyrex tubes, evacuated to 10^{-4} to 10^{-4} mm. Hg, and then sealed. Irradiations were performed at the Brookhaven National Laboratory,

Upton, Long Island. The irradiations were performed in a water-filled radiation pool in which various ^{60}Co sources were arranged to provide a range of γ-intensities.[12] Radiation dose rates were determined by using the ferrous sulfate method described by Weiss.[13] Irradiations were performed at 25°C.

Since the irradiation of the acrylamide monomer was carried out at the Brookhaven National Laboratory, considerable time elapsed before the irradiated samples could be pressurized. Fadner and Morawetz[11] reported no significant changes occurring at −78°C. in irradiated acrylamide samples. They also claim that the polymerization reaction is effectively quenched when polymerizing samples are cooled to low temperatures. Therefore all samples were immediately stored at −78°C. after irradiation and until pressurization.

Pressurization

Pressurization of the irradiated acrylamide pellets was accomplished with a belt-type die. This equipment has been described previously.[14]

Polymer Analysis

Samples were extracted immediately after pressurization with methanol, a solvent for monomer only.[10] Drying the residue *in vacuo* to constant weight gave the weight of polymer formed. This was used to confirm the titrametric analysis.

The extent of polymerization was determined by a bromine titration in methanol of the unreacted monomer.[15] Results in methanol were found to be satisfactory.

The aqueous solution of the extracted polymer was used to determine molecular weight. Viscosities of the polymer solutions were measured at 30 ± 0.05°C. in an Ubbelohde viscosimeter. Molecular weights were calculated from the intrinsic viscosity by the relationship.[16]

$$[\eta] = 4.07 \times 10^{-6} M^{1.07}$$

RESULTS AND DISCUSSION

Pressure Effects on Molecular Weight

The molecular weight of polyacrylamide obtained by solid-state polymerization increases with radiation dosage at any given dose rate. Time of irradiation was in most cases longer than the standard 60-min. post-irradiation pressurization. Table I contains the data for the molecular weight determinations. It is noted that the molecular weight of polymer formed in pressurized samples is significantly greater than in unpressurized polymerizations, when exposed to the same irradiation conditions.

The molecular weight of the polymer formed at the end of the irradiation period, measured at conversions less than 15%, is practically independent of the dose rate. Similar results were observed by Ballantine for the solid-state polymerization of acrylamide.[17]

TABLE I
Molecular Weight Data

Dose rate, rep./hr. $\times 10^{-5}$	Irradiation dose, rep. $\times 10^{-6}$	Molecular weight		
			Post-irradiation	
		End of irradiation	Not pressurized	Pressurized[a]
2.24	0.6	145,000	153,000	354,000
2.24	0.8	148,000	159,000	364,000
2.24	1.0	211,000	224,000	395,000
2.24	1.2	240,000	260,000	400,000
2.24	1.4	274,000	296,000	529,000
4.82	0.2	155,000	163,000	197,000
4.82	0.4	160,000	195,000	300,000
4.82	0.6	171,000	214,000	361,000
4.82	0.8	170,000	225,000	388,000
4.82	1.2	263,000	357,000	446,000

[a] Pressurized to 5×10^5 psi.

Application of high pressure to irradiated acrylamide has resulted in significantly higher molecular weights than with nonpressurized samples.

Nicholson and Norrish[18] studied the effect of pressure on the radical polymerization of styrene. They found that an increase in pressure and a decrease in catalyst concentration led to an increase in the average degree of polymerization. The average lifetime of growing radicals increased with increasing pressure. An investigation by Russian workers[19] on the radical polymerization of methyl methacrylate gave similar results. The polymerization will occur in the presence of hydroquinone, which is normally an inhibitor.

Wall[20] and others have studied γ-radiation-induced polymerization under pressures to 20,000 atm. and temperatures up to 250°C. These studies were conducted on perfluoroheptene, perfluorovinyl ether, carbon disulfide, and carbon dioxide. In this work, high pressures favored the production of high molecular weights.

The effects of high pressure on the molecular weight of polymers produced by solid-state polymerization were also observed in a study of the polymerization of trioxane. In a cooperative experiment with the authors, Ballantine[21] studied the effect of high pressure on the viscosity of polyoxymethylene produced by γ-ray polymerization. Samples of trioxane were pressurized at 46–55°C. at 500,000 psi prior to irradiation. Viscosity measurements of the prepressurized samples indicated considerably higher intrinsic viscosity as compared to unpressurized samples.

Pressure Effects on Polymer Conversion

A study was made of the effect of high pressure on the conversion of acrylamide to polymer initiated by high-energy ionizing radiation from a

[60]Co source. Immediately upon removal from a −78°C. storage bath, samples were compressed at 500,000 psi for 1 hr. Samples were then analyzed for polymer conversion as described above by a bromine titration.

Experimental results for acrylamide polymerizations initiated at 25°C. *in vacuo* are presented in Table II. In all of the cases, a greater degree of

TABLE II
Effects of Pressure on Polymer Conversion

Dose rate, rep./hr. $\times 10^{-5}$	Irradiation dose, rep. $\times 10^{-6}$ [a]	Conversion during irradiation, %[b]	Post-irradiation conversion, %[b]	
			Not pressurized	Pressurized[c]
2.24	0.1	1.1	0	2.8
2.24	0.2	3.1	0.7	1.0
2.24	0.4	6.8	1.8	5.5
2.24	0.6	10.2	3.0	9.3
2.24	0.8	13.6	1.7	5.4
2.24	1.0	16.2	2.8	9.4
2.24	1.2	21.4	9.0	12.6
2.24	1.4	27.7	8.6	18.4
4.82	0.1	1.8	1.2	3.9
4.82	0.2	3.3	1.6	7.5
4.82	0.4	6.9	2.0	5.8
4.82	0.6	11.4	2.7	3.6
4.82	0.8	13.8	1.6	5.5
4.82	1.0	18.7	3.4	8.6
4.82	1.2	22.1	6.2	11.1

[a] Irradiation performed *in vacuo* at 25°C.

[b] Determined by titration of available double bond.

[c] Pressurized to 5×10^5 psi.

conversion to polymer was found in samples of acrylamide which had been pressurized to 500,000 psi. Similar results were reported for the high-energy electron initiated polymerization of acrylamide.[14] In all cases, a significant increase in polymer conversion was found for pressurized samples.

Conversion to polymer under these experimental conditions appears to be independent of radiation dose rate but dependent upon the total dosage. This is true for both pressurized and unpressurized samples in the range of intensities of 0.224–0.482 Mrep./hr. Methacrylamide is reported to have constant conversion to polymer over a similar range of dose rates but at higher total dose.[15] Similar results have been obtained for the solid-state polymerization of acrylamide by exposure to γ-radiation.[10]

Conant and his collaborators[22,23] found that the rates of polymerization of a number of olefins and aldehydes were greatly increased by high pressures. He concluded that pressure helps the reactions because it aligns the monomer molecules in a way which favors the chain propagation step.

It has been shown that in the photosensitized polymerization of styrene, the initiation and termination steps are retarded by pressure, whereas the propagation step is accelerated in an exponential manner.[18]

It is well known that polymers of many substituted ethylenes can exist in stereoregular forms in which the configurations of successive asymmetric carbon atoms are either all identical (isotactic polymer) or alternate in some regular sequence (e.g., syndiotactic polymer). If ΔV^* differs for the various modes of chain growth, pressure will effect the type of stereoregularity exhibited by the polymer. A study of poly(methyl methacrylates) produced between 1 and 7500 atm. shows the effect to exist and the ratio of the propagation constants k_{iso}/k_{syn} to increase from 0.33 to 0.54 in this pressure range.[24] Isotactic growth requires a helical conformation of the radical and a strictly oriented approach by the monomer molecule. The larger (negative) ΔV^* for isotactic propagation is therefore probably associated with a greater decrease in entropy in the transition state.

There is also a very considerable effect of pressure on the structure of polyethylene. Ordinary high-pressure ethylene possesses a lower density and crystallinity compared to the low-pressure (Ziegler) polymer. This has been attributed to short "pendant" side chains.[25] At 7,000 atm. and 50–60°C., the side chains do not form, and the polymer has the high density and crystallinity characteristic of the low-pressure product.[26]

The effect of pressure on the conformation of polymers may be caused by the shift in conformational equilibrium towards the most compact conformation or by the different rates of chain propagation in the various reactive conformations. At sufficiently high pressures, both effects probably play an important role. No evidence for such stereoregulation was found in this study of high pressure polymerization of acrylamide. An x-ray examination of a number of samples did not reveal any crystallinity. The examples of stereoregulation induced by high pressure were not solid-state polymerizations. However, it should be pointed out that some polymers will not crystallize even when they can be proven to be stereoregular.[27]

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Résumé

L'effet d'une pression élvée sur la polymérisation à l'état solide initié par irradiation γ de l'acrylamide à été étudié. La conversion en polymères croissait appréciablement avec la pression appliquée. Le poids moléculaire du polymère croissait également avec la pression.

Zusammenfassung

Der Hochdruck-Nacheffekt bei der γ-Strahl-initiierten Polymerisation von Acrylamid in fester Phase wurde beschrieben. Der Polymerumsatz nahm mit dem angewandten Druck wesentlich zu. Das Molekulargewicht des Polymeren steigt mit dem Druck an.

Synthesis and Evaluation of a Series of Regular Polyampholytes*

C. H. H. NEUFELD† and C. S. MARVEL, *Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

Synopsis

A series of three true polyampholytes with unequivocally alternating acidic and basic groups attached directly to the skeletal backbone of the polymer chain have been prepared. This was accomplished by copolymerizing 3,6-diallyl-2-piperidone with the α,ω-dithiols containing 2-, 4-, and 6-methylene groups. The polymerization was carried out in an emulsion system initiated by 2,2'-azobisisobutyronitrile (AIBN), yielding soluble piperidone-containing polymers with molecular weights in the 20,000–30,000 range. The piperidone rings in the polymers were hydrolyzed by dilute sulfuric acid to yield the desired polyampholytes. Fibers were prepared by wet-spinning formic acid solutions of the polyampholyte into saturated salt solution or by melt-spinning. These fibers were quite elastic. We were unsuccessful in demonstrating that mechanical energy could be attained by the effect of pH on the fibers. Similarly, no pH effect could be elicited in Instron tests. The stress-relaxation curve showed a marked positive force–temperature effect characteristic of rubberlike materials with few crosslinks. In a check of transition temperatures, it was noted that on repeated runs the second-order transition temperature rose markedly, suggesting an irreversible change. Viscometric studies clearly demonstrated polyelectrolyte behavior. X-ray diffraction studies of the polyampholytes showed that maximum crystallinity and orientation occurred in the polymer containing as part of the repeating unit the 1,4-butane dithiol moiety.
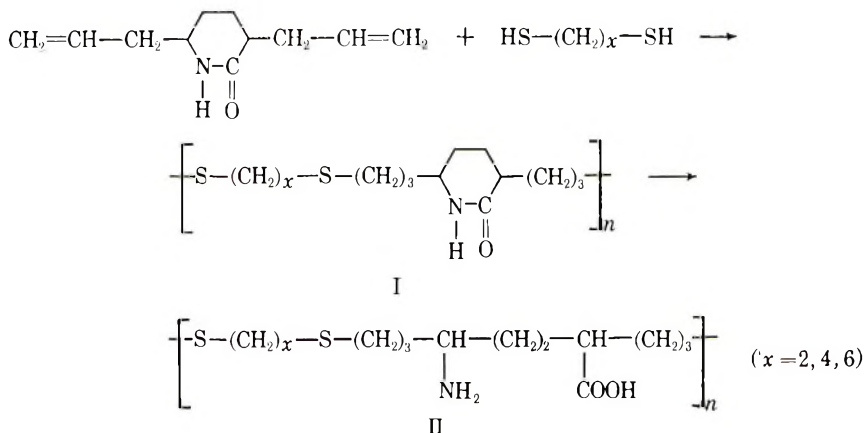
INTRODUCTION

Generally a true polyampholyte differs from a conventional polymer or polyelectrolyte molecule in that it contains both acidic and basic functions alternating regularly along the polymer chain. Naturally occurring polyelectrolytes may be typified by the protein family, high molecular weight compounds comprising sequences of some twenty amino acids. At least two factors militate against use of this class of compound for precise physical and chemical determinations. Protein preparations are usually quite inhomogeneous, and considerable effort must be devoted to structural analysis of the material before any theoretical treatment can be attached to the experimental observations.

Synthetic polyampholytes, on the other hand, can be "tailor-made" to overcome these factors. Several preparative methods have been investigated: vinyl polymerization or condensation polymerization of one monomer containing both the acidic and basic moieties, vinyl copolymerization or condensation copolymerization of two monomers each containing one of the functional groups, and chemical modification of preformed polymers. The syntheses of a number of more or less regular polyampholytes have been reported in recent years, although in some there was insufficient material available at the time to enable a complete physical characterization of the polymer.[1-4]

We have prepared a series of three true polyampholytes with unequivocally alternating acidic and basic groups attached directly to the skeletal backbone of the polymer, and have spun these into fibers as described below. One of the members of the series was prepared earlier[3] but the method chosen for its synthesis yielded a low molecular weight polymer that did not have solubility properties to make it suitable for a study of the polyampholyte properties. Our syntheses were accomplished by copolymerizing 3,6-diallyl-2-piperidone with α,ω-dithiols, followed by acid hydrolysis of the 2-piperidone ring present in the repeating unit of the polymer.

$$CH_2=CH-CH_2-\overset{}{\underset{\underset{H\ \ O}{|\ \ \|}}{\langle\ N-C\ \rangle}}-CH_2-CH=CH_2 \quad + \quad HS-(CH_2)_x-SH \quad \longrightarrow$$

$$\left[S-(CH_2)_x-S-(CH_2)_3-\overset{}{\underset{\underset{H\ \ O}{|\ \ \|}}{\langle\ N-C\ \rangle}}-(CH_2)_3 \right]_n \quad \longrightarrow$$

I

$$\left[-S-(CH_2)_x-S-(CH_2)_3-\underset{\underset{NH_2}{|}}{CH}-(CH_2)_2-\underset{\underset{COOH}{|}}{CH}-(CH_2)_3 \right]_n \quad (x=2,4,6)$$

II

EXPERIMENTAL

Preparation of 3,6-Diallyl-2-Piperidone

This monomer was prepared by a six-step synthesis from 2-carbethoxycyclopentanone combining reaction steps described by Marvel and co-workers Moyer,[3] DeTommaso,[4] and Allison.[5] Commercially available 2-carbethoxycyclopentanone was reacted with sodium shot in dry xylene, followed by allyl bromide, to produce 2-allyl-2-carbethoxycyclopentanone. This was converted to diethyl 2,5-diallyladipate by sodium ethoxide and allyl bromide. One ester group was hydrolyzed off by using potassium hydroxide in ethanol. The acid group was then converted to the acid chloride using purified thionyl chloride and pyridine. The ethyl 2,5-

diallyladipoyl chloride was subjected to the Curtius reaction yielding 4-carbethoxy-7-aminocarbethoxy-1,9-decadiene. Treatment of this compound with sodium hydride and xylene yielded 3,6-diallyl-2-piperidone. The overall yield for this series of reactions was 34.4%.

α,ω-Dithiols

1,2,-Ethanedithiol, 1,4-butanedithiol, and 1,6-hexanedithiol were purchased commercially, but were redistilled prior to use.

Preparation of Piperidone-Containing Polymers (I)

Equimolar amounts of 3,6-diallyl-2-piperidone and the dithiol, 5% siponate DS-10 emulsifier, 2% 2,2'-azobisisobutyronitrile (AIBN) initiator, and deaerated distilled water (40 ml./g. of the diallylpiperidone) were placed in a pressure bottle, flushed with nitrogen, and capped. The container was tumbled end-over-end in a 60°C. water bath for 18 hr. The product was cooled and poured into two volumes of cold methanol. The polymers were recovered by filtration and dried under vacuum. Approximately 90% conversions were realized. The products were recrystallized from chloroform–methanol. Infrared spectra (Nujol) for these bands assignable to a δ-lactam (3140 cm.$^{-1}$), to a carbonyl (1670–1680 cm.$^{-1}$), and to a secondary amide (1300 cm.$^{-1}$).

ANAL. Calcd. for I where $x = 2$ $(C_{13}H_{23}NOS_2)_n$: C, 57.11%; H, 8.48%; N, 5.12%; S, 23.44%. Found: C, 56.84%; H, 8.62%; N, 4.88%; S, 23.67%.
Calcd. for I where $x = 4$ $(C_{15}H_{27}NOS_2)_n$: C, 59.73%; H, 9.03%; N, 4.65%; S, 21.27%. Found: C, 59.18%; H, 9.03%; N, 4.54%; S, 21.49%.
Calcd. for I where $x = 6$ $(C_{17}H_{31}NOS_2)_n$: C, 61.95%; H, 9.48%; N, 4.25%; S, 19.46%. Found: C, 61.38%; H, 9.46%; N, 4.47%; S, 19.58%.

The viscosities of these piperidone-containing polymers (I) were measured in formic acid by means of a Cannon-Fenske viscometer at 30°C. Typical values were for $x = 2$: $\eta_{inh} = 0.23$ ($c = 0.413$ g./100 ml.); for $x = 4$: $\eta_{inh} = 0.18$ ($c = 0.528$ g./100 ml.); for $x = 6$: $\eta_{inh} = 0.32$ ($c = 0.493$ g./100 ml.).

Preparation of Polypampholyte (II)

This method of hydrolysis was suggested by the work of Eck and Marvel.[6] Polymer I was placed in a round-bottomed flask with 10% sulfuric acid (150 ml./g. of polymer), and refluxed for 1 hr. with efficient stirring. The reaction mixture was cooled, then neutralized with sodium hydroxide. It was stirred with periodic additions of a few drops of sodium hydroxide until the pH remained steady at 7. The polymer was allowed to settle and the supernatant was poured off. The product was washed thoroughly with water. It was dried under vacuum, ground up, and again washed with water and dried under vacuum. Quantitative yields were obtained. The polyampholyte was rubbery, and it was found to be very difficult to grind it into a mull with Nujol. We were finally successful when the product, and the mortar and pestle containing Nujol were cooled down to about

−80°C. in a Dry Ice–acetone bath prior to grinding the product. The infrared spectrum contained bands assignable to free acid (3580, 2700, 1700 cm.$^{-1}$), free amine N-H (3420, 3160 cm.$^{-1}$), and carbonyl (1640 cm.$^{-1}$).

ANAL. Calcd. for II where $x = 2$ ($C_{13}H_{25}NO_2S_2$)$_n$: C, 53.57%; H, 8.65%; N, 4.80%; S, 22.00%. Found: C, 53.10%; H, 8.32%; N, 4.46%; S, 22.21%.

Calcd. for II where $x = 4$ ($C_{15}H_{29}NO_2S_2$)$_n$: C, 56.38%; H, 9.15%; N, 4.38%; S, 20.07%. Found: C, 56.14%; H, 8.95%; N, 4.22%; S, 20.67% (residue* 1.91%).

Calcd. for II where $x = 6$ ($C_{17}H_{33}NO_2S_2$)$_n$: C, 58.75%; H, 9.57%; N, 4.03%; S, 18.45%. Found: C, 58.62%; H, 9.29%; N, 4.06%; S, 18.55% (residue 1.35%).

The viscosities of these polyampholytes (II) were measured in formic acid by means of a Cannon-Fenske viscometer at 30°C. Typical values were for $x = 2$: $\eta_{inh} = 0.27$ ($c = 0.520$ g./100 ml.); for $x = 4$: $\eta_{inh} = 0.34$ ($c = 0.430$ g./100 ml.); for $x = 6$: $\eta_{inh} = 0.32$ ($c = 0.360$ g./100 ml.).

Preparation of Fibers

Wet Spinning. The polyampholyte was dissolved in hot formic acid to yield a 20–30% solution. The solution was injected by means of a 2-ml. hypodermic syringe into a large pan of saturated salt solution while the syringe was moved through the bath. It was found that precipitation of the polymer in the form of a fiber was facilitated by holding the initial exudate of the syringe with forceps. The fibers were dried on glass frames, then washed with water.

Melt Spinning. The polyampholyte was placed in a Petri dish and warmed slowly to about 150°C. The hot polymer was touched with a spatula to which it adhered, and the spatula drawn away from the dish with a steady motion. Fibers 4–6 ft. long were obtained by this method.

RESULTS AND DISCUSSION

Viscometric Studies

Viscosities of the polyampholytes were studied as a function of pH and concentration. This was accomplished by dissolving the polyampholyte in dry dimethylformamide (DMF), determining the precise concentration of polyampholyte in 9.5 ml. of DMF–polyampholyte solution, and then determining the viscosity of 9.5 ml. of this solution, plus 0.5 ml. DMF (neutral) or 0.5 ml. DMF saturated with hydrogen chloride gas (acidic). The results are shown in Figure 1. It is noted that at low concentrations, the polyampholytes are more viscous in acid solution than in neutral solution. This behavior is expected for polyelectrolytes; at higher concentrations coulombic interaction occurs between molecules, whereas at lower concentrations this occurs within the same molecule. In the presence of acid, the amine becomes an acid salt and repels the carboxyl, causing extension of the chain, as evidenced by higher viscosity.

*Residue was sodium sulfate resulting from neutralization of sulfuric acid used in preparing polyampholyte with sodium hydroxide.
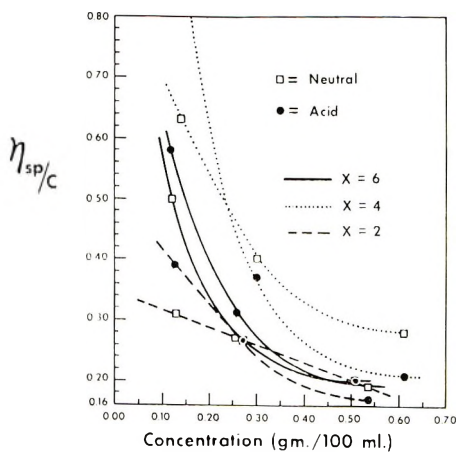
Figure 1.

Polyampholyte Properties of Fibers

Experiments were designed to demonstrate that mechanical work could be done by polyampholyte fibers. A single fiber or in some instances a bundle of fibers, $1\frac{1}{2}$ in. long, with a weight attached, was hung in a graduated column. Hydrogen chloride gas was passed upward through the column over the fiber. There was no measurable stretching or contracting of the fiber. The column was flushed out with air. Then ammonia gas was passed over the fiber. Again no change in length was noted. In other studies the fiber was hung for periods of 5 min. to 1 hr. in dilute neutral, acidic, and basic solutions. Again there was no noticeable stretching or contracting.

Stress-Relaxation Studies

Fibers made from the polyampholyte (II) in which $x = 6$ were subjected to stress-relaxation tests with an Instron universal tensile tester. The fibers were quite irregular, and naturally the thinner sections responded to loading more than the thicker sections, so conversion into stress units is not very meaningful. However, it does appear that the fibers are rather weak but quite elastic. Their stress-relaxation curves were not unlike those of a low crosslinked rubber. Some short stress-relaxation tests indicated very little crosslinking, but at the same time cycling experiments showed quite good recovery from relatively high extensions. The curves suggest that possibly some orientation occurred leaving the fiber set in a new form (cold-drawing effect).

When stretched fibers were stress-relaxed and the pH of the bath changed, no effect was evident. When the temperature was changed, a marked positive temperature effect (i.e., higher temperature, higher force) was evident. This behavior is characteristic of rubberlike materials.

Thermal Properties of Fibers

Thermal properties were measured with the use of a Perkin-Elmer DSC-1 scanning calorimeter. The specific heat, measured on a large sample (8.8 mg.) at a heating rate of 10°C./min., showed an endothermic peak centering around 64°C.; this endotherm was not reproduced on a repeat run on the same sample. Earlier measurements on a smaller sample (1 mg.) appeared to indicate a change in slope at 0°C., as well as a non-reproducible peak at 40°C. These results may indicate, when examined along with the mechanical property studies, that there is a transition region at around room temperature. The nature of this transition is uncertain, but it may represent a strain-induced ordering effect which melts out irreversibly. No unequivocal glass transition was observed. At much higher temperatures an exothermic reaction was observed at 177°C. and rapid decomposition began at 296°C.

X-Ray Diffraction Studies

X-ray photographs were taken of the polyampholytes in both bulk and fiber form. The d spacings of the polyampholytes (II) in bulk form were: $x = 2:17.56, 4.51$; $x = 4:18.03, 4.59$; and $x = 6:20.23, 4.49$. When melt-spun fibers were photographed in the relaxed state, no orientation was noted. In these studies fibers from the polyampholyte with $x = 2$ were not very crystalline. For polymer with $x = 6$, fibers were quite crystalline and there appeared to be the beginning of orientation. The maximum crystallinity and orientation was demonstrated in the fiber from the polyampholyte in which $x = 4$. It is recognized, of course, that both crystallinity and orientation can be changed by physically manipulating the sample. Stretching the high polymer usually results in increasing both the crystallinity and orientation of the molecules. Results may have been more favorable in the case of the polyampholyte with $x = 4$ when these fibers were elongated.

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Résumé

Une série de trois polyampholytes véritables avec une structure alternant avec des groupes acides et basiques attachés directement au squelette de la chaîne principale polymérique a été préparée. Ceci était obtenu par copolymérisation de la 3,6-diallyl-

2-pipéridone avec les α,ω-dithiols contenant 2, 4 et 6 groupes méthyléniques. La polymérisation était obtenue en émulsion, initiée par le 2,2'-azobisisobutyronitrile (AIBN), fournissant des polymères solubles, contenant des groupes de pipéridone, avec un poids moléculaire allant de 20.000 à 30.000. Les cycles de la pipéridone contenus dans ces polymères ont été hydrolysés par l'acide sulfurique dilué pour former les polyampholytes souhaités. Des fibres ont été préparées par filage humide des solutions dans l'acide formique de ces polyampholytes dans une solution saturée de sel ou aussi par filage à l'état fondu. Ces fibres étaient nettement élastiques. Nous n'avons pas pu montrer qu'une énergie mécanique pouvait être obtenue par l'action du pH sur ces fibres. De façon semblable aucun effet du pH n'a pu être mis en évidence par les essais à l'Itron. La courbe tension-relaxation montrait un effet nettement positif de la force en fonction de la température caractéristique de matériaux caoutchouteux, contenant peu de ponts. En ce qui concerne les température de transition, on a noté que par des essais répétés la température de transition vitreuse croissait notablement, ce qui suggère un processus irréversible. Les études viscosimétriques démontraient clairement la nature polyélectrolytique. Les études de diffraction aux rayons-X des polyampholytes montraient que la cristallinité maximum et l'orientation se présentaient dans le polymère contenant des unités dithiol-1,4-butaniques comme unités périodiques.

Zusammenfassung

Eine Reihe von drei wahren Polyampholyten mit eindeutig alternierenden sauren und basischen Gruppen direkt am Skelett der Polymerkette wurde durch Copolymerisation von 3,6-Diallyl-2-piperidon mit α,ω-Dithiolen mit 2, 4 und 6 Methylengruppen dargestellt. Die Polymerisation wurde in Emulsion bei Start durch 2,2'-Azobisisobutyronitril (AIBN) ausgeführt und lieferte lösliche piperidon-hältige Polymere mit Molekulargewichten im Bereich von 20000 bis 30000. Die Piperidonringe in den Polymeren wurden mit verdünnter Schwefelsäure zu den gewünschten Polyampholyten hydrolysiert. Fasern wurden durch Nassspinnen von Ameisensäurelösungen des Polyampholyten in gesättigte Salzlösung oder durch Schmelzspinnen hergestellt. Die Fasern waren recht elastisch. Es gelang nicht, zu zeigen dass durch den pH-Einfluss auf die Fasern mechanische Energie entwickelt werden könnte. Auch bei Instron-Tests konnete kein pH-Effekt gefunden werden. Die Spannungs-relaxationskurve zeigte einen deutlichen, für kautschukartige Stoffe charakteristischen positiven Kraft-Temperatur-Effekt. Bei einer Untersuchung der Umwandlungstemperaturen wurde festgestellt, dass bei wiederholter Bestimmung die Umwandlungstemperatur zweiter Ordnung merklich anstieg und eine irreversible Veränderung erkennen liess. Viskositätsmessungen zeigten ein eindeutiges Polyelektrolytverhaltern. Durch Röntgenbeugungsuntersuchungen an den Polyampholyten wurde nachgewiesen, dass das Maximum an Kristallinität und Orientierung beim Polymeren mit der 1,4-Butandithioleinheit als Teil des Kettenbausteins auftrat.

Polymers With Quinoxaline Units.   II.

FRANS DE SCHRYVER and C. S. MARVEL,
*Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

Synopsis

A double chain or ladder polymer was obtained by the condensation of 1,2,4,5-tetra-aminobenzene with 2,3,7,8-tetrasubstituted-1,4,6,9-tetraazaanthracene and self-condensation of 2,3-dihydroxy-6,7-diaminoquinoxaline and of 2,3-diphenoxy-6,7-diaminoquinoxaline. The polycondensations were carried out in solution or in melt. The polymers thus obtained were highly colored products which had inherent viscosities up to 2.5. The structures of the polymers were established by comparison with model compounds.

INTRODUCTION

Recent advances in thermostable polymers have shown that single-strand aromatic heterocyclic polymers have good thermal stability. It had been pointed out that a two-strand or ladder polymer seemed to offer further improvement in thermal properties.[1,2] However, most of the previously reported ladder structures were obtained by a chemical reaction on a preformed polymer[3–6] and as a result were not always completely ring-closed.

It was thought that a double chain polymer with a general formula (I) could be obtained by condensation of tetrafunctional benzene, quinoxaline, and tetraazaanthracene derivatives.


I
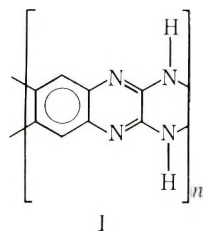
The quinoxaline unit and the tetraazaanthracene unit were chosen because of their unusually good thermal stability.[7,8]

DISCUSSION

Polymer Synthesis and Properties

The belief that polymers with recurring unit I could be obtained was based on the model reaction of an *o*-diamine with 2,3-dihydroxy,[9] 2,3-dichloro-,[10] or 2,3-diphenoxyquinoxaline.[7]

1,2,4,5-Tetraaminobenzene hydrochloride (III) and 2,3,7,8-tetrahydroxy-1,4,6,9-tetraazaanthracene (IIa) were polymerized in polyphosphoric acid. The 2,3,7,8-tetrachloro-(IIb) and the 2,3,7,8-tetraphenoxy derivatives were polymerized with 1,2,4,5-tetraaminobenzene hydrochloride under the same reaction conditions.

II   III

IIa: X = OH
IIb: X = Cl
IIc: X = OPh
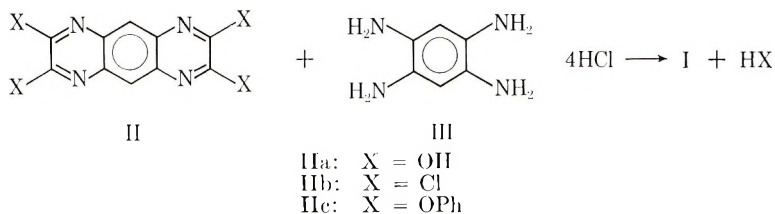
The resulting polymers were black shiny solids which did not melt below 350°C. and had inherent viscosities of 0.5–1 in acidic solvents. The ultraviolet data are reported with the respective viscosities in Table I.

Condensation of 2,3,6,7-tetrasubstituted quinoxalines resulted in a polymer with the same recurring unit but with higher molecular weight.

2,3-Dihydroxy-6,7-diaminoquinoxaline hydrochloride (IV) was polymerized in polyphosphoric acid PPA prepared from phosphorus pentoxide and ion-free water. Use of commercially available polyphosphoric acid
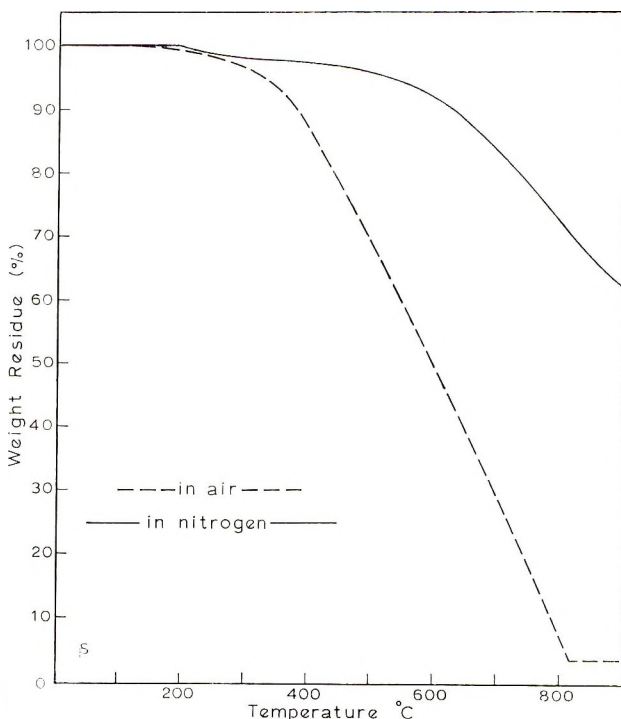

Fig. 1. Thermogravimetric analysis of I, η_{inh} = 2.5 (0.5% in methanesulfonic acid): (- - -) in air; (——) in nitrogen.

TABLE I
Data on Preparation, Inherent Viscosity, and Ultraviolet
Absorption of Poly(tetraazaanthracene)

Starting materials	Experi- mental conditions	Reaction tem- perature, °C.	η_{inb}[a]	λ_{max}, mμ[b]
IIa + III	PPA	250	0.8–1	275; 309
IIb + III	PPA	250	0.4–0.6	277; 311
IIc + III	PPA	250	0.5–0.6	
IV	PPA	250	0.8–2.5	272; 306
V	Melt	200	0.2–0.3	
		350	0.9–1	274; 309

[a] Viscosities were taken in methanesulfonic acid (0.5% solution at 30°C.).
[b] Ultraviolet data were taken in sulfuric acid.

resulted in products contaminated with metal impurities because of the chelating properties of the polymer. It was found that for the same initial concentrations, the molecular weight increased with the reaction time up to 24 hr. The inherent viscosity after 3 hr. (0.9) increased to 1.8 after 10 hr. and finally became 2.5 after 20 hr. of reaction at 250°C.
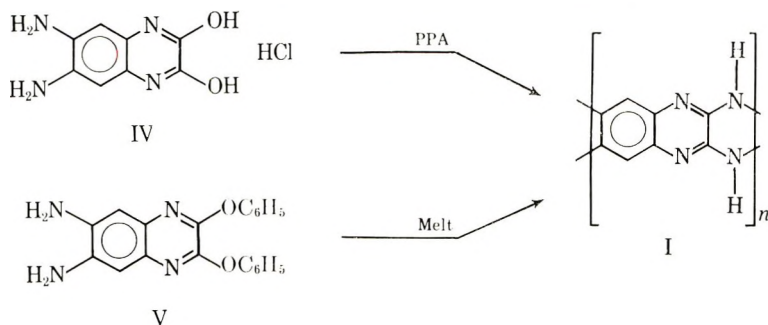

The thermogravimetric analysis (Fig. 1) showed initial weight loss in oxygen around 350°C. We believe this is due to the particular structure of this ladder, as discussed later, and not due to incomplete ring closure because the prolonged heating of the polymer in acid or base did not result in a change in viscosity.

2,3-Diphenoxy-6,7-diaminoquinoxaline (V) was condensed in melt. The prepolymer, obtained after first heating at 250°C., is soluble in dimethyl-formamide, hexamethylphosphoramide, and formic acid. The inherent viscosity of the prepolymer in methanesulfonic acid was 0.2–0.3. After the second heating cycle at 350°C., the resulting highly colored polymer was no longer soluble in the above-mentioned aprotic solvents and only 80% soluble in methanesulfonic acid. The soluble part had an inherent viscosity of 0.9–1. The ultraviolet and viscosity data of the polymers obtained from IV and V are tabulated in Table I. Ladder formation was probably incomplete.

Attempts to polymerize 2,3-diphenoxy-6,7-diaminoquinoxaline or the free 2,3-dihydroxy-6,7-diaminoquinoxaline in solution in hexamethylphosphoramide or in dimethylacetamide in a temperature range between 20 and 120°C. resulted in products with inherent viscosities below 0.1.

Polymer Structure

A study[9] on the position of the hydrogens in dihydroquinoxalino-(2,3b)-quinoxaline (VI) showed that this compound did not exist in ethanol
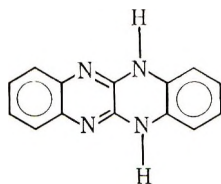
VI

solution in the p-quinoid form but that the hydrogens were found in the 5,12 position. The repeating unit (I) of the ladder structure could be compared with 5,12-dihydroquinoxalino(2,3b)quinoxaline. Due to the limited solubility, comparison was made in sulfuric acid (Table II). It was

TABLE II
Ultraviolet Data of Model Compounds[a]

Compound	λ_{max}, mμ
5,12-Diphydroquinoxalino(2,3b)quinoxaline[b]	252; 280; 290
5-Methylindolo(2,3b)quinoxaline[c]	276; 286
5,12-Dihydroquinoxalino(2,3b)phenazine[b]	270; 312.4
5,11-Dimethylquinoxalino(2,3b)quinoxaline[c]	258; 317; 325
Poly[5,12-dihydroquinoxalino(2,3b)phenazine][b]	275.4; 304.1; 334.1
Poly[5,12-dihydro-4,5,11,12-tetraazaanthracene][b]	272; 306

[a] All spectra are taken in 1-cm. cells at molar concentrations between 1.7 and 3.5 $\times$ 10^{-4}M.

[b] Measured in sulfuric acid.

[c] Measured in 95% ethanol.

found that the absorption spectrum of 5,12-dihydroquinoxalino(2,3b)quinoxaline showed a second maximum at 210 mμ compared with its ultraviolet spectrum in ethanol. This could be attributed to the ionic form VII. This was confirmed by the ultraviolet spectra of 5-methylindolo(2,3b)quinoxaline[11] (VIII), 5,11-dimethylquinoxalino(2,3b)quinoxaline (IX), 5,12-
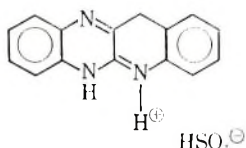
VII

dihydroquinoxalino(2,3b)phenazine,[12] and poly-[5,12-dihydroquinoxalino-(2,3b)phenazine].[13] The ultraviolet data are tabulated in Table II. The data indicate that in sulfuric acid, some percentage of the quinoid form is present. It is also possible to conclude by analogy with 5,12-dihydroquinoxalino(2,3b)quinoxaline that both hydrogens of the heterocyclic part of the polymer ladder are located in the same ring. This could explain the oxidative behavior of this type of polymer.

EXPERIMENTAL

Monomers

2,3,7,8-Tetrasubstituted-1,4,6,9-tetraazaanthracene. The preparation of these compounds has been described previously.[3a] The samples were dried intensively before use in polymerization.

1,2,4,5-Tetraaminobenzene Hydrochloride. This monomer was prepared as described or purchased from Burdick and Jackson, Muskegon, Mich., and recrystallized before use.

2,3-Dihydroxy-6,7-diaminoquinoxaline Hydrochloride. This monomer was purchased from Burdick and Jackson[14] and used as received, m.p. > 360°C.

ANAL. Calcd. for $C_8N_4H_{10}Cl_2O_2 \cdot H_2O$: C, 34.16%; N, 19.92%; H, 3.91%; Cl, 24.94%. Found: C, 33.83%; N, 19.87%; H, 4.38%; Cl, 25.33%.

2,3-Diphenoxy-6,7-diaminoquinoxaline. This monomer was purchased from Burdick and Jackson. The crude monomer was recrystallized once from ether with charcoal and twice from ethanol–water.

ANAL. Calcd. for $C_{20}N_4O_2H_{16}$: C, 69.82%; N, 16.28%; H, 4.65%. Found: C, 69.37%; N, 15.30%; H, 4.58%.

Solvents

Dimethylacetamide and hexamethylphosphoramide were dried and distilled under reduced pressure before use. Polyphosphoric acid was prepared from analytical reagent grade phosphorus pentoxide and deionized water.

Model Compounds

5,11-Dimethylquinoxalino(2,3b)quinoxaline. This compound was prepared by melt condensation of 0.82 g. N-methyl-o-phenylenediamine hydrochloride and of 0.85 g. 1,2-dihydro-3-hydroxy-1-methyl-2-oxoquinoxaline at 200°C. under nitrogen (yield 60%). The product was recrystallized twice from ethanol–water, m.p. 195–196°C.; λ_{max} in 95% ethanol: 258 mμ, $\epsilon = 13,100$; 317 mμ, $\epsilon = 39,700$.

ANAL. Calcd. for $C_{16}H_{14}N_4$: C, 73.28%; H, 5.42%. Found: C, 73.51%; H, 5.34%.

5,12-Dihydroquinoxaline(2,3b)quinoxaline. This compound was synthesized by melt condensation of 2,3-dichloroquinoxaline and o-phenylenediamine.[10] The resulting product was recrystallized from glacial acetic acid, m.p. > 360°C.

5-Methylindolo(2,3b)quinoxaline. This compound was prepared by melt condensation of N-methyl-o-phenylenediamine and isatin according to Burneziwski and Muchlewski,[11] m.p. 176°C. (lit. 175–176°C.).

5,12-Dihydroquinoxalino(2,3b)phenazine. This substance was prepared according to Badger and Petit[12] from 1,4-dihydroxy-p-benzoquinone and o-phenylenediamine.

Poly[5,12-dihydroquinoxalino(2,3b)phenazine]. The ultraviolet data of this compound were given by Dr. J. K. Stille, whose gift we gratefully acknowledge.[13]

Polymers

Polymerization in Melt of 2,3-Diphenoxy-6,7-diaminoquinoxaline

In a typical run, 3.44 g. of powdered monomer was put in a 100-ml. flask connected to a high vacuum system. After repeated deoxygenation procedures, by pulling vacuum, followed by pressurizing under nitrogen, the flask was heated very slowly under nitrogen in a wax bath up to 200°C. and kept at this temperature for 1 hr. The yellow solid melted, turned greenish, and solidified while giving off phenol. After 1 hr., the temperature was raised to 250°C. and phenol was pulled off under vacuum for 1 hr. The flask was then cooled; the solid was collected and ground. The inherent viscosity of the obtained polymer was 0.3 (0.5% in methanesulfonic acid). The prepolymer was slightly soluble in hexamethylphosphoramide, dimethyl sulfoxide, dimethylacetamide, and formic acid. A 1-g. portion of the prepolymer was heated at 350°C. for 4 hr. under vacuum. The resulting polymer was 80% soluble in methanesulfonic acid, $\eta_{inh} = 1$ (0.5% in methanesulfonic acid). The analysis indicated incomplete condensation.

ANAL. Calcd. for $C_8H_4N_4$: C, 61.52%; N, 35.92%; H, 2.56%. Found: C, 70.72%; N, 22.75%; H, 4.42%; Residue > 0.3%; P, >0.1%.

Solution Polymerization in Polyphosphoric Acid

2,3-Dihydroxy-6,7-diaminoquinoxaline Hydrochloride(IV). In a typical run, 5 g. of IV was slowly charged at 100°C. in freshly prepared polyphosphoric acid, and preheated for 1 hr. at 150°C. under nitrogen flow. When the evolution of hydrochloric acid had ended, the temperature was raised slowly (2–3°C./min.) to 250°C. The solution became more viscous and the colors changed from yellow to dark red to violet-black. This temperature was held for 24 hr. The resulting viscous solution was, while hot, poured into an ammonium hydroxide-distilled water solution and kept overnight. The solid was filtered off and extracted with water for 3 days and subsequently extracted with methanol for 14 hr. and dried.

The inherent viscosity of a sample prepared this way was 2.5 (0.5% in methanesulfonic acid). The solubility was 100%.

ANAL. Calcd. for $C_6H_4N_4$: C, 61.52%; N, 35.92%; H, 2.56%. Found: C, 59.66%; N, 34.51%; H, 2.60%; P, 0.11%; residue, 0.1%.

1,2,4,5-Tetraaminobenzene Hydrochloride and 2,3,7,8-Tetrasubstituted-1,4,6,9-tetraazaanthracene.

Tetraaminobenzene (5.6 g.) was added to 200 g. of polyphosphoric acid, heated as described above. When all the hydrochloric acid was set free, an equimolar amount of the 2,3,7,8-tetrahydroxy-tetraazaanthracene derivative (6.2 g.) was added at once. The polymerization and work-up was carried out as described above.

ANAL. Found: C, 59.58%; N, 34.48%; H, 2.65%; P, 0.11%; residue, 0.1%.

Similar runs were made for the other derivatives, and the polymers were characterized by their ultraviolet spectra.

Solution Polymerization in Organic Solvents

In a typical run, 3 g. of 2,3-diamino-6,7-diphenoxyquinoxaline was charged at room temperature to 50 cc. hexamethylphosphoramide, pressured with dry nitrogen for 1 hr. at 100°C. The temperature was raised slowly to 120°C. and kept at this point for 24 hr. The yellowish-green solution was then poured in distilled water (500 cc.) under stirring. The precipitate was filtered off and dried. The inherent viscosity was 0.08–0.1 (0.5% in methanesulfonic acid). The infrared showed presence of phenyl ether bands.

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Résumé

On a obtenu des polymères à double chaîne appelés aussi polymères à échelle, par le condensation du 1,2,4,5-tétraaminobenzène avec un anthracène-1,4,6,9-tétraazoté et 2,3,7,8-tétra substitué, et par l'auto condensation d'une 6,7-diaminoquinoxaline-2,3 dihydroxylée et une 6,7-diaminoquinoxaline-2,3-diphénoxylée. On a effectué les polycondensations en solutions ou à l'état fondu. Les polymères qui ont été obtenus étaient fortement colorés et étaient caractérisés par des viscosités intrinsèques pouvant atteindre 2.5. On a établi la structure des polymères en les comparant avec des composés modèles.

Zusammenfassung

Ein Doppelketten- oder Leiterpolymeres wurde durch Kondensation von 1,4,4,5-Tetraaminobenzol mit 2,3,7,8-tetrasubstituiertem 1,4,6,9-Tetraazaanthracen und durch Selbstkondensation von 2,3-Dihydroxy-6,7-diaminochinoxalin und von 3-Diphenoxy-6,7-diaminochinoxalin erhalten. Die Polykondensation wurde in Lösung oder in der Schmelze durchgeführt. Die so erhaltenen Polymeren bildeten tief gefärbte Produkte mit Viskositätszahlen bis zu 2,5. Die Struktur der Polymeren wurde durch Vergleich mit Modellverbindungen ermittelt.

Aromatic Polysulfonamides

F. E. ARNOLD,* S. CANTOR,† and C. S. MARVEL,
*Department of Chemistry, The University of Arizona,
Tucson, Arizona 85721*

Synopsis

Aromatic polysulfonamides have been prepared by solution polycondensation of aromatic disulfonyl chlorides and aromatic diamines with a suitable acid acceptor in such solvents as N,N-dimethylacetamide and tetramethylenesulfone. The highest molecular weight polymers were obtained by using 2,6-dimethylpyridine as the acid acceptor in tetramethylenesulfone as the solvent. Clear, translucent, brittle films of the polysulfonamides may be formed from solution or from melt.

INTRODUCTION

Various aliphatic polysulfonamides[1,2] have been prepared in high molecular weight by the reaction of benzenedisulfonyl chlorides with aliphatic diamines under the conditions of interfacial and solution polycondensation. The aliphatic polysulfonamides are known to be fiber-forming polymers which can be both melt-[3] and wet-spun.[4] They exhibit excellent stability to hydrolysis in both acidic and alkaline solutions. The present investigation was undertaken to study the preparation of completely aromatic polysulfonamides which would not only possess hydrolytic stability, but would be thermally stable due to the rigidity imposed by the aromatic rings.

RESULTS AND DISCUSSION

Melt Studies

It has been shown[5] that the diphenyl esters of methanedisulfonic acid, when treated with aniline or ammonia in a sealed tube at 160–180°C. produced the corresponding sulfonamides. Polysulfonamides derived from primary diamines and methylenedisulfonic acid esters have also been reported.[6] We believed that a fully aromatic polysulfonamide could be prepared by a melt polymerization utilizing the diphenyl ester of aromatic disulfonic acids and aromatic diamines under conditions in which phenol would be formed and removed from the reaction.

Melt polymerizations between *m*-phenylenediamine and the diphenyl ester of *m*-benzenedisulfonic acid were carried out in two stages: first, equimolar amounts of the monomers were heated under a nitrogen atmosphere to 250°C., after which the material was allowed to cool; second, the system was placed under reduced pressure (0.1 mm.) and again heated for 3 hr. at 250°C. The procedure failed to produce any polymer. In order to maintain a true 1:1 ratio of amino group to sulfonic ester necessary for a melt polymerization, the phenyl ester of metanilic acid was prepared. This monomer did not form a polysulfonamide when allowed to react at 320°C. for 3 hr., followed by the reduced pressure treatment (0.1 mm.) and further heating at 250°C. for 2 hr.

Although it has been shown[7] that phenol proved to be an excellent leaving group in the melt polymerization to form polybenzimidazoles, the results from these studies indicate that the phenyl ester of benzenedisulfonic acid is quite stable. The bis-*p*-nitrophenyl ester of *m*-benzenedisulfonic acid was prepared with the expectation that the *p*-nitrophenyl group would prove to be a better leaving group. This compound also failed to produce any polymer.

Solution Studies

No high molecular weight completely aromatic polysulfonamides have been reported. This may be attributed to the low basicity of the aromatic diamines coupled with the low reactivity of sulfonyl chloride as compared with carboxylic acid chlorides. Solution studies were carried out on a series of aromatic disulfonyl chlorides and aromatic diamines [eq. (1)] in highly polar solvents such as N,N-dimethylacetamide and tetramethylenesulfone, with an appropriate acid acceptor to pick up the hydrochloric acid formed.

$$ClSO_2-Ar-SO_2-Cl \; + \; NH_2-Ar'-NH_2 \longrightarrow \left[SO_2-Ar-SO_2-NH-Ar-NH\right]_n$$

Ar = (benzene ring) or (naphthalene)
      1,3   2,7; 1,5

(1)

Ar' = (benzene ring) or (diphenyl ether)
       1,3; 1,4   4,4'
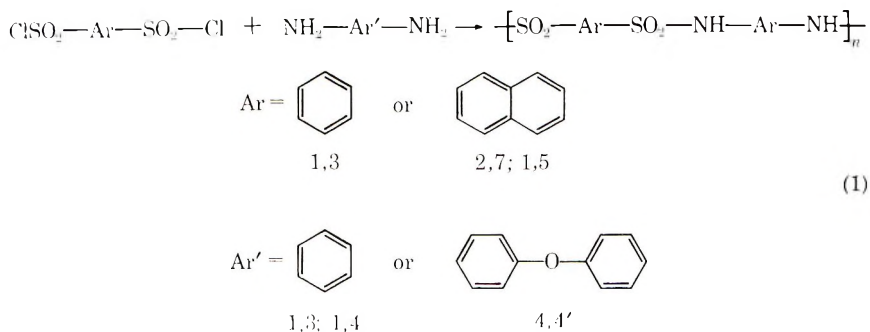
Extended reaction times were used, since the aromatic amines show a low reactivity toward aromatic disulfonyl chlorides. The polymerizations were carried out in a nitrogen-filled dry box in order to exclude all traces of moisture which would hydrolyze the disulfonyl chloride over the extended reaction time.

Three classes of acid acceptors were used in the polycondensations: acceptors such as the alkali hydrides (Table I) in which hydrogen is evolved,

heterogeneous basic inorganic acceptors (Table II), and homogeneous basic organic acceptors (Table III). The alkali hydrides gave colored polymers of low inherent viscosities indicating extensive side reaction. Polymers derived from inorganic acid acceptors were white in color, however, of low inherent viscosities. The best results were obtained with the organic acid acceptors, especially hindered 2,6-dimethylpyridine.

TABLE I

Polysulfonamides from Aromatic Diamines and Aromatic Disulfonyl Chlorides at 30°C. in N,N-Dimethylacetamide (Metal Hydride Acid Acceptors)[a]

Monomers		Acid acceptor	Reaction time, hr.	Color	η_{inh} in DMAC[b]
Diamine	Disulfonyl chloride				
m-Phenylene-	1,3-Benzene-	NaH	5	Yellow	0.04
m-Phenylene-	1,3-Benzene-	CaH₂	5	Yellow	0.06
m-Phenylene-	1,3-Benzene-	LiH	5	Yellow	0.01
m-Phenylene-	1,5-Naphthalene-	NaH	4	Brown	0.05
m-Phenylene-	1,5-Naphthalene-	CaH₂	6	Yellow	0.03
m-Phenylene-	1,5-Naphthalene-	LiH	5	—	—
m-Phenylene-	2,6-Naphthalene-	NaH	5	Brown	0.02
m-Phenylene-	2,6-Naphthalene-	CaH₂	5	Yellow	0.05
m-Phenylene-	2,6-Naphthalene	LiH	5	—	—

[a] The polymerizations were carried out with 0.01 mole of monomers/100 ml. of solvent.
[b] Inherent viscosity taken in N,N-dimethylacetamide (0.3 g./100 ml.) at 30°C.

TABLE II

Polysulfonamides from Aromatic Diamines and Aromatic Disulfonyl Chlorides in Dimethylacetamide (Inorganic Acceptors)[a]

Monomers		Acid acceptor	Reaction time, hr.	Temperature, °C.	Color	η_{inh} in DMAC[b]
Diamine	Disulfonyl chloride					
m-Phenylene-	1,3-Benzene-	Na₂CO₃	48	30	White	0.03
m-Phenylene-	1,3-Benzene-	MgCO₃	48	30	White	0.02
m-Phenylene-	1,3-Benzene-	CaCO₃	48	30	White	0.04
m-Phenylene-	1,3-Benzene-	Ca(OH)₂	48	30	White	0.05
m-Phenylene-	1,3-Benzene-	Ba(OH)₂	48	30	White	0.06
m-Phenylene-	1,3-Benzene-	Ca(OH)₂	48	−20	White	0.08
m-Phenylene-	2,6-Naphthalene-	Ca(OH)₂	48	−20	White	0.06
m-Phenylene-	1,3-Benzene-	Ba(OH)₂	48	−20	White	0.07

[a] The polymerizations were carried out with 0.01 mole of monomers/100 ml. of solvent.
[b] Inherent viscosity taken in N,N-dimethylacetamide (0.3 g./100 ml.) at 30°C.

The temperatures used for the solution polycondensations varied from −20 to 90°C. Temperatures over 90°C. led to highly colored materials. Tetramethylenesulfone proved to be a better solvent for the polymerization, since N,N-dimethylacetamide, when allowed to react with 1,3-benzenedisulfonyl chloride, formed an acetamide salt which was very hygroscopic.

TABLE III

Polysulfonamides from Aromatic Diamines and Aromatic Disulfonyl Chlorides (Organic Acid Acceptors)[a]

Monomers		Acid acceptors	Reaction time, hr.	Solvent[b]	Temperature, °C.	Color	η_{inh} in DMAC[c]
Diamine	Disulfonyl chloride						
m-Phenylene-	1,3-Benzene-	Pyridine	48	DMAC	30	Pink	0.03
m-Phenylene-	1,3-Benzene-	2,6-Dimethylpyridine	48	DMAC	30	White	0.06
m-Phenylene-	1,3-Benzene-	Pyrazine	48	DMAC	30	White	0.04
m-Phenylene-	1,3-Benzene-	2,3,5,6-Tetramethyl-pyrazine	48	DMAC	30	White	0.05
				TMS	90	—	0.10
m-Phenylene-	1,3-Benzene-	Triethylamine	48	DMAC	30	Yellow	0.03
m-Phenylene-	1,3-Benzene-	2,6-Dimethylpyridine	72	TMS[b]	90	White	0.15
m-Phenylene-	1,5-Naphthalene-	2,6-Dimethylpyridine	72	TMS	90	White	0.11
m-Phenylene-	2,6-Naphthalene-	2,6-Dimethylpyridine	72	TMS	90	White	0.06
p-Phenylene-	1,3-Benzene-	2,6-Dimethylpyridine	72	TMS	90	White	0.08
4,4'-Diphenyl oxide	1,3-Benzene-	2,6-Dimethylpyridine	72	TMS	90	White	0.19

[a] The polymerizations were carried out with 0.03 mole of monomers/60 ml. of solvent.

[b] DMAC = N,N-dimethylacetamide; TMS = tetramethylenesulfone.

[c] Inherent viscosity in N,N-dimethylacetamide (0.3 g./100 ml.) at 30°C.

Aromatic polysulfonamides with inherent viscosities greater than 0.08 precipitate from solution in a fiberlike manner. Clear, translucent films of these materials may be formed from solution or from melt. The films, however, are brittle, indicating low molecular weight material. Melt temperatures of the polymers are in the range 200–300°C. The polysulfonamides are soluble in acetone, N,N-dimethylacetamide, hexamethylphosphoramide, dimethyl sulfoxide, and partially soluble in methanol.

EXPERIMENTAL

Solvents

N,N-Dimethylacetamide was purified by drying over calcium hydride and then distilled under a nitrogen atmosphere, b.p. 163–164°C. The solvent was then transferred into a nitrogen-filled dry box and before each polymerization passed through a 12-in. column containing a 4A molecular sieve to remove the last traces of moisture.

Tetramethylenesulfone was purified by distilling under reduced pressure, b.p. 118°C./3 mm. Hg.

Monomers

Diphenyl Ester of m-Benzenedisulfonic Acid. To a solution containing 2.35 g. (0.025 mole) of phenol and 2.65 g. (0.025 mole) of sodium carbonate dissolved in 25 ml. of water and 25 ml. of acetone was added 2.75 g. (0.01 mole) of m-benzenedisulfonyl chloride. After the reaction mixture was stirred for 1 hr. a white precipitate formed and water was added. The white solid was collected and washed with water. The material was recrystallized from 95% ethanol to yield 3.0 g. (77%), m.p. 94–95°C.

ANAL. Calcd. for $C_{18}H_{14}S_2O_6$: C, 55.39%; H, 3.62%. Found: C, 55.48%; H, 3.51%.

Bis-p-nitrophenyl Ester of m-Benzenedisulfonic Acid. A procedure similar to the one used for the phenyl ester of m-benzenedisulfonic acid was employed. The pure product, m.p. 155–156°C., was recrystallized from (1:1) acetone–water mixture.

ANAL. Calcd. for $C_{18}H_{12}O_{10}N_2S_2$: C, 44.99%; H, 2.52%; N, 5.82%. Found: C, 44.80%; H, 2.60%; N, 5.71%.

Phenyl Ester of Metanilic Acid. In a 300-ml., three-necked, round-bottomed flask, fitted with a mechanical stirrer and a dropping funnel, was placed 5.5 g. (0.015 mole) of the phenyl ester of m-nitrobenzenesulfonic acid and 50 ml. of 95% ethanol. In small portions, 3.8 g. of iron filings (20 mesh), 150 ml. of water, and 4 ml. of concentrated hydrochloric acid were added. The reaction mixture was stirred at 30°C. for 3 hr. and then was filtered to remove the iron. The filtrate was neutralized by the addition

of sodium carbonate and then the ethanol was removed by distillation. The remaining aqueous solution was extracted with three 50-ml. portions of ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. Removal of the drying agent and removal of the ether produced 2.8 g. (76%) of a solid material, m.p. 71–72°C.

ANAL. Calcd. for $C_{12}H_{11}NO_3S$: C, 57.83%; H, 4.45%; N, 5.62%. Found: C, 58.15%; H, 4.57%; N, 5.79%.

1,3-Benzenedisulfonyl Chloride. The monomer was obtained commercially and purified by dissolving it in benzene and washing the organic layer with a 5% solution of sodium bicarbonate and then finally with water. The benzene solution was dried over anhydrous magnesium sulfate and treated with activated charcoal. After passing the benzene solution of the monomer through a column of activated alumina the monomer was precipitated by addition of olefin-free hexane. The resulting white crystals were dried under reduced pressure, m.p. 60–61°C.

2,6-Naphthalenedisulfonyl Chloride. In a 1-liter, round-bottomed flask fitted with a stirrer and condenser was placed a mixture of 73.7 g. (0.223 mole) of the disodium salt of 2,6-naphthalenedisulfonic acid and 110 g. of phosphorus pentachloride. The flask was placed in an oil bath and heated to 100°C. After 0.5 hr., a nonhomogeneous paste was formed. To this mixture was added 100 ml. of phosphorus oxychloride and the heating was continued for 5 hr. The excess phosphorus oxychloride was removed under reduced pressure. The dry cake material was pulverized in a mortar and transferred to a 3-liter flask. To this was added 650 ml. of distilled water and 1.6 liter of chloroform. The mixture was placed on a steam bath and heated to boiling with vigorous stirring until all of the solid dissolved. The hot chloroform solution was washed with three 150-ml. portions of 5% sodium carbonate. Then it was washed with three 100-ml. portions of warm water. While still hot, the chloroform solution was dried over anhydrous magnesium sulfate. The mixture was filtered and the volume was reduced by heating. Cooling produced 53 g. (79%) of white crystals, m.p. 226–227°C., reported[8] m.p. 225–226°C.

1,5-Naphthalenedisulfonyl Chloride. The monomer was prepared by the same method as the 2,6-isomer, yielding 54 g. (80%) of a white crystalline material, m.p. 181–183°C., reported[9] m.p. 183°C.

m-Phenylenediamine. m-Phenylenediamine was obtained commercially and recrystallized from anhydrous diethyl ether until the melting point range was within a half degree, m.p. 63–63.5°C.

p-Phenylenediamine. p-Phenylenediamine was obtained commercially and recrystallized from anhydrous diethyl ether and then sublimed at 0.10 mm. Hg, m.p. 140–141°C.

4,4'-Diaminodiphenyl Oxide. 4,4'-Diaminodiphenyl oxide was provided by E. I. du Pont de Nemours and Company; the commercial product was recrystallized from methanol and then sublimed at 0.10 mm. Hg; m.p. 186–187°C.

Polymers

Attempted Melt Polymerization from m-Phenylenediamine and the Diphenyl Ester of m-Benzenedisulfonic Acid.

In a 300-ml. round-bottomed flask, placed in a sand bath, were placed 2.00 g. (0.0185 mole) of m-phenylenediamine and 7.22 g. (0.0185 mole) of the diphenyl ester of m-benzenedisulfonic acid. The materials were thoroughly mixed and the system placed under an atmosphere of nitrogen. The flask was heated at 3°C./min. up to 250°C. and kept at that temperature for 0.5 hr. After this period, the flask was allowed to cool to room temperature and its contents were placed under reduced pressure (0.5 mm.). At this reduced pressure the flask was heated at 3°C./min. up to 250°C. and held at that temperature for 3 hr. The contents of the flask were solid, but the material dissolved in ether and, therefore, it was assumed that only starting materials were present.

Attempted Melt Polymerization from Phenyl Ester of Metanilic Acid.

In a two-necked flask was placed 0.3137 g. (0.0012 mole) of the phenyl ester of metanilic acid. The flask was fitted with a nitrogen inlet and a gas bubbler. After sweeping the flask with nitrogen for 2 hr. it was heated at the rate of 3°C./min. to 250°C. and maintained at that temperature for 2.5 hr. The color of the melt did not change during the heat treatment. The flask was then allowed to cool, placed under reduced pressure (0.5 mm.) and heated again to 250°C. for 2 hr. Examinations of the material indicated it was unreacted starting material.

Poly-1,3-benzenesulfonamide by Using Calcium Hydride.

In a nitrogen-filled dry box were mixed 1.08 g. (0.01 mole) of m-phenylenediamine, 100 ml. of N,N-dimethylacetamide, and 0.5 g. of calcium hydride powder. To this mixture was added 2.72 g. (0.01 mole) of 1,3-benzenedisulfonyl chloride as a solid in small portions. After the addition of disulfonyl chloride the reaction mixture was stirred at 30°C. for 5 hr. The solution was then filtered and the polymer was precipitated by pouring into 300 ml. of distilled water. The polymer after filtration and drying over calcium chloride under reduced pressure weighed 3 g. (83% yield). The inherent viscosity of the polymer in N,N-dimethylacetamide (0.3 g./100 ml.) at 30°C. was 0.06.

ANAL. Calcd. for $(C_{12}H_{10}S_2N_2O_4)_n$: C, 46.47%; H, 3.24%; N, 9.02%. Found: C, 46.62%; H, 3.52%; N, 9.15%.

Poly-1,3-benzenesulfonamide by Using 2,3,5,6-Tetramethylpyrazine.

To a solution containing 3.24 g. (0.03 mole) of m-phenylenediamine, 60 ml. of tetramethylenesulfone, and 3.08 g. of 2,3,5,6-tetramethylpyrazine was added 5.50 g. (0.03 mole) of solid 1,3-benzenedisulfonyl chloride over a 10-min. period. After the addition of the disulfonyl chloride, the temperature of the solution was raised to 90°C. and maintained at that temperature for 48 hr. The solution was then allowed to cool to 30°C. and the polymer was precipitated into 300 ml. of distilled water. The polymer formed was a white fibrous material and after drying over

calcium chloride under reduced pressure weighed 4 g. (58% yield). The inherent viscosity of the polymer in N,N-dimethylacetamide (0.3 g./100 ml. at 30°C. was 0.10.

ANAL. Calcd. for $(C_{12}H_{10}S_2N_2O_4)_n$: C, 46.47%; H, 3.24%; N, 9.02%. Found: C, 46.24%; H, 3.35%; N, 8.82%.

Poly-m/p-benzenesulfonamide. To a solution containing 1.08 g. (0.01 mole) of p-phenylenediamine, 2.5 ml. of 2,6-dimethylpyridine, and 50 ml. of tetramethylenesulfone was added as the solid, 2.72 g. of 1,3-benzene-disulfonyl chloride. On addition of the disulfonyl chloride the solution turned red. After heating at 90°C. for 2 hr. the solution became light yellow. The mixture was stirred for 48 hr. and then poured into 300 ml. of distilled water which precipitated a white solid. After filtration 2.5 g. (80%) of a white solid remained which showed an inherent viscosity of 0.08 in N,N-dimethylacetamide (0.3 g./100 ml.) at 30°C.

ANAL. Calcd. for $(C_{12}H_{10}S_2N_2O_4)_n$: C, 46.47%; H, 3.24%; N, 9.02%. Found: C, 46.39%; H, 3.83%; N, 8.80%.

Poly-1,3-phenylene-4,4'-oxyphenylenesulfonamide. To a solution containing 1.70 g. (0.085 mole) of oxydianiline, 2.5 ml. of 2,6-dimethylpyridine, 50 ml. of tetramethylenesulfone, was added as the solid 2.31 g. (0.085 mole) of 1,3-benzenedisulfonyl chloride. On addition of the disulfonyl chloride an orange color formed which turned lighter as the reaction proceeded. The mixture was stirred for 72 hr. at 90°C. and after cooling to room temperature was precipitated into 300 ml. of distilled water. The polymer, 2.43 g. (75%), showed an inherent viscosity in N,N-dimethylacetamide (0.3 g./100 ml.) of 0.19.

ANAL. Calcd. for $(C_{18}H_{14}S_2N_2O_5)_n$: C, 56.54%; H, 3.66%; N, 7.89%. Found: C, 55.66%; H, 3.85%; N, 7.24%.

Poly-1,3-benzene-2,6-naphthalenesulfonamide. To a solution containing 3.24 g. (0.03 mole) of m-phenylenediamine in 60 ml. of tetramethylenesulfone and 2.5 ml. of 2,6-dimethylpyridine was added 11.19 g. (0.03 mole) of 2,6-naphthalenedisulfonyl chloride as the solid under a nitrogen atmosphere. The mixture was stirred for 72 hr. at 90°C. After cooling to room temperature, the polymer was precipitated into 300 ml. of distilled water. The white polymer weighed 8.6 g. (80%) and showed an inherent viscosity in N,N-dimethylacetamide (0.3 g./100 ml.) of 0.06 at 30°C.

ANAL. Calcd. for $(C_{16}H_{12}S_2N_2O_4)_n$: C, 55.34%; H, 3.36%; N, 7.78%. Found: C, 52.93%; H, 3.60%; N, 7.58%.

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Résumé

On a préparé des polysulfonamides aromatiques par la polycondensation en solution de chlorures aromatiques de disulfonyle avec des diamines aromatiques en ajoutant un accepteur suffisamment acide, dans des solvants comme l'*N,N*-diméthylacétamide et la tétraméthylènesulfone. On a obtenu des poids moléculaires les plus élevés en employant comme accepteur acide la 2,6-diméthylpyridine et comme solvant la tétraméthylènesulfone. Ainsi on peut faire à partir de la solution ou à partir de l'état fondu, des films de polysulfonamides, clairs, translucides et cassants.

Zusammenfassung

Aromatische Polysulfonamide wurden durch Lösungspolykondensation von aromatischen Disulfonylchloriden und aromatischen Diaminen mit einem geeigneten Säureakzeptor in Lösungsmitteln wie *N,N*-Dimethylacetamid und Tetramethylensulfon dargestellt. Die höchstmolekularen Polymeren wurden mit 2,6-Dimethylpyridin als Säureakzeptor in Tetramethylensulfon als Lösungsmittel erhalten. Aus Lösung oder Schmelze Können klare, durchsichtige, spröde Polysulfonamidfilme gebildet werden.

New Synthetic Route to α-Alkylacrylonitriles and a Study of Their Homopolymerization and Copolymerization Reactions

J. KOVÁCS* and C. S. MARVEL, *Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

Synopsis

Aliphatic aldehydes have been condensed with cyanoacetic acid and the resulting olefin intermediates hydrogenated and then submitted to a Mannich-type reaction to produce α-alkylacrylonitriles with the alkyl groups ranging from C_1 to C_{12}. It was not necessary to isolate the intermediates when the reactions were carried out in acetonitrile solutions. The α-alkylacrylonitriles with C_7 or higher alkyl groups in the chains would polymerize by radical initiation in emulsion to give polymers which were sticky, rubbery products and showed adhesive characteristics. Anionic initiation did not yield polymers with the α-alkylacrylonitriles containing high alkyl groups but did convert the C_2 to C_4 alkyl-substituted acrylonitriles to low molecular weight colored products. Some copolymers of α-alkylacrylonitriles with acrylonitrile were prepared in emulsion by radical initiation. The monomer ratios in these copolymers were determined by nuclear magnetic resonance spectra.
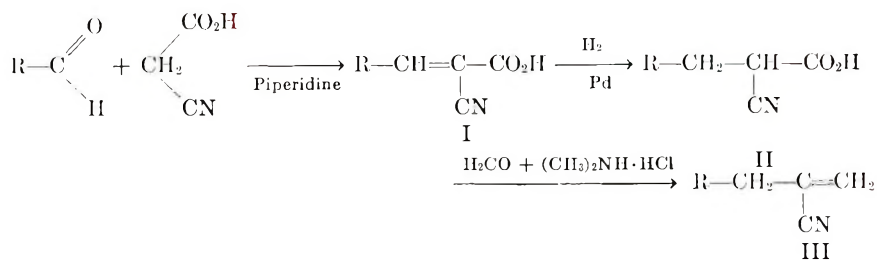
RESULTS AND DISCUSSION

Monomer Synthesis

α-Substituted alkylacrylonitriles have been made by the dehydration of the cyanohydrins of methyl ketones, but this method produces mixtures of products which are difficult to separate.[1-6] The acetates derived from the corresponding methyl ketone cyanohydrins were converted selectively to α-alkylacrylonitriles by pyrolysis.[7] Crude α-alkylacrylonitriles with alkyl groups containing two to five carbons have been obtained by dehydration of the corresponding α-alkylacrolein oximes,[8] but this method is tedious and the yield is not good.

It has now been found that by the Knoevenagel reaction with aliphatic aldehydes and cyanoacetic acid in acetonitrile, followed by reduction to the saturated derivatives by hydrogenation over palladium and subsequent use of the Mannich reaction, good yields of α-alkylacrylonitriles can be obtained.

$$R-\overset{\displaystyle O}{\underset{\displaystyle H}{C}} + \underset{\displaystyle CN}{\overset{\displaystyle CO_2H}{CH_2}} \xrightarrow[\text{Piperidine}]{} R-CH=\underset{\displaystyle CN}{\overset{\displaystyle}{C}}-CO_2H \xrightarrow[\text{Pd}]{H_2} R-CH_2-\underset{\displaystyle CN}{\overset{\displaystyle}{CH}}-CO_2H$$

$$\text{I}$$

$$\xrightarrow[]{H_2CO + (CH_3)_2NH\cdot HCl} R-CH_2-\underset{\displaystyle CN}{\overset{\displaystyle H}{C}}=CH_2$$

$$\text{II}$$

$$\text{III}$$

When the Knoevenagel reaction was carried out in water, a Michael addition reaction of cyanoacetic acid to the first olefinic acid led to glutaric acid derivatives. Acetic acid worked well as a solvent for condensation and reduction. It required high temperatures to remove the solvent before the Mannich reaction could be carried out and this led to partial decarboxylation of the cyanoacetic acid intermediate. Acetonitrile was found to be the most satisfactory solvent. The reduction step was slower in acetonitrile than in acetic acid, but the overall yield was improved.

The Mannich reaction required about 3 hr. at reflux temperatures for C_1–C_4 aldehydes. For the C_7–C_{12} aldehydes, the reaction required 5 hr.
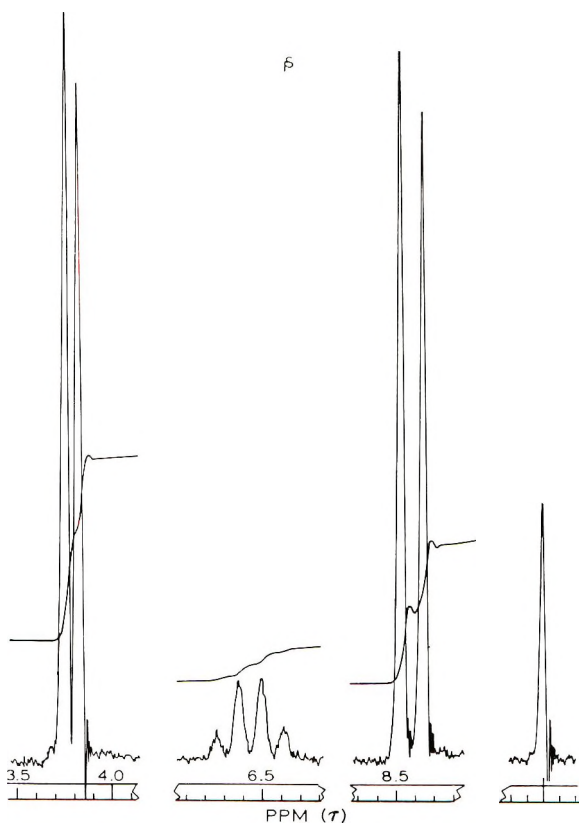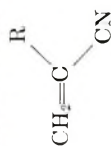

Fig. 1. NMR spectrum of 2,4-dicyano-3-methylpentadiene-1,4 (20% in D_3CCOCD_3).

TABLE I

α-Substituted Acrylonitriles

$$CH_2=C\begin{smallmatrix}R\\[4pt]CN\end{smallmatrix}$$

Run no.	R	Overall yield, %	B.p., °C./mm. Hg	n_D^{20}	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
1	CH_3	15.3	111/760	—	—	—	—	—	—	—
2	C_2H_5	30.4		1.4131	74.03	73.69	8.71	8.68	17.28	17.68
3	$n\text{-}C_3H_7$	47.0	62/52-54	1.4192	75.74	75.53	9.53	9.53	14.73	15.00
4	$n\text{-}C_4H_9$	67.6	72-73/40-41	1.4270	76.98	76.92	10.16	10.45	12.93	12.47
5	$2\text{-}C_4H_9$	50.8	68-69/44-45	1.4264	76.98	76.70	10.16	10.51	12.93	12.55
6	$n\text{-}C_7H_{15}$	68.2	111/24-25	1.4392	79.41	79.22	11.33	11.27	9.26	8.80
7	$n\text{-}C_8H_{17}$	58.8	85/2.0	1.4409	79.93	79.48	11.59	11.46	8.48	7.96
8	$n\text{-}C_9H_{19}$	43.6	83-80/0.2-0.1	1.4435	80.38	80.22	11.81	11.78	7.81	7.49
9	$n\text{-}C_{10}H_{21}$	45.6	86.0/0.25	1.4462	80.76	80.77	11.99	12.03	7.25	6.89
10	$n\text{-}C_{12}H_{25}$	19.2	107-110/0.25	1.4492	81.36	81.56	12.29	12.52	6.33	6.23
11	Neopentyl	21.7	51-52/13-14	1.4296	77.99	78.19	10.64	11.09	11.37	11.20

at reflux temperature followed by an overnight period at room temperature. With the lower alkyl groups, some cooling was necessary in the first part of the Mannich reaction to slow down the vigorous evolution of CO_2. After the reaction was finished, the acetonitrile was evaporated and the product was separated by steam distillation. The oily layer was washed with 10% sodium carbonate solution, dried and distilled under reduced pressure. The results are summarized in Table I.

This general procedure can be used for C_2–C_{12} aldehydes. For the preparation of α-methylacrylonitrile, 33% aqueous formaldehyde solution was used in the condensation. The reaction proceeded very slowly so that 3–4 days were needed for the condensation-reduction steps of the reaction. Less than 65% of the theoretical amount of hydrogen was absorbed.

An attempt to use benzaldehyde to give an α-benzylacrylonitrile did not work well, as the aromatic ring was partially reduced to give a mixture of products.

Ross and Burnett[9] condensed pivalaldehyde with sodium cyanoacetate in water and obtained β-alkylacrylic acid and derivative. In attempting this procedure, we obtained both the acrylic and glutaric acid derivatives.
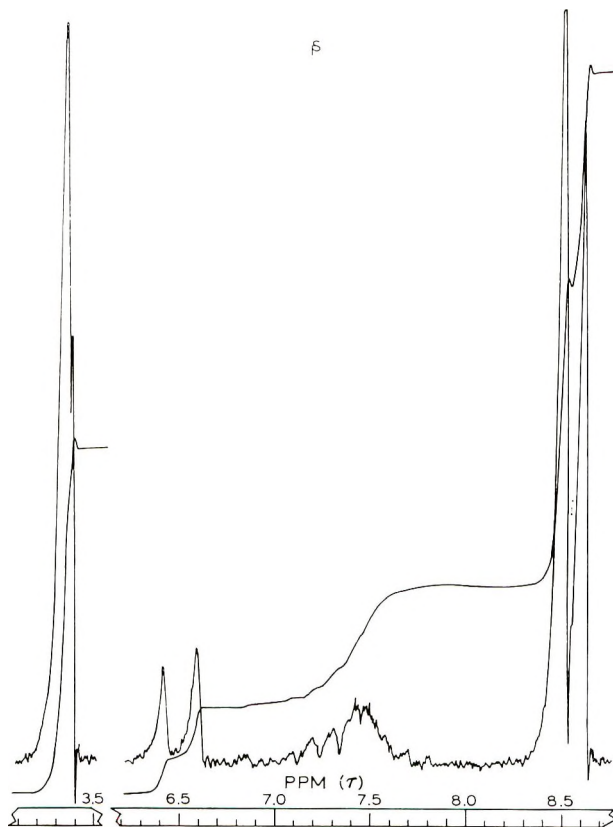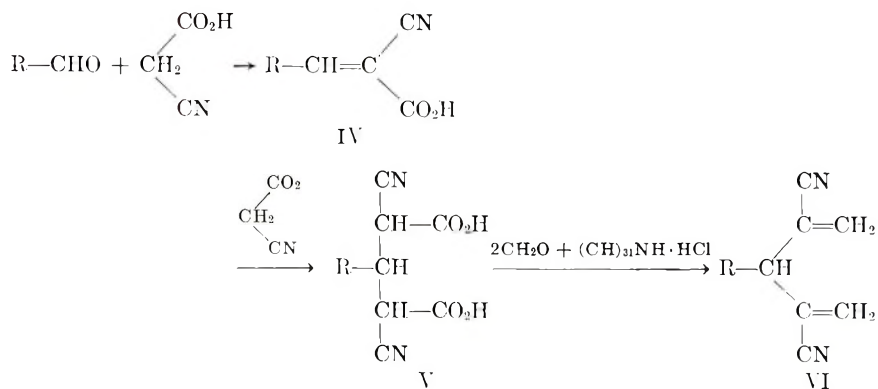

Fig. 2. NMR spectrum of 2,4-dicyano-3-isopropylpentadiene-1,4 (20% in D_3CCOCD_3).

$$\text{R—CHO} + \underset{\underset{\text{CN}}{|}}{\overset{\overset{\text{CO}_2\text{H}}{|}}{\text{CH}_2}} \longrightarrow \text{R—CH}=\text{C}\underset{\text{CO}_2\text{H}}{\overset{\text{CN}}{\diagup}}$$

$$\text{IV}$$

$$\underset{\text{CN}}{\overset{\text{CO}_2}{\underset{\diagdown}{\text{CH}_2}}} \longrightarrow \text{R—CH} \underset{\underset{\text{CN}}{|}}{\overset{\overset{\text{CN}}{|}}{\underset{\text{CH—CO}_2\text{H}}{\overset{\text{CH—CO}_2\text{H}}{}}}} \xrightarrow{\text{2CH}_2\text{O} + (\text{CH})_{31}\text{NH} \cdot \text{HCl}} \text{R—CH} \overset{\overset{\text{CN}}{|}}{\underset{\underset{\text{CN}}{|}}{\overset{\text{C}=\text{CH}_2}{\underset{\text{C}=\text{CH}_2}{}}}}$$

$$\text{V} \qquad\qquad\qquad \text{VI}$$

Using an equimolar amount of pivalaldehyde and cyanoacetic acid in alkaline solution, a product was obtained which contained 35–40% of the α-cyano-β-*tert*-butylacrylic acid and 60–65% of β-*tert*-butyl-2,4-dicyanoglutaric acid (V). The two products were separated by crystallization and identified by NMR spectra. The former product (IV) was converted to α-neopentylacrylonitrile and the second product (V) was converted to 3-*tert*-butyl-2,4-dicyanopentadiene-1,4. However, when excess pivalalde-
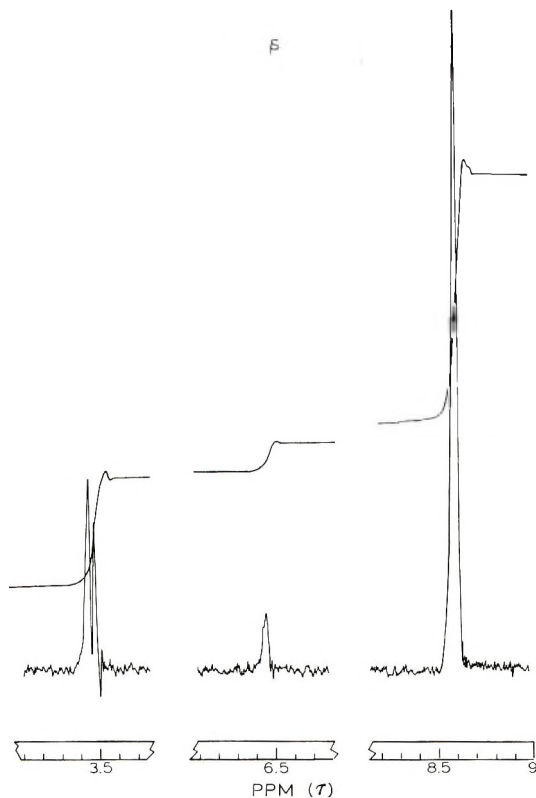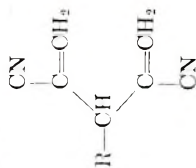

Fig. 3. NMR spectrum of 2,4-dicyano-3-*tert*-butylpentadiene-1,4 (20% in D$_3$CCOCD$_3$).

TABLE II

2,4-Dicyano-3-Substituted Pentadiene-1,4

R	Overall yield, %	Melting point, °C.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Methyl	14.6	82/1.0 mm. (b.p.)	—	—	—	—	—	—
Isopropyl	28.7	36–37	—	—	—	—	—	—
tert-Butyl	26.6	83.5	75.85	76.22	8.04	8.17	16.11	15.81

Analyses

hyde was used, and the temperature was kept low, it was possible to obtain mainly α-cyano-β-*tert*-butylacrylic acid but the yield was not satisfactory 27.8%; (see Experimental part). Hydrogenation of IV was accomplished with Raney nickel and hydrogen after neutralization with sodium carbonate
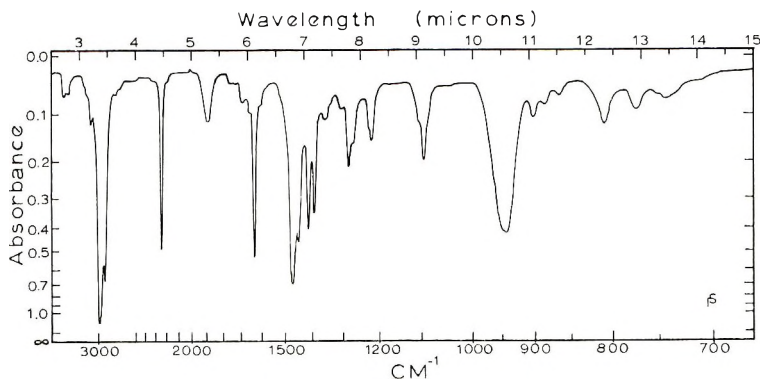
Fig. 4. Infrared spectrum of α-*n*-propylacrylonitrile (no solvent).
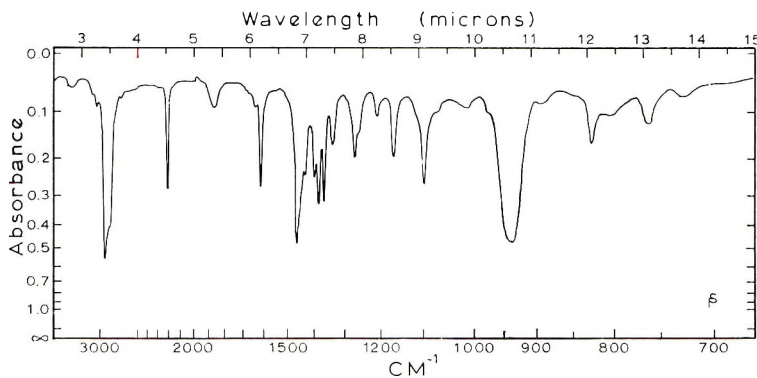
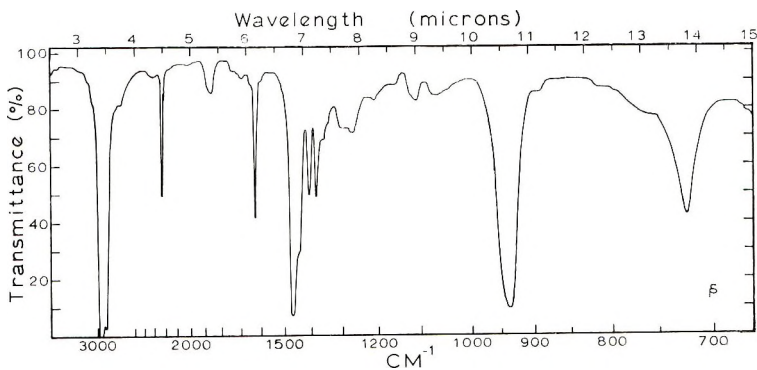Fig. 5. Infrared spectrum of α-isobutyrylacrylonitrile (no solvent).

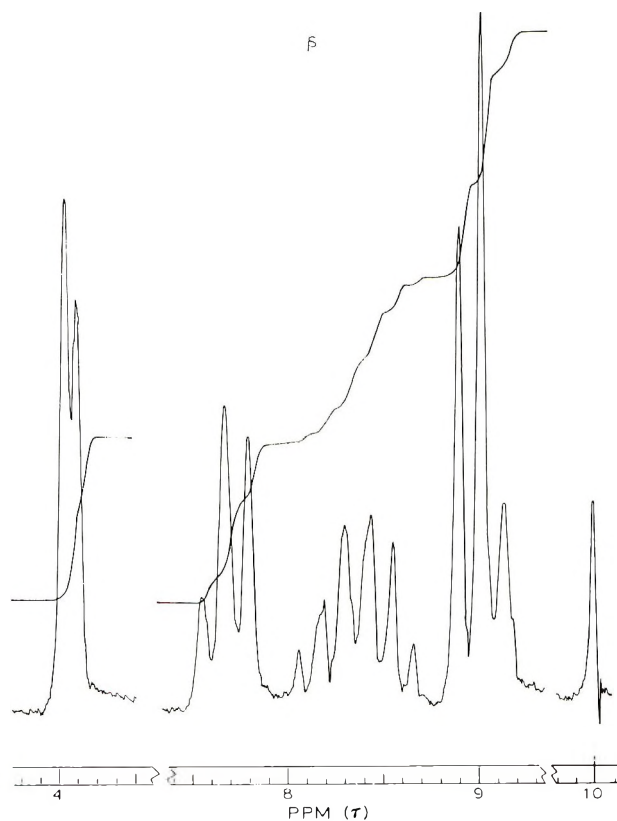Fig. 6. Infrared spectrum of α-*n*-decylacrylonitrile (no solvent).

Fig. 7. NMR spectrum of α-n-propylacrylonitrile (no solvent).

or with palladinized charcoal and hydrogen in acetonitrile solution without neutralization. The Mannich reaction was carried out in absolute alcohol or in acetonitrile solution.

Glutaric acid types (V) react with paraformaldehyde and dimethylamine hydrochloride in absolute alcohol or acetonitrile to give a rapid evolution of carbon dioxide. After evaporation of the solvent and steam distillation, the products were characterized by NMR spectroscopy (Figs. 1–3). The results are reported in Table II. The results are included for products obtained by condensation of acetaldehyde and n-butyraldehyde with cyano-acetic acid which were first carried out in aqueous solution and which produced the glutaric acid derivatives.

The structure of the α-alkylacrylonitriles was confirmed by use of infrared and nuclear magnetic resonance spectroscopy. Typical infrared spectra of the α-n-propyl-, α-isobutyl-, and α-n-decyl derivatives are given in Figures 4–6. The NMR spectra were taken either in carbon tetrachloride or on the pure liquid. In Figures 7–9 are given the NMR spectra of three α-alkyl derivatives. The peaks of the functional groups differ by 0.01 to 0.02 τ when measured in CCl_4 and in the pure liquid. Significant differences are shown between the neopentyl, isobutyl, and n-alkyl derivatives. There
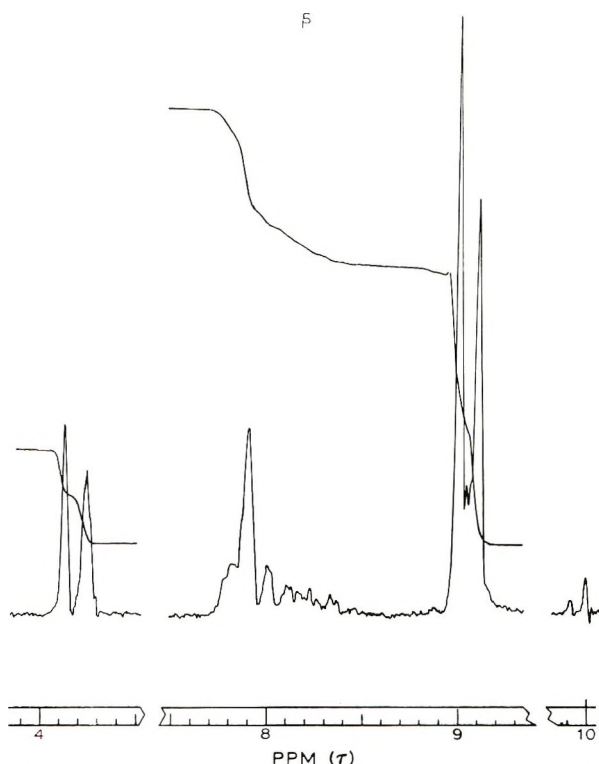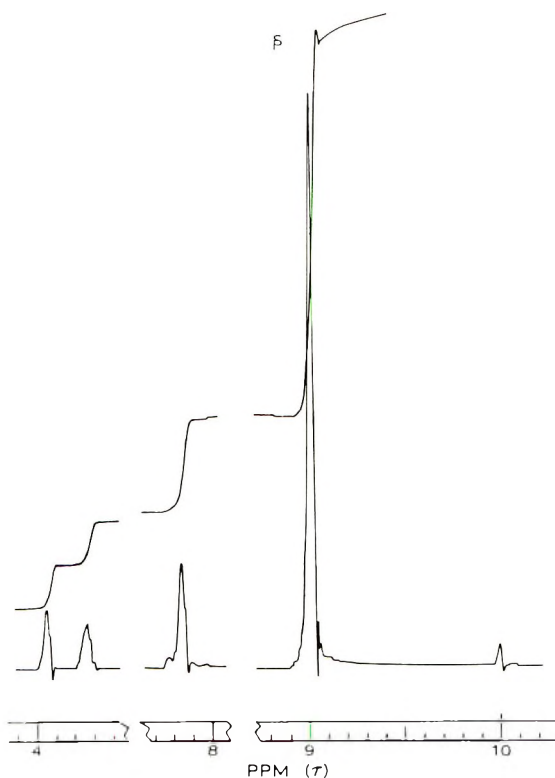
Fig. 8. NMR spectrum of α-isobutylacrylonitrile (no solvent).

is a singlet in the methyl group of the neopentyl, a doublet of the isobutyl derivative, and a triplet in the case of n-propyl. The areas under the proton peaks confirm the structure of each monomer. The other derivatives were examined and analyses were taken.

Homopolymerization Studies

Previous work has shown that α-methacrylonitrile homopolymerizes by radical initiation, but with the alkyl substituents ethyl to n-amyl, no polymerization occurred within the normal conditions. It was surprising to find that the n-heptyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl derivatives all polymerized readily in emulsion systems with potassium persulfate as the initiator. The results are tabulated in Table III. All of the polymers were slightly yellow and were sticky, rubberlike polymers which adhered to polished metal. Higher inherent viscosities were obtained with lower alkyl substituents. The polymers were soluble in tetrahydrofuran, benzene, ether, and hexane and were insoluble in dimethylformamide and dimethyl sulfoxide. Infrared spectra show no double bond absorption; a peak at 3450 cm.$^{-1}$ may indicate hydroxyl endgroups and a peak at 1680 cm.$^{-1}$ suggests some possible hydrolysis of the cyano group to yield a carboxyl derivative.

Fig. 9. NMR spectrum of α-neopentylacrylonitrile (no solvent).

TABLE III

Emulsion Homopolymerization of α-Substituted Acrylonitriles[a]
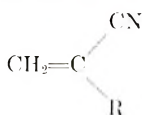
$$CH_2=C \begin{matrix} CN \\ \\ R \end{matrix}$$

R	Monomer, ml.	Potassium persulfate, g.	Emulsifier, g.	Time, hr.	Conversion, %	η_{inh}[b]
n-Heptyl	10.0	0.4	0.5	24	96.0	0.17
n-Octyl	10.0	0.4	0.5	24	95.0	0.12
n-Nonyl	10.0	0.4	0.5	24	93.8	0.13
n-Decyl	5.0	0.2	0.25	24	97.3	0.12
n-Decyl	5.0	0.05	0.25	24	70.8	0.14
n-Dodecyl	5.0	0.2	0.25	24	95.2	0.11
n-Propyl	1.8	0.1	0.25	24	No polymerization	
Neopentyl	3.0	0.06	0.125	24	Oily product	

[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end over end.

[b] Determined in tetrahydroduran as 0.5% solution at 30°C.

Homopolymerizations were carried out with anionic initiators. Natta and Dall'asta[10] obtained highly crystalline, insoluble polymers from the lower alkyl-substituted acrylonitriles. We obtained yellow polymers of low softening point, but polyneopentylacrylonitrile melted above 360°C. The polymers were readily soluble in dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and ether when methylmagnesium bromide was used as the initiator. The higher alkyl-substituted acrylonitriles (C_7–C_{12}) did not homopolymerize with mesityl- and methylmagnesium bromide initiators in tetrahydrofuran solution at low temperature. The results are summarized in Table IV.

Homopolymerization of the 2,4-dicyano-3-alkyl pentadiene-1,4 (Table II) could not be effected with radical initiators, such as benzoyl peroxide, AIBN, and redox systems. Low molecular weight polymers were obtained with anionic initiators. The results are given in Table V. All polymers were yellow and had high softening points. Many were soluble in di-methylformamide, tetrahydrofuran, dimethyl sulfoxide, pyridine, acetone, and chloroform. The polymers prepared at −78°C. were found to be more stable at elevated temperatures. They show weak carbonyl absorption in the infrared at 1620 cm.$^{-1}$ and strong double bond absorption at 1580 cm.$^{-1}$.

## Copolymers of α-Alkylacrylonitriles with Acrylonitrile

Copolymerizations were carried out in emulsion at 60°C. with potassium persulfate as initiator. It was demonstrated (Table VI) that the concentration of catalyst and emulsifier influenced the molecular weight of the copolymers. The increasing charge ratio of α-alkylacrylonitriles decreased the molecular weight (series of poly-α-n-propylacrylonitriles in Table VI) but did not influence the conversions very much. The polymer series of α-isobutylacrylonitrile shows (Table VI) that this type of monomer influences the molecular weight more than α-n-alkyl compounds. Supposedly, the chain transfer of the CH groups has more importance. Surprisingly, considerable increase in the molecular weight of the copolymers was observed as the size of the alkyl group increased.

NMR Spectral Analysis of the Copolymers

The problem of obtaining reactivity ratios in the copolymerization of pairs of monomers usually resolves itself into the problem of analysis of the copolymers. Nuclear magnetic resonance (NMR) offers a rapid and accurate method of analyses for these polymers. It has recently been applied to a number of monomer pairs.[11,12]

Some of the copolymers presented in Table VI were investigated by elemental analyses, but the results were not satisfactory. Therefore, the NMR technique was used. The area under the CH_3 proton peak at 8.95 τ is comparable with the integral of all of the protons in the copolymer and, therefore, this suggested a method for the determination of the α-alkyl-acrylonitrile content. Comparison was made between the integral of the

TABLE IV

Anionic Polymerization of α-Substituted Acrylonitriles

$$CH_2{=}C\begin{smallmatrix}CN\\[2pt]R\end{smallmatrix}$$
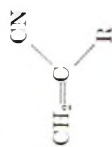
Run no.	R	Monomer, g.	Solvent type	Vol. solvent, ml.	Catalyst type	Monomer, mole-%	Temp., °C	Time, hr.	Conversion, %	η_{inh}[a]
1	n-Propyl	4.25	THF	10	CH₃MgBr	3.0	−78	72	17.5	0.088
2	n-Propyl	1.70	Toluene	20	Mg(C₂H₅)₂	~3.0	Room temp.	24	17.7	Insoluble
3	Isobutyl	2.00	Toluene	20	Mg(C₂H₅)₂	~3.0	+45	18	Trace	Insoluble
4	Isobutyl	2.00	THF	5	CH₃MgBr	3.0	−78	24	11.5	0.069
5	Neopentyl	0.85	THF	10	CH₃MgBr	5.0	−78	18	12.0	0.082
6	Neopentyl	0.85	Toluene	5	CH₃MgBr	3.0	0	24	30.0	0.062
7	Neopentyl	1.00	THF	2	CH₃MgBr	3.0	−78	72	25.0	0.076

[a] In 0.5% of the dimethylformamide solution.

TABLE V

Anionic Polymerization of 2,4-Dicyano-3-Substituted-1,4-pentadiene
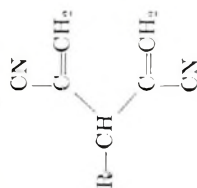
Run no.	R	Monomer g.	Solvent	Vol. solvent, ml.	Catalyst	Monomer, mole-%	Temp., °C.	Time, hr.	Conversion, %	η_{inh}[a]
1	Methyl	0.70	Toluene	5.0	Ethyl Li	3.0	0	4	23.0	0.049
2	Methyl	0.70	Toluene	5.0	CH₃MgBr	3.0	0	4	11.5	Insoluble
3	Isopropyl	0.80	Toluene	8.0	Ethyl Li	2.4	0	24	27.6	0.042
4	Isopropyl	0.80	Toluene	8.0	CH₃MgBr	3.0	0	24	25.0	Insoluble
5	tert-Butyl	0.20	THF	2.0	CH₃MgBr	3.0	−78	45	41.0	0.037
6	tert-Butyl	1.00	THF	9.0	CH₃MgBr	3.7	−78	6	8.0	—
7	tert-Butyl	0.75	THF	3.0	CH₃MgBr	5.0	0	24	10.0	0.041
8	tert-Butyl	0.50	THF	4.50	Na Ketyl	5.0	−50	17	40.0	—
9	tert-Butyl	0.50	THF	4.50	Ethyl Li	3.0	−50	16	20.0	0.0585
10	tert-Butyl	0.50	DMF	1.00	K-O-Butyl	5.0	0	24	No polymerization	—

[a] In 0.5% of the dimethylformamide solution.

TABLE VI

Copolymerization of α-Substituted Acrylonitriles and Acrylonitrile in Emulsion at 60°C. with Potassium Persulfate as Catalyst, C$_{12}$ Mercaptan as Modifier, and Sodium Dodecylbenzene Sulfonate as Emulsifier

No.	Alkyl group in α-alkyl-acrylonitriles	Recipe of acrylonitrile and α-alkyl-acrylonitrile, g./g.	Charge ratio of acrylonitrile and α-alkyl-acrylonitrile	Modifier, mg.	Potassium persulfate, g.	Emulsifier, g.	Time, hr.	Conversion, %	η_{inh} [a]	Charge ratios in the copolymers (determined by NMR) [b]	Analyses [c]		
											C, %	H, %	N, %
1	Ethyl	40/1.67	96/4	42	1.0	2.0	8	100.0	2.15	—	67.29	5.94	25.01
2	Ethyl	20.5/1.78	92/8	21	1.0	1.0	24	97.0	2.26	90.3/9.7	67.58[d]	6.14[d]	24.27[d]
											67.97	5.91	26.23
3	Ethyl	40/5.45	88/12	21	1.0	4.0	21	99.8	1.95	84.3/15.7	67.33	6.19	23.27
4	Ethyl	40/10.0	80/20	21	0.5	4.0	21	99.5	2.18	79.0/21.0	—	—	—
5	n-Propyl	20/1.25	94/6	21	1.0	1.0	24	93.2	1.40	91.3/8.7	67.25	6.13	24.01
6	n-Propyl	20/1.75	92/8	21	1.0	1.0	24	93.0	1.13	90.9/9.1	67.26	6.17	25.43
7	n-Propyl	20/2.27	90/10	21	1.0	1.0	24	97.5	1.08	88.9/11.1	67.73	6.09	24.43
8	n-Propyl	20/2.75	88/12	63	1.0	2.0	24	97.0	1.11	—	—	—	—
9	n-Propyl	20/5.0	80/20	63	1.0	2.0	24	95.2	0.97	—	—	—	—
10	n-Butyl	20/1.75	92/8	21	1.0	1.0	24	91.4	1.73	92.3/7.7	67.95[d]	6.28[d]	23.57[d]
											67.87	5.92	24.05
11	n-Butyl	20/2.27	90/10	21	1.0	1.0	24	97.4	1.37	—	67.84[d]	6.26[d]	23.19[d]
											68.38	5.84	23.27

12	n-Butyl	4.5/0.5	90/10	7	0.15	0.5	18	98.0	1.59	89.6/10.4	68.23	6.15	24.09
13	n-Butyl	40.5/5.45	88/12	42	1.0	4.0	18	100.0	1.50	—	68.01	6.64	21.78
14	n-Butyl	17.5/4.4	80/20	15	0.25	2.0	24	100.0	1.30	—	—	—	—
15	Isobutyl	9/1.0	90/10	7	0.3	0.5	18	100.0	0.43	89.7/10.3	—	—	—
16	Isobutyl	6/4.0	60/40	7	0.3	0.5	18	25.0	0.09	68.0/32.0	—	—	—
17	Isobutyl	5.3/4.7	53/47	7	0.3	0.5	18	17.0	0.08	56.0/44.0	—	—	—
18	Isobutyl	4.5/5.5	45/55	7	0.3	0.5	18	Trace	—	—	—	—	—
19	n-Heptyl	40/3.8	92/8	42	1.0	2.0	24	97.2	1.83	—	—	—	—
20	n-Heptyl	40/5.45	88/12	42	1.0	2.0	24	97.6	1.93	—	—	—	—
21	n-Heptyl	20/5.0	80/20	21	0.5	1.0	24	100.0	1.67	—	—	—	—
22	n-Octyl	10/2.50	80/20	14	0.25	0.5	24	100.0	1.86	—	—	—	—
23	n-Nonyl	10/2.5	80/70	14	0.25	0.5	24	100.0	2.29	—	—	—	—
24	n-Decyl	10/2.5	80/70	14	0.25	0.5	24	99.5	2.78	—	—	—	—
25	n-Dodecyl	10/2.5	80/20	14	0.25	0.5	24	99.0	2.12	—	—	—	—
26	Neopentyl	20/1.7	92/8	21	0.50	1.0	24	55.0	0.71	92.8/7.2	—	—	—
27	Neopentyl	20/2.64	88/12	21	0.50	1.0	24	42.2	0.64	90.3/3.9	—	—	—
28	Neopentyl	20/4.87	80/20	21	0.50	1.0	24	23.7	0.28	86.5/13.5	—	—	—
29	Neopentyl	5/2.72	65/35	7	0.125	0.25	24	10.4	0.12	—	—	—	—
30	Neopentyl	2.5/2.5	50/50	7	0.125	0.25	24	Trace	—	—	—	—	—

[a] Determined in dimethylformamide by 0.5% solution at 30°C.; all polymers were completely soluble.

[b] Water used in a charge ratio of 1:3 (monomer/water).

[c] Calculated for acrylonitrile: C, 67.92%; H, 5.69%; N, 26.39%.

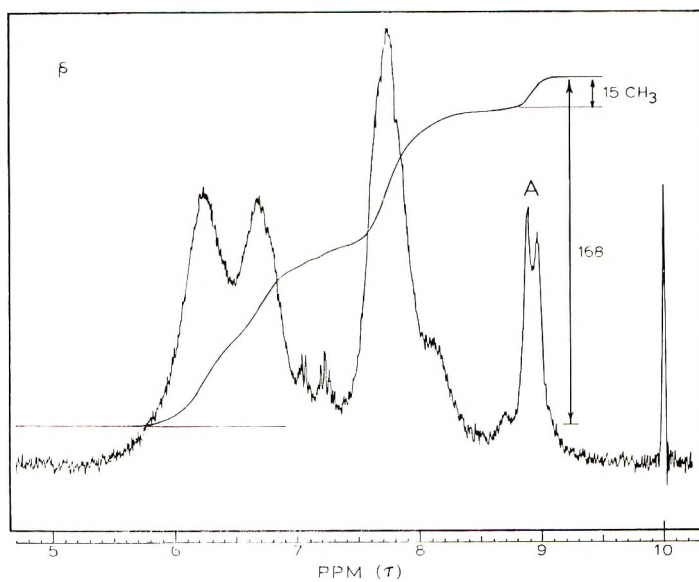[d] Determined after precipitation of the copolymers from dimethylformamide in water.

Fig. 10. NMR spectrum of copolymer acrylonitrile–α-isobutylacrylonitrile, No. 15 in
Table VI [12% DCON(CD₃)₂].

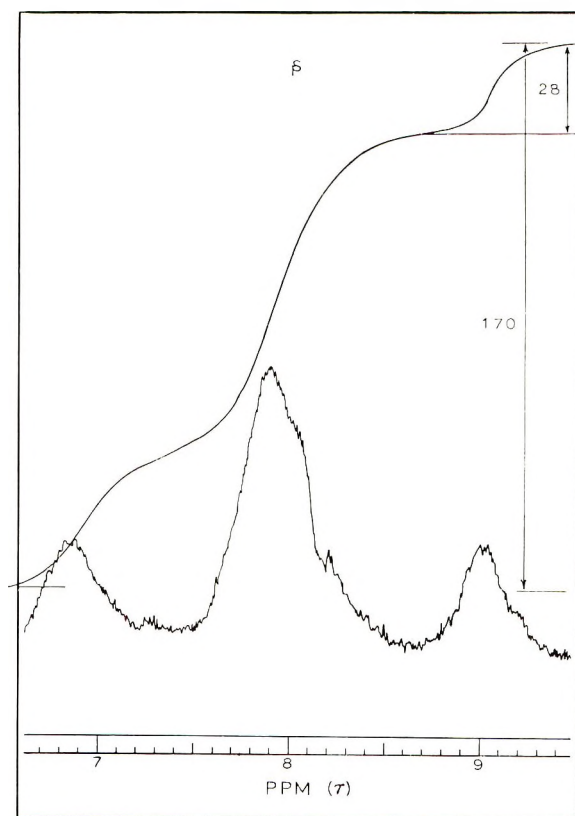Fig. 11. NMR spectrum of copolymer acrylonitrile–α-neopentylacrylonitrile, No. 28 in
Table VI [12% in DCON(CD₃)₂].
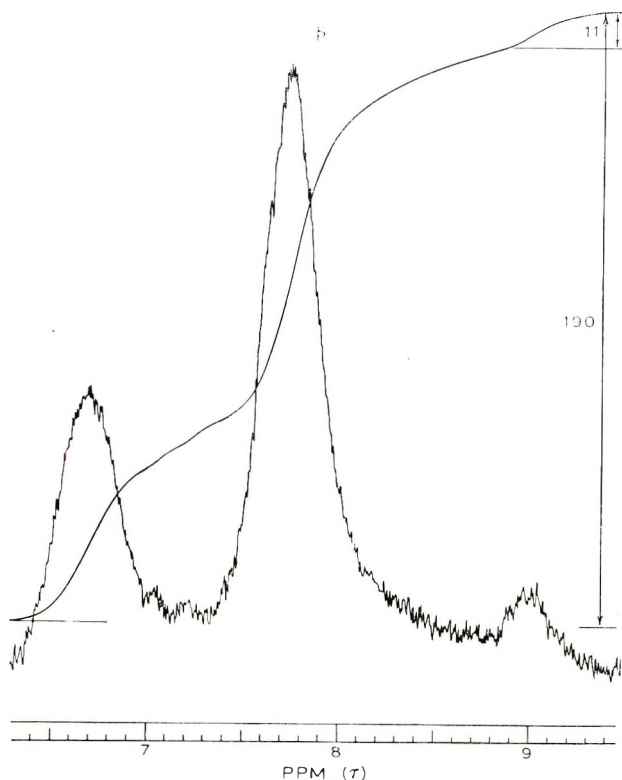
Fig. 12. NMR spectrum of copolymer acrylonitrile–α-*n*-propylacrylonitrile, No. 7 in Table VI [12% in DCON(CD₃)₂].

CH₃ proton peak (*A* in Fig. 10) 8.95 τ and the integral of all of the proton absorption (Fig. 10). Some results of the calculations of the ratios of monomers in the copolymer are presented in Table VI. Copolymers of low molecular weight (Figs. 10 and 11) have better resolution than those of high molecular weight (Fig. 12).

EXPERIMENTAL

General Method of Preparation of α-Alkylacrylonitriles

Into a 500-ml. flask, used for the hydrogenation, were placed 85 g. (1.0 mole) (in the case of *n*-dodecylaldehyde 42.5 g., 0.5 mole) of cyanoacetic acid and 100 ml. (50 ml.) of acetonitrile. After the cyanoacetic acid had dissolved, 1.2 mole (0.6 mole) of an aldehyde, 1.0 g. of palladinized charcoal (10% palladium) and while cooling, 2 ml. of piperidine was added. The hydrogenation was started immediately at a pressure of 1–3 atm. In 12–48 hr., the theoretical amount of hydrogen (1.0 mole) had been taken up and absorption ceased.

After hydrogenation, the solution was filtered from palladiumized charcoal into a 1-liter, round-bottomed flask and 81.5 g. (1.0 mole) of dimethyl-

amine hydrochloride and 36 g. (1.2 moles) of paraformaldehyde were added. The mixture was heated slowly to 90–95°C. in an oil bath. The reaction began at 70°C., and vigorous evolution of CO_2 was observed. After 3 hr. at reflux temperature, the solution was cooled, acetonitrile evaporated under vacuum, 100 ml. of water added, and the mixture steam-distilled. The oily layer was extracted with ether, dried over magnesium sulfate, the ether removed, and the residue was fractionated. The results are given in Table I.

Special Method of Preparation of α-Neopentylacrylonitrile

Into a one-liter, three-necked, round-bottomed flask, equipped with stirrer and condenser, was placed 85 g. (1.0 mole) of cyanoacetic acid dissolved in 100 ml. of water. This solution was neutralized by addition of 53.0 g. Na_2CO_3 dissolved in 150 ml. of water. Pivalaldehyde (103 g., 1.2 mole) was added under vigorous stirring, followed by 5.0 g. NaOH in 25 ml. of water. The stirring was continued for 4 hr. at 40°C. and an overnight period at room temperature. After this time, 120 ml. of concentrated hydrochloric acid was added dropwise to neutralize the solution. It was kept cold overnight, and the crystals were filtered and recrystallized from dilute ethanol (10%). A yield of 41.0 g. (27.8%) of α-cyano β-tert-butylacrylic acid, m.p. 121–125°C. was obtained. The condensation product (40 g.) was then dissolved in 100 ml. acetonitrile, 0.5 g. of palladinized charcoal (10% palladium) added, and hydrogenated. The hydrogenation was rapid and was complete after 1.5 hr.

After hydrogenation the solution was filtered from palladinized charcoal, 21.3 g. (0.261 mole) of dimethylamine hydrochloride and 9.4 g. (0.312 mole) of paraformaldehyde were added, and the mixture was heated slowly to 90–95°C. It was maintained at this temperature with stirring for 5 hr. and overnight at room temperature. The acetonitrile was evaporated, the residue steam distilled, and the oily layer was fractionated. A yield of 78.0% was obtained. The results are given in Table I.

General Method of Preparation of
3-Substituted 2,4-Dicyano-1,4-Pentadiene

Into a 500-ml., three-necked, round-bottomed flask, equipped with stirrer, condenser, and thermometer, were placed 0.264 mole of aldehyde, 189 ml. of 2.65M sodium cyanoacetate solution, and 2.43 g. of sodium hydroxide in 85 ml. of water.

The contents were then stirred vigorously. The flask was heated to 50–52°C. for 15 min. in a warm water bath. At the end of this time, the bath was removed and the stirring was continued for 2 hr. An additional 60 ml. of sodium cyanoacetate solution and 0.76 g. of sodium hydroxide in 5 ml. of water were added. The contents of the flask were reheated to 50–55°C. for 20 min. and stirring was continued for 3 hr. at room temperature. The solution was made neutral to litmus by the careful addition of concentrated hydrochloric acid. A 40–50 ml. excess of hydrochloric acid

was added to the neutral solution. The brown oil which formed was induced to crystallize by scratching the sides of the flask with a glass rod. After thorough chilling at 0°C., the crystals were removed by filtration. The required 3-alkyl-2,4-dicyanoglutaric acids were separated through fractional crystallization from dilute ethanol (10%). Yields of 38.3% 3-methyl-2,4-dicyanoglutaric acid, 67.0% 3-isopropyl-2,4-dicyanoglutaric acid, and 62.0% 3-tert-butyl-2,4-dicyanoglutaric acid were obtained.

A solution of 0.225 mole of one of the above products, 0.45 mole of dimethylamine hydrochloride, and 0.55 mole of paraformaldehyde in 80 ml. of absolute alcohol was prepared and stirred at 80°C. for 3 hr. The absolute alcohol was removed by vacuum distillation and the residue steam-distilled. The products were recrystallized from petroleum ether (30–60°C.) or distilled. Yields of 28% of 3-methyl-2,4-dicyano-1,4-pentadiene, 42.8% of 3-isopropyl-2,4-dicyano-1,4-pentadiene, and 43.0% of 3-tert-butyl-1,4-pentadiene were obtained. The last compound was sublimed at 83.5°C. to produce larger white crystals (see Table II).

Anionic Polymerization of α-Alkylacrylonitriles and 2,4-Dicyano-3-Alkylpentadiene-1,4

Solvents. Tetrahydrofuran was dried over sodium, then calcium hydride, and distilled. It was kept over lithium aluminum hydride and redistilled immediately prior to use. Toluene was dried over calcium hydride and distilled. Dimethylformamide was dried over calcium hydride and distilled under vacuum.

Catalysts. Methylmagnesium bromide was obtained from the Aropachoe Chemicals, Inc. Ethyllithium solution in benzene was obtained from the Lithium Corp. of America, Inc. Magnesiumdialkyl was prepared from the corresponding Grignard reagent.

Monomers. Monomers were distilled under nitrogen before polymerization.

Polymerization. The solvent was placed in a polymerization tube, then cooled down to the desired temperature and the tube was filled with argon. After the monomer was dissolved, the catalyst was added through a rubber stopper with a syringe. After polymerization was complete, 1 ml. of methanol hydrochloric acid solution was added and the polymer precipitated in methanol or water. Results are in Tables V and VI.

Homopolymerizations of α-Alkylacrylonitriles in Emulsion

Into a 250-ml. pressure tube was placed 0.5 g. of sodium dodecylbenzene sulfonate and under nitrogen, 50.0 ml. of water, 10.0 ml. of the monomer, and 0.4 g. of potassium persulfate were added. The emulsion was shaken for 15 min., then put in the polymerization bath at 60°C. After polymerization, the emulsion was poured into 200 ml. of water, and concentrated hydrochloric acid was added until the polymer was coagulated completely. After standing for 6–8 hr., the mixture was filtered and the polymer washed

until the filtrate was no longer acidic. For purification, the polymer was dissolved in tetrahydrofuran and precipitated in water.

Copolymerizations of Acrylonitrile with α-Alkylacrylonitrile

The copolymerizations were carried out in a 250-ml. pressure tube. Emulsifier (sodium dodecylbenzenesulfonate 1 g.) was added to the tube, and it was filled with nitrogen; 70 ml. of oxygen-free water was added followed by 25 ml. of acrylonitrile, 21 mg. of dodecyl mercaptan and the α-alkylacrylonitrile. The potassium persulfate was added without solvent. The emulsion was shaken for 15 min. and then put into the polymerization bath at 60°C. After polymerization, the emulsion was poured into a large amount of methanol, and filtered. Then the polymers were allowed to stand in a large amount of water for 24 hr. and filtered. For purification, some samples were dissolved in dimethylformamide and precipitated in water (see Table VI).

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Résumé

On a condensé des aldéhydes aliphatiques avec l'acide cyanoacétique: les intermédiaires oléfiniques résultants ont été hydrogénés et soumis ensuite à une réaction du type Mannich pour donnér des α-alcoylacrylonitriles avec des groupes alcoyles dans un domaine comprenant un nombre de C allant de C_1 à C_2. Il n'a pas été nécessaire d'isoler les intermédiaires lorsque les réactions ont eu lieu en solution dans l'acétonitrile. Les α-alcoylacrylonitriles avec des groupes alcoyles en C_7 ou supérieurs polymérisent radicalairement en émulsion pour donner des polymères collants et des produits caoutchouteux qui possèdent des caractéristiques adhésives. Par initiation anionique on n'obtient pas de polymères avec les α-alcoylacrylonitriles qui contiennent des groupes alcoyls importants, mais par contre, on obtient des produits colorés de bas poids moléculaire lorsque le substituant de l'acrylonitrile est en C_2, C_3 ou C_4. On a préparé quelque-copolymères d'α-alcoylacrylonitrile avec l'acrylonitrile par initiation radiclaire ens émulsion. Les rapports en monomères dans ces copolymères ont été déterminés par résonance nucléaire magnétique.

Zusammenfassung

Aliphatische Aldehyde wurden mit Cyanessigsäure kondensiert, die entstehenden olefinischen Zwischenprodukte hydriert und dann einer Mannich-Reaktion zur Bildung von α-Alkylacrylnitrilen mit Alkylgruppen von C_1 bis C_{12} unterworfen. Bei Durchführung der Reaktionen in Acetonitrillösung war keine Isolierung der Zwischenprodukte notwendig. Die α-Alkylacrylnitrile mit C_7- oder häheren Alkylgruppen in der Kette polymerisieren bei Radikalstart in Emulsion unter Bildung klebriger, kautschukartigir Polymerer mit Klebestoffeigenschaften. Anionischer Start ergab bei den α-Alkylacrylnitrilen mit höheren Alkylgruppen keine Polymeren, führte aber bei C-bis C_4-alkylsubstituierten Acrylnitrilen zu niedermolekularen gefärbten Produkten. Einig α-Alkylacrylnitril-Acrylnitrilcopolymere wurden in Emulsion mit Radikalstart dargesstellt. Das Monomerenverhältnis in diesen Copolymeren wurde aus den kernmagnetechen Resonanzspektren bestimmt.

Polymerization of Gaseous Diazomethane on Silicone Grease

H. KUBOTA and H. MORAWETZ, *Institute of Polymer Research, Polytechnic Institute of Brooklyn, Brooklyn, New York, 11201*

Synopsis

Dow Corning high vacuum silicone grease is a powerful catalyst for the polymerization of gaseous diazomethane. The catalytic activity is due to boric ester groups incorporated in the polysiloxane contained in the grease. The polymerization rate is proportional to the area of the interface but independent of the thickness of the grease layer, indicating that only a surface layer is involved in the catalytic action. The chain length of the polymethylene formed does not depend on the area of the interface or the pressure of the gaseous monomer. The dependence of the polymerization rate and polymer chain length on temperature is analogous to that for similar processes in homogeneous solution.

INTRODUCTION

A chance observation in our laboratory showed that Dow Corning silicone grease is a very powerful catalyst for the polymerization of gaseous diazomethane. Of the constituents of the grease, the poly(dimethyl siloxane) oil and the silica filler were found to be inert, and the catalytic activity was found to be associated with borate residues introduced into the polysiloxane chain by treatment with boric oxide.

A polymerization depending on the interaction of a gaseous monomer with a catalyst contained in a liquid phase seems to have been studied previously only by Gee et al.,[1] who followed the polymerization of butadiene gas on the surface of a hydrogen peroxide solution. It seemed, therefore, worth-while to carry out a detailed investigation of the diazomethane gas–silicone grease system.

EXPERIMENTAL

Diazomethane was synthesized from (*N*-nitrosomethyl) bis-terephthalamide (du Pont) in ethylene glycol solution by a modification of a previously reported procedure.[2] The solution was warmed from −5 to 0°C., and the evolving diazomethane gas was swept by a stream of dry nitrogen through a condenser kept at 0°C. and a trap kept at −10°C. to remove traces of water and ethylene glycol. The diazomethane was then condensed in a trap containing dibutyl phthalate cooled by liquid
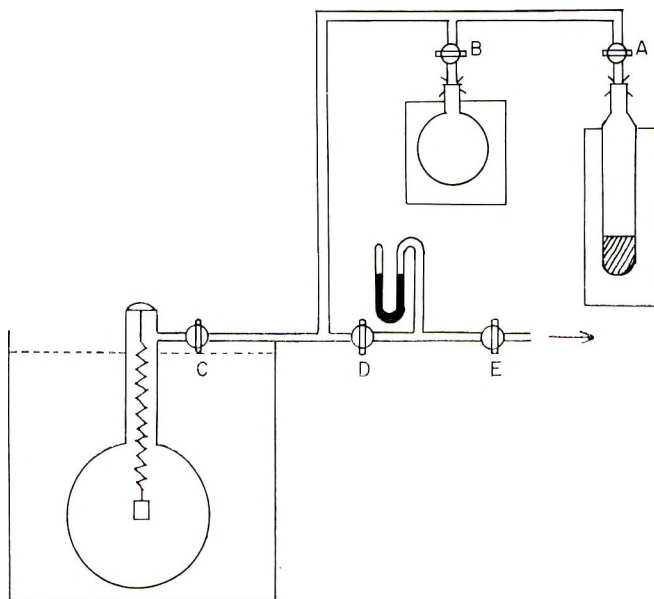
Fig. 1. Apparatus used in kinetic studies.

nitrogen. After condensing all of the diazomethane, the trap was warmed to −78°C. to allow the diazomethane and the dibutyl phthalate to mix to a viscous solution. The diazomethane was further purified by distillation under reduced pressure into another trap containing dibutyl phthalate cooled by solid carbon dioxide.

Dow-Corning high vacuum grease contained, according to the manufacturer, liquid polydimethylsiloxane with 10.3% of finely divided silica and 0.35% boric acid.

The kinetics of the polymerization were studied by the following procedure. A layer of silicone grease was pressed between an aluminum foil and a glass slide. After removal of the glass, the foil with the grease layer was weighed and suspended on a quartz helix within a thermostated reaction flask with a volume of 3170 ml. Since glass is known to catalyze the decomposition of gaseous diazomethane on prolonged contact, the inner surface was covered with a thin layer of polymethylene by filling the bulb with diazomethane at a pressure of 40 mm. Hg and keeping it for 2 days at 30°C. Any active centers in the polymethylene were then destroyed by treatment with dilute aqueous sodium hydroxide. The reaction vessel was connected to a 1-liter bulb thermostated to the same temperature as the reaction flask, the trap containing diazomethane in dibutyl phthalate, and a manometer as shown in Figure 1. After cooling the diazomethane solution to liquid nitrogen temperature, the entire system was evacuated to 10^{-3} mm. Hg. After closing the stopcocks C and E, the trap was carefully warmed to about −50°C. to allow the gaseous pressure of diazomethane to build up to the desired value. Stopcocks A and B were now closed,

and with D and E open the system was again evacuated. Now E was closed and B and C opened long enough to allow the diazomethane to enter the reaction flask. Stopcock C was now closed, the manometer reading was recorded, and the progress of the polymerization was followed by the increase of the sample weight as indicated by the extension of the quartz helix observed with a cathetometer. The manometric pressure remained approximately constant during a kinetic run, indicating that only a negligible fraction of the monomer was dissolved in the grease.

The product of the polymerization was first subjected for 200 hr. to extraction with refluxing chloroform. It was then dissolved in xylene at 130–140°C. or in decalin at 150–170°C., filtered, and precipitated into excess methanol. The material obtained in this manner had an infrared spectrum to be expected of unbranched polyethylene. Differential thermal analysis indicated a melting range of 135–141°C., and this unusually high value again suggests the absence of branching in the molecular chain. The molecular weight was estimated from the intrinsic viscosity at 135°C. in decalin containing 0.05% β-naphthylamine antioxidant, by using the relation $[\eta] = 4.6 \times 10^{-4}\overline{M}$. The viscosity measurements were carried out in a nitrogen atmosphere. The speed with which the polymer tends to degrade in the absence of antioxidant is believed to be related to the presence of some azo linkages in the chain. In some cases the temperature for viscosity determinations had to be raised to 139°C. so as to obtain a sufficient solubility of the polymer.

RESULTS AND DISCUSSION

Nature of the Catalytic Species

The high catalytic activity of the silicone grease was found to be retained in the powder remaining after extraction with boiling toluene. This treatment would be expected to remove polydimethylsiloxane, and a sample of this polymer was in fact found to be without activity. However, the silica and boric oxide known to be present in the grease were also found to be inactive. A striking observation was the loss of catalytic activity of the active ingredient on treatment with boiling methanol or boiling triethylamine.

Dr. O. K. Johannson of the Dow Corning Co. drew our attention to the possibility of an interchange reaction between the polysiloxane and boric acids which would lead to a crosslinked or less soluble polymeric product. A sample of tris(trimethylsilyl) borate $[(CH_3)_3SiO]_3B$, which he supplied to us, catalyzed powerfully the polymerization of diazomethane in ether solution. With $0.35M$ monomer and $0.028M$ catalyst, 89% of the monomer was converted to polymethylene of a molecular weight 2.8×10^5 in 21 hr. at 0°C. No reaction occurred in 24 hr. at −78°C. We found also that an active catalyst was obtained on heating 5.4 g. poly(dimethyl siloxane) fluid with 1.5 g. of boric oxide for 4 hr. in a nitrogen atmosphere at 175°C.

The catalytic activity of boric esters was previously noted by Meerwein[4] and by Korshak and Sergeyev.[5]   The cationic mechanism of the diazomethane polymerization catalyzed by BF_3 was discussed by Bawn et al.[6] and it agrees with our observation that alcohol and amine inactivate the catalyst while atmospheric oxygen does not interfere with the polymerization.

Kinetics of the Process

The following observations characterize the kinetics of the polymerization of gaseous diazomethane in contact with a layer of silicone grease.

The reaction rate is proportional to the surface area of the silicone grease but independent of the thickness of the catalyst layer (in the range of 14–28 mg./cm.²).   For instance, at 20°C. and a diazomethane pressure of 16 mm. Hg, the monomer conversion was at a rate of 8×10^{-7} mole/sec.-cm.² for surface areas from 1.5 to 7 cm.².

Ultimate monomer conversions to polymer (after 17 hr.) were in the neighborhood of 90% for initial monomer pressures above 30 mm. Hg at 27°C.   (These conversions were calculated assuming ideal gas behavior for
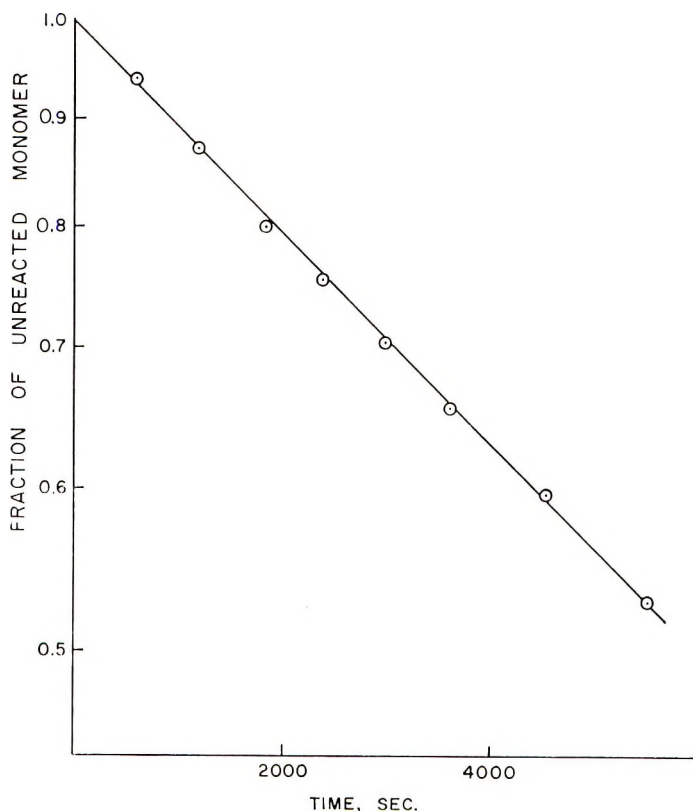

Fig. 2. First-order plot of the polymerization of diazomethane.   Temperature, 24°C.; interface area, 1.5 cm.², initial diazomethane pressure, 5.2 mm. Hg.
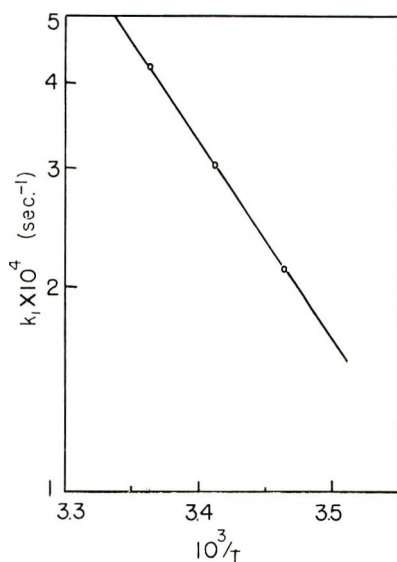
Fig. 3. Temperature dependence of the apparent initial first-order rate constant. Initial vapor pressure of diazomethane, 5 mm. Hg; interface area, 6 cm.²
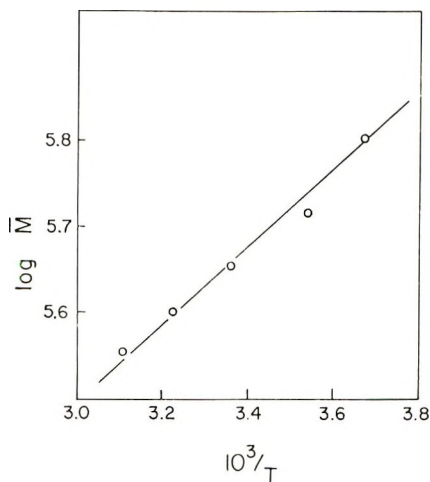

Fig. 4. Dependence of the molecular weight of polymethylene on the polymerization temperature.

the diazomethane.)   For low initial monomer pressures, the polymer yields tended to fall off, e.g., to 41% at an initial pressure of 6 mm. Hg.

The molecular weight of the polymer obtained is entirely independent of the monomer vapor pressure. With the pressure varying between 20 and 62.5 mm. Hg, the molecular weight of the polymer produced at 27 ± 2°C. remained within ±3% at 8.5 × 10⁵. The molecular weight of the polymer obtained is also independent of the surface area of the catalyst.

Plots of the logarithm of the fraction of residual monomer against time were linear up to 50% monomer conversion (Fig. 2).

The independence of the polymer chain length on the monomer pressure suggests that the chain length is governed by chain transfer to monomer. We may note that Bawn et al.[6] found the molecular weights of polymers derived from the higher diazoalkanes in the presence of BF_3 to be independent of monomer concentration, although they state specifically that the molecular weights of polymethylene increase with increasing monomer concentration.

The independence of the polymerization rate on the thickness of the catalyst layer is a most interesting feature. The catalytic species may be considered to be in a liquid phase, and we must then conclude that monomer molecules, condensing on the surface of the grease, are captured so efficiently by the cationic centers, that the probability for penetrating below a surface layer is negligible. Since the rate of collisions with the catalytic surface is proportional to the vapor pressure of residual diazomethane, first-order kinetics would be expected, unless the accumulation of polymethylene (a nonsolvent for the monomer) interferes with the condensation process. The data seem to indicate that such an effect is not significant.

The dependence of the polymerization process on temperature is depicted in Figures 3 and 4. The acceleration of the polymerization rate with increasing temperature corresponds to an apparent activation energy of 13.4 kcal./mole, quite similar to the value of 16 kcal./mole reported by Bawn and Rhodes[7] for the cupric stearate-catalyzed polymerization of diazomethane in ether solution. It may be noted that this activation energy is much lower than that observed by Shantarovich[8] for the homogeneous gas phase decomposition of diazomethane to ethylene and nitrogen ($E^{\ddagger}$ = 31.75 kcal./mole). The increase of the molecular weight of the polymethylene with a decreasing polymerization temperature corresponds to $E_p^{\ddagger} - E_{tr}^{\ddagger} = -2.1$ kcal./mole. This is also in the range characteristic of cationic polymerization processes.

A brief study of the effect of ethylene oxide vapor on the polymerization process was also undertaken. It was found that ethylene oxide reduces the molecular weight of the polymer (by about a factor of 3 when the partial pressure of ethylene oxide was 29 mm. Hg and that of diazomethane 15 mm. Hg at 24°C.), but the infrared spectrum of the product showed no evidence of ethylene oxide units in the polymer chain.

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Résumé

La graisse de silicone de Dow Corning pour vide élevé est un catalyseur puissant pour la polymérisation du diazométhane gazeux. L'activité catalytique est due à l'ester borique incorporé dans le polysiloxane contenu dans la graisse. La vitesse de polymérisation est proportionnelle à la surface de l'interface mais est indépendante de l'épaisseur de la couche de graisse ce qui indique que seulement la couche en surface est impliquée dans l'action catalytique. La longueur de chaîne polyméthylénique formée ne dépend pas de la surface de l'interface ou de la pression du monomère gazeux. La dépendance de la vitesse de polymérisation et de la longueur de chaîne polymérique en fonction de la température est analogue à celle pour des processus similaires pour une solution homogène.

Zusammenfassung

Dow Corning Silikonhochvakuumfett ist ein wirksamer Katalysator für die Polymerisation von gasförmigen Diazomethan. Die katalytische Aktivität geht auf Borsäureestergruppen zurück, die in das im Fett enthaltene Polysiloxan eingebaut sind. Die Polymerisationsgeschwindigkeit ist der Grösse der Grenzfläche proportional, aber unabhängig von der Dicke der Fettschichte, was zeigt, dass nur eine Oberflächenschichte an der katalytischen Wirkung beteilgt ist. Die Kettenlänge des gebildeten Polymethylens hängt nicht von der Grösse der Grenzfläche oder dem Druck des gasförmigen Monomeren ab. Die Abhängigkeit der Polymerisationsgeschwindigkeit und der Polymerkettenlänge von der Temperatur ist derjenigen für ähnliche Prozesse in homogener Lösung analog.

Stereospecific Polymerization of Methacrylonitrile. I.   Characterization of Crystalline Polymethacrylonitrile

YASUSHI JOH, YAHIDE KOTAKE,
TOSHIO YOSHIHARA, FUMIO IDE, and
KAZUO NAKATSUKA, *Research Laboratory,
Mitsubishi Rayon Company, Ltd., Otake, Hiroshima, Japan*

Synopsis

Methacrylonitrile (MAN) was polymerized with diethylmagnesium. Acetone-insoluble portions of the polymers are found to be crystalline. Highly crystalline portions can be isolated by further extraction of the acetone-insoluble parts with dimethylformamide (DMF). A film of DMF-insoluble fraction can be oriented uniaxially by hot-press rolling. The crystalline PMAN is insoluble in the usual solvents for amorphous PMAN because of their crystallinity and is easily soluble in CF_3COOH or $Cl_2CHCOOH$. The viscosity–molecular weight relationship was determined in $Cl_2CHCOOH$ at 30°C. as $[\eta] = 3.24 \times 10^{-3} M^{0.52}$. We found several crystalline bands in the infrared spectra, for example, at 1192 and 885 cm.$^{-1}$. Formation of the carbonyl group in the polymer is discussed, and it is concluded that it may be formed by the hydrolysis of conjugated cyclic imine or hydrolysis of the nitrile group in the polymer to acid amide.

INTRODUCTION

Recently Natta and co-workers[1] reported the syntheses of the crystalline α-alkylacrylonitrile by several organometallic catalysts. In spite of the high crystallinity of the polymers, they obtained no well-oriented sample. We also studied[2] the stereospecific polymerization of methacrylonitrile (MAN) with several organomagnesium catalysts and obtained highly crystalline polymers which can be oriented by hot-press rolling. In the present paper, some characterizations of the crystalline polymethacrylonitrile (PMAN) are described. The viscosity–molecular weight relationship for the crystalline PMAN was conveniently determined in dichloroacetic acid solution at 30°C. In the infrared spectra for the crystalline PMAN, we found several characteristic bands which are considered to be due to the crystallinity of the polymers. Formation of the carbonyl group in the polymer is also discussed.

EXPERIMENTAL

Preparation of Catalyst

Diethylmagnesium was prepared according to Schlenk's procedure[3] from Grignard reagent, special precautions being taken for exclusion of atmospheric contamination. To remove dioxane, the prepared diethylmagnesium–dioxane complex was treated at 120°C. under reduced pressure (1–2 mm. Hg) for 30 hr. The white crystals of diethylmagnesium thus obtained were powdered under a nitrogen atmosphere.

Polymerization

All manipulations were carried out under nitrogen. A three-necked separable flask equipped with stirrer and cooler was used for the polymerization. Another neck of the flask was fitted with a self-sealing rubber cap through which all the liquid reagents were added by means of syringes. To a suspension of diethylmagnesium in toluene, sufficiently purified methacrylonitrile was added dropwise with stirring at given temperatures. Polymerization started immediately, and the simultaneous appearance of a deep red color which remained during polymerization was observed. This clearly indicates the coordination between the monomer and the catalyst. When the reaction product was poured into methanol containing about 5% hydrochloric acid, the color disappeared instantly, and the polymerization stopped. The reaction mixture was allowed to stand at room temperature overnight. The precipitated white polymer was collected, washed several times with methanol, and dried *in vacuo*.

Fractionation of the Polymers

Extraction with Acetone. Crude polymers were extracted with acetone in a Soxhlet extractor for 24 hr. and were separated into soluble and insoluble parts.

Extraction with Dimethylformamide (DMF). A 1-g. portion of acetone-insoluble fraction of polymer was added to 100 ml. of dimethylformamide and treated at 100°C. for 8 hr. with stirring. The insoluble part was isolated by centrifugation, then washed thoroughly with methanol to remove the dimethylformamide, and dried *in vacuo*. The DMF-soluble part was concentrated, precipitated with methanol, and dried *in vacuo*.

Index of Solubility

The index of solubility[2] was measured as the per cent of the acetone-insoluble fraction to total yield. This value was used as one of the measure of the stereospecificity of the polymer. The index is a measure of the insoluble portion of the polymer obtained and does not represent the crystallinity of the insoluble fraction.

Viscosity

Crystalline portions of PMAN are insoluble in the usual solvents for amorphous PMAN, such as DMF and acetone. After many trials, we found that crystalline PMAN is soluble in dichloroacetic acid and that no appreciable degradation of the polymer occurs in this solution even after 2 weeks. Accordingly, in our experiments, viscosities were determined in dichloroacetic acid solutions at 30°C. in an Ubbelohde viscometer. The viscometer had a flow time of approximately 135 sec. for pure solvent, and no kinetic energy corrections were made.

Preparation of the Films

The films used for the infrared spectra and for the x-ray diffraction measurements were prepared by casting from trifluoroacetic acid solutions of the polymers at room temperature. Residual solvent can be easily removed from the films by keeping them in boiling water for 2 hr.

RESULTS

X-Ray Diffraction Measurements

Amorphous PMAN is easily soluble in many common organic solvents, for example, acetone, acetic anhydride, cyclohexanone, ethyl acetate, furfural, nitrobenzene, or pyridine. However, PMAN obtained with diethyl-
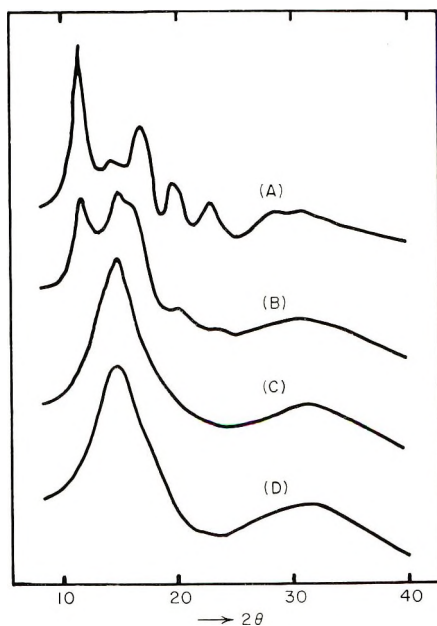

Fig. 1. X-ray diagrams for PMAN: (A) DMF-insoluble fraction; (B) DMF-soluble fraction; (C) acetone-soluble fraction; (D) radical-initiated PMAN.

magnesium is generally insoluble in the usual solvents for amorphous PMAN. For example, when the polymer was extracted with acetone, only a small portion of the polymer was extractable, and most of the polymer remained insoluble. The acetone-insoluble fractions of the polymers are crystalline. We can isolate higher crystalline portion by further extraction with dimethylformamide. Figure 1 shows the x-ray diagrams for
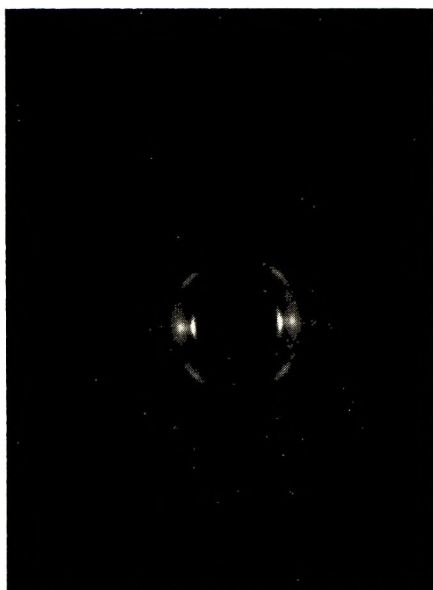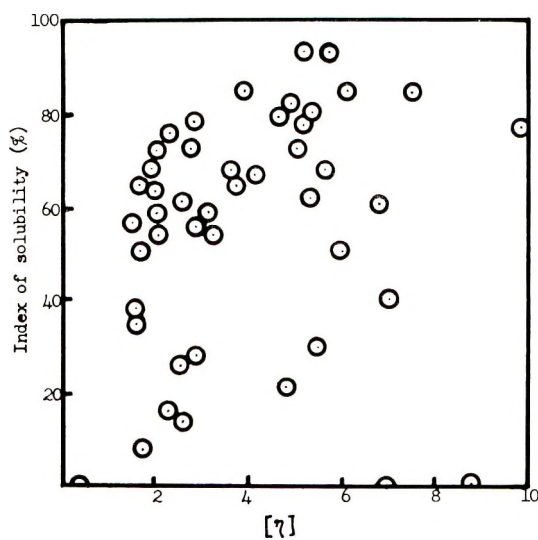

Fig. 2. X-ray fiber diagram for the DMF-insoluble fraction.

Fig. 3. Correlation between solubility index and intrinsic viscosity of polymers obtained under various conditions.

DMF-insoluble, DMF-soluble, and acetone-soluble fractions of the polymer obtained with diethylmagnesium at 70°C. together with amorphous PMAN obtained at 70°C. with a radical initiator (azobisisobutyronitrile). The DMF-insoluble fraction is highly crystalline, while the DMF-soluble fraction gives an x-ray diagram indicative of lower crystallinity. The acetone-soluble fractions are completely amorphous. The degree of crystallinity was estimated at 20% for the acetone-insoluble fraction and at 55% for the DMF-insoluble fraction. We found that the film from the DMF-insoluble fraction can be oriented uniaxially by hot-press rolling followed by drawing to about ten times the original length at 90°C. Figure 2 shows an x-ray diagram for the oriented sample.

Index of Solubility

As shown in Figure 3 there is no clear correlation between solubility index and intrinsic viscosity of the polymer. Moreover, all the polymer obtained by radical polymerization is easily soluble in acetone at room temperature, even if its intrinsic viscosity is higher than 8. This indicates that the solubility index is independent of the molecular weight and is related mainly to the stereoregularity of the polymer.

Viscosity–Molecular Weight Relationship and Huggins' Constant

The Huggins' constant k' for all fractions of the polymers obtained under various polymerization conditions were determined in dichloroacetic acid solutions at 30°C. k' for all fractions are shown to be approximately constant and are independent of the intrinsic viscosities. We obtained an average value for k' of 0.24.

The viscosity–molecular weight relationships which were determined in DMF[4] and in acetone[5] cannot be obtained for the crystalline polymers because of their insolubility in these solvents. Intrinsic viscosities for
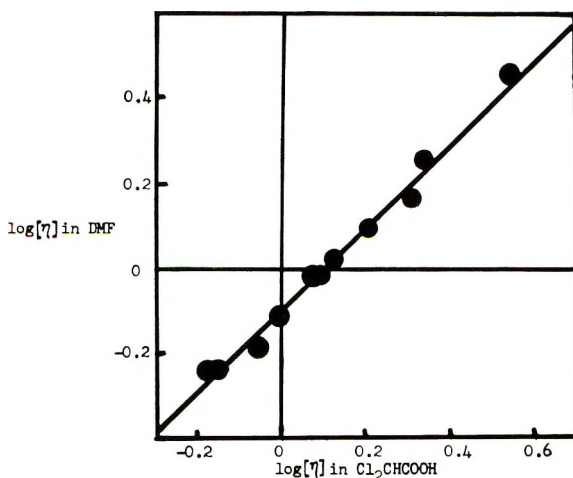

Fig. 4. Relation between intrinsic viscosities determined in $Cl_2CHCOOH$ and in DMF.

the DMF-soluble fractions were determined both in DMF and in dichloro-acetic acid. Figure 4 shows the relation between the logarithmic values of the intrinsic viscosity measured in DMF and in dichloroacetic acid. From the slope and the intercept in Figure 4, together with the viscosity-molecular weight relationship determined in DMF,[4] K and α in the equation, $[\eta] = KM^{\alpha}$ for PMAN in $Cl_2CHCOOH$ at 30°C. can be determined. Thus we obtained the following relationship:

$$[\eta] = 3.24 \times 10^{-3} M^{0.520}$$

The molecular weight of the polymers were calculated from this equation assuming that this can be applied for the DMF-insoluble crystalline poly-mers.

Infrared Spectra

Figure 5 shows the infrared spectra for (A) DMF-insoluble, (B) DMF-soluble, and (C) acetone-soluble fractions of the polymer in comparison with the radical-initiated PMAN. Evidently these polymers all give similar infrared spectra, and hence the polymers obtained with diethyl-magnesium have conventional head-to-tail sequences as in the case of the radical-initiated polymer. The infrared spectrum for the acetone-soluble fractions is especially closely similar to that of radical-initiated PMAN, no significant difference being observed between them. On the other hand, some characteristic absorption bands for the crystalline polymer are ob-
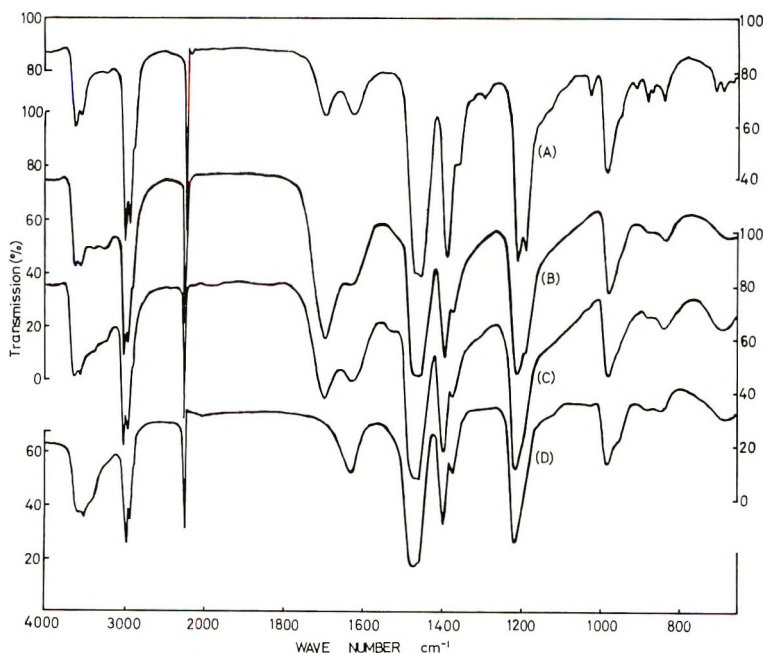

Fig. 5. Infrared spectra for PMAN: (A) DMF-insoluble, crystalline; (B) DMF-soluble; (C) acetone-soluble; (D) radical-initiated (azobisisobutyronitrile) PMAN.

served in Figure 5A, namely, the broad bands at 1210 and at 880 cm.$^{-1}$ for the amorphous polymers (Fig. 5C, 5D) are split into doublets at 1192, 1210 cm.$^{-1}$ and at 885, 875 cm.$^{-1}$ for the crystalline polymer.

It can also be seen that the absorption band at 1370 cm.$^{-1}$ for the amorphous polymer is weakened to a shoulder for the crystalline polymer. Infrared spectra for DMF-soluble fractions are intermediate between those for crystalline and amorphous polymers. For example, a shoulder at 1192 cm.$^{-1}$ was observed for this sample, as shown in Figure 5B. Absorption bands at 3640, 3560, and 1624 cm.$^{-1}$ are observed for all the polymers in Figure 5, while the observed absorption at 1697 cm.$^{-1}$ in Figures 5A, 5B, and 5C is not present in the spectrum for the radical-initiated polymer (Fig. 5D).

DISCUSSION

Solubility and Solubility Index

It is very interesting that the polymers obtained with diethylmagnesium are insoluble in the usual solvents for the amorphous PMAN. Possible reasons for their insolubility are as follows: (1) stereoregular structure and crystallinity of the polymer, (2) crosslinking in the polymer, (3) high molecular weight of the polymer which significantly reduces the solubility, (4) other structural changes in the polymer.

DMF-insoluble fractions are easily soluble in trifluoroacetic acid, dichloroacetic acid, or aqueous perchloric acid at room temperature, and no structural change was observed in the infrared spectra before and after dissolution. This indicates that there is little or no crosslinking in the polymer, and reason (2) can be ruled out. Reason (3) can be also eliminated, since there is no clear correlation between the solubility index and the intrinsic viscosity of the polymer, as shown in Figure 3. Again, the infrared spectra for the polymers obtained with diethylmagnesium closely resemble that for the PMAN obtained by radical initiation, except the absorption bands which are considered to be due to the crystallinity of the polymers. This fact also indicates that there is no significant change in the chemical structure, and reason (4) can be also ruled out. It is thus concluded that the insolubility of the polymer is certainly due to the crystallinity of the polymer.

Infrared Spectra

The absorption band at 1192 cm.$^{-1}$ and the doublets at 885 and 875 cm.$^{-1}$ are found only for the crystalline polymers. In addition, it has been recognized that these absorption bands become stronger with increasing crystallinity. These observations lead us to conclude that they are certainly crystalline-sensitive bands.

In the previous communication,[2] we reported that the observed absorption at 1624 cm.$^{-1}$ may arise from $(C=N)_x$ formed during polymerization or treatments such as extractions, film preparation, etc. However, it is
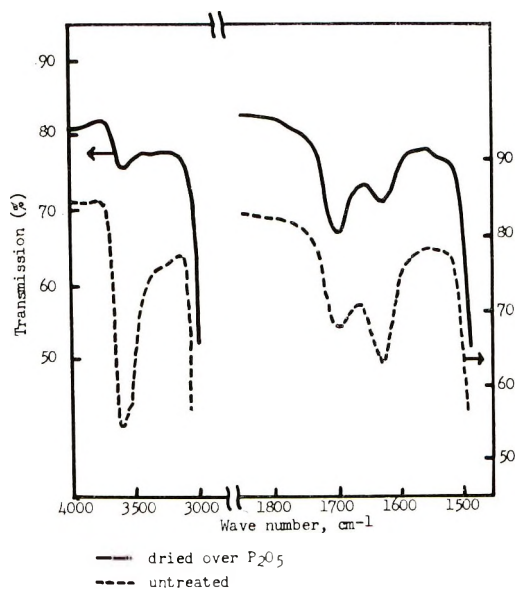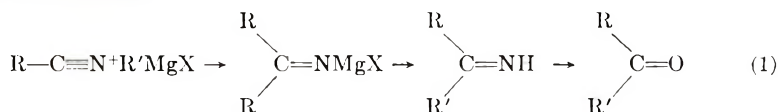
Fig. 6. Infrared spectra for PMAN: (——) dried over P_2O_5 and (--) untreated PMAN.

found that this band is not attributed to $(C=N)_x$, but to the water retained in the film, since this band, together with the bands at 3640 and 3560 cm.$^{-1}$, is weakened significantly after drying the sample over phosphorus pentoxide, as shown in Figure 6.
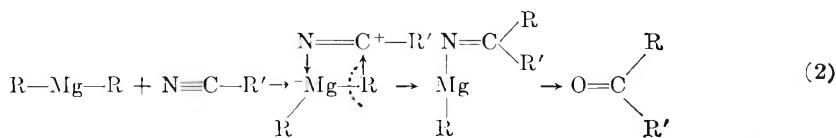
The absorption band at 1697 cm.$^{-1}$ which shows the presence of the carbonyl group in the polymer is found in every fraction of the polymers obtained with diethylmagnesium catalyst, is not observed in the radical-initiated PMAN.

The carbonyl group in the polymer may be formed by the following reactions: reaction between the catalyst and the nitrile group of the monomer or the polymer, unimolecular termination of the propagating chain, or hydrolysis of the nitrile to acid amide.

Swain[6] reported that nitrile reacts with Grignard reagent to form ketone through the scheme:

$$R\text{---}C\equiv N^+R'MgX \rightarrow \underset{R'}{\overset{R}{C}}=NMgX \rightarrow \underset{R'}{\overset{R}{C}}=NH \rightarrow \underset{R'}{\overset{R}{C}}=O \quad (1)$$

In the same manner, during the polymerization, the nitrile group of the polymer or monomer may react with diethylmagnesium. This may cause the formation of the carbonyl group in the polymer [eq. (2)].

$$R\text{---}Mg\text{---}R + N\equiv C\text{---}R' \rightarrow \underset{R}{\overset{N=C^+\text{---}R'}{Mg\text{---}R}} \rightarrow \underset{R}{\overset{N=C\overset{R}{\diagdown}R'}{Mg}} \rightarrow O=C\overset{R}{\diagdown}R' \quad (2)$$
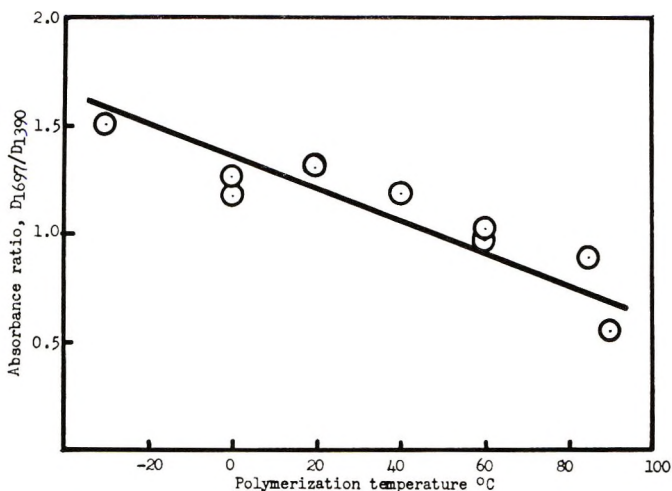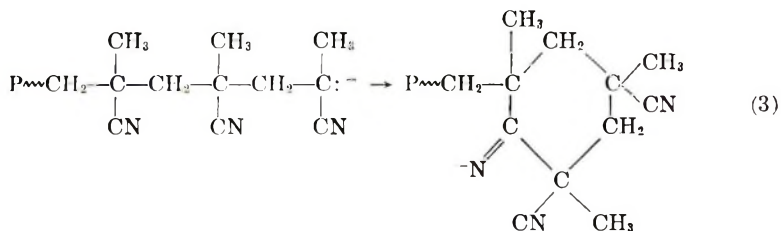
Fig. 7. Relation of absorbance ratio D_{1697}/D_{1390} to polymerization temperature.

As shown in Figure 7, the D_{1697}/D_{1390} absorbance ratio corresponding to the ratio of carbonyl and methyl group absorptions, respectively, decreased with increasing polymerization temperature. This indicates that the carbonyl in the polymer decreased with increasing polymerization temperature. It is quite unlikely that the reaction between the nitrile and diethylmagnesium is slower at higher temperatures. Furthermore, it is found that the samples with strong absorption at 1697 cm.$^{-1}$ also show an absorption band at 3200 cm.$^{-1}$. This indicates the carbonyl is present in the form of the acid amide. Consequently, explanation for the carbonyl formation by this process is not conceivable.

On the other hand, in the anionic polymerization of acrylonitrile, Otto-lenghi and Zilkha[7] reported the unimolecular termination of the propagating chain which resulted in the formation of the carbonyl at the end of the polymer chain. In the polymerization of methacrylonitrile, the same cyclization may occur as a result of the interaction of the carbanion growing end with the positive carbon of the nitrile group, so that a stable six-membered ring is obtained [eq. (3)].

$$P\text{-}CH_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{:}^{-} \rightarrow \qquad (3)$$

The imine anion is probably insufficiently basic to be able to initiate further polymerization, and on termination of the polymerization with acidic methanol, we get C=NH group, which, as known, is easily hydrolyzed to the carbonyl group, the cyclic ketone in this case. However, as already

mentioned, infrared evidence shows that the carbonyl is present in the form of the acid amide.   The imine anion may be capable of undergoing further cyclization reactions[4,8] with the pendant nitrile groups.   However, such a further cyclization could have occurred only to a small extent if at all, since the polymers obtained were almost colorless.   Subsequent hydrolysis of the conjugated imine would yield more than one acid amide group per chain.   However, the significant decrease of the absorption at 1697 cm.$^{-1}$ on extraction with DMF does not fully substantiate this explanation.

Another possible explanation for the carbonyl formation in the polymer is the hydrolysis of the nitrile in the polymer to acid amide.   Since we used methanol containing hydrochloric acid to remove the catalyst, it may be probable that acid hydrolysis of the nitrile group may occur to some extent. Interestingly, it has been demonstrated for some kinds of polymers that the hydrolysis rate of polymer is appreciably influenced by the stereoregularity of the polymer.[9-14]   In case of PMAN, we can also expect that the hydrolysis reaction is probably affected by the stereoregularity of the polymer. The higher the polymerization temperature, the higher the stereoregularity of the polymer, which may result in less reactivity for hydrolysis.   We have now no experimental data to substantiate this interpretation.   At any rate, we can not establish at present the true cause of the formation of the carbonyl in the polymer; it may be formed by hydrolysis of $(C=N)_x$ or direct hydrolysis of the nitrile group in the polymer.

The DMF-soluble fraction which is insoluble in acetone has lower crystallinity, as shown in Figure 1, and the infrared spectrum for this fraction has a strong peak at 1697 cm.$^{-1}$ as shown in Figure 5.   This fraction may be the stereoblock portion of the polymer and/or the portion which is hard to crystallize due to the presence of the amide group in the polymer, in spite of the stereoregular structure.

Detailed structural studies of the polymer are under progress and will be reported elsewhere.

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Résumé

Le méthacrylonitrile (PMAN) a été polymérisé avec le diéthylmagnésium. Des portions insolubles dans l'acétone ont été trouvées être cristallines. Les portions hautement cristallines ont été isolées par extraction ultérieures des parties insolubles dans l'acétone avec du diméthylformamide (DMF). Le film de la fraction insoluble dans le DMF peut être orientés uniaxialement par calendrage sous l'effet de la chaleur. Le PMAN cristallin est insolubl edans les solvants habituels pour le PMAN amorphe à cause de leur cristallinité. Ils sont aisément solubles dans CF_3COOH ou $Cl_2CHCOOH$. Le rapport viscosité-poids moléculaire a été déterminé dans $Cl_2CHCOOH$ à 30°C; à $[\eta] = 3.24 \times 10^{-3} M^{0.520}$ Nous avons trouvé de nombreuses bandes cristallines dans les spectres infra-rouges par exemple, à 1192 cm^{-1} et à 885 cm^{-1}. La formation de groupe carbonyle dans le polymère est discutée; on en conclu qu'il peut pêtre formé par hydrolyse de l'imine cyclique conjuguée ou par hydrolyse du groupe nitrile dans le polymère en acide amide.

Zusammenfassung

Methacrylnitril (PMAN) wurde mit Diäthylmagnesium polymerisiert. Acetonunlösliche Anteile der Polymeren erweisen sich als kristallin. Hochkristalline Anteile können durch weitere Extraktion des aceton-unlöslichen Teils mit Dimethylformamid (DMF) isoliert werden. Der Film aus der DMF-unlöslichen Fraktion kann durch Walzen auf heisser Presse uniaxial orientiert werden. Kristallines PMAN ist wegen der Kristallinität in den üblichen Lösungsmitteln für amorphes PMAN unlöslich. Es ist in CF_3COOH oder $Cl_2CHCOOH$ leicht löslich. Die Viskositäts-Molekulargewichtsbeziehung wurde in $Cl_2CHCOOH$ bei 30°C bestimmt; $[\eta] = 3.24 \times 10^{-3} M^{0.520}$. Im Infrarotspektrum wurden einige kristalline Banden, z.B. bei 1192 cm^{-1} und 885 cm^{-1} gefunden. Die Bildung der Karbonylgruppen im polymeren wird diskutiert und es wird angenommen, dass sie durch Hydrolyse konjugierter cyclischer Amine oder durch Hydrolyse der Nitrilgruppe zum Säureamid gebildet werden.

Stereospecific Polymerization of Methacrylonitrile. II. Influence of Polymerization Conditions on Polymerization and on Properties of Polymers

YASUSHI JOH, YAHIDE KOTAKE,
TOSHIO YOSHIHARA, FUMIO IDE, and
KAZUO NAKATSUKA, *Research Laboratory,
Mitsubishi Rayon Company, Ltd., Otake, Hiroshima, Japan*

Synopsis

Stereospecific polymerization of methacrylonitrile with diethylmagnesium has been studied. Polymerization temperature has an important effect on polymerization. The conversion, stereoregularity, and intrinsic viscosity of the polymer increased significantly with increasing polymerization temperature. Stereoregularity of the polymer improved with increasing the polymerization time and the monomer concentration, but it is independent of the catalyst concentration. Intrinsic viscosity of the crystalline polymer increased with increasing monomer concentration but is independent of the polymerization time and the catalyst concentration. It is suggested that two mechanisms are involved in this polymerization: coordinated anionic polymerization to form the crystalline polymer, and probably conventional anionic polymerization to form the amorphous polymer. It is found that crystalline polymer can also be obtained in homogeneous phase such as in tetrahydrofuran solvent.

INTRODUCTION

Successful synthesis[1,2] of crystalline polymethacrylonitrile (PMAN) with organomagnesium catalysts have been carried out recently, and some characterizations of the crystalline PMAN were reported in the previous paper.[3] The polymers are insoluble in the usual solvents for amorphous PMAN because of their crystallinity. It is of interest to study the influence of the polymerization conditions on stereospecific polymerization of methacrylonitrile; however no detailed study of such a polymerization has been reported so far. The purpose of this study is to examine the influence of the polymerization conditions on the polymerization and on properties of the polymers.

EXPERIMENTAL

Monomer

Methacrylonitrile (Eastman Organic Chemicals Corp.) was purified by washing with 1% aqueous sodium hydroxide solution followed by washing

with water.   It was then dried over CaCl$_2$, and fractionally distilled before use over CaH$_2$ under nitrogen.   This gave essentially a single peak when analyzed by vapor-phase chromatography; b.p. 90.3°C., n_D^{30} = 1.3942.

Catalysts

Diethylmagnesium (Et$_2$Mg) was prepared according to Schlenk's procedure as described in the previous paper.[3]   Diphenylmagnesium (Ph$_2$Mg) was also prepared in the same method from phenylmagnesium bromide.

Solvents

Toluene and heptane were treated with concentrated H$_2$SO$_4$ followed by successive washing with aqueous NaOH and water, dried over CaCl$_2$, and then distilled over metallic sodium under nitrogen.   Tetrahydrofuran was distilled before use from Na naphthalene with an excess of sodium.   Dichloroacetic acid was purified by fractional distillation over phosphorus pentoxide.   Other solvents were purified by the usual methods.   Acetone and methanol were used as received.

Polymerizations

Polymerizations were carried out in the same manner described in the previous paper.[3]   Polymers were obtained by pouring the reaction mixtures into methanol containing a small amount of hydrochloric acid.   The precipitated white polymers were collected, filtered, washed with methanol, and dried *in vacuo*.

Extraction of Polymers

Crude polymers were extracted with acetone in a Soxhlet extractor for 24 hr.   The acetone-insoluble fractions were found to be crystalline by x-ray analysis.

Index of Solubility

The index of solubility was measured as the per cent of the acetone-insoluble fraction of the total yield.   This was used as one measure of the stereoregularity of the polymer.[3]

Viscosity Measurements

Viscosities were determined in dichloroacetic acid solutions at 30°C. in an Ubbelohde viscometer which had a flow time of approximately 135 sec. for pure solvent.   No kinetic energy corrections were made.   The molecular weights of the polymers were calculated from the equation determined for DMF-soluble polymers:[3]

$$[\eta] = 3.24 \times 10^{-3} M^{0.520}$$

it being assumed that this equation can be applied for the crystalline polymers.

RESULTS

Influence of the Polymerization Temperature

Some of the results are summarized in Table I and Figures 1–3.   It is of interest that polymerization temperature has a significant effect on polymerization behavior and also on properties of the polymers.

Figure 1 shows the influence of the temperature on conversion with diethylmagnesium and diphenylmagnesium catalysts.   With diethylmagnesium catalyst (Fig. 1a), total conversion increased with increasing temperature in the range of 40 ~ 90°C. but was nearly constant at 50% con-
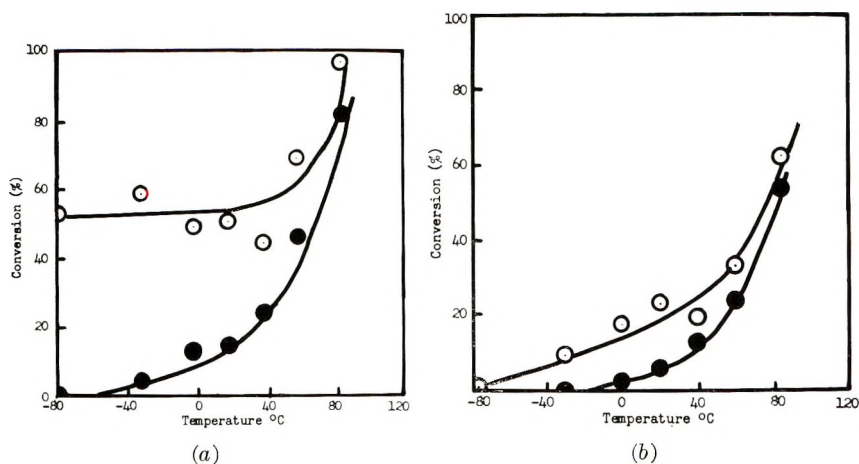

Fig. 1. Influence of polymerization temperature on conversion in the presence of (a) diethylmagnesium and (b) diphenylmagnesium: (O) total conversion; (●) conversion of acetone-insoluble fraction.   Polymerization conditions: 70 ml. toluene, 0.5 g. R$_2$Mg, 30 ml. monomer, 4 hr.
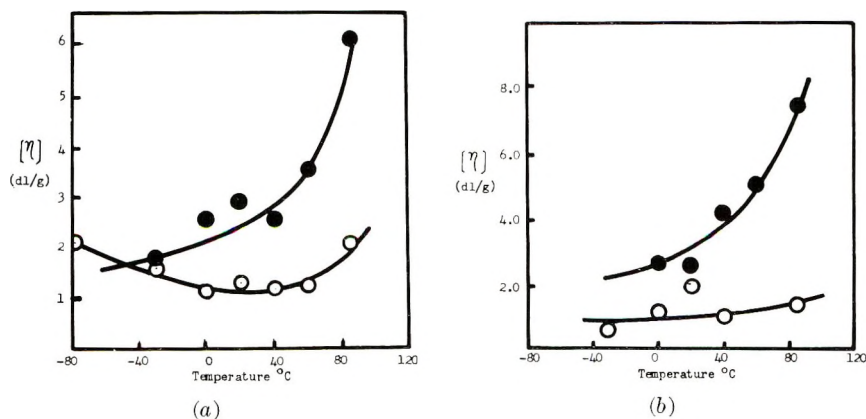

Fig. 2. Influence of polymerization temperature in the presence of (a) diethylmagnesium and (b) diphenylmagnesium on intrinsic viscosity of the polymer: (O) acetone-soluble fraction; (●) acetone-insoluble fraction.   Polymerization conditions as in Fig. 1.

TABLE I
Polymerization of Methacrylonitrile by Diethylmagnesium[a]

Polymerization temperature, °C.	Total conversion, %	Index of solubility, %	Acetone-soluble fraction		Acetone-insoluble fraction[b]		DMF-insoluble fraction	
			$[\eta]$, dl./g.	M_w	$[\eta]$, dl./g.	M_w	$[\eta]$, dl./g.	M_w
40	23.8	38.2	0.62	2.5×10^4	0.97	6.0×10^4	1.58	1.5×10^5
50	26.6	51.0	0.72	3.4×10^4	1.02	6.3×10^4	1.74	1.8×10^5
60	30.0	62.1	0.65	2.7×10^4	1.10	7.6×10^4	1.67	1.6×10^5
68	44.2	75.3	0.67	2.8×10^4	1.25	9.5×10^4	2.33	3.2×10^5
76	61.7	84.5	1.07	7.1×10^4	2.09	2.6×10^5	3.99	8.9×10^5
84	73.8	93.2	1.34	1.1×10^5	2.33	3.2×10^5	5.21	1.5×10^6

a Polymerization conditions: 0.5 g. MgEt$_2$, 370 ml. toluene, 30 ml. monomer; 4 hr.
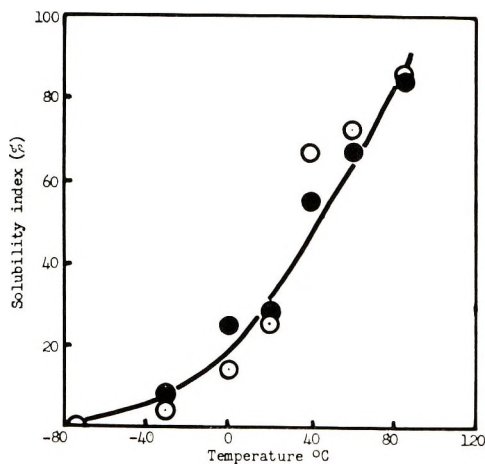b DMF-soluble.

Fig. 3. Influence of polymerization temperature on solubility index: (O) polymerization with diethylmagnesium; (●) polymerization with diphenylmagnesium. Polymerization conditions as in Fig. 1.

version at temperatures lower than 40°C. A similar trend was observed with diphenylmagnesium catalyst as shown in Figure 1b, but the catalytic activity of this catalyst is lower than that of diethylmagnesium. Almost no polymer was obtained with diphenylmagnesium catalyst at −78°C. at which amorphous polymer was obtained with 50% conversion by diethylmagnesium catalyst. Conversions of the acetone-insoluble crystalline polymers with these catalysts were markedly affected by the polymerization temperature and increased rapidly with increasing temperature.

Intrinsic viscosities for the acetone-insoluble fractions increased with increasing polymerization temperature, while those of the acetone-soluble fractions reached a minimum at about 0 ∼ 20°C. in the case of the diethylmagnesium catalyst as shown in Figure 2.

Figure 3 shows the influence of the polymerization temperature on the solubility index which can be used as one of the measure of the stereoregularity of the polymer. This value increased significantly with increasing temperature for both catalysts. It is quite interesting that polymerization rate, intrinsic viscosity of the polymer, and with the solubility index increased with increasing temperature. Generally an optimum polymerization temperature is observed[4] in stereospecific polymerizations. However, this behavior for the polymerization temperature must be a characteristic feature of the stereospecific polymerization of methacrylonitrile with these catalysts. From the Arrhenius plot of the polymerization rate, the apparent activation energy of this polymerization was estimated at 2.4 kcal./mole.

Influence of the Polymerization Time

Figure 4 shows the influence of the polymerization time on the conversion and on the solubility index of the polymer with diethylmagnesium catalyst.
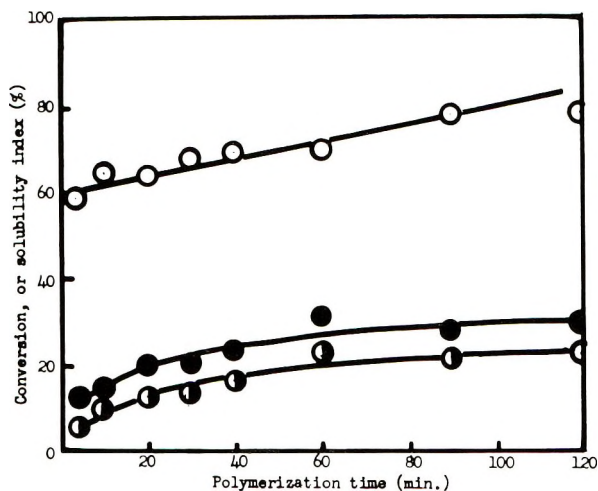
Fig. 4. Influence of polymerization time on conversion and on solubility index: (O) solubility index; (●) total conversion; (◑) conversion of acetone-insoluble fraction. Polymerization conditions: 370 ml. toluene, 0.5 g. diethylmagnesium, 30 ml. monomer, 70°C.

There is initially a rather rapid increase in conversion, followed by a long slow asymptotic increase. The solubility index increased with time in the early stage of the polymerization, then became nearly constant after 2 hr. On the other hand, intrinsic viscosities of the fractions of the polymers were approximately constant for each fraction, regardless of the polymerization time (Fig. 5).
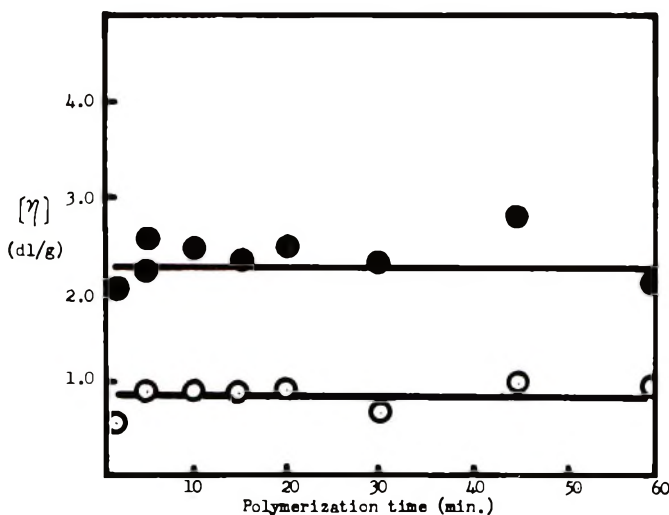

Fig. 5. Influence of polymerization time on intrinsic viscosity of the polymer: (●) acetone-insoluble fraction; (O) acetone-soluble fraction. Polymerization conditions as in Fig. 4.
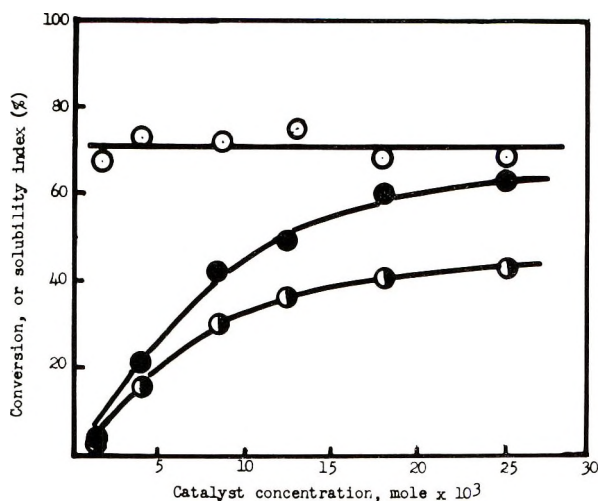
Fig. 6. Influence of catalyst concentration on conversion and solubility index: (O) solubility index; (●) total conversion: (◑) conversion of acetone-insoluble fraction. Polymerization conditions: 370 ml. toluene, 30 ml. monomer, 70°C., 1 hr.
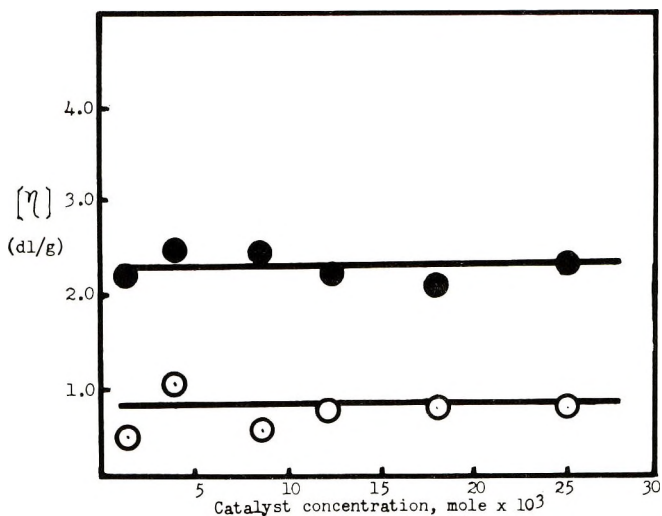

Fig. 7. Influence of catalyst concentration on viscosity: (●) acetone-insoluble fraction; (O) acetone-soluble fraction. Polymerization conditions as in Fig. 6.

Effect of the Catalyst Concentration

As shown in Figures 6 and 7, both total conversion and the conversion of the crystalline fraction increased with increasing catalyst concentration. The solubility index and the intrinsic viscosity of the polymer were approximately constant, independent of the catalyst concentration.

Influence of the Monomer Concentration

The polymerization rate is found to be proportional to the monomer concentration, as shown in Figure 8. The solubility index increased with

increasing monomer concentration. It is of interest that the intrinsic viscosity of the acetone-insoluble crystalline part increases significantly with increasing monomer concentration, while that of the acetone-soluble amorphous part is nearly constant, regardless of the monomer concentration (Fig. 9).
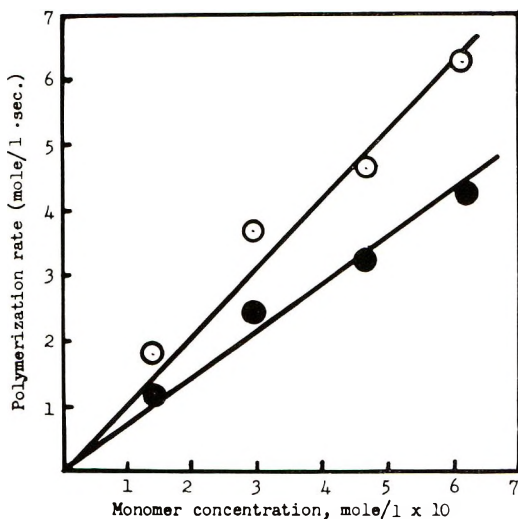
Fig. 8. Influence of monomer concentration on polymerization rate: (O) total polymerization rate; (●) polymerization rate for acetone-insoluble fractions. Polymerization conditions: toluene solvent, 0.5 g. diethylmagnesium, 70°C.

Fig. 9. Influence of monomer concentration on solubility index and on intrinsic viscosity of polymer: (◑) solubility index; (●) intrinsic viscosity of acetone-insoluble fraction; (O) intrinsic viscosity of acetone-soluble fraction. Polymerization conditions as in Fig. 8.

Influence of the Solvent

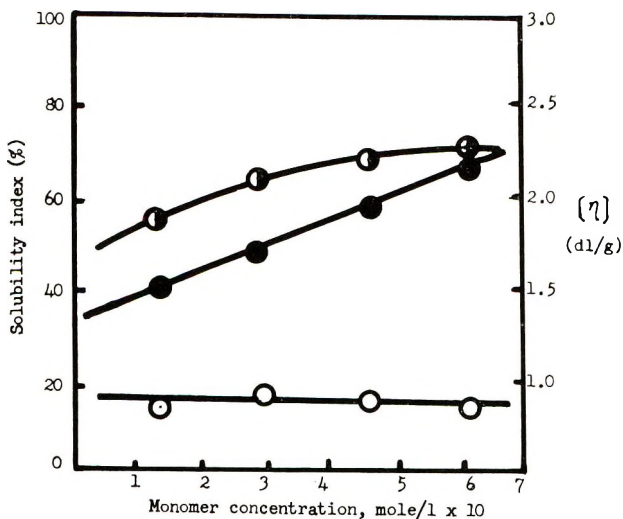The influence of the solvents on the polymerization of methacrylonitrile was examined with diethylmagnesium catalyst; some of the results are summarized in Table II. It was observed that no polymerization occurred in the solvents which have carbonyl group in the molecule, such as ethyl acetate, cylohexanone, or dimethylformamide.

TABLE II

Influence of Solvents on Polymerization of Methacrylonitrile by MgEt₂[a]

Solvent	Poly-mer-ization tem-perature, °C.	Total conversion, %	Solubility index, %	Intrinsic viscosity[b]	Molec-ular weight
Anisole	70	59.3	77.3	5.13	1.4×10^6
Dioxane	70	37.4	77.8	10.02	5.1×10^6
Tetrahydro-furan	66	39.9	75.7	3.92	8.4×10^5
Diethyl ether	35	22.0	28.9	0.82	4.2×10^4
Ethyl acetate	70	0	—	—	—
Dimethylform-amide	70	0	—	—	—
Cyclohexanone	70	0	—	—	—
Triethyl-amine-toluene[c]	70	45.3	56.7	2.20	2.8×10^5
Triethyl-amine-toluene[d]	70	48.6	66.2	1.79	2.0×10^5
Toluene	70	42.5	69.8	1.86	2.1×10^4

[a] Polymerization conditions; 0.5 g. MgEt₂, 270 ml. solvent, 30 ml. monomer, 4 hr.
[b] 30°C. in Cl₂CHCOOH for actone-insoluble parts.
[c] Toluene:triethylamine = 250:20 (volume ratio).
[d] Toluene:triethylamine = 170:100 (volume ratio).

When diethyl ether was used as solvent, polymerization activity is not so high as in hydrocarbon solvents, and the polymer obtained has lower stereoregularity. Again, the intrinsic viscosity of the polymer obtained in diethyl ether is lower than that of the polymer obtained in hydrocarbon solvent. Natta et al.[1] reported that, to obtain the stereoregular PMAN, it is necessary to use solvents which contain no electron-donor atom in the molecule. This is certainly the case with diethyl ether solvent. However, strong electron-donor solvents such as tetrahydrofuran, dioxane, or anisole do not disturb the stereospecific polymerization, and the polymers obtained in these solvents have higher stereoregularity and molecular weight than those obtained in hydrocarbon solvents.

DISCUSSION

A most interesting feature of the polymerization of methacrylonitrile with diethylmagnesium is the influence of the polymerization temperature. Polymers obtained at higher temperature have higher stereoregularity and higher molecular weights. This fact may indicate that stereospecific catalytic species are formed much more readily at higher temperature.

Considering that these stereospecific catalytic sites are formed as a result of the reaction between the monomer and the catalyst and this reaction occurs much more readily at higher temperature, this phenomenon may be reasonably interpreted. If the stereospecific catalytic species are formed in the way mentioned above, pretreated catalysts with comparable amount of the monomer at high temperature must have higher stereospecific activity even at low polymerization temperature, since the stereospecific catalytic species are already formed during pretreatment with the monomer at high temperature. However, the experimental results summarized in Table III give negative evidence, that is, the pretreated catalysts have the same stereospecific activity as untreated catalysts.

TABLE III
Effect of Pretreatment of the Catalyst with Monomer

Catalyst		Preaddition of monomer, moles	Total conversion, %[b]	Solubility index, %	Intrinsic viscosity $[\eta]$, dl./g.[c]
Compound	Moles				
MgEt$_2$	0.006	0.012	25.6	48.7	1.71
MgEt$_2$	0.006	0.006	26.4	48.9	1.03
MgEt$_2$	0.006	0.004	25.8	47.8	0.81
MgEt$_2$	0.006	0.003	24.7	47.2	0.97
MgEt$_2$	0.006	0.001	22.5	47.3	0.87
MgEt$_2$	0.006	0	25.6	51.0	1.74

[a] Pre-treatment was carried out at 90°C. for 1 hr.

[b] Polymerization conditions: 0.5 g. MgEt$_2$, 270 ml. toluene, 30 ml. monomer, 50°C., 4 hr.

[c] For acetone-insoluble fraction.

Polymerization with these organomagnesium catalysts is considered to proceed by a coordinated anionic mechanism[1] as in the case of the stereoregular polymerization of vinylpyridine with the same catalysts.[5]

In recent studies of stereoregular polymerizations, some investigators have demonstrated that there are at least two kinds of catalytic species present in catalytic systems. For example, Sakurada[6] demonstrated the presence of two kinds of catalytic species in the Ziegler type catalyst. Kato et al.[7] also reported that two mechanisms of polymerization were involved in the polymerization of methyl methacrylate with diethylmagnesium catalyst.

Similarly, in the polymerization of methacrylonitrile with diethylmagnesium, there may be two kinds of catalytic species: one, the species which induces the stereospecific polymerization by co-ordinated anionic
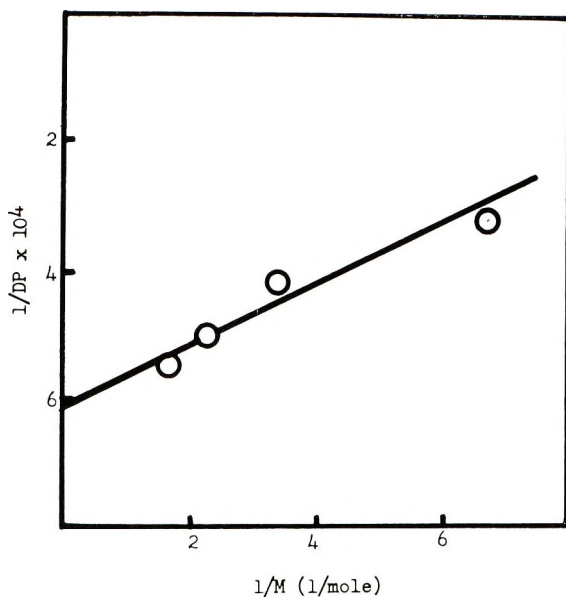
Fig. 10. Relation between 1/DP and 1/[M].

mechanism; another, the one by which amorphous polymers are formed, probably by a conventional anionic polymerization mechanism. At higher polymerization temperature, the former catalytic species may be much more reactive, and vice versa; consequently, the more highly stereoregular polymers were generally obtained at the higher polymerization temperature.

It is notable that the intrinsic viscosity of the crystalline part of the polymer increased appreciably with the monomer concentration, while that of the amorphous part was approximately constant. This also suggests that the catalytic sites for the crystalline polymer, along with the mechanism of polymerization, are different from those for the amorphous polymers. Medvedev and Gantmakher[3] and Matlack and Breslow[9] have pointed out that, in general, chain-transfer reactions in conventional anionic polymerization take place much more readily than in coordinated anionic polymerization. The acetone-soluble amorphous polymer may be formed by conventional anionic polymerization, and predominant chain-transfer reaction may control the molecular weight of the polymers. On the other hand, in the coordinated anionic polymerization, chain-transfer reactions do not occur so predominantly and hence the intrinsic viscosity of the crystalline part increased with increasing monomer concentration.

The fact that the intrinsic viscosity of the crystalline polymer is independent of the catalyst concentration and of the polymerization time indicates that this polymerization involves some chain-breaking reactions. As shown in Figure 10, 1/DP is found to be proportional to 1/[M] for the acetone-insoluble polymers. This indicates that chain-breaking reactions

in this polymerization involve monomolecular termination and chain transfer to the monomer or solvent:

$$\text{>}M_g{}^{+-}M_n + \langle\!\!\langle\ \rangle\!\!\rangle\!-CH_3 \rightarrow \text{>}M_g{}^{+-}CH_2-\langle\!\!\langle\ \rangle\!\!\rangle + HM_n$$
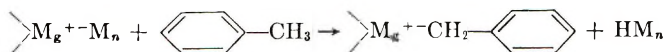
No polymerization took place in the solvents which have a carbonyl group in the molecule, probably because of the deactivation of the catalyst by the reaction between the catalyst and the solvent. The low stereo-regularity and molecular weight of the polymer obtained in diethyl ether must be due to the low polymerization temperature, since it is apparent that polymerization temperature has an important effect on the polymerization (Table I, Figs. 1–3).

Natta et al.[1] reported that diethylmagnesium which was suspended in toluene dissolved in the solvent on addition of the methacrylonitrile, but it is not so apparent in our experiments whether polymerization occurs in homogeneous phase or on the surface of the solid catalyst phase, since on addition of the monomer simultaneous precipitation of the polymer does not allow precise observation of the dissolution of the catalyst. However, it is evident that a heterogeneous phase is unnecessary for formation of crystalline polymer, because highly crystalline polymers are obtained in homogeneous phase, for example, in tetrahydrofuran solvent.

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Résumé

La polymérisation stéréospécifique du méthacrylonitrile avec le diéthylmagnésium a été étudiée. La température de polymérisation exerce un effet important sur la poly-mérisation. Le degré de conversion, la stéréospécificité et la viscosité intrinsèque du polymère croissaient de façon significative avec une augmentation de la température de polymérisation. La stéréospécificité du polymère était améliorée au augmentant la durée de polymérisation et la concentration en monomère, mais est indépendante de la concentration en catalyseur. La viscosité intrinsèque du polymère croissait avec une

augmentation de la concentration en monomère, mais était indépendante de la curée de polymérisation et de la concentration et catalyseur. On suggère que deux mécanismes ont lieu au cours de cette polymérisation, l'un est une polymérisation anionique par coordination avec formation de polymères cristallins, l'autre est probablement une polymérisation anionique conventionnelle avec formation de polymères amorphes. On a trouvé que le polymères cristallin peut également être obtenu en phase homogène, dans un solvant tel que le tétrahydrofurane.

Zusammenfassung

Die stereospezifische Polymerisation von Methacrylnitril mit Diäthylmagnesium wurde untersucht. Die Polymerisationstemperatur besass einen bedutenden Einfluss auf die Polymerisation. Umsatz, Stereospezifität und Viskositätszahl des Polymeren nahmen mit Erhöhung der Polymerisationstemperatur merklich zu. Die Stereospezifität des Polymeren verbesserte sich mit Zunahme der Polymerisationsdauer und Monomerkonzentration, sie ist aber von der Katalysatorkonzentration unabhängig. Die Viskositätszahl der kristallinen Polymeren stieg mit zunehmender Monomerkonzentration an, ist aber von Polymerisationsauer und Katalysatorkonzentration unabhängig. Es wurde angenommen, dass bei dieser Polymerisation zwei Mechanismen bestehen, der eine, eine koordinative anionische Polymerisation unter Bildung des kristallinen Polymeren und der andere wahrscheinlich eine konventionelle anionische, zur Bildung des amorphen Polymeren führende Polymerisation. Kristallines Polymeres kann auch in homogener Phase, z.B. in Tetrahydrofuranlösung erhalten werden.

Cationic and Free-Radical Polymerization of Optically Active 1-Olefins*

R. BACSKAI, *Chevron Research Company,*
Richmond, California

Synopsis

The $AlCl_3$-initiated cationic polymerization of optically active 1-olefins yields polymers of varying optical rotatory power. Polymers of (+)-3-methyl-1-pentene and (−)-4-methyl-1-hexene prepared between −78 and −55°C. in CH_2Cl_2 or *n*-heptane are almost completely optically inactive. Under identical reaction conditions (+)-5-methyl-1-heptene gives polymers of significant optical rotatory power. Alternating SO_2 copolymers of the same olefins, formed in reactions which proceed through free-radical intermediates, yield optically active products with specific rotations similar to those of low molecular weight analogs. These results are consistent with a cationic polymerization mechanism in which the growing chain undergoes intramolecular hydride shift and the asymmetric carbon atoms are converted into carbonium ions. The data also provide evidence for the lack of rearrangement in free-radical polymerization. By comparing the specific rotations of the cationic and free-radical polymers, the extent of rearrangement during cationic polymerization can be estimated. The calculations show that the 1,2-polymer in cationic poly-3-methyl-1-pentene is less than 2%, the sum of 1,2- and 1,3-polymer in cationic poly-4-methyl-1-hexene is less than 4%, and the sum of 1,2-, 1,3-, and 1,4-polymer in cationic poly-5-methyl-1-heptene is 14–20%.

INTRODUCTION

There has been considerable interest recently in polymerization reactions yielding rearranged products, i.e., polymers with repeating units other than those originally present in the monomer. A typical example of these processes, often referred to as isomerization polymerization,[1] intramolecular hydride shift polymerization,[1] or "phantom" polymerization[2] is the cationic polymerization of alkyl-substituted 1-olefins. Detailed analytical studies reported from different laboratories[1,3–5] indicate that the cationic polymerization of homologous ω-isopropyl-α-olefins gives rearranged products due to intramolecular hydride shift during polymerization. In spite of the considerable work expended in this field, there is serious disagreement between the previous investigators with regard to the extent of rearrangement.

In this paper we wish to report our work on the cationic and free-radical polymerization of optically active 1-olefins and on the use of the specific rotations of these polymers in estimating polymer composition.

EXPERIMENTAL

Materials

The monomers used in this work were synthesized by reported methods. They were redistilled before use. The boiling point, purity, and optical rotation of the monomers are shown in Table I.

TABLE I
Monomers Used in Polymerization

Monomer	Boiling point, °C.	Purity, %	Optical rotation[a]		Reported $[\alpha]_{589}$
			α_{589}^{25} [b]	$[\alpha]_{589}^{25}$	
(+)-3-Methyl-1-pentene	53.0–53.5	80.8[c,d]	+17.854°	+26.76°	+32.86°[e]
(−)-4-Methyl-1-hexene	84.5–85.5	81.4[f,g]	−1.280°	−1.83°	−2.83°[h]
(+)-5-Methyl-1-heptene	114.0	99.0[f]	+7.020°	+9.86°	+10.2°[i]

[a] 1 dm., neat.
[b] Calculated from α_{546}^{25} and α_{578}^{25}.
[c] Analysis by mass spectrometry.
[d] Contains 19.2% 4-methyl-1-pentene.
[e] 17°C., neat; data of Pino et al.[6]
[f] Analysis by vapor-phase chromatography.
[g] Contains 18.6% 5-methyl-1-hexene.
[h] 26°C., neat; data of Pino et al.[7]
[i] 25°C., neat; data of Velick and English.[8]

Sulfur dioxide (anhydrous grade, 99.98% minimum) was obtained from the Matheson Company, Inc. Before use, it was redistilled over anhydrous $CaSO_4$.

Methylene chloride and ethyl bromide were obtained from the Eastman Kodak Company. They were purified by passing through silica gel.

The $AlCl_3$ was obtained from the J. T. Baker Chemical Company (anhydrous granular, Baker Analyzed reagent). It was weighed out into screw-cap vials in a dry box before use.

Cationic Polymerization

Polymerizations were conducted with the exclusion of moisture in flamed-out glass vessels. The experimental reproducibility with respect to yield and molecular weight was satisfactory. A typical cationic polymerization was carried out as follows.

A 20-ml. glass tube equipped with a 24/40 female ground-glass joint and an appropriate adapter accommodating a thermometer, drying tube (filled with anhydrous $CaSO_4$), and side arm with rubber cap for the introduction of reactants was flamed out with a Bunsen burner. The tube was charged with 4 ml. methylene chloride and 1 ml. of catalyst solution containing 5% $AlCl_3$ dissolved in ethyl bromide. It was cooled to −75°C.

and with the aid of a hypodermic syringe 0.73 g. of (+)-3-methyl-1-pentene was added dropwise. An exothermic reaction resulted, and polymer precipitated instantaneously. During monomer addition the reaction mixture was stirred with the thermometer. Monomer addition took 13 min., and the maximum temperature was −55°C. The reaction was terminated by the addition of 10 ml. of precooled (solid CO_2–acetone) methanol. The precipitated polymer was washed with additional methanol and dried in vacuum at 80°C. The polymer yield was 0.70 g. (95.8% of theory). For purification the polymer was dissolved in n-pentane and added dropwise to an excess of methanol. The precipitated polymer was dried in vacuum and portions of it were used for intrinsic viscosity and specific rotation measurements; $[\alpha]_{589}^{25} = +0.05°$; $[\eta] = 0.20$ dl./g.

Polymerizations conducted in n-heptane proceed similarly; however, the reaction mixture gels and remains apparently homogeneous.

Free-Radical Copolymerization

Free radical copolymers of ω-alkyl-α-olefins with SO_2, shown with the example of 4-methyl-1-pentene, were prepared as follows.

The polymerization apparatus, consisting of a 6-oz., thick-walled glass bottle (Fischer and Porter Company, aerosol compatibility tube No. 110-106), equipped with a Teflon-coated magnetic stirring bar and stainless steel adapter for the introduction of reactants, was purged with nitrogen. It was cooled down in a solid CO_2–acetone bath, and SO_2 passed through anhydrous $CaSO_4$ was condensed into it. About half of the SO_2 was boiled off, and to the remaining 28 g. was added 16.8 g. of 4-methyl-1-pentene. The reaction vessel was brought to room temperature and stirred. After 75 min. a sharp increase in the viscosity of the solution was observed, and the stirrer was stopped. The reaction mixture was kept at room temperature for 16 hr. The polymerization apparatus was opened, methanol was
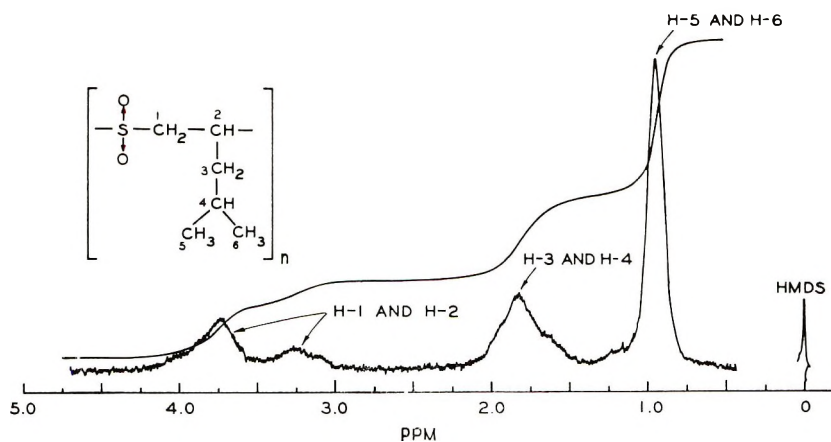

Fig. 1. 100 Mc./sec. proton magnetic resonance spectrum of free-radical 4-methyl-1-pentene/SO_2 copolymer. Polymer 8.4 wt.-% in $CHCl_3$, 30°C., hexamethyldisiloxane (HMDS) internal standard.

added, and the excess SO$_2$ was boiled off. The product, a hard white polymer, was washed with additional methanol and dried in vacuum at 80°C. The polymer yield was 7.32 g. (24.7% of theory); $\eta_{sp}/c = 3.36$ dl./g. (CHCl$_3$, 30°C.; $c = 0.1048$ g./100 ml.).

ANAL. Calcd. for the alternating 4-methyl-1-pentene/SO$_2$ copolymer: C, 48.65%; H, 8.12%; S, 21.6%. Found: c, 48.40%; H, 8.76%; S, 21.7%.

Calcd. for 3-methyl-1-pentene/SO$_2$ alternating copolymer: C, 48.65%; H, 8.12%; S, 21.61%. Found: C, 48.27%; H, 8.10%; S, 20.7%.

Calcd. for 4-methyl-1-hexene/SO$_2$ alternating copolymer: C, 51.85%; H, 8.64%; S, 19.75%. Found: C, 51.86%; H, 8.76%; S, 19.0%.

In some instances where the reaction did not start spontaneously, a few drops of cumene hydroperoxide was added as an initiator.

Polymer Characterization

Optical rotations at 546 and 578 mμ were measured with a Carl Zeiss photoelectric polarimeter (accuracy: ±0.005°). The rotation at 589 mμ was calculated by using eq. (1):

$$\alpha_{589} = \left\{ \frac{\alpha_{578}/(\alpha_{546} - \alpha_{578})}{[\alpha_{578}/(\alpha_{546} - \alpha_{578})] + 1.3727} \right\} \alpha_{546} \qquad (1)$$

The polymers used in optical activity measurements were purified by dissolving them in pentane followed by precipitation with methanol.

Repeated purification did not change the optical rotatory power of the polymers. This is shown in Table II.

TABLE II
Effect of Purification on the Optical Rotatory
Power of Cationic Poly-5-methyl-1-heptene

Sample	c, g./ml.	Optical rotation[a]		$\dfrac{[\alpha]^{25}_{589} \text{ Cationic}}{[\alpha]^{25}_{589} \text{ Free radical}} \times 100^c$
		α^{25}_{589} [b]	$[\alpha]^{25}_{589}$	
Polymer A				
1st Precipitation	0.0831	+0.329°	+3.96°	24.0
2nd Precipitation	0.1000	+0.407°	+4.07°	24.7
Polymer B				
1st Precipitation	0.1282	+0.491°	+3.83°	23.3
2nd Precipitation	0.1155	+0.448°	+3.88°	23.6

[a] 1 dm., CCl$_4$.
[b] Calculated from α^{25}_{546} and α^{25}_{578}.
[c] Calculated from data of this table and Table IV.

Intrinsic viscosities were determined in CCl$_4$ at 30°C. (unless otherwise noted).
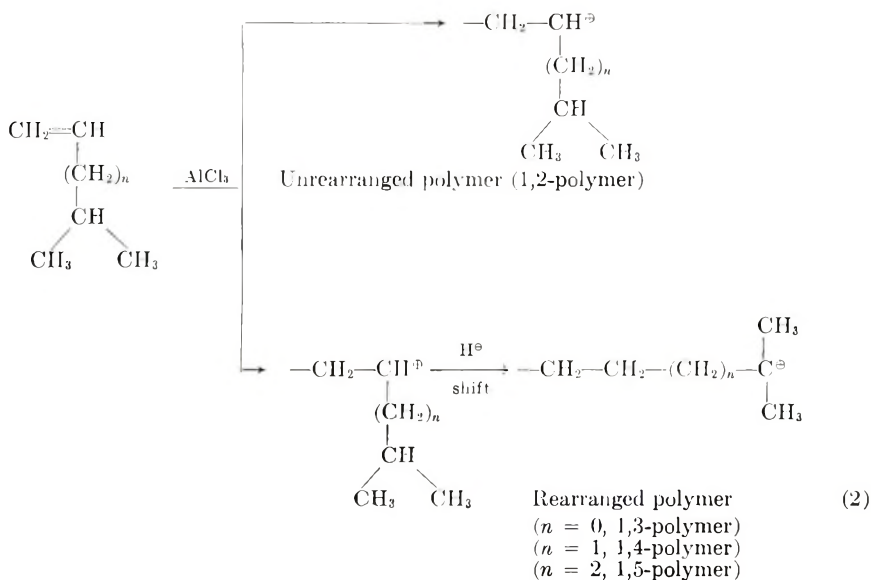
Proton magnetic resonance spectra were obtained with a Varian HA-100, 100 Mc./sec. nuclear magnetic resonance spectrometer.

RESULTS AND DISCUSSION

Cationic Polymers

It is generally agreed[1] that the cationic polymerization of ω-isopropyl-α-olefins, such as 3-methyl-1-butene, 4-methyl-1-pentene, and 5-methyl-1-hexene, involves an intramolecular hydride shift resulting in rearranged products. These polymers, depending on the monomer enchainment, are designated as 1,3-, 1,4-, and 1,5-polymers to distinguish them from the unrearranged or 1,2-polymers.

The reactions leading to unrearranged and rearranged polymers, respectively, can be represented as shown in eq. (2).

$$
\begin{array}{c}
\text{—CH}_2\text{—CH}^{\ominus} \\
\mid \\
(\text{CH}_2)_n \\
\mid \\
\text{CH} \\
\diagup \quad \diagdown \\
\text{CH}_3 \quad \text{CH}_3
\end{array}
\qquad \text{Unrearranged polymer (1,2-polymer)}
$$

$$
\begin{array}{c}
\text{CH}_2\!=\!\text{CH} \\
\mid \\
(\text{CH}_2)_n \\
\mid \\
\text{CH} \\
\diagup \quad \diagdown \\
\text{CH}_3 \quad \text{CH}_3
\end{array}
\xrightarrow{\ \text{AlCl}_3\ }
$$

$$
\begin{array}{c}
\text{—CH}_2\text{—CH}^{\oplus} \\
\mid \\
(\text{CH}_2)_n \\
\mid \\
\text{CH} \\
\diagup \quad \diagdown \\
\text{CH}_3 \quad \text{CH}_3
\end{array}
\xrightarrow[\text{shift}]{\text{H}^{\ominus}}
\begin{array}{c}
\quad\quad\quad\quad \text{CH}_3 \\
\quad\quad\quad\quad \mid \\
\text{—CH}_2\text{—CH}_2\text{—(CH}_2)_n\text{—C}^{\ominus} \\
\quad\quad\quad\quad \mid \\
\quad\quad\quad\quad \text{CH}_3
\end{array}
$$

Rearranged polymer   (2)
$(n = 0, \text{1,3-polymer})$
$(n = 1, \text{1,4-polymer})$
$(n = 2, \text{1,5-polymer})$

The driving force of the rearrangement is the transformation of secondary carbonium ion into the thermodynamically more stable tertiary carbonium ion. Further structural possibilities arise in the case of monomers where $n \neq 0$, since intramolecular hydride shifts can occur involving the hydrogen on the methylene groups. Indeed, the existence of such polymer structures has been postulated, too.[5]

Reports on the relative amounts of the different polymer structures obtained under cationic polymerization conditions are contradictory. Thus, Edwards and Chamberlain[3] reported that 3-methyl-1-butene polymerized by AlCl$_3$ yields 100% rearranged polymer over the entire temperature range (-73 to $0°C$.) investigated. However, Kennedy and coworkers[9] have estimated that the same monomer gives about 30% unrearranged polymer at -78 to $-96°C$. under practically identical reaction conditions. For the cationic polymers of 4-methyl-1-pentene produced in CH$_3$Cl with AlCl$_3$ between -73 and $-78°C$., the former group[3] claimed "predominant" 1,4-polymerization while Wanless and Kennedy[10] calcu-

lated 60% 1,4-polymer structure, 7% 1,3-polymer structure, and 33% 1,2-polymer structure. These structure determinations were based on proton magnetic resonance[3,9] and infrared[5] analysis of the polymers and were also in apparent agreement with the gas chromatographic analysis of polymer pyrolysis degradation products.

There are less data available on the cationic polymers of the analogous ω-(sec-butyl)-α-olefins, such as 3-methyl-1-pentene, 4-methyl-1-hexene, and 5-methyl-1-heptene. Since these monomers are homologs of the respective ω-isopropyl-α-olefins, they are also expected to polymerize by rearrangement. This has been confirmed for the cationic polymer of racemic 4-methyl-1-hexene, and based on infrared and proton magnetic resonance analysis, the reaction was postulated to give complete rearrangement.[11] The spectroscopic analysis of the cationic poly-ω-(sec-butyl)-α-olefins investigated in our laboratory is also consistent with polymer structures formed through intramolecular hydride shifts. The proton magnetic resonance absorptions attributed to methyl groups attached to a quaternary carbon atom,[12] and the infrared absorptions between 720 and 755 cm.$^{-1}$ characteristic for the methylene rocking vibrations of two, three, or four contiguous methylene groups, provide good evidence for the rearrangement. However, due to insufficient resolution, we find it difficult to evaluate quantitatively the extent of rearrangement by either of these methods.
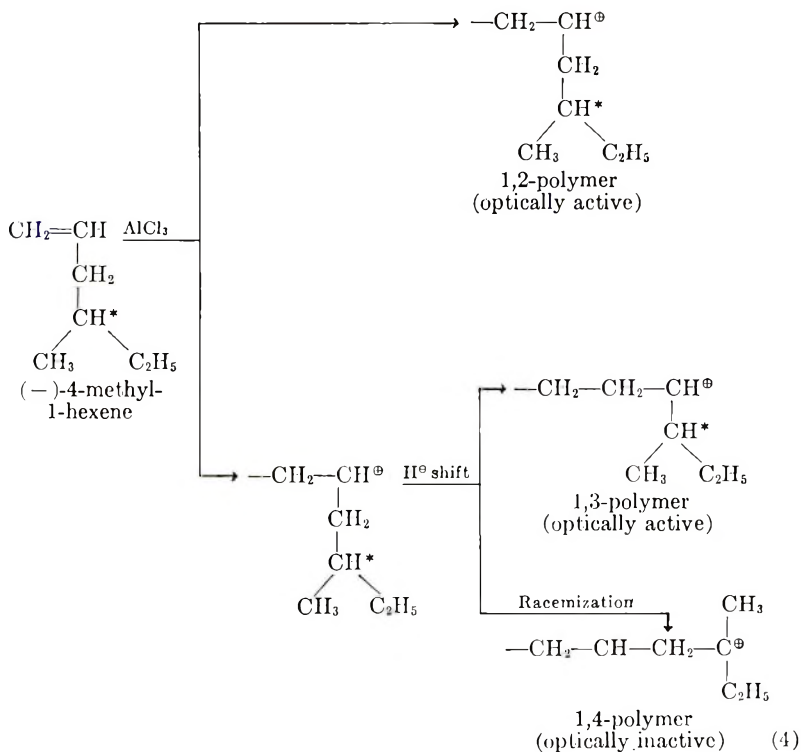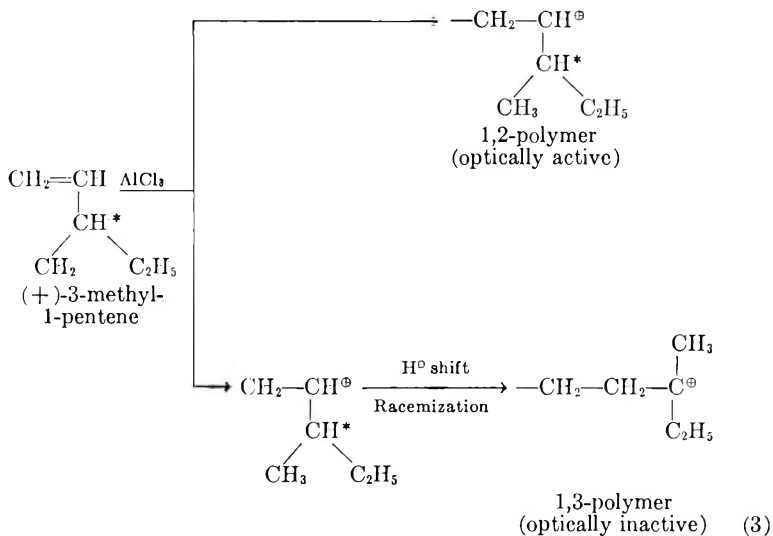
In our work we have taken a different approach to estimate the polymer composition in cationic polymers of ω-(sec-butyl)-α-olefins. The method is based on the measurement of the optical rotatory power of polymers obtained by the cationic polymerization of optically active monomers. If, as a result of intramolecular hydride shift, the asymmetric carbon atom of the growing chain is converted into a stable tertiary carbonium ion (long lifetime), then it is expected that the polymers will be optically inactive. This prediction is based on the experience gained from a large number of organic reactions, where it has been shown that optically active compounds undergoing carbonium ion reactions on the asymmetric carbon atom racemize totally if the lifetime of the carbonium ion is long.[13] If the rearrangement is incomplete and not all of the asymmetric carbon atoms of the reacting monomers are converted into carbonium ions, the resulting polymer will be optically active. It follows that the optical rotatory power of polymer mixtures will depend on the relative amounts of different polymeric structures.

Possible reaction sequences leading to optically active and inactive polymers are shown in eqs. (3)–(5). In formulating these reactions, the question whether some of the reactions proceed through one longer-range hydride shift or through a series of 1,2-hydride shifts has not been considered, since it is irrelevant to this discussion.

Low-Temperature Polymerization

A summary of low temperature cationic polymerization experiments conducted at -78 to $-55°C.$ with optically active 3-methyl-1-pentene, 4-

methyl-1-hexene, and 5-methyl-1-heptene is presented in Table III. For comparison, the specific rotations of the corresponding free-radical SO_2 copolymers discussed later are shown in Table IV. Table V shows the reproducibility of cationic polymerizations with regard to the optical rotatory power of poly-5-methyl-1-heptene obtained.

$$-CH_2-CH^\oplus$$
$$\overset{|}{CH^*}$$
$$CH_3 \quad C_2H_5$$
1,2-polymer
(optically active)

$$CH_2=CH \quad AlCl_3$$
$$\overset{|}{CH^*}$$
$$CH_2 \quad C_2H_5$$
(+)-3-methyl-
1-pentene

$$CH_2-CH^\oplus \xrightarrow[\text{Racemization}]{H^\circ \text{ shift}} -CH_2-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C^\oplus}}$$
$$\overset{|}{CH^*}$$
$$CH_3 \quad C_2H_5$$

1,3-polymer
(optically inactive)   (3)

$$-CH_2-CH^\oplus$$
$$\overset{|}{CH_2}$$
$$\overset{|}{CH^*}$$
$$CH_3 \quad C_2H_5$$
1,2-polymer
(optically active)

$$CH_2=CH \quad AlCl_3$$
$$\overset{|}{CH_2}$$
$$\overset{|}{CH^*}$$
$$CH_3 \quad C_2H_5$$
(−)-4-methyl-
1-hexene

$$-CH_2-CH^\oplus \xrightarrow{H^\ominus \text{ shift}}$$
$$\overset{|}{CH_2}$$
$$\overset{|}{CH^*}$$
$$CH_3 \quad C_2H_5$$

$$-CH_2-CH_2-CH^\oplus$$
$$\overset{|}{CH^*}$$
$$CH_3 \quad C_2H_5$$
1,3-polymer
(optically active)

$$\xrightarrow{\text{Racemization}} -CH_2-CH-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C^\oplus}}$$

1,4-polymer
(optically inactive)   (4)

$$\begin{array}{c}
-CH_2-CH^{\oplus} \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
CH^* \\
\diagup \quad \diagdown \\
CH_3 \quad C_2H_5 \\
\text{1,2-polymer} \\
\text{(optically active)}
\end{array}$$

$$\begin{array}{c}
CH_2=CH \quad \underline{AlCl_3} \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
CH^* \\
\diagup \quad \diagdown \\
CH_3 \quad C_2H_5 \\
(+)\text{-5-methyl-} \\
\text{1-heptene}
\end{array}$$

$$\begin{array}{c}
-CH_2-CH_2-CH^{\oplus} \\
| \\
CH_2 \\
| \\
CH^* \\
\diagup \quad \diagdown \\
CH_3 \quad C_2H_5 \\
\text{1,3-polymer} \\
\text{(optically active)}
\end{array}$$

$$\begin{array}{c}
-CH_2CH^{\oplus} \quad \underline{H^{\ominus}\ shift} \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
CH^* \\
\diagup \quad \diagdown \\
CH_3 \quad C_2H_5
\end{array}$$

$$\begin{array}{c}
-CH_2-CH_2-CH_2-CH^{\oplus} \\
| \\
CH^* \\
\diagup \quad \diagdown \\
CH_3 \quad C_2H_5 \\
\text{1,4-polymer} \\
\text{(optically active)}
\end{array}$$

Racemization

$$\begin{array}{c}
CH_3 \\
| \\
-CH_2-CH_2-CH_2-CH_2-C^{\oplus} \\
| \\
C_2H_5 \\
\text{1,5-polymer} \\
\text{(optically inactive)}
\end{array}$$

$$(5)$$

If it is assumed (the validity of this assumption will be discussed later) that the free-radical alternating SO_2 copolymers contain the olefinic monomer exclusively in 1,2-enchainment, then the composition of cationic polymers can be estimated.* The figures in the last column of Table III represent the per cent of 1,2-polymer in cationic poly-3-methyl-1-pentene, the per cent of 1,2- and 1,3-polymer in cationic poly-4-methyl-1-hexene, and the per cent of 1,2-, 1,3-, and 1,4-polymer in cationic poly-5-methyl-1-heptene; calculated from the specific rotations of the cationic polymers and from those of the free-radical copolymers. The data show that by using either of two different polymerization solvents the amount of 1,2-polymer formed in the low-temperature cationic polymerization of (+)-3-methyl-1-pentene is less than 2%. Similarly, with (−)-4-methyl-1-hexene the sum of 1,2- and 1,3-polymer is low and does not exceed 4%. However, con-

* For the calculation the reported specific rotations of the 1,2-polymers obtained by Ziegler catalysts are of little use owing to their abnormally high optical rotatory power attributed to the helical conformation of the polymers in solution.[14]

TABLE III

Optical Rotatory Power of Low-Temperature Cationic Polymers of $(+)$-3-Methyl-1-pentene, $(-)$-4-Methyl-1-hexene and $(+)$-5-Methyl-1-heptene[a]

Polymer	Polymerization solvent	Polymerization temperature, °C.	Conversion, %	$[\eta]$, dl./g.[b]	c, g./ml.	$\alpha_{589}^{25,\,d}$	Optical rotation[c] $[\alpha]_{589}^{25}$	$\dfrac{[\alpha]_{589}^{25}\text{ Cationic}}{[\alpha]_{589}^{25}\text{ Free radical}} \times 100$[e]
Poly-3-methyl-1-pentene	CH₂Cl₂	−75 to −55	95.8	0.20	0.0920	~0.005°	+0.05°	0.2
Poly-4-methyl-1-hexene	CH₂Cl₂	−72 to −63	96.2	0.41	0.0859	+0.079°	+0.92°	4.0
Poly-5-methyl-1-heptene	CH₂Cl₂	−77 to −61	92.5	0.33	0.1316	+0.353°	+2.68°	16.3
Poly-3-methyl-1-pentene	n-Heptane	−78 to −69	100.0	0.34	0.0554	+0.022°	+0.40°	1.9
Poly-4-methyl-1-hexene	n-Heptane	−76 to −64	100.0	0.46	0.0728	+0.015°	+0.21°	0.9
Poly-5-methyl-1-heptene	n-Heptane	−77 to −69	100.0	0.42	0.1352	+0.326°	+2.41°	14.6

[a] Polymerization: 4 ml. solvent, 1 ml. 5% AlCl₃ in C₂H₅Br, ~1 ml. monomer (added to catalyst solution), 10–13 min.

[b] CCl₄, 30°C.

[c] 1 dm., CCl₄.

[d] Calculated from α_{546}^{25} and α_{578}^{25}.

[e] Calculated from data of this table and Table IV.

siderably larger amounts 14–20%, of optically active polymer representing
the 1,2-, 1,3-, and 1,4-polymer is obtained from (+)-5-methyl-1-heptene.
This latter result is attributed to a depression of the hydride shift as the
length of the path over which it must occur increases.[3]

It is difficult to ascertain to what extent the results of this structure
analysis, carried out on the cationic polymers of ω-(sec-butyl)-α-olefins with
the aid of optically active monomer, can be extrapolated to the correspond-
ing cationic poly-ω-isopropyl-α-olefins. However, owing to the similarity
of the respective monomers, major differences in the structure of polymers
formed under analogous conditions would be unexpected. Indeed, com-
parison of the data of Edwards and Chamberlain[3] with those reported in

TABLE IV

Optical Rotatory Power of Free-Radical Alternating SO_2 Copolymers of
(+)-3-Methyl-1-pentene, (−)-4-Methyl-1-hexene,
and (+)-5-Methyl-1-heptene

Polymer	η_{sp}/c, dl./g.[a]	Optical rotation[b]		
		c, g./ml.	α_{589}^{25} [c]	$[\alpha]_{589}^{25}$[d]
(+)-3-Methyl-1-pentene/SO_2 copolymer	0.28[e]	0.0468	+0.560°	+21.13°
(−)-4-Methyl-1-hexene/SO_2 copolymer	0.11[f]	0.0521	+0.731°	+23.19°
(+)-5-Methyl-1-heptene/SO_2 copolymer	0.70[g]	0.0619	+0.650°	+16.46°

[a] $CHCl_3$, 30°C.
[b] 1 dm., $CHCl_3$.
[c] Calculated from α_{546}^{25} and α_{578}^{25}.
[d] For the calculation of $[\alpha]_{589}^{25}$ only the olefin portion of the copolymer is included in the concentration term.
[e] $c = 0.1474$ g./100 ml.
[f] $c = 0.1024$ g./100 ml.
[g] $c = 0.1040$ g./100 ml.

this work, indicates that there is no significant difference between the po-
lymerization behavior of the two homologous series of ω-alkyl-α-olefins.
In contrast, the analytical results of Kennedy and co-workers reported for
the composition of cationic poly-3-methyl-1-butene[9] and poly-4-methyl-1-
pentene[10] are different from those of the analogous poly-3-methyl-1-pentene
and poly-4-methyl-1-hexene described in this work. This is quite unex-
pected, and the anomaly requires clarification.

In order to confirm that the loss of optical activity is the consequence of
intramolecular hydride shifts occurring during the course of cationic po-
lymerization, auxiliary experiments had to be carried out to rule out other
alternatives.

TABLE V

Reproducibility of Polymer Optical Rotatory Power in Cationic Poly-5-methyl-1-heptene[a]

Solvent	Polymerization, temperature, °C.	Conversion, %	$[\eta]$, dl./g.[b]	c, g./ml.	Optical rotation[c]		
					α_{589}^{25} [d]	$[\alpha]_{589}^{25}$	$\dfrac{[\alpha]_{589}^{25}\ \text{Cationic}}{[\alpha]_{589}^{25}\ \text{Free radical}} \times 100$[e]
CH_2Cl_2[f]	−76 to −67	62.5	0.25	0.1017	+0.289°	+2.84°	17.3
CH_2Cl_2	−77 to −61	92.5	0.33	0.1316	+0.353°	+2.68°	16.3
CH_2Cl_2	−76 to −68	68.3	0.20	0.1155	+0.382°	+3.30°	20.1
n-Heptane[f]	−76 to −71	100.0	0.42	0.0840	+0.202°	+2.41°	14.6
n-Heptane	−77 to −69	100.0	0.42	0.1352	+0.326°	+2.41°	14.6
n-Heptane	−77 to −71	51.8	0.29	0.0717	+0.243°	+3.38°	20.5

[a] Polymerization: 4 ml. solvent, 1 ml. 5% $AlCl_3$ in C_2H_5Br, ~1 ml. (+)-5-methyl-1-heptene (added to catalyst solution), 13–15 min.

[b] CCl_4, 30°C.

[c] 1 dm., CCl_4.

[d] Calculated from α_{546}^{25} and α_{578}^{25}.

[e] Calculated from data of this table and Table IV.

[f] In this polymerization the methanol used to deactivate the catalyst was not precooled.

TABLE VI
Optical Rotatory Power of Starting (+)-3-Methyl-1-pentene,
Recovered (+)-3-Methyl-1-pentene, and Cationic
Poly-3-methyl-1-pentene

Compound	Optical rotation[a]		
	c, wt.-%[b]	α_{589}^{25} [c]	α_{589}^{25}/C
Starting			
(+)-3-methyl-1-pentene	10.90[d]	+4.544°	+0.417
Recovered			
(+)-3-methyl-1-pentene	9.12[d]	+3.810°	+0.418
Poly-3-methyl-1-			
pentene[e]	3.33[f]	+0.035°	+0.011

[a] 1 tube.

[b] Due to the higher reactivity of 3-methyl-1-pentene[17] these values are corrected for the 4-methyl-1-pentene content of the compounds.

[c] Calculated from α_{546}^{25} and α_{578}^{25}.

[d] Solvent: CH_2Cl_2.

[e] Polymerization: 20 ml. CH_2Cl_2, 5 ml. (+)-3-methyl-1-pentene, 1 ml. 3.3% $AlCl_3$ in C_2H_5Br (added to monomer solution), −75 to −60°C., 30 sec.   Conversion: 33.9%; $[\eta] = 0.16$ dl./g.

[f] Solvent: CCl_4.

The possibility of monomer racemization before polymerization was excluded by interrupting the reaction at partial conversion and recovering the monomer.   Such an experiment is summarized in Table VI.

It can be seen that the specific rotation of the recovered monomer is identical to that of the starting monomer while the polymer shows very weak optical rotation.   The fact that (+)-5-methyl-1-heptene yields polymers of considerable optical rotatory power, indicates that the small specific rotation observed with some of the other products (see Table III) is not caused by polymer racemization.   This was also confirmed, as shown in Table VII, by measuring the specific rotation of poly-5-methyl-1-heptene polymerized for different times.

These data show that the specific rotation of poly-5-methyl-1-heptene, within the limits of experimental error, is independent of polymerization time.   If the initially formed polymer would undergo racemization, then the polymer obtained with the longer polymerization time would have a significantly lower specific rotation.

Finally, speculations based on the racemization of the growing chain leading to optically inactive 1,2-polymer as illustrated on the example of (+)-3-methyl-1-pentene [eq. (6)] have to be rejected because this scheme
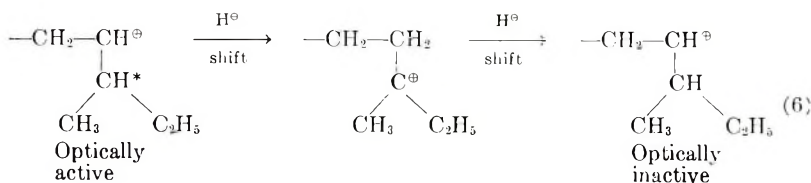
TABLE VII. Optical Rotatory Power of Cationic Poly-5-methyl-1-heptene Polymerized for Different Times[a]

Polymerization time, min.	Polymerization temperature, °C.	Conversion, %	$[\eta]$, dl./g.[b]	Optical rotation[c]			
				c, g./ml.	α^{25}_{589},[d]	$[\alpha]^{25}_{589}$	$\dfrac{[\alpha]^{25}_{589} \text{ Cationic}}{[\alpha]^{25}_{589} \text{ Free radical}} \times 100$[e]
2	−76 to −68	21.5	0.17	0.1000	+0.407°	+4.07°	24.7
8	−76 to −61	54.4	0.17	0.1155	+0.448°	+3.88°	23.6

[a] Polymerization: 4 ml. CH₂Cl₂, ~1 ml. (+)-5-methyl-1-heptene, 1 ml. 5% AlCl₃ in C₂H₅Br (added to the monomer solution); [b] CCl₄, 30°C.; 1 dm., CCl₄; [d] calculated from α^{25}_{546} and α^{25}_{578}; [c] calculated from data of this table and Table IV.

TABLE VIII. Optical Rotatory Power of High-Temperature Cationic Polymers of (+)-3-Methyl-1-pentene, (−)-4-Methyl-1-Hexene, and (+)-5-Methyl-1-heptene[a]

Polymer	Polymerization temperature, °C.	Conversion, %	$[\eta]$, dl./g.[b]	Optical rotation[c]			
				c, g./ml.	α^{25}_{589},[d]	$[\alpha]^{25}_{589}$	$\dfrac{[\alpha]^{25}_{589} \text{ Cationic}}{[\alpha]^{25}_{589} \text{ Free radical}} \times 100$[e]
Poly-3-methyl-1-pentene	−3 to +9	64.0	0.10	0.07	0	0	0
Poly-4-methyl-1-hexene	+3 to +6	85.2	0.21	0.08	0	0	0
Poly-5-methyl-1-heptene	+3 to +11	72.2	0.14	0.0745	+0.004°	+0.05°	0.3

[a] Polymerization: 4 ml. CH₂Cl₂, 1 ml. 5% AlCl₃ in C₂H₅Br, ~1 ml. monomer (added to catalyst solution), 15 min.; [b] CCl₄, 30°C.; 1 dm., CCl₄; [d] calculated from α^{25}_{546} and α^{25}_{578}; [e] calculated from data of this table and Table IV.

calls for the transformation of a tertiary carbonium ion into the thermodynamically less stable secondary carbonium ion. The unlikelihood of such a reaction is well documented in carbonium ion chemistry.[15] Furthermore, there is no evidence for transformation of a tertiary carbonium to a secondary carbonium ion in the analogous isobutene polymerization either.[16]

High-Temperature Polymerization

The cationic polymerization of optically active 1-olefins conducted at relatively high temperature (-3 to $+11°C.$) yields optically inactive products. The respective experiments are summarized in Table VIII.

Initially, the lack of optical activity in these polymers was interpreted as being evidence for total rearrangement during polymerization.[17] However, later studies have shown that the optically active polymer of (+)-5-methyl-1-heptene loses its optical activity rapidly when subjected to polymerization conditions. This is shown in Table IX.

TABLE IX

Effect of 0°C. Polymerization Conditions on the Optical Rotatory Power of Preformed Cationic Poly-5-methyl-1-heptene[a]

Reaction time, min.	Optical rotation[b]			
	C, g./ml.	α_{589}^{25} [c]	$[\alpha]_{589}^{25}$	$\dfrac{[\alpha]_{589}^{25} \text{ Cationic}}{[\alpha]_{589}^{25} \text{ Free radical}} \times 100$[d]
0[e]	0.0840	$+0.202°$	$+2.41°$	14.6
0.15	0.0724	$+0.005°$	$+0.69°$	4.2
15	0.0744	0	0	0

[a] For 0.1–0.2 g. of optically active polymer dissolved in 1 ml. CH_2Cl_2 at 0°C.; 0.2 ml. 5% $AlCl_3$ in C_2H_5Br added to polymer solution; reaction stopped with methanol; isolated polymer dried in vacuum.

[b] 1 dm., CCl_4.

[c] Calculated from α_{546}^{25} and α_{578}^{25}.

[d] Calculated from data of this table and Table IV.

[e] Starting polymer.

An unequivocal interpretation of these results is presently not possible. The lack of optical activity may be a consequence of intramolecular hydride shifts, as discussed above, or it might be caused by "secondary" reactions occurring at the asymmetric carbon atom of the originally optically active polymer. The configurational stability of poly-5-methyl-1-heptene formed at -61 to $-76°C.$ (see Table VII) contrasts sharply with the configurational instability observed at 0°C. (Table IX). This may be caused by the fact that the cationic polymers precipitate instantaneously when prepared at low temperature (as opposed to the polymers prepared at 0°C. where the system remains homogeneous), and in that way become unavailable for "secondary" reactions. However, the depression of the rate of the secondary reactions at low temperature is also a distinct possibility.

Free-Radical Polymers

The fact that cationic polymerization of ω-alkyl-α-olefins leads to rearranged polymers and coordinated anionic polymerization of the same olefins with the use of Ziegler-Natta catalysts produces unrearranged polymers,* raises the important question: What is the structure of the free-radical polymers?

Although alkyl radical or hydrogen atom shifts have not been detected in ordinary organic reactions,[19] the rearrangement of the secondary radical into a tertiary radical is energetically favorable.[20a] The possible reactions are illustrated in eq. (7) for the example of 3-methyl-1-pentene.
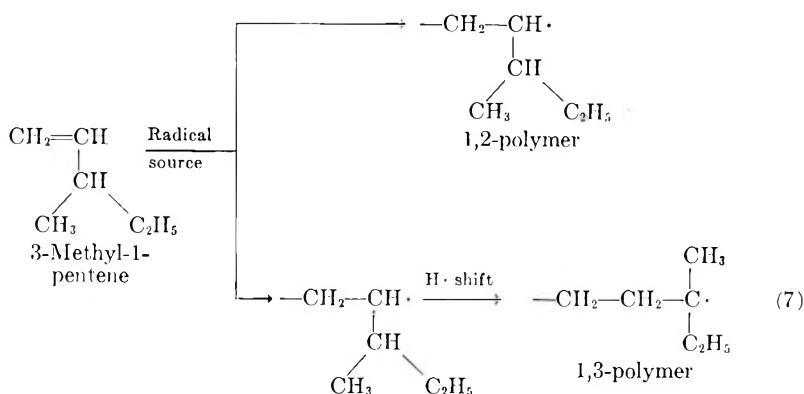
Since there are no methods known to produce high molecular weight homopolymers of 1-olefins by free-radical initiation, we have prepared the SO_2 copolymers. These reactions proceed through free-radical intermediates and yield the alternating 1-olefin/SO_2 copolymer.[21] Thus the copolymers are suitable for studying the structure of the olefinic component formed under free-radical conditions.

Alternating SO_2 copolymers of (+)-3-methyl-1-pentene, (−)-4-methyl-1-hexene, and (+)-5-methyl-1-heptene show high optical rotation (Table IV). The specific rotations of these copolymers are of the same order of magnitude as that of a low molecular weight analog, (+)-2,4-dimethylhexane.[22] The formation of optically active polymers indicates that the asymmetric carbon atom of the monomers is not converted by rearrangement into a free radical during polymerization [eqs. (8)–(10)]. Such a process, based on our knowledge on the stereochemistry of free radicals,[20b] would lead to optically inactive products. Therefore, this evidence argues in favor of a 1,2-structure for the free-radical polymers.

Additional evidence for the 1,2-structure of the free-radical polymers can be obtained from a study of the proton magnetic resonance spectra. The proton magnetic resonance spectrum of a 4-methyl-1-pentene/SO_2 copolymer is presented in Figure 1. The resolved peaks correspond to the

---

* This is known from x-ray diffraction[18] and proton magnetic resonance[3,4,9] studies.

$$CH_2{=}CH$$
$$\underset{CH_3 \quad C_2H_5}{\overset{CH^*}{|}}$$
(+)-3-Methyl-
1-pentene
$$+ SO_2$$

→ $-SO_2-CH_2-CH\cdot$ 1,2-polymer
$$\underset{CH_3 \quad C_2H_5}{\overset{CH^*}{|}}$$ (optically active)

$[\alpha]_{589}^{25} = +21.1°$

✗ → $-SO_2-CH_2-CH_2-\overset{CH_3}{\underset{C_2H_5}{\underset{|}{\overset{|}{C}}}}\cdot$ 1,3-polymer
(optically inactive)   (8)

$$CH_2{=}CH$$
$$\overset{|}{CH_2}$$
$$\underset{CH_3 \quad C_2H_5}{\overset{CH^*}{|}}$$
(−)-4-Methyl-
1-hexene
$$+ SO_2$$

→ $-SO_2-CH_2-CH\cdot$ 1,2-polymer
$$\overset{|}{CH_2}$$
$$\underset{CH_2 \quad C_2H_5}{\overset{CH^*}{|}}$$ (optically active)

$[\alpha]_{589}^{25} = +23.2°$

✗ → $-SO_2-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{C_2H_5}{\underset{|}{\overset{|}{C}}}}\cdot$ 1,4-polymer (optically inactive)   (9)

$$CH_2{=}CH$$
$$\overset{|}{CH_2}$$
$$\overset{|}{CH_2}$$
$$\underset{CH_3 \quad C_2H_5}{\overset{CH^*}{|}}$$
(+)-5-methyl-
1-heptene
$$+ SO_2$$

→ $-SO_2-CH_2-CH\cdot$ 1,2-polymer
$$\overset{|}{CH_2}$$
$$\overset{|}{CH_2}$$
$$\underset{CH_3 \quad C_2H_5}{\overset{CH^*}{|}}$$ (optically active)

$[\alpha]_{589}^{25} + 16.5°$

✗ → $-SO_2-CH_2-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{C_2H_5}{\underset{|}{\overset{|}{C}}}}\cdot$ 1,5-polymer (optically inactive)

(10)

$$CH_3-CH-CH_3$$
$$\overset{|}{CH_2}$$
$$\underset{CH_3 \quad C_2H_5}{\overset{CH^*}{|}}$$
2,4-Dimethylhexane
$[\alpha]_{589} = +18.7°$

protons CH_3, $CH_2 + CH$, and the H adjacent to sulfur. Their ratio is 2.04:1.10:1.00, respectively, approximating fairly well the theoretical 2:1:1 ratio expected for a copolymer containing 4-methyl-1-pentene in 1,2-enchainment. A 1,4-enchainment of 4-methyl-1-pentene would require a proton ratio of 3:2:1, respectively.

This result, in agreement with the optical activity data discussed above,

proves that the free-radical copolymerization of alkyl-substituted 1-olefins proceeds either totally or at least predominantly without rearrangement.

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Résumé

La polymérisation cationique initiée au chlorure d'aluminium des oléfines-1 optiquement actives fournit des polymères de pouvoir rotatoire optique variable. Les polymères de (+)-3-méthyl-1-pentène et de (−)-4-méthyl-1-hexène préparés entre −78°C et −55°C dans le CH₂Cl₂ ou le *n*-heptane, sont presque complètement inactifs du point de vue optique. Dans des conditions de réactions identiques le (+)-5-méthyl-1-heptène fournit des polymères de pouvoir rotatoire optique important. Des copolymères alternants de SO₂ des mêmes oléfines formés au cours de réaction radicalaire, fournissent des produits optiquement actifs de rotation spécifique similaire à celle des analogues de faibles poids moléculaires. Ces résultats sont consistants avec un mécanisme de polymérisation cationique où la chaine de croissance subit un glissement de l'hydrure intramoléculaire et où les atomes de carbone assymétriques sont transformés en ions car-

bonium. Les résultats fournissent également une preuve pour l'absence d'un réarrangement en cours de polymérisation radicalaire. En comparant la rotation spécifique de polymères cationiques et radicalaires, le degré de réarrangement en cours de polymérisation catinique peut être estimé. Les calculs montrent que le polymère-1,2 dans le poly-3-méthyl-1-pentène cationique est inférieur à 2%, la somme de 1,2 et de 1,3 polymère dans le poly-4-méthyl-1-hexène cationique est inférieur à 4% et la somme de polymère 1,2, 1,3 et 1,4 dans le poly-heptène-1-5-méthyl est de 14-20%.

Zusammenfassung

Die AlCl₃-gestartete kationische Polymerisation optisch aktiver 1-Olefine liefert Polymere mit wechselendem optischen Drehungsvermögen. Zwischen −78°C und −55°C in CH₂Cl₂ oder n-Heptan dargestellte Polymere von (+)-3-Methyl-1-penten und (−)-4-Methyl-1-hexen sind optisch fast völlig inaktiv. Unter identischen Reaktionsbedingungen liefert (+)-5-Methyl-1-hepten Polymere mit wesentlichem optischen Drehungsvermögen. Alternierende, durch radikalische Prozesse gebildete SO₂-Copolymere der gleichen Olefine sind optisch aktive Stoffe mit einer spezifischen Drehung von ähnlicher Grösse wie diejenige von niedermolekularen analogen Verbindungen. Die Ergebnisse entsprechen einem kationischen Polymerisationsmechanismus, bei welchem die wachsende Kette eine intramolekulare Hydridverschiebung erleidet und die asymmetrischen Kohlenstoffatome in Carboniumionen umgewandelt werden. Weiters zeigen sie auch, dass bei radikalischer Polymerisation keine Umlagerung eintritt. Durch Vergleich der spezifischen Drehung der kationischen und radikalischen Polymeren kann das Ausmass der Umlagerung während der kationischen Polymerisation bestimmt werden. Die Berechnung zeigt, dass das 1,2-Polymere in kationischem Poly-3-methyl-1-penten weniger als 2%, die Summe von 1,2- und 1,3-Polymerem in kationischem Poly-4-methyl-1-hexen weniger als 4% und die Summe von 1,2- 1,3- und 1,4-Polymerem in kationischem Poly-5-methyl-1-hepten 14-20% betragen.

Uranyl Ion-Sensitized Polymerization of Acrylamide and Methacrylamide in Aqueous Solution

K. VENKATARAO and M. SANTAPPA,

*Department of Physical Chemistry, University of Madras,
Madras, India*

Synopsis

The kinetics of polymerization of the vinyl monomers, acrylamide and methacrylamide, photosensitized by uranyl ions in homogeneous aqueous acid medium was studied systematically. Monochromatic radiation of wavelengths 365, 405, and 436 mμ was used for irradiation. Uranyl perchlorate in aqueous perchloric acid (pH = 0–2) was used as the sensitizer to ensure that only uncomplexed UO_2^{2+} ions existed in the solution. Polymerization was found to proceed without any induction period, the steady state being attained in about 10–20 min., and was followed by the measurement of the rate of monomer disappearance by bromine addition method. The chain lengths of the polymers were determined by viscometry. It was observed that there was no change in the initiator concentration, $[UO_2^{2+}]$, during polymerization. The dependence of the rate of polymerization on variables like light intensity, light absorption fraction by the active species, wavelength, monomer concentration, hydrogen ion concentration, temperature, nature of the acid used ($HClO_4$ and H_2SO_4), viscosity of the medium etc., were studied. A kinetic reaction scheme is proposed and discussed in the light of the experimental results. Certain rate parameters were calculated. The mechanism of photosensitization by uranyl ions with specific reference to primary photochemical act, initiation of polymerization etc., are discussed.

INTRODUCTION

The photochemistry of uranyl ions was and indeed still is a subject of extensive research. Conclusions from the investigations were often contradictory and sometimes even confusing. Uranyl ions were used to photosensitize the decomposition of oxalic acid[1–10] and other aliphatic acids.[11–17] Formation of a quinquevalent uranyl ion, U^{5+} or UO_2^+ species, as an intermediate in the photoreduction of uranyl ion by sugars was inferred by Heidt and Moon.[18] Alternative mechanisms (electron transfer and energy transfer) for the oxidation of organic compounds by uranyl ions in light have been suggested.[19] Oxidation studies with the use of sugars,[18] aliphatic acids,[14,17] and aldehydes[20] led to the conclusion that a photosensitive cluster, uranyl ion–organic compound, is formed prior to photoexcitation. Uranyl ions have also been used successfully as photoinitiators of vinyl polymerization.[21–27] The termination mechanism was found not to involve uranyl ions and the effect of hydrogen ion on the rate of polymerization

was found to be very complex.[21] Mahadevan and Santappa[26] studied the kinetics of polymerization of methyl methacrylate, methyl acrylate, acrylonitrile etc., with uranyl perchlorate by light of λ = 365, 313, 405, and 436 mμ in aqueous media, and concluded that the initiation of polymerization was by radicals formed in an electron transfer reaction between the monomer and the excited uranyl ions. We felt studies on this UO_2^{2+}-monomer system in homogeneous and nonprecipitating media would be desirable for understanding the nature of the primary photochemical act, initiation of polymerization, etc. With this end in view, photoinitiated polymerization of acrylamide and methacrylamide (which yield water-soluble polymers) by UO_2^{2+} has been studied, and the nature of the initiation etc., initiation etc., have been discussed in the light of experimental results.

EXPERIMENTAL

Light Sources and Monochromatic Radiation

Two types of light sources were used: a 250-w. high-pressure mercury vapor lamp (Mazda ME/D box type fitted with glass windows, supplied by B. T. H. Co., U.K.) and a 125-w. bulb-type ultraviolet lamp (Mazda MBW/U, also supplied by B. T. H. Co.). The lamps were connected to the mains through the stabilizing chokes and power factor capacitors, external voltage stabilizers being used to minimize the effect due to fluctuations in the supply voltage. The first lamp was used for obtaining light of wavelengths 405 and 436 mμ and the second type for light of wavelength 365 mμ. The light from the lamp was condensed and made parallel by a quartz biconvex lens, and the resulting beam was allowed to pass through a series of filter solution combinations[28] for isolating the required monochromatic wavelengths. To obtain light of wavelength 365 mμ, the second type of lamp was used without any filters (purity of the line $\sim$98% of 365 mμ).

Reaction Cell

A parallel beam of light consisting of monochromatic radiation was allowed to fall on the reaction cell which was kept in a thermostat with quartz windows. The reaction cell (4.6 cm. light path, and 4.6 cm. diameter) was a cylindrical vessel (capacity 75 ml.) fused at both ends with flat, optically clear, quartz plates and had two outlet tubes of standard B-14 cones for deaeration of the system.

Reagents

All the chemicals used in the preparation of reagents were the purest available (AnalaR B. D. H., G. R., E. Merck, or Riedel products). Distilled water, doubly distilled over alkaline permanganate in an all-glass Quickfit set-up and then passed through Biodeminrolit resin (Permutit Co., U.K.) was used for preparation of reagents etc. Stock solutions of uranyl per-

chlorate were prepared by the method given by Heidt and Moon.[18] Uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (AnalaR B. D. H.), was repeatedly heated with concentrated (60%) perchloric acid (E. Merck G. R.) till all the volatile acid was removed. Roughly four to five heatings were found to be enough to remove all the nitric acid, and further treatment showed no difference in the spectral properties and the kinetic behavior of the solution. Uranyl sulfate was prepared in the same way by fuming uranyl nitrate with concentrated (36N) sulfuric acid (AnalaR B. D. H.). Uranous perchlorate was prepared by electrolytic reduction of the uranyl salt with platinum gauze electrodes. Perchloric acid (E. Merck, G. R., ca. 60% $HClO_4$) and sulfuric acid (AnalaR B. D. H., ca. 36N) were employed. Sodium perchlorate for adjustment of ionic strength was prepared by mixing equimolar volumes of perchloric acid and sodium hydroxide. Acrylamide (American Cyanamid Co.) and Methacrylamide (Rohm and Haas) were used. Acrylamide was recrystallized[29] from warm chloroform solution; a white, crystalline solid (m.p. 84.5°C.) was obtained. Methacrylamide was purified by recrystallization from benzene–ethanol mixture (4:1 by volume) twice and drying the solid under vacuum for about 12 hr. The product was a white, crystalline solid (m.p. 109.8°C.). Potassium ferrioxalate, used for actinometry, was prepared[31] from potassium oxalate and ferric chloride and purified by recrystallization from warm water. Solvents like methanol, ethanol, chloroform, benzene, and acetone were distilled immediately before use, and middle cuts were used. Deaeration of the system was done by nitrogen, freed from traces of oxygen by Fieser's solution.[32]

Estimations

Stock solutions of uranyl perchlorate were standardized by reduction of the former to the U^{4+} state (by Jone's reductor[33]) and titration of the latter against standard potassium permanganate. Free acid in the uranyl perchlorate stock solution was determined by the ion-exchange resin method.[34] The purity of the monomers used and the strength of the monomer solutions were estimated by bromine addition to the double bond[35] of the former. A typical experiment was as follows. The reaction mixture containing uranyl salt, monomer, acid, and neutral salt were taken in the reaction cell and deaerated with nitrogen for about 75 min. in the dark. The reaction cell was then placed in a thermostat maintained at 35 ± 0.01°C. by means of a toluene regulator and hot-wire vacuum switch relay (Gallenkamp) in the path of the monochromatic light and irradiated for 10–30 min. The rate of monomer disappearance was followed by estimating the monomer concentration before and after irradiation by bromometry. There was no induction period, and the rate attained a steady state in a short time (10–20 min.). Methods for estimating the U^{4+} ions possibly formed were: (1) thiocyanate method[37] based on colorimetry; (2) measurement of absorbancies of U^{4+} ion in 1M acid at 670 mμ; and (3) reaction of the U^{4+} with ferric chloride (0.01M) and o-phenanthroline (0.1M) reagent at pH 2.0 to

give the Fe^{2+}–o-phenanthroline complex, which was estimated colori-
metrically at 510 mµ. The last method[36] was very sensitive and can
measure U^{4+} concentrations down to $10^{-6}M$. Absorbancies for computing
light absorption fraction by the active species etc., were measured in a
Hilger-Watts Uvispek H-700 spectrophotometer. The light intensity of
the mercury vapor lamp was measured by potassium ferrioxalate acti-
nometry.[31] The amount of ferrous ion formed as Fe^{2+}–o-phenanthroline
complex was estimated spectrophotometrically at 510 mµ in the Hilger
Uvispek spectrophotometer. The polyacrylamide was precipitated from
the reaction mixture by addition of methanol and purified by reprecipita-
tion from water. The purified samples were dried, and the viscosities of
0.1% solutions in $1.0M$ sodium nitrate measured in a Polymer Consultants
Ltd. Ubbelohde viscometer thermostated to $30 \pm 0.01°C$. in a viscometric
bath designed for precision viscometry (Krebs Electrical and Manufac-
turing Co., New York). From the measured viscosities, the number-
average molecular weight of polyacrylamide was calculated by using
the Mark-Houwink relationship between limiting viscosity number and
molecular weight[29] at 30°C.

$$[\eta] = 6.8 \times 10^{-4}(\bar{M}_n)^{0.66}$$

KINETIC RESULTS

Uranyl ion was found to be an efficient initiator of photopolymerization
of acrylamide and methacrylamide in aqueous acid media. Most of the
experiments were conducted in perchloric acid and some in sulfuric acid
medium to study the effect of anions. The pH was kept below 2.0 in all
cases to avoid hydrolysis of U^{6+}, and variation of hydrogen ion concentra-
tion was done within this limit. All experiments were done under de-
aerated conditions (since presence of oxygen inhibited the reaction) and at
constant ionic strength ($\mu = 0.2$ with acrylamide and $\mu = 0.3$ with meth-
acrylamide). In the case of polymerization of methacrylamide, polymer
precipitated at high conversions (ca. 15–20%), making the measurements
inaccurate; therefore experiments were restricted to conversions up to
10%, where no precipitation of polymer occurred. The effect of variation
of light absorption fraction, light intensity, monomer concentration, hy-
drogen ion concentration, wavelength of light, temperature, ionic strength
and viscosity of the medium on the rate of monomer disappearance were
studied in detail. It was observed that no change in the concentration of
uranyl ion occurred during the reaction or no uranous ion was produced.

Effect of Monomer Concentration

The rate of monomer disappearance was found to be proportional to the
3/2 powers of monomer concentration in the case of both acrylamide and
methacrylamide (Fig. 1). Chain lengths of polyacrylamide were found
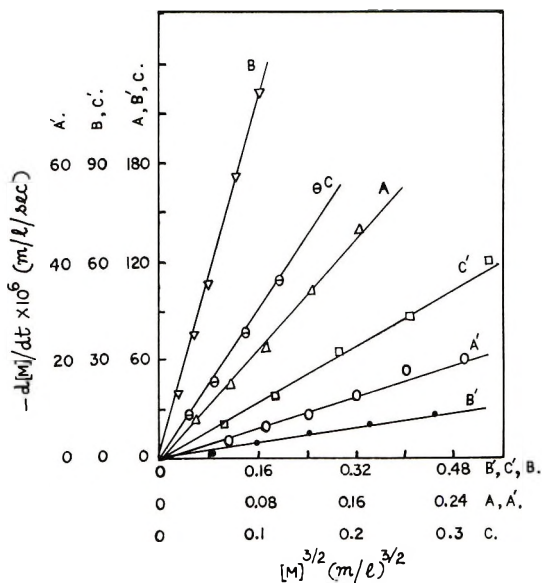to be proportional to the first power of monomer concentration.

Fig. 1. Plots of $-d[\text{M}]/dt$ vs. $[\text{M}]^{3/2}$: (A) acrylamide, 436 mμ; (B) acrylamide, 405 mμ; (C) acrylamide, 365 mμ; (A') methacrylamide, 436 mμ; (B') methacrylamide; 405 mμ; (C') methacrylamide, 365 mμ.

Effect of Light Absorption Fraction

The light absorption fraction (the fraction of light absorbed by the system) was varied by varying the concentration of the uranyl ion, which was the only light-absorbing species. The rate of monomer disappearance was
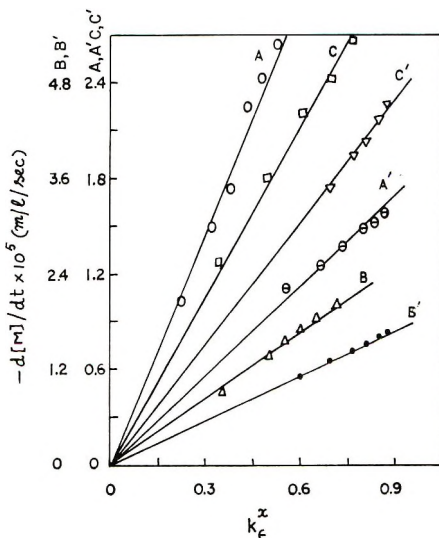

Fig. 2. Plots of $-d[\text{M}]/dt$ vs. k_ϵ^x: (A) acrylamide $(x = 0.5)$ 436 mμ; (B) acrylamide, 405 mμ; (C) acrylamide, 365 mμ; (A') methacrylamide $(x = 0.35)$ 436 mμ; (B') methacrylamide, 405 mμ; (C') methacrylamide, 365 mμ.

proportional to square root of light absorption fraction in the case of acrylamide (Fig. 2). With methacrylamide, dependence of the rate of monomer disappearance on $K_\epsilon^{0.35}$, where k_ϵ is the light absorption fraction, was noticed (Fig. 2). Chain lengths of polyacrylamide were found to be inversely proportional to the square root of light absorption fraction.

Effect of Light Intensity I

The rate of monomer disappearance was proportional to $I^{0.5}$ in the case of acrylamide (Fig. 3) and $I^{0.35}$ in the case of methacrylamide (Fig. 3). Chain lengths of polyacrylamide were found to be inversely proportional to the square root of light intensity.
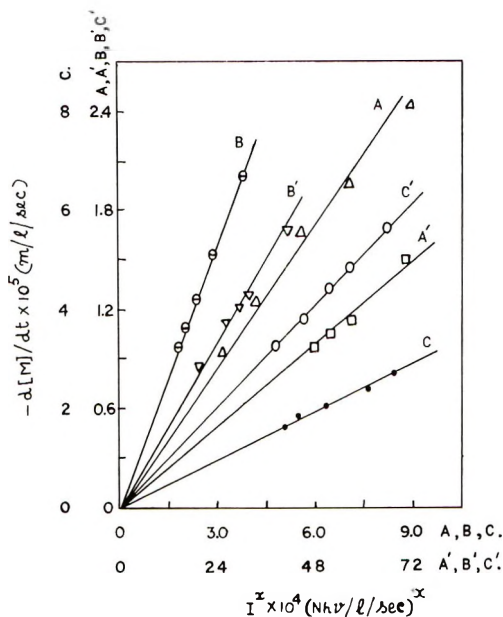
Fig. 3. Plots of $-d[M]/dt$ vs. I^x: (A) acrylamide ($x = 0.5$) 436 mμ; (B) acrylamide, 405 mμ; (C) acrylamide, 365 mμ; (A') methacrylamide ($x = 0.35$) 436 mμ; (B') methacrylamide, 405 mμ; (C') methacrylamide, 365 mμ.

Effect of Hydrogen Ion Concentration

The rate of monomer disappearance decreased with increase in hydrogen ion concentration, and plots of $(-d[M]/dt)^{-2}$ versus $[H^+]$ gave straight lines with definite intercepts on the y axis (Fig. 4). The chain length of polyacrylamide increased with increasing $[H^+]$. The polymers prepared at high acid concentrations were insoluble, probably due to some kind of crosslinking.

Effect of Viscosity

The rate of monomer disappearance increased with increasing viscosity of the medium, the variation in the latter being effected by addition of
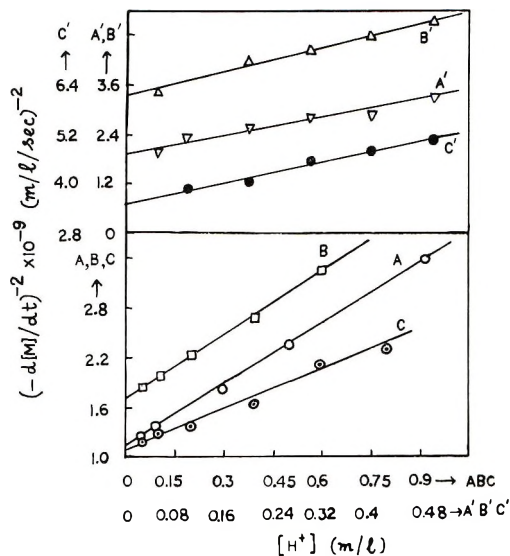
Fig. 4. Plots of $(-d[\mathrm{M}]/dt)^{-2}$ vs. $[\mathrm{H}^+]$: (A) acrylamide 436 mμ; (B) acrylamide, 405 mμ; (C) acrylamide, 365 mμ; (A') methacrylamide, 436 mμ; (B') methacrylamide, 405 mμ; (C') methacrylamide, 365 mμ.

a glycerol–water mixture. Also, the chain length of the polyacrylamide formed increased with increasing viscosity of the medium.

Effect of Temperature

Temperature had little effect on the rate of the reaction, and approximate calculation of overall activation energy, gave values of $\Delta E \approx 2.9$ kcal. for acrylamide and $\Delta E \approx -1.8$ kcal. for methacrylamide polymerizations, indicating that the reaction was a pure photochemical one.

Effect of Ionic Strength

A sixfold increase in ionic strength of the medium increased the rate by about 15%.

Effect of the Anion

The polymerization of acrylamide was repeated with uranyl sulfate in aqueous sulfuric acid as the initiator to study the effect of change in anion. The rate of polymerization remained unaffected by change in anion under comparable conditions.

KINETIC SCHEME AND DISCUSSION

The sequence of reactions (1)–(6) would explain most of the results. Formation of photosensitive cluster:

$$\mathrm{UO_2^{++}} + \mathrm{M} \underset{\overleftarrow{}}{\overset{K_1}{\rightleftharpoons}} (\mathrm{UO_2^{y+}M}) \tag{1}$$
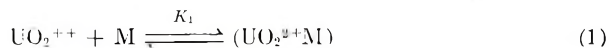
Here $(UO_2^{2+}M)$ is the photosensitive cluster, M is the monomer (acrylamide or methacrylamide) and K_1 is the equilibrium constant for the cluster.

Excitation of the cluster:

$$(UO_2^{++}M) + h\nu \underset{k_d}{\overset{k'_\epsilon I}{\rightleftharpoons}} (UO_2^{2+}M)^* \tag{2}$$
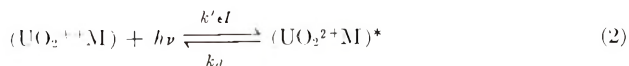
k'_ϵ is the light absorption fraction of the complex, I is the light intensity, and k_d is the rate constant for the dark back-reaction, deactivating the excited photosensitive cluster by encounter with a third body.

Dissociation of the excited cluster and energy transfer to monomer:

$$(UO_2^{++}M)^* \xrightarrow{k_i} UO_2^{2+} + X \tag{3}$$
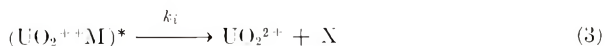
X denotes the free-radical fragment produced from the monomer.

Initiation of polymerization:

$$X + M \rightarrow X\text{—}M\cdot \tag{4}$$

Propagation:

$$X\text{—}M\cdot + M \xrightarrow{k_p} X\text{—}M\text{—}M\cdot \tag{5}$$

Termination:

$$(X\text{—}M_n)\cdot + (M_m\text{—}X)\cdot \xrightarrow{k_t} (X\text{—}M_{m+n} - X) \tag{6}$$
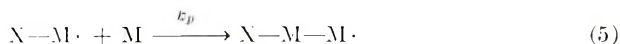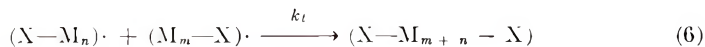
The light absorption fraction k'_ϵ by the complex may be expressed in terms of total light absorption fraction k_ϵ by all the species in the system, assuming that the extinction coefficients of the cluster and free uranyl ion are almost the same.

$$k'_\epsilon = k_\epsilon K_1[M]/(1 + K_1[M]) \tag{7}$$

Since under experimental conditions $K_1[M] \ll 1$, eq. (7) becomes

$$k'_\epsilon = k_\epsilon K_1[M] \tag{8}$$

It is further assumed that the salt formation equilibrium of the monomer with hydrogen ion,

$$M + H^+ \underset{}{\overset{K_2}{\rightleftharpoons}} (MH^+) \tag{9}$$
$$\text{(inactive)}$$
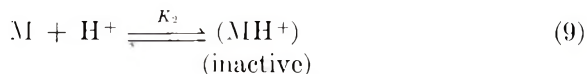
would interfere in the formation of the cluster [eq. (1)] and consequently in the initiation of polymerization. The free monomer concentration $[M]_f$ may therefore be expressed in terms of total monomer concentration $[M]_0$,

$$[M]_f = [M]_t/(1 + K_2[H^+]) \tag{10}$$

Using the usual steady-state assumptions for the concentrations of radicals and excited photosensitive cluster and also the nonvariation of rate con-

stants with size of the polymer radical, we get the expression for rate of monomer disappearance and for chain length n:

$$\frac{-d[\mathrm{M}]}{dt} = \frac{k_p k_i^{1/2} K_1^{1/2}}{k_t^{1/2}(k_d + k_i)^{1/2}} \cdot \frac{k_\epsilon^{1/2} I^{1/2}[\mathrm{M}]_t^{3/2}}{(1 + K_2[\mathrm{H}^+])^{1/2}} \tag{11}$$

$$n = \frac{2k_p(k_d + k_i)^{1/2}}{k_t k_i^{1/2} K_1^{1/2}} \cdot \frac{[\mathrm{M}]^{1/2}(1 + K_2[\mathrm{H}^+])^{1/2}}{k_\epsilon^{1/2} I^{1/2}} \tag{12}$$

In the photoinitiated polymerization of acrylamide and methacrylamide sensitized by uranyl ions, the most probable primary photochemical reaction appears to be the excitation of the photosensitive cluster formed between uranyl ion and monomer. The formation of the cluster prior to excitation is indicated by the slight increase in absorbancy of the uranyl salt solution on adding the monomer. The excited photosensitive cluster then decomposes in a unimolecular reaction to give radicals. In fact, the independence of rates of monomer disappearance on ionic strength and the inhibition of the reaction by oxygen show the free-radical nature of the reaction. The production of radicals appears to be by the transfer of excitation energy from the uranyl ion to the monomer in the excited cluster. This view is in contrast to that of Mahadevan and Santappa,[26] who maintained that the primary photochemical reaction was one of excitation of the free uranyl ion and that radical-ions (from the monomer) were formed by electron transfer from the monomer to the excited uranyl ion in a secondary dark reaction. They were led to this view mainly by the small reduction ($<5\%$) of U^{6+} to U^{4+} which they noted by employing the colorimetric method of estimation of U^{6+} by ammonium thiocyanate.[37] With the homogeneous conditions of our experiments and the refined methods for the estimation of U^{4+} employed by us, no reduction of uranyl ion during the course of polymerization was noticed, however. Special methods used to detect very low concentrations ($\sim10^{-6}M$) of uranous ions[36] did not indicate that the U^{4+} was produced in our experiments. Further, values of $k_t K_1(k_i + k_d)$, which can be taken as a measure of the rate of initiation, evaluated by us were so high (Table I) that measurable concentrations of
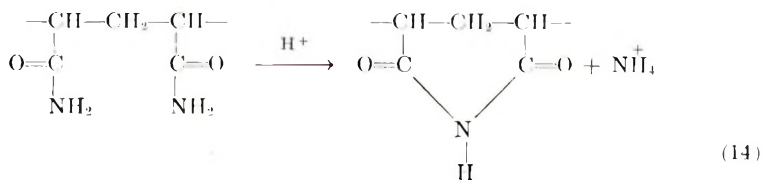
TABLE I
Values of K_i and $k_p K_i^{1/2}/k_t^{1/2}$

Monomer	Wavelength, $m\mu$	Medium	$k_p K_i^{1/2}/k_t^{1/2}$, l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$	K_i, sec.$^{-1}$ [a]
Acrylamide	365	HClO$_4$	1.997	0.2262
Acrylamide	405	HClO$_4$	2.370	0.3184
Acrylamide	436	HClO$_4$	1.825	0.1889
Acrylamide	436	H$_2$SO$_4$	1.836	0.1912
Methacrylamide	436	HClO$_4$	0.0144	0.0473
Methacrylamide	405	HClO$_4$	0.0308	0.2154
Methacrylamide	365	HClO$_4$	0.0205	0.0957

[a] Calculated assuming Dainton's[29,30] values for $k_p/k_t^{1/2}$: acrylamide = 4.2 l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$; methacrylamide = 0.2099 l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$.

uranous ion should have been produced if an electron-transfer reaction was important. Estimation of small differences in $[U^{6+}]$ by colorimetry by Mahadevan and Santappa[26] were perhaps well within limits of experimental errors, and adsorption of small quantities of U^{6+} by the precipitating polymer, under their experimental conditions probably contributed to this error (always within 5%). The rate of monomer disappearance was found to be dependent on $[M]^{1/2}$, indicating that the termination was by mutual interaction. This was in accordance with the results of the earlier workers.[21,26] Incidentally, this result indicated that uranyl ions were poor terminators of polymerization. Chain lengths of polyacrylamide were proportional to the first power of monomer concentration, while the reaction scheme would ascribe a square-root dependence of the latter. $-d[M]/dt$ was proportional to k_t^x and I^x, where $x = 0.5$ for acrylamide and $x = 0.35$ for methacrylamide. The dependence of 0.5 powers of k_t and I as well as $3/2$ powers of monomer concentration conclusively proved that the termination was one of mutual type. The discrepancy in the normal k_t and intensity exponent ($\sim$0.5) in the case of methacrylamide indicated that possibly some other term of termination such as by primary radicals X, was also taking place in addition to the mutual termination in this respect. Similar observations were made by Toppet et al.[38] in the dye-sensitized photopolymerization of acrylamide where the rate depended on $I^{0.35}$ and [sensitizer]$^{0.5 \to 0}$. The chain lengths of polyacrylamide depend on $k_t^{-1/2}$ and $I^{-1/2}$ as expected from the mechanism given. The decrease in rate and chain length with increasing $[H^+]$ and the straight-line plots of $(1/\text{rate})^2$ versus $[H^+]$ were explained by assuming reaction (9) above, $M + H^+$ competing with reaction $M + U^{6+} \to$ photosensitive cluster. Such salt formation [reaction (9)] was reported to take place between acrylamide and concentrated sulfuric acid.[38]

$$CH_2=CHCONH_2 + H_2SO_4 \to CH_2=CHCONH_2 \cdot H_2SO_4 \qquad (13)$$

The polymers prepared at high acid concentrations were insoluble, probably due to imide linking, catalyzed by acids.[39]

$$\begin{array}{ccc} -CH-CH_2-CH- & & -CH-CH_2-CH- \\ | & | & \xrightarrow{H^+} \quad | \qquad | \\ O=C & C=O & O=C \qquad C=O + N\overset{+}{H}_4 \\ | & | & \qquad \searrow \quad \swarrow \\ NH_2 & NH_2 & \qquad N \\ & & \qquad | \\ & & \qquad H \end{array} \qquad (14)$$

The low temperature coefficients and low overall activation energy for $-d[M]/dt$, $\Delta E = 2.9$ kcal. for acrylamide and $\Delta E = -1.8$ kcal. for methacrylamide (cf. $\Delta E = 1.5$ kcal. for the polymerization of methacrylic acid by uranyl ions) indicated that the reaction was a pure photochemical one. Increasing viscosity of the medium increased the rate of polymerization and chain lengths, due to the fact that termination rate decreased and became progressively diffusion-controlled with increasing viscosity. Similar observations were made by Oster et al.[40] in their study on the poly-

merization of acrylamide sensitized by riboflavin. The overall rate constants $k_p K_i^{1/2}/k_t^{1/2}$, where $K_i^{1/2} = k_i^{1/2} K_1^{1/2}/(k_d + k_i)^{1/2}$, were calculated from the plots of $-d[\mathrm{M}]/dt$ versus k_e^x, I^z and $[\mathrm{M}]^{3/2}$, where $x = 0.5$ for acrylamide and 0.35 for methacrylamide, assuming $(1 + K_2[\mathrm{H}^+])^{1/2} \sim 1$, under experimental conditions. K_i vaues at various wavelengths of light were calculated using Dainton's values for $k_p/k_t^{1/2}$ for mutual termination[29–30] since they cannot be determined directly (Table I). The K_i values were highest for $\lambda = 405$ mμ and lowest for $\lambda = 436$ mμ. Most of the experiments were done with uranyl perchlorate in perchloric acid medium (pH = 0–2.0), where the former exist as uncomplexed and unhydrolyzed UO_2^{2+} ions. Uranyl sulfate in dilute sulfuric acid medium (pH = 0–2.0) was used as the photosensitizer with a view to study the effect of complexing on the initiator efficiency; peculiarly enough, the rate constants did not change with change in the nature of the anions. This again lent support to the view that the secondary dark reaction was one of energy transfer and not electron transfer, for the nature of the anions may affect the rate of the latter.

These studies on the photopolymerization of acrylamide and methacrylamide indicate the occurrence of energy transfer in the excited cluster Further studies on similar systems may throw much light on the behavior of uranyl ions as photoinitiators of polymerization.

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Résumé

La cinétique de polymérisation de monomères vinyliques tels que l'acrylamide et le méthacrylamide photosensibilisés par des ions uranyles en milieu acide aqueux a été étudiée systématiquement. Une radiation monochromatique de longueur d'onde de 365 mμ, 405 mμ et 436 mμ a été utilisée pour l'irradiation. Le perchlorate d'uranyle dans l'acide perchlorique (pH = 0 à 2) a été utilisé comme sensibilisateur pour s'assurer qu'uniquement les ions UO_2^{++} existent en solution. La polymérisation se passe sans aucune période d'induction, l'état stationnaire étant attient après 10–20 minutes, il était suivi par la mesure de la vitesse de disparition du monomère par la méthode d'addition de brome. Les longueurs de chaîne de ces polymères ont ét édéterminées par viscosimétrie. On a observé qu'il n'y avait pas de variation de concentration en initiateur (UO_2^{2+}), au cours de la polymérisation. La dépendance de la vitesse de polymérisation vis à vis des variables telles que l'intensité lumineuse, la fraction de lumière absorbée par les espèces actives, la longueur d'onde, la concentration en monomères la concentration en ion hydrogène, la température, la nature des acides utilisés ($HClO_4$ et H_2SO_4), la viscosité du milieu, etc. a été étudiés. On propose un schéma de réaction cinétique et le discute en fonction des résultats expérimentaux. Certains paramètres cinétques ont été calculés. On discute d'un mécanisme de photosensibilisation par des ions uranyle en faisant appel à l'acte photochimique primaire, à l'initiation de la polymérisation, etc.

Zusammenfassung

Die Kinetik der durch Uranylionen photosensibilisierten Polymerisation der Vinylmonomeren Acrylamid und Methacrylamid in homogenem, wässrigen sauren Medium wurde systematisch untersucht. Zur Bestrahlung wurde monochromatisches Licht der Wellenlänge 365 mμ und 405 mμ sowie 436 mμ verwendet. Uranylperchlorat in wässriger Perchlorsäure (pH = 0 bis 2) bildete den Sensibilisator, so dass nur nichtkomplexierte UO_2^{2+} Ionen in der Lösung vorhanden waren. Die Polymerisation verlief ohne jede Induktionsperiode, der stationäre Zustand wurde in etwa zehn bis zwanzig Minuten erreicht und wurde durch Messung der Geschwindigkeit des Monomerver-

brauches nach der Bromadditionsmethode verfolgt. Die Kettenlänge der Polymeren wurde viskosimetrisch bestimmt. Während der Polymerisation trat keine Änderung der UO_2^{2+}-Konzentration auf. Die Abhängigkeit der Polymerisationsgeschwindigkeit von Lichtintensität, Anteil der Lichtabsorption durch die aktive Spezies, Wellenlänge, Monomerkonzentration, Wasserstoffionenkonzentration, Temperatur, Natur der verwendeten Säure ($HClO_4$ und H_2SO_4), Viskosität des Mediums etc. wurde untersucht. Ein kinetisches Reaktionsschema wird vorgeschlagen und im Lichte der Versuchsergebnisse diskutiert. Einige Geschwindigkeitsparameter werden berechnet. Photosensibilisierungsmechanismen durch Uranylionen mit besonderer Berücksichtigung des photochemischen Primärakts, des Polymerisationsstarts etc. werden diskutiert.

Conformation of Polyesters Adsorbed on Solid Surfaces

PAUL PEYSER,* DANIEL J. TUTAS,
and ROBERT R. STROMBERG, *Institute for Materials Research,
National Bureau of Standards, Washington, D.C. 20234*

Synopsis

The conformation of a polyester, poly(ethylene *o*-phthalate), of relatively low molecular weight was studied after adsorption. The extension of the adsorbed molecule in a poor solvent on several planar metal surfaces was studied by ellipsometry and the fraction *p* of attached groups on colloidal silica particles in a good solvent was determined by the shift in the infrared absorption frequency between free and adsorbed carbonyl groups. In contrast to previously reported results for polystyrene, the extension normal to the surface remained constant ($\sim$70 A.) while the concentration of polymer in the adsorbed film increased during the adsorption period. The value of *p* (0.34 for MW = 5400) is relatively high and was independent of surface population for the range of solution concentrations measured. Differences between these results and those for polystyrene are interpreted as resulting from differences in interaction energy and chain stiffness.

INTRODUCTION

The adsorption of flexible polymer molecules on solid surfaces has received considerable attention in recent years. Many of these studies, both theoretical and experimental, have been directed toward a determination of the conformation of the adsorbed molecule. All theoretical treatments predict a "flattened" molecule with a large number of polymer–surface contacts for large interaction energies. However, for small interaction energies, both large and small loops of the polymer chain normal to the surface have been predicted, depending on the theoretical treatment.

In previous papers[1,2] from this laboratory we have described the results of measurements of the extension of polystyrene molecules normal to an adsorbing metallic surface upon adsorption from cyclohexane at approximately the theta temperature. Under equilibrium conditions for maximum absorption this extension was found to increase linearly with the square root of the molecular weight for a molecular weight range of 76,000–1,900,000. (Some deviation from linearity was found for a molecular weight of 3,300,000.) The sizes of the measured root-mean-square average

extensions were near the calculated root-mean-square end-to-end distances of a polymer with one end attached to a reflecting boundary or to a surface with an absorbing boundary one step behind it.* These results were interpreted to indicate that the conformation of polystyrene adsorbed under these conditions is close to that of a random coil.

In this paper we are concerned with the conformation of a relatively low molecular weight condensation polymer, poly(ethylene o-phthalate), adsorbed on oxide surfaces. The adsorption of a series of linear, noncrystalline polyesters has been reported,[4] and the adsorption and the temperature dependence of the reversibility of adsorption of poly(ethylene o-phthalate) from chloroform solution on glass have been studied.[5] Here we are reporting the results of a study of the extension of the adsorbed polymer molecule normal to the surface, and of the fraction of polymer segments attached to the surface. The measurements were carried out *in situ*, the extension being determined by ellipsometric measurements, and the fraction of segments attached, by measuring the relative amounts of free and bound carbonyl by means of infrared spectroscopy.

MEASUREMENT TECHNIQUES

Ellipsometry

The extension of the adsorbed molecule from the surface was studied by means of ellipsometry. The method is based on the measurement of changes in the state of polarization of light upon reflection from a surface. With this technique, by measuring the optical constants of a bare reflecting surface and of a film-coated surface one can calculate the thickness and refractive index of the film overlaying that surface. The basic principles, techniques, and calculations have been reviewed or described elsewhere.[6-8] and will not be discussed here. The application of the technique to the study of polymer adsorption on metallic surfaces has also been previously given.[1,2,8a]

The metal slides were cleaned as described below and placed under ethyl acetate in an adsorption cell on the ellipsometer. The cell was maintained at a constant temperature by an appropriate jacket. The windows of the cell were normal to the incident light. The optical constants of the metal surfaces were determined with the surface under the solvent with the use of triple reflection techniques to achieve greater sensitivity.[1,8a] The solvent was exchanged for polymer solution without moving the metal surfaces. Measurements of the change in the state of polarization as a result of the adsorption of polymer were made on the identical locations for which the optical constants of the metal surfaces had been obtained.

Two parameters are measured: Δ, a relative phase difference for light polarized with its electric vector in the plane of incidence to that polarized

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* DiMarzio[3] has concluded that the use of such an absorbing barrier, rather than a reflecting barrier, is required for the proper counting of the number of conformations of a molecule near a surface.

normal to the plane of incidence, and tan ψ, the ratio of the magnitude of the reflection coefficients for these two polarizations. These parameters are then used to compute the thickness and refractive index of the adsorbed layer[7] (which we refer to also as a "film"). The technique permits the measurement of these quantities *in situ* with the adsorbed polymer in contact with the solution. As the adsorbed polymer film is a mixture of polymer and solvent, the refractive index can be used to determine the composition of the adsorbed layer and together with the thickness, the amount of polymer adsorbed per unit area.

Infrared

Upon attachment of a molecule to a surface, the wavelength of one or more infrared absorption peaks for the molecule can be shifted owing to the attachment. There is usually a corresponding change in the extinction coefficient of the shifted peak. If the original and shifted peaks are well separated, the fraction p of an adsorbed polymer molecule which is attached to the surface can be determined from the spectrum of the adsorbed polymer. A method to use this absorption shift for polymer absorption studies was described by Fontana and Thomas[9] and modified by Peyser.[10] The method of analysis most suitable can vary somewhat from case to case. The method used here will be described only in sufficient detail to enable the reader to understand the method and to describe additional modifications in the method and calculations. More detailed descriptions can be found elsewhere.[9−11]

Since the peaks are not well separated, one must resort to a differential spectral analysis. Such a differential spectrum is obtained between a cell containing only the original polymer solution and a cell containing the polymer adsorbed on silica suspended in polymer solution. This latter cell contains, therefore, adsorbed molecules comprising attached groups and unattached groups, as well as nonadsorbed molecules. A typical differential spectrum obtained for the polyester system is given in Figure 1. Upon adsorption, as a result of the attractive energy between the silica and the carbonyl group, there is a small shift to a higher wavelength for the carbonyl absorption band of attached polyester groups. Peak 1 is due to the unattached groups and peak 2 to the attached groups. As a differential spectrum, peak 1 represents the difference between the original concentration of carbonyl groups and the reduced concentration of unattached groups after adsorption. There is some overlap of peak 2 on peak 1. The optical density of peak 1 was measured relative to a base line obtained by extrapolating the absorption due to the silica (peak 3) to the vicinity of peak 1. (The baseline is shown by a dashed curve.)

If it is assumed that both carbonyl groups on an adsorbed polyester segment are attached to the surface (see Discussion), then the fraction p of attached segments is related to the optical density (OD) of peak 1 by[10]

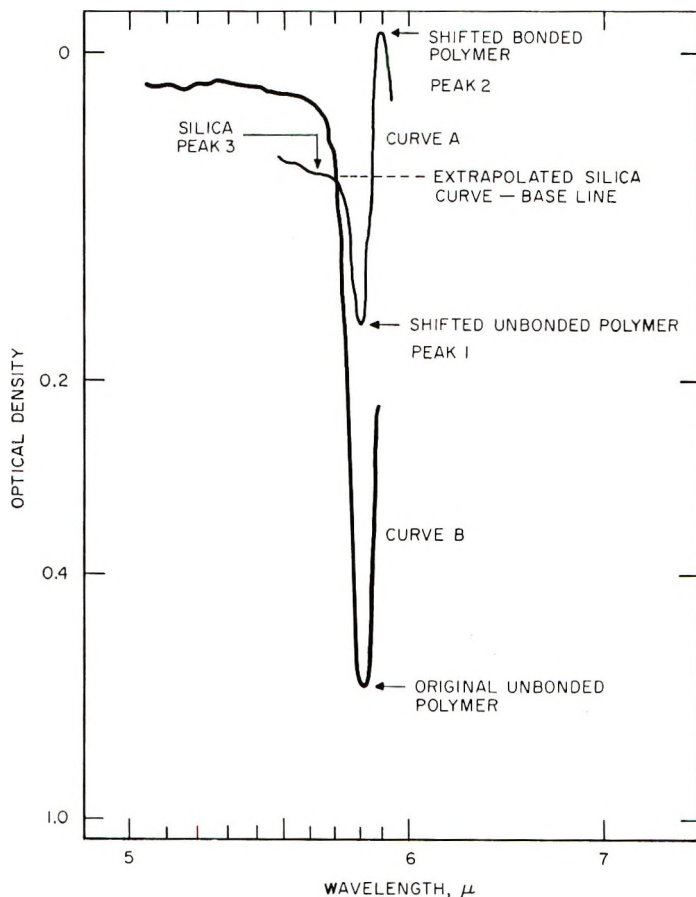$$p = [(OD) + \epsilon_1 c'] / Lc(\epsilon_1 - \epsilon_2)$$

Fig. 1. Infrared spectra: (*A*) typical differential spectrum between a solution of polymer of a given concentration in the sample beam of the spectrophotometer vs. a solution of polymer of the same concentration mixed with silica (the difference between the optical density at the maximum of peak 1 and the dashed line is proportional to *p*); (*B*) polymer solution solvent.

where L is the cell length, c is the difference between the original concentration of polymer and the final concentration, ϵ_1 is the extinction coefficient for the free segments at peak 1, ϵ_2 is the extinction coefficient of the attached segments at peak 1 (overlap), and c' is the difference in concentration between polymer solution in both cells (allows for volume of silica).

The final solution concentration and hence the value of c was determined by ultraviolet absorption measurements at 276 mμ after adsorption. A spectrum of only attached polymer segments can be obtained by adjusting the path length of the reference cell until peak 1 is just removed. The overlap, and thus the value of ϵ_2, can be estimated from this spectrum. An error in this estimate will result in only a relatively small error in p. It should be noted that a determination of $(\epsilon_1 - \epsilon_2)$ is necessary to determine the absolute value of p, but not its relative value. A measurement of

OD/Lc is sufficient to show a change in p with final solution concentration.

EXPERIMENTAL DETAILS

The polymer used in this study was the linear saturated polyester, poly-(ethylene o-phthalate), which had been prepared by refluxing ethylene glycol and phthalic anhydride in a molar ratio of 1:1 for various times to obtain the desired average molecular weights. The purification and fractionation of the samples has been previously described.[5] The number-average molecular weights were obtained by endgroup analysis.

The solvents, ethyl acetate and chloroform, were of reagent grade, dried over calcium chloride, and freshly distilled prior to use.

Several metals were used as adsorption surfaces for the ellipsometry measurements. These included steel gage blocks, and chromium, gold, or copper that had been electrodeposited on such gage blocks. The finish of these gage blocks was given by the manufacturer as 0.09 μin. (root-mean-square average). Chrome surfaces cut from commercial ferrotype plate were also used as an adsorbing surface. The steel gage blocks were washed with hot solvents to remove grease films, dried, flamed, and placed while still warm in the adsorption cell under solvent. Immediately after electroplating, the electrodeposited blocks were thoroughly washed with water and hot solvent and stored under liquid until ready to use. Immediately prior to use they were flamed and placed while still warm in the adsorption cell under solvent. The ferrotype-plate specimens were cleaned with warm sulfuric acid–dichromate cleaning solution, washed with hot distilled water, dried, flamed, and placed while still warm in the adsorption cell under solvent. The polyester (MW = 7400) was adsorbed from ethyl acetate at 34°C. for the ellipsometry measurements.

The silica used for the determination of the value of p was of the type prepared by the vapor-phase hydrolysis of a silicon compound. It is reported by the manufacturer to have a surface area of 175–200 m.²/g., which is external, i.e., the material is nonporous, and the particle size is reported to be 0.015–0.020 μ. The material was preconditioned in a room maintained at 50–60% R.H. prior to use in adsorption experiments, and the adsorption tubes were filled with the adsorbent under these conditions. The tubes were then filled with chloroform solutions of the polymer and rotated end over end at 35°C. for at least 24 hr. before the measurements to determine p were carried out. The molecular weights of the polymers used for these measurements were 5400 and 2500.

RESULTS

The Drude equations[12] that were used to calculate the thickness and refractive index of a film from the experimental values of Δ and ψ obtained by ellipsometry are for a homogeneous film. However, in this study we would expect the "film" to exist as an inhomogeneous mixture of adsorbed
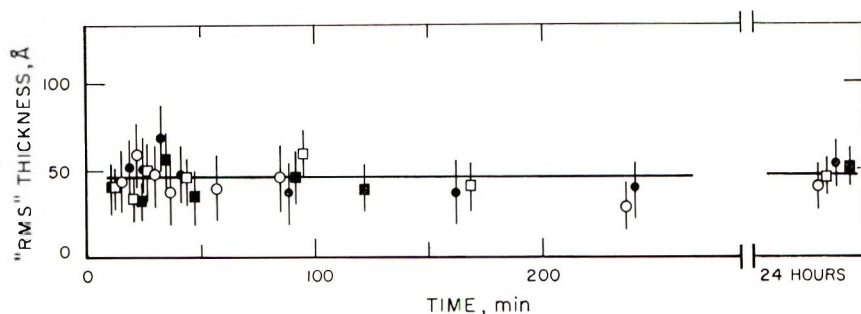
Fig. 2. Extension of adsorbed poly(ethylene o-phthalate) molecule, MW = 7400 normal to chrome ferrotype surface during the adsorption period; solvent, ethyl acetate; concentration, 0.28 mg./ml. The different symbols represent different samples and the open and closed points represent separate measurements made on the same sample.
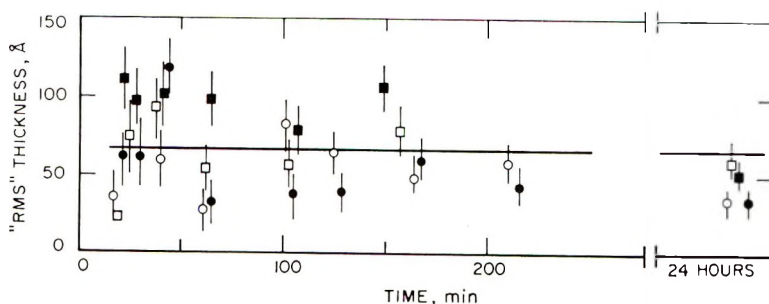

Fig. 3. Extension of adsorbed polymer molecule, MW = 7400, normal to steel surface during the adsorption period; solvent, ethyl acetate; concentration, 0.28 mg./ml. The different symbols represent different samples and the open and closed points represent separate measurements made on the same sample.

polymer and solvent, with the polymer concentration decreasing with the distance from the surface. Relations between the average value obtained with a homogeneous film model and those for several possible distributions have been determined by McCrackin and Colson.[8b] Some recent theoretical treatments[13,14] of the segment distribution normal to the surface for isolated polymer molecules have indicated that under certain conditions, except for a very short distance from the surface,[14] the distribution can be well represented by an exponential function. Although our ellipsometric experiments were for much larger surface concentrations of polymer and for somewhat smaller molecules than those treated, we have chosen the exponential distribution as the best approximation. We have, therefore, divided the value of the thickness obtained using the Drude equations for a homogeneous film by 1.5, the factor to obtain a root-mean-square average thickness, t_{rms}, for an exponential distribution.[2,8b]

Typical curves are given in Figures 2 and 3 showing the extension of the adsorbed polymer normal to the surface during the adsorption period. The extension is expressed in Angstrom units as the root-mean-square (rms)
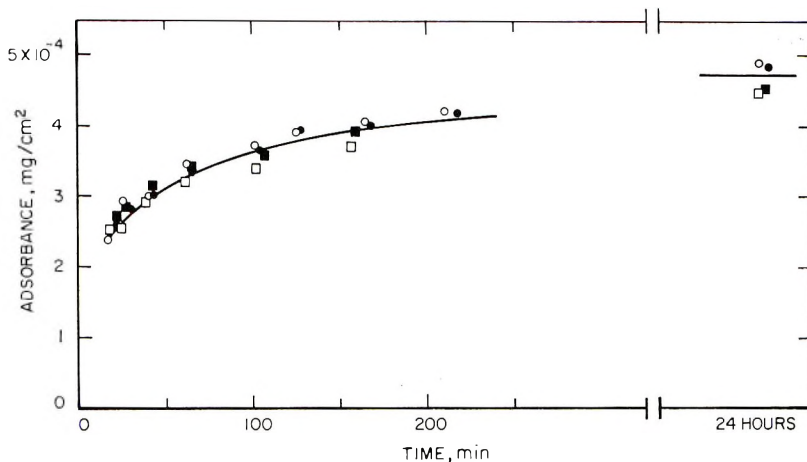
Fig. 4. Adsorbance of polymer, MW = 7400, on steel surface during the adsorption period; solvent, ethyl acetate; concentration, 0.28 mg./ml. The different symbols represent different samples and the open and closed points represent separate measurements made on the same sample.
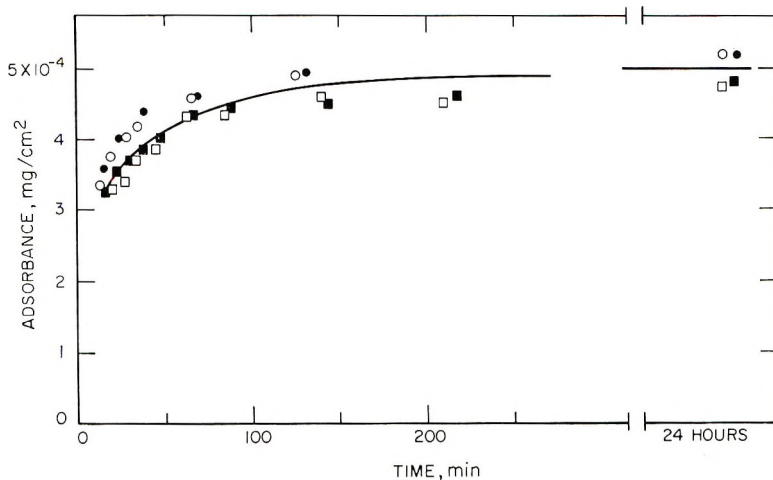

Fig. 5. Adsorbance of polymer, MW = 7400, on electrodeposited chromium during the adsorption period. The different symbols represent different samples and the open and closed points represent separate measurements made on the same sample.

average thickness of the adsorbed polymer–solvent film on the metallic surface. The different symbols in each figure represent different samples; the open and the closed points represent different locations measured on the same sample. The extension is observed to remain constant during the entire period of adsorption in which measurements were made. Precise measurements could not be made during the first few minutes of the adsorption period.

Although the extension of the polymer chain remained constant during this time interval, the adsorbance (amount of polymer adsorbed per unit

Average Equilibrium Values for the Adsorption of Poly(ethylene o-phthalate) from Ethyl Acetate on Metal Surfaces

Surface	Root-mean-square thickness, A.	Absorbance $\times 10^4$, mg./cm.^{2}	Polymer in film, wt.-%
Chrome, ferrotype	50	5.9	59
Chromium, electrodeposited	70	5.0	36
Steel	70	4.7	33
Gold, electrodeposited	70	4.9	35

area) increased with time until a final adsorbance value was attained. Typical curves are shown in Figures 4 and 5. Since the solutions were not stirred during the adsorption process, the rate of adsorption cannot be determined from these measurements. Several hours were required before a final adsorbance value was attained. The value obtained for a 24-hr. period did not change with longer time periods.

Figures 2–5 are typical for the four metal surfaces studied by ellipsometry. The average root-mean-square thickness values and the final average equilibrium adsorbance values are given in Table I. Except for the chrome ferrotype surface, the root-mean-square thickness is approximately 70 A. and the adsorbance is about 5×10^{-4} mg./cm.^{2}. This results in an adsorbed polymer film consisting of approximately 35% polymer (w/w).
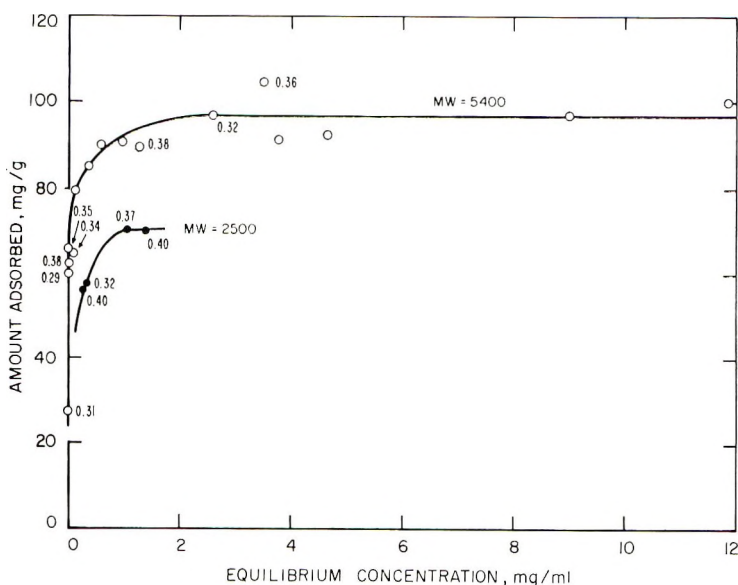
Fig. 6. Adsorption isotherms of polymer from chloroform on silica at 35°C. expressed as milligrams of polymer/g. of silica. The numbers on the figure represent the value of p obtained at that point.

The extension from the chrome ferrotype surface was somewhat lower, and as the adsorbance was slightly greater, the concentration of the polymer in the film was relatively much larger than for the other surfaces.

Adsorption isotherms for the adsorption of two molecular weight fractions of the poly(ethylene o-phthalate) from chloroform solution on silica are given in Figure 6. The results are expressed in milligrams of polymer adsorbed per gram of silica. The amount adsorbed is larger for the higher molecular weight fraction, as would be expected. The values of p associated with the isotherms are given in this figure and are relatively constant for each isotherm. The average value of p is approximately 0.34 for the 5400 molecular weight fraction and 0.37 for the 2500 molecular weight fraction. As can be seen from the curves, there is some experimental variation among the individual points. However, there is no observable trend at either molecular weight for an increase or decrease in p as the amount adsorbed increases.

DISCUSSION

The results of this study on a polar polymer can be compared with the results of investigations on the adsorption of a nonpolar molecule, polystyrene. In both cases the nature of the surface is the same or very similar: a metal presumably covered with an oxide layer and adsorbed gases, and silica, exposed to air prior to use.

Under the conditions previously studied[2,15] (adsorption from a theta solvent on the types of surfaces described above) the extension of the adsorbed polystyrene molecule normal to the surface was dependent upon the competition among polymer molecules for surface adsorption sites. When the competition was small, as would occur at short absorption times or at low solution concentrations, the molecule was relatively flat. As the adsorption period continued and additonal molecules arrived at the surface, segments of the earlier arrivals were assumed to be desorbed and replaced by segments of the newer arrivals, resulting in an increased average extension. Increased extensions also occurred for higher solution concentrations. A decrease in p, the fraction of segments adsorbed, with an increase in adsorbance for a somewhat different system, has also been reported[11] for polystyrene, supporting these conclusions. At maximum adsorbance the molecule attains a conformation that is close to that of a random coil at a boundary.

The behavior of the polar polyester adsorbing on these surfaces is markedly different from that of the polystyrene. Although the adsorbance increased during the adsorption period until a constant value was attained (Figs. 4 and 5), the extension of the molecule normal to the surface remained constant during this period (Figs. 2 and 3). As shown in Figure 6, for a given molecular weight the value of p is independent of the equilibrium adsorbance value for the range studied. A similar behavior for p has been reported for two other polymers containing carbonyl groups, a poly(alkyl methacrylate)[9] and poly(methyl methacrylate).[11] The constant value of p

indicates that the conformation remains unchanged with increasing solution concentration and surface population, in contrast to the behavior exhibited by the polystyrene under the conditions studied.

The specific values of p, averaging 0.34 for the 5400 molecular weight fraction and 0.37 for the 2500 molecular weight material, were calculated on the basis that both of the carbonyl groups in a segment are simultaneously bound to the surface. Fontana and Thomas[9] determined the extinction coefficients for the adsorbed carbonyl of n-dodecyl isobutyrate and di-n-dodecyl-3,3-dimethyl glutarate and found them to be identical and independent of surface coverage, indicating that the two carbonyl groups are simultaneously adsorbed. We attempted to determine the extinction coefficient for the adsorbed carbonyl of di-n-butyl phthalate, as an analog of a segment of poly(ethylene o-phthalate). Unfortunately, there was no measurable adsorption from chloroform solution on the silica surface. Similar results[4] were obtained previously for di-n-butyl sebacate.

The studies that we are reporting here for the poly(ethylene o-phthalate) involve the use of a different type of surface for the determination of p than that used for the determination of the extension, as well as two different solvents. We realize that the energetics of solid–polymer, solid–solvent, and polymer–solvent are different for the two studies. However, in both cases the adsorbent surface is most probably an oxide with a pre-adsorbed layer of gas. To a first approximation, the surface energies of the solids should be similar. The ethyl acetate, used for the extension measurements, is a poor solvent, and chloroform, used for the determination of p, is a good solvent. Also, as discussed below, the geometrical structure is different for the two systems studied. Hence, the numerical values of p or the extension may not be directly comparable for the two systems. However, in both cases the constant values of p and of extension inferred a stable and fixed conformation with changing surface population, either during the adsorption process or with solution concentration.

The relatively high values of p reported here infer a very flat molecule with very short loops extending into the solution. They were determined for a system in which the diameter of the adsorbent particle is small and comparable to the dimensions of a polymer molecule. It is reasonable to expect that each adsorbed polymer molecule is attached to more than one particle and that a particle may be attached to more than one molecule. For a given molecular conformation, then, attachments are possible to portions of the molecule which are unattached in the case of adsorption on an infinite planar surface. It is probable, then, that the values of p reported here are larger than those occurring in the ellipsometry experiments due, in part, to differences in the geometry of the two surfaces. The difference in polymer–solvent interaction for the two systems studied also can result in somewhat different conformations.

The value of 50–70 Å. for the root-mean-square extension for adsorption on a plane surface from a poor solvent indicates that in this case each molecule has only very few, but relatively large, loops extending into the

TABLE II

Adsorbance Values for Polyesters Adsorbed under Different Conditions

Polymer	Mol. wt.	Solvent	Temp., °C.	Adsorbent	Adsorbance $\times 10^4$, mg./cm.^{2}	Ref.
Poly(ethylene o-phthalate)	7400	Ethyl acetate	34	Metals	5.0	
"	5400	Chloroform	35	Silica[a]	0.5	
"	2500	"	"	"	0.4	
"	5400	"	50	Glass[b]	0.7	5
Poly(neopentyl succinate)	4400	"	30	Glass[c]	0.9	4
"	"	Toluene	"	"	2.2	4
"	"	Chloroform	"	Silica[a]	0.3	4
"	"	"	"	Alumina[d]	0.1	4
Poly(neopentyl phthalate)	2000	n-Heptane	20	Silica gel[e]	1.6	19

[a] Particle size 0.015–0.020 μ, nonporous.

[b] Powder, composition described in ref. 5.

[c] Type E powder, composition described in ref. 4.

[d] Porous.

[e] Wide pore.

solution. This leads to the conclusion that the value of p is small or that the attachments to the surface are in the form of relatively long trains. For a high interaction energy and a molecule that is hindered in its flexibility by the oxygen atoms in and near the backbone, trains of consecutive attachments and one or two long loops per molecule appear to be reasonable. This is consistent with the decrease in the ratio of the number of loops (or trains) to the number of repeating units that occurs with increase in chain stiffness, as shown theoretically by Hoeve et al.[16] for an isolated molecule.

The stiffness in the chain of the polyester molecule may be the cause of the observed constant value of the extension during the adsorption period. The rate of additional attachments of new trains of an adsorbed molecule could be small, compared to polystyrene, and at the solution concentration used here, vacant sites on the surface would be occupied by new arrivals before a very flat conformation could be achieved. It is possible that some readjustment of early arrivals occurs, with an increase or a decrease in extension with time. However, because of this effect and the small size of the molecule, such a difference in extension would be less than the experimental precision of the measurements and not observed.

It is possible that a higher portion of the total surface area is occupied in the case of the polyester adsorption compared to the adsorption of polystyrene. The concentration of polymer in the film adsorbed from the very poor solvent, ethyl acetate, is, as shown in Table I, approximately 35 wt.-% for three of the surfaces studied and higher for the fourth. For polystyrene adsorbed from cyclohexane at the theta temperature, the poly-

mer concentration in the film is approximately 10% at all molecular weights.[2] The use of non-theta solvents for polystyrene would probably result in lower concentration values.

The adsorbance values given here can be compared with those obtained for polyesters adsorbed from several solvents on high surface energy adsorbents. Some such values are listed in Table II. Adsorption from a good solvent, such as chloroform, on a nonporous system results in adsorbance values that are relatively independent of the adsorbent. In the case of an adsorbent with a small pore structure, such as alumina, the surface area available to the polymer is reduced, and the amount adsorbed per unit area is lower. For adsorption from poor solvents, such as toluene and n-heptane, the quantity of polymer adsorbed is significantly increased. Adsorption from ethyl acetate results in still higher adsorbance values.

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Résumé

Après adsorption on a étudié la conformation d'un polyester, le polyéthylène-*o*-phtalate, d'un poids moléculaire relativement bas. Par éllipsométrie, on a fait des recherches sur l'extension de la méthode adsorbée dans un solvant pauvre, sur différentes plaques métalliques; on a aussi déterminé p c'est-à-dire la fraction de groupes attachés

à des particules colloïdales de silice dans un bon solvant par le glissement de la fréquence entre les groupes carbonyles libres et adsorbés dans l'infra-rouge. En contradiction avec des résultats antérieurs pour le polystyrène, l'extension normale sur la surface reste constante (~70 Å) alors que pendant l'adsorption la concentration du polymère dans le film adsorbé augmente. Pour les concentrations employées, la valeur de p est relativement élevée (0.34 pour un poids moléculaire = 5400) est indépendante de la population à la surface. On suppose que la différence entre ces résultats et ceux obtenus pour le polystyrène doit être attribuée à une différence d'énergie d'interaction et de rigidité de la chaîne.

Zusammenfassung

Die Konformation eines verhältnismässig niedermolekularen Polyesters, Polyäthylen-o-phthalat, nach Adsorption wurde untersucht. Die Ausdehnung des adsorbierten Moleküls in einem schlechten Lösungsmittel an mehreren ebenen Metalloberflächen wurde ellipsometrisch ermittelt und der Bruchteil, p, an gebundenen Gruppen an kolloiden Kieselsäureteilchen in einem guten Lösungsmittel durch die Verschiebung der Infrarotabsorptionsfrequenz zwischen freien und absorbierten Carbonylgruppen bestimmt. Im Gegensatz zu früher für Polystyrol mitgeteilten Befunden blieb die Ausdehnung normal zur Oberfläche konstant (~70 Å), während die Polymerkonzentration im adsorbierten Film während der Adsorptionsperiode anstieg. Der Wert für p (0,34 für MW = 5400) ist verhältnismössig hoch und war von der Oberflächenbedeckung im untersuchten Lösungskonzentrationsbereich unabhängig. Die Unterschiede zwischen den hier erhaltenen Ergebnissen und denjenigen für Polystyrol werden auf Unterschiede in der Wechselwirkungsenergie und Kettensteifigkeit zurückgeführt.

Polymerization of Styrene with the $VOCl_3$–$AlEt_2Br$ Catalyst System

L. C. ANAND, A. B. DESHPANDE, and S. L. KAPUR,

National Chemical Laboratory, Poona, India

Synopsis

The rate of polymerization with the $VOCl_3$–$AlEt_2Br$ catalyst system at 30°C. in *n*-hexane reached a maximum at an Al/V molar ratio of 1.5. At this ratio, the rate of polymerization was first-order with respect to catalyst and second-order with respect to monomer concentrations. The apparent activation energy calculated was 6.4 kcal./mole. Diethylzinc was found to act as a chain transfer agent. However, the molecular weights of polymers obtained were low. The possibility of bromide-containing catalyst sites acting in the termination reaction has been investigated. The average valence of vanadium is discussed in relation to molecular weights.

Introduction

Since the discovery of the Ziegler catalyst system,[1] various transition metal halides in combination with organometallic compounds have been employed for the polymerization of styrene and other unsaturated hydrocarbons. Depending on the nature of the catalyst components employed,[2] each combination has its characteristic behavior in polymerization. Ziegler catalyst systems prepared with halide-containing organometallic compounds have produced entirely different results from those having organometallic compounds without halides. Natta[3] has reported that in the polymerization of propylene with $TiCl_3$ in combination with different organometallic compounds, stereospecificity increased in the order: $AlEt_3$ < $AlEt_2Cl$ < $AlEt_2Br$ < $AlEt_2I$.

Polymerization of vinyl monomers and olefins by the use of $AlEt_2Cl$ in combination with various transition metal halides has been extensively reported in the literature whereas only a few studies are known with the use of $AlEt_2Br$ in the Ziegler type catalyst. Dubose et al.[4] have reported that the $TiCl_4$–$AlEt_2Br$ catalyst system polymerizes propylene and styrene, the former stereospecifically; when $MgBr_2$ was present with the catalyst system, stereospecific polystyrene was obtained. The $VOCl_3$–$AlEt_2Br$ system is similar to the $TiCl_4$–$AlEt_2Br$ system but it has not yet been used for any polymerization reaction. In this communication some observations on the polymerization of styrene with the use of the $VOCl_3$–$AlEt_2Br$ system are reported.

Experimental

All the experiments were carried out inside a dry glove box and under nitrogen.

Styrene was freed of inhibitor by washing with 5% alkali solution followed by washing several times with water and was stored over anhydrous Na_2CO_3. Prior to use, styrene was freshly distilled under reduced pressure at 55°C. and dried over activated silica gel.

n-Hexane was purified by treatment with concentrated H_2SO_4, washed with water, and dried overnight over anhydrous $CaCl_2$. After distillation, it was stored over sodium wire. It was refluxed over sodium under bubbling nitrogen for 12 hr., redistilled, and stored over activated silica gel inside the dry box.

$VOCl_3$ was prepared[5] by reacting 1 mole of V_2O_5 with 2 moles of anhydrous $AlCl_3$ at about 400°C. and distilled out as brown liquid. After redistillation under anhydrous conditions, a lemon-yellow liquid was obtained. A stock solution (0.5M) was prepared in n-hexane.

$AlEt_2Br$[6] was obtained by reacting magnalium alloy (Al 70%, Mg 30%) with C_2H_5Br (in molar proportion) and distilled under reduced pressure (1 mm.) at 68°C. Aluminum was estimated[7] volumetrically by EDTA complexometric titration, which showed high purity of material. A stock solution of 0.5M concentration was prepared in n-hexane.

$ZnEt_2$ was prepared[8] by reacting C_2H_5Br and C_2H_5I with Zn–Cu alloy (Zn 92%, Cu 8%) and distilled at 110°C. under nitrogen atmosphere.

The valence of vanadium in catalyst complex was estimated by potentiometric titration[9] at 80°C. under bubbling nitrogen. The catalyst complex was decomposed with $4N$ H_2SO_4 and titrated against $0.0432N$ $CeSO_4$ solution. An Ampot potentiometer was used for the experiments.

Polymerization

All the reagents were added with hypodermic all-glass syringes fitted with stainless steel needles. The reagents were added in an Erlenmeyer flask (50 ml.) fitted with a B_{19} cone joint in the following order: solvent, $VOCl_3$ solution, and $AlEt_2Br$ solution. The catalyst complex so formed was aged for a given time and at this stage monomer was introduced into the system. The flask was stoppered tightly with a well-greased B_{19} socket joint and maintained at a thermostatically controlled constant temperature. The reaction mixture was stirred vigorously with specially fabricated magnetic stirrer.[10] After a specific time of reaction, the polymer was precipitated with large amount of methanol containing 5% HCl and left overnight to settle down well. It was washed thoroughly with methanol and separated over a weighed crucible with a sintered glass disk and dried to constant weight.

Molecular weights were determined viscometrically in benzene at 25°C. by using the relationship:[11]

$$P_n = 1770[\eta]^{1.4}$$

Results and Discussion

A dark brown color developed instantaneously on mixing the two catalyst components which was unchanged regardless of variation in concentration of catalyst components; a precipitate was also formed.   As seen

TABLE I
Effect of Aging of Catalyst on Polymerization of
Styrene with VOCl₃–AlEt₂Br[a]

No.	Aging time, min.	Yield, g.	[η]	Molecular weight
1	10	0.6626	0.141	11,900
2	20	0.7639	0.124	9920
3	30	0.6693	0.135	11,480
4	60	0.4536	0.090	6690
5	1440	0.2210	0.077	5060

[a] Polymerization conditions: VOCl₃ = 0.002 mole/l.; styrene = 5 ml. (1.74 mole/l.); AlEt₂Br = 0.003 mole/l.; reaction time = 15 min.; Al/V ratio = 1.5.   Temp., 30°C.

in Table I, the catalyst system was aged for periods of time from 10 min. to 24 hr.   It was observed that after 30 min. aging of catalyst, the rate of polymerization and molecular weight of polymer decreased with time, indicating decomposition of the catalyst system.   In order to have a catalyst system of constant activity all the experiments were carried out after 20
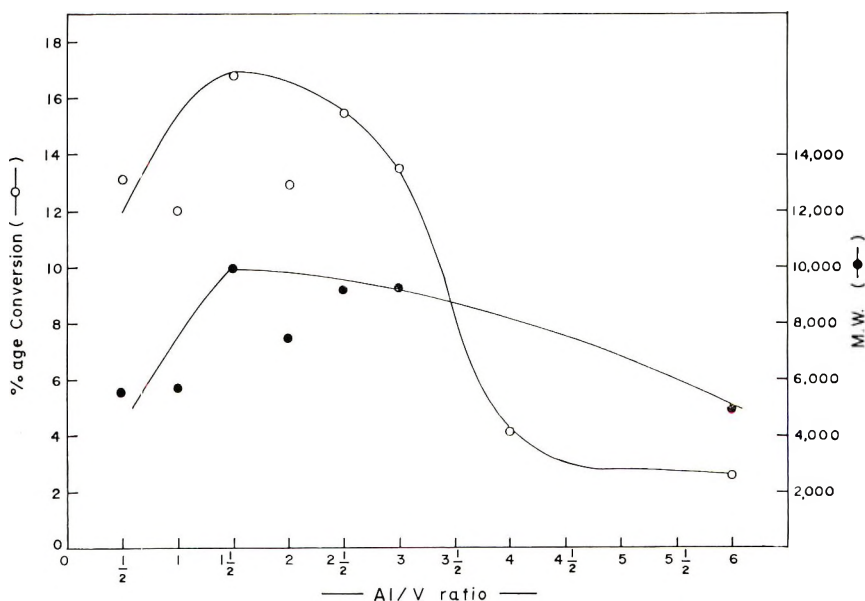
Fig. 1. Effect of Al/V ratio on (O) conversion and (●) molecular weight in polymerization of styrene by VOCl₃–AlEt₂Br. Total volume = 25 ml.; VOCl₃ = 0.002 mole/l.; styrene = 5 ml.; aging time = 20 min; reaction time = 15 min.; temperature = 30°C.
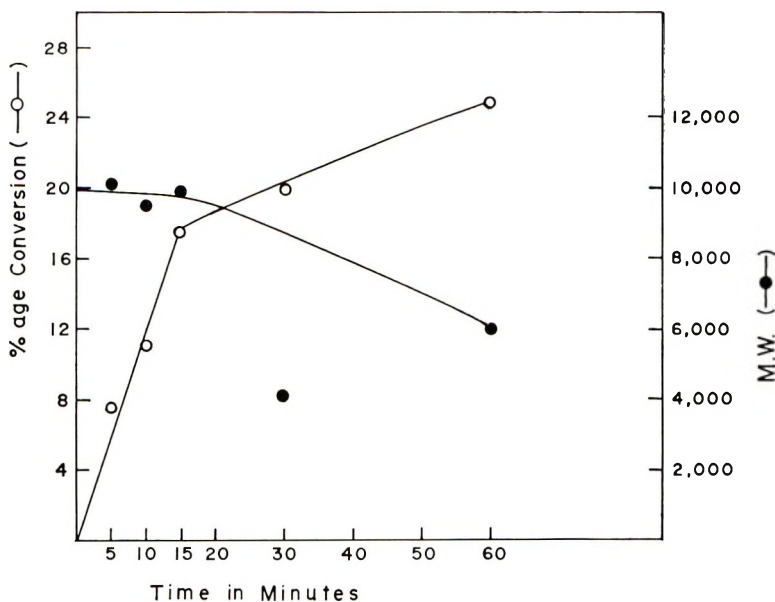
Fig. 2. Plot of (○) conversion and (●) molecular weight vs. time. Total volume = 25 ml.; VOCl₃ = 0.002 mole/l.; AlEt₂Br = 0.003 mole/l.; Al/V ratio = 1.5; styrene = 5 ml.; aging time = 20 min.; temperature = 30°C.
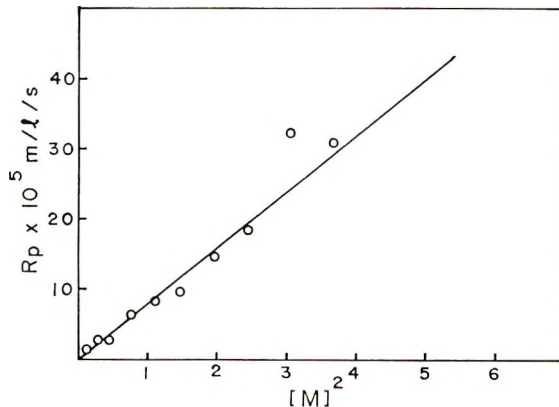

Fig. 3. Effect of monomer concentration on (○) the rate of polymerization. Total volume = 25 ml.; VOCl₃ = 0.002 mole/l.; AlEt₂Br = 0.003 mole/l.; Al/V ratio = 1.5; aging time = 20 min.; reaction time = 15 min.; temperature = 30°C.

min. aging of the catalyst system. It is known[12,13] that particular catalyst sites are formed corresponding to variation of ratio of catalyst components. In this case also, the rate of polymerization was maximum at an Al/V ratio of 1.5 and at this ratio the molecular weight of polymer was also maximum (see Fig. 1). Hence it can be assumed that Ziegler-type catalyst sites with maximum activity are available at the Al/V ratio of 1.5.

The rate of polymerization at an Al/V ratio of 1.5 was also constant only up to the first 15 min. (Fig. 2) and then decreased, probably due to covering of catalyst sites with precipitated polymer in n-hexane. Similar covering of catalyst sites with polymer has been reported[14] in the polymerization of ethylene and styrene.
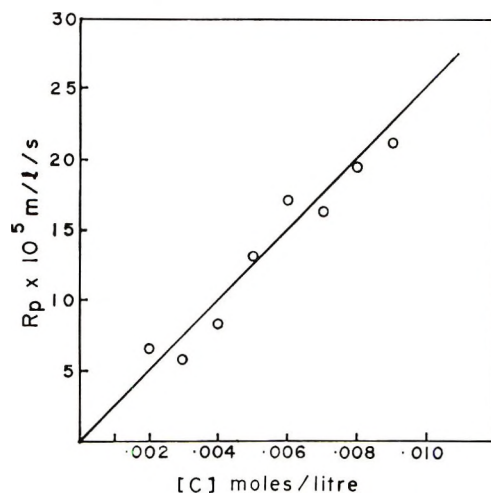

Fig. 4. Effect of catalyst concentration on (○) the rate of polymerization. Total volume = 25 ml.; Al/V ratio = 1.5; styrene = 2.5 ml.; aging time = 20 min.; reaction time = 15 min.; temperature = 30°C.
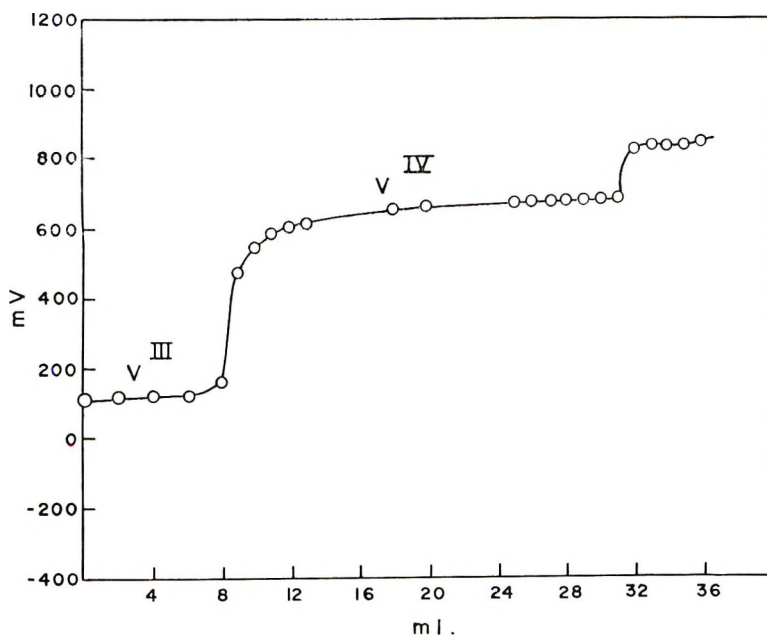
Fig. 5. Valence distribution of vanadium at Al/V ratio of 1.5. VOCl₃ = 2 ml. (0.5M); H₂SO₄ = 25 ml. (4N); temperature = 80°C.; CeSO₄ = 0.043N; V(III) = 8 ml.; V(IV) = 15 ml. Average valence = 3.65.

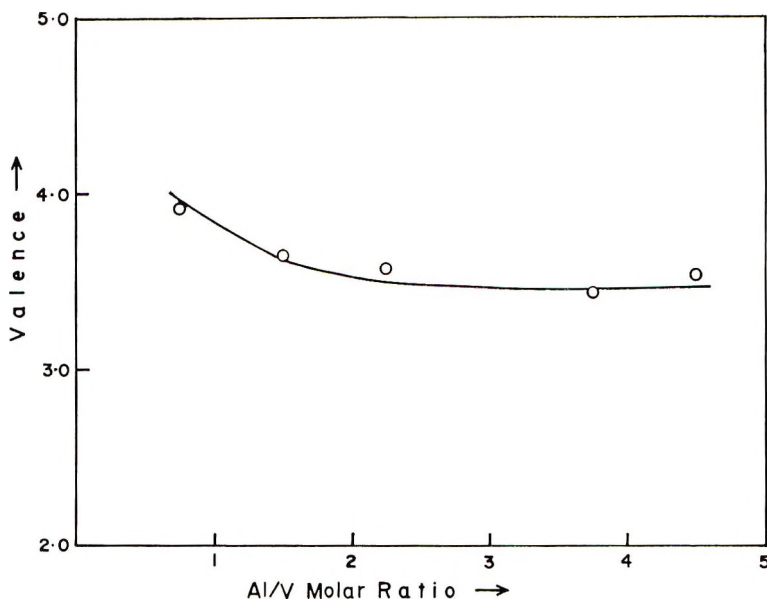Fig. 6. Average valence of vanadium at different ratios of Al/V: VOCl₃ = 2 ml.
(0.5M); H₂SO₄ = 25 ml., (4N); temperature = 80°C.; CeSO₄ = 0.043N.

The variation of polymerization rate with catalyst and monomer concentrations was studied at an Al/V ratio of 1.5 and was restricted to 15 min. reaction time. The reaction was first-order with respect to catalyst and second-order with respect to monomer concentration (Figs. 3 and 4), and rate constants calculated (K = 2.99 × 10⁻² sec./mole²-l.² with respect to monomer and K = 3.99 × 10⁻² sec./mole²-l.² with respect to catalyst) represented a very high activity of the catalyst system. The second-order relation with respect to monomer can be explained on the basis of a Rideal or Langmuir-Hinshelwood mechanism, as was done by Gaylord et al.[15]

The molecular weight of polymer obtained was very low, i.e., in the range of 4000–12,000. Similarly, the AlEt₂Cl–TiCl₄ catalyst[16] system yields a low molecular weight polymer as compared to the AlEt₃–TiCl₄ catalyst system. Further, the average valence of vanadium in the catalyst complex was found to be 3.65 (Fig. 5) and at different ratios of Al/V, it is in the range of 3.5–4 (Fig. 6). This, no doubt, indicates that the catalyst complex is mostly tetravalent. A tetravalent catalyst complex like Li alkyl–TiCl₄[17] has been reported to be highly reactive, however yielding low molecular weight polymer.

The molecular weight of polymer did not change significantly with increasing concentrations of catalyst and monomer, indicating termination through chain transfer with monomer and catalyst sites. In case of the AlEt₂Cl–TiCl₄ catalyst system, it is also reported that chain termination takes place with monomer and catalyst sites.[16]

In order to observe the effect of certain catalyst sites containing bromide on the termination reaction, C_2H_5Br was added to the VOCl₃–AlEt₃ polymerization system. A very small decrease in rate of polymerization and molecular weight was observed. However, when an increasing amount of C_2H_5Br was used with the classical Ziegler catalyst ($TiCl_4$–AlEt₃), it acted as a chain transfer agent (Tables II and III).

With all these probable factors responsible for chain termination, $AlEt_2Br$ can act as chain transfer agent since with increasing concentration of $AlEt_2Br$, the molecular weight decreased (Fig. 1). Under these circumstances, it is only natural that the molecular weight of polymer would be very low and at the same time the rate of polymerization would be very high.

TABLE II
Effect of Ethyl Bromide on Polymerization
of Styrene with VOCl₃–AlEt₃[a]

No.	EtBr concn., mole/l.	Yield, g.	Molecular weight
1	—	0.1329	82,410
2	0.002	0.1091	79,500
3	0.010	0.1105	79,370
4	0.020	0.1112	77,050

[a] Polymerization conditions: reaction time = 1 hr.; styrene = 10 ml. (3.5 mole/l.); aging time = 20 min.; VOCl₃ = 0.02 mole/l.; ratio Al/V = 2. Temp., 40°C.

TABLE III
Effect of Ethyl Bromide on Polymerization of Styrene with $TiCl_4$–AlEt₃[a]

No.	EtBr concn., mole/l.	Yield, g.	Molecular weight
1	—	0.0526	72,770
2	0.001	0.0728	53 010
3	0.002	0.0649	50,860
4	0.020	0.1324	31,880
5	0.060	0.1449	27,610

[a] Polymerization conditions: reaction time = 1 hr.; styrene = 10 ml. (3.5 mole/l.); aging time = 20 min.; $TiCl_4$ = 0.02 mole/l.; ratio Al/Ti = 3. Temp., 40°C.

Further, the mechanism of polymerization can be understood from the studies of activation energy and effect of adding zinc diethyl to the polymerization reaction. The activation energy calculated from a plot of log R_p versus reciprocal absolute temperature (Fig. 7) was 6.4 kcal./mole, which falls in the range of activation energy (5–12 kcal./mole) obtained for many Ziegler-type catalyst systems like $TiCl_4$–AlEt₃ and $TiCl_3$–AlEt₃.[18,19] With the addition of ZnEt₂ to VOCl₃–AlEt₂Br system, there was initially a sudden decrease in molecular weight (Table IV) but there was little effect with the further increase in concentration of ZnEt₂. A decrease in molecular weights has been reported with the addition of ZnEt₂ to classical $TiCl_4$–AlEt₃ Ziegler catalyst also.[20]
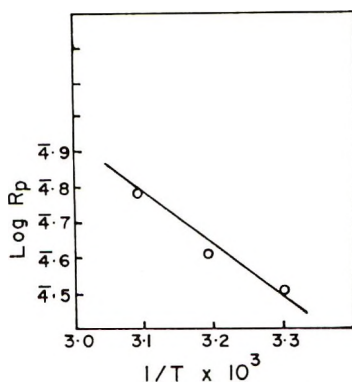
Fig. 7. Activation energy. $VOCl_3$ = 0.002 mole/l.; $AlEt_2Br$ = 0.003 mole/l.; Al/V ratio = 1.5; styrene = 5 ml.; aging time = 20 min.; reaction time = 15 min.

TABLE IV

Effect of $ZnEt_2$ on the Polymerization of Styrene with $VOCl_3$–$AlEt_2Br$[a]

No.	$ZnEt_2$ concn., moles/l.	Yield, g.	Molecular weight
1	—	0.7639	9930
2	0.0002	0.5456	2110
3	0.0004	0.2213	2140
4	0.001	0.1271	2270
5	0.002	0.1079	2770
6	0.01	0.1037	3650

[a] Polymerization conditions: styrene = 5 ml. (1.74 mole/l.); reaction time = 15 min., $VOCl_3$ = 0.002 mole/l.; aging time = 20 min.; ratio Al/V = 1.5. Temp., 30°C.

In short, this catalyst system is responsible for polymerization of styrene by a coordinated anionic mechanism like other classical Ziegler catalyst systems, but due to different terminating reactions, molecular weights are low.

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Résumé

La vitesse de la polymérisation du styrène, catalysée par VOCl₃–AlEt₂Br à 30°C dans le n-hexane, atteignait un maximum quand le rapport Al/V était égal à 1.5. Alors, en accord avec les systèmes catalysés par les initiateurs classiques de Ziegler, la vitesse de polymérisation était du premier ordre par rapport à la concentration en catalyseur et en monomère; apparemment l'énergie d'activation calculée était de 6.4 Kcal/mole et on avait trouvé que le diéthyl zinc agissait comme un agent de transfert de chaîne. Et pourtant les poids moléculaires obtenus des polymères étaient très bas. On avait suggéré la possibilité d'une terminaison catalysée par des bromures. On a discuté la valence du vanadium en relation avec les poids moléculaires.

Zusammenfassung

Die Polymerisationsgeschwindigkeit von Styrol mit dem Katalysatorsystem VOCl₃–AlEt₂Br bei 30°C in n-Hexan besitzt bei einem Al/V-Verhältnis 1,5 ein Maximum. Bei diesem Verhältnis war, in Ubereinstimmung mit klassischen Ziegler-Katalysatorsystemen, die Polymerisationsgeschwindigkeit von erster Ordnung in Bezug auf Katalysator- und Monomerkonzentration, die scheinbare Aktivierungsenergie wurde zu 6,4 Kcal/Mol berechnet und Diäthylzink erwies sich als Kettenüberträger. Die Molekulargewichte der erhaltenen Polymeren waren aber sehr niedrig. Die Möglichkeit der Wirksamkeit von bromhältigen Katalysatorplätzen bei der Abbruchsreaktion wurde untersucht. Die Beziehung der mittleren Vanadinvalenz zum Molekulargewicht wird diskutiert.

NOTES

Hydrogen-Transfer Polymerization of Cinnamide

Hydrogen-transfer polymerization by basic catalyst has been reported by many authors for acrylamide,[1-4] methacrylamide,[1,5] p-styrenesulfonamide,[6] maleimide,[7] crotonamide,[8] and other monomers. In the present experiment the hydrogen-transfer polymerization of cinnamide, a β-substituted acrylamides, to poly-β-phenyl-β-alanine by basic catalyst was investigated.

In the polymerization of cinnamide various solvents, such as dimethylformamide (DMF), pyridine, dimethyl sulfoxide (DMSO), etc., were used. The catalytic effect of several basic compounds, such as sodium (dispersion), sodium tert-butoxide, n-butyllithium, and sodium methoxide, was investigated. Table I records the results for several runs.

TABLE I
Effect of Solvent and Catalyst in the Polymerization of Cinnamide

Catalyst	Solvent	Reaction temperature, °C.[a]	Yield of polymer, %	Reduced viscosity of polymer[b]
n-BuLi	DMF	120	55	0.04
n-BuLi	DMF	140	50	0.06
n-BuLi	—[c]	160	92	0.05
n-BuLi	DMAc	140	5	0.04
n-BuLi	Pyridine	90	35	0.05
Na	DMF	140	50	0.05
Na	Pyridine	90	25	0.04
CH₃ONa	DMF	140	40	0.04
C₂H₅ONa	DMF	140	35	0.05
tert-BuOK	DMF	140	35	0.04
tert-BuONa	Pyridine	90	25	0.04
Na alkoxide of d-borneol	Pyridine	100	54	0.07

[a] Reaction time 5 hr.

[b] Measured at concentration of 0.5 g./100 ml. of DMF at 30°C.

[c] Bulk polymerization.

The reduced viscosity of polymers did not change markedly on varying the catalyst and was scarcely affected by the concentration of catalyst. n-Butyllithium and sodium dispersion in DMF gave high yield of polymer (50–60%). In chlorobenzene and toluene, no polymer was obtained, though acrylamide gave polymer of high viscosity in high yield in these solvents. With the sodium alkoxide of d-borneol, which is an optically active catalyst, polymerization occurred, and the polymer obtained had no optical activity. The polymerization of cinnamide was carried out at temperatures ranging from −78°C. to 160°C. in DMF with n-butyllithium as a catalyst. At temperatures below 80°C., no polymer was obtained, and at higher temperatures the polymerization proceeded to give polymer in high yield. The decomposition point of polymers was

about 230°C. The polymers were soluble in DMF, DMSO, m-cresol, and dichloroacetic acid.

In the infrared spectrum of the polymer obtained here, the characteristic absorption band (amide II band) of a monosubstituted amide appeared at 1530 cm.$^{-1}$ and absorptions characteristic of the ethylenic group appeared at 2850 and 2900 cm.$^{-1}$. In addition to these absorptions, C–H out-of-plane deformation due to the terminal olefinic double bond was observed at 965 cm.$^{-1}$. The infrared spectrum of β-cinnamoylamino-β-phenylpropionamide as a model compound gave the same absorptions as the polymers.

The polymer was hydrolyzed with hydrochloric acid. When the hydrolyzate was subjected to paper chromatography and amino acid analysis, only β-phenyl-β-alanine was found as amino acid. In addition to β-phenyl-β-alanine, an oily product was obtained in the hydrolyzate which was found to correspond to β-chloro-β-phenylpropionic acid by thin-layer chromatography with n-hexane as a developing solvent ($R_f = 0.48$ by methyl red). This result showed that the hydrogen-transfer polymerization of cinnamide occurred, and the polymer should be terminated by an ethylenic double bond. When 0.396 g. of polymer (η_{sp}/c 0.04) obtained in DMF with Na as catalyst was hydrolyzed with 12N hydrochloric acid, the hydrolyzate contained 0.118 g. of an oily product. The oily product gave a single spot by methyl red and was determined to be β-chloro-β-phenylpropionic acid by thin-layer chromatography. The residue (0.248 g.) obtained from hydrochloric acid solution gave a single ninhydrin-positive spot and was determined to be β-phenyl-β-alanine hydrochloride by amino acid analysis. From this hydrolysis data, the degree of polymerization is estimated to be about three if the polymer has one double bond per molecule.

The presence of the terminal C=C double bond suggests that the initial step of the polymerization involves proton abstraction of amide hydrogen with base. The fact that only oligomers were obtained may be due to the charge transfer of the growing anion chain to monomer. A steric effect by the phenyl group of the monomer may also play a part.

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Yoshio Iwakura
Nobuo Nakabayashi
Kazutsune Sagara
Yoshifumi Ichikura

Department of Synthetic Chemistry
Faculty of Engineering
University of Tokyo
Bunkyo-ku, Tokyo, Japan

Decay of the ESR Signal in Ultraviolet-
Irradiated Poly(methyl Methacrylate)

The same ESR spectrum is obtained when bulk samples of poly(methyl methacrylate), PMMA, are exposed to various types of radiation.[1] It has been a controversy whether the spectrum arises from a single free radical[2-7] or two different radicals.[8-12] Observations have been made that some resonance lines in the spectrum appear to decay at a faster rate than others and they have been interpreted as evidence for the existence of two separate radicals. A typical derivative display of the ESR spectrum is shown in Figure 1a, which consists of nine lines with alternating intensities. Some authors have described it as a five-line spectrum interleaved with a four-line spectrum having a smaller peak intensity. These two groups of lines are the ones observed to decay at different rates. In the present work, we have investigated the decay of the ESR signal in ultraviolet-irradiated PMMA in an attempt to determine whether a single radical or two separate radicals are involved.
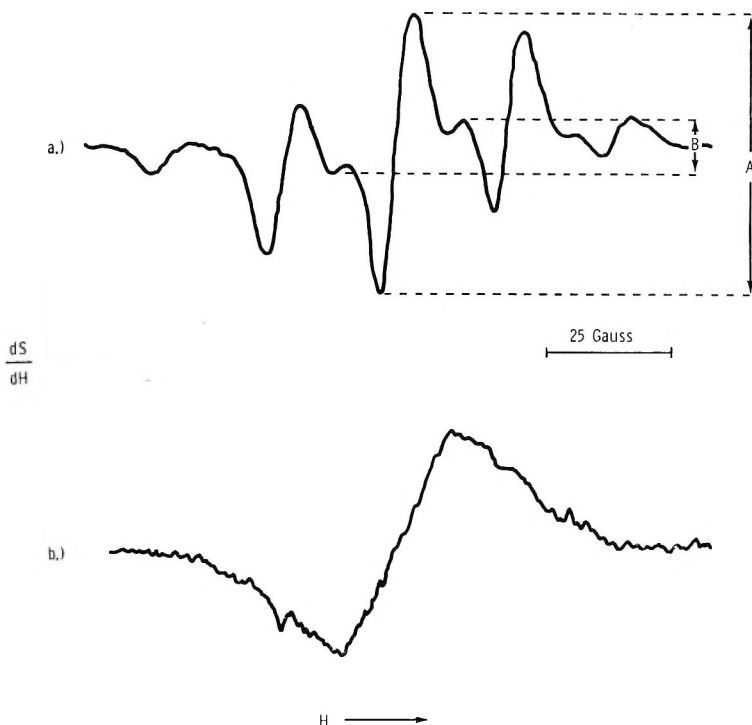

Fig. 1. ESR spectra of PMMA: (a) derivative of typical ESR spectrum in irradiated PMMA; (b) ESR signal remaining after continued heating at 80°C. Note: amplitudes of Fig. 1b have been increased by approximately five times over Fig. 1a.

Experimental

The ESR measurements were made at approximately 9.5 Gc./sec. with the use of a standard reflection spectrometer. Magnetic field modulation was used which resulted in a derivative presentation of the signal as shown in Figure 1a.

The polymer samples were placed in quartz tubes, evacuated, and sealed at 10^{-2} mm. Hg. The irradiation was carried out by placing the tube in the center of a Rayonet photochemical reactor which provides light primarily at 2537 A. The irradiation was

nominally carried out at room temperature, although some warming of the samples occurred (to approximately 40°C.). The decay was observed at room temperature.

The PMMA was prepared from monomer which had been distilled twice. Dissolved oxygen was removed from the monomer by a freeze-melt technique in which the sample was successively flushed with dry, oxygen-free nitrogen gas, frozen, and evacuated. The monomer was then allowed to polymerize slowly in bulk at room temperature, without the use of initiator or radiation. Scrapings from the resulting polymer rod were used to prepare several samples all of which behaved similarly as those reported on here.

Results and Discussion

The parameters A and B in Figure 1a were used to measure the intensity of the five-line and four-line spectra, respectively. These are essentially the parameters which have been used by other investigators. (It would be desirable to obtain the relative amplitudes of the five-line and four-line spectra from a fit of the experimental spectrum to a theoretically calculated one. However, at the present time, uncertainties in the number of lines,[5,13,14] their linewidths,[5] and their relative positions[14] make such a calculation of doubtful value, especially during a change in the form of the spectrum.) Figure 2 shows typical results for the decay of A (five-line spectrum) and B (four-line spectrum) following exposure to ultraviolet light. The behavior of A can be described by the expression:

$$A = A_0 \exp \{-kt^{1/2}\} \tag{1}$$

where k is the decay constant and A_0 is the value of A at $t = 0$ when the irradiation was discontinued and the decay began to be monitored. The corresponding rate equation is:

$$dA/dt = -\frac{1}{2} A (k/t^{1/2}) \tag{2}$$

This behavior can be described by considering each radical which produces the resonance A as being surrounded by a sphere of influence. Outside of this sphere is a uniform distribution of impurity particles, each of which can react instantaneously with the radical once it has diffused inside the sphere of influence. This problem has been discussed in general terms by Chrandrasekhar[15] and Waite.[16] Campbell and Looney[10] have successfully applied it specifically to the decay of the ESR signal in PMMA, although little mention of their work appears in the literature.

The agreement of our data (on A) with eq. (1) leads us to conclude that the decay in the evacuated and sealed sample tubes is also due to impurities such as residual monomer and/or degradation products and that the rate of decay is controlled by the diffusion of these impurities. Other descriptions of the decay have attributed it to radical recombination[11,17] and to an impurity[18] but without considering the diffusion of the impurity as a controlling factor.

The data of Figure 2 show that not only do A and B decay at different rates but that the decay of B is not described by the same expression as A. The different decay rates for A and B have been observed in all studies but one[3] and cannot be seriously questioned. On the other hand, the success of the single radical picture[2,6] in predicting spectra for deuterated samples leads us to consider other possible interpretations of the decay data than that the five-line and four-line spectra arise from separate radicals.

One obvious alternative explanation (although it has not been suggested in the literature) is that the nine-line spectrum is superimposed on an additional spectrum which decays at a different rate. In support of this suggestion, we have observed that, while heating the sample at 110°C. for 30 min. completely destroyed the ESR signal, a rather broad single resonance (Fig. 1b) remained after continued heating at 80°C. It is interesting to note that the derivative peaks appear at the positions where B (the four-line spectrum) is measured. Similar results have been reported by Bullock and Sutcliffe,[13] although they observed a poorly resolved quartet which they interpreted as the

four-line spectrum of the normal PMMA signal. However, the stability of the spectrum in Figure 1b and the observed decay of B with time suggest two separate contributions to B. The resonances of the five-line spectrum are sufficiently narrow that the decay of B cannot be attributed to changes in the outer extension of these lines. The derivative display in Figure 1b shows a greater contribution from the stable line to B than to A. In addition, the large amplitude of A further reduces the importance of the small contribution from the stable line to the decay rate. Assuming that there is zero contribution to A and that there is no decay of the stable line at room temperature, it should be possible to find some constant, B_0, such that $B - B_0$ decays in the same manner as A if our alternative explanation of the decay is correct. This is seen to be satisfied by B-13 in Figure 2.
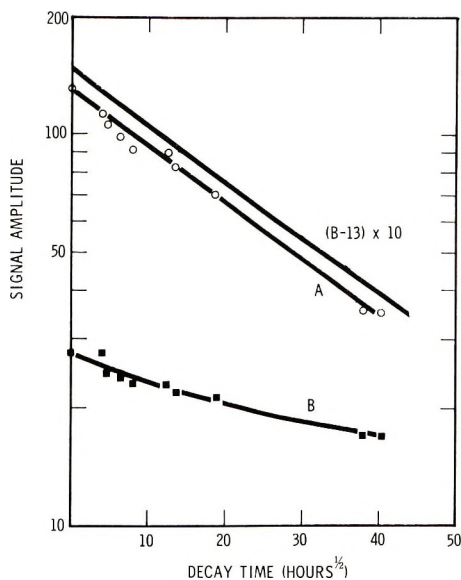

Fig. 2. Decay of (A) five-line spectrum, (B) four-line spectrum (B-13) corrected four-line spectrum for ultraviolet-irradiated PMMA.

It is of interest to note that although Campbell and Looney[19] present their results as evidence for two separate radicals, their data can also be treated and explained in the same manner as we have suggested. Furthermore, the B_0 for their data is sufficiently small relative to the initial amplitude that the difference in the decay rates of the five-line and four-line spectra cannot be easily detected in the early stage (until the amplitude decays to about one-third of the initial value). It might be noted that this is the same range of decay over which Symons[3] observed no relative change in the five-line and four-line spectra.

In conclusion, our data show that the decay of the ESR signal in irradiated PMMA can be explained by the combination of the radicals with impurities such as residual monomer and/or degradation products. The rate of decay is controlled by the diffusion of the impurities. Furthermore, the change in the form of the spectrum as decay occurs does not necessarily require the five-line and four-line spectra to arise from two separate radicals. It is possible that instead the nine-line spectrum is superimposed on an additional spectrum of greater stability.

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R. E. MICHEL
F. W. CHAPMAN
T. J. MAO

General Motors Research Laboratories
Warren, Michigan 48090

Elemental Organic Compounds. Part XX. Ethylene Dimerization to Butene-1

The oligomerization of ethylene to obtain various low molecular weight products has been investigated for a long time and includes the Alfene Process[1] for the production of α-olefins.

Selective dimerization has been achieved with some success over BF_3,[2] pure Ni,[3] Co–charcoal,[4] nickel oxide–silica–alumina,[5-8] aluminosilicate,[9] trialkylaluminum–titanates,[10] and trialkylaluminum–zirconates,[11] triethylaluminum–nickel acetylacetone,[12] or ethyl-aluminum sesquichloride–nickel carbonyl–triphenylphosphine.[13]

However, in most of the cases, the catalysts are complex mixtures of several components or the selectivity for butene-1 production is not prominent.

We report a novel unicomponent organometallic catalyst, dicyclopentadienylnickel (nickelocene) for the highly selective dimerization of ethylene to butene-1.

A solution of nickelocene (1 g.) in n-heptane (50 ml.) was placed in a 300-ml. autoclave under nitrogen pressure. Ethylene was charged at a pressure of 600 psi. The autoclave was heated at 200°C. for 18 hr., during which period the pressure decreased from 2600 to 1500 psi, indicating a reaction. After cooling to room temperature, the autoclave was vented and the released gas was collected in a trap cooled by a Dry Ice–acetone bath. The colorless liquid thus obtained (5 ml.) was found, by gas chromatography, to consist of butane, butene-1, trans-butene-2 and cis-butene-2, in a ratio of 1:1198:89:56 (89% butene-1). The catalyst was decomposed, and some higher oligomers were also detected in the reacted solution. Due to isomerization, the butene-1 content dropped to ca. 20% when the reaction was conducted at 300°C.

A logical mechanism is presented in eqs. (1).
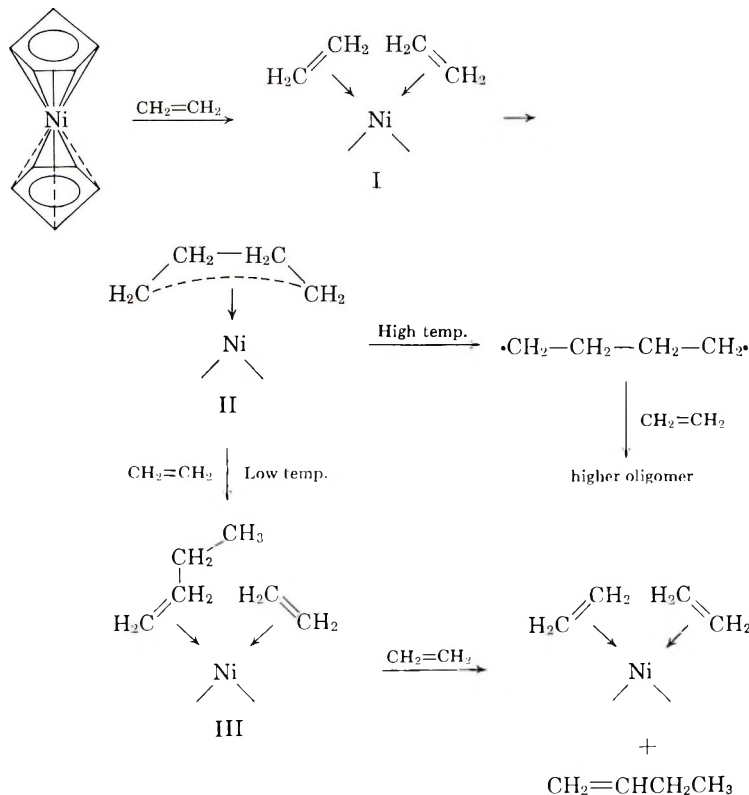
Since nickelocene has two unpaired electrons in its antibonding orbital, it may be attacked by ethylene releasing the cyclopentadienyl rings while forming a π-complex (I) with ethylene. Then, dimerization occurs by the coupling of ethylene on the surface of the nickel metal (II). Simultaneously (possibly, this may be the true driving force for dimerization) another ethylene attacks the complex and yields selectively a butene-1 complex (III) by the shift of a hydrogen radical. No further coupling occurs on the metallic surface because the bulkiness of the dimer prevents the metal orbital overlap with another ethylene molecule.

After the butene-1 is expelled from the complex III by an approaching ethylene, the interaction proceeds in the same manner. Thus, the reaction continues catalytically. However, at higher temperatures, a biradical propagation reaction may occur soon after the initial interaction of the ethylene molecules. The butene-1 complex (III) does not form under these conditions because of the retardation of the proton shift by thermal agitation producing higher oligomers. Solid polymers are not evaluated since the ethylene pressure is not high enough. Thermodynamically, it is difficult to obtain pure butene-1 at high temperatures due to isomerization.

In the case of butadiene cyclooligomerization by the use of a zero-valent nickel catalyst, the intermediate π-complex is isolable.[14] However, in our case, the intermediate is too unstable to be isolated.

This proposed mechanism of π-type dimerization on an active metal surface is one example of catalysis at the atomic level which has been described already.[15]

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Department of Chemistry   Minoru Tsutsui*
New York University   Takashi Koyano†
Bronx, New York 10453

* To whom all correspondence should be directed.

† Present address: Central Research, Toa Nenryo Co., Saitama-Ken, Japan.

Elemental Organic Compounds. Part XXI. Polymerization of Ethylene by Dibenzenechromium

It has recently been reported that the polymerization of butadiene takes place on surfaces of various transition metal atoms such as Ti, Cr, Fe, Co, and Ni, each of which is formed by the decomposition of corresponding organic derivatives.[1]

The polymerization mechanism can be explained by the concept of catalysis at the atomic level which, when created, increases the activity of the transition metal towards addition polymerization by means of stimulated interaction of π-electrons of the monomer with the metal d orbitals. The oligomerization of butadiene by a zero-valent nickel atom has also been interpreted by essentially the same mechanism.[2]

We have, however, been able to dimerize a monoolefin, ethylene, selectively on atomic nickel which was produced by the decomposition of nickelocene.[3]

We have now found another example of this type of ethylene polymerization catalyst. A solution of dibenzenechromium (0), 1.1 g. in nitrogen-saturated n-heptane (50 ml.), was placed in a 300-ml. autoclave under a nitrogen atmosphere. Ethylene was charged into the autoclave to 630 psi. The pressure did not change on prolonged heating at 200°C. for 16 hr. However, at 250°C. and 2800 psi, a rapid decrease to 1100 psi was observed after 7 hr. The catalyst was found decomposed in the cooled autoclave. The white solid polyethylene formed was dissolved in hot xylene and boiled with hydrochloric acid three times to remove the catalyst and was reprecipitated several times with xylene–methanol. The purified polymer weighed 3.7 g. According to infrared analysis, it seems to have contained only an internal $trans$ double bond (965 cm.$^{-1}$) as the unsaturated bond. The density was 0.966 g./cc. by the density-gradient tube method. This value corresponds to 88% crystallinity.[4]

The melting point observed under a polarization microscope was 126°C. The intrinsic viscosity measured in tetralin at 130°C. was 0.99, from which the molecular weight calculated by Tung's equation was 34,000.[5]

On the basis of these findings, it appears that the polymerization reaction may proceed through atomic level catalysis, since the reaction commences at a temperature close to the decomposition point[6] of dibenzenechromium.

The $trans$ double bond in the polymer implies that the double bond was fixed to the catalyst during the propagation reaction and the chain grew from both sides independently. Thus, the mechanism of eqs. (1) is postulated.
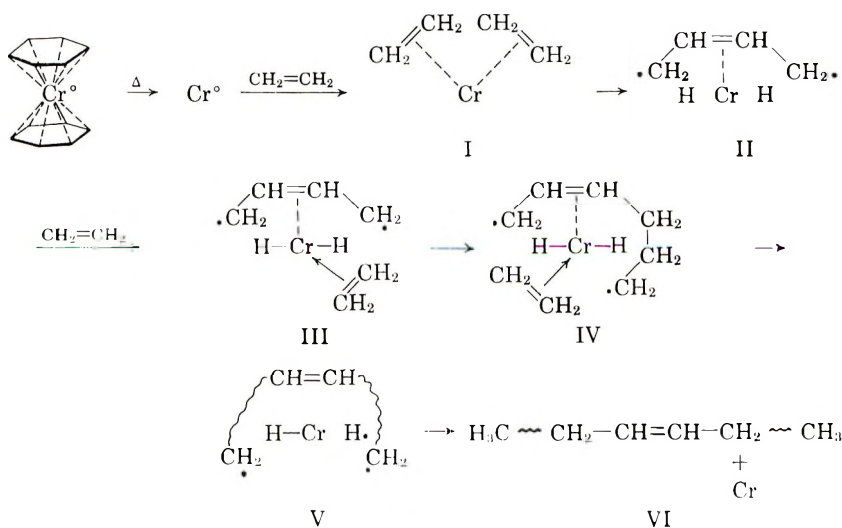
Soon after metallic chromium is formed from the thermal decomposition of dibenzene-chromium, the surrounding ethylene molecules start interacting with the vacant d orbitals of the metal to form π-bonding (I). Since the active chromium atoms shows a strong ability to dehydrogenate organic groups forming chromium hydride,[7] the ethylene ligands form a biradical olefinic chain (III).

Each radical can add additional ethylene molecules assisted by the central metal which can interact with the ethylene π-system (III, IV). Thus, the successive radical propagation continues catalytically until hydrogen radicals from the decomposition of chromium hydride finally terminate the reaction. During the course of the polymerization, the internal double bond is preserved by π-bonding to the catalyst. As a result of the restricted propagation on the metal surface, an unusually high density polyethylene is produced in spite of a sort of radical type polymerization.

The polymerization of ethylene by dibenzenechromium has already been reported. However, the active species is derived from the treatment of dibenzenechromium with oxygen before use[8,9] and does not constitute catalysis at the atomic level. The polyethylene thus produced had a considerably high molecular weight, 898,000 or 1,660,000, and a high melting point, 135–140°C. The double bonds were predominantly the terminal vinyl type. The polymerization mechanism has not been elucidated.

Several factors contribute to the difference in catalysis between nickel (VI) and chromium at the atomic level. Presumably, it is due partly to the difference in electronic configuration and geometry. Zero-valent nickel forms tetrahedral complexes, while zero-valent chromium can accept as many as six ligands in an octahedral environment. Thus, the intermediate dimerized chromium complex can couple more easily with additional ethylene molecules. Evidently, the nickel complex breaks as additional ethylene molecules approach the metal perpendicular to the square plane.

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Minoru Tsutsui*
Takashi Koyano†

Department of Chemistry
New York University
Bronx, New York 10453

* To whom all correspondence should be directed.
† Present address: Central Research, Toa Nenryo Company, Saitama-Ken, Japan.

Preparation of Hydroxyl-Terminated Polysiloxanes by Diborane Reduction of Corresponding Acids

Polysiloxanes containing terminal carboxyl groups have been prepared previously by equilibration of octamethylcyclotetrasiloxane with 5,5,7,7-tetramethyl-5,7-disila-6-oxaundecane-dioic acid[1,2] by use of a sulfuric acid catalyst. Reduction of these acids with lithium aluminum hydride produced glycols which showed infrared absorption at 2120 cm.$^{-1}$ (Si—H), indicating cleavage of Si—O bonds.[2]

This communication describes the use of diborane to reduce the acids smoothly to glycols without apparent formation of Si—H linkages. The reductions were carried out at 10°C. in tetrahydrofuran, and the molecular weights of the glycols were determined by acetic anhydride–pyridine endgroup titration.[3]

EXPERIMENTAL

Materials

Diborane was obtained from the Metal Hydrides Company as a 1M solution of BH$_3$ in tetrahydrofuran.

Octamethylcyclotetrasiloxane was obtained from the K and K Laboratories, Inc.

5,5,7,7-Tetramethyl-5,7-disila-6-oxaundecanedioic acid was prepared by the method of Mulvaney and Marvel.[1]

Preparation of Carboxyl-Terminated Polysiloxane

Reaction of 105 g. of octamethyltetrasiloxane, 19.5 g. of 5,5,7,7-tetramethyl-5,7-disila-6-oxaundecanedioic acid, and 3.3 ml. of concentrated sulfuric acid according to the procedure of Kojima et al.[2] yielded 107 g. (86%) of polymer. The inherent viscosity of the product was 0.026 (measured as an 0.5% solution in toluene at 30°C.). The molecular weight determined from neutralization equivalent titration with methanolic sodium hydroxide was 1926.

ANAL. Calcd. for a molecular weight of 1926: C, 35.04%; H, 8.30%; Si, 35.14%; Found: C, 34.72%; H, 7.92%; Si, 34.50%.

Reduction of Carboxyl-Terminated Polysiloxane with Diborane

A solution of 85 g. of carboxyl-terminated polysiloxane (M.W. 1926) in 750 ml. of tetrahydrofuran was cooled to 10°C. in a nitrogen atmosphere. Then 280 ml. of 1M diborane solution in tetrahydrofuran was added over a 1.5-hr. period. When the addition had been completed, the mixture was allowed to warm to 20°C. and was decomposed by addition of a solution of 120 ml. of methanol in 300 ml. of tetrahydrofuran. Some foaming occurred during this step. The solvents were removed under reduced pressure, and the residue was dissolved in 500 ml. of ether and 400 ml. of hydrochloric acid. The ether layer was washed with water until neutral and dried over magnesium sulfate. Removal of solvents followed by drying in a vacuum oven at 40°C. for 16 hr. gave 77 g. (91%) of liquid hydroxyl-terminated polysiloxane. The inherent viscosity of the polymer was 0.034 (measured as an 0.5% solution in toluene at 30°C.). Hydroxyl endgroup titration gave a molecular weight of 2008. The infrared spectrum of the polymer showed no Si—H absorption.

ANAL. Calcd. for a molecular weight of 2008: C, 35.06%; H, 8.50%; Si, 35.41%; Found: C, 35.97%; H, 8.60%; Si, 35.53%.

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J. K. Hecht*
C. S. Marvel

Department of Chemistry
University of Arizona
Tucson, Arizona

BOOK REVIEW

Macromolecular Syntheses, Vol. II. J. R. Elliott, Ed. Wiley, New York, 1966. ix + 124. $6.50.

Macromolecular Syntheses is a series patterned after the highly successful *Organic Syntheses* put out by the same publisher. As in Volume I, a wide variety of polymer types is included, and sufficient detail is included so that even an experimenter who had never made a polymer before could expect to get the molecular weight and yield specified. There are a total of 30 preparations, ranging from simple slurry polymerization of acrylonitrile to a complex Diels-Alder polymer.

A polymer, to be useful, must be of a reasonably high molecular weight and must be tractable in some way so that something can be done with it after it is made. *Macromolecular Syntheses* is to be criticized in that the editorial policy is to accept and publish preparations where only low molecular weight products are formed, which in some cases are not even clearly characterized, simply to illustrate a new principle. To pick a few, "poly-*p*-phenylene" is characterized simply as "a light brown powder," "poly-β-alanine," and "poly-*p*-xylylidene" give very low molecular weight products.

In general, however, the selection and characterization is good, and this book belongs on the bookshelf of every practicing polymer chemist.

Tod W. Campbell

Research Manager
Orlon-Lycra Technical Division
E. I. du Pont de Nemours & Company
Waynesboro, Virginia   22980