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The Formylation of Cellulose

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Synopsis

The reaction between formic acid and disordered cellulose is described. It is shown that a degree of substitution as high as 2.5 can be readily obtained without any catalyst. There is no evidence of any difference between the formylation behavior of this cellulose up to the monoformate level and that beyond this level. Formic acid produces ordered, inaccessible regions in disordered cellulose; this behavior reduces the value of the latter material as a calibration standard in formylation studies and also throws doubt on the basic value of formylation as a method of measuring disorder in cellulose. There is evidence that native celluloses formylate less rapidly per unit amount of hydrogen-bond-disordered material than do regenerated celluloses; this may be associated with the fibrillar nature of the native celluloses.

INTRODUCTION

The esterification of cellulose with formic acid has been studied by several workers[1–11] and developed as a method of measuring the degree of disorder and accessibility of cellulose.[3–5,10] It is assumed that the formic acid penetrates and esterifies the less ordered parts of the structure, and the rate and extent of esterification are, therefore, related to the degree of structural disorder. The relative amounts of disorder in different celluloses can thus be investigated by comparison of their rates of formylation, and this procedure is adopted by some workers.[7,11] To convert the formylation values into a quantitative measure of accessible, disordered cellulose it is necessary to relate the values to some standard.

This has been attempted in two ways. The first procedure, that adopted by Tarkow and Stamm,[4] was to assume that one of the hydroxyls in the anhydroglucose unit esterifies much more rapidly than the other two; there is some evidence that this is the case with starch.[6] Thus, a completely accessible cellulose would react, within a time dependent on acid concentration and temperature, to give the monoformate, and the accessibility of a sample would be simply the ratio of the formylation produced by this treatment to the formylation corresponding to the monoformate. Some workers consider that the primary hydroxyl is the one that reacts rapidly.[4,6] It has been found,[5,8] however, that the rate of formylation of the two remaining hydroxyl groups is not insignificant, and levels of formylation in excess of the monoformate can be achieved without much difficulty; it has been suggested[8] that the formylation values of Tarkow and Stamm[4] are low because of the low ratio of formic acid to cellulose employed by these workers. The second procedure for converting formylation values into accessibilities is to compare the rate of formylation with that of a completely accessible sample; dextrin and starch have been employed as standards for this purpose.[3,5] This method seems to be preferable to the first procedure in that it does not necessarily assume any marked difference in the rates of formylation of the three hydroxyl groups on the anhydroglucose unit; it does, however, assume that the rate of formylation of starch and dextrin is the same as that of cellulose, and this assumption has been criticized by Tarkow and Stamm.[4]

Some workers[5,9] have studied the formylation of cellulose at different temperatures; a gradual increase in the degree of formylation with increase in temperature was found. This behavior is thought to be a reflection of the range of degrees of accessibility and of lateral order present in the cellulose structure; that is, the higher the temperature, the higher the degrees of lateral order in regions accessible to the acid. On this basis diagrams representing the distribution of degrees of lateral order in various celluloses were constructed.

These procedures for interpreting formylation values in terms of fractions of accessible, disordered material are to some extent suspect. The main purpose of the work described in this paper was to put the formylation method on a sounder quantitative basis. It was thought that this could be achieved by the use of a specially prepared cellulose film as a completely accessible standard. This film, the preparation and properties of which are described briefly below and in detail elsewhere,[12] is at least 97% hydrogen-bond-disordered, as measured by the infrared-deuteration technique.[12–14] A second aim of the present work was to investigate the claim[3–5] that formylation treatments do not produce any additional crystallization in cellulose samples, since any such crystallizing effect of formic acid would tend to invalidate the method; the 97%-disordered cellulose would obviously seem to be a suitable material for investigations of the crystallizing tendency of a treatment.

EXPERIMENTAL

Preparation of Disordered Cellulose Film

Thin films of secondary cellulose acetate were saponified in a 1% solution of sodium hydroxide in ethanol for 1 day at room temperature.[12] The saponified films were washed in ethanol and dried in air for several days. The complete removal of acetate groups in each batch of saponified film was confirmed by the absence of the infrared carbonyl band near 1725 cm.$^{-1}$. The dried films used in most of the work were 4–8 μ thick, that is, suitable for infrared spectroscopy. For a few experiments, as indicated below, films about 20 μ thick were prepared.

Formylation Technique

Samples of approximately 0.5 g. of dried cellulose were formylated at 30°C. in mixtures of formic acid and water of concentrations 60–100% by weight formic acid. The mass-to-volume ratio of cellulose to acid was approximately 1 g. in 100 ml. The reaction was terminated after the desired time either by removal of the sample or by addition of ethanol or an ethanol and water mixture (3:1 v/v); this precipitated any dissolved cellulose formate. The cellulose formate was freed from formic acid either by evaporation or by washing (see below).

Determination of Formyl Contents

The extents of esterification of a range of partially formylated samples were determined by a modified Eberstadt technique,[15–17] in which the formyl cellulose is saponified in aqueous solutions of sodium hydroxide. For some of these samples the formyl contents thus obtained could be plotted against the absorbance of the 1725 cm.$^{-1}$ carbonyl band of the material, measured relative to the absorbance of the 2900 cm.$^{-1}$ CH band (to eliminate so far as possible effects resulting from variations in film thickness). The relation so obtained was reasonably linear, at least to just above the monoformate level of substitution, and enabled the formyl contents of some of the samples remaining as coherent films after formylation to be measured with reasonable accuracy from the infrared spectra. A simple infrared method such as this is much faster and easier to carry out than an Eberstadt determination and is suitable for use even with very small film samples. At higher degrees of formylation the film was broken up and partially or completely dissolved by the formic acid. In these cases the degree of formylation of the cellulose formate (broken film or precipitated material or both) was always measured by the Eberstadt method.

Infrared Measurements

All infrared measurements were made on a Grubb-Parsons double-beam spectrophotometer. Measurements of three types were carried out: first, to confirm the absence of acetate groups in the disordered cellulose films as prepared; second, to determine the degree of formylation of treated celluloses (a sodium chloride prism was employed for these two types of measurement); and, third, to study the degree of hydrogen bond order in partially formylated films by means of the deuteration technique;[13,14] a lithium fluoride prism was used for these measurements. For infrared measurement the films were mounted in brass cells with calcium fluoride windows and evacuated to dryness. The films were deuterated in these cells by being immersed in the saturated vapor of a reservoir of 99.7% deuterium oxide, in the absence of air, for 15 min. at room temperature. The deuterated films were freed from excess D_2O by evacuation. A brief discussion of the principles of the infrared-deuteration method and the calculation of the fractions of ordered material is given below.

Periodate Oxidation

Samples were oxidized in 0.04*M* sodium metaperiodate for 68 hr. at room temperature in the dark, to give an indication of the number of glycol groupings in celluloses at various levels of formylation.[6,18–20]

RESULTS AND DISCUSSION

The Nature of the Disordered Cellulose Studied in This Paper

The purpose of this section is to summarize the preparation and properties of the highly disordered cellulose films studied in the present work; this is essential for a full appreciation of some of the results presented in this paper. A full description of the nature of this type of disordered cellulose is in course of publication;[12] other workers have described similar methods of preparing disordered celluloses.[21–26]

For clarity it is first necessary to describe briefly the infrared-deuteration technique as applied to cellulose.[13,14] In this method the cellulose is immersed in an excess of deuterium oxide; the absorbed deuterium oxide converts the OH groups to OD groups in the accessible parts of the structure. With normal types of cellulose the exchange reaction is in two stages, a rapid stage, followed by a slow one; a fraction of the OH groups remain unexchanged even after prolonged treatment; that is, these OH groups are inaccessible to deuterium oxide, at least on any practicable time scale. Infrared study of the OH- and OD-stretching bands of the dried, partially deuterated product at the end of the initial rapid exchange enables the proportion of readily accessible cellulose to be measured. These infrared investigations also show that with regard to hydrogen bonding cellulose can be divided into two components. In the first component, which comprises the rapidly exchanged portion of the cellulose, the hydrogen bonding is disordered in character; the OH band of this component is thus broad and featureless. In the second component, which comprises the slowly accessible and inaccessible portions of the cellulose, the hydrogen bonding is regular and ordered in character and gives rise to an OH band showing characteristic peaks and shoulders.[13,14,27] In undeuterated cellulose, therefore, the OH band is a combination of these two components.

In cotton about 40% of the OH groups are "hydrogen-bond-disordered" and readily accessible (that is, they deuterate within about 15 min. in saturated deuterium oxide vapor at 20°C.[28]). In textile viscose rayons about 75% of the OH groups are hydrogen-bond-disordered. The characteristic and important feature of the disordered cellulose film used in the present formylation study is that it is at least 97%, and often as much as 99%, hydrogen-bond-disordered. The infrared OH stretching band of this material is broad and featureless with virtually no "ordered" component.

Deuteration rapidly removes practically the whole of this OH band, leaving at most a very weak band, usually of the cellulose II type; the material is, therefore, practically completely accessible to deuterium oxide. So far as the infrared-deuteration technique is concerned, in fact, this type of cellulose has all of the properties of the hydrogen-bond-disordered components of normal types of cellulose.

These highly disordered celluloses are produced, as indicated above, by the regeneration of films or fibers of cellulose derivatives in non-aqueous solutions, followed by washing in non-aqueous solvent and drying in air. The method outlined above, namely the saponification of secondary cellulose acetate in ethanolic solutions of sodium hydroxide, is very satisfactory, but it is emphasized that other derivatives and non-aqueous regenerating systems give similar results. Careful removal of foreign molecules (regenerating agent or non-aqueous solvent) from the cellulose does not lead to any increase in order; that is, the hydrogen-bond disorder cannot in general be attributed to the effect on the structure of impurities of this kind. It should, in fact, be pointed out that the samples of disordered cellulose film used in this work contained practically no sodium hydroxide and very little (never more than 2% by weight, and usually less than 1%) ethanol. There is no doubt, therefore, that the very high hydrogen-bond disorder of the cellulose is directly associated with the absence of water in the preparative processes; water seems to be essential for the development of order in the hydrogen-bonding system in cellulose, as has been emphasized by Manley and his associates.[24–26] These disordered celluloses do, in fact, "crystallize" rapidly in water, giving products very similar in type and amount of hydrogen-bond order to ordinary textile viscoses (about 25% hydrogen-bond order of the cellulose II type); they are, however, reasonably stable in air at humidities up to 60–70%.

The hydrogen-bond-disordered character of the celluloses is confirmed by moisture-regain measurements; the regain of a 98%-disordered cellulose at 57% R.H. and 20°C. was 16.75 g. of H_2O per 100 g. of cellulose, which is close to the value calculated from the known relation between hydrogen-bond disorder and moisture regain.[28] X-ray studies confirm the low degree of lateral order of these "non-aqueous regenerated" celluloses; the diffractograms show very poor three-dimensional order.

Stability of Formyl Celluloses to Washing

It has been suggested[1,2,8] that the cellulose formates are somewhat unstable to treatment in water and to heating. Figure 1 shows the effect of prolonged treatment in water and ethanol at 16°C. on the formyl content of partially formylated, disordered celluloses. The decrease in the formyl content is slow in both liquids, particularly ethanol. It is unlikely that this slow decrease is the result of the removal of free formic acid, and it is considered probable that some decomposition of the formate is taking place. It is probable that any free formic acid in the film would wash out rapidly (within, say, 1 hr.); thus, washing in water or ethanol, particularly the

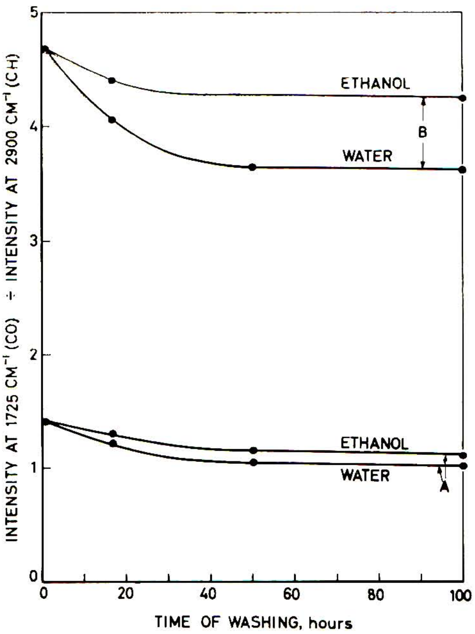

Fig. 1. Effect of washing in water and in ethanol on intensity of 1725 cm.$^{-1}$ carbonyl band of formylated disordered cellulose. Samples of disordered cellulose formylated in 100% formic acid at 30°C. for 0.5 hr. (A) and 2.5 hr. (B).

latter, seems to be a satisfactory method of removing free acid without appreciable decomposition of the formate. In the present experiments a 3:1 v/v mixture of ethanol and water was used for washing the formylated samples, except those to be used for measurement of the degree of order; with these, the formic acid was removed either by evaporation (under vacuum in the later stages) or by washing in ethanol only, since water tends to crystallize disordered cellulose.

There was no appreciable effect on the formyl contents of formylated samples that had been washed for a few hours, when these samples were heated to 100°C. in air for times up to 24 hr.

Rate and Extent of Formylation of Disordered Cellulose

Figure 2 illustrates the rate of formylation of disordered cellulose in three concentrations of formic acid. The formylation was initially rapid, gradually leveling off to a slow rate. The leveling-off degrees of substitution (D.S.) in 100%, 90%, and 83% by weight formic acid were 2.5, 1.3, and 0.8, respectively (the value for completely formylated cellulose is, by definition, 3). The effect of the concentration of formic acid in the range 60–100 % is clearly shown in Figure 3.

It is clear from Figure 2 that the formylation values show a considerable scatter; the scatter is particularly marked between different batches of disordered cellulose. Part of this scatter must be the result of slight variations

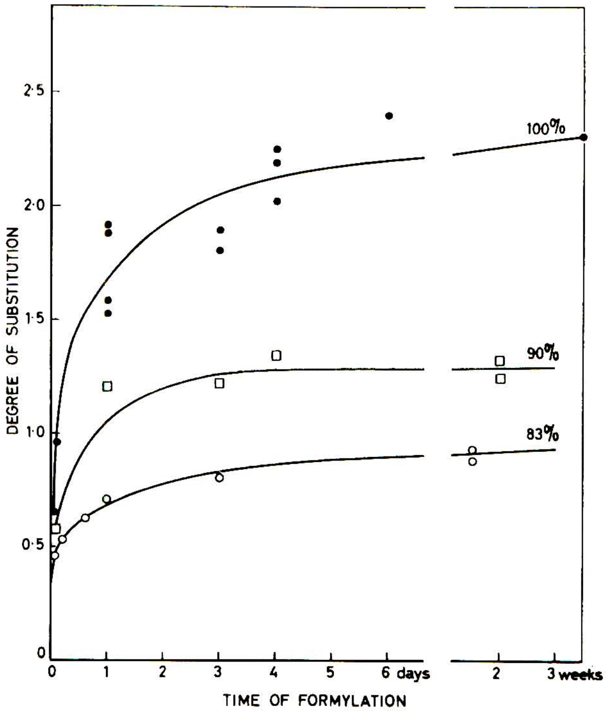

Fig. 2. Rate of formylation of disordered cellulose in mixtures of formic acid and water at 30°C. Concentration of formic acid shown as weight/weight percentage.

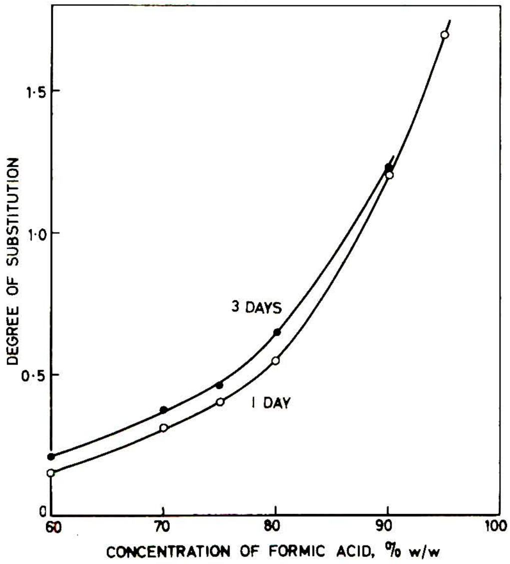

Fig. 3. Effect of concentration on formylation of disordered cellulose in mixtures of formic acid and water at 30°C. Samples formylated for 1 day and 3 days, as indicated on the figure.

in the formylation technique from batch to batch and of error in the determination of formyl content, but part probably reflects genuine structural differences between the different samples. Very recent results on the alcoholysis of disordered cellulose, obtained in these laboratories, support the conclusion that different batches of disordered cellulose, though they may be similar in that they contain no more than 3% of hydrogen-bond-ordered material, yet may differ very markedly in reactivity towards certain reagents. This variability may be associated with differences in the void and capillary structure, these differences probably arising from variations in the method of drying of the disordered cellulose.

At concentrations of formic acid of more than 90% the disordered cellulose film gradually broke up and dissolved within a few days; the breaking up of the film and the amount of dissolved material gradually increased with time up to an overall D.S. in the region of 1.5, at which stage all the ester was dissolved. The rate of dissolution depended somewhat upon the batch of disordered film, possibly as a result of slight differences in the amount of ordered cellulose in these films (0–3%) and also upon the thickness of the film; 20 μ film dissolved significantly faster than 4–8 μ film. In one experiment the degree of substitution of the undissolved (broken-up) film was compared with that of the dissolved component, the overall D.S. being about 1.2; no significant difference was observed.

The facility with which partially formylated disordered cellulose dissolved indicates that all regions of the structure are reasonably accessible to 100% formic acid. Celluloses that contained crystalline regions, even at D.S. values of about 1.5, were much more resistant to swelling and dissolution in 100% formic acid. Despite this high degree of accessibility of disordered cellulose to formic acid it was found that the formylation treatment produced regions in the structure which are to some extent ordered. This important result is described and discussed in detail below.

Figures 2 and 3 show no clear indication of any marked discontinuity in the rate of formylation of disordered cellulose at the monoformate level of substitution; D.S. values as high as 2.5 can be readily obtained without any catalyst. This suggests that there are no marked differences in the rate of formylation of the three hydroxyl groups in the anhydroglucose unit, in disagreement with the opinions held by other workers.[4] This point was further investigated by oxidizing partially formylated samples with aqueous solutions of sodium metaperiodiate; this oxidizing agent oxidizes only the glycol groupings of secondary hydroxyls in the cellulose and thus provides a means of obtaining a measure of the degree of substitution of secondary hydroxyls.[6] In assessing the significance of these oxidation results it is necessary to make two assumptions. The first is that neither the presence of formyl groups nor the crystallizing action of the aqueous periodate solution renders the formylated samples less accessible to the solution than the unsubstituted samples. The crystallization of disordered cellulose films in water is described elsewhere.[12] The presence of formyl groups in esterified samples would be expected, if anything, to decrease the amount of order produced by the aqueous oxidizing solution, and thus this first assumption seems reasonable. The second assumption is that the formylation of primary hydroxyl groups does not decrease the rate of oxidation of the secondary glycol groups.

Experimental error in these oxidation measurements was considerable, for reasons not fully understood at present, but the results obtained (Table I) show clearly that formylation to a D.S. of less than 1 caused a marked decrease in the extent of the oxidation compared with that for unformylated samples; on the basis of the above two assumptions, this indicates that a significant degree of formylation of secondary hydroxyl groups takes place at levels of substitution lower than the monoformate.

TABLE I
Extent of Reaction After 68 hr. of Oxidation at Room Temperature, of Samples of Different Degrees of Substitution, Expressed as the Percentage of that Obtained for Unformylated Disordered Cellulose

Deg. of substitution	0.77[a]	0.72[a]	0.44[b]	0.40[b]	0
Reaction, %	11 ± 6	7 ± 6	73 ± 5	81 ± 8	100 ± 10

[a] Prepared by treating disordered cellulose for 15 hr. in 90% w/w formic acid (two batches).

[b] Prepared by treating disordered cellulose for 4.5 hr. in 83% w/w formic acid (two batches).

It should perhaps be emphasized that this conclusion—that there are no marked differences in the rates of formylation of the three hydroxyl groups—may apply only to regenerated celluloses. It may be that with native celluloses, in which the accessible hydroxyl groups are situated mainly on the surfaces of fibrillar structures, differences between the three groups may be observed as a result of different accessibilities of the groups to the acid; in regenerated celluloses the three groups are more likely to be equally accessible.

Crystallization of Disordered Cellulose in Formic Acid

Samples of disordered cellulose film that had been treated in formic acid were studied by the infrared-deuteration technique.[13,14] The films were formylated in 100% formic acid, freed from formic acid by evaporation or washing in ethanol, and deuterated for 15 min. at room temperature in saturated deuterium oxide vapor. Infrared measurements of these deuterated samples, after drying, showed that the partially formylated samples contain hydroxyl groups that are resistant to deuteration (Fig. 4); this probably means that the samples contain regions which are inaccessible and to some extent ordered. The proportion of deuteration-resistant hydroxyl groups increased as the time of formylation was increased. Two hours was the maximum time of formylation that could be studied easily, because of the tendency of the films to disintegrate after longer treatments.

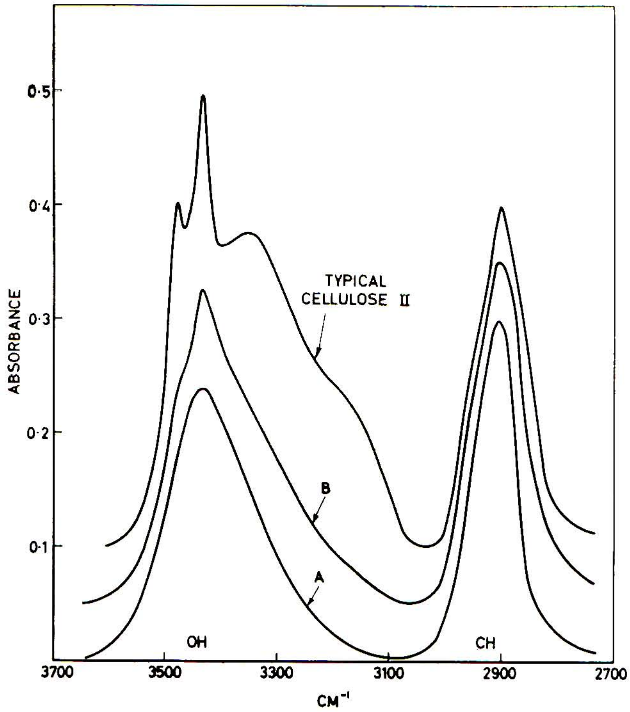

Fig. 4. Hydroxyl stretching band of the hydrogen-bond-ordered regions produced in disordered cellulose by treatment in 100% formic acid. Samples deuterated for 15 min. in saturated deuterium oxide vapor. The difference between A and B is described in the text.

At this stage the D.S. was only about 0.6, so effects of formyl groups on the infrared deuteration behavior could probably be ignored to a first approximation. It is not possible from the spectra in Figure 4 to make an accurate estimate of the fraction of deuteration-resistant OH groups, that is of the fraction of ordered material; however, by comparing the absorbance of the 3400 cm.$^{-1}$ OH band after deuteration with that of the 2900 cm.$^{-1}$ CH band (as an internal "thickness standard") it is possible to arrive at an approximate value for this fraction on the assumption that this OH/CH ratio is related to the fraction of inaccessible OH groups by a factor similar to the factor appertaining to ordinary regenerated celluloses.[13,14,28,29] On this basis the fraction of deuteration-resistant OH groups in the film rises during formylation to as much as 10–20%. The nature of this inaccessible material is not fully understood. The shape of the OH band in Figure 4 suggests that it is, to some extent at least, hydrogen-bond-ordered, as distinct from the readily exchanged material. Sometimes the band has the simple shape of the type shown as cure A in Figure 4; this shape is similar to that given by samples containing cellulose IV,[27,29] though x-ray evidence so far obtained lends no support to this. On other occasions the band shape appears to be a mixture of this simple shape and a component with the characteristic "cellulose II" band shape (curve B in Fig. 4). This point is being investigated further.

Whatever the nature of this inaccessible component, the fact that formic acid can, at least in some circumstances, produce such regions in cellulose is important from two points of view. First, it clearly detracts from the use of disordered cellulose as a calibration standard. It is apparent from the rates of dissolution that the deuteration-resistant material produced by the formic acid formylates much more rapidly than the crystalline regions of ordinary cellulose (see below) and may formylate as rapidly as the disordered regions; nevertheless, the possible effect of this material on the rate of formylation in the early stages cannot be ignored (in the latter stages of the reaction the cellulose is in solution). The second, and more important, point is that this tendency to produce inaccessible regions in cellulose clearly renders the formylation technique of doubtful value as a means of studying order and disorder in cellulose. It may be that in partially ordered celluloses the formic acid will have little effect on the order; a few measurements of disordered cellulose after crystallizing the latter in boiling water, to give a cellulose containing about 25% hydrogen-bond-ordered material, did not, in fact, reveal any marked change in order on subsequent treatment in formic acid. It would, however, be difficult to be certain that this was always the case.

As would be expected, the addition of water to the formic acid increases the rate of crystallization of the disordered cellulose and changes the shape of the hydroxyl band of the ordered regions from those illustrated in Figure 4, curves A and B, to that characteristic of cellulose II (Fig. 4);[13,14] the amount of ordered material produced at equilibrium gradually increases from the value of 10–20% in 100% formic acid to that of 25% in 60:40 w/w formic acid and water (25% is characteristic of disordered cellulose crystallized in pure water). It is clear, therefore, that crystallization effects can not readily explain the dependence of the rate of formylation and of the "leveling off" formyl content on the proportion of water in the formic acid solution; the effect of water on the formylation behavior is far too pronounced, unless it is supposed that the mixtures of formic acid and water produce ordered, inaccessible regions of a type not detected by the infrared-deuteration technique. Any such regions would, however, have to be extensive in amount to produce the difference in the extent of formylation between 100 and 60% formic acid (Fig. 3).

The Effect of Hydrogen-Bond Order on the Rate of Formylation

The rate of formylation of the following films was investigated and compared: (*a*) disordered cellulose, (*b*) disordered cellulose, crystallized by immersion in water at room temperature for 10 sec., (*c*) disordered cellulose crystallized in boiling water for 5 min., (*d*) disordered cellulose crystallized by immersion in 18% w/w NaOH solution for 15 min., followed by boiling in water for 10 min.,[30] (*e*) bacterial cellulose film. The approximate percentages of hydrogen-bond-ordered material in these celluloses, as measured

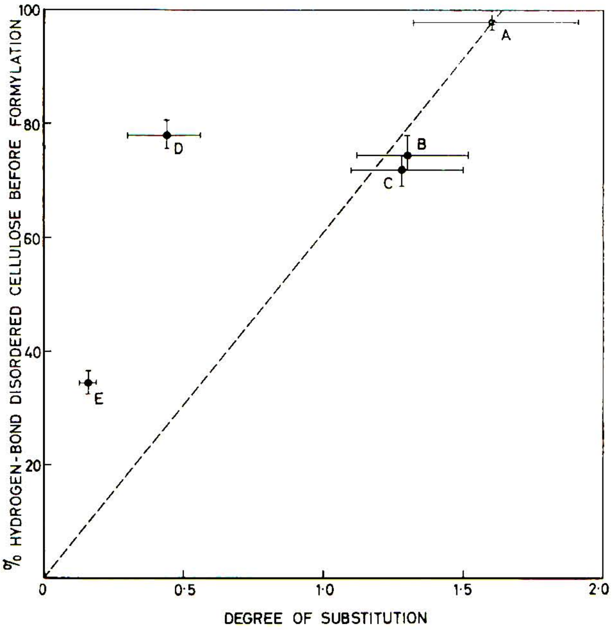

Fig. 5. Formylation of cellulose in relation to the fraction of hydrogen-bond-disordered material. Samples treated for 1 day in 100% formic acid at 30°C. The scatter of results is as indicated on the figure: point A, disordered cellulose; point B, disordered cellulose crystallized in water at room temperature; point C, disordered cellulose crystallized in boiling water; point D, disordered cellulose crystallized in sodium hydroxide solution; point E, bacterial cellulose film.

by infrared-deuteration techniques, were (*a*) 0–3, (*b*) 25, (*c*) 30, (*d*) 20, and (*e*) 65.[28] The ordered material in samples (*a*) to (*d*) was cellulose II in character, to judge from the infrared spectrum; the perfection of this ordered cellulose was high in sample (*d*). Sample (*e*) has crystalline regions of the cellulose I type. The general shape of the plot of formylation against time was similar for all the samples: a rapid initial reaction followed by a slow one. The scatter of results was unexpectedly large, especially so between batches of films prepared at different times; as mentioned earlier, some of this scatter is due to error in the determination of formyl content and to slight variation in the formylation technique, but part is probably the result of genuine differences between the films. All the films other than the disordered cellulose remained in a coherent form during the formylation treatment. The degree of formylation after 1 day at 30°C. in 100% formic acid is plotted in Figure 5 against the fraction of hydrogen-bond-disordered material present in the original films. The two quantities are clearly related, although the relation is complicated by other factors. This is in general agreement with the results of Tarkow and Stamm,[4] who found that their formylation values were related to moisture-regain results (it has been shown[28,31,32] that the moisture regain is linearly related to the fraction of hydrogen-bond-disordered material in cellulose). Figure 5 shows that the alkali-treated disordered cellulose and the bacterial cellulose formylate more slowly than would be expected from the fractions of hydrogen-bond-disordered cellulose present in them. The reason for the slow formylation of the alkali-treated samples may be a "hornification" of the structure caused by the alkali treatment;[33] the high degree of swelling during the latter and the drying from this high state of swelling may seal up voids, capillaries, fibrillar surfaces, etc., within the cellulose. Such a "hornification" process might be expected to have a greater effect on the accessibility of the structure to formic acid than on the accessibility to deuterium oxide because of the difference in molecular size. The low rate of formylation of the bacterial cellulose may reflect the largely fibrillar nature of this type of cellulose. Much of the hydrogen-bond-disordered material in bacterial cellulose probably is situated at the surfaces between fibrils and may therefore be less accessible to formic acid than the disordered component of regenerated cellulose, in which some, at least, of the disordered component may exist in distinct regions. Where comparisons are possible, published results on regenerated celluloses and cotton tend to agree with these conclusions. Regenerated celluloses[3,5,10] have a degree of formylation after 16 hr. in 90% formic acid of about 70–85% that of disordered cellulose, as measured in the present experiments, that is, similar to the two crystallized samples (Fig. 5); this fraction is approximately the same as the fraction of hydrogen-bond-disordered material in these celluloses.[13,28] Cotton, which has a fibrillar structure, behaves similarly to bacterial cellulose; the degree of formylation[3,5] is about 20–25% that of disordered cellulose, compared with the fraction of hydrogen-bond-disordered material, which is 42%.[28]

SUMMARY AND CONCLUSIONS

This paper describes the formylation of cellulose in relation to the hydrogen-bond order in the latter. Emphasis is placed on a study of the reaction between formic acid, and between mixtures of formic acid and water, and a cellulose containing not more than 3% of hydrogen-bond-ordered material. This "disordered cellulose" reacts readily with the formic acid, and degrees of substitution in the region of 2.5 can be easily obtained without any catalyst; the formyl cellulose dissolves in the formic acid at D.S. values of about 1.5, indicating complete accessibility to the reagent. The rate and extent of formylation decreases rapidly as the content of water in the formic acid is increased. There is no obvious indication of any difference in the formylation behavior up to the monoformate level, compared with that beyond this level; measurements of the oxidation of partially formylated samples in periodate solutions indicate that substantial numbers of secondary hydroxyl groups in the cellulose are formylated at degrees of substitution of less than 1. Thus, there is no support for the suggestion that the formylation of cellulose tends to "level out" at the monoformate stage or that the formylation takes place initially, or principally, at the primary hydroxyl groups. It is recognized, however, that differences in the relative rates of formylation of the primary and secondary hydroxyl groups may exist with native celluloses, in which the accessible groups are largely confined to the surfaces of fibrillar structures. Disordered cellulose is found to "crystallize" readily in 100% formic acid (and even more readily, of course, in mixtures of formic acid and water). This tendency of formic acid to produce ordered, inaccessible regions clearly lessens the usefulness of disordered cellulose as a "calibration standard" for the formylation method of measuring disorder and also throws doubt on the basic value of the method. It is shown that there is a rough, general relation between the rate of formylation of a cellulose and the fraction of hydrogen-bond-disordered material in the cellulose. There is some evidence that native celluloses formylate less per unit amount of disordered material than do regenerated celluloses; this may be related to the fibrillar nature of the native celluloses.

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Résumé

La réaction entre l'acide formique et la cellulose désordonnèe est décrite. On montre qu' un degré de substitution aussi élevé que 2.5 peut facilement être obtenu sans catalyseur. Il n'y a pas d'évidence d'une quelconque différence dans le comportement à la formylation de cette cellulose désordonnée jusqu' au niveau monoformiate comparé à son comportement au delà de ce niveau. L'acide formique produit dans la cellulose désordonnée des régions ordonnées inaccessibles. Ce comportement réduit la valeur de ce dernier matériau comme étalon de calibrage pour des études de formylation et ainsi jette un doute sur la valeur fondamentale de la formylation comme méthode de mesure de désordre dans la cellulose Il est évident que des celluloses naturelles sont moins rapidement formylées par unité de lien hydrogène-matériau désordonné que les celluloses régénérées; ceci peut être associé à la nature fibrillaire de la cellulose naturelle.

Zusammenfassung

Die Reaktion von Ameisensäure mit Cellulose mit ungeordneten Bereichen wird beschrieben. Es wird gezeigt, dass ein Substitutionsgrad bis zu 2,5 ohne jeden Katalysator leicht erhalten werden kann. Es bestehen keine Hinweise auf irgendeinen Unterschied im Formylierungsverhalten dieser Cellulose bis zur Monoformiatstufe im Vergleich zu demjenigen oberhalb dieser Stufe. Ameisensäure erzeugt in nicht geordneter Cellulose geordnete, unzugängliche Bereiche; dieses Verhalten verringert den Wert letzteren Materials als Eichstandard für Formylierungsuntersuchungen und lässt auch am grundsätzlichen Wert der Formylierung als Methode zur Messung ungeordneter Bereiche in Cellulose zweifeln. Es wird gezeigt, dass native Cellulose weniger rasch, und zwar pro Mengeneinheit an Material ohne Wasserstoffbindungsordnung, formyliert wird als regenerierte Cellulose; das kann mit der fribrillären Natur der nativen Cellulose zusammenhängen.

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Stereoregular Condensation Polymers. I. Synthesis and Comparison of Optically Active and Inactive Polycamphorates and Polycamphoramides*

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Synopsis

Optically active and inactive polycamphorates and polycamphoramides were prepared by polycondensation of *d*- and *dl*-camphoryl dichloride with 1,4-butanediol, bisphenol A, and piperazine. The higher melting and more crystalline properties of optically active stereoregular condensation polymers compared to inactive atactic forms appear consistent with results from optically active isotactic and inactive atactic addition polymers.

INTRODUCTION

In a study of the correlation between the structure and properties of macromolecules, the effect of the asymmetry in the polymer is of interest. Price and co-workers have shown that the optically active isotactic addition polymers: *d*- and *l*-polypropyleneoxide,[1] *d*- and *l*-polyconidine,[2] and *d*- and *l*-polypropyleneimine[3] were higher melting than the corresponding inactive atactic forms.

In order to determine just what effect this asymmetry in the polymer chains had on the physical properties of the condensation polymers, it was necessary to prepare the polymers from both a racemic and an optically active bifunctional monomer, which contains at least one asymmetric carbon away from the reaction center. One of the readily available optically active dibasic acids for this purpose appeared to be *d*-camphoric acid. This dibasic acid seemed to be a good example for study, since both *d*- and *dl*- forms are commercially available and the optically active *d*- form would produce an optically active condensation polymer with the asymmetric center in the main chain to produce an effect on the properties.

RESULTS AND DISCUSSION

A preliminary study on the preparation of polycamphorates and polycamphoramides showed that direct condensation of commercial *d*- and *dl*-

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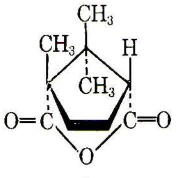
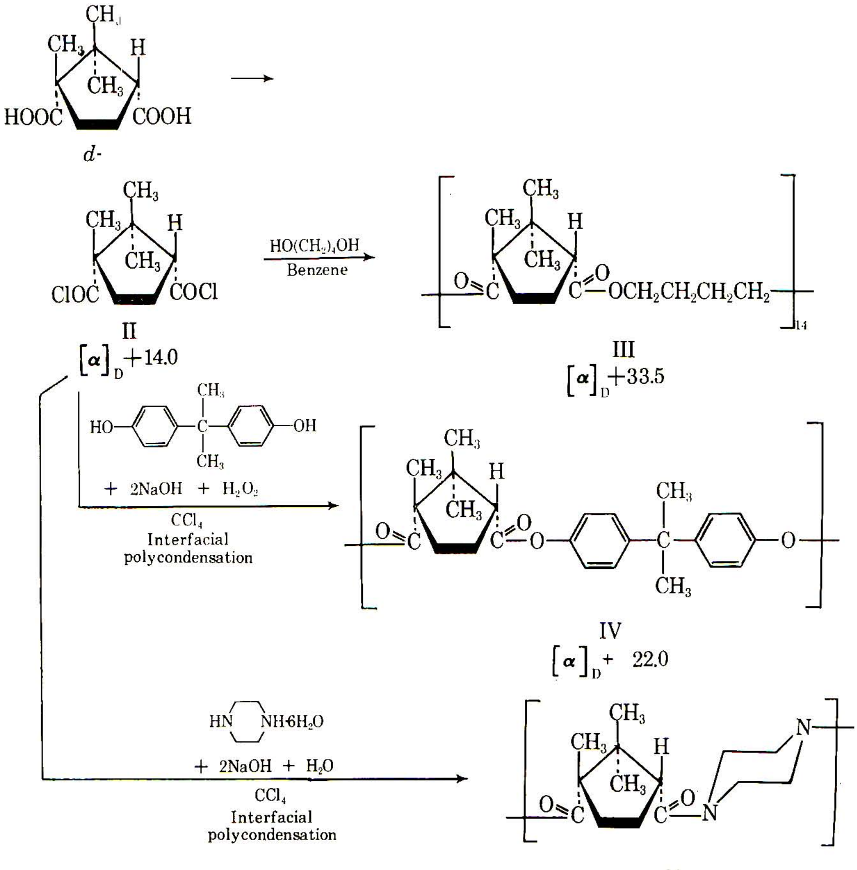
camphoric acids, which are mainly *cis*-acids, gives intramolecular formation of the six-membered anhydride ring (I).



I

However, polycamphorates and polycamphoramides were readily obtained from camphoryl dichloride as the monomer. Conversion of camphoric acid to camphoryl dichloride by phosphorus pentachloride in petroleum ether was almost quantitative.[4,5]



The comparison of physical properties of optically active stereoregular and inactive nonstereoregular polycamphorates and polycamphoramides is in agreement with the theoretical considerations which suggest that the optically active stereoregular condensation polymers are higher melting than inactive nonstereoregular forms.

The x-ray powder diagrams of poly(*cis-d*-camphoryl piperazine) and its *cis-dl*-isomer as shown in Table I indicated almost identical interplanar spacings but the intensities of the *cis-d*-polymer are four times stronger than those for the *cis-dl-* polymer.

TABLE I
Interplanar Spacings and Intensities from X-Ray Diagrams of Poly(*cis-d*-camphoryl Piperazine) and Its *cis-dl*-Isomer

	Spacing, A.	Intensity
Poly(*cis-d*-camphoryl piperazine)	5.53	Very strong
Poly(*cis-dl*-camphoryl piperazine)	5.54	Weak

The differences in water contents of poly (*cis-d*-camphoryl piperazine) found with interfacial and homogeneous polymerization conditions may suggest differences in arrangements of repeating units in the polymer chains, i.e., head-to-head and head-to-tail.

EXPERIMENTAL

Materials

d- and *dl*-Camphoric acid used in this work were commercially available without additional purification. The commercial grade acids are mainly in *cis* forms with less than 5% as *trans* isomer. The other isomeric impurity in commercial *d*-acid is *dl*-isomer.

Monomers

***d*-Camphoryl Dichloride (II).** To a stirred suspension of 244.3 g. (1.17 moles) of phosphorus pentachloride in 450 ml. of petroleum ether was added during 45 min. at 0°C. 116.0 g. (0.58 mole) of commercial *d*-camphoric acid, $[\alpha]_D^{25} = +45.7$ ($c = 10$ in isopropyl alcohol), m.p. 181–183°C. The stirring mixture was allowed to warm to room temperature for 1 hr. This homogeneous liquid was evacuated on the steam bath under reduced pressure. The residual liquid was distilled, 90°C./0.5 mm. (bath temperature 140–150°C.), to yield 137.1 g. (99%) of *d*-camphoryl dichloride, $[\alpha]_D^{25} = +14.0$ ($c = 4$ in benzene); lit.[5] b.p. 140°C./10 mm.).

ANAL. Calcd. for $C_{10}H_{14}O_2Cl_2$: C, 50.65%; H, 5.95%; Cl, 29.90%. Found: C, 50.85%; H, 5.71%; Cl, 29.73%.

***dl*-Camphoryl Dichloride.** The same procedure was followed as above. From commercial *dl*-camphoric acid was obtained *dl*-camphoryl dichloride; b.p. 92°C./0.5 mm., $[\alpha]_D^{25.0} = 0$ ($c = 4$ in benzene).

Found: C, 50.87%; H, 6.15%; Cl, 29.76%.

***cis-d-* and *dl*-Camphoryl Dichlorides.** These dichlorides were prepared by the same procedure as above except that the starting materials were *cis-d-* and *dl*-camphoric acids.

***cis-d*-Camphoric Acid.** A solution of 100 g. of commercial *d*-camphoric acid (m.p. 181–183°C.) in 500 ml. of acetic anhydride was refluxed for 3 hr. and evaporated under reduced pressure on steam bath to dryness. A benzene solution of this residual solid was washed with aqueous sodium bicarbonate and water and was dried with anhydrous sodium sulfate. The residual solid obtained on evaporation of benzene was recrystallized from benzene; yield 80 g. (88%) of *cis-d*-camphoric anhydride, m.p. 210–212°C. A solution of 75 g. of this anhydride and 120 g. of potassium hydroxide pellets in 500 ml. of water was extracted with benzene, acidified, and again extracted with benzene. This second benzene extract was washed with water and dried with anhydrous sodium sulfate. The residual solid obtained on evaporation of benzene was recrystallized from ethyl acetate and benzene; yield 77 g. (82%), m.p. 187°C., $[\alpha]_D^{25} = +49.3$ (c = 1.4 in ether); lit. m.p. 187°C., $[\alpha]_D = +47.7$ in ethanol.

ANAL. Calcd. for $C_{10}H_{16}O_4$: C, 59.98%; H, 8.05%. Found: C, 59.94%; H, 8.23%.

***cis-dl*-Camphoric Acid.** The same procedure was followed as above. From 100 g. of commercial *dl*-camphoric acid (m.p. 201–203°C.) was obtained crystalline *cis-dl*-camphoric anhydride; yield 76.0 g. (84%), m.p. 224–225°C. From 73 g. of this *cis-dl*-camphoric anhydride was obtained crystalline *cis-dl*-camphoric acid; yield 73 g. (91%), m.p. 201–202°C., $[\alpha]_D^{25.0} = 0.00$ (c = 4 in ether); lit.[6,8] m.p. 202–203°C.

ANAL. Calcd. for $C_{10}H_{16}O_4$: C, 59.98%; H, 8.05%. Found: C, 60.22%; H, 8.11%.

Polycamphorates

Poly(tetramethylene *d*-Camphorate) (III). To a stirred solution of 23.0 g. (0.097 mole) of *d*-camphoryl dichloride in benzene was added at room temperature 8.7 g. (0.097 mole) of 1,4-butanediol. The solid was dissolved in benzene and washed with 10% aqueous potassium hydroxide, then with dilute acid, until the washing became neutral, and finally with an excess of water. Poly(tetramethylene *d*-camphorate) was recovered by benzene sublimation of the frozen benzene layer; yield 19.2 g. (78%), $[\alpha]_D^{25.0} = +33.5°$ (c = 4 in benzene), molecular weight 3,600 (ca. 14 repeating units) by endgroup (i.e., COOH) determination.

ANAL. Calcd. for $(C_{14}H_{22}O_4)_2$: C, 66.13%; H, 8.66%. Found: C, 66.34%; H, 8.38%.

Poly(*d*-Camphoryl Bisphenol A) (IV). To a vigorously stirred solution of 29.5 g. (0.129 mole) of 2,2-bis(4-hydroxyphenyl)propane (i.e., bisphenol A) and 10.4 g. (0.260 mole) of sodium hydroxide pellets in 200 ml. of water was added a solution of 30.7 g. (0.129 mole) of *d*-camphoryl dichloride in 200 ml. of carbon tetrachloride. The stirring mixture was allowed to stand for 1 hr. The sticky middle layer formed by addition of water was separated and evacuated under reduced pressure at room temperature to afford 44.5 g. of white powdery polymer; m.p. 62–64°C., $[\alpha]_D^{26.0} = +22.0$ ($c = 4$ in benzene), $[\eta] = 0.01$ (benzene, 29.0°C.).

ANAL. Calcd. for $(C_{25}H_{28}O_4)_n$: C, 76.50%; H, 7.19%. Found: C, 76.29%; H, 7.19%.

The same procedure was followed as above, except the starting material was *dl*-camphoryl dichloride; a soft and tacky product was obtained.

Polycamphoramides

Poly(*d*-Camphoryl Piperazine) (V). To a vigorously stirred solution of 28.0 g. (0.144 mole) of piperazine hexahydrate and 11.6 g. (0.288 mole) of sodium hydroxide in 600 ml. of water was added at 0°C. a solution of 34.2 g. (0.144 mole) of *d*-camphoryl dichloride in 200 ml. of carbon tetrachloride. The stirring mixture was allowed to warm to room temperature for 1 hr. The white solid was collected by filtration, washed with water, benzene, and ether and dried over phosphorus pentoxide to afford nearly quantitative yield of the polymer, m.p. (in sealed tube) 403°C. (dec.) with preliminary browning.

ANAL. Calcd. for $(C_{14}H_{22}O_2N_2 \cdot {}^1/_2H_2O)_n$: C, 64.82%; H, 8.93%. Found: C, 64.41%; H, 8.86%.

The same procedure as above was followed, except that the *dl*-camphoryl dichloride was used. The *dl*-polymer obtained melted (in sealed tube) at 340°C. (dec.) and was soluble in *m*-cresol and *o*-chlorophenol, while the *d*-polymer was insoluble.

Poly(*cis*-*d*-Camphoryl Piperazine). A solution of 32.5 g. of *cis*-*d*-camphoryl dichloride (b.p. 88°C./0.45 mm.) in 20 ml. of anhydrous ether was added during 30 min. at 0°C. to a stirred solution of 11.7 g. of anhydrous piperazine in 300 ml. of anhydrous ether. An addition of 28 g. of triethylamine was followed and then the stirred mixture was allowed to warm to room temperature for 1 hr. The white solid was collected by filtration, washed with water and dissolved in chloroform. This chloroform solution was washed with 10% aqueous sodium hydroxide, dilute acetic acid, and finally with water. The white polymer obtained by addition of ether to the chloroform layer was dried over phosphorus pentoxide under reduced pressure; yield 30 g. (34%), m.p. (in sealed tube) 420°C. (dec.), $[\alpha]_D^{25.0} = +14.7$ ($c = 1.3$ in CH_2Cl_2), $[\eta] = 0.12$ (methylene chloride, 24.5°C.).

ANAL. Calcd. for $(C_{14}H_{22}O_2N_2 \cdot {}^1/_3H_2O)_n$: C, 65.59%; H, 8.91%. Found: C, 65.66%; H, 8.73%.

The identical procedure described above was followed with the exception that the starting material was *cis*-*dl*-camphoryl dichloride (b.p. 119°C./1.5 mm.). From *cis*-*dl*-camphoryl dichloride was obtained almost quantitative yield of poly(*cis-dl*-camphoryl piperazine), m.p. (in sealed tube) 380°C. (dec.), $[\alpha]_D^{25.0} = 0.000$ ($c = 1.5$ in ether), $[\eta] = 0.11$ (methylene chloride, 24.8°C.).

ANAL. Calcd. for $(C_{14}H_{22}O_2N_2\cdot{}^3/_4H_2O)_n$: C, 63.72%; H, 8.98%; N, 10.61%. Found: C, 63.57%; H, 9.04%; N, 10.10%.

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Résumé

Des polycamphorates et des polycamphoramides optiquement actifs et inactifs ont été préparés par polycondensation du dichlorure de *d*- et de *dl*-camphoryle avec le 1,4-butanediol, le bisphénol-A et la pipérazine. Le point de fusion plus élevé et les propriétés plus cristallines des polymères de condensation stéréoréguliérs, et optiquement actifs, comparés aux polymères atactiques inactifs sont en accord avec les résultats obtenus au départ des polymères d'addition, optiquement actifs isotactiques et atactiques inactifs.

Zusammenfassung

Optisch aktive und inaktive Polyester und Polyamide der Camphersäure wurden durch Polykondensation von *d*- und *dl*-Camphoryldichlorid mit 1,4-Butandiol, Bisphenol A und Piperazin hergestellt. Der höhere Schmelzpunkt und die grössere Kristallinität optisch aktiver, sterisch regel mässig gebauter Kondensationspolymerer gegenüber inaktiven, ataktischen Formen treten in Ubereinstimmung mit den an optisch aktiven, isotaktischen und inaktiven, ataktischen Additionspolymeren erhaltenen Ergebnissen auf.

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Mechanism of Ziegler-Natta Polymerization of Propylene and α-*d*-Propylene

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Synopsis

Rates of propylene homopolymerization and α-*d*-propylene–propylene copolymerization were determined by using constant-pressure polymerization conditions. It could be demonstrated that the rate of propylene homopolymerization was constant under the conditions used. However, the initial rate of copolymerization was faster and decreased with time to the rate obtained for propylene homopolymerizations. The higher initial copolymerization rate was attributed to the stabilization of potentially active centers in solution when the deuterated monomer was present. These active centers are assumed to be formed by reactions of tetravalent titanium with monomer. These active centers, which are formed in solution, are said to be destroyed by isotopically controlled reactions, i. e., abstraction of the hydrogen or the α-deuterium atom from these monomer-alkylated species in solution or at the interface. These active centers are believed to be adsorbed and/or chemisorbed onto the precipitated catalyst surface and to be responsible for a polymer of considerably lower steric order. This scheme predicts a stereoregular polymer of high molecular weight produced by polymerization on a Ti(III) surface and a largely amorphous polymer of lower molecular weight produced by adsorbed and/or chemisorbed species. This prediction was verified by fractionation of the deuterated polymers into crystalline and amorphous portions.

INTRODUCTION

The studies of transition metal catalysis for the polymerization of olefins have been and continue to be intimately involved with tetravalent and trivalent titanium halides in association with aluminum alkyls and alky halides. In what is, perhaps, the most thorough study of transition metal catalysis, using a highly crystalline form of titanium trichloride (α-$TiCl_3$) and triethylaluminum for the stereospecific polymerization of propylene in heptane, Natta[1] has shown that the use of trivalent titanium produces polymers of higher stereospecificity than the use of tetravalent titanium. Therefore, recent studies have been mainly concerned with the use of trivalent rather than tetravalent titanium halides.

In his classical study, Natta[1] showed the point of attachment of the growing polymer chain to be at the β carbon of propylene. He described the

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mechanism of propagation as coordinate anionic. He also inferred the placement of a partial positive charge on the catalyst component and a partial negative charge at the end of the growing polymer chain. Although the nature of the active site could not be clearly demonstrated, it was believed to be a bimetallic–monomer complex. The termination reaction was believed to occur primarily by chain transfer with monomer, during which a hydride ion was transferred to the α carbon of propylene from the α carbon of the last monomer unit in the polymer chain, thus producing a terminated polymer chain and a site capable of further polymerization.

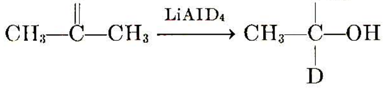
On the basis of the work of Natta,[1] it was strongly believed that the use of α-*d*-propylene should result in a strong isotope effect during the termination reaction for polymer formation. In addition, it has been suggested by Furukawa[2] that a change of substituent at the α carbon of the olefin could affect, in these heterogeneous systems, not only the termination mechanisms but also the mode of coordination and stability of the coordinate complex, e.g., the possibility existed of additional factors of unknown magnitude which could cloud an isotope effect of the termination reaction.

A relatively complete review of literature references pertaining to formation and destruction of active centers during Ziegler-Natta catalyses has been presented earlier.[3] The available literature data and results obtained for the polymerization of α-deuterostyrene[3] indicate that higher polymerization rates as well as higher polymer molecular weights should be obtainable for α-deuteropropylene compared to propylene with the use of the $TiCl_4$–$Al(C_2H_5)_3$ catalytic system. The body of this paper deals with an attempt to demonstrate similarities and anticipated differences between the polymerization of α-*d*-propylene and α-*d*-styrene with the use of the same $TiCl_4$–$Al(C_2H_5)_3$ catalytic systems. These similarities and differences should be noted if the suggested mechanism for formation and destruction of active centers using a $TiCl_4$–$Al(C_2H_5)_3$ is valid.[3]

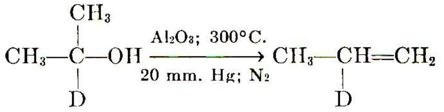
EXPERIMENTAL

Monomers

α-*d*-Propylene. α-*d*-Propylene was prepared by using a method based on the procedure of Shiner[4] as shown in eqs. (1) and (2).



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{LiAlD_4} CH_3-\underset{\underset{\displaystyle D}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH \qquad (1)$$



$$CH_3-\underset{\underset{\displaystyle D}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[20\ mm.\ Hg;\ N_2]{Al_2O_3;\ 300°C.} CH_3-\underset{\underset{\displaystyle D}{|}}{C}H{=}CH_2 \qquad (2)$$

To a slurry of 15 g. (0.355 mole) $LiAlD_4$ (isotopic purity 90%+) in 200 ml. of anhydrous ether (freshly distilled from $LiAlH_4$) was added

91 g. (1.56 mole) of freshly distilled acetone over a period of 4 hr. The mixture was stirred for 24 hr. at reflux. The slurry was then cooled, and a solution of 87 ml. of concentrated H_2SO_4 in 500 ml. of water was slowly added. The ether layer was then separated, and the water layer was extracted with fresh ether in a continuous extractor for 7 days. The ether layers were then distilled through a packed column until most of the ether was separated. The residue was then distilled through a concentric column (120 plates) to give 71.3 g. (81%) of α-deuteroisopropanol.

Analysis of the deuterated isopropanol by infrared and mass spectroscopy showed the majority of the product to be α-deuteroisopropanol. The remainder was mainly dideuterated and perhaps trideuterated isopropanol, mainly as α,β-dideuteroisopropanol. The deuterated isopropanol was contaminated with some nondeuterated isopropanol and with a compound or compounds containing ethyl groups. These can be attributed to either ether or ethanol or both. The relative amount of these compounds in the isopropanol was slight but significant. It is not possible to explain the presence of these impurities in the product at this time.

A 65.0 g. portion of the isopropanol–α-deuteroisopropanol mixture was pyrolyzed in a column of granulated alumina at 300°C. and slight vacuum. The product was trapped in an acetone–Dry Ice bath and with a liquid nitrogen bath. It was redistilled through a column of activated molecular sieves and stored in a stainless steel high pressure container. The yield of α-deuteropropylene was 32.1 g. (70.0%).

Analysis of the above-prepared α-deuteropropylene by mass spectroscopy indicated that it had the following composition: propylene (—C_3H_6), 43.4 mole-%; α-deuteropropylene (—C_3H_5D), 42.5 mole-%; 2,3-dideuteropropylene (—$C_3H_4D_2$), 14.1 mole-%.

These conclusions have also been confirmed by the infrared spectrum of the propylene. Analysis of the spectrum, especially in the C–D region at 2260 cm.$^{-1}$, reveals the existence of mainly a monodeuterated propylene and a minor amount of dideuterated propylene. Examination of the spectrum of the obtained polypropylene shows that the methylene absorption is very sharp. This confirms the fact that the propylene is deuterated at the α position or at the 2,3 positions. Therefore there is little, if any, deuteration at the 1 positions of propylene. These conclusions agree fairly well with the known spectra of deuterated propylene[5] and of deuterated polypropylenes.[6]

Propylene. Research grade propylene was obtained from the Phillips Petroleum Company, Bartlesville, Oklahoma. It was purified by passing it through a drying tower of Drierite and molecular sieves.

Solvents

Highest purity n-heptane was obtained from the Phillips Petroleum Co., Bartlesville, Oklahoma. It was further purified by refluxing with concentrated sulfuric acid, and neutralized by stirring overnight with anhydrous potassium carbonate. It was then refluxed over calcium hydride and distilled. The heptane was stored over activated molecular sieves and chips of calcium hydride under an atmosphere of nitrogen.

Catalysts

Titanium tetrachloride ($TiCl_4$) was obtained from Fisher Scientific Co., New York City. It was vacuum-distilled just prior to use (74.5°C./110 mm. Hg).

Triethylaluminum ($AlEt_3$), obtained in a $^1/_2$-lb. lecture bottle from the Ethyl Corporation, was distilled just prior to use (94°C./8 mm. Hg).

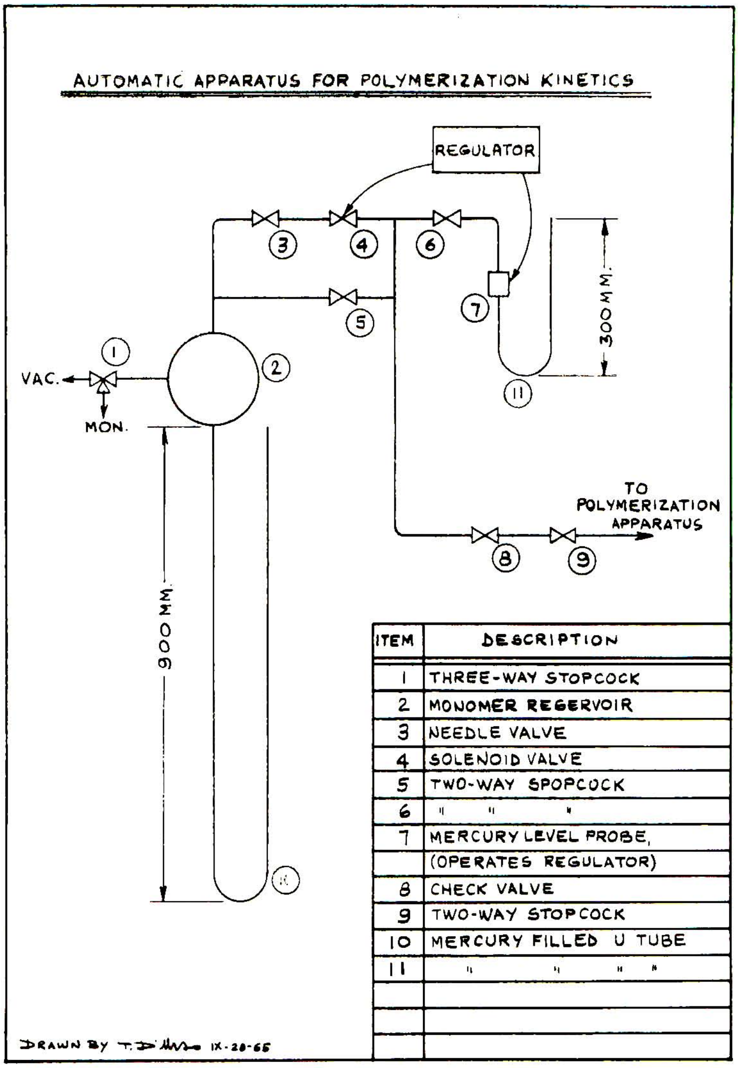
Preparation of Standard Catalyst Solutions

Standard solutions of titanium tetrachloride and triethylaluminum in purified *n*-heptane were prepared according to a previously described procedure.[7] Two solutions were prepared: 0.29*F* solution of titanium tetrachloride and 0.42*F* solution of triethylaluminum.

Polymerization Technique

Description of Apparatus. A schematic of the stationary part of the apparatus is shown in Figure 1. It consists of a monomer reservoir and a pressure-control system. The monomer reservoir system consists of a glass sphere (2) about 200 ml. in volume. It is connected to a manometer (10) made of 3-mm. precision-bore capillary tubing. Finally, it is connected by two paths to a mobile polymerization apparatus shown as Figure 2. One of the paths is controlled manually by a stopcock (5), and the other is controlled electronically and serves to maintain constant pressure at the polymerization side of the apparatus. This path is made up of a vernier-controlled needle valve (3) purchased from the Nupro Co., and by a solenoid valve (4) from the Hoke Co. The solenoid valve is opened or closed depending on the pressure at the other polymerization apparatus side of the reservoir system. This pressure is measured by a manometer (11). Thus, when the pressure at the manometer (11) decreases because of uptake of monomer, the mercury level is activated. The mercury level probe is part of a Thermo-Watch regulator, purchased from Instruments for Research and Industry, Cheltenham, Pennsylvania. When the probe is activated, solenoid valve (4) is opened, permitting entrance of monomer from the high-pressure side, i.e., the reservoir, to the low-pressure side, i.e., the polymerization apparatus. After enough monomer has been introduced into the low-pressure side, the pressure increases, deactivating the probe, which automatically closes the solenoid valve (4). Normally, while measurements are in progress, the solenoid is activated two to six times per minute, and each activation lasts about 1 sec. Stopcock (5), the alternate path to the polymerization apparatus, is used to evacuate the system and saturate the solvent with monomer. It is closed when the polymerization rates are being measured.

The mobile part of the polymerization apparatus is shown as Figure 2. It is attached to the stationary part of the apparatus through joint (L). It



ITEM	DESCRIPTION
1	THREE-WAY STOPCOCK
2	MONOMER REGERVOIR
3	NEEDLE VALVE
4	SOLENOID VALVE
5	TWO-WAY SPOPCOCK
6	" " "
7	MERCURY LEVEL PROBE,
	(OPERATES REGULATOR)
8	CHECK VALVE
9	TWO-WAY STOPCOCK
10	MERCURY FILLED U TUBE
11	" " " "

Fig. 1. Automatic apparatus for polymerization kinetics: (1) three-way stopcock; (2) monomer reservoir; (3) needle valve; (4) solenoid valve; (5, 6) two-way stopcocks; (7) mercury level probe (operates regulator); (8) check valve; (9) two-way stopcock; (10, 11) mercury-filled U tube.

is made up of two sections, (E) and (K). Section (E) is about 2 cm. in diameter and 10 cm. long. It contains a close-fitting ribbon stirrer which is used to stir the catalyst mixture. Section (K) is a sphere, about 100 ml. in capacity, where the polymerization actually occurs.

Pretreatment of the Apparatus. The mobile section of the apparatus was placed in a constant-temperature oil bath and connected through joint (L) to the stationary section, by using a clamp. The oil bath, which contains a magnetic stirrer, was elevated so that the lower part of the mobile section was just above the stirrer. The oil level was then just below stopcock (G). The whole apparatus was evacuated through stopcock (1). It was then filled with dry nitrogen. This process was repeated several times, and finally the apparatus was evacuated.

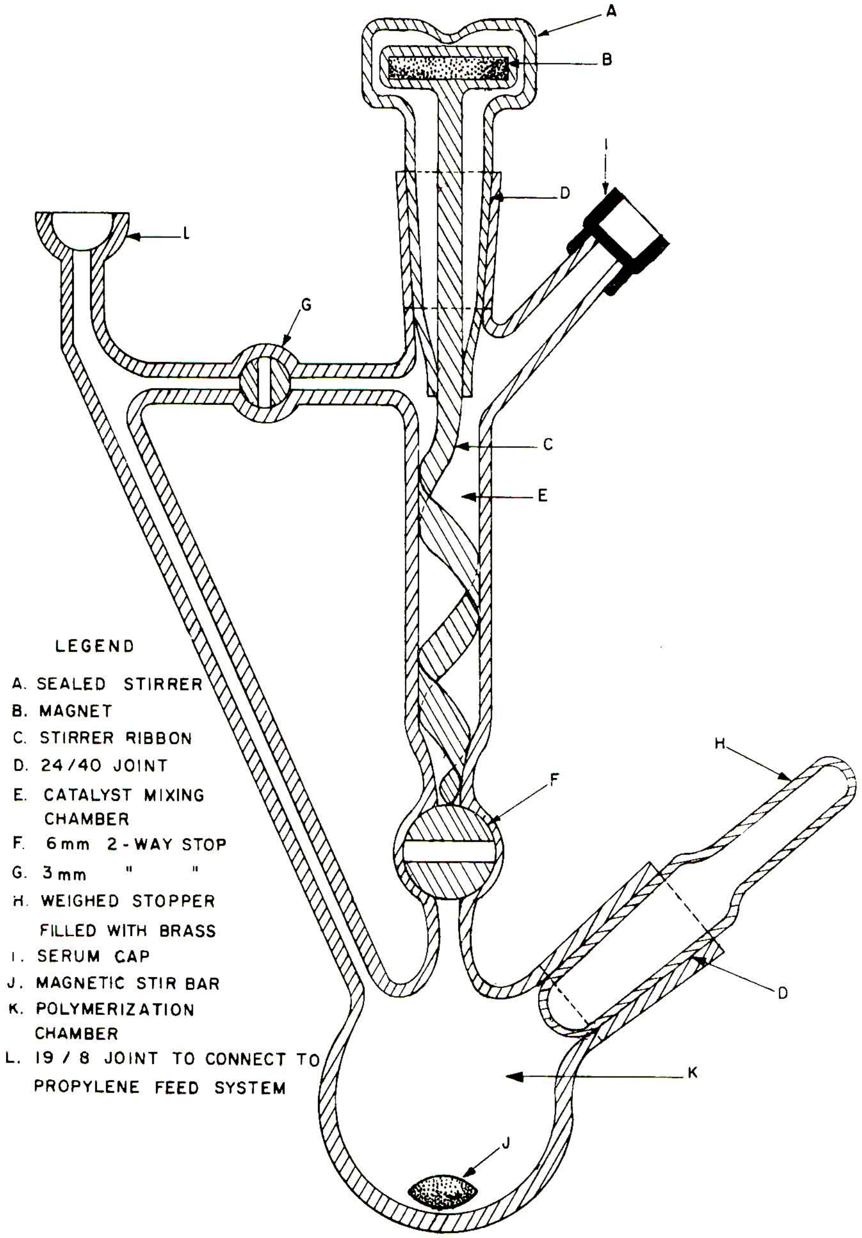


Fig. 2. Polymerization apparatus: (A) sealed stirrer; (B) magnet; (C) stirrer ribbon; (D) 24/40 joint; (E) catalyst mixing chamber; (F) 6-mm. two-way stopcock; (G) 3-mm. two-way stopcock; (H) weighed stopper, filled with brass; (I) serum cup; (J) magnetic stir bar; (K) polymerization chamber; (L) 19/8 joint to connect to propylene feed system.

Charging of the Monomer. With stopcocks (5) and (6) closed, monomer was introduced so that the reservoir was at a pressure of 1500–1600 mm. absolute. Then with stopcock (9) closed, 45 ml. of solvent was added through the serum cap (I). Stopcocks (F) and (G) were closed and stopcocks (5) and (9) were opened. The magnetic stirrer was started, and solvent was saturated with monomer. In the final phases of the operation, stopcock (5) was closed, and the saturation was maintained by the regulator. The solvent was saturated to a pressure of 802 ± 1 mm. Hg.

Preparation of Catalyst. One hour after the solvent was saturated, the catalyst solutions were added through serum cap (I) into chamber (E). Normally a measured volume of standard titanium tetrachloride solution was first added and the sealed magnetic stirrer (C) was turned on. A measured volume of standard triethylaluminum solution was next added over a period of about 10 sec. The finely divided, heterogeneous catalyst thus formed was allowed to age for a specific period of time, normally 30 min., before it was added to the monomer solution.

Addition of Catalyst to the Monomer. Just before the end of the aging period, the catalyst solution was vented to bring it back to atmospheric pressure. Stopcock (9) was then closed. Stopcock (G) was opened and finally stopcock (F) was opened. After all the liquid had transferred to the polymerization chamber, both stopcocks, (F) and (G), were closed, the ribbon stirrer was stopped, and stopcock (9) was then opened. This point marked the beginning of the measured polymerization (time = 0).

Measurement of Polymerization Rates. At the instant that stopcock (9) was opened, the solenoid valve automatically opened to bring the pressure back to 802 mm. Hg. Readings of the pressure of the reservoir (2) were taken every minute with a cathetometer, the change of the height (Δh) of mercury in manometer (10) being measured versus time t. The rates obtained were calculated as $\Delta h/t$. A conversion of rates from $\Delta h/t$ as millimeters per hour to millimoles per hour was accomplished by multiplication by an appropriate factor. The evaluation of this factor required knowledge of the volume of the reservoir chamber (2), as discussed below.

Determination of Volume of Reservoir Chamber. Before any experiments were run, the volume of the reservoir chamber (2) was calculated. This was accomplished as follows. A small bulb was attached to the stationary section of the apparatus where normally the mobile section was attached. Reservoir (2) was then filled with nitrogen to 900 mm. Hg pressure. The pressure at the bulb was recorded by reading manometer (11), and the pressure at the reservoir was recorded by reading manometer (10). Valve (5) was now opened and the equilibrium pressure was recorded. This procedure was repeated again for a slightly larger bulb. The volume difference C between the two bulbs was determined by weighing the bulbs empty and filled with water, and calculating the difference of the volume of water which each bulb contains.

Assuming constant (room) temperature, we can obtain eq. (3):

$$P_{\mathrm{A}}V_{\mathrm{A}} + P_{\mathrm{B}}V_{\mathrm{B}} = P_{\mathrm{F}}(V_{\mathrm{A}} + V_{\mathrm{B}}) \tag{3}$$

where P_A is initial pressure at reservoir (2), V_A is volume of the reservoir, P_B is pressure at bulb (B), V_B is volume of bulb (B) and connecting lines, P_F is equilibrium pressure in reservoir (2) and bulb (B), and $V_A = k_1V_B$ where

$$k_1 = (P_F - P_B)/(P_A - P_F) \tag{4}$$

Similarly, using the larger bulb we can obtain eq. (5):

$$P'_AV_A + P'_BV'_B = P'_F(V_A + V'_B) \tag{5}$$

and

$$V_A = k_2V'_B \tag{6}$$

where

$$k_2 = (P'_F - P'_B)/(P'_A - P'_B)$$

since $V'_B = V_B + C$, where C is the computed difference in total volume,

$$V_A = k_1k_2C/(k_1 - k_2) \tag{7}$$

where k_1 and k_2 are constants given above. By using the calculations described above, the volume of the reservoir V_A was computed to be 190 ± 5 ml.

Once the volume of the reservoir V_A was calculated, the multiplication factor which was used to convert polymerization rates from millimeters per hour to millimoles per hour is calculated by eq. (8):

$$\Delta P = \Delta nRT/V \tag{8}$$

Since these experiments were conducted at room temperature conditions, and since the changes in pressure were slight, the ideal gas equation appears justified. Thus by using the values: $R = 62.4$ mm. Hg-l./mole-°K., $T = 300$°K. = 23°C., $V = 0.190$ liters, $\Delta n/\Delta P$ is calculated to be 1.02×10^{-2} mmole of gas/mm. Hg pressure.

Polymer Isolation and Characterization. After completion of a run with the apparatus described in Figures 1 and 2, stopcock (9) was closed and the serum cap (I) was removed. Then, 2 ml. of methanol was added and stopcock (F) was opened. After a few minutes, the magnetic stirrer was turned off, and the mobile apparatus was disconnected from the stationary apparatus. Finally, the stopper (H) was removed, and the contents were placed in a 600 ml. beaker containing 10 ml. of concentrated hydrochloric acid in 200 ml. of methanol. The flask was stirred over a magnetic stirrer for 15 min. and then heated on a steam bath for 15 min. Finally, the three-phase mixture was allowed to stand overnight. The solution was decanted, and fresh solution of 10 ml. hydrochloric acid in 200 ml. of methanol was added. It was stirred for 15 min., and the resulting white polymer was filtered, washed with methanol, then acetone, and finally dried in a vacuum oven at ca. 60°C. overnight and weighed. Yields are reported at this point. Hot tetralin was used to dissolve the polymer.

The hot, very viscous polymer solution was filtered by gravity through paper and the polymer was precipitated in ethanol. Tetralin was used as a solvent for the determination of intrinsic viscosities. In all cases the viscosities were determined at 97.5°C. by dilution of 0.2–0.1% polymer solutions.

The crystallinity of several of the polymers was determined by low-angle x-ray scattering. All the polymers showed large degrees of crystallinity. Infrared spectra of the polymers were obtained as powders in most cases. Efforts to characterize homopolymers and copolymers of propylene and 2-deuteropropylene by nuclear magnetic resonance (NMR) using diphenyl ether as the solvent at 135°C. were not successful. Only a broad polymer absorption was obtained.

Fractionation of Polymers. A method of fractionation was devised to fractionate several of the polymers into crystalline and amorphous fractions. The weighed, reprecipitated polymer was initially cut into small pieces. It was then dispersed in 1000 times its weight of *n*-heptane and stirred overnight with a magnetic stirrer. The solution was filtered by gravity over a sintered glass filter of medium porosity. The swelled polymer precipitate was then washed repeatedly with acetone and vacuum-dried at ca. 60°C. overnight and weighed. The above isolated fraction is the crystalline fraction. The polymer solution filtrate was concentrated to $^1/_{100}$ its initial volume in an oil bath and finally added to acetone. The precipitated polymer was filtered, vacuum-dried overnight at ca. 60°C., and weighed. The above isolated fraction is the amorphous fraction.

RESULTS

Homopolymerization of Propylene

Homopolymerization rates for propylene were determined at three $TiCl_4$ concentrations, all other conditions remaining constant. Product viscosities were determined over the same $TiCl_4$ concentration range. A single run was performed at one-half the usual catalyst aging time (15 instead of 30 min.) for the lowest $TiCl_4$ concentration. A summary of these data appears as Table I. Data obtained at a 30-min. catalyst aging time indicate the following.

(*1*) Only one rate of polymerization was observed over the whole experimental time range of 1 hr., i.e., initial rate = final rate.

(*2*) Polymerization rate at a single $TiCl_4$ concentration can be reproduced with a relative mean deviation (RMD) of 5%. Polymerization rates appear to increase slightly with increasing $TiCl_4$ concentrations.

(*3*) Polymer intrinsic viscosities appeared to increase with decreasing $TiCl_4$ concentrations. The viscosities are low enough to permit straight-line extrapolation with ease for determinations of intrinsic viscosities in tetralin at 97.5°C.

Since no attempt was made to keep the stirring rate constant, the results appear to be independent of stirring rates used here, not implying, however,

TABLE I
Rates of Propylene Polymerization[a]

Aging time, min.	$TiCl_4$, mmole/l.	Total volume, ml.	Initial rate, mole/l.-hr.	Final rate, mmole/l.-hr.	Yield, g.	[η] (97.5°C., tetralin), dl./g.
15	8.89	49.5	112	58.6	0.203	3.45
30	8.89	"	41.4 [b]	41.4	0.116 [d]	
"	"	"	48.9	48.9	0.120	
"	"	"	44.4	44.4 [c]	0.105	
"	"	"	41.8	41.8	0.146	4.02 [h]
"	"	"	44.8	44.8	0.119	
30	11.4	51.0	49.8 [e]	49.8	0.160 [g]	
"	"	"	48.0	48.0 [f]	0.144	3.92
"	"	"	49.6	49.6	0.148	
30	13.9	52.5	49.5 [i]	49.5 [j]	0.134	3.80
"	"	"	50.7	50.7	0.151	3.75
"	"	"	52.6	52.6	0.165 [k]	

[a] Reaction conditions: Al/Ti = 2.86; temp. = 54.50 ± 0.05°C.; pressure = 802 ± 2 mm. Hg.

[b] Avg. = 44.3 ± 2.1 mole/l.-hr.; RMD = 4.7%.

[c] Avg. = 44.3 ± 2.1 mole/l.-hr.

[d] Avg. = 0.121 ± 0.010 g.; RMD = 8.3%.

[e] Avg. = 49.1 ± 0.8 mole/l.-hr.; RMD = 1.6%.

[f] Avg. = 49.1 ± 0.8 mole/l.-hr.

[g] Avg. = 0.151 ± 0.006 g.; RMD = 4.0%.

[h] Avg. = 3.87 ± 0.10; RMD = 2.6%.

[i] Avg. = 50.9 ± 0.1 mole/l.-hr.; RMD = 2.2%.

[j] Avg. = 50.9 ± 1.1 mole/l.-hr.

[k] Avg. = 0.150 ± 0.011 g.; RMD = 7.3%.

that stirring cannot be a function when variations become excessive. The isolated results obtained at a 15-min. catalyst aging time indicate that an almost 200% increase in initial rate can be achieved in this manner. This high initial rate dropped to a final rate which approached that rate observed throughout at a 30-min. catalyst aging time. This increase in initial rate yielded a considerable increase in isolable product, and a product of lower intrinsic viscosity than that obtained at a 30-min. catalyst aging time. These data, while isolated, are relevant to the observations made for propylene and *α-d*-propylene copolymerizations discussed below.

Copolymerization of Propylene and 2-Deuteropropylene

Copolymers of propylene and 2-deuteropropylene were prepared at a constant 2-deuteropropylene monomer feed concentration. The polymerizations were conducted for a period of 1 hr. During this time and for all catalyst concentrations, an initial rate ca. 10 times the initial rate of polypropylene formation was observed, which rapidly decreased with time. The final rate measured after a period of about 40 min. appeared to be the same as the rate obtained under similar conditions with propylene homopolymerization. The inaccuracies in determining the initial rates are large, since they were experimentally difficult to control. These results are shown in Table II. It is of interest that while an approximate 10-fold increase of initial rate could be obtained for α-*d*-propylene compared to propylene, this initial rate increase did not appear to be a function of $TiCl_4$ concentrations within these experimental errors, nor was it correspondingly reflected in the amount of polymer isolated; e.g., same low molecular weight product may not have been isolated.

TABLE II

Rate of Copolymerization of Propylene and 2-Deuteropropylene[a]

Aging time, min.	$TiCl_4$, mmole/l.	Total volume, ml.	Initial rate, mmole/l.-hr.	Final rate, mmole/l.-hr.	Yield, g.	$[\eta]$ (97.5°C., tetralin), dl./g.
30	8.89	49.5	500 ± 100	44.6[b]	0.200[c]	3.74
30	8.89	49.5	700 ± 200	46.5	0.220	3.60
30	11.4	51.0	450 ± 150	51.2[d]	0.231[e]	
30	11.4	51.0	500 ± 100	49.2	0.228	3.58
60	11.4	51.0	550 ± 100	49.2	0.190	
30	13.9	52.5	550 ± 100	50.5[f]	0.241[g]	
30	13.9	52.5	500 ± 100	50.9	0.250	3.31

[a] Reaction conditions: 56.6% α-*d*-propylene; Al/Ti = 2.86; $T = 54.50 \pm 0.05$°C.; $P = 802 \pm 2$ mm. Hg.

[b] Avg. = 45.6 ± 1.0 mole/l.-hr.

[c] Avg. = 0.210 ± 0.010 g.

[d] Avg. = 49.9 ± 0.9 mole/l.-hr.

[e] Avg. = 0.225 ± 0.015 g.

[f] Avg. = 50.7 ± 0.2 mole/l.-hr.

[g] Avg. = 0.246 ± 0.005 g.

The viscosities of the polymers may indicate a slight decrease compared with those of products obtained by the homopolymerization of propylene and appeared to increase with decreasing titanium concentration.

Fractionation of Polymers

Fractionation of several of the deuterated copolymers with *n*-heptane as solvent at room temperature revealed that the deuterated copolymers were composed of two distinct fractions. The soluble fractions had an average intrinsic viscosity of 1.34, as compared with an average intrinsic viscosity of 3.6 for unfractionated polymer, and constituted 51% of the total unfractionated polymer. The low-angle x-ray diffraction pattern revealed the polymer to be largely amorphous. The insoluble fraction had an average intrinsic viscosity of 7.5. It constituted 49% of the total polymer. X-ray patterns revealed the insoluble polymer to be almost completely crystalline. Fractionation of the propylene homopolymers, which had an intrinsic viscosity of 3.9, revealed only an insoluble crystalline fraction. These x-ray patterns are shown in Figure 3.

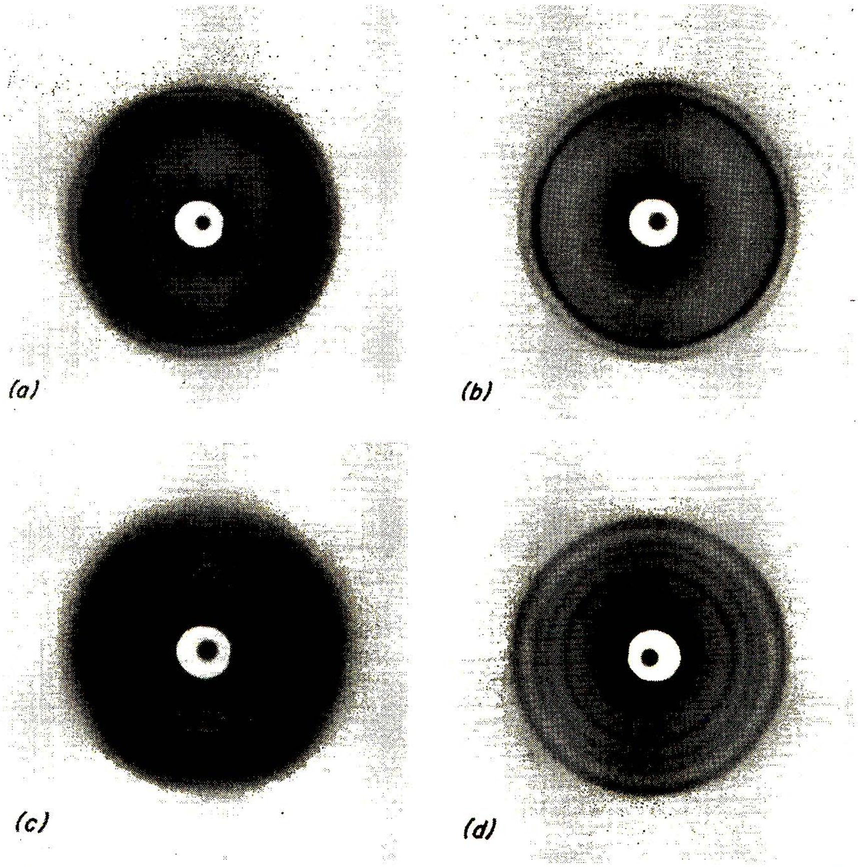


Fig. 3. X-ray diffraction patterns of: (*a*) unfractionated deuterated copolymer, $[\eta]$ (97.5°C., tetralin) = 3.6; (*b*) insoluble fraction of the deuterated copolymer, $[\eta]$ (97.5°C., tetralin) = 7.5; (*c*) soluble fraction of the deuterated copolymer, $[\eta]$ (97.5°C., tetralin) = 1.3; (*d*) unfractionated polypropylene homopolymer, $[\eta]$ (97.5°C., tetralin) = 3.9.

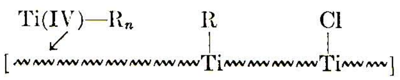
DISCUSSION

Data presented in this paper can be explained by assuming polymerization mechanisms disclosed earlier[3] for styrene and α-*d*-styrene with the same heterogeneous TiCl_4–$\text{Al(C}_2\text{H}_5)_3$ catalyst system.

The formation of potential active centers in the absence of monomer is believed to result in at least two distinct types: an insoluble, trivalent and/or divalent partially alkylated titanium surface

$$[\sim\sim\overset{\text{Cl}}{\overset{|}{\text{Ti}}}\sim\sim\sim\sim\overset{\text{R}}{\overset{|}{\text{Ti}}}\sim\sim]$$

and a soluble, tetravalent alkylated titanium species $[\text{Ti(IV)}—\text{R}_n]$ which can be adsorbed and/or chemisorbed onto the surface formed *in situ:*



$$[\overset{\text{Ti(IV)}—\text{R}_n}{\overset{\swarrow}{\sim\sim\sim\sim\sim\sim\sim\sim}}\overset{\text{R}}{\overset{|}{\text{Ti}}}\sim\sim\sim\sim\overset{\text{Cl}}{\overset{|}{\text{Ti}}}\sim\sim]$$

Formation of alkylated titanium species is believed to occur in solution after the initial formation of a Lewis acid–base adduct which is considerably ionic in character [$\mathrm{Ti}^{\mathrm{IV}\delta+}\ldots{}^{\delta-}\mathrm{AIR}$]. Soluble, tetravalent, alkylated titanium species are then believed to be produced by a unimolecular rear-

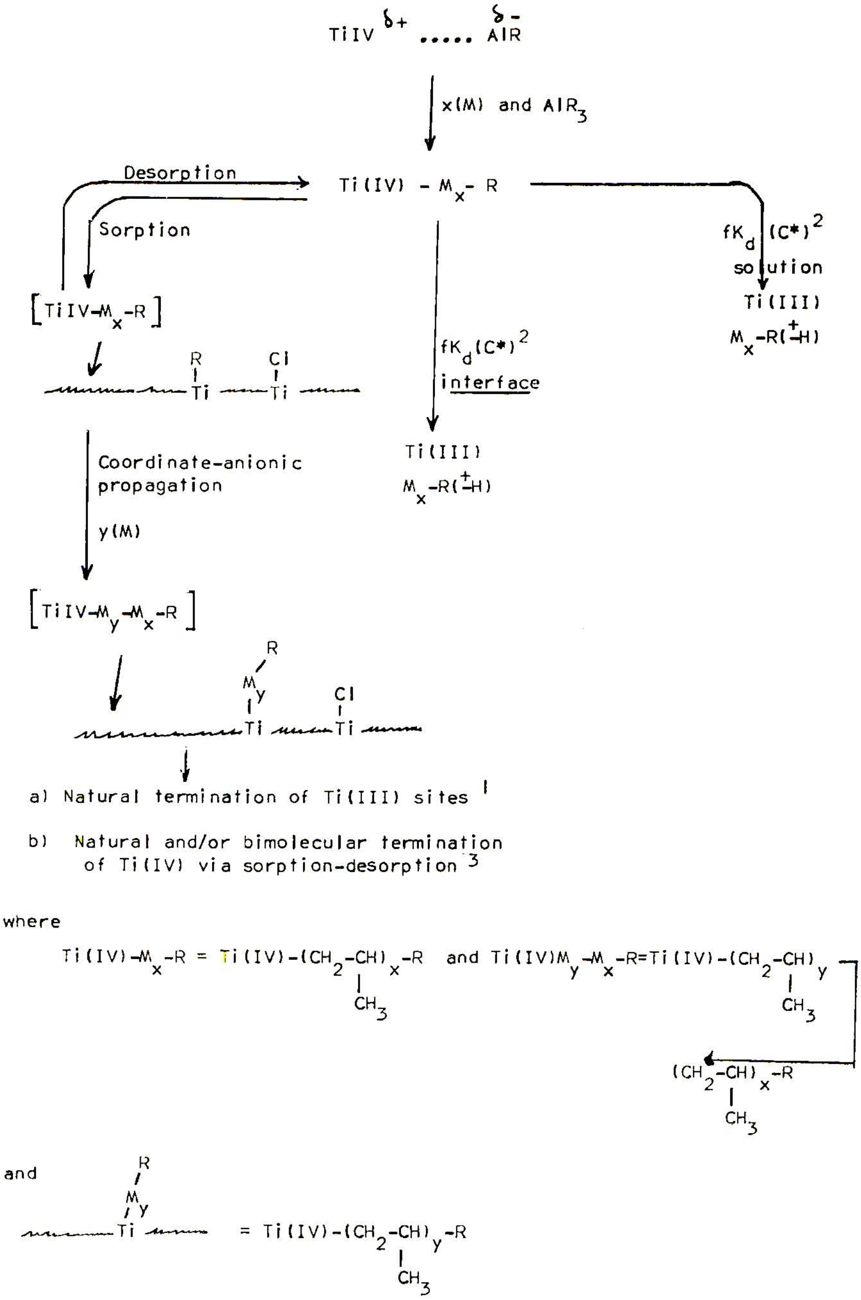


Figure 4.

rangement of the Lewis acid-base adducts, and/or by a reaction of these adducts with excess aluminum alkyl. Formation of the insoluble trivalent and/or divalent titanium species is believed to be the result of a bimolecular disproportionation of soluble, tetravalent, alkylated titanium species [Ti(IV)—R_n]. With increasing catalyst aging time, Ti(IV) solution and Ti(IV) adsorbed and/or chemisorbed species should diminish, leaving, at infinite aging time, an essentially pure alkylated Ti(III) surface. Consequently, since for the suggested mechanism of active center formation[3] both Ti(IV) and Ti(III) species are potential active centers for monomers which can stabilize a carbonium ion (e.g., styrene, propylene), the overall rate of polymerization should be inversely proportional to catalyst aging time. The above would certainly predict an initial rate higher than a final rate for both propylene and α-*d*-propylene at sufficiently low catalyst aging times. The data in Table I indicate that a 15 min. catalyst aging time can produce higher initial rates than a 30-min. catalyst aging time for propylene. The data in Table II indicate that α-*d*-propylene containing monomer mixtures exhibit a very much higher initial rate at a 30-min. catalyst aging time than 100% propylene. It is suggested that this behavior is a direct result of the isotopically controlled rate of decomposition of solution-formed, monomer-alkylated Ti(IV) potential active centers, assuming that, at a catalyst aging time of 30 min., the concentration of Ti(IV) potentially active center is equal for propylene and α-*d*-propylene but less than that available at a catalyst aging time of 15 min. Only α-*d*-propylene by virtue of a reduced decomposition rate involving the α-*d*-position can produce enough surviving species to show this potentially available rate increase.

A summary of this mechanism of polymerization and active center formation and destruction[3] based on styrene is given schematically in Figure 4 for propylene.

In summary then, the observed rate of polymerization V_p is assumed to be the sum of at least two distinct rates:

$$V_p\ (\text{observed}) = V_{p1}\ [\text{cationic Ti(IV) species}] + V_{p2}\ [\text{coordinate anionic Ti(III) species}]$$

As catalyst aging time approaches zero, V_{p2} is expected to approach zero, yielding:

$$V_p\ (\text{observed}) \cong V_{p1}$$

This produces cationically formed, lower molecular weight, primarily atactic and amorphous oligomers and polymers.

Conversely, at very long catalyst aging times, V_{p1} is expected to approach zero, yielding:

$$V_p\ (\text{observed}) \cong V_{p2}$$

The product in this case is tactic, crystalline, high molecular weight polymer.

The extent of interference via V_{p1} can be enhanced by deuteration of the α position of propylene.

The x-ray patterns shown in Figure 3 clearly indicate the enhancement of V_{p1} for the α-*d*-propylene case. The x-ray diagram of the crystalline homopolypropylene (Fig. 3*d*) does not exactly match the x-ray diagram obtained for the crystalline fraction of the deuterated copolymers. Nevertheless, both crystalline fractions are expected to be the product of identical processes. One reason for this discrepancy may be the fact that Ti(IV)—M_x—R species may have a sufficiently long lifetime to be responsible for a fraction of largely crystalline Ti(IV)—M_y—M_x—R. Another factor may be the incomplete removal of Ti(IV)—M_x—R species by the fractionation.

The results obtained for α-*d*-propylene–propylene copolymerizations discussed above were expected and consequently reinforce the mechanisms published earlier for this catalyst system.[3] These expected results then represent the similarities which were anticipated based on the styrene–α-*d*-styrene work.

In addition to the expected similarities there are also evident from Figure 3 the expected differences. The viscosities of the crystalline fractions are substantially higher than those of the amorphous fractions, indicating again that the α hydrogen of propylene is involved in the termination step for coordinate-anionic polymerization. None of the styrene or α-*d*-styrene copolymers showed any degree of crystallinity probably because, as stated earlier,[3] the majority (if not all) of the polymer was formed cationically using Ti(IV) species in solution and/or those adsorbed on the Ti(III) surface. Stating it another way, the tendency for styrene to polymerize cationically is substantially larger than for propylene under any given situation which allows for both cationic and coordinate-anionic polymerizations.

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Résumé

L'homopolymérisation du propylène et la copolymérisation de α-*d*-propylène-propylène ont été étudiées du point de vue de leur vitesse utilisant une pression constante et

des conditions de polymérisation identiques. On a pu démontrer que les vitesses de homopolymérisation de propylène étaient constantes dans les conditions utilisées. Toutefois, la vitesse initiale de copolymérisation est plus rapide et décroissait avec le temps de façon à atteindre la vitesse obtenue pour l'homopolymérisation du propylène. La vitesse de copolymérisation initiale plus élevée était attribuée à la stabilisation des centres actifs potentiels en solution lorsque le monomère deutéré est présent. Ces centres actifs étaient formés par réaction de titane tétravelant avec le monomère. Ces centres actifs étaient formés en solution et étaient détruits par des réactions contrôlées isotopiquement; c'est-à-dire, l'abstraction d'hydrogène ou d'un atome de α-deutérium au départ des monomères en solution ou à l'interface. Ces centres actifs étaient absorbés ou chémisorbés sur la surface du catalyseur précipité qui était responsable pour un polymère d'ordre stérique considérablement plus faible. Ce schéma prédit un polymère stéréorégulier de poids moléculaire élevé produit par polymérisation sur une surface Ti(III) et un polymère fortement amorphe de poids moléculaire plus bas produit par les espèces absorbées ou chémisorbées. Cette prédiction a été vérifiée par fractionnement des polyméres deutérés en portions cristallines et amorphes.

Zusammenfassung

Die Geschwindigkeit der Propylenpolymerisation und der α-d-Propylen–Propylencopolymerisation wurde bei konstantem Druck bestimmt. Es konnte gezeigt werden, dass die Geschwindigkeit der Homopolymerisation von Propylen unter den gewählten Bedingungen konstant ist. Die Anfangsgeschwindigkeit der Copolymerisation war dagegen grösser und nahm mit der Versuchsdauer auf den für die Homopolymerisation von Propylen erhaltenen Wert ab. Die höhere Anfangsgeschwindigkeit der Copolymerisation wurde der Stabilisierung potentiell aktiver Zentren in Lösung bei Anwesenheit des deuterierten Monomeren zugeschrieben. Es wird angenommen, dass diese aktiven Zentren durch Reaktion des vierwertigen Titans mit Monomerem entstehen. Diese in Lösung gebildeten aktiven Zentren sollen durch eine Reaktion mit Isotopeneffekt zerstört werden, nämlich durch Abstraktion des Wasserstoff- oder α-Deuteriumatoms von der monomer-alkylierten Spezies in Lösung oder an der Grenzfläche. Weiters wird angenommen, dass die aktiven Zentren an der Oberfläche des ausgefällten Katalysators adsorbiert oder chemisorbiert werden und für die Bildung eines Polymeren von beträchtlich geringerer sterischer Ordnung verantwortlich sind. Dieses Schema lässt ein stereoreguläres, durch Polymerisation an einer Ti-(III)-Oberflächer erzeugtes hochmolekulares Polymeres und ein weitgehend amorphes, durch adsorbierte oder chemisorbierte Spezies erzeugtes Polymeres von niedrigerem Molekulargewicht erwarten. Diese Erwartung wurde durch Fraktionierung der deuterierten Polymeren in kristalline und amorphe Anteile bestätigt.

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Stereospecific Polymerization of Methacrylonitrile. III. Some New Catalysts for Isotactic Polymethacrylonitrile

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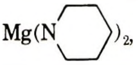
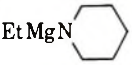
Synopsis

Some classes of organometallic catalysts what induce stereospecific polymerization of methacrylonitrile have been found. They include organolithium aluminum compounds of the type $LiAlR_4$, $Li[R_3AlOAlR_2]$, and $Li[R_3AlN(R)AlR_2]$, organosodium aluminum compounds of the type $NaAlR_4$, organolithium zinc compounds of the type $LiZnR_3$ and Li_2ZnR_4, organomagnesium aluminum compounds of the type $RMg[AlR_4]$ and $Mg[AlR_4]_2$, and organomagnesium compounds containing an Mg–N bond, such as , , and their related compounds. One of the features of the polymerization with these catalysts was that the crystalline polymers were formed at moderately high temperatures. Total conversion, solubility index, and molecular weight of the polymer increased with increasing polymerization temperature, as observed in the case of polymerization with diethylmagnesium catalyst. Catalysts with an Mg–N bond were found to be highly effective for the stereospecific polymerization. The acetone-insoluble fractions of the polymers gave x-ray diagrams identical to the crystalline polymer produced with diethylmagnesium. This indicates that the acetone-insoluble crystalline polymers produced with these catalysts have an isotactic structure. The viscosity–molecular weight relationship for crystalline polymer was conveniently determined in $Cl_2CHCOOH$ at 30°C.; $[\eta] = 2.27 \times 10^{-4} M^{0.754}$.

INTRODUCTION

In spite of considerable recent development in the field of the stereospecific polymerization of polar monomers there has been very little work done on the stereospecific polymerization of the monomers containing a nitrile group.[1]

Recent work in this laboratory has demonstrated that crystalline polymethacrylonitrile can be successfully obtained with organometallic catalysts.[2,3] The present paper is concerned with some classes of the new catalysts that are found to be effective in the polymerization of methacrylonitrile, leading to the formation of the crystalline polymer at moderately high temperatures.

All the crystalline polymers obtained with the catalysts used in the present study gave x-ray diagrams that were substantially identical with that of the crystalline polymer obtained by diethylmagnesium.[2] The structural studies made in this laboratory showed that the crystalline polymer has an isotactic structure.[4] One of the most characteristic features of these catalysts is that they induce stereospecific polymerization only at moderately high temperatures.

EXPERIMENTAL

Materials

Monomer. Methacrylonitrile (Eastman Organic Chemicals Corp.) was purified by successive washing with 1% sodium hydroxide aqueous solution followed by water. After drying over $CaCl_2$ it was fractionally distilled immediately 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 (b.p. 90°C., n_D^{23} 1.3990).[5]

Solvents. Dichloroacetic acid was purified by fractional distillation over phosphorus pentoxide. Other solvents were purified by the usual methods, as described in the previous paper.[6] Acetone and methanol were used without further purification.

Catalysts

BuLi. A hexane solution of *n*-butyllithium supplied by Foot Mineral Co. was used as catalyst. The concentration was periodically checked by the method of Kamiensky.[7] This analytical procedure has been compared with the usual double titration method of Gilman et al.[8] and found to give satisfactory agreement. The catalyst solution was stored at −20°C.

$AlEt_3$ and $ZnEt_2$. Triethylaluminum and diethylzinc, supplied by Ethyl Corporation and by Wako Chemical Drug Co., respectively, were used without further purification.

$LiAlEt_3Bu$, $NaAlEt_4$, and Related Compounds. $LiAlEt_3Bu$ was prepared *in situ* by mixing equimolar amounts of $AlEt_3$ and BuLi in inert solvent. $NaAlEt_4$ was prepared from NaOEt and $AlEt_3$ according to the following reaction:

$$AlEt_3 + NaOEt \rightarrow Na[AlEt_3OEt]$$

$$Na[AlEt_3OEt] + AlEt_3 \rightarrow Na[AlEt_4] + AlEt_2OEt$$

Thus, 6 g. of NaOEt, which had been pulverized into uniform, fine particles, was suspended in 100 ml. of heptane and kept at −78°C. To this mixture was introduced under nitrogen atmosphere 113 ml. of toluene solution containing 20% $AlEt_3$. Upon warming up to room temperature the reaction between NaOEt and $AlEt_3$ took place instantaneously. At the end of the reaction the reaction product was completely soluble. On standing at −20°C. overnight $NaAlEt_4$ crystallized out. It was then purified by recrystallization from a toluene–heptane mixture under nitrogen atmosphere; m.p. 125°C. A modified catalyst, for example $NaAlEt_3(NPh_2)$, was prepared *in situ* by the reaction between $NaAlEt_4$ and an equimolar quantity of diphenylamine, $LiAlEt_2Bu(NPh_2)$ was prepared from $AlEt_2NPh_2$ and BuLi.

$EtMg[AlEt_4]$ and $Mg[AlEt_4]_2$. $EtMg[AlEt_4]$ was prepared in toluene from the reaction of $MgEt_2$ with an equimolar amount of $AlEt_3$. $Mg[AlEt_4]_2$ was prepared in the same way from $MgEt_2$ and 2-mole equivalents of $AlEt_3$. These complexes were soluble in hydrocarbons, and toluene solution was used as catalyst.

$Li[Et_3AlOAlEt_2]$ and Related Catalysts. $Li[Et_3AlOAlEt_2]$ was prepared by the method described by Tani et al.[9] from LiOH and $AlEt_3$ in toluene according to the reaction

$$LiOH + AlEt_3 \rightarrow LiOAlEt_2 + EtH$$

$$LiOAlEt_2 + AlEt_3 \rightarrow Li[Et_3AlOAlEt_2]$$

It was purified by recrystallization from a toluene–hexane mixture. The crystallized product was colorless needles, which melted at about 90°C. A modified catalyst, $Li[Et_2(NPh_2)AlOAlEt_2]$, was prepared from $LiOAlEt_2$ and $AlEt_2NPh_2$.

$Li[Et_3AlN(Ph)AlEt_2]$. $Li[Et_3AlN(Ph)AlEt_2]$ was also prepared according to Tani's procedure:[10]

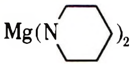
$$PhNH_2 + BuLi \rightarrow PhNHLi + BuH$$

$$PhNHLi + 2AlEt_3 \rightarrow Li[Et_3AlN(Ph)AlEt_2] + EtH$$

The product was colorless needles, which melted at 133°C.

$LiZnEt_2Bu$, $Li_2ZnEt_2Bu_2$, and Related Compounds. $LiZnEt_2Bu$ and $Li_2ZnEt_2Bu_2$ were prepared *in situ* by mixing $ZnEt_2$ and a stoichiometric quantity of BuLi in toluene. Amine-modified catalyst, for example $LiZnEtBu(NPh_2)$, was prepared through the reaction of $ZnEt_2$ and an equimolar amount of diphenylamine, followed by mixing with BuLi. Other modified catalysts were prepared by the similar methods.

An "isolated catalyst" was prepared, for example, in the following manner. To a hexane solution of $ZnEt_2$ an equivalent quantity of diphenylamine was introduced at room temperature under nitrogen stream. To this reaction mixture a stoichiometric amount of *n*-BuLi in toluene was added dropwise at ambient temperature. A white precipitate was formed, and this was filtered, washed with hexane several times, and dried under nitrogen. This white powder was "isolated catalyst, $LiZnEtBu(NPh_2)$." "Isolated $Li_2ZnBu_2(NPh_2)_2$" was prepared as follows. A hexane solution of $ZnEt_2$ was allowed to react with a toluene solution of diphenylamine in a molar ratio of 1:2 at room temperature. 2-mole equivalents of ethane were evolved, and the reaction product was completely soluble in the solvent. To this reaction mixture a stoichiometric amount of *n*-butyllithium was introduced dropwise with vigorous stirring at room temperature. A white precipitate formed, which was collected, filtered, and washed several times with *n*-hexane and then dried *in vacuo*.

Organomagnesium Compounds with Mg–N Bond. These compounds were all prepared *in situ* through the reaction of $MgEt_2$ with a stoichiometric amount of amine in inert solvent. The typical preparation procedure was as follows. To a suspension of $MgEt_2$ in toluene 2-mole equivalents of piperidine were introduced dropwise at room temperature under nitrogen atmosphere. After stopping of the gas evolution it was heated to a boil for a few minutes, then allowed to stand at room temperature for about 30 min. After completion of the reaction the product was completely soluble in toluene. This solution was  catalyst.

Polymerizations

A representative polymerization procedure is described below. The reaction vessel was a 500-ml. three-necked separable flask equipped with a mechanical stirrer, reflux condenser, and inlet and outlet tubes for nitrogen gas. One neck of the flask was covered by a rubber serum-bottle cap. After the flask was flushed with dry nitrogen, 270 ml. of purified toluene was introduced with a syringe through the serum cap. The catalyst was then added by means of a hypodermic syringe inserted through the rubber cap. The solution was then warmed to a given temperature, and the reaction was started by injecting 30 ml. of methacrylonitrile with a syringe in the same fashion. Polymerization started immediately, and in every case there was a simultaneous appearance of a deep red color, which remained during the polymerization. A positive nitrogen pressure was maintained during the polymerization. After the appropriate time a crude polymer was isolated by pouring the reaction mixture into methanol containing a small amount of hydrochloric acid and then allowing the mixture to stand at room temperature overnight. The precipitated white polymer was collected, filtered, washed several times with methanol, and dried *in vacuo*.

Solubility Index

The solubility index, which represents a percent value of acetone-insoluble fraction to total polymer, was determined according to the method described in another paper.[6]

Viscosity Measurement

Viscosities were determined for the acetone-insoluble fractions in $Cl_2CHCOOH$ at 30°C. in an Ubbelohde viscometer, which had a flow time of approximately 133 sec. for pure solvent; no kinetic energy corrections were made.

Viscosity–Molecular Weight Relationship and Molecular Weight Determination

In a series of this investigation Hayashi et al.[11] in this laboratory determined the viscosity–molecular weight relationship in DMF for polymethacrylonitrile by the Archibald ultracentrifugal method, using radical-initiated polymer. They give the relationship

$$[\eta] = 2.33 \times 10^{-4} M_w^{0.73} \quad \text{(at 30°C. in DMF)}$$

In the present study, with the DMF-soluble fractions, these values and the values for viscosities determined in $Cl_2CHCOOH$ were used for obtaining K and α in the equation $[\eta] = KM^{\alpha}$ for the crystalline polymer. Seventeen sets of the data were used for determining K and α and gave $K = 2.27 \times 10^{-4}$ and $\alpha = 0.754$.

Thus we have the following relationship for the $Cl_2CHCOOH$ solution:

$$[\eta] = 2.27 \times 10^{-4} M^{0.754} \quad \text{(in } Cl_2CHCOOH \text{ at } 30°C.)$$

In the present investigation molecular weights were calculated by assuming that this relationship could also be applied for the DMF-insoluble, highly crystalline materials.

RESULTS

$LiAlEt_3Bu$, $NaAlEt_4$, and Related Catalysts

The results of the polymerization of methacrylonitrile with $LiAlEt_3Bu$ and $NaAlEt_4$ are summarized in Table I. These catalysts were not very effective in stereospecific polymerization, from the low conversions and the low values of the solubility index of the resulting polymers. However, the acetone-insoluble fraction was found to be crystalline by x-ray examination.

Some results of the polymerization with a catalyst modified with diphenylamine are listed in Table II. The modification of the catalysts with diphenylamine gave remarkable effects. The solubility indexes of the resulting polymers increased and, more interestingly, the crystallinity of the acetone-insoluble fractions obtained with the modified catalysts was much higher than those with the unmodified ones; see Table III.

TABLE I

Polymerization[a] of Methacrylonitrile with $NaAlR_4$ and $LiAlR_4$

Catalyst	Mole	Solvent	Polymerization temp., °C.	Polymerization time, hr.	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]
$NaAlEt_4$	0.006	Toluene	50	4	Trace	—	—
$NaAlEt_4$	0.006	"	70	4	3.8	37.6	0.87
$NaAlEt_4$	0.006	"	90	4	5.0	49.6	2.15
$LiAlEt_3Bu$	0.005	"	−78	7	Trace	—	—
$LiAlEt_3Bu$	0.005	"	0	7	Trace	—	—
$LiAlEt_3Bu$	0.005	"	40	7	5.0	21.8	0.46
$LiAlEt_3Bu$	0.005	"	70	7	20.7	38.3	1.59
$LiAlEt_3Bu$	0.005	"	90	7	27.8	54.4	3.29
$LiAlEt_3Bu$	0.005	*n*-Heptane	0	4	3.9	3.2	1.36
$LiAlEt_3Bu$	0.005	"	50	4	10.7	16.2	0.36
$LiAlEt_3Bu$	0.005	"	90	4	20.2	26.5	0.65
$LiAlH_4$	0.013	Toluene	70	4	0	—	—

[a] Polymerization conditions: solvent, 270 ml.; monomer, 30 ml.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

TABLE II
Polymerization[a] of Methacrylonitrile with $LiAlR_3NPh_2$ and Related Compounds

Catalyst	Mole	Polymerization temp., °C.	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
$LiAlEt_2Bu(NPh_2)$	0.005	0	Trace	—	—	—
$LiAlEt_2Bu(NPh_2)$	0.005	25	Trace	—	—	—
$LiAlEt_2Bu(NPh_2)$	0.005	50	2.5	47.6	0.39	1.9×10^4
$LiAlEt_2Bu(NPh_2)$	0.005	70	9.1	59.8	1.02	6.9×10^4
$LiAlEt_2Bu(NPh_2)$	0.005	90	16.0	63.4	2.61	2.43×10^5
$NaAlEt_3(NPh_2)$	0.006	70	3.5	34.6	1.05	7.2×10^4
$NaAlEt_2(NPh_2)_2$	0.006	70	3.0	30.2	0.97	6.5×10^4
$NaAlEt(NPh_2)_3$	0.006	70	3.3	32.6	0.95	6.3×10^4

[a] Polymerization conditions: toluene, 270 ml.; monomer, 30 ml.; polymerization time, 4 hr.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

The total conversion and the solubility index increase with increasing polymerization temperature in the case of modified and of unmodified catalysts. These phenomena were observed with all the catalysts dealt with in the present study and seemed to be characteristic features in the stereospecific polymerization of methacrylonitrile. When $LiAlH_4$ was used as catalyst, no polymer was obtained under these polymerization conditions. $LiAlEt_3Bu$ has been found to be an effective catalyst for other polar monomers, such as methylmethacrylate,[12] but a low temperature such as −78°C. is necessary to form the stereospecific polymer. In the case of methacrylonitrile no polymer was obtained at such a low temperature, and the crystalline polymer was obtained only at moderately high temperatures.

The crystallinity of polymers obtained with this class of catalyst depends on the kind of catalyst and also on the polymerization conditions. These are summarized in Table III.

$LiZnEt_2Bu$, $Li_2ZnEt_2Bu_2$, and Related Catalysts

Table IV shows the results of the polymerization of methacrylonitrile with $LiZnEt_2Bu$ and related catalysts. Polymers were obtained in good yields, and about 40% of the resulting polymers were insoluble in acetone.

The results of polymerization with $Li_2ZnEt_2Bu_2$ and related catalysts are given in Table V. The total conversion and solubility index of the polymer were somewhat higher than those obtained with $LiZnEt_2Bu$ catalysts. With catalysts modified by diphenylamine the solubility index of the resulting polymer increased, although the total conversion was slightly lowered. It is very interesting that the crystallinities of the acetone-insoluble fractions from modified catalysts are much higher than those from unmodified ones; see Figure 1. This modification effect was also observed in $LiAlEt_3Bu$ and $NaAlEt_4$ catalysts (see also Table III).

Table VI shows the results of polymerization with "isolated catalyst." It is very interesting that these organolithium zinc complex catalysts gave polymer in comparatively good yield at 0°C., although the solubility index of the polymer was rather low. On the other hand, little or no polymer was obtained at 0°C. with $LiAlEt_3Bu$, $NaAlEt_4$, or the related catalysts (see Tables I and II).

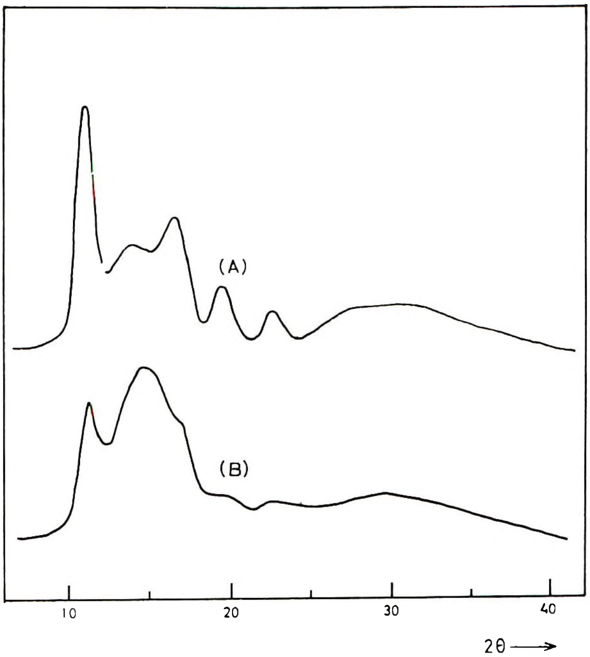


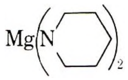
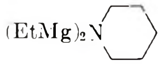
Fig. 1. X-ray diagram of acetone-insoluble fractions: catalysts (*A*) $LiZnEt_2NPh_2$ and (*B*) $LiZnEt_2Bu$.

Li[$Et_3AlOAlEt_2$] and Related Catalysts

Recent publications by Tani et al.[9,10] have disclosed the new types of stereospecific catalyst for isotactic polyacetaldehyde. These include, for example, Li[$Et_3AlOAlEt_2$] and Li[$Et_3AlN(Ph)AlEt_2$].

Attempts at the polymerization of methacrylonitrile with these catalysts at low temperatures were unsuccessful. No polymer was obtained with these catalysts at −78°C., at which temperature very highly crystalline polyacetaldehyde was formed in good yields. However, it has been found that the crystalline polymethacrylonitrile can be formed with these catalysts at high temperature, such as 90°C. Some results are listed in Table VII. It is of great interest that the acetone-insoluble fractions of the polymers obtained with these catalysts are highly crystalline. An x-ray diffraction diagram of the acetone-insoluble fraction obtained with Li[$Et_3AlN(Ph)AlEt_2$] is shown in Figure 2. The crystallinity is approxi-

TABLE III
Catalysts for Stereospecific Polymerization[a] of Methacrylonitrile

Catalyst	Catalytic activity	Solubility index of polymer	Intrinsic viscosity[b]	Crystallinity of acetone-insol. fraction
BuLi	+ + +	(+ + +)[c]	1.8	(−)
$LiAlEt_3Bu$[d]	+	+ +	1.6	+ + +
$LiAlEt_2BuNPh_2$[d]	+	+ + +	1.0	+ + + +
$NaAlEt_4$[d]	+	+	0.9	+ +
$NaAlEt_3NPh_2$	+	+	1.1	+ + + +
$NaAlEt_2(NPh_2)_2$	+	+	1.0	+ + + +
$NaAlEt(NPh_2)_3$	+	+	1.0	+ + + +
$LiZnEt_2Bu$	+ +	+ +	1.0	+
$LiZnEtBuNPh_2$[e]	+ +	+ +	1.3	+ + +
$Li_2ZnEt_2Bu_2$	+ + +	+ +	1.2	+
$Li_2ZnEtBu_2NPh_2$[d,e]	+ + +	+ + +	1.1	+ +
$EtMg[AlEt_4)$	+	+ + +	3.2	+ + +
$EtMg[AlEt_3NPh_2]$[f]	+ +	+ + +	3.0	+ + + +
$Mg[AlEt_4]_2$	+	+ + +	3.7	+ + +
$(EtMg)_2NPh$[e]	+ +	+ + + +	2.6	+
$EtMgNPh_2$	+ +	+ + +	2.0	+
$Mg(NPh_2)_2$	+ +	+ + +	2.0	+
$Li[Et_3AlOAlEt_2]$[d]	+	+ + +	1.2	+ + +
$Li[Et_3AlN(Ph)AlEt_2]$	+	+ + +	1.8	+ + + +
Et_2Mg[d,e]	+ +	+ + +	1.9	+ +
Et_2Mg[f]	+ + +	+ + +	5.1	+ + + +
Et_2Mg[g]	+ + +	+ + + +	10.0	+ +
Et_2Mg[h]	+ + +	+ + + +	3.9	+
	+ + +	+ + +	2.6	+
	+ + +	+ + +	2.8	+

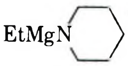
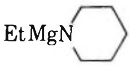
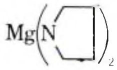
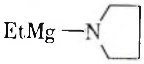
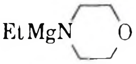
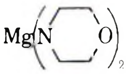
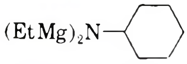
(continued)

mately comparable to those of the DMF-insoluble fractions obtained with $MgEt_2$ catalyst.

$EtMg[AlEt_4]$ and $Mg[AlEt_4]_2$

Formation of complexes between $MgEt_2$ and $AlEt_3$ has been reported by Ziegler,[13] and structures with "electron-deficient" or "single-electron" bonds have also been discussed. Unlike $MgEt_2$, these complexes are soluble in hydrocarbons. Table VIII shows some results of polymerization with these catalysts. The solubility index and molecular weight of the polymer obtained in toluene was much higher than those obtained in heptane. This phenomenon was also observed with $MgEt_2$ catalyst[6] and $LiAlEt_3Bu$ catalyst (see Table I).

TABLE III (*continued*)

Catalyst	Catalytic activity	Solubility index of polymer	Intrinsic viscosity[b]	Crystallinity of acetone-insol. fraction
 [f]	++++	++++	4.5	+
 [g]	++++	++++	5.7	+
$MgEt(NEt_2)$	++	+++	1.9	+
$Mg(NEt_2)_2$	++	+++	2.2	+
	++++	++++	1.6	+
	++++	++++	1.7	+
	++	+++	1.8	++
	++	+++	1.9	++
	+++	+++	2.2	+

[a] Polymerization conditions: toluene, 270 ml.; monomer, 30 ml., polymerization temp., 70°C.

[b] Approximate values determined in $Cl_2CHCOOH$ at 30°C.

[c] Insoluble in acetone (extreme swelling) but very soluble in dimethylformamide.

[d] Polymerization temp., 90°C.

[e] Heterogeneous catalyst.

[f] Solvent: anisole.

[g] Solvent: dioxane.

[h] Solvent: tetrahydrofuran.

TABLE IV

Polymerization[a] of Methacrylonitrile with $LiZnR_3$ and Related Compounds

Catalyst	Polymerization temp., °C.	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
$LiZnEt_2Bu$	70	48.1	36.7	1.03	7.1×10^4
$LiZnEt_2Bu$	90	63.9	44.0	1.18	8.4×10^4
$LiZnEtBu(NPh_2)$	70	44.5	41.8	1.32	9.6×10^4
$LiZnEtBu(NPh_2)$	90	34.3	40.2	1.91	1.62×10^5

[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.005 mole; monomer, 30 ml.; polymerization time, 4 hr.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

TABLE V
Polymerization[a] of Methacrylonitrile with Li_2ZnR_4 and Related Compounds

Catalyst	Polymerization temp., °C.	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
$Li_2ZnEt_2Bu_2$	90	76.3	43.0	1.73	1.40×10^5
$Li_2ZnEt_2Bu_2$	70	64.7	38.4	1.16	8.2×10^4
$Li_2ZnEtBu_2(NPh_2)$	70	68.7	54.2	1.14	8.0×10^4
$Li_2ZnEtBu_2(NPh_2)$	90	65.6	49.3	2.22	1.96×10^5

[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.005 mole; monomer, 30 ml.; polymerization time, 4 hr.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

TABLE VI
Polymerization[a] of Methacrylonitrile with "Isolated" $LiZnEtBu(NPh_2)$ and $Li_2ZnBu_2(NPh_2)_2$

Catalyst	Temp., °C.	Conversion, %	Index of solubility, %
$LiZnEtBu(NPh_2)$	70	67.6	48.4
$LiZnEtBu(NPh_2)$	0	59.0	15.5
$LiZnEtBu(NPh_2)$	−78	0	—
$Li_2ZnBu_2(NPh_2)_2$	70	69.0	28.5
$Li_2ZnBu_2(NPh_2)_2$	0	75.3	27.2

[a] Polymerization conditions: toluene, 50 ml.; catalyst, 0.7 g.; monomer, 20 ml., polymerization time, 4 hr.

TABLE VII
Polymerization[a] of Methacrylonitrile with $Li[Et_3AlOAlEt_2]$ and $Li[Et_3AlN(Ph)AlEt_2]$

Catalyst	Polymerization temp., °C.	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
$Li[Et_3AlOAlEt_2]$	90	15.3	65.7	1.18	8.4×10^4
$Li[Et_2(Ph_2N)AlOAlEt_2]$	90	10.0	30.7	1.75	1.43×10^5
$Li[Et_3AlN(Ph)AlEt_2]$	70	11.8	59.7	1.80	1.50×10^5

[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.005 mole; monomer, 30 ml.; polymerization time, 4 hr.

[b] Determined at 30°C. for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

TABLE VIII

Polymerization[a] of Methacrylonitrile with $EtMg[AlEt_4]$ and $Mg[AlEt]_2$

Catalyst	Solvent	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
$EtMg[AlEt_4]$	Toluene	18.4	67.9	5.62	6.74×10^5
$EtMg[AlEt_4]$	Heptane	18.8	24.6	2.50	2.30×10^5
$Mg[AlEt_4]_2$	Toluene	26.2	63.0	5.17	5.96×10^5
$Mg[AlEt_4]_2$	Heptane	25.5	16.2	2.20	1.94×10^5

[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.006 mole; monomer, 30 ml.; polymerization temperature, 70°C.; polymerization time, 7 hr.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

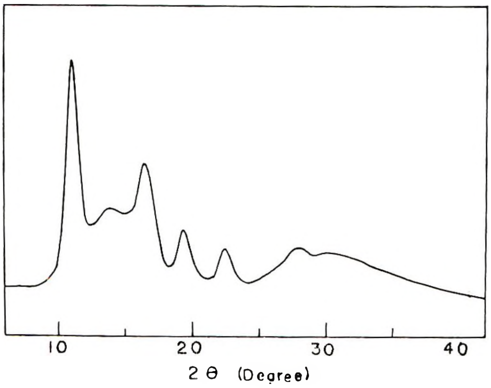


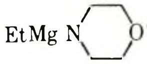
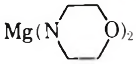
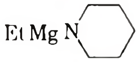
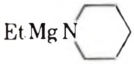
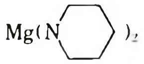
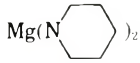
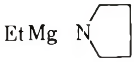
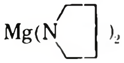
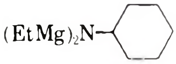
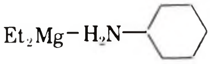
Fig. 2. X-ray diagram of acetone-insoluble fraction obtained with $Li[Et_3AlN(Ph)AlEt_2]$.

Organomagnesium Compounds with Mg–N Bond

Some results of polymerization with organomagnesium catalysts containing an Mg–N bond are summarized in Table IX. These catalysts were found to be much more effective for the polymerization of methacrylonitrile than $MgEt_2$ catalyst. Especially the catalysts with piperidine or pyrrolidine rings were shown to be strikingly effective for stereospecific polymerization, from the high conversions and high solubility indexes of the polymers. It should be noted, however, that the crystallinity of the resulting acetone-insoluble fraction of the polymers is not so high. The effect of the polymerization temperatures on polymerization with ethylpiperidinomagnesium is shown in Table X. Total conversion, molecular weight, and solubility index increased with increasing polymerization temperature. This temperature effect on polymerization is very interesting. This was observed with all the catalysts dealt with in the present study.

The effects of the solvent on the polymerization with this catalyst were

TABLE IX
Polymerization[a] of Methacrylonitrile with Organomagnesium Catalysts Containing Mg–N Bond

Catalyst	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
$EtMgNPh_2$[d]	51.9	60.7	2.00	1.70×10^6
$Mg(NPh_2)_2$[d]	41.3	61.7	2.35	2.13×10^5
$EtMgNEt_2$[d]	72.9	66.4	1.91	1.62×10^5
$Mg(NEt_2)_2$[d]	72.5	65.5	2.19	1.93×10^5
[d]	41.5	68.2	1.80	1.50×10^5
[d]	48.0	68.9	1.88	1.58×10^5
	76.8	68.5	2.62	7.44×10^5
[d]	76.2	71.5	3.00	2.92×10^5
	81.1	70.7	2.58	2.40×10^5
[d]	78.4	69.1	2.77	2.63×10^5
[d]	89.2	76.2	1.71	1.40×10^5
[d]	93.0	73.3	1.64	1.32×10^5
	53.2	74.2	2.22	1.97×10^5
 (1:1)	49.9	71.1	1.91	1.62×10^5
$(EtMg)_2NPh$	33.9	72.5	2.55	2.35×10^5
$(EtMg)_2NPh$	42.4	68.7	1.88	1.58×10^5
$Et_2Mg–H_2NPh$[d] (1:1)	20.9	77.5	3.07	3.00×10^5

---

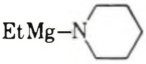
[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.006 mole; monomer, 30 ml.; polymerization temperature, 70°C.; polymerization time, 4 hr.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

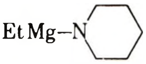
[d] "*In situ*" catalyst.

examined; the results are shown in Table XI. Ethers, such as anisole and dioxane, are more efficient solvents than hydrocarbons for stereospecific polymerization. The same phenomenon was also observed with $MgEt_2$ catalyst.[6] Natta and Dall'Asta[1] have described how, to obtain stereoregular polymethacrylonitrile, it is necessary to use solvents that essentially contain no electron-donor atoms in the molecule. However, in our

TABLE X
Effect of Polymerization Temperatures on the Polymerization[a] of Methacrylonitrile Catalyzed by 

Polymerization temp., °C.	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
90	81.4	68.2	3.00	2.92×10^5
70	71.5	62.0	2.57	2.39×10^5
50	60.6	48.4	2.07	1.78×10^5
0	54.8	43.8	1.70	1.39×10^5

[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.006 mole; monomer, 30 ml.: polymerization time, 4 hr.
[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.
[c] Calculated for acetone-insoluble fractions.

TABLE XI
Effect of Solvents on the Polymerization[a] of Methacrylonitrile Catalyzed by 

Solvent	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
Toluene	77.7	59.0	2.85	2.74×10^5
Anisole	93.0	80.7	4.56	5.10×10^5
Dioxane	95.4	80.6	5.70	6.87×10^5

[a] Polymerization conditions: toluene, 270 ml.; catalyst, 0.006 mole; monomer, 36 ml.; polymerization temperature, 70°C.; polymerization time, 4 hr.
[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.
[c] Calculated for acetone-insoluble fractions.

experiments strong electron-donor solvents, such as anisole or dioxane, did not disturb the stereospecific polymerization but the polymers obtained in these solvents had higher solubility indexes (see Table XI).

BuLi

Some of the results of the polymerization of methacrylonitrile with BuLi under various polymerization temperatures are shown in Table XII. Butyllithium has high catalytic activity over a wide range of polymerization temperatures. It is quite notable that the polymers obtained with it were tremendously swollen by acetone extraction with a Soxhlet extractor, but they were very soluble in DMF and gave completely amorphous x-ray diagrams.

TABLE XII
Polymerization[a] of Methacrylonitrile with BuLi

Catalysts	Polymerization temp., °C.	Conversion, %	Index solubility,[b] %	Intrinsic viscosity[c]	Mol. wt.[d]
BuLi	−78	52.0	65.0	1.82	1.52×10^5
BuLi	−30	63.3	83.8	2.19	1.93×10^5
BuLi	0	33.0	70.4	2.16	1.90×10^5
BuLi	Room temp.	82.0	75.7	2.03	1.75×10^5
BuLi	70	71.3	70.5	1.94	1.65×10^5

[a] Polymerization conditions: toluene, 60 ml.; monomer, 20 ml.; catalyst, 0.0016 mole; polymerization time, 3.5 hr.

[b] Polymers were tremendously swollen by acetone extraction with a Soxhlet extractor and were very soluble in DMF. These polymers were completely amorphous by x-ray diagram.

[c] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[d] Calculated for acetone-insoluble fractions.

Effect of Additives to $MgEt_2$

The effects of some additives to $MgEt_2$ were examined and are summarized in Table XIII. All the additives reduced the catalytic activity of the $MgEt_2$ catalyst.

TABLE XIII
Effect of Some Additives to $MgEt_2$ on the Polymerization[a] of Methacrylonitrile

Catalyst	Added compound	Add. compd. to Et_2Mg, mole ratio	Conversion, %	Index of solubility, %	Intrinsic viscosity[b]	Mol. wt.[c]
Et_2Mg	Acetylacetone	0.5	29.3	72.4	1.99	1.70×10^5
Et_2Mg	Acetylacetone	1.0	11.6	68.6	2.16	1.90×10^5
Et_2Mg	$PhCH_2OH$	1.0	8.3	68.9	1.91	1.62×10^5
Et_2Mg	$PhCH_2OH$	2.0	10.7	61.0	1.69	1.38×10^5
Et_2Mg	*n*-Butylaldehyde	1.0	33.8	71.6	2.33	2.09×10^5
Et_2Mg	*n*-Butylaldehyde	2.0	18.8	65.7	3.36	3.40×10^5
Et_2Mg	Dimethylformamide	1.0	18.8	65.7	2.00	1.72×10^5
Et_2Mg	Dimethylformamide	2.0	2.5	56.7	3.46	3.54×10^5
Et_2Mg	Dimethyl sulfoxide	1.0	28.6	54.1	1.34	9.8×10^4
Et_2Mg	Dimethyl sulfoxide	2.0	30.4	42.8	1.16	7.3×10^4
Et_2Mg	—	—	42.5	69.8	1.86	1.56×10^5

[a] Polymerization conditions: toluene, 270 ml.; Et_2Mg, 0.006 mole; monomer, 30 ml.; polymerization temperature, 70°C.; polymerization time, 4 hr.

[b] Determined at 30°C. in $Cl_2CHCOOH$ for acetone-insoluble fractions.

[c] Calculated for acetone-insoluble fractions.

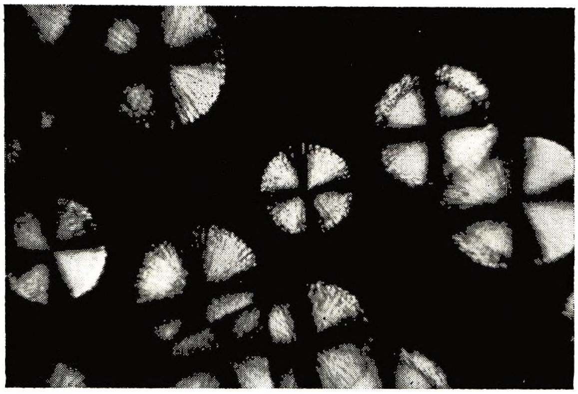
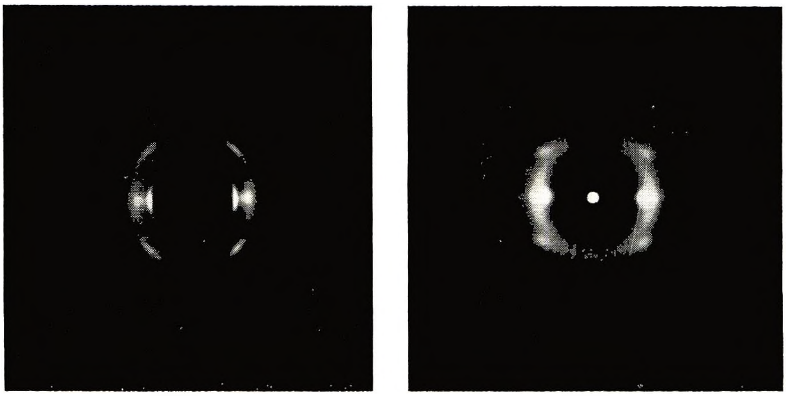


Fig. 3. Spherulite of crystalline polymethacrylonitrile.



Type I Type II

Fig. 4. X-ray fiber diagrams of oriented crystalline polymethacrylonitrile: (left) type I, (right) type II.

For a comprehensive survey of the stereospecific activities of the catalysts some typical catalysts and some features of the resulting crystalline polymers are summarized in Table III.

A gradual removal of the solvent from the films that were cast from CF_3-COOH solutions of the acetone-insoluble fractions of polymethacrylonitrile easily formed spherulites. Figure 3 shows one of the examples of the spherulite of the crystalline polymethacrylonitrile. Figure 4 shows the x-ray fiber diagrams for the oriented sample of the crystalline polymethacrylonitrile. Two types of crystalline modifications were found, and a 4_1 helix structure was proposed for type II of the structures.[4] Figure 5 shows the infrared spectra of the crystalline polymethacrylonitrile and the conventional polymer obtained with a radical initiator. Crystalline-sensitive bands are observed at 1370, 1192, 910, 882, 873, 839, 711, and 690 cm.$^{-1}$ for the crystalline polymer.

The infrared spectra under polarized light for the stretched film of the crystalline polymer showed clearcut infrared dichroism, as shown in Figure 6. Detailed structural studies of the polymer are in progress.

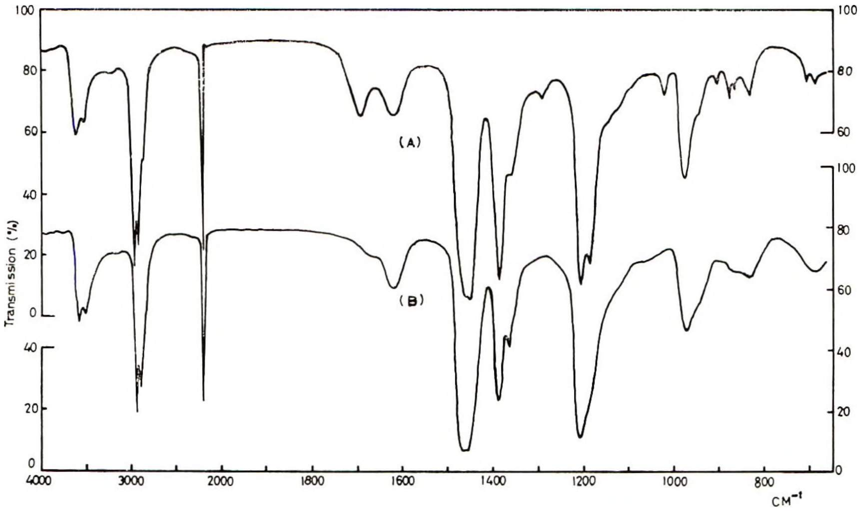


Fig. 5. Infrared spectra of polymethacrylonitrile: (*A*) crystalline and (*B*) conventional polymer obtained with radical initiator.

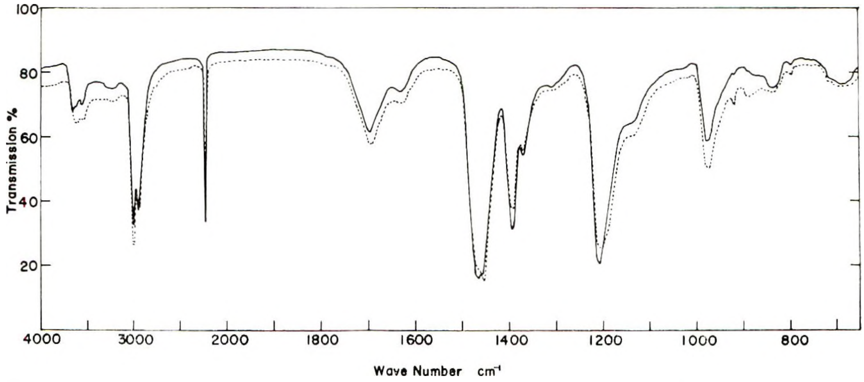


Fig. 6. Polarization spectra of highly crystalline polymethacrylonitrile polarized (- - -) parallel and (——) perpendicular to the direction of stretch.

DISCUSSION

Viscosity–Molecular Weight Relationship

The viscosity–molecular weight relationships available for polymethacrylonitrile are $\overline{\mathrm{DP}}_n = 0.92[\eta]^{1.81}$ for the acetone solution, as given by Mesrobian and Fuhrman,[14] and $[\eta] = 3.06 \times 10^{-3} M^{0.503}$ for the DMF solution, as given by Overberger et al.[5] These relationships are not applicable to the crystalline polymers because of the insolubility of the crystalline polymers in these solvents. In another paper[15] we gave the following relationship for the crystalline polymethacrylonitrile in $Cl_2CHCOOH$ solution:

$$[\eta] = 3.24 \times 10^{-3} M^{0.520} \quad \text{(in Cl}_2\text{CHCOOH at 30°C.)}$$

This was determined by using the DMF-soluble fractions for a cross-comparison with the data obtained in DMF and in $Cl_2CHCOOH$, combined with Overberger's relationship (in DMF), which was also determined by the same cross-comparison method from Mesrobian's relationship (in acetone). Therefore, the reliability of our relationship, which involves the double derivation from Mesrobian's relationship via Overberger's, is not very high. So in the present study we again conveniently determined the viscosity–molecular weight relationship for the crystalline polymer by a cross-comparison method, using Hayashi's equation, which was determined in a complete solution study of polymethacrylonitrile in DMF by means of the Archibald ultracentrifugal method. Although the problem is raised whether the highly crystalline material which is insoluble in DMF will exhibit chain dimensions in $Cl_2CHCOOH$ that are identical with those of a much less crystalline fraction soluble in DMF, the relationship is useful, at present, in developing this investigation, for all attempts at a complete solution study with our crystalline polymer in $Cl_2CHCOOH$ have been unsuccessful, because the strongly acidic, powerful solvent spoils the equipment.

Polymerization

One of the most considerable developments in stereospecific polymerization has been the utilization of the organometallic compounds. A case in point is methacrylonitrile.

It seems very surprising that the conversions, intrinsic viscosities, and solubility indexes increase with increasing polymerization temperature with all the catalysts used in the present investigation. The reason for these temperature effects[6] on the stereospecific polymerization of methacrylonitrile is obscure at present.

Polymerization with these stereospecific catalysts probably proceeds by a so-called coordinated anionic mechanism, as in the case of polymerization with $MgEt_2$ catalyst.[1,6] Coordination of the monomer to the catalyst was shown by the simultaneous appearance of a deep red color, which was considered to be a result of the formation of a charge-transfer complex between the catalyst and the nitrile group of the monomer.

The explanation of the coordinated anionic mechanism has been that the monomer first coordinates to the active site of the catalyst and then inserts itself in the propagating chain end. The temperature effect of the polymerization is probably due to the requirement of a rather high activation energy for the insertion of the monomer, which is strongly coordinated to the metal through the nitrile group.

In case of $LiZnR_3$, Li_2ZnR_4, $LiAlR_4$, and related catalysts more than 50% of the resulting polymers are extractable with acetone.

A question may arise whether free alkyllithium, which is capable of initiating a polymerization to amorphous polymer, is present, from the following equilibriums in these catalytic systems:

$$\mathrm{LiAlR_4} \rightleftarrows \mathrm{LiR} + \mathrm{AlR_3}$$

$$\mathrm{LiZnR_3} \rightleftarrows \mathrm{LiR} + \mathrm{ZnEt_2}$$

$$\mathrm{Li_2ZnR_4} \rightleftarrows \mathrm{LiR} + \mathrm{LiZnR_3} \rightleftarrows \mathrm{2LiR} + \mathrm{ZnR_2}$$

However, when polymerization was carried out at low temperatures, i.e. −78°C., no polymer was obtained, whereas butyllithium initiates polymerization at that low temperature (see Table XII).

Accordingly, it is concluded that free alkyllithium is not present in the catalytic system, at least at such low temperatures as −78°C. The fact that the value of the solubility index increased with polymerization temperature, along with the fact that the acetone-insoluble fraction obtained with the organolithium zinc complex is crystalline, strongly suggests that free alkyllithium is not present or, if any, is negligible in the catalytic system even at higher temperatures. If a significant amount of free alkyllithium is liberated through equilibrium at higher temperature, the solubility index must decrease with temperature, or the crystallinity of the acetone-insoluble fraction must be reduced, because alkyllithium has a high catalytic activity over a wide range of polymerization temperatures, and the polymers obtained by this catalyst are completely amorphous.

Another piece of experimental evidence which shows that the formation of the acetone-soluble amorphous polymer is not due to the presence of free alkyllithium in the catalytic system is given in the results of "isolated catalyst," which formed the amorphous polymer in a ratio comparable to that of *in situ* catalyst, because the "isolated catalyst" was obtained as a white powder, from which free alkyllithium was completely removed by washing with *n*-hexane.

The reason why all the catalysts dealt with in the present investigation can form both crystalline and amorphous polymers is not clear. Probably there are at least two kinds of catalytic species, one being the species that induces stereospecific polymerization by a coordinated anionic mechanism and another being the one from which amorphous polymers are formed, probably by a conventional anionic mechanism. It seems that, for example, the aggregation of the catalysts may play an important role in the formation of stereospecific catalytic species. More detailed discussions are beyond the scope of our present study.

Another interesting feature of the stereospecific polymerization of methacrylonitrile is that highly crystalline polymers are formed by completely homogeneous catalysts. These include $\mathrm{LiAlR_4}$, $\mathrm{LiZnR_3}$, $\mathrm{Li_2ZnR_4}$, $\mathrm{Li[Et_3AlOAlEt_2]}$, $\mathrm{Li[Et_3AlN(Ph)AlEt_2]}$, $\mathrm{EtMg[AlEt_4]}$, and $\mathrm{Mg[AlEt_4]_2}$. We think it is a very rare case in which stereospecific polymerization occurs in homogeneous phase at such a high temperature.

As shown in Table XIII, additives to $\mathrm{MgEt_2}$ gave only reductions of the catalytic activities of the catalysts, while the value of the solubility index of the resulting polymer remained almost constant. This fact suggests that the Mg–O bond, different from the Mg–N bond, has no catalytic activity in the polymerization.

Infrared spectra for all the polymers obtained by these organometallic catalysts show the presence of a carbonyl group in the polymer. The formation of the carbonyl group has been briefly discussed in another paper[15] but is not well documented so far. Careful studies of this problem have recently been made in this laboratory, and it has been elucidated that imino anion formed by a monomolecular termination of the propagating chain end in a cyclization reaction successively attacked the vicinal pendant nitrile groups in the polymer chain so as to form the conjugated cyclic imines, which were hydrolyzed to acid amides during catalyst decomposition with acidic methanol. The results of this extensive study will be reported in a future publication.

Detailed structural studies of the crystalline polymethacrylonitrile will be reported in future publications.

The authors wish to express their appreciation to F. Ide, K. Nakatsuka, N. Yamada, and T. Isoshima for their continued encouragement and interest in this work. The authors are also indebted to H. Kado and Miss A. Furuki, who performed much of the experimental work, and to H. Yoshiyama for the x-ray diffraction measurements.

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Résumé

Certaines classes de catalyseurs organométalliques qui induisent la polymérisation stéréospécifique du méthacrylonitrile ont été trouvées. Celles-ci incluent des composés aluminium-organolithiens du type $LiAlR_4$, $Li[R_3AlOAlR_2]$, $Li[R_3AlN(R)AlR_2]$, des composés aluminium-organosodés du type $NaAlR_4$, des composés zinc-organolithiens du type $LiZnR_3$, Li_2ZnR_4, des composés aluminium-organomagnésiens du type RMg-

$[\mathrm{AlR_4}]$, $\mathrm{Mg[AlR_4]_2}$ et et des composés organomagnésiens contenant des liens Mg–N tels que Mg(N )$_2$, EtMgN , et leurs composés voisins. Un des phénomènes de la polymérisation avec ces catalyseurs est la formation de polymères cristallins à des températures modérément élevées. La conversion totale, l'indice de solubilité, et le poids moléculaire du polymère croissen avec une augmentation de la température de polymérisation tel qu'on a observé dans le cas de la polymérisation au moyen d'un catalyseur de diéthyle magnésium. Les catalyseurs avec des liens Mg–N sont hautement efficaces pour la polymérisation stéréospécifique Les fractions de polymères insolubles dan l'acétone donnent des diagrammes de rayons-X identiques à celui du polymère cristallin obtenu par le diéthyle magnésium. Ceci indique que les polymères cristallins insolubles dans l'acétone obtenus au moyen de ces catalyseurs ont une structure isotactique. La relation viscosité–poids moléculaire pour le polymère cristallin a été déterminée de façon conventionnelle dans l'acide dichloroacétique à 30°C; $[\eta] = 2.27 \times 10^{-4} M^{0.754}$.

Zusammenfassung

Einige Gruppen organometallischer Katalysatoren, welche die stereospezifische Polymerisation von Methacrylnitril induzieren, wurden gefunden. Dazu gehören lithium-aluminium-organische Verbindungen vom Typ $\mathrm{LiAlR_4}$, $\mathrm{Li[R_3AlOAlR_2]}$, $\mathrm{Li[R_3AlN(R)\text{-}AlR_2]}$, natrium-aluminium-organische Verbindungen vom Typ $\mathrm{NaAlR_4}$, lithium-zink-organische Verbindungen vom Typ $\mathrm{LiZnR_3}$, $\mathrm{Li_2ZnR_4}$, magnesium-aluminium-organische Verbindungen vom Typ RMg $[\mathrm{AlR_4}]$, $\mathrm{Mg[AlR_4]_2}$ und magnesium-organische Verbindungen mit einer Mg–N-Bindung wie Mg(N )$_2$, EtMgN  sowie verwandte Verbindungen. Eines der Merkmale der Polymerisation mit diesen Katalysatoren ist die Bildung kristalliner Polymerer bei mässig hohen Temperaturen. Gesamtumsatz, Löslichkeitsindex und Molekulargewicht des Polymeren nahm, wie im Falle der Polymerisation mit Diäthylmagnesium als Katalysator, mit Erhöhung der Polymerisationstemperatur zu. Katalysatoren mit einer Mg–N -Bindung zeigten sich als hochwirksam für die stereospezifische Polymerisation. Die acetonunlöslichen Fraktionen der Polymeren lieferten die gleichen Röntgendiagramme wie das mit Diäthylmagnesium erhaltene kristalline Polymere. Das zeigt, dass die mit diesen Katalysatoren gebildeten aceton-unlöslichen kristallinen Polymeren eine isotaktische Struktur besitzen. Die Viskositäts–Molekulargewichtsbeziehung für das kristalline Polymere konnte in $\mathrm{Cl_2CHCOOH}$ bei 30°C gut bestimmt werden; $[\eta] = 2{,}27 \times 10^{-4} M^{0{,}754}$.

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Cyclopolycondensations. VII. Preparation of Aromatic Poly(ureido Acids) by the Low-Temperature Solution Polymerization and Cyclodehydration to Fully Aromatic Polyquinazolinediones*

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Synopsis

Fully aromatic polyquinazolinediones (IV) of high molecular weight were obtained by thermal cyclodehydration of aromatic poly(uredio acids) (III) prepared by the polyaddition reaction of 4,4′-diaminobiphenyl-3,3′-dicarboxylic acid (I) with aromatic diisocyanates (II). From the kinetic study of reactions of model systems (anthranilic acid with phenyl isocyanate) in the presence of a variety of basic catalysts, it was established that tertiary amines had the highest catalytic activity for the formation of ureido linkage. The optimum polymerization conditions were determined by the study of reaction variables such as monomer concentration, polymerization temperature, monomer ratio, and catalyst concentration. The effect of polarity and purity of organic solvents and reactants was also studied.

INTRODUCTION

The demand for thermally stable polymers has generated a great deal of research on the syntheses of new polymers of aromatic or pseudo-aromatic systems. Previous publications[1-4] from this laboratory described the syntheses of new fully aromatic polymers containing quinazolinedione structure by melt polymerization and solution polymerization in polyphosphoric acid.

In the present paper, the authors wish to report the details on the study of low-temperature solution polymerization of aromatic poly(ureido acids) (III) in organic solvents and the fully aromatic polyquinazolinediones (IV) by thermal cyclodehydration of an open chain precursor. The general reaction scheme for the formation of polyquinazolinedione is shown in eqs. (1) and (2), where Ar represents an aromatic nucleus.

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For part VI of this series see Yoda et al.[1]

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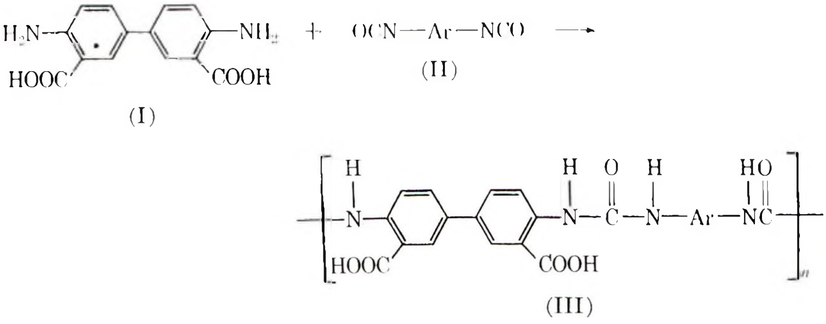
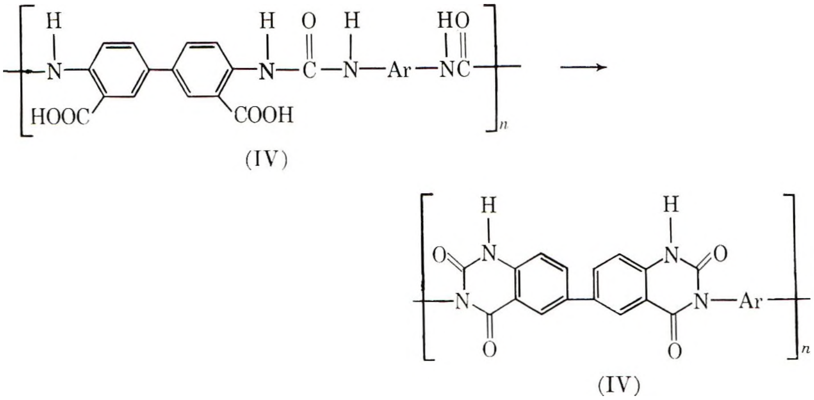


(1)



(2)

The characteristic features of cyclopolycondensation for this polymer involve the formation of a soluble, open-chain precursor (III) of high molecular weight by a polyaddition reaction, followed by thermal cyclodehydration along the polymer chain to obtain insoluble polyquinazolinedione (IV) of outstanding thermal stability.

The present paper gives a detailed account of the study on reaction variables of low-temperature solution polymerization, such as catalyst concentration, reaction temperature, and monomer concentration as well as purity of reactants and solvent. Furthermore, the model reaction of anthranilic acid with phenyl isocyanate was studied, and the rate of reaction was determined with a variety of basic catalysts.

EXPERIMENTAL

Materials

4,4′-Diaminobiphenyl-3,3′-dicarboxylic acid(I)[3] was prepared from *o*-nitrobenzoic acid by benzidine rearrangement. The monomer was carefully purified by recrystallization followed by vigorous vacuum drying. Commercially available aromatic diisocyanates were subjected to recrystallization from *n*-hexane and vacuum distillation before use. *N*-Methyl-2-pyrrolidone (NMP), tetramethylenesulfone (TMS), *N*,*N*′-dimethylacetamide (DMAc), *N*,*N*′-dimethylformamide (DMF), and hexamethylphosphoramide (HMPA) were dried with calcium hydride and distilled under reduced pressure in the presence of phosphorus pentoxide. Pyridine was dried with potassium hydroxide and distilled.

Polymerization

The general procedure for the preparation of a poly(ureido acid) is as follows. A 100 ml. flask fitted with a Teflon-sealed stirrer, nitrogen inlet, drying tube, and stopper was carefully flamed to remove traces of water on the glass walls and allowed to cool under a stream of dry nitrogen. A calculated amount of 4,4′-diaminobiphenyl-3,3′-dicarboxylic acid was dissolved in specified solvent together with a certain amount of basic catalysts and the polymerization system maintained at specified reaction temperature. An equimolar amount of aromatic diisocyanate was added to the flask through a dried powder funnel. When the solution became extremely viscous, additional solvent was added to give efficient stirring of the polymerization system.

Model Reactions

***N*-(Phenylcarbamoyl)anthranilic Acid.** Each model reaction is carried out at constant temperature in a thermostat with mechanical stirring. The rate of reaction of anthranilic acid with phenyl isocyanate in the presence of various catalysts was determined by the analysis for unreacted phenyl isocyanate as described in the following procedure. To a solution of 1.37 g. (0.01 mole) of anthranilic acid and 0.0005 mole catalyst in 50 ml. of NMP was added 50 ml. of a solution of 1.19 g. (0.01 mole) of phenyl isocyanate in NMP. Stirring was started and aliquots of the solution pipetted at constant intervals into a 100 ml. Erlenmeyer flask. A 10 ml. portion of 0.2*N* *n*-butylamine solution in NMP containing 50 ml. of water and a drop of phenolphthalein indicator was added to the flask; then the excess *n*-butylamine was titrated with 0.1*N* aqueous hydrochloric acid solution. The phenyl isocyanate remaining is calculated by the amount of hydrochloric acid consumed by the titration. The *N*-(phenylcarbamoyl)anthranilic acid thus obtained had a melting point at 184–185°C. (lit.,[5] m.p. 181°C.).

ANAL. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.63%; H, 4.72%; N, 10.93%. Found: C, 65.70%; H, 4.74%; N, 10.90%.

3-Phenyl-2,4(1H,3H)-quinazolinedione. A 3.0 g. portion (0.01 mole) of *N*-(phenylcarbamoyl)anthranilic acid was dissolved in 30 ml. of ethanol, and 30 ml. of concentrated hydrochloric acid was added with mechanical stirring. The reaction mixture was heated at 110°C. for 2 hr. under reflux. After the solution was cooled to room temperature, the product was precipitated out and filtered. Recrystallizations from ethanol afforded colorless needles in 88% yield; m.p. 280–281°C. (lit.,[6] m.p. 280°C.).

ANAL. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58%; H, 4.23%; N, 11.76%. Found: C, 70.36%; H, 4.17%; N, 11.45%.

RESULTS AND DISCUSSION

Effect of Basic Catalysts in Polymerization

The rate of polymerization of 4,4′-diaminobiphenyl-3,3′-dicarboxylic acid (BDC) with aromatic diisocyanates in the absence of catalyst is extremely slow; only oligomer is obtained under the polymerization conditions described for low-temperature solution polymerization owing to the low rate of the polyaddition reaction. The low rate of addition of amino group to isocyanate is attributed to the anchimeric effect of the carboxyl *ortho* substituent, in which the basicity of the amino group is decreased by the electron-withdrawing effect of the carbonyl group, and accordingly, the reactivity to isocyanate of the active hydrogen of the amino group diminishes considerably. In order to increase the rate of reaction, the catalytic effect of organic bases such as pyridine, triethylamine, triethylenediamine, (1,4-diazabicyclo[2.2.2]octane), and di(n-butyl)tin dilaurate was studied, and the rate of reaction of anthranilic acid with phenyl iso-

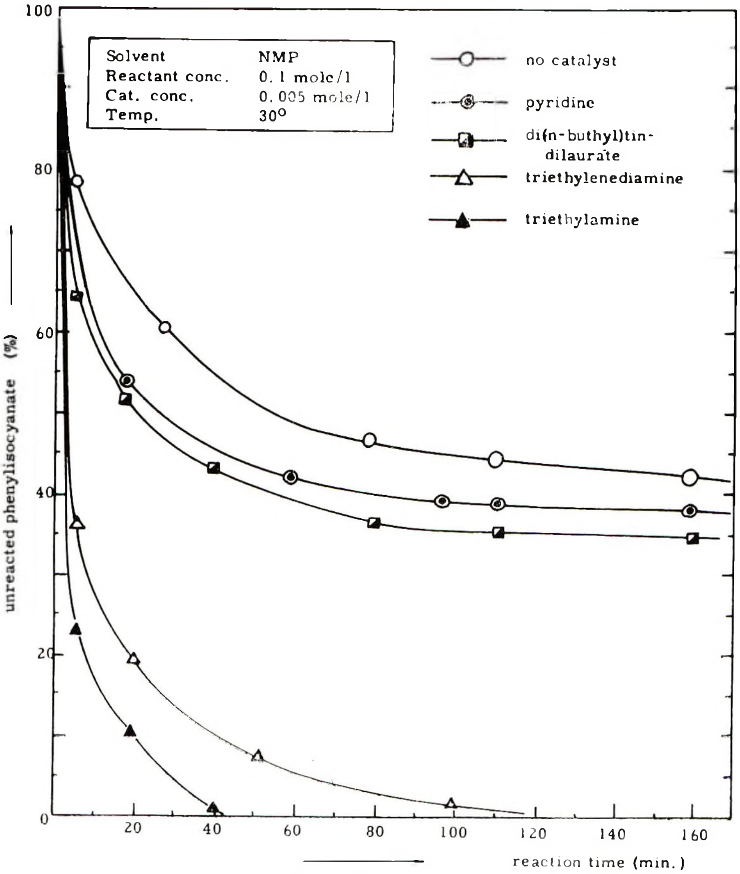


Fig. 1. Reaction of phenyl isocyanate and anthranilic acid in the presence of various catalysts.

cyanate was determined by analysis for unreacted phenyl isocyanate. The experimental results are described in Figure 1. The rate constant was calculated from the initial rate of reaction, which deviates slightly from the second-order reaction as shown in Table I. A close correlation between basicity of catalyst and the rate of reaction is observed, and the rate of reaction and the pK_a values of catalysts are summarized in Table I.

TABLE I
Reaction Rates of Anthranilic Acid and Phenyl Isocyanate

Catalyst	Reaction rate, l./mole-sec. × 10^2	pK_a[a]
None	0.86	—
Pyridine	1.25	5.19
Di(*n*-butyl)tin dilaurate	1.70	—
Triethylenediamine	11.1	8.7
Triethylamine	18.7	10.7

[a] In H_2O.[7]

The following conclusions are drawn from the experimental results obtained in the study of model reactions. (*1*) The reaction of anthranilic acid with phenyl isocyanate is accelerated remarkably in the presence of basic catalyst, especially tertiary amines. The catalytic activity increases with increasing basicity of basic catalyst. (*2*) Organotin compounds widely used for urethane formation by the reaction of alcohol with isocyanate have no appreciable catalytic effect on the reaction of aromatic *o*-aminocarboxylic acid derivatives with aromatic isocyanate.

Low-Temperature Solution Polymerizations

From the study of model reactions, tertiary amine is expected to be effective as a catalyst for the polymerization of BDC with aromatic diisocyanates. The optimum reaction conditions were determined in the presence of basic catalysts, and the effects of catalyst concentration, monomer ratio, and reaction temperature on the degree of polymerization as well as purity of reactant and solvent effect were studied. The polymerization of BDC and its dihydrochloride dihydrate with 4,4′-diisocyanatodiphenyl ether was carried out at a BDC/diisocyanatodiphenyl ether reactant ratio of 1/1 in NMP at 25°C. for 2 hr. The initial and final monomer concentrations were 8 and 3%, respectively, and 2 moles (based on 1 mole of monomer) of triethylamine was added as a catalyst. The effect of monomer composition on the inherent viscosity of the polymer was studied as described below. $BDC \cdot 2HCl \cdot 2H_2O$ affords a polymer with η_{inh} (25°C., 0.5% in concentrated H_2SO_4) = 0.16. BDC contaminated with a trace of hydrogen chloride yields a polymer with η_{inh} = 0.24. In both cases the polymer solution became opaque in the course of polymerization. When purified BDC is employed, polymer having an inherent viscosity of 0.50 was obtained. These data indicate that BDC must be

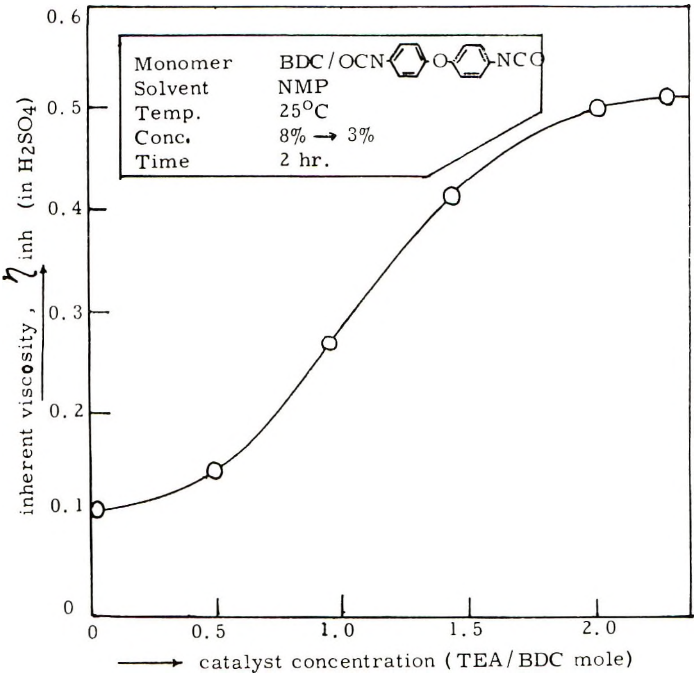


Fig. 2. Effect of catalyst concentration on the degree of polymerization.

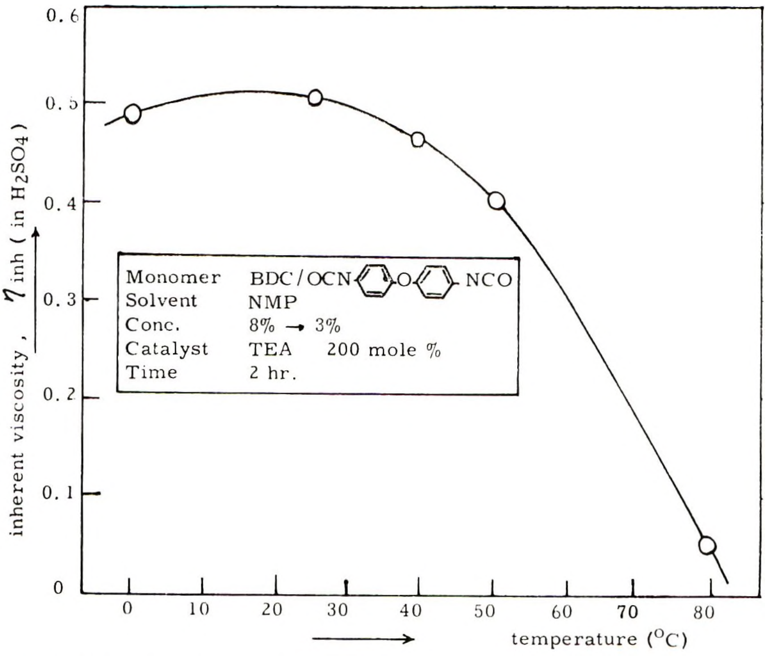


Fig. 3. Effect of polymerization temperature on the degree of polymerization.

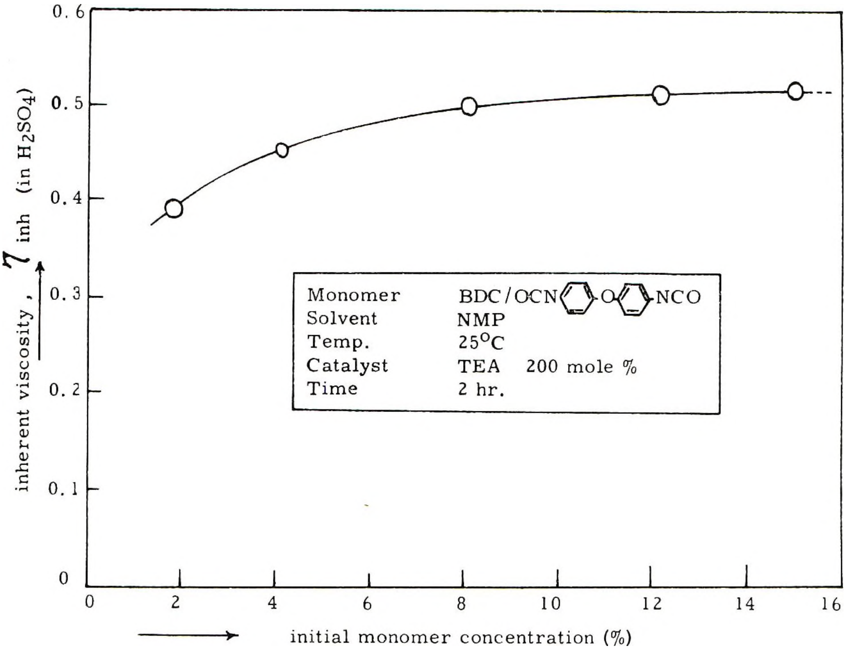


Fig. 4. Effect of initial monomer concentration on the degree of polymerization.

free of hydrogen chloride, because of triethylamine hydrochloride salt formation results in a heterogeneous polymerization system in which the rate of polymerization is decreased and the molecular weight of the poly(ureido acid) is lower. *N*-Methyl-2-pyrrolidone is found to afford an open-chain polymer of the highest molecular weight as shown in Table II.

The effect of catalyst concentration on the degree of polymerization was studied (Fig. 2). Equimolar amounts of amine and BDC carboxyl affords a polymer of the highest molecular weight.

The inherent viscosities of the poly(ureido acid) at different polymerization temperatures are plotted in Figure 3. The dissociation of the ureido linkage to amine and isocyanate is presumed to be one of the causes for

TABLE II

Effect of Solvent on the Degree of Polymerization[a]

Solvent	Polymer η_{inh}[b]
DMSO	—[c]
DMF	0.15
Pyridine	0.19[d]
TMS	0.28
NMP	0.50

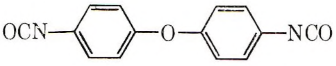
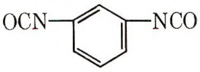
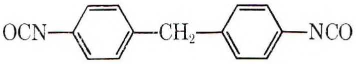
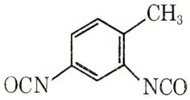
[a] Reaction conditions are the same as those described above.

[b] 25°C., 0.5% polymer in concentrated H_2SO_4.

[c] Polymerization did not occur and BDC was recovered quantitatively.

[d] Resulting polymer precipitated out in pyridine.

TABLE III
Polymerization of BDC with Various Aromatic Diisocyanates[a]

Wt. BDC, g.	Aromatic diisocyanate	Wt. diisocyanate, g.	Wt. triethylamine, g.	η_{inh} of polymer In H_2SO_4	In NMP
1.36		0.80	1.01	0.55	—
1.36		1.26	1.01	0.50	1.80
1.36		0.80	1.01	0.40	2.54
1.36		1.25	1.01	0.31	1.32
1.36		0.87	1.01	0.17	—

[a] Polymerization was carried out in NMP at 24°C. The initial monomer concentration was about 8%.

[b] 25°C. polymer concentration.

the decrease in molecular weight of the polymer at higher temperatures. The effect of initial monomer concentration on the molecular weight of the poly(ureido acid) is described in Figure 4. It was found that a higher initial monomer concentration favors an increase in both the rate of polymerization and the molecular weight of poly(ureido acid).

The optimum polymerization conditions for the polymerization of BDC with aromatic diisocyanates were employed to prepare a variety of aromatic poly(ureido acids) as summarized in Table III.

A transparent film can be cast from the *N*-methyl-2-pyrrolidone solution of poly(ureido acids) having inherent viscosities above 0.3 (0.5% polymer concentration in concentrated sulfuric acid).

The triethylamine salt of poly(ureido acid) is prepared by reacting an equimolar amount of triethylamine and 4,4′-diamonobiphenyl-3,3′-dicarboxylic acid and polymerizing with 4,4′-diisocyanatodiphenyl ether in *N*-methyl-2-pyrrolidone; the product is precipitated in benzene/methanol (1:1) solvent. Similarly, the polyurea acid is prepared by the treatment of the amine salt of the poly(ureido acid) with an aqueous hydrochloric acid and washed thoroughly with distilled water.

Fully aromatic polyquinazolinediones (IV) of excellent thermal stability are obtained by treatment at 250–300°C. for 5–30 min. under vacuum or in air of the polyureido acids prepared by low-temperature solution polymerization. Cyclodehydration[8,9] along the main chain of the poly(ureido acid) amine salt (III′) to polyquinazolinedione (IV) in eq. (3) was

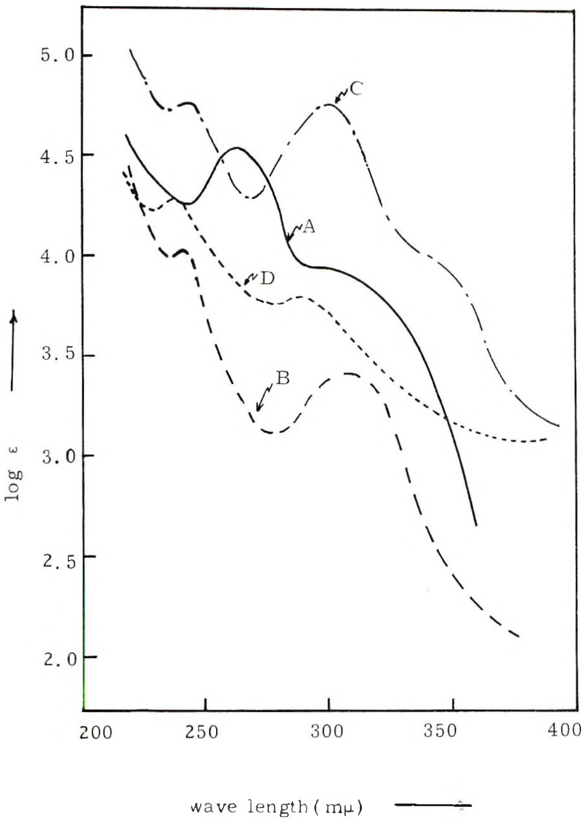
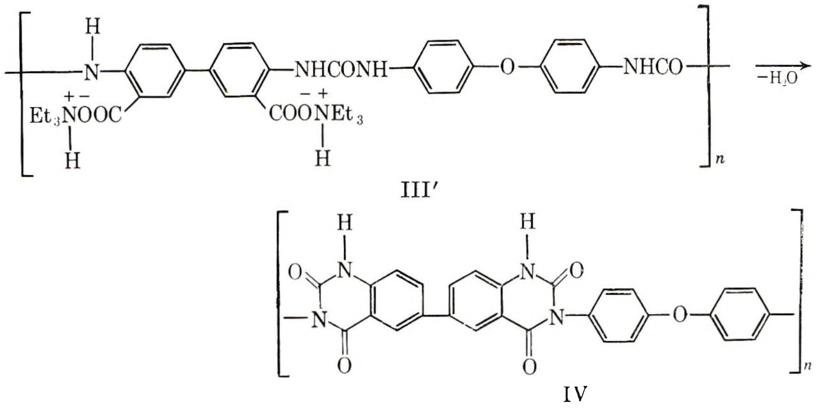


Fig. 5. Ultraviolet spectra of (*A*) *N*-(phenylcarbamoyl)anthranilic acid (99.5% ethanol); (*B*) 3-phenyl-2,4-(1H, 3H)-quinazolinedione (99.5% ethanol); (*C*) poly(ureido acid) methyl ester (film); (*D*) polyquinazolinedione (film).

confirmed from the infrared spectra by the disappearance of the carbonyl stretching vibration of the carboxyl group at 1680 cm.$^{-1}$ and the observation of a new carbonyl absorption band at 1725 cm.$^{-1}$ of 4-carbonyl of quinazolinedione ring structure.[10]



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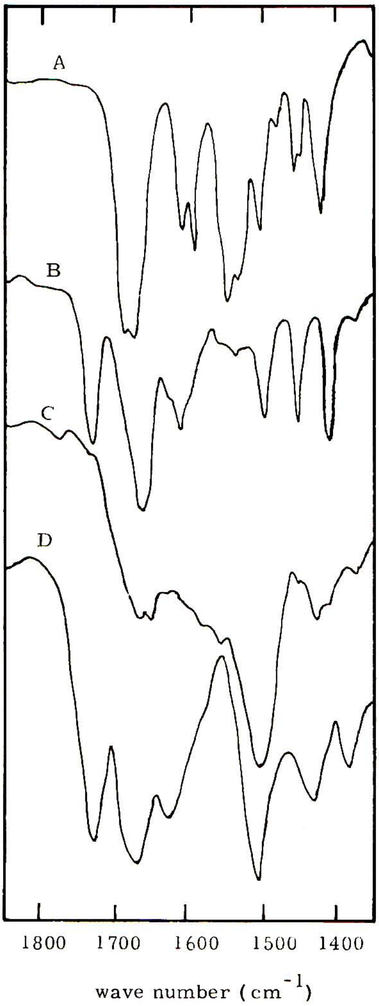

Fig. 6. Infrared spectra of (*A*) *N*-(phenylcarbamoyl)anthranilic acid; (*B*) 3-phenyl-2,4-(1H, 3H)-quinazolinedione; (*C*) poly(ureido acid); (*D*) polyquinazolinedione.

ANAL. Calcd. for polyquinazolinedione, $(C_{28}H_{16}O_5N_4)_n$: C, 65.21%; H, 4.38%; N, 10.18%. Found: C, 64.93%; H, 4.61%; N, 10.31%.

The ultraviolet and infrared spectra of the model compounds are closely related to those of the corresponding polymers, as shown in Figures 5 and 6.

Based on the results of elemental analyses and infrared and ultraviolet spectra, it is fully established that the aromatic polyquinazolinediones are obtained by the intramolecular cyclodehydrations along the polymer main chain as expected from the model reactions. Moreover, the outstanding thermal stabilities of the resultant heterocyclic polymers as described in Figure 7 definitely support the formation of rigid aromatic heterocyclic polymers containing the quinazoline ring system. The infrared spectra of the poly(ureido acid), polyquinazolinedione, and 3-phenylquinazolinedione are shown in Figure 6. The changes in infrared spectra for the polymer are closely related to those found for the reaction of the model ureido acid (*A*) to the corresponding 3-aryl quinazolinedione (*B*) in Figure 6. The polyquinazolinedione thus obtained is highly resistant to hydrolytic degradation by strong acid or alkali and is insoluble in most organic solvents.

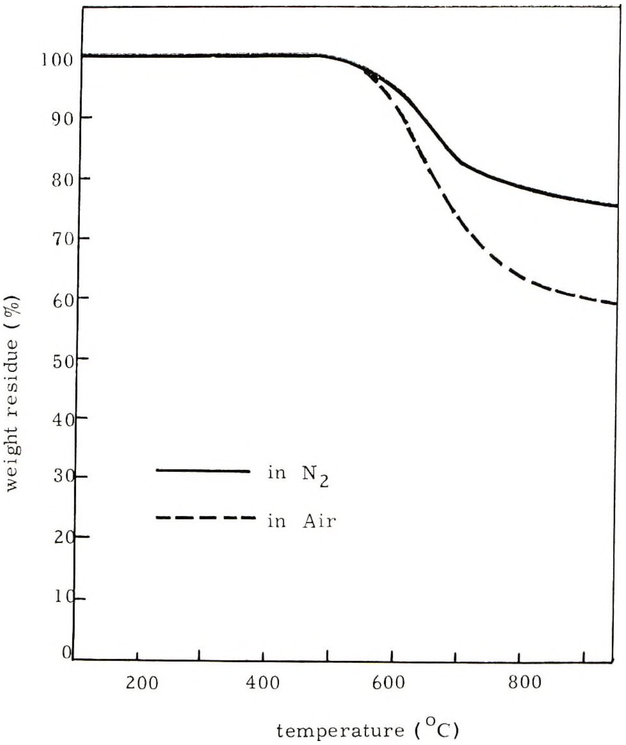

Fig. 7. Thermogravimetric analysis curves of polyquinazolinedione in nitrogen and in air.

The thermal stability of the fully aromatic polyquinazolinediones prepared from aromatic diaminodicarboxylic acid with various aromatic diisocyanates were measured in nitrogen and in air by the thermogravimetric method as shown in Figure 7. The quinazolinedione polymers have thermal stabilities which are comparable to those of aromatic polyimides,[11] polybenzimidazoles,[12] and polybenzoxazoles.[13] When the film was heated above 350–900°C. in the presence of oxygen, oxidative degradation occurred simultaneously with dehydration.

The authors wish to thank Dr. M. Ishitani, who carried out the ultraviolet spectral measurements. Thanks are also due to Messrs. Y. Ebata and T. Mizushima for the elemental and thermogravimetric analyses.

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Résumé

Des polyquinazolinediones (IV) complètement aromatiques, de poids molédulairs élevé ont été obtenus par cyclodeshydratation thermique d'acides polyuréiques aromatiques (III) préparés par réaction de polyaddition d'acide 4,4′-diaminobiphényl-3,3′-dicarboxylique (I) avec des diisocyanates aromatiques (II). Au départ d'une étude cinétique des réactions modèles de l'acide anthranilique avec l'isocyanate de phényle en présence de différents catalyseurs basiques, on a trouvé que les amines tertiaires exerçaient l'activité catalytique la plus élevée en vue de la formation de liens uréides. Les conditions de polymérisation optimums ont été déterminées par l'étude des variables de la réaction telles que les concentrations en monomère, les températures de polymérisation, le rapport en monomère et les concentrations en catalyseurs aussi bien que l'effet de la polarité et de la pureté des solvants organiques et des réactifs.

Zusammenfassung

Vollaromatische Polychinazolidindione (IV) hohen Molekulargewichts wurden durch thermische Cyclodehydratisierung aromatischer Polyureidsäuren (III) hergestellt, die ihrerseits durch eine Polyadditionsreaktion zwischen 4,4′-Diaminobiphenyl-3,3′-dicarbonsäure (I) und aromatischen Diisocyanaten (II) erhalten worden waren. Durch die kinetische Untersuchung der Modellreaktion von Anthranilsäure mit Phenylisocyanat in Gegenwart einer Reihe basischer Katalysatoren liess sich beweisen, dass tertiäre Amine die höchste katalytische Aktivität für die Ausbildung von Ureidbindungen besitzen. Durch die Untersuchung sowohl der Reaktionsvariablen wie Monomerkonzentration, Polymerisationstemperatur, Monomerverhältnis und Katalysatorkonzentrationen, als auch des Einflusses der Polarität und der Reinheit der organischen Lösungsmittel und Reaktanten wurden die optimalen Bedingungen für die Polymerisation bestimmt.

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Anionic Graft Polymerization of Methyl Acrylate to Protein Functional Groups*†

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Synopsis

Graft polymerization of methyl acrylate to functional groups in proteins was studied with model compounds and with whole gluten proteins. Polymerization was carried out in the presence of sodium hydride or sodium in dimethyl sulfoxide. Initiation proceeds by an anionic mechanism, and the rate-determining step is the production of the initially formed carbanion. The rate of disappearance of methyl acrylate was followed via gas chromatography. Amino acid analyses indicated that the functional groups of the amino acids, as well as the peptide bonds, were acting as the initiation sites in proteins. Reaction rates of the functional groups were determined on model compounds in the presence of sodium and sodium hydride. With both the model compounds and the proteins, polymerization was initially rapid and then leveled off, although rates depended on the concentration of activator and acrylate. Methoxyl group analyses of modified model compounds and proteins indicated that from 5 to 10 methyl acrylate residues were introduced per reactive site.

INTRODUCTION

Graft polymerization of various unsaturated monomers to naturally occurring polymeric substrates has been widely investigated in attempts to improve their mechanical, chemical, thermal, and other properties. Graft polymerization to cellulose has been recently reviewed by Krässig and Stannett.[2] Starch has been copolymerized to acrylic acid derivatives by redox systems, irradiation, and ozonization.[3,4] Wool has been modified with various vinyl monomers by radiation.[5] Throughout such studies, ionic initiation techniques have attracted little attention, and little work has been carried out in a single-phase solution.[6] In their work on grafting of vinyl monomers to cellulose, Zilkha et al.[7] and Schwenker and Pacsu[8] found that anionic polymerization conditions can be used to initiate grafting in non-aqueous solvents such as ammonia, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide (DMSO).

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† For preceding paper see Krull and Friedman.[1]

Sodium hydride and sodium produce carbanions from DMSO.[9–11] Ledwith and McFarlane[10] conclude that the DMSO anion is 7 × 10^6 times more basic than the *tert*-butyl anion. Therefore, in the presence of almost any proton donor, the DMSO anion would abstract a proton and generate a new anion. For example, in the polymerization of acrylamide to poly-β-alanine, with strong bases, Tani et al.[12] have shown that at least part of the polymerization is initiated by the amide anion of acrylamide. Thus, it would be expected that more acidic functional groups, such as sulfhydryl and hydroxyl, would also initiate polymerization.

This investigation is a continuation of our systematic studies on the chemical modification of functional groups in proteins with α,β-unsaturated compounds.[13–15] Model compounds containing functional groups as in proteins, as well as gluten proteins, were reacted with methyl acrylate in DMSO in the presence of either sodium or sodium hydride. The addition of an activated electron-donating group to a conjugated, polarized double bond in an aprotic solvent is essentially a Michael addition,[16] except that termination does not occur after monoaddition. Since Michael additions occur with amino and sulfhydryl functional groups present in proteins, although at vastly different rates,[13–15] it would be expected that poly-Michael-type additions would occur with proteins under aprotic conditions.

EXPERIMENTAL

Materials

DMSO (Baker) was dried over calcium hydride for about 24 hr. and then distilled under vacuum immediately before use.[17] Methyl acrylate (Eastman) was dried over anhydrous potassium carbonate and then distilled before use. Sodium hydride in mineral oil was obtained from Metal Hydrides and sodium metal from Baker. Benzylamine and benzyl mercaptan (Eastman) were distilled under vacuum. Benzamide (Fisher) was purified by sublimation. Succinamic acid was prepared from succinic anhydride (Eastman) by the method described by Jeffery and Vogel;[18] 3-mercaptopropionic acid (Aldrich) was distilled under reduced pressure; 3-aminopropionic acid (Calbiochem) and 3-hydroxypropionic acid (Aldrich) were used without further purification.

Wheat gluten was isolated by the procedure of Jones et al.[19] and vacuum-dried for 24 hr. at 100°C. before using.

Graft Polymerizations

All reactions were carried out under an atmosphere of nitrogen and with stirring by means of a magnetic stirrer. With the model systems, 0.01 mole of the compounds was used in sufficient DMSO and acrylate to make a total volume of 100 ml. The acrylate was added at both a 10-fold and a 100-fold molar excess over the number of reactive groups.

The following is a typical reaction procedure. Whole wheat gluten, 2 g. (a 2-g. portion of whole gluten contains a total of 8.4 mmole of amide, amino, guanidino, hydroxyl, and thiol groups[20]), was placed into a flask, dried for 24 hr. at 100°C. in a vacuum oven, and stored under dry nitrogen. The flask was then equipped with a magnetic stirrer, a nitrogen balloon, and a 1 ml. pipet (for removal of samples), and a pressure-equalized dropping funnel. To this reaction vessel, under a stream of nitrogen, was added the appropriate quantity of DMSO required to make the concentration of the final reaction mixture 1% in protein. Two reactions were usually run, one with a 10-fold excess of acrylate and another with a 100-fold excess. The 10-fold excess required 84 mmole of methyl acrylate or 7.5 ml. The 100-fold excess required 74.6 ml. of methyl acrylate. Therefore the protein was dissolved in 192.5 ml. of DMSO in one run and in 125.4 ml. in the other.

When the protein had dissolved in the DMSO, an equimolar quantity (8.4 mmole) of sodium or sodium hydride in mineral oil was added. Sodium took about 4 hr. to react. After this time, acrylate was added, and the reaction was allowed to proceed.

At various intervals, 1-ml. portions were removed from the reaction mixture to determine the decrease in acrylate concentration. These aliquots were diluted to 10 ml. with a solution composed of 0.5–4.0% tetrahydrofuran (as internal standard for gas chromatography analysis of the acrylate), and 4% acetic acid (as a proton source for quenching the polymerization) in DMSO. About 2 μl. of these samples was analyzed by gas chromatography.

Larger samples were removed from the reaction mixture at various times and the products from each of these were isolated by neutralization with acetic acid, followed by dialysis against water until free of acrylate and DMSO, and dried either by lyophilization or rotatory evaporation.

Solvents and volatile reactants for the reactions with model compounds were removed with a rotary evaporator connected to a vacuum pump. An ion-exchange procedure[1] was used to remove DMSO in cases where evaporation or dialysis could not be applied.

Gas Chromatography

Gas-liquid chromatography was carried out on an F&M Model 810; equipped with a disk integrator and a 6 ft. × $^1/_8$ in. column of Carbowax 20M, 10% on Chromasorb G, 80–100 mesh. The analysis was run at 60°C. for 2 min., to elute the tetrahydrofuran and the acrylate, and then the column was heated to 180°C. for 4 min. to drive off DMSO and other materials. The internal standard eluted in about 30 sec. and the acrylate in about 55 sec. The decrease in acrylate as a function of time was determined by comparison with a standard plot of area ratios of solutions of known weight ratios.[21]

Amino Acid Analysis

To 2 ml. of the reaction mixture was added 2 ml. of glacial acetic acid to quench the polymerization. The unreacted acrylate was removed under reduced pressure. The sample was then hydrolyzed by the addition of 20 ml. of constant-boiling HCl and refluxed for 24 hr. The HCl was removed by concentration under vacuum, and the samples were diluted to 10 ml. with pH 2.2 citrate buffer and analyzed. Amino acid analyses were carried out on a Phoenix Precision Instrument Co. accelerated amino acid analyzer, Model K-8800.[22]

To analyze for cysteine and cystine, as cysteic acid, DMSO was removed by dialysis, the product was oxidized with performic acid,[23] and then hydrolyzed as previously described.

Degree of Polymerization of Grafts

The average degree of polymerization (DP) of the grafts was computed by dividing the number of introduced methoxyl groups[24] by the number of reactive sites in the model compound or protein.

RESULTS AND DISCUSSION

Initiation of Polymerization by Model Functional Groups

Sodium or sodium hydride can extract a proton from the DMSO,[9–11] and the resulting anion may then initiate polymerization. In the presence of functional groups which contain active hydrogen, such as thiol, amino, hydroxyl, amido, or guanido, however, it was expected that sodium hydride or sodium would preferentially react with these rather than with DMSO. The resulting functional group anions should then initiate polymerization

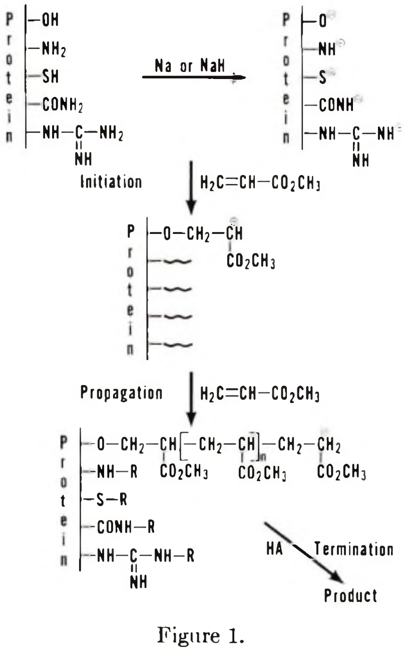


Figure 1.

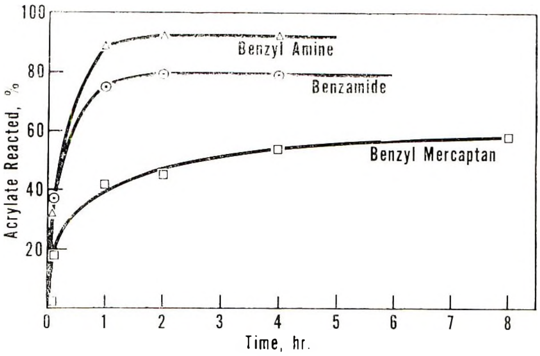


Fig. 2. Rate of decrease of methyl acrylate during reaction with benzyl derivatives (Na as activator).

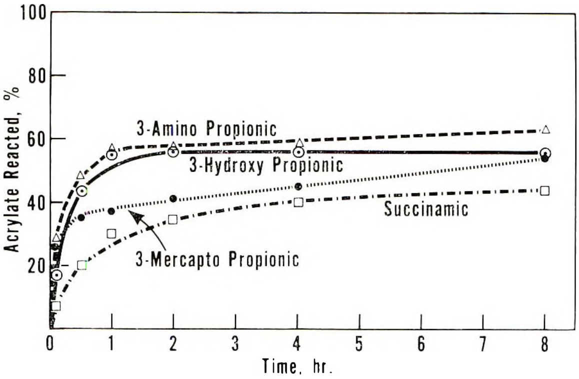


Fig. 3. Rate of decrease of methyl acrylate during reaction with 3-propionic acid derivatives (Na as activator).

as illustrated in Figure 1. To demonstrate that DMSO does not initiate polymerization under these conditions to form an ungrafted homopolymer, the products which resulted from reaction of methyl acrylate with benzyl amine and benzamide were analyzed for sulfur. Both of these products contained only 0.04% sulfur. This sulfur could come from limited DMSO-initiated nongrafted homopolymer or from trace amounts of DMSO not removed from the product.

To gain information on the relative reactivities of the various functional groups present in proteins, polymerization studies were first carried out with several series of model compounds containing these functional groups. The first series consisted of benzylamine, benzamide, and benzyl mercaptan. These compounds were reacted with a 10-fold excess of methyl acrylate in the presence of equimolar quantities of sodium (Fig. 2). Initially, the methyl acrylate is rapidly consumed, and after 1–2 hr. there is a decrease in rate of consumption. Benzylamine consumes around 90%, benzamide 80%, and benzyl mercaptan less than 60% methyl acrylate after about 4 hr., at which time the reaction is essentially complete. Relative reactivities of these model compounds are probably related to basicities of their conjugate bases. The anion formed from benzylamine is probably a stronger base than the corresponding anion from benzamide, which is stabilized by resonance. The sulfur anion is the weakest base in this series. Reaction rates of methyl acrylate with 3-mercapto propionic, 3-aminopropionic, 3-hydroxypropionic, and succinamic acids, determined under the same conditions as with the benzene derivatives, are shown in Figure 3. The amide, succinamic acid, reacts more slowly than benzamide. The overall extent of reaction for all the functional groups attached to propionic acid side chains is decreased as compared to the benzene derivatives.

The next series of polymerization studies was carried out with cysteine and glutathione. Amino acid analysis at various intervals showed a time-dependent decrease in unmodified amino acid content. For example, when cysteine was reacted with a 10-fold excess of methyl acrylate, with equimolar sodium, for 24 hr., 4.0% of the cysteine was recovered unmodified. With reduced glutathione under the same conditions, 4.3% of the cysteine was recovered. Thus, the difference in the quantity of cysteine remaining is small, whether its α-amino group is blocked or exposed. Also, it should be noted that from hydrolysates of the glutathione reaction product, 20% of the *N*-terminal glutamic acid and only 69% of the glycine were recovered. The glutamic acid decrease is due to the reaction with the free amino group. The partial loss of glycine cannot be as readily explained, although it is well known that glycine peptide bonds are labile to alkaline conditions. However, in the absence of methyl acrylate, no loss of glycine occurs under these conditions as evidenced by amino acid analysis.

The type of model compound exhibited little influence on the DP of the graft. Methyl acrylate (10-fold excess, equimolar in sodium) when polymerized onto any of the model compounds gave grafts with DP's of 4–8.

Initiation of Polymerization by Protein Functional Groups

Wheat gluten, the protein used in these studies, was reacted under the same conditions as the model compounds. The concentration of activator added to the proteins in DMSO was based on the concentration of reactive functional groups present in the gluten. Not included was the concentration of the secondary peptide amide bonds of the protein.

To ascertain whether homopolymerization takes place in the presence of proteins attempts were made to extract any homopolymer from the proteins with hot and cold benzene. Little, if any, homopolymer is formed. Evidently, the reactive sites on the protein are more acidic than the methylsulfinyl carbanion and give up their proton to the carbanion.

The decrease in methyl acrylate concentration with time when sodium was reacted on an equimolar basis to the functional groups is shown in Figure 4. Initially, there is a rapid loss of methyl acrylate, both in the reaction with a 10-fold excess and that with a 100-fold excess. Both reactions are essentially complete after about $1^1/_2$ hr. The 10-fold excess re-

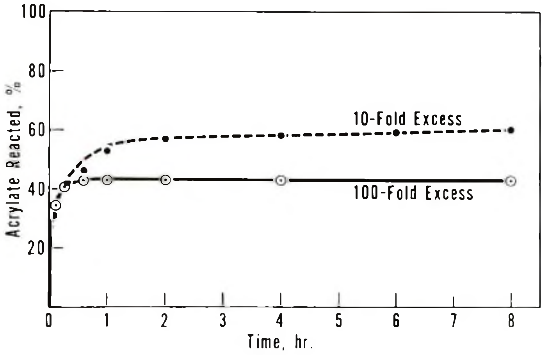


Fig. 4. Rate of decrease of methyl acrylate during reaction with wheat gluten (Na as activator).

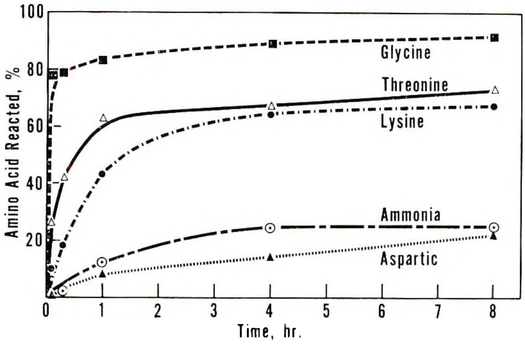


Fig. 5. Decrease in amino acid content of product hydrolysates with time during reaction with wheat gluten (Na as activator). Disappearance of arginine, cysteine, and tyrosine was complete in 5 min.

action consumes about 60% of the available acrylate and the 100-fold about 40%.

The decrease in amino acids in a reaction with equimolar sodium (8.4 mmoles/2 g.) and a 10-fold excess of methyl acrylate (84 mmole/2g.) is shown in Figure 5 and Table I. The reaction initially is rapid and reaches a plateau after 1–2 hr.

In this reaction, the basic amino acids histidine and arginine, as well as cysteine and tyrosine, are immediately consumed. The functional groups in these amino acids are the most reactive to this system. The functional groups of threonine, serine, and lysine also are rapidly consumed until about 70% of these amino acids are reacted.

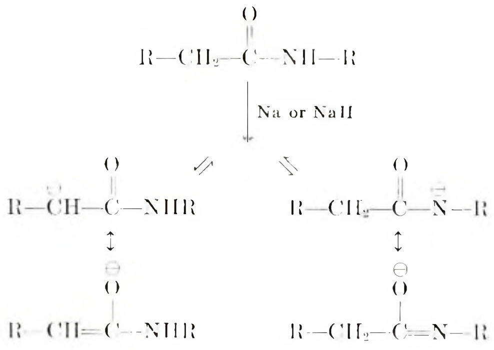
Glycine in the protein is also modified as it was in the glutathione. Glycyl residues react until about only 10% remain. There is a smaller decrease in other amino acids, such as aspartic, previously assumed to be nonreactive to this system. Since the decrease is quite general for most of the "nonreactive" amino acids, the peptide bonds of the protein must participate in the reaction. Glycine with no side chain offers the least

TABLE I
Amino Acid Content of Wheat Gluten Modified with Methyl Acrylate (MA) with Sodium as Activator

Sodium concn., mmole	8.4	0.84	0.84	8.4	8.4	8.4	8.4
MA concn., mmole	—	84	84	84	84	840	840
Time, hr.	4	1	8	1	8	1	8
Amino acid contents, μmole/g. N							
Lysine	0.359	0.350	0.230	0.206	0.121	0.046	Trace
Histidine	0.672	0	0	0	0	0	0
Ammonia	6.71	7.736	7.486	14.43	12.30	4.763	2.481
Arginine	0.923	0.114	Trace	0	0	0	0
Aspartic	0.993	0.941	0.866	0.884	0.826	0.336	0.219
Threonine	1.132	1.046	0.925	0.443	0.323	0.137	0.056
Serine	2.819	1.109	1.080	0.320	0.141	0.099	0.039
Glutamic	16.46	10.02	10.04	9.887	9.131	4.656	2.610
Proline	6.931	6.963	6.307	5.928	5.111	2.908	2.157
Glycine	2.888	2.575	1.689	0.499	0.232	0.920	0.037
Alanine	1.447	1.422	1.403	0.876	0.838	0.412	0.287
$^1/_2$ Cystine	0.409	Trace	Trace	0	0	0	0
Valine	1.807	1.791	1.710	1.392	1.303	0.588	0.493
Methionine	0.528	0.470	0.372	Trace	Trace	Trace	Trace
Isoleucine	1.646	1.614	1.570	1.124	1.126	0.687	0.491
Leucine	3.122	2.665	2.544	1.835	1.808	1.038	0.713
Tyrosine	0.874	0	0	0	0	0	0
Phenylalanine	1.764	0.849	0.803	0.495	0.434	0.244	0.157

steric hindrance to the incoming acrylate and is therefore modified most extensively. Amino acids with bulky side chains are less readily consumed.

Initiation of anionic polymerization by the mechanism illustrated in eqs. (1) could explain the decrease in glycine and other nonreactive amino



(1)

acids. Hydrogen atoms on the carbon adjacent to carbonyl groups are known to be acidic and could participate with a strong base in the indicated acid–base equilibria. The same considerations would also apply to the amide hydrogens of the peptide bonds. In this manner the peptide backbone of the protein could provide additional sites for initiation.

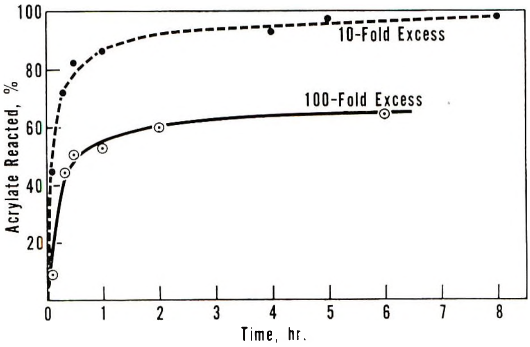


Fig. 6. Rate of decrease of methyl acrylate during reaction with wheat gluten (NaH as activator).

When sodium hydride was used as the activator with whole gluten in equimolar quantities (Fig. 6), again there is the characteristic rapid consumption of methyl acrylate. The 10-fold excess reaction consumes almost all the methyl acrylate and the 100-fold excess more than 60%. Consumption of methyl acrylate is concentration-dependent since the total consumption of this vinyl compound is about six times greater in the 100-fold excess reaction than in the 10-fold. The reaction with sodium hydride utilizes a greater percentage of the methyl acrylate than the comparable reaction with sodium.

With sodium hydride the amino acid residues are modified at a different rate than in the sodium reaction (Table II). When equimolar sodium hydride (8.4 mmole/2 g.) and 10-fold excess of methyl acrylate (84 mmole/2 g.) have been reacted with gluten, all cysteine, histidine, and arginine, and only about 25% of the tyrosine are consumed after 4 hr. The amino acids are modified to a lesser extent here than in the sodium reaction under the same conditions. Fewer amino acids are modified and larger quantities of methyl acrylate are consumed with sodium hydride than with sodium. Thus, sodium hydride gives fewer grafts of greater molecular weights than does sodium.

To establish whether activator concentration affects the degree of polymerization, wheat gluten was reacted with methyl acrylate in the presence of $^1/_{10}$ of the stoichiometric amount of sodium or sodium hydride. A comparison of the results in Figure 7 to those in Figures 4 and 6 demonstrates that the degree of polymerization is a function of activator concentration because a decrease in sodium or sodium hydride causes a corresponding decrease in methyl acrylate consumption.

In proteins, where the sites are more numerous and less accessible, the methyl acrylate (10-fold excess, equimolar sodium) grafts had DP's in the range 2–4. When the acrylate concentration was increased to 100-fold excess (sodium equimolar), the maximum DP of a graft was about 8. When equimolar sodium hydride was used as the activator, the DP's of grafts ranged from 5 to 20, depending on the concentration of acrylate

TABLE II
Amino Acid Content of Wheat Gluten Modified with Methyl Acrylate (MA) with Sodium Hydride as Activator

Sodium hydride concn., mmole	Blank	8.4	0.84	0.84	8.4	8.4	8.4	8.4
MA concn., mmole	—	—	84	84	84	84	840	840
Time, hr.	0	4	1	8	1	8	1	8
Amino acid contents, μmole/g. N								
Lysine	0.364	0.362	0.204	0.110	0.142	0.129	0.110	0.101
Histidine	0.688	0.644	0	0	0	0	0	0
Ammonia	16.55	11.84	8.39	7.74	8.298	6.847	6.496	4.543
Arginine	0.950	0.901	0.632	0.616	Trace	Trace	0	0
Aspartic	0.971	0.956	0.947	0.935	0.982	0.936	0.610	0.553
Threonine	1.197	1.168	1.155	1.148	0.946	0.624	0.270	0.218
Serine	2.844	2.863	1.404	1.359	0.583	0.511	0.220	0.149
Glutamic	16.93	17.13	10.20	10.19	10.19	8.923	10.19	10.17
Proline	6.973	6.942	6.919	6.915	6.892	6.688	6.766	6.582
Glycine	2.873	2.814	2.474	2.345	0.953	0.638	0.241	0.188
Alanine	1.457	1.448	1.408	1.366	1.408	1.059	0.957	0.890
$^1/_2$ Cystine	—	—	Trace	Trace	0	0	0	0
Valine	1.801	1.809	1.762	1.766	1.753	1.673	1.411	1.358
Methionine	0.536	0.516	0.497	0.433	0.476	0.420	0.306	0.277
Isoleucine	1.623	1.617	1.530	1.497	1.553	1.497	1.504	1.433
Leucine	3.110	3.108	2.618	2.578	2.191	2.024	2.174	2.021
Tyrosine	1.232	0.826	0	0	0	0	0	0
Phenylalanine	1.836	1.709	0.856	0.790	0.844	0.737	0.791	0.590

present. Thus, the sodium-activated polymerization, which modified more amino acid residues, produces grafts of smaller length than the sodium hydride-activated reaction.

The results of this study demonstrate for the first time that protein functional groups can act as initiation sites for anionic polymerizations in homo-

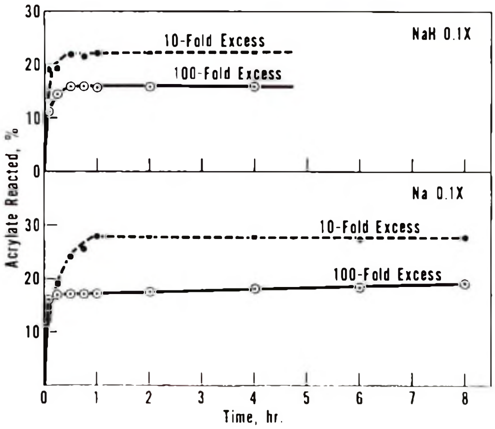


Fig. 7. The effect of decreasing activator concentration to one tenth of stoichiometric (see text) on the rate of decrease of methyl acrylate during reaction with wheat gluten.

geneous solutions. The absence of known monoaddition products of lysine and cysteine[25] in hydrolyzates of grafted proteins provides further evidence for polymerization rather than monoaddition. The results also indicate that anions from peptide bonds and/or carbanions located adjacent to carbonyl groups of peptide bonds may participate in the polymerization reactions.

Since reaction rates of various functional groups present in proteins differ initially but are similar in later stages, it would appear that the initiation step is rate-controlling. Various aspects of the described anionic graft polymerization will be explored in future publications.

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Résumé

La polymérisation greffée de l'acrylate de méthyle aux groupes fonctionnels des protéines a été étudiée avec des composés modèles et avec des protéines gluténiques. La polymérisation a été effectuée en présence d'hydrure de sodium ou de sodium dans le diméthylsulfoxyde. L'initiation résulte d'un mécanisme anionique et l'étape détermin-

ante de vitesse consiste en la production du carbanion initialement formé. La vitesse de disparition de l'acrylate de méthyle est suivie par chromatographie gazeuse. Les analyses des acides aminés indiquent que les groupes fonctionnels d'acides aminés aussi bien que les liens peptidigues, agrissent comme site d'initiation au sein des protéines. Des vitesses de réaction des groupes fonctionnels ont été déterminées au départ de composés modèles en présence de sodium ou d'hydrure de sodium. Aussi bien avec les composés modèles qu'avec les protéines, la polymérisation était initialement rapide puis diminuait bien que les vitesses dépendaient de la concentration de l'activateur et de l'acrylate. L'analyse des groupes méthoxyles de composés modèles modifiés et des protéines indiquait que cinq à dix résidus acrylate de méthyle étaient introduits par sites réactionnels.

Zusammenfassung

Die Pfropfpolymerisation von Methylacrylat auf funktionelle Gruppen in Proteinen wurde an Modellverbindungen und an Glutenproteinen untersucht. Die Polymerisation wurde in Gegenwart von Natriumhydrid oder Natrium in Dimethylsulfoxyd ausgeführt. Der Start erfolgt nach einem anionischen Mechanismus und der geschwindigkeitsbestimmende Schritt ist die anfängliche Bildung des Carbanions. Die Geschwindigkeit des Verbrauches von Methylacrylat wurde gaschromatographisch bestimmt. Aminosäureanalysen zeigten, dass sowohl die funktionellen Gruppen der Aminosäuren als auch die Peptidbindungen als Initiatoren in den Proteinen wirken. Die Reaktionsgeschwindigkeit für die funktionellen Gruppen wurde an Modellverbindungen in Gegenwart von Natrium und Natriumhydrid bestimmt. Bei den Modellverbindungen und bei den Proteinen war die Polymerisation am Anfang rasch und verlangsamte sich später; die Geschwindigkeit war aber von Aktivator- und Acrylatkonzentration abhängig. Methoxygruppenanalysen an modifizierten Modellverbindungen und Proteinen zeigten, dass pro reaktive Stelle 5 bis 10 Methylacrylatreste eingeführt werden.

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Alkyl Vinyl Esters of Brassylic (Tridecanedioic) Acid*

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Synopsis

Brassylic acid was partially esterified at 77°C. in toluene solution with ethyl, 2-methylpentyl, or nonyl alcohol and with *p*-toluenesulfonic acid used as catalyst. Half-esters were isolated from the respective reaction mixtures in yields of 28, 34, and 32% after reaction times of 2, 6, and 8 hr. Both recovered brassylic acid and byproduct dialkyl ester were successfully used as starting materials in subsequent esterifications. Consequently, conversion of starting materials to half-ester would be increased in a process that involved continuous recycling of byproducts. Alkyl hydrogen brassylates were vinylated at 165°C. for 8 hr. with acetylene at 360 psig. The zinc salt generated *in situ* from zinc oxide served as catalyst and toluene as solvent. Yields were 80–88% and purities of products were 94–95%. Samples of 2-methylpentyl vinyl brassylate and nonyl vinyl brassylate of much higher purity were obtained by preparative gas–liquid chromatography or molecular distillation. Physical properties and experimental conditions for gas–liquid chromatographic analyses of both the alkyl hydrogen and alkyl vinyl brassylates are reported.

INTRODUCTION

The suitability of alkyl vinyl esters of dicarboxylic acids as comonomers for internally plasticized poly(vinyl chloride) has been examined.[1] One factor that affects the internal plasticization by vinyl esters of monocarboxylic acids is the chain length of the acid.[2] The longest straight-chain dicarboxylic acid available in commercial quantities as dimethyl ester[3] is brassylic (tridecanedioic) acid. This product is obtained from erucic (*cis*-13-docosenoic) acid. Currently erucic acid is derived from imported rapeseed oil, but a richer source is a newly developed domestic oilseed crop, *Crambe abyssinica* Hochst. ex R. E. Fries, the seed oil of which contains 55–60% of erucic acid as the glyceride ester.[4] Since dialkyl brassylates are excellent low-temperature plasticizers,[5] building alkyl vinyl brassylates into a polymer as internal plasticizers to avoid leaching and volatilization might provide useful products.

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Among the dialkyl brassylates, the bis(2-methylpentyl) ester is the best plasticizer when all properties are considered. Accordingly, 2-methylpentyl vinyl brassylate was selected as one of the comonomers to be prepared. The other two, ethyl vinyl and nonyl vinyl brassylates, were chosen to determine the effects of a small and a large saturated alkyl. Copolymerization of these alkyl vinyl brassylates with vinyl chloride and the internal plasticization achieved will be reported later.

Alkyl hydrogen esters of short-chain dicarboxylic acids have previously been prepared from: (*a*) dicarboxylic acids by half-esterification[6] or equilibration,[7] (*b*) dialkyl esters by half-saponification,[8] and (*c*) monomeric anhydrides by alcoholysis.[9] Alkyl vinyl esters have been made from alkyl half-esters by direct vinylation,[10] by transesterification,[11] or via the corresponding chlorides by reaction with the mercuric derivative of acetaldehyde.[8] Alkyl vinyl esters have also been produced from salts of alkyl half-esters by reaction with vinyl haloformates.[12]

In this investigation, half-esterification followed by vinylation with acetylene was the most convenient route to the desired alkyl vinyl esters of the long-chain dibasic acid, brassylic acid.

EXPERIMENTAL

Materials and Analytical Methods

Brassylic acid from ozonolysis of erucic acid[13] was recrystallized twice from xylene to a purity of 99.0%. Ethanol was treated with sodium metal and distilled at atmospheric pressure to give a purity of 98.7%. 2-Methylpentanol (Union Carbide) and nonanol (Aldrich) were fractionally distilled to respective purities of 99.8 and 99.9%. For the purified 2-methylpentanol, $n_D^{25} = 1.4160$ (reported[14] 1.4172), and for nonanol, $n_D^{25} = 1.4388$ (reported[15] 1.4388). The purities of starting materials and products were determined by gas–liquid chromatography (GLC) under conditions given in Table I. Thin-layer chromatography (TLC) was conducted with silica gel G plates and hexane–ethyl ether (80/20) as the solvent. Infrared absorption spectra of 5% solutions of half-esters in carbon tetrachloride were obtained on a Perkin-Elmer Model 337 Infracord spectrophotometer; spectra of alkyl vinyl esters were secured from the compounds as liquid films. Neutralization equivalents,[17] saponification equivalents,[18] and iodine values[19] were determined by conventional methods.

Preparation of Half-Esters

Details of preparation and purification of each half-ester are given in Table II. The following general procedure was used. A 1-liter, three-necked flask equipped with a condenser, mechanical stirrer, and thermometer was placed in a water bath maintained at 77°C. Into the flask were introduced 48.86 g. (0.2000 mole) of brassylic acid, 1.26 g. (0.0066 mole) of *p*-toluenesulfonic acid monohydrate (Eastman), 0.2000 mole of the ap-

TABLE I
Gas-Liquid Chromatography of Brassylic Acid Esters and Their Starting Materials

Compound	ECL[a]	Liquid phase[b]	Column temperature, °C.	Equipment[c]
Ethanol	—	Apiezon L 20%	60	A
Ethyl brassylate	17.0	Apiezon L 10%	220	B
Ethyl methyl brassylate	16.3	Apiezon L 10%	220	B
Methyl brassylate	16.7	Apiezon L 10%	220	B
Methyl brassylate	15.7	Apiezon L 10%	220	B
Methyl brassylate	20.3	Resoflex 446 3%	208	C
Methyl 2-methylpentyl brassylate	23.3	Resoflex 446 3%	208	C
2-Methylpentanol	—	Apiezon L 20%	80–160	A
2-Methylpentyl hydrogen brassylate	29.6	Resoflex 446 3%	208	C
2-Methylpentyl brassylate	26.8	Resoflex 446 3%	208	C
2-Methylpentyl vinyl brassylate	23.6	Resoflex 446 3%	208	C
2-Methylpentyl vinyl brassylate	23.6	Resoflex 446 15%	205	D
Nonanol	—	Apiezon L 10%	220	B
Nonyl brassylate	31.0	JXR 3%	115–330	E
Nonyl methyl brassylate	24.0	JXR 3%	115–330	E
Nonyl vinyl brassylate	24.5	JXR 3%	115–330	E
Nonyl vinyl brassylate	24.5	JXR 3%	110–320	F
Vinyl brassylate	20.8	Resoflex 446 3%	208	C

[a] Equivalent chain length based on methyl *n*-alkanoates as reference.[16] Linear plot of retention time versus ECL used for programmed temperature GLC.

[b] Solid support for Apiezon L = acid-washed, silylated, 60/80-mesh Chromosorb W; Resoflex 446 = acid-washed, 60/80-mesh Celite 545; JXR = 100/120-mesh Gas Chrom Q (Applied Science).

[c] Equipment: A = F&M Model 810, flame ionization detector, 10 ft. × 1/8 in. stainless steel coiled column, helium 25 ml./min./50 psig; B = Burrell Model K-5, thermal conductivity detector, 275 × 0.6 cm. glass U-column, helium 40 ml./min./40 psig. (carrier gas reduced to 10 ml./min./10 psig. for nonanol); C = Burrell Model K-5, thermal conductivity detector, 125 × 0.3 cm. glass U-column, helium 30 ml./min./30 psig.; D = Aerograph Autoprep Model A-700, thermal conductivity detector, 5 ft. × 1/4 in., stainless steel coiled column, helium 60 ml./min./50 psig., 0.1 ml. sample per injection; E = F&M Model 810, flame ionization detector, 2 ft. × 1/8 in., stainless steel column, helium 100 ml./min./100 psig; F = F&M Model 810, thermal conductivity detector, 2 ft. × 1/8 in., stainless steel column, helium 35 ml./min./40 psig., 0.1 ml. sampler per injection.

propriate alcohol, and 500 ml. of toluene. The reaction mixture was heated for the time specified in Table II, and the products were then cooled overnight at the temperatures indicated. The precipitate, predominantly brassylic acid, was removed by filtration. The half-ester content in the precipitate was 10–12, 3–8, and 1–2% for ethyl, 2-methylpentyl, and nonyl hydrogen brassylate, respectively. The small quantity of brassylic acid remaining in the filtrate was removed by passing the filtrate through a 4.4-cm. I.D. column containing 150 g. of silicic acid and washing the column with 350–400 ml. of toluene. After adjustment to the volume given in

TABLE II
Preparation of Brassylic Acid Half-Esters

	Esterification			Crystallization			Product[a]			
							Yield, %			
Half-ester	Alcohol charged, g.	Time at 77°C., hr.	Temperature for cooling and filtration, °C.	Volume of toluene solution, ml.	Temperature, °C.	Time, hr.	A	B	C	Purity of A, %
Ethyl hydrogen brassylate	9.21	2	1	500	−78	4	28	48		99.1
2-Methylpentyl hydrogen brassylate	20.43	6	−18	500	−78	4	34	42	42	99.2
Nonyl hydrogen brassylate	28.85	8	25	1250	−18	16	32			99.5

[a] A, From fresh starting materials; B, total from one fresh run and one recycling of the recovered brassylic acid; C, total from one fresh run and one recycling of both the recovered brassylic acid and the crude dialkyl brassylate.

Table II, the combined eluate was cooled to the crystallization temperature (Table II). The alkyl hydrogen brassylate which crystallized was filtered in the cold (1°C.) and washed with cold (crystallization temperature) toluene. The filtrate from the crystallization contained dialkyl brassylate (60–80%) and unrecovered alkyl hydrogen brassylate (15–35%).

The brassylic acid-rich precipitate was recycled without affecting the yield by following the foregoing procedure after adding fresh brassylic acid and alcohol to give a total of 0.200 mole each of the brassylic and alcoholic moieties. In one instance the crude dialkyl brassylate was also included as "starting material" in a recycling experiment. Yields B and C in Table II were calculated from the total brassylic acid employed. This total included the brassylic acid used in the original esterification and that added as "make-up" starting material in the recycling experiment.

Analytical samples of solid ethyl and nonyl hydrogen brassylates were prepared by three recrystallizations from *n*-hexane. An analytical sample of liquid 2-methylpentyl hydrogen brassylate was made by silicic acid column chromatography for which chloroform was used as solvent. Samples were analyzed for purity by TLC and by GLC of their corresponding methyl esters prepared by reaction with diazomethane (Table I). Physical constants were determined by conventional methods.

Vinylation

The following general procedure was employed: A 300-ml. stainless-steel autoclave equipped with a magnetic stirrer and cooling coil was charged with 0.61 g. (0.0075 mole) of zinc oxide (Baker analyzed reagent), 0.0900 mole of half-ester, and a weight of toluene equal to 83% of the half-ester used. The autoclave was inserted into an electric heater and flushed with acetylene. Vinylation proceeded with stirring at 165°C. under 360 psig. maintained by periodically refilling the autoclave with acetylene. The reaction was stopped after 8 hr., during which time sufficient acetylene had been absorbed to provide an 80–90% conversion. Products were removed from the autoclave and filtered. To remove traces of catalyst and unreacted starting material, the filtrate was introduced into a 3.2-cm. I.D. column packed with a mixture of 50 g. of alumina, 25 g. of Celite, and 25 g. of active carbon and was eluted with 400 ml. of toluene. Upon removal of solvent a faint yellow liquid remained. Products were 94–95% pure, and yields were 80–88%.

For characterization, 1 g. samples of 2-methylpentyl vinyl brassylate and nonyl vinyl brassylate were further purified by preparative GLC (Table I). Larger samples (6–12 g.) of the pure compounds were collected after four or five passes through an ASCO 50 rota-film molecular still. For polymerization 100 g. quantities of 2-methylpentyl vinyl brassylate were freed of the crosslinking agent, divinyl brassylate, by its selective removal from the bulk product in a single pass through the molecular still. Further purification of ethyl vinyl brassylate was, however, not achieved by either molecular distillation, preparative GLC, or fractional crystallization.

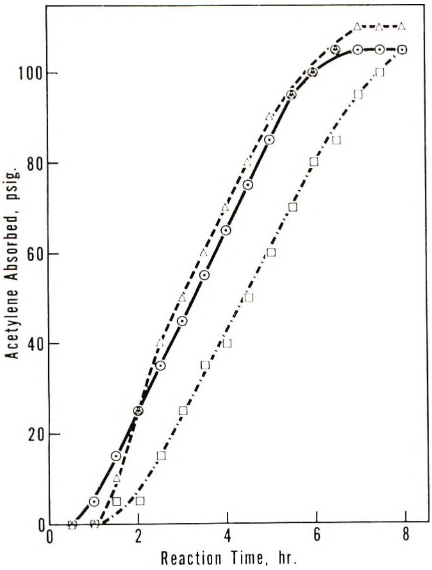

Fig. 1. Uptake of acetylene during vinylation of (△) ethyl hydrogen brassylate, (⊙), 2-methylpentyl hydrogen brassylate, and (□) nonyl hydrogen brassylate.

The final highly purified samples were examined by TLC to confirm the absence of any contaminating polymers.

RESULTS AND DISCUSSION

To avoid excessive discoloration during half-esterification a temperature (77°C.) below reflux (110°C.) was used. The reaction times were the minimum times at which an equilibrium mixture of unreacted brassylic acid, half-ester, and dialkyl ester (in 1:2:1 molar ratio) was achieved in

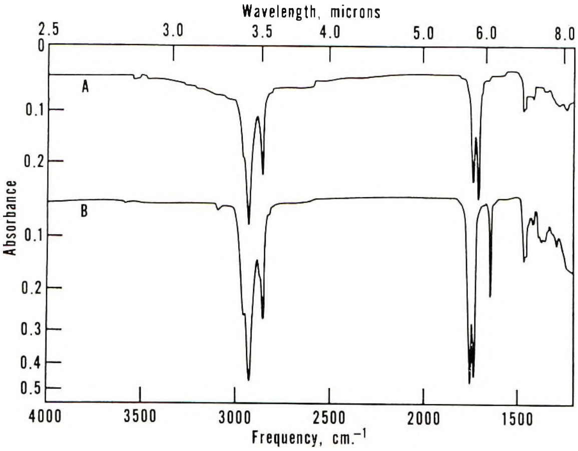

Fig. 2. Portions of infrared spectra: (*A*) nonyl hydrogen brassylate (2% in chloroform); (*B*) 2-methylpentyl vinyl brassylate (liquid film).

TABLE III
Analyses and Physical Constants of Brassylic Acid Esters

		Neutralization equivalent		Saponification equivalent		Iodine value				
Ester	Purity, %	Calcd.	Found	Calcd.	Found	Calcd.	Found	Melting point, °C.	n_D^{25}	Sp. gr.$_{25}^{25}$
Ethyl hydrogen brassylate	99.6	272.4	272.8	136.2	136.9			60.0–61.0[a]		
2-Methylpentyl hydrogen brassylate	99.8	331.3	328.5	164.3	164.0			22.5–24.5	1.4509	0.9502
Nonyl hydrogen brassylate	99.9	370.6	374.0	185.3	186.8			50.0–51.0		
Ethyl vinyl brassylate	93.7					85.1	81.8	21.0–21.8	1.4485	0.9532
2-Methylpentyl vinyl brassylate	99.9					71.6	70.0	5.8–6.3	1.4506	0.9320
Nonyl vinyl brassylate	99.4					64.0	63.2	23.8–24.3	1.4528	0.9240

[a] Reported melting points 56–57°C.,[22] 42–43°C.[23]

preliminary experiments. Although the half-ester content of the reaction mixture at equilibrium is 50%, continuous recycling of byproducts should eventually give essentially quantitative conversion of brassylic acid to half-esters (Table II). Because colored impurities accumulated in the diester fraction and interfered with the subsequent crystallization of half-ester, yield C in Table II is no greater than yield B. To take full advantage of the potential yield increase by recycling, a purification step to remove the contaminants should be incorporated.

While our work was in progress, Freidlin et al.[11,20] reported preparation of alkyl vinyl esters of succinic (C_4), glutaric (C_5), adipic (C_6), azelaic (C_9), and sebacic (C_{10}) acids via transesterification. They also mentioned success in direct vinylation of alkyl hydrogen adipate but failure with alkyl hydrogen succinate.[21] Our direct vinylation of half-esters gave satisfactory results. The procedure we used involves preparation of the catalyst (zinc salt of the half-ester) *in situ*. Acetylene uptake ceased before the end of the 8 hr. reaction time when ethyl and 2-methylpentyl half-esters were the starting materials, but not with the nonyl hydrogen brassylate. Nevertheless, the yields of alkyl vinyl brassylates were substantially the same in all three reactions. Even though the starting materials (half-esters) contained no brassylic acid, all vinylation products contained 1–2% divinyl brassylate, as well as 3–6% dialkyl brassylate. Where differences in molecular weight were great enough, these impurities could be removed by molecular distillation or preparative gas–liquid chromatography. The pure ethyl vinyl brassylate was, however, not obtainable by these methods because of its similarity in molecular weight to divinyl and diethyl brassylates.

The reported yields are an average of at least five preparations, except for yield C (Table II) which is an average of two preparations. The listed purities are the alkyl hydrogen brassylate and alkyl vinyl brassylate contents determined by gas–liquid chromatography (see Table I). The trace contaminants in the half-ester preparations were half-esters of the homologous undecanedioic and pentadecanedioic acids. TLC of the alkyl vinyl brassylate samples showed no contamination by polymers. The chemical constants listed in Table III and the C and H analysis observed for the analytical samples were in good agreement with their calculated values. All half-esters and alkyl vinyl esters were soluble (0.1 g./ml.) in acetone, acetonitrile, carbon tetrachloride, chloroform, dioxane, ethyl ether, *n*-hexane, methanol, and toluene but were insoluble in water. The infrared spectra of half-esters showed a double carbonyl peak at 5.85 μ (carboxylic acid, stronger) and 5.75 μ (alkyl ester, weaker). The spectra of alkyl vinyl ester had a vinyl peak at 6.08 μ (C=C stretch) and a double carbonyl peak at 5.78 μ (alkyl ester) and 5.70 μ (vinyl ester), the shorter wavelength of the latter being due to the electron-withdrawing property of the vinyl group.[24] Another absorption peak of the vinyl group at 3.24 μ (CH_2 asymmetric stretch) was seen, but it was weak. The strength of the methylene peak at 3.42 μ increases as the number of methylene groups increases from the ethyl to nonyl esters.

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Reference to commercial products does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

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Résumé

L'acide brassylique a été estérifie partiellement à 77°C. en solution toluénique avec l'alcool éthylique, 2-méthylpentylique, ou nonylique et en présence d'acide *p*-toluènesulfonique comme catalyseur. Les hemiesters ont été isolés au départ de leur mélange de réaction respectif avec des rendements de 28, 34 et 32% après des durées de réaction de

2, 6 et 8 heures. L'acide brassylique recupéré et l'ester dialcoylé formé comme produit secondaire, ont été utilisés avec succès comme matériaux de départ pour des estérifications subséquentes. En conséquence, la conversion des matériaux de départ en hémiesters pourrait être augmentée dans un processus qui comporterait le recyclige continuel des produits secondaires. Les brassylates acides d'alcoyle ont été vinylés à 165°C durant 8 heures avec de l'acétylène à 360 psig. Le sel de zinc engendré *in situ* au départ d'oxyde de zinc faisait fonction de catalyseur et le toluène était utilisé comme solvant. Les rendements s'élevaient à 80–88% et de la pureté des produits atteignaient 94–95%. Des échantillons de vinylbrassylate de 2-méthylpentyle et de nonyle de degré de pureté plus élevé, ont été obtenus par chromatographie préparative gaz–liquide ou par distillation moléculaire. Les propriétés physiques et les conditions expérimentales pour les analyses chromatographiques gaz–liquide, à la fois des brassylates hydrogène acide d'alcoyle et vinylalcoyle ont été rapportées.

Zusammenfassung

Brassylsäure wurde bei 77°C in Toluollösung mit Äthyl- 2-Methylpentyl- oder Nonylalkohol mittels *p*-Toluolsulfonsäure als Katalysator partiell verestert. Die Halbester wurden aus den entsprechenden Reaktionsmischungen in Ausbeuten von 28, 34 und 32% nach Reaktionsdauern von 2, 6 and 8 h isoliert. Die zurückgewonnene Brassylsäure und der als Nebenprodukt erhaltene Dialkylester wurden erfolgreich als Ausgangsmaterial für weitere Veresterungen verwendet. Daher würde die Umwandlung der Ausgangsprodukte in Halbester in einem Verfahren mit kontinuierlicher Wiedereinführung der Nebenprodukte erhöht werden. Alkylhydrogenbrassylate wurden mit Acetylen bei 360 psig bei 165° durch 8 h vinyliert. Das in situ mit Zinkoxyd gebildete Zinksalz diente als Katalysator und Toluol al Lösungsmittel. Die Ausbeuten betrugen 80–88% und die Reinheit der Produkte lag bei 94–95%. 2-Methylpentyl-vinylbrassylat- und Nonylvinylbrassylatproben von viel höherer Reinheit wurden durch präparative Gas–Flüssigchromatographie oder Molekulardestillation erhalten. Physikalische Eigenschaften und Versuchsbedingungen für gas–flüssigchromatographische Analysen von Alkylhydrogen- und Alkylvinylbrassylaten werden angegeben.

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Solid-State Polymerization Studies. I. 2-Vinylnaphthalene Post-Polymerization Initiated by ^{60}Co γ-Irradiation

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Synopsis

^{60}Co γ-irradiated 2-vinylnaphthalene was obsreved to post-polymerize in the solid phase. Plots of conversion versus time indicated a 14% limiting conversion of monomer to polymer. The post-polymerization was found to be first-order in monomer with an Arrhenius activation energy of 19.0 kcal./mole.

Introduction

The polymerization of 2-vinylnaphthalene is well documented in the literature. In addition to being polymerized by conventional free-radical initiators, e.g., benzoyl peroxide, the monomer has been polymerized or copolymerized with organolithium compounds[1] and carbonium salts such as tropylium hexachloroantimonate.[2] Koton[3] polymerized the monomer in bulk at 100–10°C. and found the reaction to be unimolecular with an activation energy 18.8 kcal./mole. Yura[4] compared several techniques for the polymerization and found the degree of polymerization followed the order solid phase > emulsion > bulk > solution while the rate of polymerization followed the order bulk > solution > emulsion > solid phase. All the reactions are reported to be unimolecular except the solid-phase reaction, whose order was not determined. Later, Yura[5] polymerized the monomer under pressure in the solid state and found the reaction to be first order.

This laboratory has investigated the kinetic parameters of the γ-induced solid-state post-polymerization of 2-vinylnaphthalene.

Experimental

The 2-vinylnaphthalene was a technical grade obtained from Aldrich Chemical Company. This compound was purified by recrystallizing five times from a 90% aqueous methanol solution. The monomer was then dried in a vacuum desiccator to yield a pure white crystalline compound melting at 67°C. Then 3-g. portions of this monomer were sealed under

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high vacuum in Pyrex ampules and irradiated in a nominally 28,000-c. ^{60}Co γ-facility. The dose rate was determined by the Fricke dosimeter ($G = 15.5$).

Irradiations were performed at −78°C. at intensities from 104 to 161 krad/hr. The samples were post-polymerized in a cryogenic bath at temperatures ranging from −20 to 41°C. At temperatures above 41°C. the reaction rate was too fast to be followed conveniently, and below −21°C. no appreciable polymerization occurred.

There is a major problem in determining the yield of any solid-state polymerization reaction due to the possibility of the polymerization of trapped radicals on solution of the polymer–monomer mixture. In order to circumvent this problem, the polymer in this study was isolated by rapidly dissolving the reaction mixture in benzene that contained hydroquinone and precipitating with excess methanol. However, it appears that a small amount of polymer was formed either during the isolation of the polymer or during irradiation. The polymer was filtered and redissolved in benzene and reprecipitated with methanol and then vacuum-dried to constant weight.

Results and Discussion

Figure 1 shows the post-polymerization of 2-vinylnaphthalene in the temperature range −10 to 24°C. Here the per cent conversion versus time in hours is plotted for an intensity of 161 krad/hr. and a total dose of

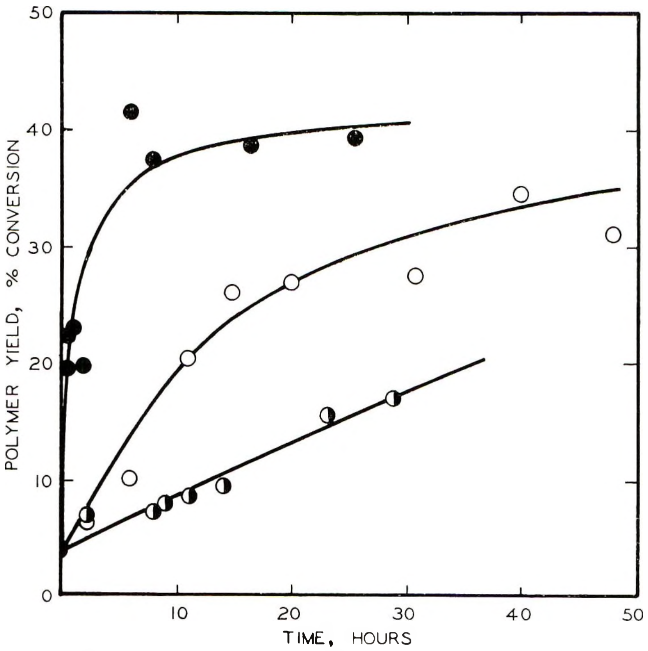

Fig. 1. Polymer yield vs. time for ^{60}Co γ-polymerization of 2-vinylnaphthalene: (◑) −10°C.; (○) 0°C.; (●) 24°C. Dose, 8.7×10^6 rad; intensity, 1.6×10^5 rad/hr.

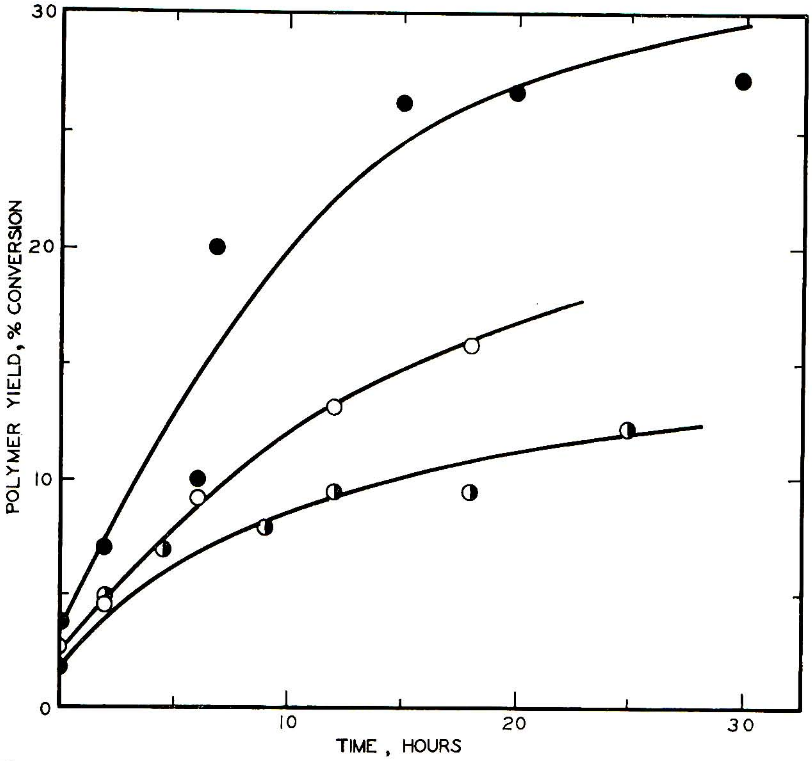

Fig. 2. Polymer yield vs. time for ^{60}Co γ-polymerization of 2-vinylnaphthalene at various doses: (●) 8.7 × 10^6 rad; (○) 7.0 × 10^6 rad; (◑) 5.0 × 10^6 rad. Intensity, 1.61 × 10^5 rad/hr.

8.7 Mrad. Although no data were collected beyond 50 hr. it appears reasonable to assume that the system would approach a limiting conversion of approximately 41%.

In Figure 2 the per cent conversion is plotted against time in hours for an intensity of 161 krad/hr. and doses ranging from 5 to 8.7 Mrad at a temperature of 0°C. This figure shows that the limiting conversion increases with the total dose.

The expression derived by Chapiro[6] for post-polymerization in the gel phase for liquid-phase polymerization is

$$-\,dm/dt = k_p[\mathrm{M}^*][\mathrm{M}] \tag{1}$$

where [M] is the monomer concentration, [M*] is the concentration of the active species at any time *t*, and k_p is the rate constant for the propagation step. Due to the lack of mobility of monomer in the crystal lattice it is conceivable that active polymerization sites could be trapped in regions void of monomer, a portion of the monomer thus being made unavailable for polymerization.† If the assumed limiting conversion of 41% as shown

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† Presently under investigation in this laboratory is a study of validity of the assumption that active polymerization sites are trapped in the polymer matrix.

in Figure 1 is considered to be all of the monomer that is available for polymerization under these irradiation conditions, then $(a - x)$ may be substituted for [M], where a is the limiting conversion of the monomer and x is the amount of monomer converted to polymer. This yields eq. (2):

$$-d(a-x)/dt = k_p[\mathrm{M}^*][a-x] \tag{2}$$

Upon integrating, eq. (2) becomes

$$\ln[a/a-x] = k_p[\mathrm{M}^*]t \tag{3}$$

In Figure 3, log $[a/(a-x)]$ is plotted against time in hours for the data at -10 and 0°C. and shows a linear relationship with slopes equal to $k_p[\mathrm{M}^*]$.

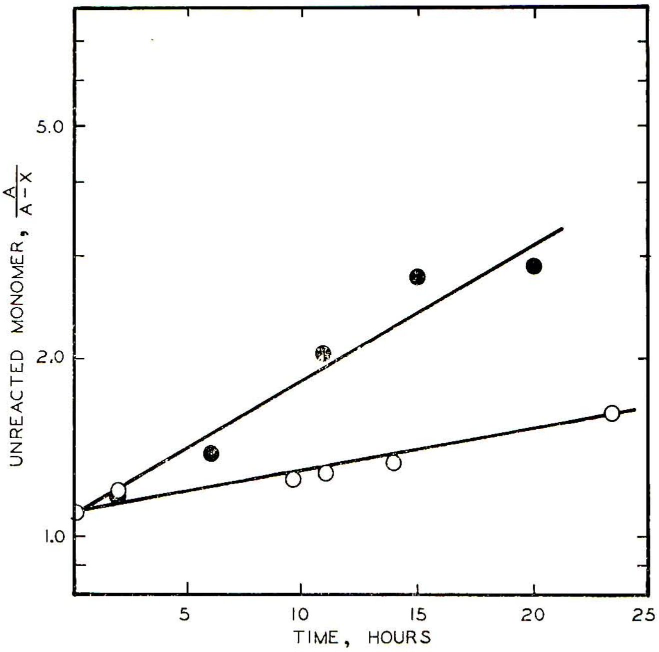

Fig. 3. Log fraction unreacted monomer vs. time for ^{60}Co γ-polymerization of 2-vinylnaphthalene: (O) -10°C.; (●) 0°C. Dose 8.7×10^6 rad; intensity 1.6×10^5 rad/hr.

The linear relationships observed in Figure 3 indicates that the postpolymerization of 2-vinylnaphthalene is first order with respect to monomer. This observation is consistent with the results of previous studies by Yura[5] and Koton.[3] In addition, the concentration of the active species appears to remain constant during the early stages of the reaction.

In Figure 4, the initial rate of polymerization is plotted against the reciprocal of the absolute temperature. The slope yields an Arrhenius activation energy of 19.0 kcal./mole. This activation energy is not significantly different from those of Koton,[3] where the polymerization was initiated thermally in the bulk liquid phase. The value found from these

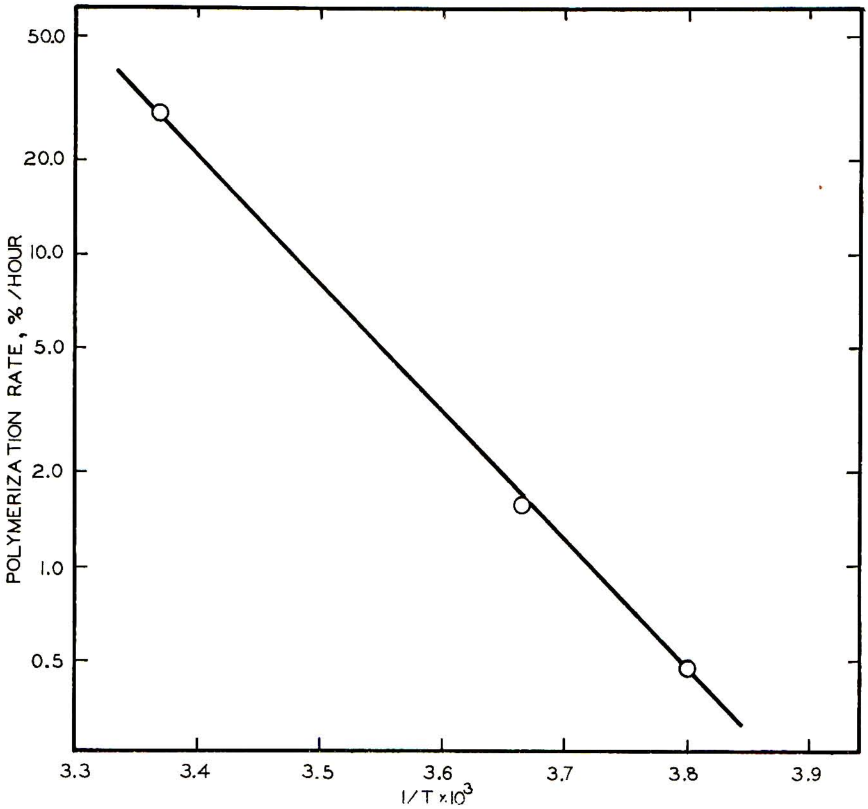

Fig. 4. Initial rate of polymerization vs. reciprocal of absolute temperature for temperature dependency for ^{60}Co γ-polymerization of 2-vinylnaphthalene.

data is similar to activation energies reported for several other vinyl systems that polymerize in the solid state.[7]

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Résumé

On a observé que le 2-vinylnaphthalène irradié par les rayons-γ émis par le Co^{60} postpolymérisait en phase solide. En portant graphiquement le degré de conversion du monomère en polymère en fonction du temps, on a observé un degré de conversion-limite situé à 14%. La postpolymérisation est du premier ordre par rapport au monomère et il lui correspond une énergie d'activation de 19.0 kcal/mole.

Zusammenfassung

Eine Nachpolymerisation in fester Phase wurde bei ^{60}Co-γ-Bestrahlung von 2-Vinylnaphthalin beobachtet. Das Umsatz-Zeitdiagramm liess einen Grenzumsatz von 14% für die Monomer-Polymerumwandlung erkennen. Die Nachpolymerisation war von erster Ordnung in bezug auf das Monomere mit einer Arrhenius-Aktivierungsenergie von 19,0 kcal/Mol.

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Gel Permeation Properties of Cellulose. I. Preliminary Comparison of Unmodified and Crosslinked, Decrystallized Cotton Cellulose

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Synopsis

Decrystallized cotton cellulose was found to have gel permeation properties comparable to those of the highly crosslinked dextran and polyacrylamide gels used in chromatography. Partial separations of pairs of sugars, ranging in molecular weight from 120 to 738, were studied by determining the optical rotations of fractions eluted from chromatographic columns, employing a sensitive automatic polarimeter. The elution volumes of individual sugars of known molecular weights provide a quantitative measure of changes produced in the cellulose polymer structure by crosslinking. A significant difference was found between unmodified cellulose and the same material crosslinked by formaldehyde treatment; although crosslinking reduced permeability to larger molecules, the crosslinked material was found to be more permeable than the untreated cellulose to compounds having molecular weights below approximately 1000.

INTRODUCTION

Methods based upon gel permeation, in which the separation of compounds of a variety of classes is dependent upon their molecular weights, have found wide application in chromatography following the development by Porath and Flodin[1] of crosslinked gel media of graded permeability. These insoluble polymers have the property of swelling in aqueous solutions with imbibition or "regain" of water which occupies pores of differing sizes, making them selectively more permeable to solutes of decreasing molecular weights. The effective ranges of different grades of these polymers are controlled by the degree of crosslinking; regain values range from as high as 20 (g./g. of dry gel) down to approximately 1 in the most highly crosslinked polymers. High regain gels are used for the separation of proteins and other macromolecules, while the grade having minimum regain has been shown to be effective in separating sugars and oligosaccharides of molecular weights up to approximately 1000.

Cotton cellulose, decrystallized by ball-milling, undergoes swelling in water; its regain was found to be somewhat greater than that of a sample of the highly crosslinked dextran which is used as a medium for chromatography. The amorphous cellulose may be used in conventional chromatographic columns for investigation of its microporous structure by determining the gel permeation properties with respect to compounds of relatively low molecular weights and of known molecular structures and dimensions. Sugars and oligosaccharides are ideally suitable for this purpose, being readily soluble in water and compatible with cellulose, to which they are similar chemically. Their high optical activities make it possible to monitor the column eluates precisely with a highly sensitive automatic polarimeter. Crosslinking the cellulose would be expected to have an effect similar to that produced in dextran gels, i.e., narrowing the range of molecular weights to which the material is permeable. Quantitative differences in permeability could thus provide a measure of the effectiveness of various treatments of the amorphous cellulose, and possibly throw light upon the molecular structure of the cellulose polymers.

The objective in gel permeation, as in other chromatographic techniques, is to effect complete separation of mixtures of solutes in a minimum of time. Materials that will permit development of the columns at high rates of flow are especially desirable, and equilibrium of solutes with the gel system is seldom approached and probably never attained under the conditions generally used. For the investigation of cellulose polymer properties and structure, precise determinations of the elution curves for individual compounds are required. A condition essential for interpretation of the results of such measurements is that the solutes approach local equilibrium closely in each horizontal elemental volume of gel material throughout the development of the column. Flow rates of only 1–2 ml./cm.^{2}/hr. were used in this work, with the result that the relationship of elution volume to molecular weight was found to be simpler than that obtained under nonequilibrium conditions.[2–4]

This report describes preliminary experiments in which partial separations of selected pairs of sugars established the gel permeation properties of decrystallized cellulose, permeability of the cellulose particles being less by the higher molecular weight sugar, which is the first of each pair to be eluted. Individual sugars covering the lower part of the range of permeability, of molecular weights of 120–738, were used in systematic determinations carried out with a sample of ball-milled cotton cellulose and with a part of the same material which was crosslinked with formaldehyde to a high level. Empirical measurements by this technique, under standardized conditions, can be used to obtain information on accessibility of the amorphous regions of cotton and changes in accessibility produced by various chemical modifications.

EXPERIMENTAL

Equipment and Methods

Columns 50 cm. long fabricated from ordinary 1.8-cm. (diameter) Pyrex tubing were used in the initial experiments. These were packed with two different samples of unmodified cellulose, designated UM-1 and UM-2, and with one sample of crosslinked cellulose, XL-1. Resistance to flow of water through the densely packed materials resulted in very low effluent rates; the stopcocks fitted to the bottoms of the columns were left open during operation.

Smaller columns of 1.5-cm. diameter precision bore tubing, 40 cm. in length (from Pharmacia Fine Chemicals, Inc.), were used in experiments on comparable samples of unmodified and crosslinked celluloses, UM-3 and XL-2. These columns had fittings designed to permit more accurate introduction of the sugar solutions, and to reduce the volume of effluent below the column packing to 0.3 ml. After the small volume of sugar solution had penetrated the top layer of cellulose, the system was filled completely with water up to the level in the supply reservoir. These flasks were fed in turn by Mariotte flasks which maintained a constant level that could be adjusted to provide the desired rates of flow within the limits possible for each type of column material.

The procedure described by Flodin and Kupke[5] for preparing cellulose columns for zone electrophoresis and recommended for chromatography with Sephadex[6] was followed in packing the columns. A 50-cm. extension tube was used, and the funnel from which the slurry of material was introduced was fitted with a stirrer operating at 1 rpm, ensuring slow and uniform settling of the bed with a horizontal surface at all times. A weighed amount of cellulose with sufficient water to form a thin suspension was agitated for 5 min. in a high-speed blender, and the slurry was poured into the funnel, below which the entire column and extension tube system had been filled with water. A sample of the cellulose was taken at the time of mixing for moisture determination by drying over phosphorus pentoxide, in order to estimate the weight of dry material in each column. As the amount required to form columns of the desired height was not known, an excess was used and packing was terminated when a bed of 25–30 cm. had formed. The suspension above this bed level was decanted quantitatively, filtered, and dried over phosphorus pentoxide to determine its weight, the dry weight in the column being obtained by difference.

The first column, UM-1, had a bed height of only 15.5 cm., but served to demonstrate that partial separation of sugars could be effected. A larger number of experiments were performed with columns UM-2 and XL-1 which had bed heights of 20.0 and 22.7 cm., respectively. The two smaller (1.5 cm. diameter) columns, UM-3 and XL-2, were filled as nearly as possible to the same height, approximately 27 cm.

Rates of development were low, ranging from 1.0 to 2.5 ml./cm.^{2}/hr. in most experiments, necessitated by the high resistance to flow of the columns. A siphon control of the fraction collector used in a few early experiments was replaced by a timing mechanism which was more satisfactory, but did not yield exactly equal volumes for the individual fractions. The fractions were collected in tared tubes, and volumes were determined by weight. This made it possible to determine peak elution volumes more precisely and to correct polarizations to a standard volume for the fractions collected in each experiment. The volumes collected ranged from 2 to 4 ml. in different experiments and sufficed for displacement of the polarimeter cell. Samples of sugars, in amounts ranging from approximately 5 to 25 mg., were applied to the columns in volumes of 0.5, 1.0, or 1.5 ml., which were allowed to sink into the top of the column packing before collection of eluate was begun. Void volumes of all columns were taken to be the elution volumes of blue dextran;[6] this colored, high molecular weight substance also served to show that packing was uniform. Concentrations of solutes in the fractions were determined with the ETL-NPL automatic polarimeter which has a sensitivity and accuracy of 0.0002°. This polarimeter is type 143A, distributed by Bendix Corp. for Bendix-Ericcson, Ltd. Elution curves were established by plotting the polarizations, corrected for variations in volume, at the mid-point of elution of each of the fractions containing sugars. Recoveries of 90–100% were obtained, as measured by the total polarizations in the standard volume for individual sugars or, in the case of mixtures, by the total net polarizations.

Materials

The cotton cellulose samples for UM-1 and XL-1 were prepared from 80 × 80 print cloth which was desized and scoured but not bleached. Material for samples UM-2, UM-3, and XL-2 was desized, scoured, and bleached. The material was decrystallized and reduced to a particle size suitable for use in the columns by grinding in a Wiley mill, followed by ball-milling in a vibratory mill of the type described by Hermans and Weidinger;[7] details are specified for each sample. Crosslinked cellulose samples were prepared by applying the form D treatment with formaldehyde and acid catalyst, as described by Chance et al.,[8] to the decrystallized cellulose. The procedure was essentially the same for both samples XL-1 and XL-2. The cellulose was stirred continuously for 5–5.5 hr. at 23°C. in a solution consisting of 5.4% formaldehyde, 5.4% hydrochloric acid, 70.5% glacial acetic acid, and 18.7% water. The ratio of solution volume to weight of air-dried cotton was 52.8 ml./g. for sample XL-1 and 62.4 ml./g. for XL-2. The suspension of reacted cellulose was concentrated to a slurry by filtration, dispersed in 350 ml. 1*N* NaOH, diluted to 1 liter with ice, and left standing overnight. The treated cotton was separated by filtration and washed with hot tap water, dispersed in 700 ml. of 2% NaOH for 5 hr., filtered, and rinsed with dilute acetic acid followed by distilled water.

Sample UM-1. This was decrystallized by ball-milling 10-g. batches for 4 hr.; approximately 20 g. was used in the short column employed in preliminary experiments. This column was dismantled after having been used for 10 weeks, and an x-ray diffractogram[9] of the dried cellulose suggested a very slight increase in crystallinity over that of the original ball-milled sample.

Sample UM-2. This was prepared by ball-milling 5-g. batches for 2 hr. Approximately 22 g. was used to pack the column to a height of 20 cm.

Crystallinity was nil as determined by x-ray examination of the original material before filling the column.

Sample UM-3. This sample was decrystallized by ball-milling 5-g. batches for 2 hr. as for sample UM-2. A sufficient quantity was prepared so that half of the material could be treated with formaldehyde to produce sample XL-2. The x-ray examination showed this material to be completely decrystallized.

Sample XL-1. A separate batch of print cloth decrystallized as for sample UM-1 by ball-milling 10-g. batches for 4 hr. was treated with formaldehyde to a level of 5.3% CH_2O. Approximately 20.5 g. was required to pack the column to a height of 23 cm.; crystallinity was very low as determined prior to filling the column.

Sample XL-2. This crosslinked sample was prepared from half of the material used for UM-3, treated with formaldehyde to a level of 5.2% CH_2O. Crystallinity was nil, the gel fraction was 1.0,[10] and the distention index was 5.2.[11]

Four of the six sugars used were of high purity, fully adequate for this work, as shown by their specific rotations in a subsequent table. Erythrose is available only in the form of a sirup of about 40% concentration; quantities applied to the columns were determined on the basis of its specific rotation. Fructose and maltose were obtained from Pfanstiehl as Levulose, C.P., Special, and maltose, C.P. grade, respectively. A determination by carbon column chromatography had shown the maltose to contain less than 0.25% glucose. Raffinose was obtained from Calbiochem as A grade (lot 35890). Both stachyose and D-erythrose were products of Nutritional Biochemical Corporation, control Nos. 4849 and 7400, respectively. Glucose was Baker's Analyzed, reagent grade, dextrose, anhydrous. For determining void volumes, blue dextran, molecular weight (avg.) 2×10^6, was obtained from Pharmacia Fine Chemicals, Inc.

RESULTS

Separation of Mixtures

Numerous experiments were conducted with pairs of sugars consisting of a dextrorotatory and a levorotatory compound to establish the mechanism as that of gel permeation. Typical results are illustrated in Figure 1 by the separation of stachyose from erythrose on cellulose sample XL-1. The initial fractions of eluate are dextrorotatory, containing a preponderance of the high molecular weight stachyose, while the final fractions contain principally the small molecules of levorotatory erythrose, to which the cellulose is more permeable. The peak elution volumes indicated by maxima of the dextro- and the levorotatory branches of this elution curve are in the ratios 1.22 and 1.60, respectively, relative to the elution volume of dextran, which was 32.0 ml. for this column. The curve represents the net polarizations of the fractions, most of which are mixtures of the two sugars; therefore, the ratios of elution volumes do not coincide with those that have been obtained for the same sugars individually. Total sugars were determined in aliquots of the fractions by the phenol–sulfuric acid colorimetric method.[12] This resulted in the dashed elution curve of Figure 1, the peak volume of which has a ratio of 1.49 relative to dextran.

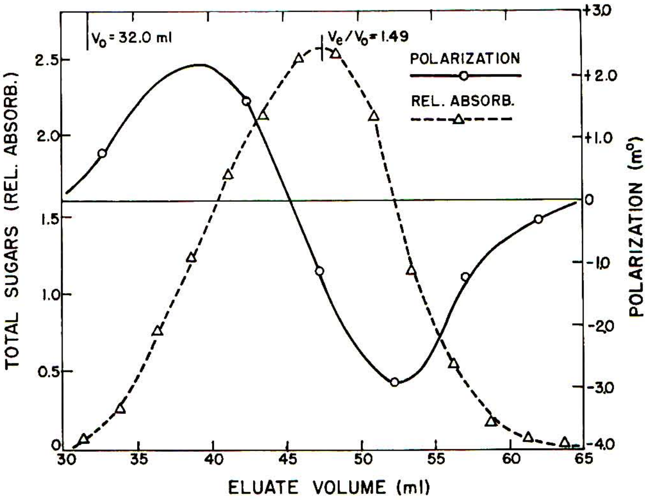

Fig. 1. Partial separation of stachyose (0.96 mg.) from erythrose (3.41 mg.) on column of sample XL-1; (O) curve of net polarization; (△) elution curve of total sugars by colorimetric method.[12]

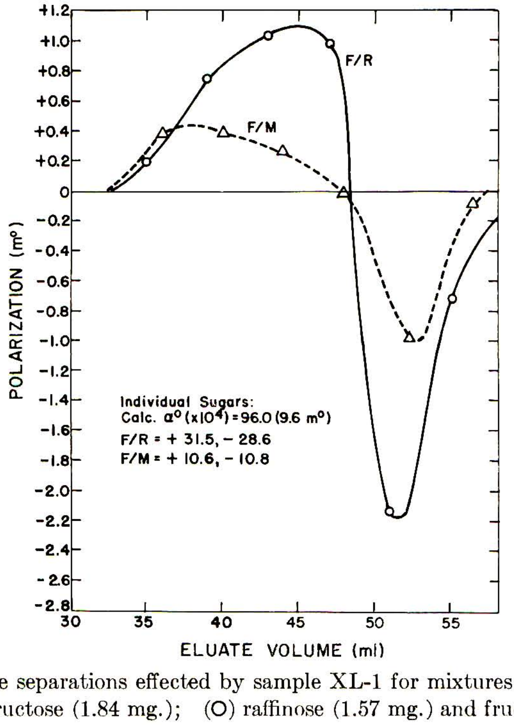

Fig. 2. Percentage separations effected by sample XL-1 for mixtures of: (△) maltose (1.29 mg.) and fructose (1.84 mg.); (O) raffinose (1.57 mg.) and fructose (1.84 mg.).

In Figure 2 are presented the results of two experiments with sample XL-1 on the separation of fructose from raffinose and from maltose, respectively. The quantity of each was so chosen that its total polarization in the fractions collected, corrected to a volume of 4.0 ml., would be 9.6 m° (rotations are expressed in millidegrees; 1 m° = 0.001°). A greater degree of separation of fructose is effected from the higher molecular weight raffinose than from the lower molecular weight maltose. The total net dextro- and levopolarizations obtained by partial separation are approximately equal, since those of the mixtures applied to the column were zero. The values obtained, expressed as a percentage of the calculated total polarization of the individual sugars, 9.6 m°, provide an index of the degree of separation in each case. Separation of the fructose from maltose is approximately 11%, while that from raffinose is approximately 31%.

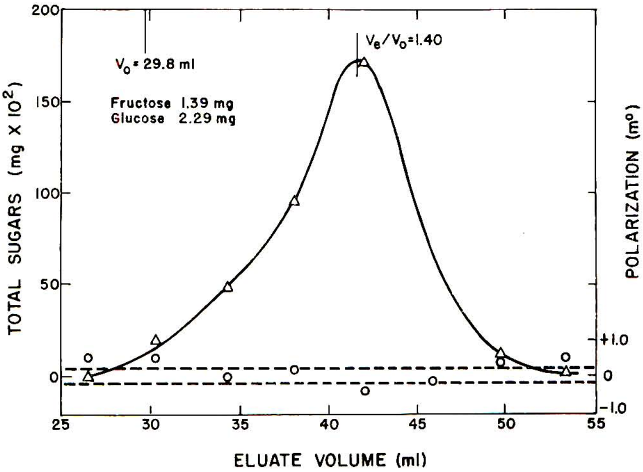

Fig. 3. Elution curve from sample column UM-1 of (O) a mixture of glucose (2.29 mg.) and fructose (1.39 mg.) showing no separation detectable by net polarization of fractions; (Δ) of total sugars determined by colorimetric method;[12] (--) limit of sensitivity of polarimeter ± 0.2 m°.

Evidence that the separation of sugars is governed predominantly, if not entirely, by molecular size was obtained in an experiment with fructose and glucose on sample UM-1, results of which are presented in Figure 3. These sugars were applied as a mixture in the proportions necessary to make the net polarization 0°. None of the fractions obtained had a polarization greater than ±0.5 m°; since the sensitivity of the polarimeter is 0.2 m°, the variations are not significant. The trend toward a small positive rotation in the initial and final fractions is attributable to the larger quantity of glucose which was required to balance the rotation of fructose in the mixture. Elution of total sugars was determined by the colorimetric method.[12] Both sugars have an elution volume ratio of 1.40 relative to that of dextran, determined from the peak volume of this elution curve.

TABLE I
Partial Separation of Pairs of Sugars

		Elution volume ratios referred to V_0				
Samples	V_0, ml.	Stachyose	Raffinose	Maltose	Fructose	Erythrose
UM-1	29.4	—	1.10	—	1.45	—
		—	—	—	1.40	1.40 (Glucose)
UM-2	40.3	—	1.20	—	1.43	—
		—	1.15	—	—	1.39
		—	1.14	—	—	1.38
UM-3	23.0	1.21	—	—	—	1.32
XL-1	32.5	—	—	1.10	1.59	—
		—	1.38	—	1.56	—
		1.22	—	—	—	1.60
		1.28	—	—	1.50	—
		—	1.22	—	1.45	—
		—	1.25	—	1.43	—
XL-2	22.4	—	1.33	—	1.55	—

Data from these and other experiments on the separation of pairs of sugars are assembled in Table I. Consistent results were obtained in effecting separations by molecular size, although the reproducibility of the ratios of elution volumes was not as satisfactory as that obtained with individual sugars in the more precisely constructed columns used with samples UM-3 and XL-2.

Experiments with Individual Sugars

All of the determinations made with individual sugars were conducted with samples UM-3 and XL-2 in the 1.5-cm. diameter columns which had almost identical dimensions. Dry weights of samples used and volumes characterizing each column are assembled in Table II. The volumes are defined as: V_t, total volume of the column occupied by cellulose particles and external water; V_0, external, or void volume measured by the peak

TABLE II
Characteristic Volumes of Cellulose Columns

	Celluloses			
	Unmodified, UM-3		Crosslinked, XL-2	
	Total,		Total,	
Column volumes	ml.	ml./g.	ml.	ml./g.
Total volume V_t	46.60	3.330	47.10	3.440
Void volume V_0	23.00	1.642	22.40	1.635
Solid volume V_s	8.80	0.629	8.62	0.629
Regain volume V_r	14.80	1.059	16.08	1.176
Internal volume V_i	6.93	0.500	9.94	0.760
Weight of solid, g.	14.0	—	13.7	—

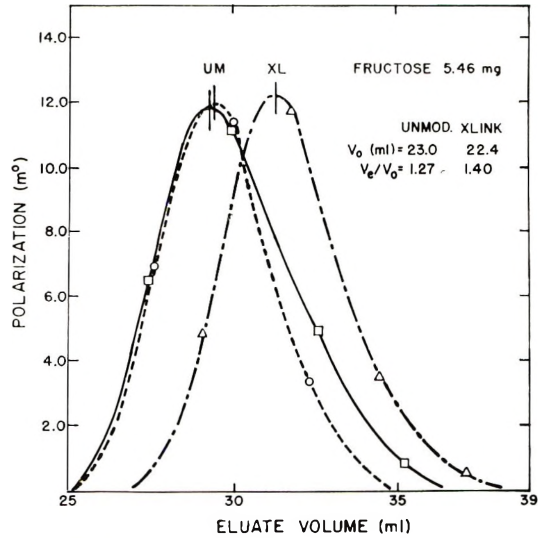

Fig. 4. Reproducibility of determinations of elution volumes V_e for fructose: (△) from sample XL-2 at 1.03 ml./cm.^{2}/hr.; (□) from sample UM-3 at 0.98 ml./cm.^{2}/hr.; (O) from sample UM-3 at 1.41 ml./cm.^{2}/hr.

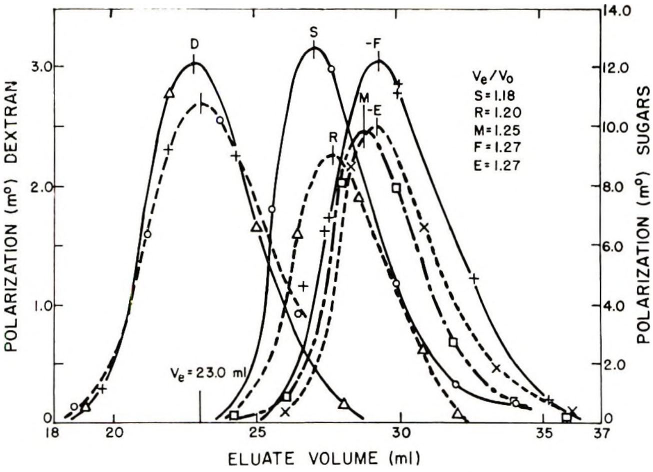

Fig. 5. Elution curves for (D) dextran, (S) stachyose, (R) raffinose, (M) maltose, (F fructose, and (E) erythrose for sample UM-3; V_e/V_0 ratios relative to dextran.

elution volume of blue dextran; V_s, volume occupied by dry solid, estimated from its weight and density; and V_r, total internal water volume, or regain, obtained by difference, $V_t - (V_0 + V_s)$. The molecular density of the solid was assumed to be 1.59, the theoretical value calculated from the unit cell dimensions of crystalline cellulose.[13] The elution volume of an individual sugar is designated as V_e. The effective internal solvent volume, V_i, is less than the regain, V_r, for reasons that will be discussed below, and was obtained from extrapolation of the curves of Figure 7.

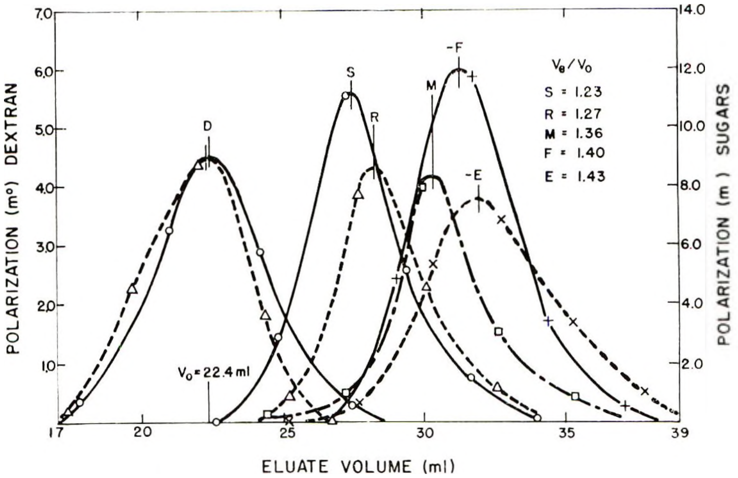

Fig. 6. Elution curves and elution volume ratios for (D) dextran, (S) stachyose, (R) raffinose, (M) maltose, (F) fructose, and (E) erythrose for sample XL-2.

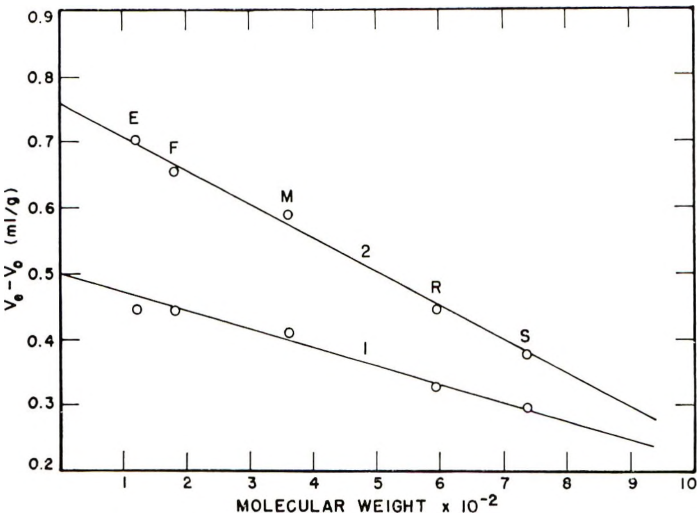

Fig. 7. Relation of ($V_e - V_0$) to molecular weights of the five sugars (E) erythrose, (F) fructose, (M) maltose, (R) raffinose, and (S) stachyose for (*1*) sample UM-3, and (*2*) sample XL-2. Lines are best fit from equations a and b of Table III.

Performance of the smaller columns was checked by a few experiments with pairs of sugars which showed that these samples of unmodified and crosslinked cellulose effected partial separations of pairs of sugars to the same extent as had the columns of samples UM-1, UM-2, and XL-1. The reproducibility with which peak elution volumes could be located is illustrated by the elution curves of Figure 4. This experiment was made with fructose on sample UM-3 to show that the peak elution volume is not altered by changing the rate of flow. A difference of less than 0.2 ml. re-

TABLE III

Elution Volumes of Individual Sugars from Columns of Unmodified and Crosslinked Celluloses

			Sample UM-3					Sample XL-2				
					$V_e - V_0$					$V_e - V_0$		
Sugars	Sugar mol. wt.	$[\alpha°]_{546}^{20°}$	V_e, ml./g.	V_e/V_0	Obs.	Calc.[a]	Diff., %	V_e, ml./g.	V_e/V_0	Obs.	Calc.[b]	Diff., %
Erythrose	120	−48.5	2.086	1.27	0.444	0.466	−5.0	2.340	1.43	0.698	0.703	+0.7
Fructose	180	−104.5	2.086	1.27	0.444	0.449	−1.1	2.290	1.40	0.667	0.654	−1.9
Maltose·$1H_2O$	360	+153.8	2.052	1.25	0.410	0.398	+3.0	2.225	1.36	0.575	0.589	+2.4
Raffinose·$5H_2O$	594	+122.7	1.970	1.20	0.328	0.333	−1.5	2.079	1.27	0.448	0.443	−1.1
Stachyose·$4H_2O$	738	+155.8	1.937	1.18	0.295	0.292	+1.0	2.012	1.23	0.380	0.376	−1.1
Dextran, reference (V_0)	2×10^6	+182.1	1.642	(1.00)	—	—	—	1.636	(1.00)	—	—	—

[a] $V_e - V_0 = 0.500 - 0.282 \times 10^{-3} \times \text{MW}$.

[b] $V_e - V_0 = 0.760 - 0.515 \times 10^{-3} \times \text{MW}$.

sulted from increasing the rate from 0.98 to 1.41 ml./cm.^{2}/hr. Greater tailing of the curve for the low flow rate is attributable to increased diffusion and spreading of the sample band, but this does not affect the peak volume measurement significantly. A determination with the same amount of fructose on the crosslinked cellulose sample, XL-2, resulted in a significantly larger peak elution volume at a rate of development approximately equal to that of the lower rate used with the unmodified cellulose sample, UM-3. These columns had almost equal void volumes, determined with dextran, as shown in Table II. The fructose ratios relative to these void volumes are 1.275 for unmodified cellulose, and 1.405 for the crosslinked sample. Reproducibility of volume measurements is good, in view of the necessity for collecting the eluate in fractions of approximately 2 ml. minimum volumes required for polarization, providing only four or five points for plotting each elution curve.

Parallel series of measurements with each of the five sugars were carried out on the unmodified cellulose, UM-3, and on the crosslinked sample, XL-2. Results are presented graphically in Figures 5 and 6; data for the elution volumes, calculated for unit weight of cellulose samples, and the elution volume ratios are assembled in Table III. Permeability of the celluloses is measured by the volume displacements of the sugars relative to dextran, given by $V_e - V_0$. From data in Table III, the relation of these values for each sample to the molecular weights of the sugars is shown graphically in Figure 7. A simple, inverse linear relation is indicated between $V_e - V_0$ and molecular weights rather than an inverse relation to the logarithm of the molecular weight which is commonly observed in gel permeation studies with columns of dextran or polyacrylamide gels that are eluted at higher rates of flow.[2]

DISCUSSION

The use of cotton decrystallized by ball-milling was dictated by the necessity for reducing the material to a particle size suitable for uniform packing of the chromatographic columns. Fibrous cotton cellulose, of which a maximum of approximately 30–45% may be accessible,[14] was anticipated to provide insufficient internal volume for accurate measurement of differences in peak elution volumes. Accessible hydroxyl groups, whether in regions or on surfaces, are the sites of reaction in treatment of fibers with crosslinking agents. By treating the decrystallized samples with formaldehyde to a high level of reaction, i.e., ca. 5% CH_2O, material was produced which is considered representative of that portion of the fiber which is modified by crosslinking. The possibility exists that the course or extent of reaction may not be the same in decrystallized cotton as that in amorphous regions of fibers, as mechanical degradation during ball-milling causes a reduction of the molecular weight.[15] Experiments with cotton samples treated with formaldehyde prior to ball-milling will be necessary to explore this possibility.

Experiments with pairs of sugars, comprising a high molecular weight dextrorotatory compound and a low molecular weight levorotatory compound, provided the most sensitive means of detecting and measuring partial separations. The degree of separation effected at low rates of flow was not great enough to permit differentiation of the sugars by the colorimetric method of monitoring, as illustrated in Figure 1. Appearance of preponderantly dextrorotatory mixtures in the earlier fractions of eluate, followed by predominantly levorotatory fractions as elution was completed, established the mechanism to be that of gel permeation in which solutes are eluted in the order of decreasing molecular size. Quantitative differences in permeability resulting from crosslinking can be measured empirically by the separation of pairs of sugars applied to the sample columns in the proportions required to make the total net polarization zero. The peak volumes corresponding to the dextro- and levorotatory maxima of the net polarization curves differ from the elution volumes obtained by eluting the same sugars separately and are not simply related to their molecular weights.

The results obtained by eluting sugars and polysaccharides of known molecular sizes and configurations can be used to estimate certain quantitative differences in permeability related to the change in polymer structure produced by crosslinking amorphous cellulose. While the total internal water content or regain value V_r of sample UM-3 is almost as large as that of the crosslinked sample XL-2, the effective internal solvent volumes V_i found by extrapolation of the curves of Figure 7 are 0.500 ml./g. for the unmodified cellulose and 0.760 ml./g. for the crosslinked sample. In the untreated cellulose, 52.8% of the internal water is bound and is not available as effective solvent volume; crosslinking results in a decrease of the proportion of bound water to 35.2%. Blocking of hydroxyl groups by reaction with formaldehyde evidently makes the cellulose less hydrophilic, reducing its water binding capacity and increasing the permeable volume occupied by mobile water solvent. This change is accompanied by alteration of the size distribution of internal spaces or "pores" within the gel. A larger proportion of the internal volume V_i is distributed among spaces that are permeable to the lower molecular weight sugars, while spaces within the unmodified cellulose that were permeable to the largest molecules appear to have been eliminated. Intercepts with the abscissa of the curves of Figure 7 suggest that the limit of permeability is reduced significantly, from a molecular weight of 1775 for unmodified cellulose, to 1475 for the crosslinked cellulose. Both the lower limit of permeability and the larger internal volume V_i of the crosslinked sample tend to increase differences in elution volumes V_e of individual sugars in comparison with those obtained for the unmodified cellulose.

Differences of the observed values of $(V_e - V_0)$ from those given by the linear equations (footnotes a and b in Table III) are within the limits of experimental error, in view of the possible variations to which the measurements are subject: e.g., the small columns were not jacketed to maintain constant temperature, and evaporation from the eluate during collection periods ranging up to 20 hr. did not affect the weights of the fractions equally. A compromise was necessary in collecting the minimum volume of 2 ml. of each fraction required for displacement of the small polarimeter cell, and for obtaining four to six points for plotting the elution curves from which elution volumes were estimated. Rates of flow and the technique for determining successive polarizations of the fractions collected were kept as nearly identical as possible for determinations with all five sugars on each of the columns; variations for individual points did not greatly affect the reproducibility of the elution volumes estimated from the peaks of the curves.

The accuracy of determinations of the complete elution curves will probably be improved by use of larger columns jacketed to maintain constant temperatures, by continuous monitoring of the eluates for individual sugars with a differential refractometer, or by polarimetric determinations for a larger number of fractions. More significant data pertaining to the dimensions of permeable spaces occupied by water within the cellulose polymer particles may be obtained by analysis of such elution curves, from which heats of sorption and other thermodynamic relationships may be calculated.[16] It is unlikely that the inverse linear relationship of relative elution volumes to molecular weights of the sugars can be attributed to diffusion of solute molecules into the gel through cylindrical, or otherwise geometrically simple and uniform pores, or that the distribution of solute under equilibrium conditions would be a function of molecular and mean pore radii.[17] By analogy with the mechanism that has been established for sorption by molecular sieves,[18] a more plausible explanation would be that the observed selective sorption of the sugars is due to the high capacities of both cellulose[19] and sugars[20,21] for hydrogen bonding of water. A particular sugar will reach equilibrium in permeating the cellulose polymer gel when it occupies those spaces within the internal solvent volume in which steric restriction of the molecules is such that translational, and possibly one or more rotational degrees of freedom are replaced by vibrational degrees of freedom.[16] Under these conditions, the equilibrium distribution of solute between the available internal solvent and the surrounding solution would be related simply to the size of the sugar molecule, i.e., its molecular weight.

From thermodynamic data on the sorption of sugars and oligosaccharides of increasing molecular weights up to the limit of permeability of cellulose, it should be possible to make useful inferences as to the molecular dimensions and structure of the cellulose polymer which forms the gel matrix. Actual distances between polymer chains would be greater than those calculated from internal spaces of the sizes necessary to restrict the solute molecules, because of the intervening layers of water molecules bound by both the cellulose and the sugar molecules. It is planned to extend this study with suitable homologous series of oligosaccharides, and to develop a theoretical basis for detailed interpretation of the data obtainable from their characteristic elution curves.

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Résumé

La cellulose de coton décristallisée présente des propriétés d'imprégnation de gel comparables à celles du dextrane fortement ponté de des gels de polyacrylamide utilisés en chromatographie. La séparation partielle de paires de sucres, d'un poids moléculaires variant de 120 à 738, a été étudiée en déterminant les rotations optiques des fractions éluées sur des colonnes chromatographiques, un utilisant un polarimètre automatique sensible. Les volumes d'élution des différents sucres de poids moléculaire connu, fournissent une mesure quantitative des variations produites dans la structure de polymère cellulosique par le pontage. Une différence importante a été trouvée entre la cellulose non modifiée et la même substance pontée par traitement au formaldéhyde. Bien que le pontage réduise la perméabilité à l'égard de molécules plus grandes, la substance pontée est plus perméable que la cellulose non traitée aux composés ayant des poids moléculaires situés en-dessous de 1.000.

Zusammenfassung

Dekristallisierte Baumwollcellulose besitzt, wie gefunden wurde, Gelpermeationseigenschaften, die mit denen hochvernetzter Dextrane und Polyacrylamidgele, wie sie in der Chromatographie verwendet werden, vergleichbar sind. Die teilweise Trennung von je

zwei Zuckern mit Molekulargewichten zwischen 120 und 738 wurde durch Bestimmung der optischen Drehung der aus den Chromatographiersäulen eluierten Fraktionen untersucht, wobei ein empfindliches automatisches Polarimeter verwendet wurde. Die Elutionsvolumina einzelner Zucker bekannten Molekulargewichts stellen ein quantitatives Mass für die Veränderungen dar, die durch Vernetzung in der Polymerstruktur der Cellulose hervorgerufen werden. Ein bedeutender Unterschied wurde zwischen unmodifizierter Cellulose und demselben Material nach Vernetzung durch Behandlung mit Formaldehyd gefunden: Obwohl die Vernetzung die Permeabilität für grossere Moleküle herabsetzte, wies den Ergebnissen zufolge das vernetzte Material für Verbindungen mit einem Molekulargewicht unterhalb etwa 1000 eine höhere Permeabilität als die unbehandelte Cellulose auf.

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Effect of Chemical Reagents on the Fine Structure of Cellulose. Part IV. Action of Caustic Soda on the Fine Structure of Cotton and Ramie

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Synopsis

An x-ray study has been made of the changes in lateral order that take place on the treatment of cotton and ramie with different concentrations of caustic soda at 0 and 20°C. When mercerization conditions are reached it is found that there is an increase in lateral disorder in the fibrils. The x-ray diagrams from samples treated in the higher concentrations of caustic soda reveal a residual diffraction effect that can be interpreted in terms of a special type of cellulose sheet. This result implies one extreme of lateral disorder that is present in the fine structure of these materials. Indication is given how these lateral disorder phenomena can affect reactivity.

INTRODUCTION

The modern views on the fine structure of cotton and other native cellulosic fibers have been reviewed by Warwicker et al.,[1] and it has been shown that the current fringe-micellar theory is no longer tenable. In replacement of this theory it became clear that cotton and ramie have to be regarded as built from elementary fibrils about 100 A. thick with a possibility that even these units may be aggregates of a smaller unit 35 A. thick.[2] On the basis of such elementary fibrils it is clear that the thickness is commensurate with the thickness of a single crystallite in the older fringe-micellar theory. The only question that then arises is whether extensive disordered regions exist along the length of the fibril, and the consensus of evidence now shows that, even along the length, the disordered regions can only be amicroscopic (i.e., less than 50 A. long). The disorder in these amicroscopic regions is more of the nature of imperfections in crystallites than of gross disorder as envisaged by the so-called amorphous regions in the fringe-micellar theory. The elementary fibrils must therefore be considered as crystalline along their length with small regions of imperfection at intervals. As a further corollary, these crystalline elementary fibrils are thought to be more perfect near their core, with imperfection in the position of chains near their surface that allows reaction to take place. For this reason Ruck[3] prefers to describe this model of structure as a cable model, since he envisages the different layers in the elementary fibril as layers of wrapping round a cable. It would seem, however, simpler to call this model the crystalline fibril theory, provided that it is realized that these fibrils can contain deviations from perfect crystalline order. Of importance, therefore, is a measure of the imperfections and also a measure of the accessibility to the imperfect surfaces where reaction can take place. In cotton and ramie there is a void distribution that allows a limited accessibility to different sized molecules, and such a void distribution can be altered by treatment of cotton and ramie, particularly by swelling agents, so that some way of defining this system of holes is necessary.

Superimposed on this fine structure is the morphology of each particular fiber, which itself can modify reaction on native fibers as pointed out in a previous paper.[4] In the present paper, however, attention is paid to the fine structural features of cotton and ramie and an attempt is made to produce concepts and parameters that will help to define the fine structure outlined above, as well as to show how this structure is modified by the use of caustic soda as a swelling agent.

The study of the disorder is made from an examination of x-ray diagrams, and accessibility is defined in relation to moisture sorption. Further development of the ideas outlined in this paper is in progress, and therefore this paper is preliminary to a more extensive study of fine structure of cotton.

EXPERIMENTAL, RESULTS, AND DISCUSSION

Details of Samples

The Texas cotton used for these experiments was pressure-scoured and solvent-extracted. It was found to be essentially pure cellulose, and the outer cellulosic primary wall was intact. The ramie was given a mild bleach and also solvent-extracted; it consisted of a single cellulose wall with an S-twist 6° to the axis. Further details of these samples are given in a previous paper,[4] in which the treatment with caustic soda and subsequent washing and drying treatments are described.

Width-Swelling Measurements

A determination of the amount of swelling that each sample had undergone was made by the microscopical measurement of the width swelling of fibers of cotton and ramie in different concentrations of caustic soda at 0 and 20°C. The measurements with cotton were made at the widest part of the hair. Each determination was the mean of 200 separate measurements.

The curves for ramie (Fig. 1) have the same shape at 0 and 20°C. It is well known that the width swelling[5] of cotton hairs is restricted by the presence of the primary wall and greater swelling can be achieved if this is ruptured. The sharper peak for the width swelling of cotton (Fig. 2) with caustic soda of concentrations 2–5N at 0°C. is connected with the bursting of the primary wall during swelling[4] in this range of concentration. It is

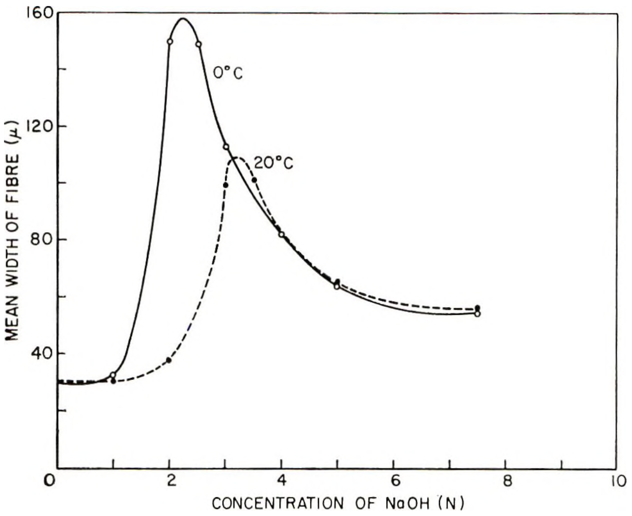

Fig. 1. Width swelling of ramie in caustic soda solutions.

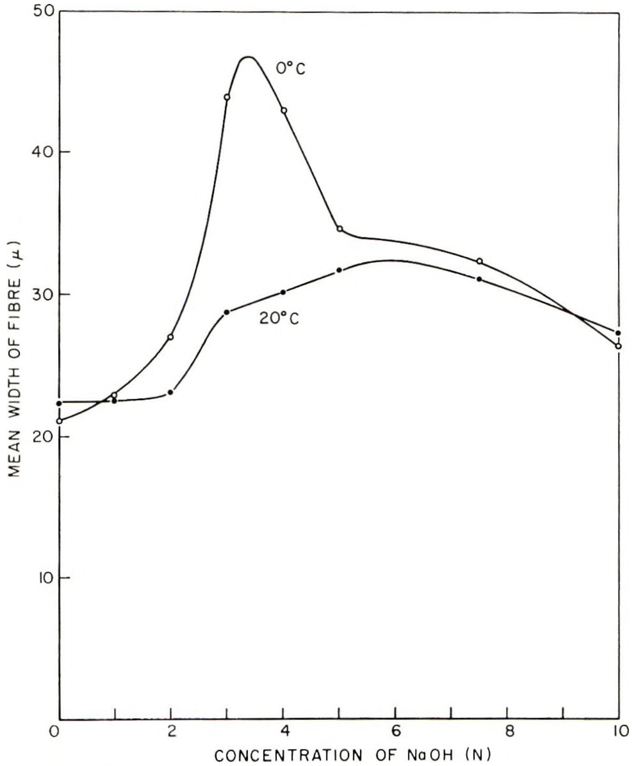

Fig. 2. Width swelling of cotton hairs in caustic soda solutions.

also clear that for the higher concentrations of caustic soda the width swelling of cotton is little affected by temperature differences.

Moisture Sorption

Treatment of samples of native cellulose with caustic soda brings about a product that has a greater reactivity only if the reagent has a swelling action. One method of measuring the accessibility of the structure to such reagents is by water sorption. A simple method of recording the water sorption is by measurement of the moisture content defined as the percentage water content of the sample in equilibrium with an atmosphere of 66% R.H.

All samples were therefore conditioned to 66% R.H. in a chamber over saturated aqueous sodium nitrite solution at 20°C. The moisture content was determined by heating weighed samples to 110°C. for 16 hr. and determining the dry weight on cooling. The results are shown in Figure 3. All curves show similar features, i.e., a rapid rise in moisture content after a definite concentration of caustic soda had been used. The concentrations of caustic soda at which this change occurs are lower at 0 than at 20°C. and corresponding changes for ramie occur at lower concentrations than for cotton. With ramie for concentrations where complete mercerization appears to have been achieved (about $4N$ sodium hydroxide), the changes produced in the structure do not produce large differences in moisture sorption either by the use of higher concentrations of caustic soda or by a change in temperature. Cotton is not greatly affected by the temperature of treatment for concentrations of caustic soda greater than $7N$, but between $4N$ and $7N$ there is a greater change of moisture sorption with cotton

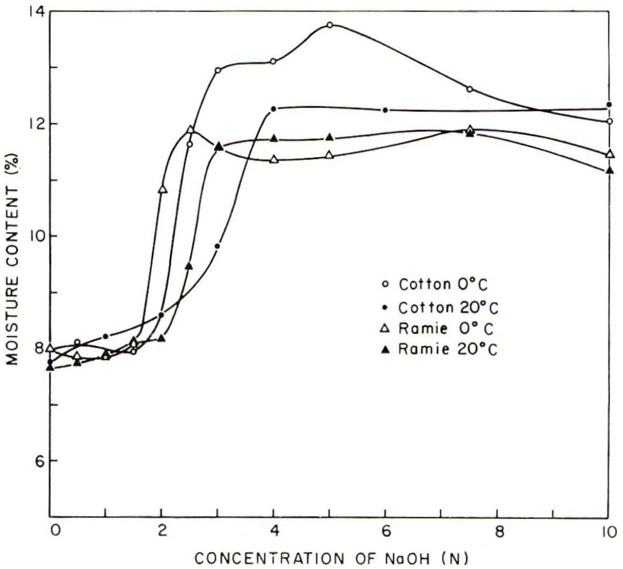

Fig. 3. Moisture content of cotton and ramie after treatment with caustic soda.

than with ramie at 0 than at 20°C. The technical use of high concentrations of caustic soda in mercerization processes to eliminate temperature effects is thus explained. The greater reactivity of cotton at 0°C. after treatment with caustic soda of 2–5*N* concentration is also probably associated with the bursting of the primary wall that occurs under these conditions.[4]

X-Ray Diffraction

Most of the details of the preparation of the equatorial scans from the x-ray diagrams were essentially similar to those described in a previous paper on azimuthal scans.[4] However, for the present purpose a semi-cylindrical camera of radius 5.73 cm. was used which was fitted with a narrow vertical subsidiary camera containing a standard cellulose I sample. A portion of the film was blanked off during exposure and a step-wedge was subsequently superimposed on this portion of film. Thus the final x-ray photograph gave in addition to the pattern to be investigated, a narrow vertical powder pattern of cellulose I and a step-wedge.

The main pattern was measured on a microdensitometer along the equator across the principal peaks for values of 2θ between 8° and 32°. The standard cellulose I pattern and the step-wedge also were measured. All densities could be converted to intensity units by reference to the step-wedge, and an allowance for the scatter background was made. Reference to the intensity of the main peak of the standard cellulose I pattern allowed all the photographs to be placed on a comparable scale of intensities. However, a further complication arises because of the known differences in x-ray orientation of the different specimens,[4] and a correction factor was required to allow for orientation differences if comparison of equatorial scans was to be carried out.

The orientation correction was derived from a consideration of the diffraction conditions.

It is considered that the intensity arises from a distribution of reciprocal lattice points on a sphere. The diffracted beam that produces the given reflection corresponds to the intersection of this sphere with the sphere of reflection. If a narrow band of the sphere is considered and the density of reciprocal lattice points is given by $f(\phi)$, the number of reciprocal lattice points in the band is $f(\phi)\delta A$, where δA is the area of the band. Now from Figure 4,

$$\delta A = 2\pi d^* \cos \phi \, d\phi$$

The total number of reciprocal lattice points on the sphere is:

$$N = 2\pi \, d^* \int_{-\pi/2}^{+\pi/2} f(\phi) \cos \phi \, d\phi$$

The measured intensity at a point in the arc corresponding to ϕ is proportional to $f(\phi)$.

Thus

$$N \alpha\ 2\pi d^* \int_{-\pi/2}^{+\pi/2} I(\phi) \cos \phi \, d\phi$$

d^* will be the same for all diagrams at the same value of 2θ, and since comparison of intensities at different values of 2θ is not required, it can be ignored.

Thus if each value of I on an azimuthal scan is multiplied by $\cos \phi$ and the result plotted against the azimuthal angle ϕ, the area under this derived curve gives the required integral. In practice it is only necessary to consider half the azimuthal curve from the center at maximum intensity to zero at the tail, and if the orientation of all arcs is considered to be the same then only the 002 azimuthal scan need be used. Since experiments have shown that this latter assumption is valid the final correction was derived from the 002 azimuthal scan for the given experiment. This scan was first scaled to give the same maximum intensity as that for the corresponding equatorial peak, the values of I multiplied by $\cos \phi$ and the area under the curve from the centre outwards then found. A convenient parameter to represent this area was the integral breadth derived by dividing the area by the total height of the peak. If the intensities of the equatorial scan are multiplied by this integral breadth all equatorial scans are then free from differences due to orientation factors.

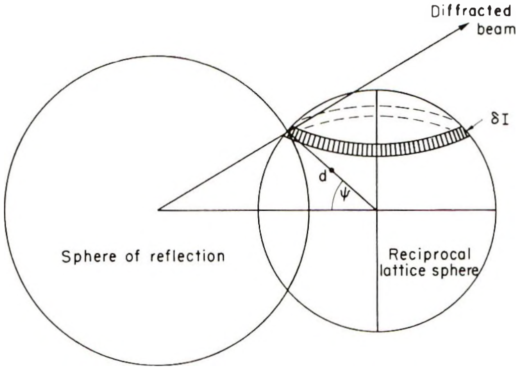

Fig. 4. Diffraction conditions for the orientation correction.

Analysis of Equatorial Scans

Changes in the equatorial scans from those derived from x-ray diagrams of cellulose I do not occur until a given concentration of caustic soda has been used: this concentration is different for the different native celluloses. For ramie changes can be detected in the equatorial scans with samples treated with 2.5N caustic soda at 20°C. or 2.0N caustic soda at 0°C. Corresponding concentrations of cotton are 3.0N at 20°C. and 2.0N at 0°C.

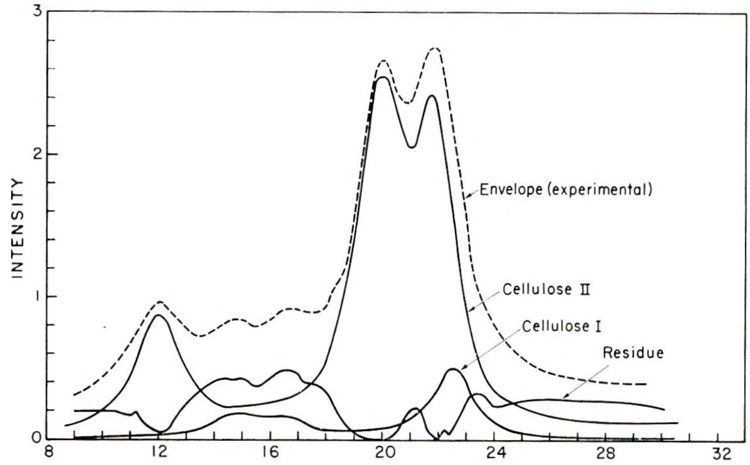

Fig. 5. Equatorial scan from cotton treated with 4N caustic soda at 20°C.

To effect an analysis of the scans from the remaining samples that could be mixtures of cellulose I and cellulose II, the equatorial scan from untreated ramie was taken as that for cellulose I, and an equatorial scan from Fortisan, a highly oriented cellulose II, was taken as the standard cellulose II scan.

The justification for the use of these equatorial scans from ramie and Fortisian to represent cellulose I and cellulose II lies in the fact that an analysis of them by a method similar to that described by Gjönnes et al.[6] has shown that these scans can be decomposed into crystalline peaks only, with little if any residual diffraction from other structural components. The implication of this fact for native celluloses has been dealt with by Gjönnes et al.;[6] the implication for Fortisan is similar and will be published with other data later.

It is possible to fit these two scans in different ratios to the experimental scans so that the majority of the envelope is fitted by the sum of the two standard scans. This fitting procedure was largely done by trial and error, but an indication of the correct ratios of the two standard scans can be obtained from the experimental scans by noting that the scan of cellulose I makes only a small contribution to the intensity at $2\theta = 12°$, whereas the scan of cellulose II gives an appreciable contribution. Every equatorial scan for samples treated with caustic soda at concentrations above those necessary for changes to be detectable was analysed in the way described; Figure 5 shows an analysis for cotton treated with 4*N* caustic soda.

The result of this analysis showed that in almost every case the envelope could be analysed into three components, cellulose I, cellulose II, and a residual component. The quantities of each component in any given envelope depended on the sample. The cellulose I fraction could not be detected for the ramie samples treated with 2.5–5.0*N* caustic soda at 0°C.

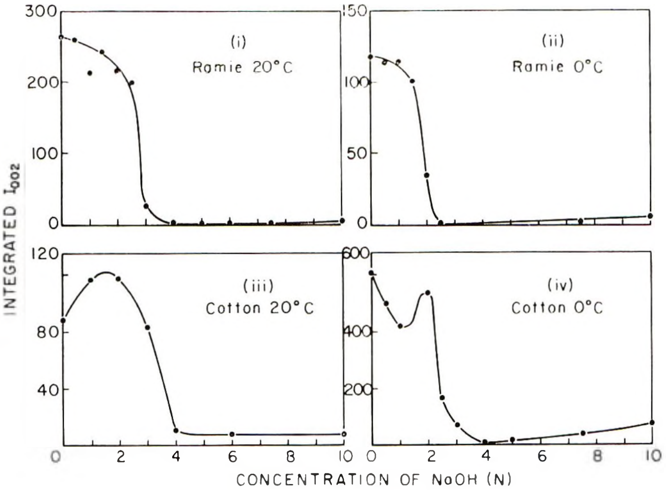

Fig. 6. Cellulose I content of samples of ramie and cotton treated with caustic soda.

but it was detected for ramie treated with higher concentrations. Cellulose I fractions, however, were detected in all cotton samples at 0 and 20°C. in which changes brought about by caustic soda were detected, and also for corresponding samples of ramie at 20°C. The implication from this is that even under the best mercerizing conditions with loose fibers, complete change of crystal lattice from cellulose I to cellulose II does not occur with cotton, and only for a restricted range of caustic soda concentrations at 0°C. for ramie.

Since it is possible to separate the contribution of the cellulose I from the total contribution it is possible to determine lateral order according to the method of Marchessault and Howsmon.[8] To apply this method it is necessary to give a quantitative measure of the cellulose I content at different concentrations of caustic soda. The equatorial scans corrected in the way described should be comparable with one another, so that a measure of the cellulose I content can be obtained by determining the integrated intensity of the 002 peak. A quantity proportional to this integrated intensity is found by multiplying the height of the (002) peak, after orientation correction, by the half width of the 002 peak of the equatorial scan. The 002 peak is almost free from overlap of other reflections, and so the half width measured in degrees (2θ) on the original scan is close to the correct half width of a separated peak. One assumption had to be made that the separated cellulose I fractions had the same half width of the 002 peak as the original standard scan. Although this assumption may be in error, it cannot have a large effect on the subsequent values, especially when taken in relation to the values that can be directly determined.

The integrated intensities of the 002 peak were then plotted against caustic soda concentration; the results are shown in Figure 6 and in Tables I–IV.

TABLE I

Ramie at 20°C.

Sodium hydroxide, N	Half width 002 (2θ)	I_{002}	Integrated intensity ×10	Slope
0	1.0°	26.6	266	−1.2
0.5	1.0°	26.2	262	−1.6
1.0	0.9°	23.4	211	−2.4
1.5	0.9°	25.8	245	−3.6
2.0	0.95°	24.0	216	−4.8
2.5	0.9°	20.87	198	−8.8
3.0	0.9°	3.17	28	−14.4
3.5	—	—	—	−1.6
4.0	0.9°	0.87	8	
5.0	0.9°	0.69	6	
7.5	0.9°	0.51	5	
10.0	0.9°	1.96	20	

TABLE II

Ramie at 0°C.

Sodium hydroxide, N	Half width 002 (2θ)	I_{002}	Integrated intensity ×10	Slope
0	1.00°	11.9	119	−0.4
0.5	0.95°	12.0	114	−0.8
1.0	1.10°	10.5	115.5	−1.4
1.5	1.20°	8.45	101	−3.4
2.0	0.90°	4.08	36.7	−12.6
2.5	—	—	—	−0.8
3.0	—	—	—	0
4.0	—	—	—	
5.0	—	—	—	
7.5	0.9°	0.40	3.6	
10.0	0.9°	0.69	6.2	

TABLE III

Cotton at 20°C.

Sodium hydroxide, N	Half width 002 (2θ)	I_{002}	Integrated Intensity ×10	Slope
0	0.90°	9.8	88	+2.4
1.0	0.90°	11.9	107	+1.2
2.0	0.90°	12.0	108	−1.0
3.0	0.85°	9.9	84	−6.2
4.0	0.9°	1.22	11	−1.2
5.0	—	—	—	0
6.0	0.9°	0.85	8	
10.0	0.9°	0.86	8	

TABLE IV
Cotton at 0°C.

Sodium hydroxide, N	Half width 002 (2θ)	I_{002}	Integrated intensity $\times 10$	Slope
0	0.9°	68	612	−22
0.5	0.9°	55.5	500	−22
1.0	0.95°	40.75	387	−3
1.5	0.8°	52	416	+21
2.0	0.9°	60	540	0
2.5	0.8°	21.1	169	−47
3.0	0.9°	7.90	71	−10
3.5	—	—	—	−7
4.0	0.9°	0.48	4	0
5.0	0.9°	1.94	17	
7.5	0.9°	4.69	42	
10.0	0.9°	9.03	81	

It is seen that the integrated intensity of the 002 reflection for ramie always decreases with concentration of caustic soda at 0 and 20°C., even when changes in the shape of the cellulose I pattern cannot be detected, i.e., at concentrations below 2.0 and $2.5N$, respectively. This result implies that some cellulose I crystalline material has been removed from the total structure. Such a removal could be by the splitting or by an increased disorder of the fibrils so that the coherent cellulose I structure is decreased, especially if the surfaces are the sites of disordered chains.

With cotton at 20°C., on the other hand, there is an increase in the integrated intensity of the 002 reflection, followed by a decrease before the critical concentration ($3.0N$) is reached. Somewhat similar results with cotton have been reported by Nelson and Mares.[9] At 0°C. the corresponding graph is more complicated [Fig. 6(*iv*)] but still retains a region where an increase in the integrated intensity of the 002 peak occurs. Thus caustic soda has an effect on the fine structure of cotton before any penetration of the fibrils with subsequent change in crystal lattice takes place. It is suggested that these changes are associated with the penetration of the finer voids of the structure by caustic soda allowing a better re-ordering of the chains on the surface of the fibrils, i.e., by interfibrillar swelling, but the difference in behavior from that of ramie must in some way be connected with the difference in morphology of the two fibers. The more complicated behavior of cotton at 0°C. is probably due to the splitting of the primary wall that is known to occur in concentrations of caustic soda around 2.0–$3.0N$.

These graphs also clearly define the transition range over which a change of crystal structure from cellulose I to cellulose II takes place. The slope of these curves at different concentrations of caustic soda were determined and the Marchessault and Howsmon[8] type of analysis was applied. The final slope was given in units of intensity per unit of concentration (normal-

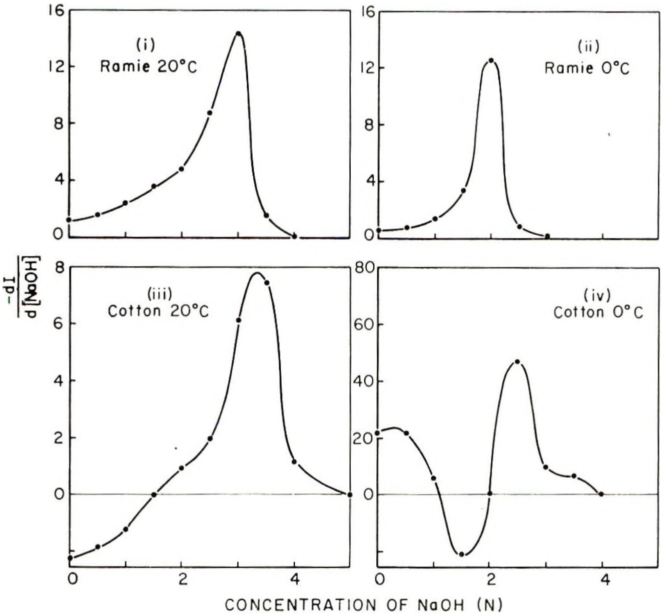

Fig. 7. Lateral order distributions derived from equatorial scans for samples of ramie and cotton treated with caustic soda.

ity). The slope is usually negative, but due to the changes discussed above there are regions of positive slope for cotton. A plot of the slope against caustic soda concentration gives the distribution curve necessary for the Marchessault and Howsmon analysis (Fig. 7). The general conclusion that can be deduced from these curves is that the width of the main peak of distribution is small, and hence the distribution of order of both cotton and ramie is narrow. Similar curves (Fig. 8) can be derived from the moisture sorption results and bear out this general conclusion. It may also be deduced that the distribution of order in ramie is narrower than that in cotton. However there are differences between the distribution of order found by the use of results for experiments done at 0 and 20°C. so that there must be other complicating factors than would be expected from a straightforward application of the Marchessault and Howsmon analysis.

Although this type of analysis gives information with regard to the fine structural changes taking place before and during the transition of the cellulose I crystal structure to that of cellulose II, it does not give information about the lateral order and fine structure of the mercerized cellulose. This information can be obtained from the difference scans for those experiments in which caustic soda concentrations have been used beyond the transition range. The equatorial scans from these experiments show that the main component is that of cellulose II, but the difference scans show clearly that there are residual diffraction effects that only in small part can be attributed to a cellulose I component. This residual component was not

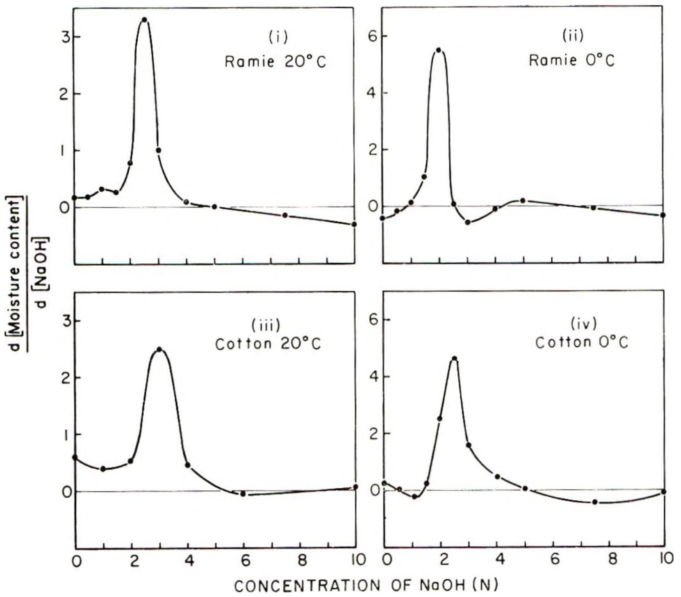

Fig. 8. Lateral order distributions derived from moisture contents for samples of ramie and cotton treated with caustic soda.

very easily detectable in the early stages of the transition but was clearly present for all other samples treated with higher concentrations of caustic soda for ramie and cotton at 0 and 20°C.

Such an analysis as described above is illustrated in Figure 5. The residual effects for $2\theta > 22°$ can be attributed to the neglect of peaks that are known to occur in this region. Similarly the values of the residues for $2\theta < 8°$ are partly due to diffraction effects again not included in the analysis. The most important features to discuss are the peaks in the difference scan at $2\theta = 12$–$19°$ and that centered about $2\theta = 21°$. The latter peak arises because the cellulose II pattern of Fortisan is more resolved than that of the cellulose II fraction of the experimental material, i.e., the $10\bar{1}$ and 002 peaks are broader for the experimental material than the corresponding peaks from Fortisan used in the analysis; this is quite evident by an examination of the total envelope of diffraction given by the experimental material. If, therefore, a cellulose II pattern had been subtracted with the correct breadth of peaks indicated by the envelope then the peak in the difference scan centered at $2\theta = 21°$ would be eliminated, the residual effects for $2\theta > 22°$ and $< 8°$ could be reduced but the broad residual peak at $2\theta = 12$–$19°$ would still remain although sharpened and reduced in intensity. The presence of such a residual diffraction effect has already been suggested by Gjönnes, Norman, and Viervoll[6] in their analysis of the diffraction pattern from mercerized wood pulp. These authors attribute this residue to the presence of amorphous material having a diffraction pattern similar to that given by dry-ground cellulose. In the present case the residue is from highly oriented material and it is unlikely that it represents completely disordered material.

A possible explanation of the residual peak with $2\theta = 12°-19°$ is that it arises from the presence of material that diffracts in the manner of isolated cellulose sheets of the type described by Warwicker and Wright.[7] These sheets are composed of cellulose chains with their hydrophobic surfaces in contact and the hydroxyl groups projecting from the surface of the sheet, i.e., the sheets are one chain thick and extend by the piling of chains on top of one another. Such an aggregate could give a peak in the region discussed and the residual peak then would be an indication of the residual quantity of sheets that have not properly integrated into a crystalline arrangement. If this explanation is correct, this residual peak then indicates a special type of disorder in which there is good order in two dimensions, but poor lateral order in the third direction, i.e., it is the extreme case of the lateral disorder present in the structure after swelling. By the position of the diffraction peak produced from these sheets, their essential structure is probably that found in the structure of cellulose I which is built up from such sheets, and not that found in the structure of cellulose II. For the observed diffraction effects it is, however, only necessary for the sheets to be isolated in the sense that coherent diffraction cannot take place between the surface of the sheet and the cellulosic layer next to it, i.e., that a cleavage has taken place in successive (101) planes causing a cellulose sheet to be isolated by minute cracks, the size of which need only be of the order of one wavelength ($\lambda = 1.54$ A.) wide. This means that the sheet isolated in this way can exist within a fibril and not be a separate entity. It is also plausible that a similar explanation can be given for dry-ground cellulose where it can be envisaged that the disorder is between sheets of chains, i.e., disorder in the (101) planes of the crystal structure only, and not completely random chains as the term "amorphous" implies. If this explanation of dry-ground cellulose is correct, then the explanation by Gjönnes et al.[6] and the one given here are virtually identical. Further work to give a more mathematical treatment of this concept is in progress.

The samples that give a cellulose II pattern thus have two types of lateral order, one that results in a broadening of the peaks of the cellulose II pattern, and one that arises from a complete disruption of the crystalline lattice sufficient to virtually isolate individual sheets of cellulose. The broadening of the peaks can arise either by lateral disorder or by a diminution of the fibrillar width: probably both factors play a part, and the factor of diminution of size can also be connected with the isolation of sheets in the manner discussed. Thus the lateral disorder forms a spectrum of disorder. Work is now in progress to attempt to express this disorder in terms of the breadth of peaks and to devise some measure of the residual diffraction peak.

These diffraction effects just described were found with all samples of cotton and ramie treated with caustic soda of concentration $4N$ or above at 0 and 20°C. The total envelopes from these scans, however, show variations in shape due to the varying cellulose I contents of the samples; an estimate of these can be obtained by reference to Figure 6. Once these cellulose I fractions have been removed, then the remaining envelope can be analyzed in the way discussed.

It can thus be concluded that in the process of mercerization of cotton and ramie lateral disorder is produced in the fibrils, together with some splitting of the fibrils along their length, probably by cleavage in the (101) plane. The reactivity of such a system will therefore depend on the accessibility of the disordered surfaces to the reagents used for any particular reaction. Such accessibility then depends on the void distribution between fibrils and any swelling of the whole system brought about during the reaction. Since all these factors can be influenced by the way in which the material is dried after treatment with caustic soda and washing, it is thus highly important to define precisely the drying conditions in preparing samples for reaction after a caustic soda treatment. It is equally important to define the conditions of the reaction, viz., whether swelling, and thus increased access to the reactive surfaces, can take place. Failure to observe the correct conditions after treatment can lead to products that cannot react with nonswelling reagents: this situation has been found in acetylation. It is thus of extreme importance to cellulose chemistry to be able to define the fine structure of cellulosic materials.

SUMMARY AND CONCLUSIONS

The width swelling of cotton and ramie fibers in a series of caustic soda solutions of different concentration at 0 and 20°C. is described. Indication of the bursting of the primary wall of cotton is given at 0°C.

Moisture contents are given as a measure of accessibility to water of structures produced from cotton and ramie by treatment with caustic soda.

Lateral order of the samples produced after treatment with caustic soda is studied by an analysis of the microdensitometer scans of the equatorial reflections of the x-ray diagrams.

It is shown that, except for a few experiments with ramie at 0°C., all the treated samples of cotton and ramie contain residual cellulose I components even after treatment in good mercerization conditions.

A plot of the integrated intensity of the (002) reflexion of the cellulose I component against caustic soda concentration defines the transition range. These curves are analyzed by the method of Marchessault and Howsmon.[8] It is found that the lateral order of ramie is slightly better than that of cotton, but both fibers possess high lateral order. General confirmation of these results is obtained by a similar analysis carried out with the moisture contents.

The analysis of the equatorial scans for samples treated with caustic soda concentrations greater than those in the transition range show that the main component is cellulose II. However, besides the small cellulose I component detected in most of the experiments, all experiments show a residual diffraction peak at $2\theta = 12-19°$. This residual diffraction peak is explained in terms of a special type of cellulose sheet and is the extreme example of lateral disorder. There is, therefore, a spectrum of lateral order.

It is concluded that in the mercerization treatment, besides a lattice change to cellulose II, a greater lateral disorder is introduced in the fibrils and, in the extreme, separated sheets of cellulose can be formed. The consequences to reactivity are indicated.

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Résumé

Une étude aux rayons-X à été effectuée concernant les changements d'ordre latéral qui ont lieu lors du traitement du coton et de la ramie à différentes concentrations en soude caustique à 0 et 20°C. Lorsque les conditions de mercerisation sont atteintes, on trouve qu'il y a une augmentation de désordre latéral au sein des fibriles. Les diagrammes aux rayons-X, au départ d'échantillons traités à des concentrations plus élevées en soude caustique, montrent des effets de diffraction résiduelle qui peuvent être interprétés sur la base d'un type spécial de feuillet celluloisque. Ce résultat implique un désordre latéral extrême qui se présente dans la structure fine de ce matériau. On montre comment ce désordre latéral peut affecter la réactivité.

Zusammenfassung

Die bei der Behandlung von Baumwolle und Ramie mit verschieden konzentrierter kaustischer Soda bei 0° und 20°C auftretenden Änderungen der Querordnung wurden röntgenographisch untersucht. Bei Erreichen von Merzerisierungsbedingungen tritt, wie gefunden wurde, eine Verringerung der Querordnung in den Fäserchen auf. Die Röntgen-Diagramme von Proben, die mit höheren Konzentrationen kaustischer Soda behandelt worden waren, zeigen einen Restbeugungseffekt, der durch einen speziellen Typ einer Celluloseschicht gedeutet werden kann. Dieses Ergebnis deut ein Extrem an lateraler Unordnung an, das in der Feinstruktur dieser Materialien vorliegt. Es werden Hinweise gegeben, wie diese Phänomene der lateralen Unordnung die Reaktivität beeinflussen können.

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Synthesis and Polymerization of 1,3-Bis-(2,3-epoxypropylphenyl)tetramethyldisiloxanes and Related Compounds

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Synopsis

1,3-Bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane and its *meta* isomer were synthesized and subsequently cured with *m*-phenylenediamine. Dielectric properties of the cured resin derived from the *para* isomer were measured between 25 and 100°C. The ambient temperature dielectric constant of the resin at 1 kc./sec. was 3.4, its dissipation factor was 0.01, and its volume resistivity was 10^{14} ohm-cm. at 500 v. d.c. Several allylphenylsiloxanes were also prepared by the cohydrolysis of allylphenyldimethylethoxysilane with dimethyldiethoxysilane, bis(dimethylethoxysilyl)benzene, and methyltriethoxysilane. Preliminary epoxidation studies on these latter materials were also carried out.

INTRODUCTION

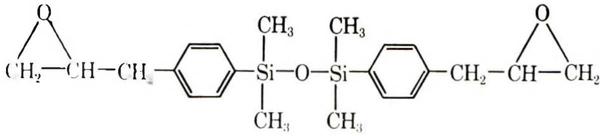
Over the past ten years published reports on epoxysilicones have averaged about two per year. Research in this area has thus been somewhat meager and has generally been prompted by the need for silicone resins and elastomers with certain physical properties and curing characteristics generally attributed to epoxy resins. In contrast, the need for heat- and ethylene oxide-sterilizable dielectric compounds, suitable for use in an aerospace environment, prompted the work reported herein.

Epoxysilicone prepolymers have most commonly been prepared by the reaction of epoxy prepolymers, or mixtures of polyols and epoxy prepolymers, with polyalkoxysilanes such as dimethyldiethoxysilane, ethyltriethoxysilane, etc.[1,2] They have, however, also been prepared by the epoxidation of unsaturated silicones. For example, the cohydrolysis of dimethyldichlorosilane with cyclohexenyltrichlorosilane produces a cyclohexenyl-substituted silicone which can be epoxidized with hydrogen peroxide in acetic acid.[3] Tetramethyltetravinylcyclotetrasiloxane has also been epoxidized by using acetyl peroxide in a sodium acetate-buffered acetic acid solution.[4]

Another method involves the platinum-catalyzed addition of silanes, containing Si–H bonds, to vinyl-substituted epoxy compounds such as monoepoxidized vinylcyclohexene.[5] Two more well-defined epoxysilicones which have been reported are 1,3-bis(epoxypropoxy)tetramethyldisiloxane[6] and 1,4-bis[(2,3-epoxypropoxy)dimethylsilyl]benzene.[7] In addition to these, the diglycidyl ether of the condensation product resulting from the reaction of 2,2-bis(*p*-hydroxyphenyl)propane with 1,3-bis(chloromethyl)tetramethyldisiloxane[8] and the diglycidyl ethers of various monoalkylmonoalkylenepolysiloxanes[9] have also been prepared. The compound most closely resembling the disiloxanes which are the subject of this paper is 1,3-bis[*p*-(2,3-epoxy-2-methylpropyl)phenyl]tetramethyldisiloxane.[8] Its preparation was accomplished via the perbenzoic acid epoxidation of the parent diallyl compound. Physical properties of this epoxy compound were not reported, however, nor were characterization tests described.

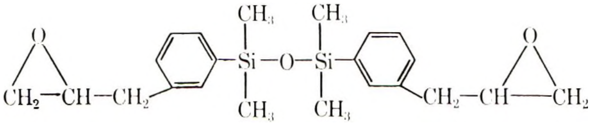
RESULTS AND DISCUSSION

Efforts made to develop epoxysilicones suitable for conformal coating applications were directed toward the synthesis of 1,3-bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane (I), the homologous *meta* isomer (II), and several analogous higher molecular weight siloxanes (III–V).



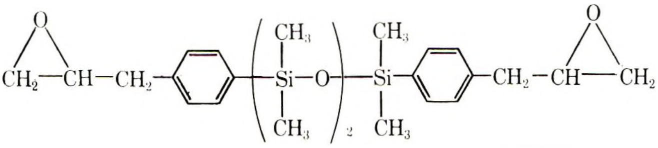
1,3-Bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane

I



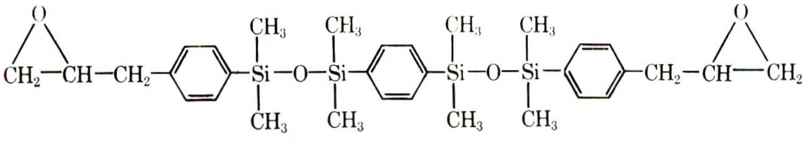
1,3-Bis[*m*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane

II



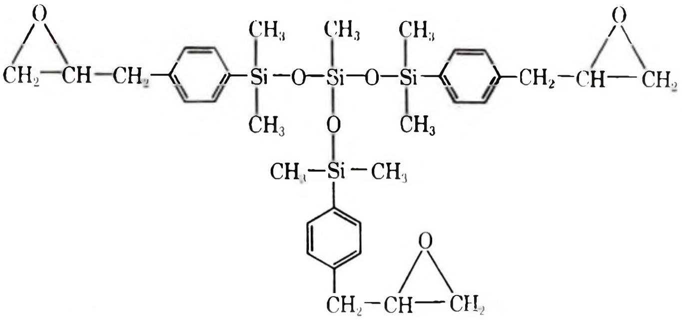
1,5-Bis[*p*-(2,3-epoxypropyl)phenyl]hexamethyltrisiloxane

III



1,4-Bis{[*p*-(2,3-epoxypropyl)phenyldimethylsiloxy]dimethylsilyl}benzene

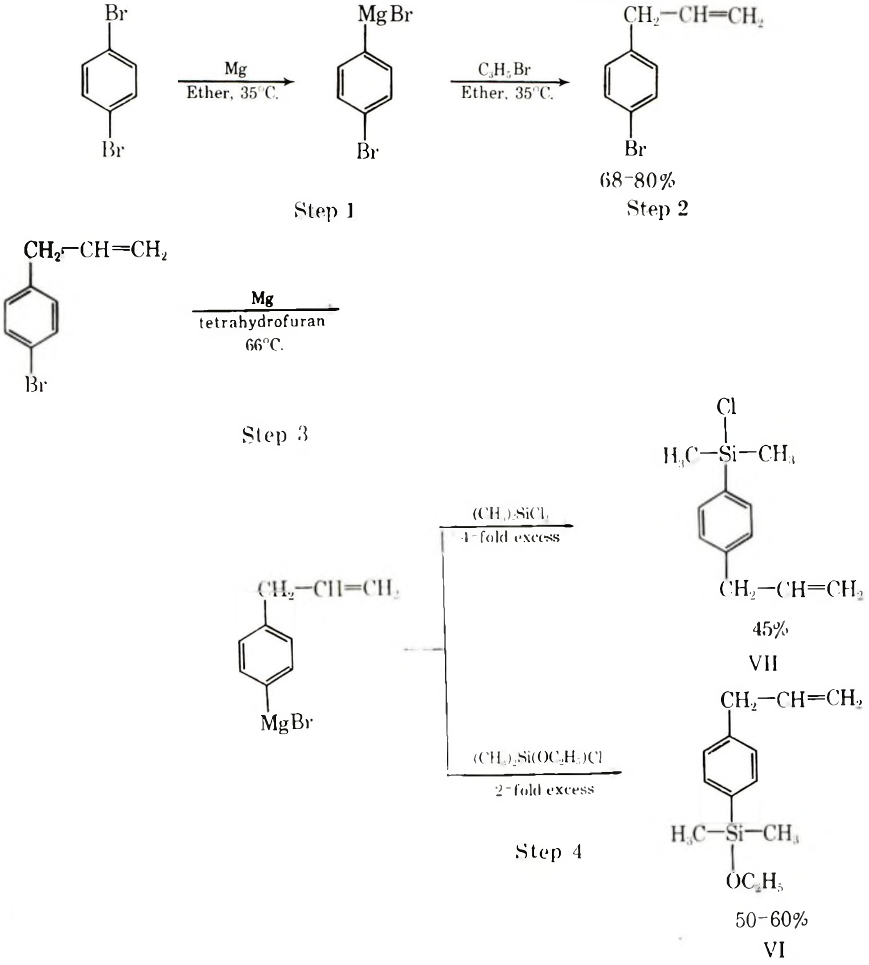
IV



Methyltris[p-(2,3-epoxypropyl)phenyldimethylsiloxy]silane

V

Several key intermediates were common to each of these epoxy-silicones. Undoubtedly, the most important of these intermediates were *p*-allylphenyldimethylethoxysilane (VI), the analogous chlorosilane (VII), and the *meta* isomers of these compounds. Their structures and methods of synthesis are shown in eqs. (1) and (2).



In the first step of this process, either *m*- or *p*-dibromobenzene may be used. The *meta* isomer has an advantage over the *para* isomer in that it is a liquid readily soluble in ether and thus is more convenient to monitor into the reaction mixture. The low solubility of the *para* isomer in ether renders it less convenient to use, particularly in large-scale preparations; however, it can be added in small portions in the solid state. Yields from these reactions have generally been about 70 ± 10%, although lower yields were observed when difficulties were encountered in keeping the reactions under control due to excessively rapid addition rates. The refractive index of the *p*-allylbromobenzene (n_D^{23}) was 1.5522 and the boiling point was 62°C./3 torr, 80°C./5–6 torr, 96°C./14 torr, and 117°C./35 torr.

Conversion of the allylbromobenzene to allylphenylmagnesium bromide (step 3) was generally carried out in tetrahydrofuran because the reaction is rather sluggish and gives much poorer yields in ethyl ether. After preparation, the Grignard reagents were added dropwise to excess quantities of either dimethyldichlorosilane or dimethylchloroethoxysilane. With a fourfold molar excess of dimethyldichlorosilane a yield of 43% of allylphenyldimethylchlorosilane was obtained, whereas with the dimethylchloroethoxysilane yields of 50–60% were obtained when the ethoxy compound was used in a twofold excess. The use of the ethoxy compound does, however, have a disadvantage in that its purification is difficult. It is generally contaminated with both the dichlorosilane from which it is made and with dimethyl diethoxysilane. Furthermore, its synthesis by the partial ethanolysis of dimethyldichlorosilane as illustrated in eq. (3)

$$(CH_3)_2SiCl_2 + C_2H_5OH \rightarrow (CH_3)_2Si(OC_2H_5)Cl \qquad (3)$$

is wasteful, since yields were about 40% when a 3°C. boiling range was collected, 50% when a 12°C. boiling range was collected, and 67% when a 20°C. boiling range was collected. The apparent boiling point of the pure compound is 90°C. at atmospheric pressure.

m-Allylphenyldimethylethoxysilane prepared from dimethylchloroethoxysilane distills at 95 ± 5°C./5 torr. Its refractive index varied between 1.49 and 1.50 at ambient temperature, due to the variation in the amount of *m*-allylphenyldimethylchlorosilane which it contains, since the chlorosilane has a refractive index (n_D^{23}) of 1.5139. This contamination was of little concern since both compounds hydrolyze to the same disiloxane. It has been noted that when the ethoxysilane was treated with ethanol prior to distillation, the chlorosilane therein was esterified, and foaming, which was always encountered during distillation, was drastically reduced. Infrared spectra of the *m*- and *p*-allylphenyldimethylethoxysilanes are shown in Figures 1 and 2, respectively.

An elemental analysis was carried out on a sample of *m*-allylphenyldimethylethoxysilane with a refractive index (n_D^{23}) of 1.4919 by the Elek. Microanalytical Laboratory, Los Angeles, California.

ANAL. Calcd.: C, 70.96%; H, 9.16%; Si, 12.77%. Found: C, 68.55%; H, 9.07%; Si, 12.19%.

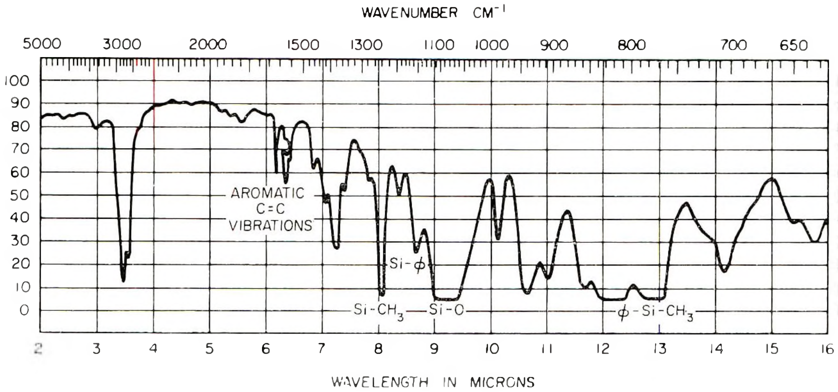


Fig. 1. Infrared spectrum of *m*-allylphenyldimethylethoxysilane.

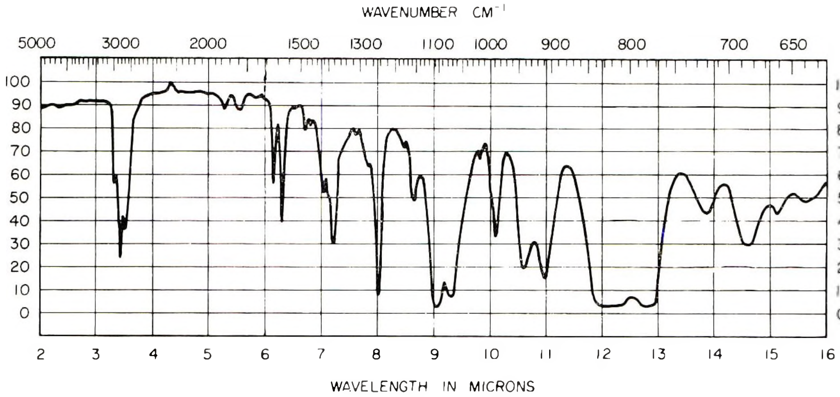
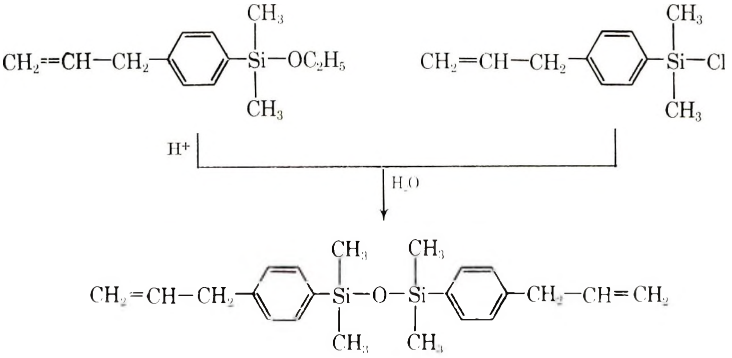


Fig. 2. Infrared spectrum of *p*-allylphenyldimethylethoxysilane.

A sample of the homologous *para* isomer free of halosilane boiled at about 100°C./9 torr or 70–75°C./0.2 torr and had a refractive index (n_D^{23}) of 1.4965.

Both allylphenyldimethylchlorosilane and allylphenyldimethylethoxysilane are suitable for the preparation of di- and polysiloxanes. Hydrolysis of either compound produces dimer (VIII), as shown in eq. (4).



VIII

(4)

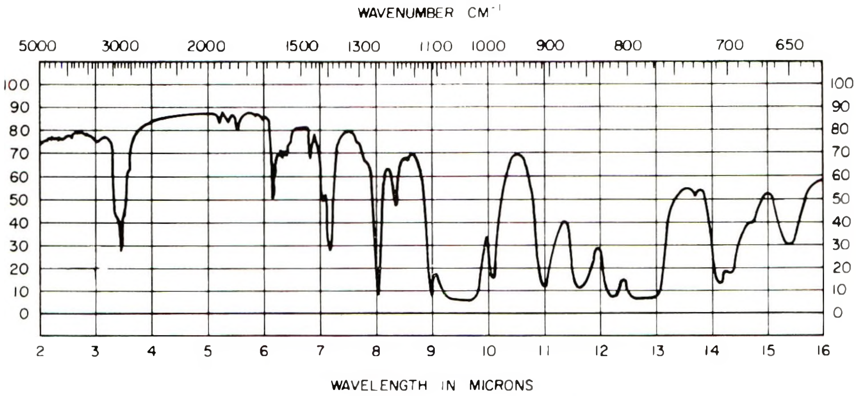


Fig. 3. Infrared spectrum of 1,3-bis(*m*-allylphenyl)tetramethyldisiloxane.

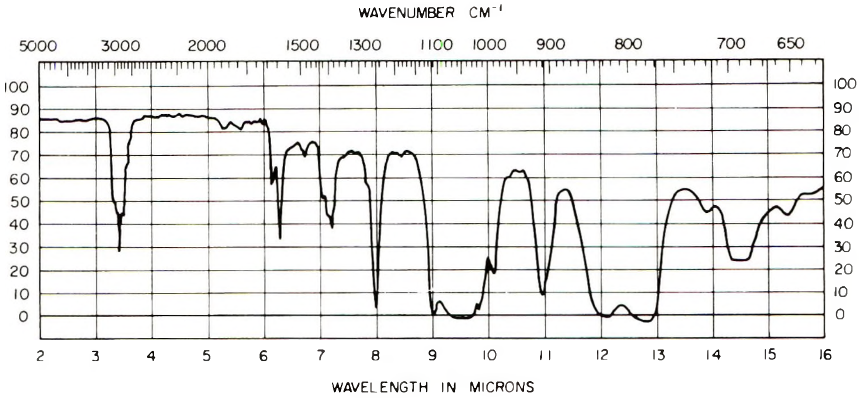


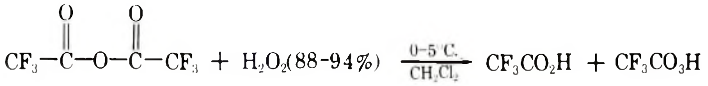
Fig. 4. Infrared spectrum of 1,3-bis(*p*-allylphenyl)tetramethyldisiloxane.

Both the *meta*- and *para*-substituted disiloxanes can be distilled under high vacuum. The *meta* isomer has been collected at 130°C./0.003 torr and at 150–155°C./1.3 torr, whereas the *para* isomer has been collected at 130–140°C./0.010 ± 0.006 torr and at 120–130°C./0.002 torr. The refractive index of the *meta* isomer (n_D^{23}) was always 1.5208 ± 0.0009, and that of the *para* isomer was 1.5206 ± 0.0006. At least three independent values, from different preparations, were obtained on each of these compounds. Infrared spectra of both isomeric disiloxanes are shown in Figures 3 and 4.

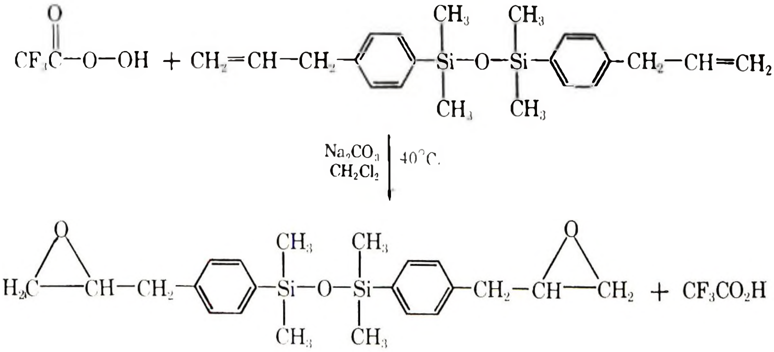
Elemental analyses carried out on two independently synthesized samples of the *meta*-substituted disiloxane supported the proposed structure.

ANAL. Calcd.: C, 72.20%; H, 8.26%; Si, 15.35%. Found (sample 1): C, 72.43%; H, 8.14%; Si, 13.48%. Found (sample 2): C, 71.14%; H, 8.14%; Si, 15.22%.

Epoxidation of the bis(allylphenyl)tetramethyldisiloxanes was carried out with freshly prepared trifluoroperacetic acid following a modified procedure described by Eisch and Trainor.[10] This procedure is illustrated in eqs. (5) and (6).



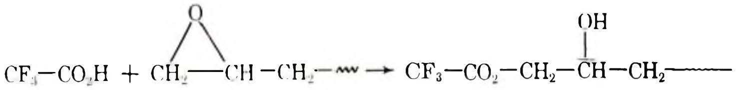
$$CF_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CF_3 + H_2O_2(88\text{-}94\%) \xrightarrow[CH_2Cl_2]{0\text{-}5°C.} CF_3CO_2H + CF_3CO_3H \qquad (5)$$



(6)

IX

A considerable number of epoxidation experiments which were carried out at 0–8°C. proved unsatisfactory, in that the bisepoxy compounds which were obtained were always contaminated with fluorinated esters resulting from the addition of trifluoracetic acid to the epoxy compound [eq. (7)].



(7)

These esters could not be removed readily by vacuum distillation.

Evidence for the addition came from infrared spectroscopy. Absorption peaks observed in many of the epoxysilicones at 1170 and 1200 cm.$^{-1}$ can be attributed to C—F absorptions and this was verified by the deliberate addition of trifluoroacetic acid to a sample of the epoxy silicone. Also observed was absorption at 1770 cm.$^{-1}$ which was attributed to the carbonyl groups and absorption at 3300 cm.$^{-1}$ which was attributed to the hydroxyl groups. These absorptions are absent when the epoxidations are carried out in refluxing methylene chloride (40°C.). The deliberate addition of trifluoroacetic acid to a sample of epoxysilicone also supported the assignment of absorptions at 965 and 752 cm.$^{-1}$ to the epoxy groups. These latter absorptions disappeared as a result of the addition. This observation was important because all of the generally recognized epoxy group absorptions were masked by Si—O, Si—C_6H_5, Si—CH_3, and other functional groups.

Contamination by fluoroester was considered serious because its removal by molecular distillation was not readily accomplished. Furthermore, epoxysilicones containing fluoroester often polymerized into viscous fluids when distillation was attempted. This was attributed to the liberation of trifluoroacetic acid, which acted as a polymerization catalyst at the elevated temperatures. Epoxidations carried out in methylene chloride below 8°C. tended to yield solutions which were acidic to dry, wide-range indicator paper. This proved to be an excellent technique for testing for complete removal of free acid. Moist indicator paper did not necessarily show this acidity, probably due to bleaching of the litmus in the presence of water. Problems encountered with low temperature epoxidations were thus attributed to the failure of the suspended carbonates to absorb spent acids in the reaction mixture at a sufficiently high rate.

Epoxidations carried out at 40°C. were always free of C—F, C=O, and OH absorptions. Furthermore, the use of excess trifluoroperacetic acid was necessary at the elevated temperature as long as sufficient carbonate was present, whereas in the lower temperature epoxidations excess peracid was always very detrimental.

Elemental analyses carried out on a distilled sample of 1,3-bis[*m*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane gave the following results.

ANAL. Calcd. for $C_{22}H_{30}Si_2O_3$: C, 66.38%; H, 7.60%; Si, 14.11%. Found: C, 66.57%; H, 7.59%; Si, 14.15%.

This fraction was molecularly distilled at about 90 ± 10°C./10^{-3} torr and had a refractive index (n_D^{23}) of 1.5251. The best fraction of *para* isomer isolated from a low temperature epoxidation had the following analysis.

ANAL. Calcd. for $C_{22}H_{30}Si_2O_3$: C, 66.38%; H, 7.60%; Si, 14.11%. Found: C, 68.29%; H, 7.87%; Si, 15.36%.

This fraction was distilled at 100–125°C./5×10^{-4} torr and had a refractive index (n_D^{23}) of 1.5162.

An undistilled sample of 1,3-bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane isolated from an epoxidation which was carried out at 40°C. and in which the theoretical amount of peracid was used had the following analysis.

ANAL. Calcd. for $C_{22}H_{30}Si_2O_2$: Si, 14.73% (50% epoxidized). Calcd. for $C_{22}H_{30}Si_2O_3$: Si, 14.11% (100% epoxidized). Found for sample 6: Si, 14.86%.

An infrared spectrum of this product showed that it was free of C—F, C=O, and OH groups. Its equivalent weight was found to be 401 rather than 200 as calculated, and thus it appeared to have only 50% of its allyl groups epoxidized. This was supported by the elemental analysis. Thus, it was concluded that whereas epoxidations carried out at 40°C. produce epoxy compounds with virtually no fluoroester contamination, they must be carried out in the presence of a significant excess of peracid to achieve complete epoxidation. Such a peracid excess could not be tolerated below 10°C.

Epoxidations at 40°C. were subsequently carried out with 50% and 100% theoretical excess of peracid without producing products contaminated with trifluoroacetic acid–epoxy addition compounds. Reactions

TABLE I

Expt. no.	Theoretical excess peracid, %	Carbonate/anhydride mole ratio	Product		
			Equiv. wt.[a]	Yield, %	n_D^{23}
5	0	3.0	440	69	1.5245
6	0	3.2	401	100	1.5245
7	50	3.0	367	72	1.5248
8	50	3.0	333	—	—
9	100	3.0	295	57	1.5260
10	100	2.0	232	67	1.5270
11	100	1.5	217	85	1.5268

[a] Theoretical value 200.[11]

which produced the most complete epoxidation were those utilizing 100% excess peracid and a sodium carbonate/trifluoroacetic anhydride ratio of about 1.5. Results of several typical epoxidations are shown in Table I.

An infrared spectrum of the 1,3-bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane (experiment 10) is shown in Figure 5. Infrared absorptions at 750 and 970 cm.$^{-1}$ appear to be assignable to the epoxy groups. These assignments have not been proven conclusively, however.

Dielectric properties of *m*-phenylenediamine-cured samples of the 1,3-bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane have been measured. Analyzed equivalent weights of the epoxysilicones were used in all cases. The compositions of these cured epoxysilicones are presented in Table II and their dielectric properties are listed in Table III.

An examination of these dielectric property data shows that the best sample of cured unfilled 1,3-bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane was sample A. Its dielectric constant at 1 kc./sec. increased from 3.4 to 4.4 when heated from 25 to 100°C., while its dissipation factor increased from 1 to 3.8%. Analogous resin filled with 15 wt.-% of silica microballoons (Eccospheres SI from Emerson and Cuming, Inc., Los

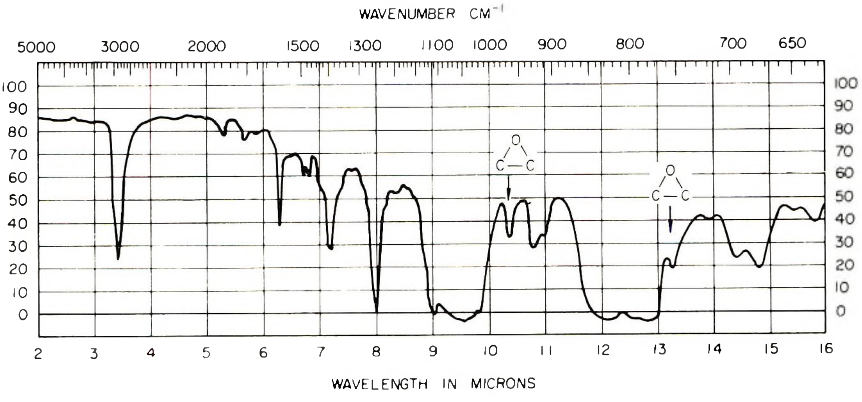


Fig. 5. Infrared spectrum of 1,3-bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane.

TABLE II
Composition of Various Cured Epoxysilicones

		Epoxysilicone[a]		Epon X-24[b]		Filler[c]	Amine[d]			
Specimen no.	Epoxy-silicone no.	Weight, g.	Equivalents[e]	Weight, g.	Equivalents[e]	Weight, g.	Weight, g.	Equivalents	Cure	Comments
A	12	4.0	0.014				0.50	0.02	60 hr. at 85°C. + 3.5 hr. at 100°C. in N_2	Rigid tan disk
B	13	5.02	0.018				0.49	0.018	16 hr. at 80°C. + 8 hr. at 100°C. in N_2	Clear amber flexible disk
C	13	5.02	0.018			0.97	0.49	0.018	16 hr. at 80°C. + 8 hr. at 100°C. in N_2	Light tan rigid disk
D	13	3.07	0.011	1.87	0.011		0.59	0.022	16 hr. at 80°C. + 8 hr. at 100°C. in N_2	Cured sample not completely homogeneous
E	13	3.07	0.011	1.87	0.011	0.98	0.59	0.022	16 hr. at 80°C. + 8 hr. at 100°C. in N_2	Only 50% filled due to flotation
F	14	4.67	0.010				0.27	0.010	16 hr. at 85°C. + 4 hr. at 100°C. in N_2	Flexible disk

[a] 1,3-Bis(*p*-epoxypropylphenyl)tetramethyldisiloxane. Not applicable to specimen F.

[b] Shell Chemical Company, equiv. wt. approximately 80.

[c] Silica microballoons, Eccospheres SI dried at 250°C. (Emerson and Cuming).

[d] *m*-Phenylenediamine.

[e] Based on analyzed equivalent weights.

TABLE III

Dielectric Properties of Various Epoxysilicone Specimens (1.90 in. Diameter, 0.09 in. Thick)

Specimen no.	Isomer[a]	Dielectric constant (at 1 kc./sec.)			Dissipation factor (at 1 kc./sec.), %			Volume resistivity, megohm-cm. at 500 v. d.c.		
		25°C.	50°C.	100°C.	25°C.	50°C.	100°C.	25°C.	50°C.	100°C.
A	P	3.4	3.8	4.4	1.0	1.7	3.8	2×10^8	2×10^6	4×10^3
B	P	3.8	3.9	6.7	2.7	2.7	6.3	4×10^7	2×10^6	3×10^4
C	P	2.3	3.0	3.2	2.0	4.6	10.9	3×10^7	1×10^6	7×10^3
E	P	2.5	2.9	4.0	1.3	2.9	14.8	2×10^7	3×10^6	2×10^4
F	[b]	3.2	3.6	6.3	3.9	6.8	14.5	3×10^7	2×10^6	7×10^3

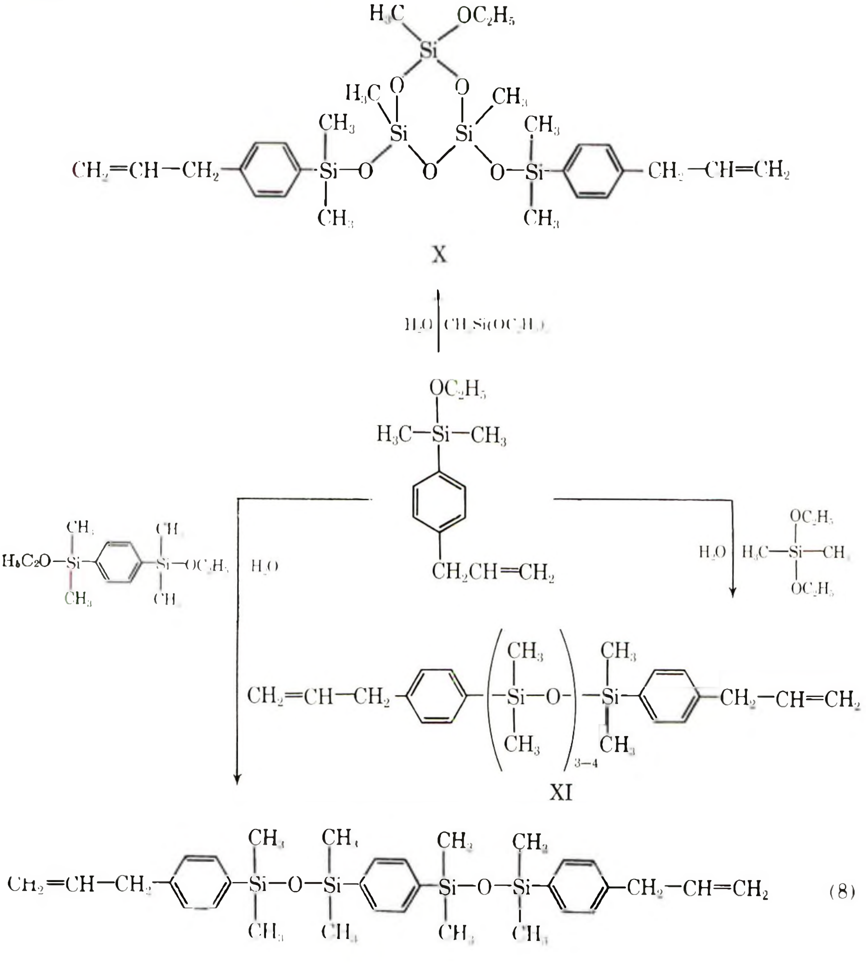
[a] P refers to the *para* isomer of 1,3-bis(epoxypropylphenyl)tetramethyldisiloxane.

[b] Epoxidized cohydrolysis product of *p*-allylphenyldimethylethoxysilane and methyltriethoxysilane.

Angeles, California) (sample C) had dielectric constants which varied from 2.3 to 3.2 between 25 and 100°C. and dissipation factors which varied from 2.0 to 10.9% within this temperature range or from 2.0 to 4.6% between 25 and 50°C.

Siloxane Copolymers

Allylphenyldimethylchlorosilane and the allylphenyldimethylethoxysilanes are also useful in cohydrolysis reactions with other chloro- or ethoxysilanes. Such cohydrolyses may be used to produce various types of higher molecular weight allylphenylsiloxanes. Three such reactions which were carried out in this study include the cohydrolysis of *p*-allylphenyldimethylethoxysilane with methyltriethoxysilane, with dimethyldiethoxysilane, and with 1,4-bis(dimethylethoxysilyl)benzene. These reactions are illustrated in eqs. (8) to demonstrate the utility and potential of the basic compounds described earlier.



XII

Cohydrolysis reactions do not, of course, yield single compounds as products, but rather yield mixtures of allylphenylsiloxanes. Each reaction product contained bis(allylphenyl)tetramethyldisiloxane and lower-boiling cyclosiloxanes as well as the desired cohydrolysis products. For the purpose of this program, only the lower-boiling cyclosiloxanes needed to be removed prior to epoxidation and polymerization. Studies were made nevertheless to determine the structure of high boilers after removal of the bis(allylphenyl)tetramethyldisiloxane. Analysis of the epoxidized bis-(allylphenyl)polydimethylsiloxane showed that the nonvolatile cohydrolysis product XI contained on the average a little more than three repeating dimethylsiloxy units.

ANAL. Calcd. for $C_{28}H_{48}Si_5O_{4.5}$:* Si, 23.52%; M.W. 597. Calcd. for $C_{26}H_{42}Si_4O_{3.5}$:* Si, 21.48%; M.W. 523. Found: Si, 21.96%; M.W. 572.

The equivalent weight of this epoxy compound was found to be 1089, and thus only 25% of its allyl groups were epoxidized. A significant portion of the dimethyldiethoxysilane used in this cohydrolysis ended up as cyclosiloxane and was removed by vacuum distillation.

In the cohydrolysis of *p*-allylphenyldimethylethoxysilane with methyltriethoxysilane, the nonvolatile siloxane which was isolated appeared to be primarily an incompletely hydrolyzed trisiloxane X. Analysis of this undistilled high-boiling fraction gave the following results.

ANAL. Calcd. for $C_{27}H_{44}Si_5O_6$: C, 53.59%; H, 7.33%; Si, 23.21%. Found (undistilled product): C, 53.03%; H, 7.64%; Si, 23.34%. Found (distilled fraction): C, 55.45%; H, 7.68%.

The presence of unreacted ethoxy groups in the product was not expected, although the hydrolysis was carried out under very weakly acidic conditions. The reaction thus warrants re-examination with the use of more vigorous hydrolysis conditions. The major portion of the reaction product distilled at about 165°C./10^{-4} torr, had a refractive index (n_D^{23}) of 1.4943 and was primarily the bis(*p*-allylphenyl)tetramethyldisiloxane.

In the cohydrolysis of *p*-allylphenyldimethylethoxysilane with 1,4-bis-(dimethylethoxysilyl)benzene, a nonvolatile siloxane was obtained which after epoxidation had an equivalent weight of 491. The theoretical value is 287. Elemental analyses have not been obtained. Apparently, this epoxidation was only 58% complete. Nevertheless, when the epoxy compound was reacted with an equivalent amount of *m*-phenylenediamine, it cured to a flexible tough elastomer when heated at 100°C. in nitrogen for 2 days, then in air for $2^1/_2$ days. A simple flexibility test carried out at about −70°C. showed the elastomer to be tough and nonbrittle at this temperature.

Optimum epoxidation processes had not been developed at the time the three previously described copolymers were epoxidized. The process ultimately developed for the epoxidation of the bis(allylphenyl)tetrameth-

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* Fractional units are used here because the compound was incompletely epoxidized.

yldisiloxanes, namely, the use of 100% excess peracid, epoxidation temperatures of 40°C., and sodium carbonate/trifluoracetic anhydride molar ratios of 1.5 or less, would currently be recommended.

EXPERIMENTAL

Synthesis of *p*-Bromoallylbenzene

To a slurry of dry magnesium (245 g., 10 g.-atoms) in anhydrous ether (6.4 liter) was gradually added, in small portions, solid *p*-dibromobenzene (2360 g., 10 mole) after the reaction was initiated with a small amount of ethylmagnesium iodide. The reaction flask was cooled in an ice-water bath throughout the reaction to maintain control; however, reflux was maintained by carefully monitoring the rate of dibromobenzene addition. In this manner, the addition was completed within $2^1/_2$ hr. Reflux was then continued for 1 hr. by an auxiliary heat source.

Allyl bromide (1295 g., 10.7 mole) in anhydrous ether (1 liter) was then added slowly to the Grignard reagent at a rate which permitted controlled reflux. Upon completion of this reaction the reaction mixture was cautiously poured over acidified ice. The ether phase was then separated and the aqueous phase was washed with fresh ether. Combined ether layers were then distilled. The *p*-allylbromobenzene (1534 g., 78%) was collected at 60–63°C./3 torr.

Synthesis of *m*-Bromoallylbenzene

A solution of *m*-dibromobenzene (571 g., 2.42 mole) in absolute ether (200 ml.) was gradually added to a slurry of magnesium (60 g., 2.5 g.-atoms) in absolute ether (200 ml.) after initiating the reaction with iodine and ethyl iodide. After the exothermic phase of the reaction was over the mixture was heated at reflux for 1 hr. with the use of an auxiliary heat source. Allyl bromide (300 g., 2.5 mole) was then added dropwise to the reaction mixture at such a rate as to maintain control. When the addition was completed, heating was maintained for $^1/_2$ hr. The reaction mixture was cooled, then poured over a mixture of hydrochloric acid and ice. Separation of the two phases yielded an ether phase which was washed with water and dried over calcium sulfate. Fractional distillation of the ether solution yielded 335 g. (70%) of *m*-allylbromobenzene (b.p./35 torr = 117°C.).

Synthesis of Dimethylethoxychlorosilane

Anhydrous ethanol (276 g., 6 mole) was added dropwise to dimethyldichlorosilane (1032 g., 8 mole). When the reaction subsided, the mixture was heated at reflux for 1 hr. and was then distilled. Unreacted dichlorosilane (125 g.) was recovered at 58–62°C. Then several other fractions were collected, namely, II, 89 g., 76–82°C.; III, 66 g., 82–89°C.; IV, 299 g., 89–95°C.; V, 100 g., 95–97°C. The latter two fractions represent 2.90 mole or 36% of theoretical.

Synthesis of *m*-Allylphenyldimethylethoxysilane

m-Bromoallylbenzene (250 g., 1.27 mole) was dissolved in anhydrous tetrahydrofuran (400 ml.) and the solution was then gradually added to a slurry of magnesium (34 g., 1.42 g.-atoms) in anhydrous tetrahydrofuran. The addition took about 1 hr. after the reaction had been initiated with iodine and ethylmagnesium iodide. When the addition was completed, the mixture was heated at reflux for 1 hr. This Grignard solution then was added gradually to dimethylchloroethoxysilane (294 g., 2.13 mole) while keeping the reaction cool with an ice bath. When the addition was complete, the reaction mixture was heated at reflux for 1 hr., then diluted with petroleum naphtha. It was then filtered and fractionally distilled to yield 147 g. of pure product (b.p. = 90–100°C./5 torr, n_D^{23} = 1.5028). Another fraction was recovered by redistillation of the forerun. This fraction weighed 27 g., had a boiling point of 85–110°C./5 torr and a refractive index of n_D^{23} = 1.5040. The combined 174 g. (0.79 mole) of product represents 62% of the theoretical yield.

Synthesis of *p*-Allylphenyldimethylethoxysilane

p-Allylbromobenzene (332 g., 1.68 mole) in an equal volume of dry tetrahydrofuran was added dropwise, with constant stirring, to dry magnesium (43.1 g., 1.74 g.-atoms) in 644 ml. dry tetrahydrofuran. The reaction was initiated with a few grams of freshly prepared ethylmagnesium iodide. The mixture had to be heated at the beginning, but then even reflux was maintained, during addition, with an ice bath. After addition, the mixture was stirred at reflux for $^3/_4$ hr. The resulting Grignard reagent was decanted into a dropping funnel, and added dropwise, with constant stirring, to dimethylethoxychlorosilane (451 g., 3.28 mole) in an equal volume of dry tetrahydrofuran. After initial heating, an ice bath had to be used to keep the reaction at even reflux. After addition, the mixture was stirred at reflux for 2 hr. The product was taken up in hexane, and solids were separated out by filtration. Absolute ethanol (80.0 g., 1.74 mole) was then added and the mixture was stirred for 1 hr. at ambient temperature. After initial evaporation of solvent, the crude product weighed 298 g. It was then distilled under vacuum, yielding the following fractions: 1F2: 70–75°C./0.2 torr, 126.0 g. net, n_D^{24} = 1.4965; 2F1: 60–70°C./0.5 torr, 30.6 g. net, n_D^{24} = 1.4930; 2F2: 70–76°C./0.5 torr, 32.3 g. net, n_D^{25} = 1.4993. Redistillation of 1F2 yielded the following: 3F1: 70–73°C./0.5 torr, 94.3 g. net, n_D^{25} = 1.5006. (The redistillation of 1F2 was run because of the presence of impurities, as indicated in the infrared absorption spectra.)

Synthesis of *p*-Allylphenyldimethylchlorosilane

To a slurry of magnesium (113 g., 4.65 g.-atoms) in anhydrous tetrahydrofuran (2 kg.) was added *p*-bromoallylbenzene (833 g., 4.23 mole) at such a rate that moderate reflux was maintained. The reaction was initiated with a small amount of ethylmagnesium iodide. Upon completion of the addition, reflux was continued for 1 hr. using an auxiliary heat source.

The cooled Grignard reagent thus prepared was then placed into a dropping funnel and added dropwise to freshly distilled dimethyldichlorosilane (2184 g., 16.9 mole) over a 2 hr. period. Stirring was then continued for 1 hr. and the reaction mixture was then filtered to remove precipitated salts. These salts were washed with petroleum ether. Tetrahydrofuran and unreacted dimethyldichlorosilane were then removed in large part from the filtrate by distillation. The petroleum ether from the salt wash was then combined with the undistilled crude allylphenyldimethylchlorosilane and the mixture was filtered. Simple distillation of the filtrate gave low-boiling material and 738 g. of allylphenyldimethylchlorosilane (b.p. = 70–100°C./5 torr).

Fractional distillation of the impure product was then carried out using a packed column. The purified allylphenyldimethylchlorosilane (382 g., 1.82 mole, n_D^{23} = 1.5139) distilled at 102–103°C./5 torr. This represents a 43% yield.

Synthesis of Bis(*p*-allylphenyl)tetramethyldisiloxane by Hydrolysis of *p*-Allylphenyldimethylchlorosilane

p-Allylphenyldimethylchlorosilane (382 g., 1.82 mole) was added dropwise to water (1.5 liter) while stirring vigorously. When the reaction was completed, the mixture was cooled and the two phases were separated. Distillation of the disiloxane was then carried out at 6×10^{-3} torr, and the fraction boiling between 130 and 140°C. was collected. It weighed 300 g. (0.82 mole) and represented a 90% yield. Its refractive index (n_D^{23}) was 1.5209.

Synthesis of 1,3-Bis(*p*-allylphenyl)tetramethyldisiloxane by Hydrolysis of *p*-Allylphenyldimethylethoxysilane

A mixture of water (10 ml.) and glacial acetic acid (1 ml.) was gradually added to *p*-allylphenyldimethylethoxysilane (74.4 g., 0.34 mole), b.p. 60–85°C./0.5 torr. After shaking vigorously, the two phases were separated and the upper layer was collected and distilled at 0.015 torr. Two fractions of product were recovered: I, 23.7 g., b.p. 130–140°C./0.015 torr, n_D^{22} = 1.5206; II, 24.7 g., b.p. 130–140°C./0.015 torr, n_D^{22} = 1.5193. The total yield of product (48.4 g., 0.14 mole) represents a 77% yield.

Synthesis of 1,3-Bis(*m*-allylphenyl)tetramethyldisiloxane by Hydrolysis of *m*-Allylphenyldimethylethoxysilane

Water (1.5 ml., 0.086 mole), which had been slightly acidified (one drop of glacial acetic acid per 10 ml. water), was added to *m*-allylphenyldimethylethoxysilane (16.7 g., 0.076 mole) with constant stirring. The mixture was stirred for 48 hr. at room temperature. A total of 3.3 g. of water–ethanol mixture was then distilled from the crude product at 1 atm.

No further purification of the product was attempted, since 1.5 g. of a fraction distilled under vacuum (133°C. 3×10^{-3} torr) had a refractive index of $n_D^{23} = 1.5210$, while that of the undistilled portion was $n_D^{23} = 1.5208$. Infrared spectrograms were run on both distilled and undistilled products.

ANAL. Calcd.: C, 72.20%; H, 8.26%; Si, 15.35%. Found (undistilled product): C, 72.43%; H, 8.14%; Si, 13.48%.

Epoxidation of 1,3-Bis(*p*-Allylphenyl)tetramethyldisiloxane (Experiment 5)

Trifluoroperacetic acid was prepared by the dropwise addition of a solution of trifluoroacetic anhydride (106 g., 0.504 mole) in methylene chloride (110 ml.) to a stirred mixture of hydrogen peroxide (89%, 15.7 g., 0.410 mole) in dry methylene chloride (50 ml.) at a temperature of 0–5°C.

The peracid was not used immediately but was allowed to set for 3 hr., during which time the temperature gradually rose to ambient. It was then added dropwise to a slurry of 1,3-bis(*p*-allylphenyl)tetramethyldisiloxane (75.0 g., 0.205 mole) and anhydrous powdered sodium carbonate (163 g., 1.52 mole) in dry methylene chloride (75 ml.) while maintaining reflux throughout the addition and for $^1/_2$ hr. after. After cooling, inorganic salts were removed by filtration and the solvent was removed by distillation. The epoxy compound was then heated at about 85°C./3×10^{-4} torr to remove low-boiling material. It then weighed 54.2 g. and had an equivalent weight of 440.

A second portion of the diallyl compound was epoxidized (experiment 6) as described above, except that 79.8 g. (0.218 mole) of diolefin, 113 g. (0.512 mole) of anhydride, 16.7 g. (0.410 mole) of peroxide, and 173 g. (1.65 mole) of sodium carbonate were used. In this case the peracid was used immediately after being prepared. The final product weighed 85 g. and had an equivalent weight of 401.

Another epoxidation (experiment 8) was carried out as described above, with the use of 11.2 g. (0.522 mole) of trifluoroacetic anhydride, 1.65 g. (0.0432 mole) of 89% hydrogen peroxide, 5.3 g. (0.0122 mole) of bis(allylphenyl)tetramethyldisiloxane, and 17 g. of sodium carbonate. The epoxy compound was heated at about 80°C. and 3×10^{-4} torr to remove volatiles. It then weighed 4.5 g. and had an equivalent weight of 333. It should be noted that a 50% theoretical excess of peracid was used in this experiment.

Epoxidation of 1,3-Bis(*p*-allylphenyl)tetramethyldisiloxane

50% Excess Peracid–Triple Carbonate (Experiment 7). Trifluoroacetic anhydride (107 g., 0.51 mole) in an equivalent volume of methylene chloride was added dropwise to a slurry of hydrogen peroxide (89%, 15.8 g., 0.414 mole) in methylene chloride (30 ml.) while keeping the temperature below 5°C. After addition, stirring was continued for 15 min.

The fresh peracid was then added dropwise to a slurry of the diolefin (50 g., 0.136 mole) and anhydrous powdered sodium carbonate (162 g., 1.53 mole) in methylene chloride (200 ml.) while maintaining reflux throughout the addition and for 30 min. thereafter. Salts were then filtered out and fresh carbonate (15 g.) was added. After 15 min. the carbonate was filtered out. Solvent was removed by distillation, and the epoxy compound was devolatilized at 80°C./10^{-4} torr. Its equivalent weight was 367.

100% Excess Peracid–Triple Carbonate (Experiment 9). Trifluoroacetic anhydride (142 g., 0.676 mole) in methylene chloride (140 ml.) was added dropwise to a stirred slurry of hydrogen peroxide (89%, 21.0 g., 0.55 mole) in methylene chloride (60 ml.) while keeping the reaction temperature at 0–5°C. throughout the addition and for 15 min. thereafter. The cold peracid was then placed in a cooled dropping funnel and added dropwise to a slurry of bis(allylphenyl)tetramethyldisiloxane (50 g., 0.137 mole) and dry powdered sodium carbonate (215 g., 2.03 mole) in methylene chloride (200 ml.). The reaction was run at reflux. Upon completion of the reaction the inorganic salts were removed by filtration and fresh carbonate (15 g.) was added and the mixture stirred for 15 min. Again inorganics were removed by filtration. Solvent was then removed by simple distillation, and the epoxy compound was heated at 70–75°C./5×10^{-3} torr for about 12 hr. to remove volatiles. Its equivalent weight was 295. The yield was 31 g. (57%).

100% Excess Peracid–Double Carbonate (Experiment 10). This experiment was carried out in the same manner as experiment 9 except that 143 g. of Na_2CO_3 (1.35 mole) was used rather than 215 g. This represents a molar ratio of sodium carbonate to trifluoroacetic anhydride of 2:1 rather than 3:1 as used previously. The peracid addition was completed in 1 hr. by using an ice bath to help dissipate the heat of reaction. The epoxidation reaction was carried out at total reflux, even though the flask was cooled in ice. The epoxy compound weighed 36 g. and had an equivalent weight of 232. The yield was 67% of theoretical.

100% Excess Peracid-One and One-Half Carbonate (Experiment 11). Trifluoroacetic anhydride (416.5 g., 1.983 mole) in methylene chloride (400 ml.) was added dropwise to a well-stirred slurry of hydrogen peroxide (89%, 61.4 g., 1.61 mole) in methylene chloride (180 ml.) while keeping the reaction temperature at 0–5°C. throughout the addition. The cold peracid was then placed in a cooled dropping funnel and added dropwise to a slurry of bis(allylphenyl)tetramethyldisiloxane (147.4 g., 0.402 mole) and dry finely powdered sodium carbonate (315 g., 2.97 mole) in methylene chloride (600 ml.). This took about $1^1/_4$ hr., during which time total reflux was maintained even though the flask was being cooled externally. Upon completion of the reaction the inorganic salts were removed by filtration, washed with methylene chloride, and the combined filtrates were treated with additional carbonate (approximately 50 g.) for 15 min. and refiltered. Solvent was then removed by simple distillation and the epoxy compound was heated overnight at 75 ± 5°C./10^{-3} torr to remove residual volatiles. The product weighed 137 g. and had an equivalent weight of 217. The yield was 85%; n_D^{23} = 1.5268.

Cohydrolysis of *p*-Allylphenyldimethylethoxysilane and Methyltriethoxysilane

An aqueous acetic acid solution was prepared by adding ten drops of glacial acetic acid to 5.83 g. (0.648 equiv.) of distilled water. Part of this solution (3.2 g., 0.324 equiv. H_2O) was added dropwise with constant stirring to a mixture of *p*-allylphenyldimethylethoxysilane (95.0 g., 0.432 equiv.) and methyltriethoxysilane (6.4 g., 0.108 equiv.). The reaction temperature was kept at 45–50°C. during the addition. Another portion of the methyltriethoxysilane (6.4 g., 0.108 equiv.) was then added to the reaction mixture, after which the remainder of the aqueous acetic acid solution was added dropwise, with constant stirring, at 45–50°C.

After the reaction mixture had become homogeneous, an additional quantity of distilled water (3 g.) was added, and the whole mixture was stirred for 1 hr. at 45–50°C.

Ethanol and excess water were distilled from the reaction mixture at 20 torr, the temperature being allowed to reach 80°C. Distillate (35 ml.) was collected in a cold trap. A high vacuum distillation was then carried out on a molecular still, yielding four fractions as follows: F1: 84°C./10^{-4} torr, 11.8 g., n_D^{24} = 1.5053; F2: 85–96°C./10^{-4} torr, 16.2 g., n_D^{24} = 1.4986; F3: 165°C./10^{-4} torr, 22.2 g., n_D^{24} = 1.4943; F4: ≥ 165°C./10^{-4} torr, 5.9 g. n_D^{24} = 1.4895.

Cohydrolysis of *p*-Allylphenyldimethylethoxysilane with Dimethyldiethoxysilane

Distilled water (7.3 g., 0.40 mole), which contained one drop of glacial acetic acid, was added dropwise with constant stirring to a mixture of *p*-allylphenyldimethylethoxysilane (89.2 g. 0.40 mole) and dimethyldiethoxysilane (30.0 g. 0.20 mole). The mixture was vigorously stirred at ambient temperature for about 18 hr. Absolute ethanol (40 ml.) was then added and the mixture was heated at reflux for 1 hr. After removal of the ethanol by simple distillation, all other low-boiling material was removed at 85°C./10^{-3} torr. The undistilled product weighed 48 g., which represented a 55% yield. Low-boiling products weighed 12.2 g.

Epoxidation of Bis(*p*-allylphenyl)polymethylsiloxane

The cohydrolysis product of the experiment above was used in this epoxidation. Trifluoroacetic anhydride (27.9 g., 0.133 mole) in methylene chloride (25–30 ml.) was added dropwise to a stirred slurry of hydrogen peroxide (88%, 4.0 g., 0.102 mole) in methylene chloride at 0–5°C. When the reaction was completed, the peracid solution was added dropwise with constant stirring to a mixture of the diallyl compound (45.0 g., 0.102 mole) and anhydrous powdered sodium carbonate (42.2 g., 0.399 mole) in methylene chloride (75 ml.). The reaction mixture was maintained at reflux during the addition and for 30 min. thereafter. It was then filtered to remove inorganic salts. These salts were washed with methylene chloride, and the organic phases were combined and retreated with fresh carbonate. After setting overnight and refiltering, most of the solvents were removed by simple distillation and the low-boiling products were removed at 90°C./10^{-3} torr. The nonvolatile product weighed 36.6 g., which was 76% of theory.

Cohydrolysis of *p*-Allylphenyldimethylethoxysilane with *p*-Bis(dimethylethoxysilyl)benzene

Bis(dimethylethoxysilyl)benzene (46.0 g., 0.080 mole, b.p. 110–115°C./2 torr) and *p*-allylphenyldimethylethoxysilane (35.2 g., 0.160 mole) were mixed together, and acidified water (2.9 g., 0.16 mole, plus 0.3 drops acetic acid) was added. The mixture was stirred vigorously for about 16 hr. at ambient temperature. When excess water, ethanol, and low-boiling products were removed at 70°C./10^{-3} torr, the undistilled product weighed 40.5 g. (60% of theory) and had an equivalent weight of 491.

Epoxidation of 1,4-Bis[(*p*-allylphenyldimethylsiloxy)-dimethylsilyl]benzene

Trifluoroperacetic acid was prepared by the dropwise addition of a solution of trifluoroacetic anhydride (31.6 g., 0.150 mole) in methylene chloride (35 ml.) to a stirred mixture of methylene chloride (35 ml.) and hydrogen peroxide (4.66 g., 89%, 0.122 mole) at 0–5°C. The freshly prepared peracid was then added dropwise to a slurry of 1,4-bis[(*p*-allylphenyldimethylsiloxy)dimethylsilyl]benzene (35.0 g.) and anhydrous powdered sodium carbonate (47.8 g., 0.45 mole) in methylene chloride (75 ml.). Reflux was maintained throughout the addition and was continued for $^1/_2$ hr. after the addition was complete. After cooling, the inorganic salts were removed by filtration. Solvent was then removed by distillation, and the epoxy compound was heated at about 95°C./5×10^{-4} torr to remove all volatile constituents. A yield of 18.4 g. of epoxy compound was obtained, which had an equivalent weight of 491.

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Résumé

Le tétraméthyldisiloxane-1,3-bis[*p*-(2,3-epoxypropyl)phényl] et son isomère *méta* ont été synthétisés et ultérieurement traités avec la *m*-phénylènediamine. Les propriétés diélectriques de la résine traité dérivée de l'isomère *para* ont été mesurées entre 25 et 100°C. Sa constante diélectrique à température de chambre à 1 Kc était de 3.4, son facteur de dissipation était de 0.01 et sa résistivité de volume était de 10^{14} ohm-cm sous 500 volts dc. De nombreux allylphénylsiloxanes ont été également préparés par cohydrolyse de l'allylphényldiméthylethoxysilane avec le diméthyldiéthoxysilane, le bis(diméthyléthoxysilyl)benzène, et le méthyltriéthoxysilane. Des études d'époxydation préliminaires sur ces derniers matériaux ont également été effectuées.

Zusammenfassung

1,3-Bis[*p*-(2,3-epoxypropyl)phenyl]tetramethyldisiloxan und sein *meta*-Isomeres wurden hergestellt und nachher mit *m*-Phenylendiamin gehärtet. Die dielektrischen Eigenschaften des vom *para*-Isomeren abgeleiteten Harzes wurden zwischen 25° und 100°C gemessen. Das Harz besass bei 1 kHz bei Raumtemperatur eine Dielektrizitätskonstante von 3,4, einen Dissipationsfaktor von 0,01 und einen spezifischen Volumswiderstand von 10^{14} Ohm·cm. bei 500 Volt Gleichspannung. Durch Cohydrolyse von Allylphenyldimethyläthoxysilan mit Dimethyldiäthoxysilan, Bis(dimethyläthoxysilyl)-benzol und Methyltriäthoxysilan wurden auch mehrere Allylphenylsiloxane hergestellt. An diesen letztgenannten Substanzen wurden auch Voruntersuchungen über deren Epoxydierung durchgeführt.

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Radiation-Induced Polymerization of 1,1,2-Trichlorobutadiene

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Synopsis

The γ-ray-induced polymerization of 1,1,2-trichlorobutadiene, m.p. -48.5°C., was investigated in the temperature range from $+55$ to -196°C. In the liquid state, the following results were obtained: (*1*) the rate decreases with decrease of temperature (E_a = 8.0 kcal./mole); (*2*) the dose rate dependences of rate and of molecular weight are 0.49 and -0.25, respectively; (*3*) the reaction is inhibited by DPPH; (*4*) the structure of the polymer is predominantly 1,4 units. It was concluded that the liquid-state polymerization proceeds by a radical mechanism, and the radical yield was found to be 19.7. In the solid state, the following results were obtained: (*1*) the rate is considerably higher than in the liquid state immediately above the melting point and gradually decreases with decrease of temperature (E_a = 0.34 kcal./mole); (*2*) the dependence of the rate on dose rate is unity while the molecular weight is independent of the dose rate; (*3*) the reaction rate is unaffected by DPPH and accelerated by dimethylformamide; (*4*) the structure of the polymer, 3,4 units, is completely different from that of the polymer obtained in the liquid-state polymerization. The solid-state polymerization is probably of a different nature and is not well elucidated.

INTRODUCTION

It has been reported that the radiation-induced polymerization of butadiene[1,2] and isoprene[3,4] proceeds by an ionic mechanism as well as by a radical mechanism. The structure of the resulting polymers is specific to the reaction mechanism. Suprun and Soboleva[5] have shown that potassium persulfate-initiated polymerization of 1,1,2-trichlorobutadiene gives a polymer containing both 1,4 and 3,4 additions. In the present study, the polymerization of 1,1,2-trichlorobutadiene was carried out in the temperature range from $+55$ to -196°C. The structure of the resulting polymers was elucidated from the nuclear magnetic resonance and infrared spectra. It was found that the polymerization behavior and the structure of the polymer obtained in the solid-state polymerization were considerably different from those obtained in the liquid-state polymerization.

EXPERIMENTAL

The monomer was prepared by the method described previously[6] and purified by repeated drying with calcium hydride followed by distillation prior to use (b.p. 57.5°C./38 mm. Hg). Reagent-grade solvents were used after distillation and drying. The monomer in a glass ampule was degassed by a successive freezing-melting procedure and then sealed under a vacuum of about 10^{-6} mm. Hg. The ampule was then irradiated by γ rays from a ^{60}Co source in the temperature range from +55 to −196°C. After irradiation the contents of the ampule were diluted with benzene and poured into a large excess of cold methanol. The precipitated polymer was collected on a sintered glass filter disk, dried *in vacuo,* and weighed. The per cent conversion calculated from the weight of the isolated polymer was checked by determination of the unchanged monomer with vapor-phase chromatography with a Perkin-Elmer vapor fractometer Model-188.

The polymer samples used for the characterization were purified by repeated precipitation from benzene solution by methanol. The number-average molecular weight was determined osmometrically in benzene solution with a Hitachi-Perkin-Elmer vapor-pressure osmometer Model-115.

Infrared spectra were obtained with a grating infrared spectrometer, Hitachi Model EPI-G, by using the potassium bromide pellet technique. The NMR spectra were obtained with a Japan Electron Optics Laboratory Co. JNH4H-100 spectrometer operating at 100 Mc./sec. The resonance position, given in τ units, is for a carbon tetrachloride solution at 60°C. Tetramethylsilane was used as an internal reference.

RESULTS

Polymerization of 1,1,2-Trichlorobutadiene

As shown in Figure 1, the per cent conversion increases linearly with irradiation time up to a conversion of several per cent. There is no induction period except in the polymerization at −196°C., where a limiting con-

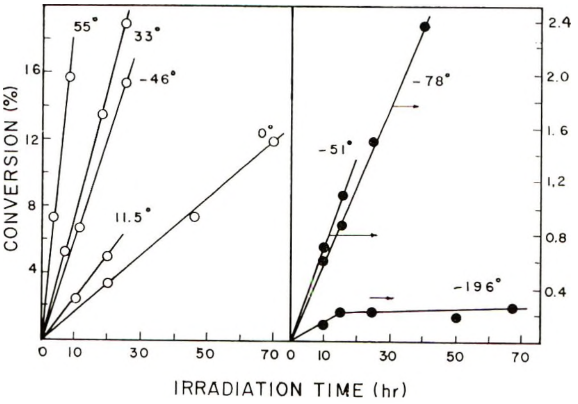

Fig. 1. Relationship between per cent conversion 1,1,2-trichlorobutadiene and irradiation time at various temperatures at a dose rate of 3.16×10^4 rad/hr.: (O) liquid, (●) solid. The scale of the ordinate for the curve at −46°C. is one hundredth of the scale in the figure.

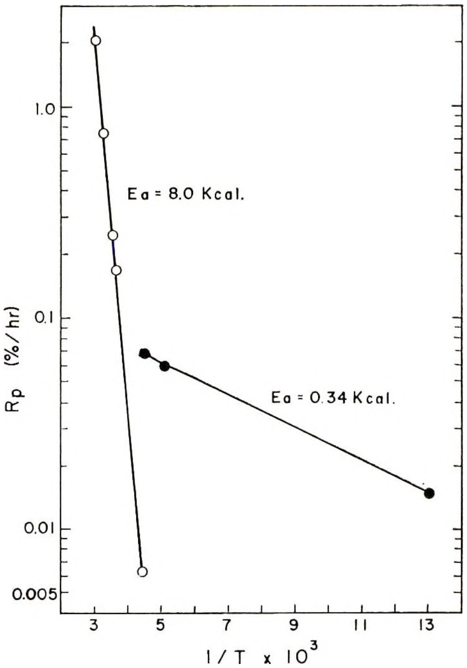

Fig. 2. Activation energies for polymerization at a dose rate of 3.16 × 10^4 rad/hr.: (O) liquid, (●) solid.

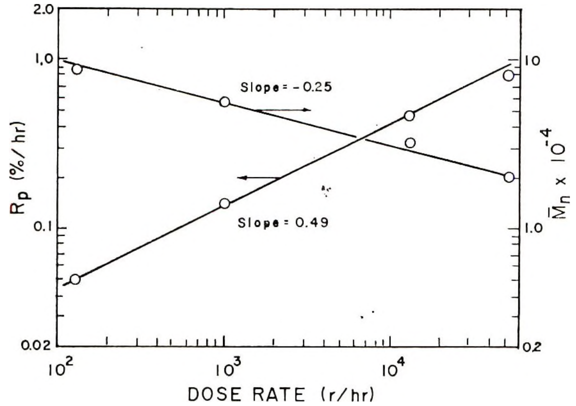

Fig. 3. Dependences of rate of polymerization and molecular weight on dose rate at an irradiation temperature of 25°C.

version of about 0.2% was reached. Figure 2 shows the influence of temperature on the rate of polymerization. The rates decrease linearly with decrease of temperature in the liquid-state polymerization. At −51°C., where the monomer solidifies, the rate increases sharply and again decreases linearly with decrease of temperature, although the slope of the line is not as sharp as that in the liquid-state polymerization. The overall activation

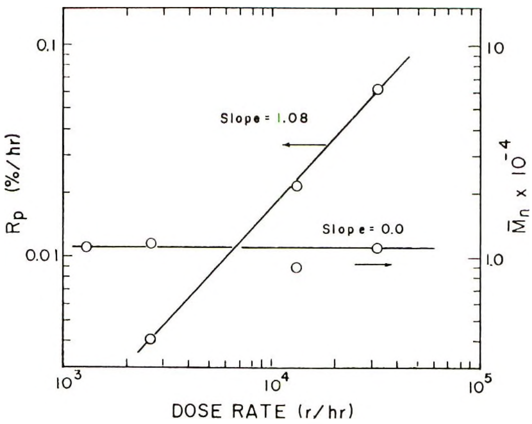

Fig. 4. Dependences of rate of polymerization and molecular weight on dose rate at an irradiation temperature of −78°C.

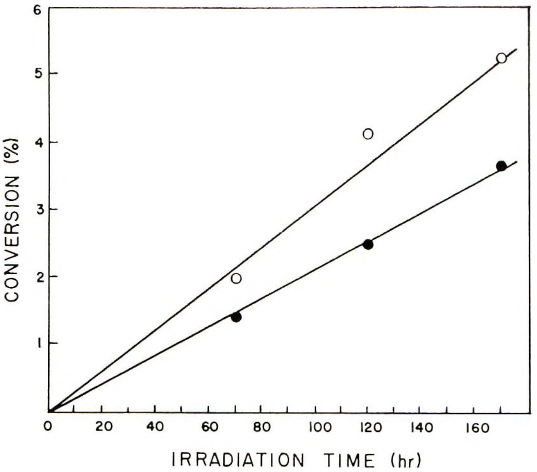

Fig. 5. Effect of dimethylformamide on polymerization of 1,1,2-trichlorobutadiene at −78°C. at a dose rate of 1.3×10^4 rad/hr.: (○) monomer containing 50 mole-% dimethylformamide, (●) pure monomer.

energies were calculated to be 8.0 and 0.34 kcal./mole in the liquid- and solid-state polymerizations, respectively.

Figures 3 and 4 represent the dose rate dependences of the initial rate of polymerization and of the initial molecular weight at 25°C. (liquid state) and at −78°C. (solid state), respectively. The following results were obtained: at 25°C., Rate $\propto$ (dose rate)$^{0.49}$, $\bar{M}_n \propto$ (dose rate)$^{-0.25}$; at −78°C., Rate $\propto$ (dose rate)$^{1.08}$, $\bar{M}_n \propto$ (dose rate)$^{0.0}$. The molecular weight of the polymer obtained at −78°C. was considerably lower than of that obtained at 25°C.

In a preliminary experiment on the effect of oxygen on the polymerization, inhibition was observed in the liquid-state polymerization and re-

TABLE I
Effect of DPPH on the Polymerization

Temperature, °C.	Physical state	Total dose, Mrad	Conversion, % DPPH added (2 wt.-%)	No DPPH
25	Liquid	0.31	0.26	12.0
0	Liquid	0.62	0.0	5.7
−46	Liquid	0.38	0.0	0.043
−51	Solid	0.47	0.63	1.09
−78	Solid	0.91	1.75	1.52

tardation in the solid-state polymerization. The effect of DPPH on the polymerization is shown in Table I. DPPH inhibits the liquid-state polymerization, while it has no effect in the solid-state polymerization. It is generally known that an amine solvent such as dimethylformamide accelerates the anionic polymerization. In Figure 5, a comparison of the polymerization rate in the solid state at −78°C. of pure monomer with that of monomer containing 50 mole-% of dimethylformamide is shown. It is evident from the figure that dimethylformamide accelerates the solid-state polymerization.

Structure of Poly-1,1,2-trichlorobutadiene

In the polymerization of 1,1,2-trichlorobutadiene, the 1,4-, 1,2-, and 3,4-additions are possible, leading to the following structures, respectively: $-\mathrm{CCl_2-CCl{=}CH-CH_2}-$, $-\mathrm{CCl_2}-\underset{|}{\mathrm{CCl}}-\mathrm{CH{=}CH_2}$, and $\mathrm{CCl_2{=}CCl}-\underset{|}{\mathrm{CH}}-\mathrm{CH_2}-$. Polymer samples prepared at +55, 0, −78, and −196°C. were investigated.

The NMR spectra of the monomer and polymers are shown in Figure 6. The spectrum of the monomer shows two groups of peaks centered at τ 3.1 and τ 4.4 due to the nonterminal and terminal olefinic protons. The coupling constants between the vicinal protons in the double bond were found to be 17 cps for *trans* and 10 cps for *cis*. These values are in good agreement with the values reported[7] for compounds of the same type. The chemical shifts of the nonterminal olefinic proton, and the *trans*- and *cis*-terminal protons were τ 3.13, τ 4.22, and τ 4.54, respectively.

The spectrum of polymer A obtained at −196°C. shows peaks at τ 6.92 and τ 8.22 in 1:1.8 area ratio. These peaks are assigned to the methin proton and the methylene protons, respectively, in $\mathrm{CCl_2{=}CCl}-\underset{|}{\mathrm{CH}}-\mathrm{CH_2}-$ groupings. Since there is no peak at lower field, the absence of olefinic protons was confirmed. With polymer B, obtained at −78°C., weak peaks at τ 6.47 appear in addition to the peaks τ 6.92 and τ 8.22 (the

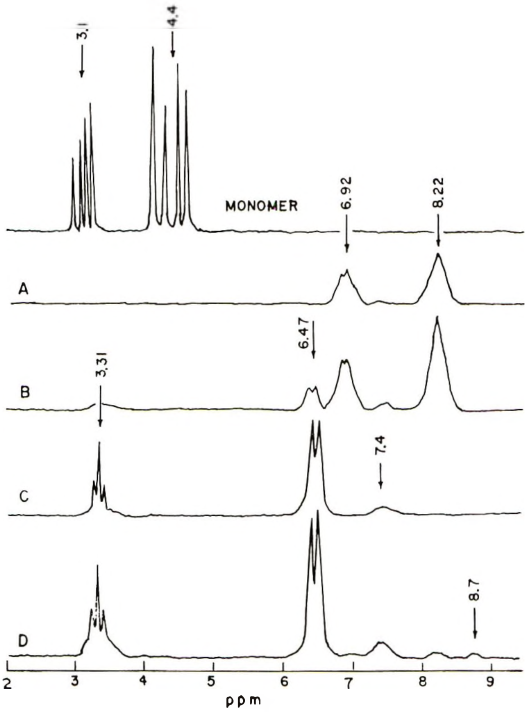

Fig. 6. NMR spectra of 1,1,2-trichlorobutadiene and its polymers prepared at (A) -196°C.; (B) -78°C.; (C) 0°C.; (D) $+55$°C.

area ratio of the last two peaks was 1:2.0). These are due to $=C-CH_2-CCl_2-$ protons in 1,4 units as mentioned below. From the area ratio of the τ 6.47 peaks to the τ 8.22 peak, the relative concentration of 1,4 units was calculated to be about 12 mole-%. It was concluded, therefore, that the polymer obtained at -196°C. is composed of 3,4 units and the polymer obtained at -78°C. consists of 3,4 units and a small amount of 1,4 units.

The spectrum of polymer D obtained at $+55$°C., which is similar to that of polymer C obtained at 0°C., shows peaks at τ 3.31 and τ 6.47. These peaks are assigned to the olefinic proton and the methylenic protons, respectively, in $-CCl_2-CCl=CH-CH_2-$ groupings, their chemical shifts being compared with those of the protons in $=CCl-CH=$ (τ 3.13) of the monomer and in $-CCl_2-CH_2-CCl_2-$ (τ 6.01).[8] The triplet and doublet splittings of the peaks and the 1:2.0 area ratio support this assignment. Besides these main peaks, weak peaks at τ 7.4 and τ 8.7 appear (the latter peak is absent from polymer C). The τ 7.4 peak may be assigned to the methylenic protons of a $-CCl_2-CCl=CH-CH_2-CH_2-CH=CCl-CCl_2-$ structure which would result from a head-to-head 1,4 addition. It was concluded, therefore, that the polymers prepared in the liquid-state polymerizations at $+55$ and 0°C. contain predominantly 1,4 units.

The infrared spectra of the polymers, as shown in Figure 7, exhibit notable differences in the regions around 3000 and 1600 cm.$^{-1}$ and the region

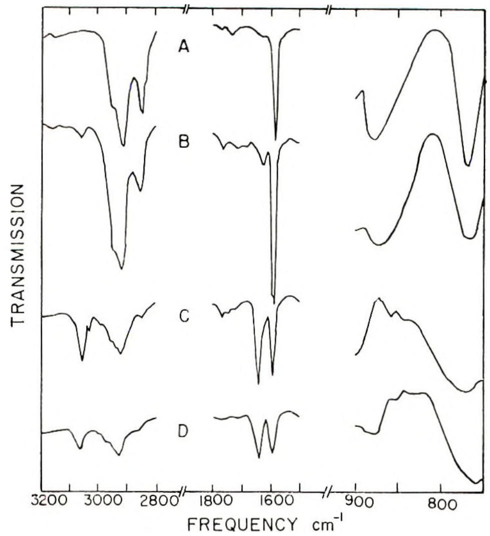

Fig. 7. Infrared spectra of poly-1,1,2-trichlorobutadiene prepared at (A) −196°C.; (B) −78°C.; (C) 0°C.; (D) +55°C.

between 850 and 800 cm.$^{-1}$, depending upon the physical state during polymerization. Polymers A and B prepared by solid-state polymerization exhibit a strong band at 2920 cm.$^{-1}$ due to the saturated C—H stretching vibration and a sharp band at 1590 cm.$^{-1}$. The 1590 cm.$^{-1}$ band is assigned to C=C stretching vibration of the trichlorovinyl double bond resulting from 3,4 additions, by comparing with those of 1,1,2-trichloro-1-butene-3-ol[6] and 1,1,2-trichloropropene-1.[9] In polymer B prepared at −78°C., a weak band is displayed at 3060 cm.$^{-1}$ and is accompanied by the 1625 cm.$^{-1}$ band. These bands were assumed to arise from 1,4 additions as described below.

Polymers C and D prepared by liquid-state polymerization show additional bands at 3060 and 1640 cm.$^{-1}$, the bands at 2920 and 1590 cm.$^{-1}$ being decreased in intensity. The 3060 and 1640 cm.$^{-1}$ bands are assigned to the olefinic C—H stretching vibration and C=C stretching vibration in $—CCl_2—CCl=CH—CH_2—$ groupings resulting from 1,4 addition. The peak frequencies corresponding to the 1640 cm.$^{-1}$ band have been reported to be 1653 cm.$^{-1}$ (*cis* form) and 1662 cm.$^{-1}$ (*trans* form) in 1,4 addition of chloroprene,[10] and about 1650 cm.$^{-1}$ in 1,4 addition of isoprene.[11] Furthermore, although no maximum was seen because of overlapping, the absorption in the region between 850 and 800 cm.$^{-1}$, which seem to be characteristic of 1,4-polybutadiene, was observed with polymers C and D but not with polymers A and B. The frequencies of the corresponding absorption have been reported to be 826 cm.$^{-1}$ in polychloroprene[10] and 843 and 815.5 cm.$^{-1}$ in polyisoprene.[11]

These infrared spectra of the polymers are consistent with the findings from the NMR spectra.

DISCUSSION

In liquid-state polymerization the reaction is inhibited by radical inhibitors such as DPPH, and the structure of the resulting polymer, predominantly 1,4 units, is similar to that of a polymer prepared from a conventional radical polymerization in an emulsion system.[5] Moreover, the rate is proportional to the square root of the dose rate. These findings indicate that the polymerization proceeds by a free-radical mechanism.

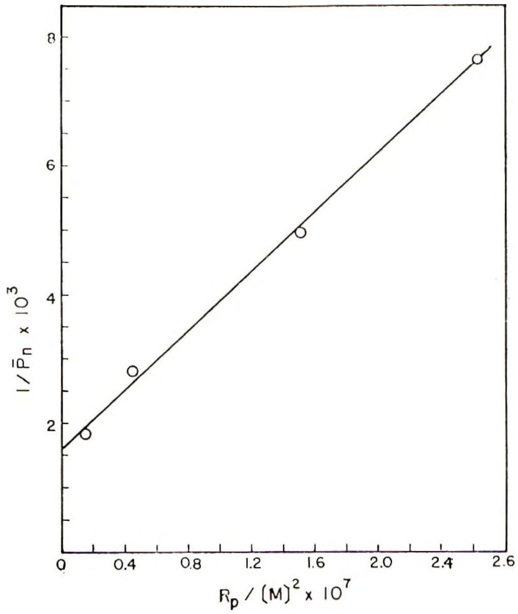

Fig. 8. Relationship between $1/\bar{P}_n$ and $R_p/[M]^2$ for polymerization of 1,1,2-trichlorobutadiene at 25°C.

Figure 8 shows the reciprocal of the degree of polymerization, $1/\bar{P}_n$, plotted versus the rate of polymerization, R_p, on the basis of the experimental data of Figure 3. A linear relationship was obtained given by eq. (1).

$$1/\bar{P}_n = 1.6 \times 10^{-3} + 2.4 \times 10^4 R_p/[M]^2 \qquad (1)$$

From this equation, the value of the transfer constant with monomer was shown to be 1.6×10^{-3}. The rate of initiation, G_i, was calculated from the value of $k_t/2k_p^2$ [2.4×10^4 from eq. (1)], and the radical yield, G_r, was derived from the value of R_i. These values are presented in Table II. The G_r values ranged from 12.6 (for high dose rate) to 19.7 (for low dose rate). Such variation in the G_r value with dose rate was reported in the cases of styrene and methyl methacrylate.[12] The higher value is more reliable, as the rate of production of free radicals tend to reach a saturation value at higher dose rates.

TABLE II
Radiation-Chemical Yields for the Production of Free Radicals Derived from Kinetic Data (Irradiation Temperature 25°C.)

I, rad/sec.	R_p, mole/l.-sec. × 10^6	R_i, mole/l.-sec. × 10^8	G_r, radicals/ 100 e.v.
14.2	19.4	23.7	12.6
3.61	11.2	7.92	16.6
0.28	3.33	0.58	19.0
0.036	1.22	0.094	19.7

From the following findings it has been concluded that the solid-state polymerization of styrene[13] and acrylonitrile[14] at low temperature proceeds by an ionic mechanism: (*1*) the activation energies are negative or very small, (*2*) monomers containing a radical scavenger are easily polymerized, (*3*) the rates are first-order with respect to the dose rate, and (*4*) the molecular weights of the polymers are independent of the dose rate. It has also been concluded that the low temperature polymerization of 1,3-dienes such as butadiene[1,2] and isoprene[3,4] proceeds by an ionic mechanism. This is based on the following evidence: (*1*) the activation energy is negative, (*2*) the reaction rate is unaffected by radical inhibitors and reduced by pyridine, (*3*) the rate is proportional to the first power of the dose rate, (*4*) the structure of the polymer is similar to that of the cationically polymerized polymer.

For the present solid-state polymerization of 1,1,2-trichlorobutadiene, the results are summarized as follows: (*1*) the rate increases sharply when the monomer solidifies, and the activation energy (0.34 kcal./mole) is very much lower than that found for the liquid-state polymerization (8.0 kcal./mole); (*2*) the rate is first-order with respect to the dose rate, and the molecular weight of the polymer is independent of the dose rate; (*3*) the reaction rate is unaffected by DPPH and accelerated by dimethylformamide.

Dose rate dependence of the rate of polymerization and of the molecular weight as found in this solid-state polymerization study are also seen in the case of the solid-state polymerization of acrylamide in which the reaction proceeds by a radical mechanism,[15] and hence the above-mentioned results are not considered conclusive evidence for an ionic mechanism. However, attention should be paid to the remarkable change in the structure of polymers (3,4 units in solid-state polymerization, predominantly 1,4 units in liquid-state polymerization). In order to establish the reaction mechanism, a preliminary experiment on the polymerizations in solution at −78°C., by ionic catalysts such as *n*-BuLi, sodium naphthalene, $BF_3 \cdot O(Et)_2$, $TiCl_4$–$Al(Et)_3$, and $Al(Et)_3$–H_2O was tried. No polymer could be obtained. Though the polymerization in the solid state seems to proceed by an ionic mechanism, more extensive work will be required to decide the reaction mechanism unquestionably.

We wish to thank Japan Electron Laboratory Co. for the measurement of NMR spectra and Mr. Takaari Yumoto of our Institute for supplying the monomer.

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Résumé

La polymérisation induite par irradiation γ du 1,1,2-trichlorobutadiène, (point de fusion -48.5°C) a été étudiée dans un domaine de température de $+55$ à -196°C. A l'état liquide les résultats suivants ont été obtenus: (*1*) la vitesse décroît avec une diminution de la température ($E_a = 8.0$ Kcal/mole); (*2*) la dépendance de la vitesse en fonction de la dose était de 0.49 et en ce qui concerne le poids moléculaire de -0.25; (*3*) la réaction est inhibée par DPPH; (*4*) la structure du polymère est essentiellement 1.4. On en conclut que la polymérisation à l'état liquide résulte d'un mécanisme radicalaire et que le rendement radicalaire est de 19.7. A l'état solide, les résultats suivants ont été obtenus: (*1*) la vitesse est notablement plus élevée qu'à l'état liquide bien que au-dessus du point de fusion elle décroît graduellement avec une diminution de température ($E_a = 0.34$ Kcal/mole); (*2*) la dépendance de la vitesse en fonction de la vitesse de dose est unitaire alors que le poids moléculaire est indépendante de cette dose; (*3*) la vitesse de réaction n'est pas affectée par le DPPH et est accélérée par le diméthylformamide; (*4*) la structure du polymère essentiellement du type 3,4 est entièrement différente de celle du polymère obtenu pour la polymérisation à l'état liquide. La polymérisation a l'état solide est probablement d'une nature différente qui n'a pas encore été bien élucidée.

Zusammenfassung

Die durch γ-Strahlen angeregte Polymerisation von 1,1,2-Trichlorbutadien (Fp. 48,5°C) wurde im Temperaturbereich von $+55$ bis -196°C untersucht. Im flüssigen Zustand wurden folgende Resultate erhalten: (*1*) Die Geschwindigkeit wird mit abnehmender Temperatur kleiner ($E_a = 8{,}0$ Kcal/Mol), (*2*) die Dosisleistungsabhängigkeit der Geschwindigkeit und des Molekulargewichts beträgt 0,49 bzw. $-0{,}25$, (*3*) die Reaktion wird durch DPPH inhibiert, (*4*) das Polymere weist überwiegend 1,4-Verküpfungen auf. Daraus wurde geschlossen, dass die Polymerisation im flüssigen Zustand nach einem radikalischen Mechanismus verläuft; die Radikalausbeute beträgt dabei, wie gefunden wurde, 19.7. Für den Festzustand ergaben sich folgende Resultate: (*1*) Die

Geschwindigkeit ist wesentlich höher als im flüssigen Zustand unmittelbar über dem Schlemzpunkt und nimmt mit fallender Temperatur allmählich ab (E_a = 0,34 Kcal/Mol), (*2*) die Geschwindigkeit ist der Dosisleistung direkt proportional, während das Molekulargewicht unabhängig von der Dosisleistung ist, (*3*) die Reaktionsgeschwindigkeit bleibt durch DPPH unbeeinflusst und wird durch Dimethylformamid erhöht, (*4*) die Struktur des Polymeren (3,4-Verknüpfung) ist von der des im flüssigen Zustand erhaltenen Polymeren vollständig verschieden. Die Polymerisation im Festzustand ist wahrscheinlich anderer Natur und ist nicht vollständig aufgeklärt.

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Polynomial Expansion of Log Relative Viscosity and Its Application to Polymer Solutions

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Synopsis

Solomon and Ciuta's equation has been deduced from first principles and has been shown to be merely an algebraic consequence of the definition of intrinsic viscosity. Secondly, a consequence of this equation that $[\eta]c$ should be linear with $\sqrt{2\eta_{sp} - 2 \ln \eta_{rel}}$ with unit slope, is found to be fairly accurate when examined against literature and our own data, and so this equation is commended not only for single-point determination of $[\eta]$ but also for representing viscosity variation with concentration up to $\eta_{sp} < 0.60$. Thirdly, higher-order approximations are found to be less suitable. Other consequences of Solomon and Ciuta's equation are discussed.

Solomon and Ciuta[1] have proposed an equation [eq. (7)] for a single-point determination of intrinsic viscosity $[\eta]$. Narr et al.[2] have deduced this equation from Huggins' viscosity equation,[3] and Ibrahim and Elias[4] have derived this by combining Huggins' equation[3] with Kraemer's equation.[5] Recently Deb and Chatterjee[6] have derived another equation of the same type [eq. (9)] by eliminating K from Schulz and Blaschke's equation.[7] The purpose of the present note is to examine closely the algebraic foundation of the proposed relations, when it turns out that these relations follow from the mere definition of intrinsic viscosity $[\eta]$; secondly we have investigated herein the validity of these equations for representation of viscosity variation with concentration for dilute polymer solution.

Since relative viscosity η_{rel} by definition is given by $\eta_{rel} = 1 + \eta_{sp}$ where η_{sp} is specific viscosity, we can take logarithm of both sides and expand as follows:

$$\ln \eta_{rel} = \ln (1 + \eta_{sp}) = \eta_{sp} - {}^1/_2\, \eta_{sp}^2 + {}^1/_3\, \eta_{sp}^3 - {}^1/_4\, \eta_{sp}^4 + \dots \quad (1)$$

On retaining the first term only, we get

$$\ln \eta_{rel} = \eta_{sp} = \psi_1 \dots \quad (2)$$

which should be valid at infinite dilution. On retaining up to the second term we get

$$\ln \eta_{rel} = \eta_{sp} - {}^1/_2\, \eta_{sp}^2 \quad (3)$$

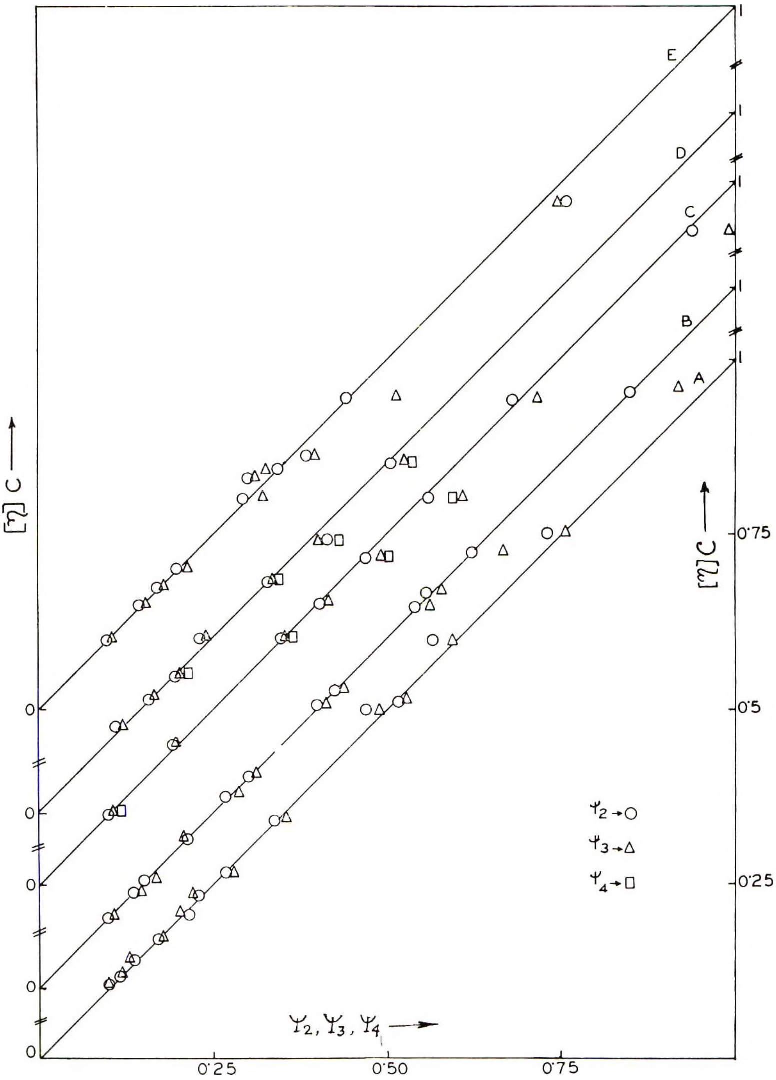

Fig. 1. $[\eta]c-\psi$ plots of literature data: (*A*) Baysal's[8] data on poly(methyl methacrylate) in chloroform; (*B*) Billmeyer's[9] data on poly(methyl methacrylate) in ethylene dichloride; (*C*) Wagner's[10] data on poly(vinyl acetate) in acetone; (*D*) Philipp's[11] data on cellulose acetate in methyl glycol; (*E*) Philipp's[11] data on cellulose acetate in acetone.

If η_{sp} is supposed to be represented by a polynomial series in c (concentration), i.e.,

$$\eta_{sp} = [\eta]c + Kc^2 + \dots \tag{4}$$

where K is related to the well-known Huggins constant K' by the relation $K = K'[\eta]^2$, we can substitute this value for η_{sp} in eq. (3) in the quadratic term to obtain

$$\ln \eta_{\mathrm{rel}} = \eta_{sp} - {}^1/_2([\eta]c + K'[\eta]^2c^2 + \dots)^2 \tag{5}$$

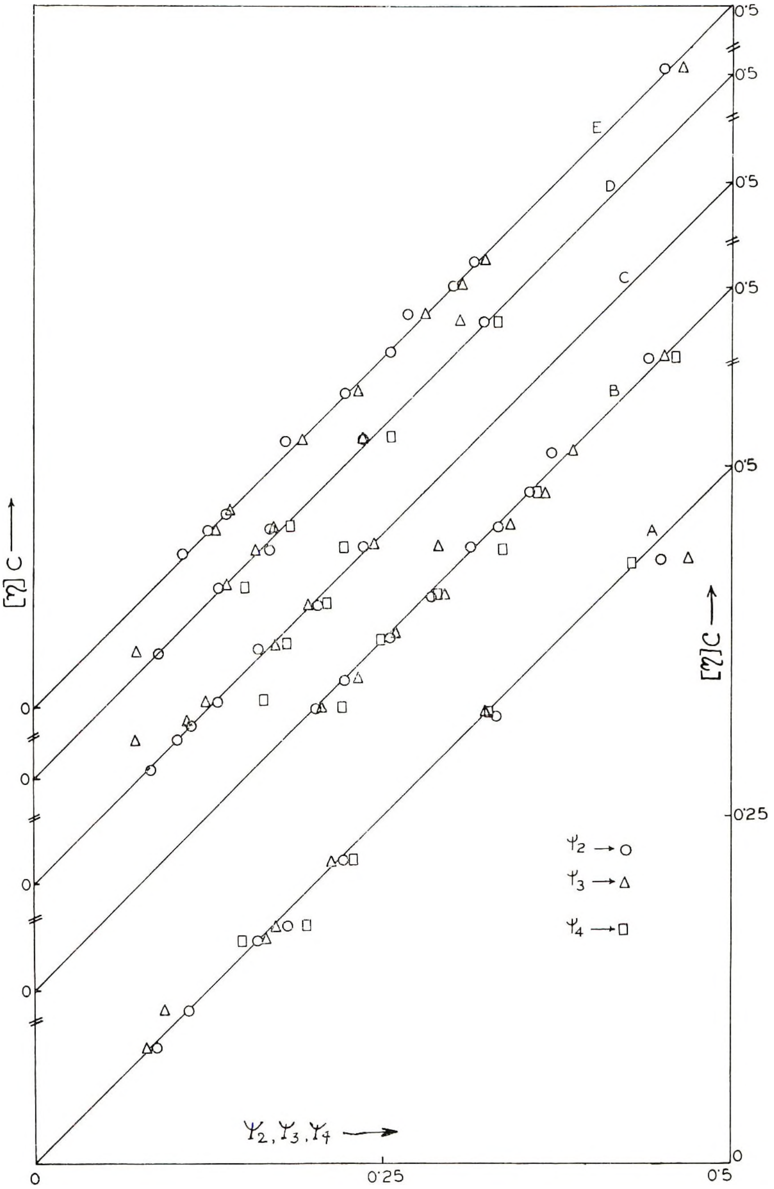

Fig. 2. $[\eta]c$–ψ plots: (*A*) Wissler's[12] data on glycogen triacetate; (*B*) our data on copolymer of methyl methacrylate and styrene in benzene at 30°C.; (*C*) our data on poly-*m*-vinyltoluene in ethyl acetate at 30°C.; (*D*) our data on poly-*m*-vinyltoluene in cyclohexane at 30°C.; (*E*) our data on poly(ethyl acrylate) in methyl ethyl ketone at 30°C.

Including the first term involving K' in the quadratic expression, we obtain

$$[\eta]c = \sqrt{2\eta_{sp} - 2 \ln \eta_{rel} - 2K'[\eta]^3c^3} \tag{6}$$

Since the term involving K' in eq. (6) is negligible in comparison to the second term, we can ignore this and get the relation

$$[\eta]c = \sqrt{2\eta_{sp} - 2\ln\eta_{\mathrm{rel}}} = \psi_2 \tag{7}$$

which is the equation of Solomon and Ciuta. If the cubic term is included, the equation becomes

$$\ln\eta_{\mathrm{rel}} = \eta_{sp} - {}^1/_2\eta_{sp}{}^2 + {}^1/_3([\eta]c + K'[\eta]^2c^2 + \ldots)^3$$

On retaining the term involving K' in the cubic expression this becomes

$$[\eta]c = \sqrt[3]{3\ln\eta_{\mathrm{rel}} - 3\eta_{sp} + {}^3/_2\,\eta_{sp}{}^2 - 3K'[\eta]^4c^4} \tag{8}$$

In this case also the term involving K' is negligible in comparison to others and thus we get

$$[\eta]c = \sqrt[3]{3\ln\eta_{\mathrm{rel}} - 3\,\eta_{sp} + {}^3/_2\eta_{sp}{}^2} = \psi_3 \tag{9}$$

which is the equation of Deb and Chatterjee,[6] who derived the same from Schulz and Blaschke's[7] equation in an attempt to improve upon the accuracy of Solomon and Ciuta's equation.[1] Similarly, including up to the biquadratic term and retaining the term involving K' of the expanded biquadratic expression we get

$$[\eta]c = \sqrt[4]{4\eta_{sp} - 2\eta_{sp}{}^2 + {}^4/_3\eta_{sp}{}^3 - 4\ln\eta_{\mathrm{rel}} - 4K'[\eta]^5c^5} \tag{10}$$

For the same reason as stated above, the term involving K' of eq. (10) can be ignored, leading to the equation

$$[\eta]c = \sqrt[4]{4\eta_{sp} - 2\eta_{sp}{}^2 + {}^4/_3\,\eta_{sp}{}^3 - 4\ln\eta_{\mathrm{rel}}} = \psi_4 \tag{11}$$

It appears that we can include more and more terms to get better and better agreement with experiment (however, see below). The following points deserve special mention.

In deriving eq. (7), (9), or (11), only the first term involving K' of the quadratic, cubic, or biquadratic expansion was accepted and the others were ignored. This is normally permissible only if they are negligible compared to the first term. Here, they are often not so, but still this gives fairly accurate results because the error is largely cancelled out by the leading term in the next higher polynomial. For example, in expansion of ${}^1/_3\eta_{sp}{}^3$,

$${}^1/_3\eta_{sp}{}^3 = {}^1/_3[\eta]^3c^3 + {}^1/_3K^3c^6 + K[\eta]c^3\eta_{sp}$$

Deb and Chatterjee[6] accepted only the term ${}^1/_3[\eta]^3c^3$ but neglected two other terms. The term $K[\eta]c^3\eta_{sp}$ is not negligible in comparison to ${}^1/_3[\eta]^3c^3$, but this does not introduce much error here because the leading term of $-{}^1/_4\eta_{sp}{}^4$ is almost equal to this and so almost cancels it out. Similarly, in the deduction of Solomon and Ciuta's equation,[1] Narr et al.[2] have neglected the term higher than c^2, and a similar justification exists. Thus

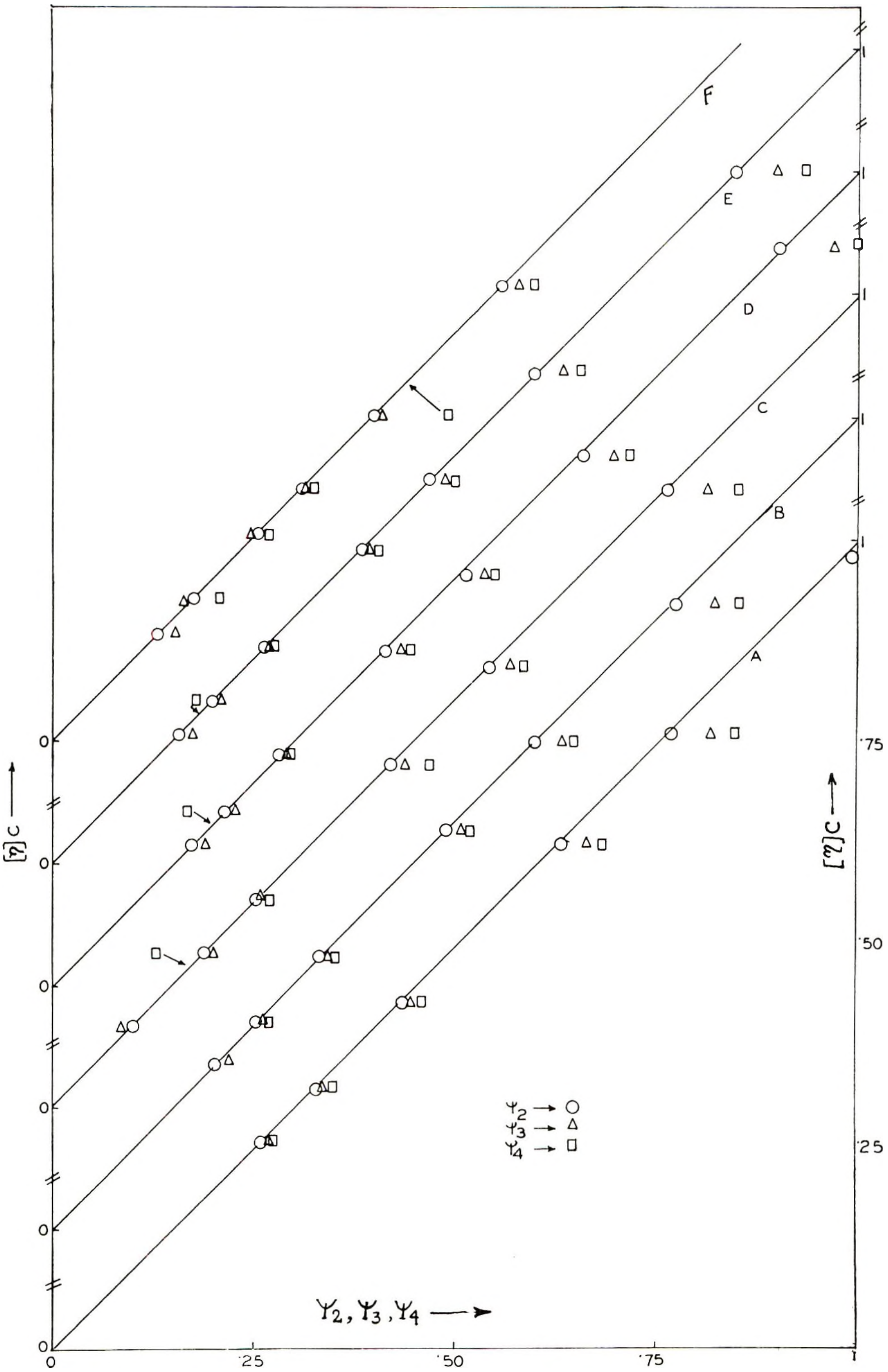

Fig. 3. $[\eta]c$–ψ plots of Kapur's[13] data on poly(vinyl acetate) in acetone at 30°C.: (*A*) fraction Ia; (*B*) fraction Ib; (*C*) fraction Id; (*D*) fraction IIa; (*E*) fraction IIb; (*F*) unfractionated sample I.

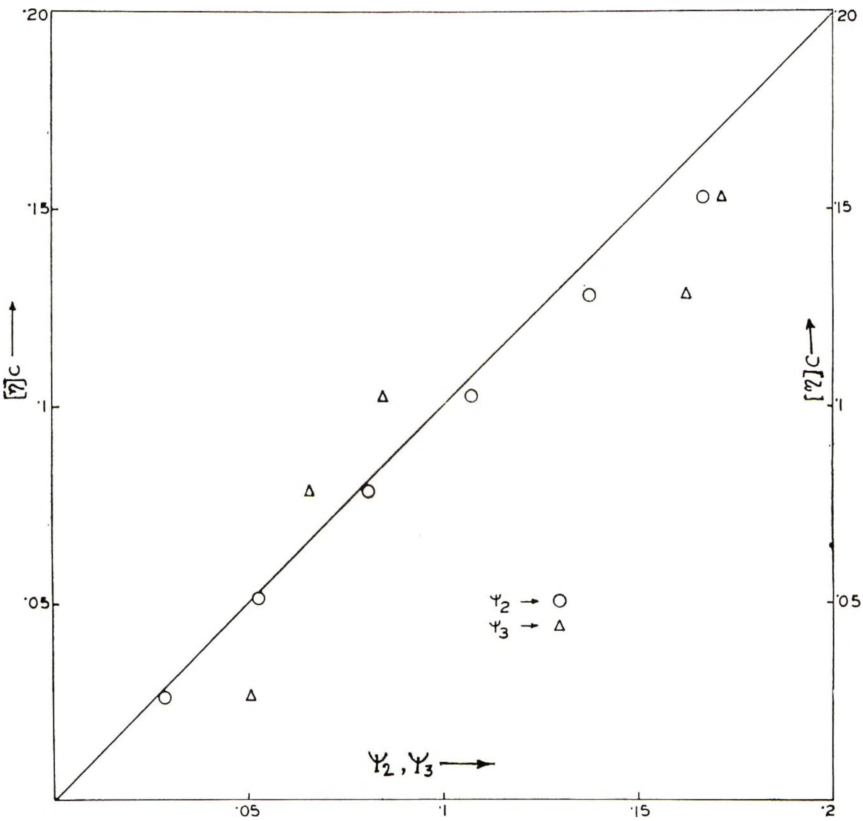

Fig. 4. $[\eta]c$–ψ plots of literature[14] data on sucrose solution in water at 20°C.

Solomon and Ciuta's equation[1] is valid due to a fortunate cancellation of alternate positive and negative terms.

The prime condition of validity of these eqs. (7), (9), and (11) is evidently $\eta_{sp} < 1$. For the usual accuracy, use of $\eta_{sp} < 0.6$ gives satisfactory results.

The most remarkable feature of eqs. (7), (9), and (11) is that they contain no adjustable parameter and give directly the value of $[\eta]$ from a single determination of relative viscosity, a feature well illustrated by Solomon and Ciuta[1] and also by Deb and Chatterjee.[6]

Another feature of these equations is that if we plot $[\eta]c$ against ψ_2, ψ_3, or ψ_4 we should get a straight line of unit slope passing through the origin for all polymers in all solvents at all temperatures in dilute solution. Experimentally, this is found to be true under the condition, $\eta_{sp} <$ ca. 0.6 i.e., $[\eta]c <$ ca. 0.75. This is graphically illustrated for a number of systems in Figures 1–4 from published data and data from our own laboratory. The agreement is quite satisfactory.

It appears from the method of deduction of eqs. (7), (9), and (11), that eq. (11) would be somewhat better than eq. (9) which in turn would be somewhat better than eq. (7); but when these equations were closely examined with experimental data by plotting $[\eta]c$ versus ψ, the case was found not to be so. In fact, eq. (7) is generally found to be at least as good as, if not better than, eq. (9), while eq. (11) was in general of poor validity [results of eq. (11) are plotted in a few cases only]. This is probably due to the increased sensitivity of eq. (11) as it contains a biquadratic term and thus a slight error in the determination of $[\eta]$ is magnified in the above plot. For the same reason, eq. (9) offers no advantage over eq. (7). We therefore conclude that for fairly dilute polymer solutions Solomon and Ciuta's equation[1] is good enough and is the equation of choice.

An important conclusion from our derivation is that the remarkably simple equation of Solomon and Ciuta[1] not containing any adjustable parameter [as also eqs. (9), (11), and higher order ones] is merely an algebraic consequence inherent in the definition of intrinsic viscosity $[\eta]$ and is in no way dependent on Huggins' equation,[3] Schulz and Blaschke's equation,[7] Kraemer's equation,[5] or for that matter any other equation of similar type as supposed by Narr et al.,[2] Ibrahim and Elias,[4] and Deb and Chatterjee,[6] respectively, and the $[\eta]$ value obtained by using Solomon and Ciuta's equation[1] would be identical with the value obtained by the usual linear extrapolation of η_{sp}/c versus c to infinite dilution, as the two procedures are mathematically equivalent. Solomon and Ciuta's equation[1] is strongly commended either for determination of $[\eta]$ or for representing viscosity variation with concentration not only for high polymers but also for other solutes, say, sugar, by determining the limiting slope of the c versus ψ_2 plot.

There is one difficulty with Solomon and Ciuta's equation.[1] This equation predicts that at low viscosity ($\eta_{sp} < 0.6$ as per our finding), plots of η_{sp} versus c, or log η_{rel} versus c, or the usual η_{sp}/c versus c should not intersect each other for all polymers in all solvents. This requirement appears to be extremely stringent, but since it is inherent in Solomon and Ciuta's equation,[1] it is very likely to be experimentally valid. The vast amount of presently available experimental data needs scrutiny from this standpoint to elucidate further this remarkable consequence of Solomon and Ciuta's equation.[1]

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Résumé

L'équation de Solomon et Ciuta a été déduite au départ du premier principe et est essentiellement une conséquence algébrique de la définition de la viscosité intrinsèque. Une conséquence de cette expression, à savoir que $[\eta]c$ serait linéaire par rapport à $\sqrt{2\eta_{sp} - 2 \ln \eta_{rel}}$ avec une tengente unitaire est remarquablement précise lorsque elle est examinée en comparaison avec la littérature et nos propres résultats, et ainsi cette équation est recommandée non seulement pour la détermination par un seul point de $[\eta]$ mais également pour représenter la variation de viscosité avec la concentration jusque $\eta_{sp} < 0.60$. Troisièmement, des approximations d'ordre plus élevés, ont été trouvées moins utiles. D'autres conséquences de l'équation de Solomon et Ciuta sont discutées.

Zusammenfassung

Die Gleichung von Solomon und Ciuta wurde aus Grundprinzipien hergeleitet und stellt, wie gezeigt wurde, lediglich eine algebraische Konsequenz der Definition der Viskositätszahl dar. Weiters ist die als Konsequenz dieser Gleichung auftretende Linearität zwischen $[\eta]c$ und $\sqrt{2\eta_{sp} - 2 \ln \eta_{rel}}$, wobei die Neigung eins beträgt, wie an Hand von Literaturdaten und eigenen Ergebnissen festgestellt wurde, mit be friedigender Genauigkeit erfüllt. Aus diesem Grund ist diese Gleichung nicht nur für die Bestimmung von $[\eta]$ aus einem einzigen Messpunkt, sondern auch für die Darstellung der Konzentrationsabhängigkeit der Viskosität bis zu $\eta_{sp} < 0{,}60$ zu empfehlen. Darüberhinaus wurde gefunden, dass Näherungen höherer Ordnung weniger gut geeignet sind. Weitere Konsequenzen der Solomon-Ciuta-Gleichung werden einer Diskussion unterzogen.

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On the Chromophore of Polyacrylonitrile

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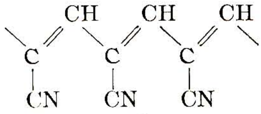
Synopsis

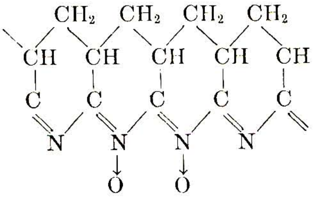
Further evidence is presented to show that the chromophore of polyacrylonitrile is formed by polymerization of the nitrile groups, rather than by dehydrogenation of the polymer backbone. The polyimine structure formed is resistant to hydrolysis; hence, the nitrogen content of hydrolyzed polymer increases with increased chromophore formation.

When polyacrylonitrile (PAN) is subjected to heat or to treatment with base, the polymer becomes colored. The intensity of the color depends upon the intensity and duration of the treatment. Many authors have concerned themselves with the chemical structure of the chromophore so produced[1]; in particular Conley and Bieron[2] have suggested a simple olefin bond conjugated with a nitrile group, whereas Berlin et al.[3] and Fester[4–6] have proposed that the polymer is dehydrogenated by heat to form a polyene with pendant nitrile groups (I).



I

On the other hand, Peebles and Brandrup[1] cite evidence for a system of conjugated imine and nitrone groups (II) formed by polymerization of the nitrile groups either by heat or by base followed by addition of oxygen.



II

Fester cites spectra and hydrolysis data for heat-degraded PAN and polymethacrylonitrile (PMAN) to show that chemically different mechanisms are responsible for the formation of color in these polymers. We will defer a detailed discussion of the interpretation of ultraviolet and infrared spectra to later publications; in this paper we wish to consider the visible color formed by base or by heat. We will cite additional data to show that Fester's data are also consistent with the imine-nitrone hypothesis and therefore does not unequivocally support C=C formation. Further, we wish to show that PMAN is a poor choice for a model compound.

If the PAN chromophore is formed by polymerization of the pendent nitrile groups, then it should be possible to polymerize nitrile groups which are not structurally held in position by a carbon matrix. Indeed, Peebles and Brandrup polymerized isobutyronitrile, succinonitrile, and 2,4-dicyanopentane either by base or by heat in the presence of oxygen. These polymers are rather resistant to hydrolysis and are very deeply colored. A 1% solution of polysuccinonitrile in methanol is black. Thus, if the PAN chromophore is formed by nitrile polymerization, then the colored polymer should contain some residual nitrogen after hydrolysis, the amount of residual nitrogen increasing with increased reaction time. We repeated Fester's experiments by heating PAN for short periods of time at 240°C. to form materials which varied from a light cream color to a dark cinnamon brown. The residual nitrogen content, after hydrolysis with 50 wt.-% H_2SO_4 is shown in Figure 1 as a function of time at 240°C., along with Fester's data. Furthermore, PAN was degraded by base to a dark red-black color, isolated, and then refluxed either with 50 wt.-% sulfuric acid or with 25% NaOH for 6 hr. No color change was observed. Polysuccinonitrile, prepared by reaction with diethylamine was also resistant to acid hydrolysis. These results show that colored PAN and imine-nitron polymers (polysuccinonitrile) contain nonhydrolyzable nitrogen.

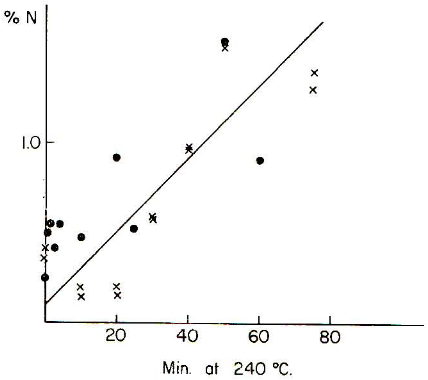


Fig. 1. Residual nitrogen in PAN after hydrolysis by 50 wt.-% H_2SO_4: (×) present work; (●) data of Fester.[4]

Fester observed no change in color on reaction of the colored, hydrolyzed PAN with diazomethane, followed by reduction with $LiAlH_4$, whereas the colored, hydrolyzed PAN could be easily oxidized with $KMnO_4$ to a colorless product. He interprets this to mean that the chromophore is in the carbon backbone.

Our experience, based on reactions with the model compounds cited above, leads us to conclude that the imine-nitrone structure would not be hydrolyzed by H_2SO_4 (demonstrated), methylated by diazomethane (hypothesized) or reduced by $LiAlH_4$ (demonstrated[1]). However, the imine-nitrone structure is easily oxidized to a colorless substance.[1] If only part of the nitrile groups participated in the color formation reaction, the remaining unreacted nitrile groups should react as specified by Fester.

We believe that the chromophore in PAN, formed either by base or by heat, is a conjugated imine-nitrone system. Prolonged heating of PAN in an oxygen atmosphere at high temperature will convert the PAN into the nonflammable form described by Vosburgh.[7] When the latter reaction occurs, dehydrogenation of the carbon backbone probably does occur.

We now wish to show that PMAN is an unfortunate choice for a model compound of PAN. These polymers are the only readily available materials with nitrile groups in the proper juxtaposition and connected by a carbon backbone. Deeply colored materials can be formed from these polymers by either heat or base attack. However, the chromophore of PMAN is easily bleached. Merely dissolving the colored polymer in a solvent, then adding acid, base, or salt will cause the solution to become almost colorless,[8] whereas colored PAN is stable under these same conditions. Thus, when PMAN is subjected to the same type of reactions described by Fester, the deep color of PMAN is destroyed by treatment with H_2SO_4. The generally accepted chromophore of PMAN is the conjugated imine system, but why then is PMAN unstable whereas PAN is stable? One can speculate that the methyl groups of PMAN cause the chromophore to be unstable in solution, perhaps because the polyimine is structurally prevented from forming a stable endgroup, hence the chromophore is easily depolymerized. Thus, the significant tests for the structural identity of the PAN chromophore must depend on studies of the conjugated imine-nitrone systems formed directly from small molecules rather than by formation of a ladder polymer as in PMAN.

Experimental

PAN powder (1 g.) was intimately mixed with 70-g. 300-mesh glass beads to disperse the heat generated by the exothermic reaction which occurs at 240°C. The polymers were heated in a muffle furnace for the requisite time, then freed of beads by sieving. Polymer ($^1/_2$ g.) was refluxed with 50 wt.-% H_2SO_4 for 8 hr., allowed to cool, dispersed in methanol, and precipitated with ether repeatedly until the methanol was acid-free and thus free of hydrolyzed nitrogen. The polymer was then dried, dissolved in 98% formic acid, and freeze-dried to a fluffy film. Nitrogen analysis was by the Dumas method.

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Résumé

On apporte une preuve nouvelle de ce que le chromophore du polyacrylonitrile est formé par polymérisation des groupes nitriliques plutôt que par déshydrogénation de la chaîne principale polymérique. La structure du polyimide formé est résistante à l'hydrolyse; dès lors la teneur en azote du polymère hydrolysé croissait avec une formation dechromophore croissante.

Zusammenfassung

Es wird weiteres Beweismaterial geliefert, um zu zeigen, dass der Chromophor des polyacrylnitrils eher durch Polymerisation der Nitrilgruppen als durch Dehydrierung der Hauptkette des Polymeren gebildet wird. Die dabei entstehende Polyiminstruktur ist hydrolysenbeständig; daher steigt der Sickstoffgehalt eines hydrolysierten Polymeren mit dem Ausmass der Chromophorenbildung an.

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Radical Copolymerization of Crotonyl Compounds with Styrene

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Synopsis

The monomer reactivity ratios for the radical copolymerization of crotononitrile (CN), methyl crotonate (MC), and *n*-propenyl methyl ketone (PMK) with styrene (St) were measured at 60°C. in benzene and little penultimate unit effect was shown for these systems. The values obtained were: St–CN, $r_1 = 24.0$, $r_2 = 0$; St–MC, $r_1 = 26.0$, $r_2 = 0.01$; St–PMK, $r_1 = 13.7$, $r_2 = 0.01$. The rate of copolymerization and the viscosity of the copolymer decreased markedly as the molar fraction of the crotonyl compound in the monomer mixture increased. The Q–e values were also calculated to be as follows: CN, $e = 1.13$, $Q = 0.009$; MC, $e = 0.36$, $Q = 0.015$; PMK, $e = 0.61$, $Q = 0.024$. A linear relationship was obtained between the e values of the crotonyl compounds and their Hammett constants σ_m.

INTRODUCTION

The radical homopolymerization of crotonyl compounds is very difficult due to their being 1,2-disubstituted olefins, but the copolymerization with styrene by use of a radical initiator, is easy. Many workers have investigated the copolymerization of crotonyl compounds, such as crotonic acid,[1-4] crotonaldehyde,[5] butyl crotonate,[6] crotonamide,[7] and crotononitrile,[8] with vinyl monomers.

In the present work, crotononitrile (CN), methyl crotonate (MC), and *n*-propenyl methyl ketone (PMK) were copolymerized with styrene (St), and the copolymerizability of these crotonyl compounds and the effect of the substituted groups in the crotonyl compounds on the Alfrey-Price Q,e values is discussed. Moreover, the fact[8-11] that a penultimate unit effect exists in the copolymerization system of a monomer which has a strongly polar group, such as a nitrile or carbonyl group, led the authors to discuss this point in detail.

EXPERIMENTAL

Materials

Crotononitrile (CN) was a commercially available reagent. The *trans* isomer, which was the main component separated from it by means of gas chromatography, was dried over calcium sulfate and distilled under nitrogen before use; b.p. 45–46°C./64 mm. Hg.

Methyl crotonate (MC) was a commercially available reagent, and it was purified before use by the method used for the purification of methyl methacrylate; b.p. 127–128°C.

n-Propenyl methyl ketone (PMK) was prepared by the aldol condensation of acetoaldehyde with acetone. It was distilled under nitrogen after drying over calcium sulfate; b.p. 43–44°C./81 mm. Hg.

Styrene (St) was a commercially available reagent. The inhibitor was removed from the reagent by washing with alkali, and it was distilled under nitrogen before use; b.p. 54°C./30 mm. Hg.

Benzoyl peroxide was precipitated from chloroform with methanol.

Benzene was purified before use by the usual method.

Copolymerization Procedure

The copolymerization was carried out in a tube containing the required amounts of the two monomers, the initiator, and the solvent. The tube was degassed, sealed off under vacuum, and placed in a constant temperature bath (60 ± 0.01°C.) and the copolymerization was carried out up to 10% conversion. After the copolymerization, the contents of the tube were poured into a large amount of methanol to precipitate the product; the precipitate was washed thoroughly with methanol and then weighed.

Analysis of Copolymer

The composition of the resulting copolymer was determined by elementary analyses (N for crotononitrile and C, H for methyl crotonate and *n*-propenyl methyl ketone).

Viscosity Measurements

The viscosity of the copolymer was measured in benzene solution at 25°C. in an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Monomer Reactivity Ratio

The results of the copolymerization for each system, crotononitrile, methyl crotonate, and *n*-propenyl methyl ketone, with styrene are shown in Tables I, II, and III, and the composition curves for these are shown in Figures 1, 2, and 3.

It is reasonable, from the failure of crotonyl compounds to homopolymerize, that the reactivity of the copolymerization was low, and that the content of the crotonyl compound in the copolymer was small compared with the initial amount of monomer for all the crotonyl compounds. The monomer reactivity ratios r_1, r_2 were obtained from the equation of Fineman and Ross:[12]

$$F(f-1)/f = r_1F^2/f - r_2 \tag{1}$$

TABLE I
Results of Copolymerization of St–CN System in Benzene at 60°C., [BPO] = 2.41 × 10^{-2} mole/l.

	Feed monomer					
Expt. no.	[St] × 10^{-1}, mole/l.	[CN] × 10^{-1}, mole/l.	[CN], mole-%	Time, hr.	Conversion, %	Copolymer CN, mole-%[a]
0	40.59	0	0	2	3.72	0
4	27.29	18.82	40.90	3	3.76	2.94
5	23.42	22.89	49.43	3.5	3.68	3.64
6	18.56	28.11	60.23	4.5	3.75	6.49
7	14.01	31.98	69.54	6	3.79	7.24
8	9.28	37.65	80.23	7	2.84	15.14
9	4.67	41.82	89.96	8	1.48	19.69

[a] Calculated from N elementary analysis.

TABLE II
Results of Copolymerization of St–MC System in Benzene at 60°C., [BPO] = 2.41 × 10^{-2} mole/l.

	Feed monomer					
Expt. no.	[St] × 10^{-1}, mole/l.	[MC] × 10^{-1}, mole/l.	[MC], mole-%	Time, hr.	Conversion, %	Copolymer MC, mole-%[a]
11	40.54	0	0	2	3.72	0
12	36.54	4.56	11.09	2	3.33	2.0
13	32.48	9.13	21.94	3	4.24	2.7
14	28.42	13.69	32.51	4	4.57	3.3
15	24.36	18.26	42.84	5	4.47	3.0
16	20.30	22.82	52.92	7	4.91	4.3
17	16.24	27.38	62.76	10	4.54	4.3
18	12.18	31.35	72.01	15	5.01	7.6
19	8.12	36.51	81.80	18	3.36	11.1
20	4.06	41.08	89.92	20	0.90	21.1

[a] Calculated from C,H elementary analysis.

where F is the molar ratio ($[M_1]/[M_2]$) of the feed monomers, and f is the molar ratio ($d[M_1]/d[M_2]$) in the copolymer. For the data of Tables I–III, $F(f - 1)/f$ was plotted against F^2/f as shown in Figures 4–6.

From the slopes and the intersects of the above straight lines, the monomer reactivity ratios were determined, as shown in Table IV.

If $r_2 = 0$, eq. (1) reduces to:

$$(f - 1) = r_1 F \tag{2}$$

Therefore the relationship between $(f - 1)$ and F is a straight line passing through the origin. In fact, proportional relationships were obtained, as shown in Figure 7.

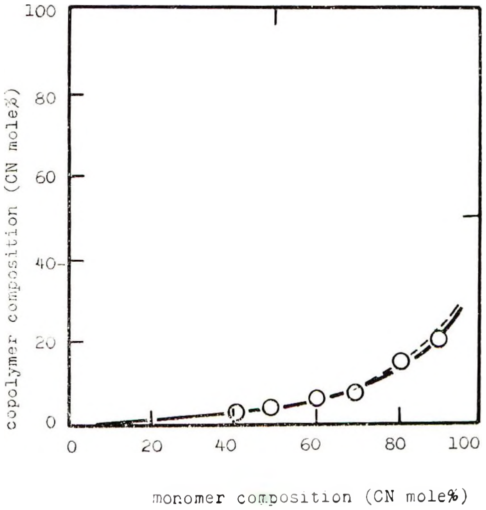

Fig. 1. Composition curve for St–CN copolymer: (——) terminal model, $r_1 = 24.0$, $r_2 = 0$; (- - -) penultimate model, $r_1 = 23.0$, $r_1' = 20.0$, $r_2 = r_2' = 0$.

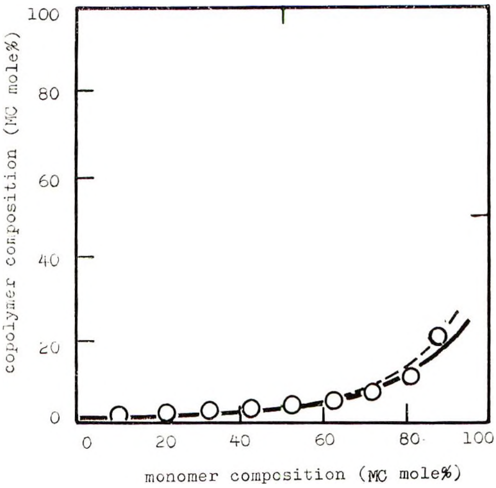

Fig. 2. Composition curve for St–MC copolymer: (——) terminal model, $r_1 = 26.0$, $r_2 = 0.01$; (- - -) penultimate model; $r_1 = 27.0$, $r_1' = 33.0$, $r_2 = r_2' = 0$.

Figure 7 indicates that the penultimate unit effect, which is generally accepted in the case of the styrene–acrylonitrile[11] and styrene–crotononitrile[9] systems, did not need to be considered. Nevertheless, it was attempted to treat the results in this work on the basis of the penultimate unit effect.[10] The reactivity of polymer radical is determined not only by its terminal unit, but also by the nonterminal units of the radical. If the terminal and penultimate units alone are considered to be influential, and

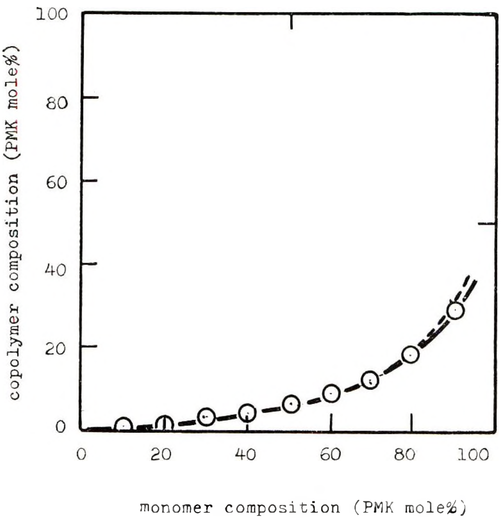

Fig. 3. Composition curve for St–PMK copolymer: (——) terminal model, $r_1 = 13.7$; $r_2 = 0.01$; (- - -) penultimate model, $r_1 = 14.0$, $r_1' = 11.1$, $r_2 = r_2' = 0$.

TABLE III
Results of Copolymerization of St–PMK System in Benzene at 60°C., [BPO] = 2.4×10^{-2} mole/l.

Expt. no.	Feed monomer [St] $\times 10^{-1}$, mole/l.	[PMK] $\times 10^{-1}$, mole/l.	[PMK], mole-%	Time, hr.	Conversion, %	Copolymer PMK, mole-%[a]
21	40.59	0	0	1	1.86	0
22	35.96	4.04	10.09	1.5	2.55	0.4
23	31.90	8.08	20.21	2	2.96	1.7
24	27.84	12.12	30.33	3	3.80	3.3
25	23.78	16.16	40.46	4	4.15	4.1
26	19.82	20.20	50.60	6	4.92	6.5
27	16.24	24.24	59.88	6	3.75	9.1
28	12.18	27.61	69.38	10	4.57	12.8
29	8.12	31.65	79.58	16	4.06	12.8
30	4.06	38.45	90.45	33	2.48	29.6

[a] Calculated from C,H elementary analysis.

TABLE IV
Copolymerization Parameters of Crotonyl Compounds with St (M_1)

M_2, R in $CH_3CH{=}CHR$	Terminal model $r_1(=k_{11}/k_{12})$	$r_2(=k_{22}/k_{21})$	e_2	Q_2	Penultimate model[a] $r_1(=k_{111}/k_{112})$	$r'_1(=k_{211}/k_{212})$	r'_1/r_1
CN	24.0	0	1.13	0.009	23.0	20.0	0.8
$COOCH_3$	26.0	0.01	0.36	0.015	27.0	33	1.2
$COCH_3$	13.7	0.01	0.61	0.024	14.0	11.1	0.7

[a] Assuming $r_2(=k_{222}/k_{221}) = 0$, $r'_2(=k_{122}/k_{121}) = 0$.

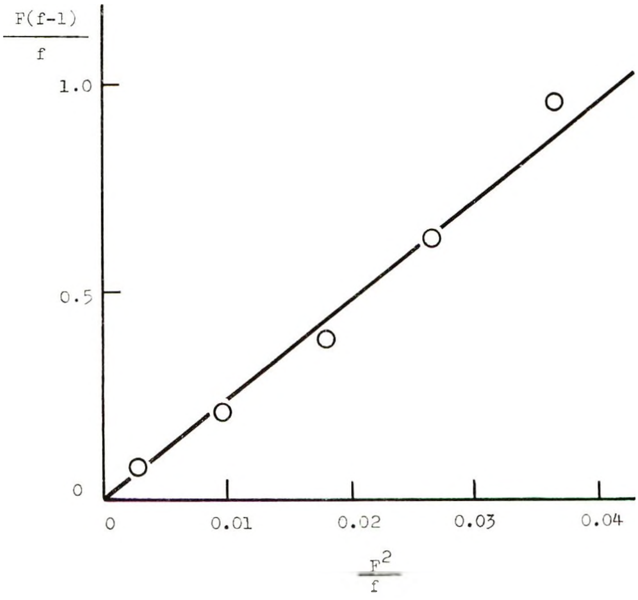

Fig. 4. Fineman-Ross plot for St(M_1)–CN (M_2) system.

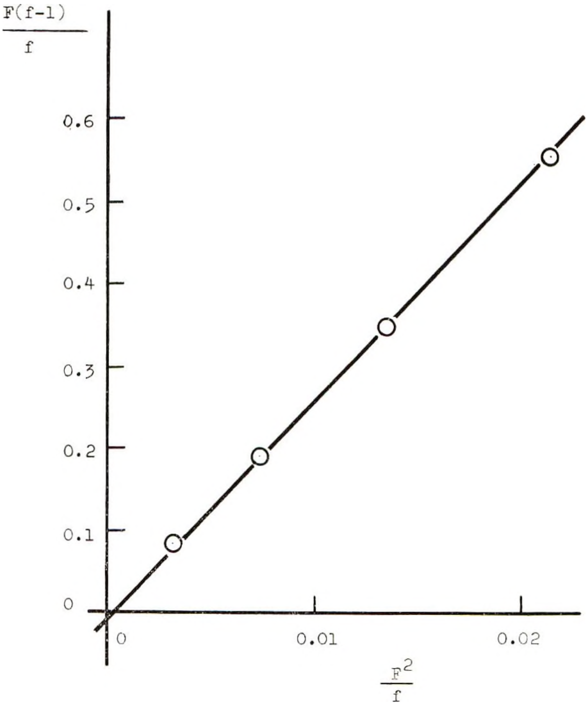

Fig. 5. Fineman-Ross plot for St(M_1)–MC (M_2) system.

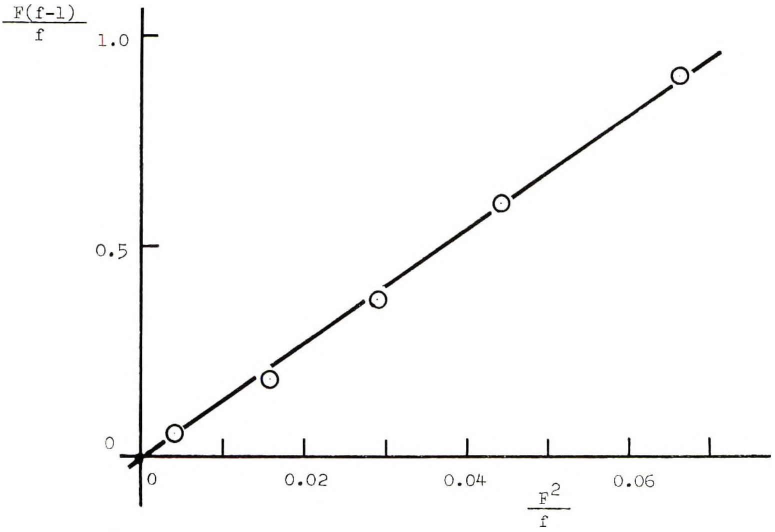

Fig. 6. Fineman-Ross plot for St (M_1)–PMK (M_2) system.

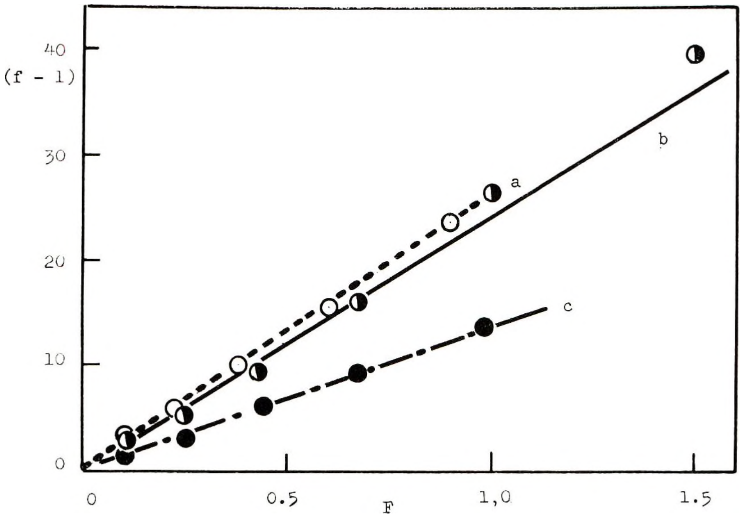

Fig. 7. Plots of $(f-1)$ vs. F: (*a*) St–MC system; (*b*) St–CN system; (*c*) St–PMK system.

if $r_2 = r'_2 = 0$, then the modified kinetic scheme requires five propagation steps and two new reactivity ratios:

$$M_1M_1\cdot + M_1 \xrightarrow{k_{111}} M_1M_1M_1\cdot$$
$$M_1M_1\cdot + M_2 \xrightarrow{k_{112}} M_1M_1M_2\cdot$$
$$M_2M_1\cdot + M_1 \xrightarrow{k_{211}} M_2M_1M_1\cdot$$
$$M_2M_1\cdot + M_2 \xrightarrow{k_{212}} M_2M_1M_2\cdot$$
$$M_1M_2\cdot + M_1 \xrightarrow{k_{121}} M_1M_2M_1\cdot$$

where

$$r_1 = k_{111}/k_{112}$$

$$r'_1 = k_{211}/k_{212}$$

The corresponding copolymer composition equation is:

$$(f - 1) = r'_1F(1 + r_1F)/(1 + r'_1F) \qquad (3)$$

if $1/r'_1 = 0$, eq. (3) reduces to:

$$(f - 2) = r_1F$$

and a linear relationship results. The results of the determinations using equation (3) are shown in Table IV.

In Table IV, r_1'/r_1, which is the degree of the penultimate unit effect, is nearly unity. Therefore, from the above two facts, even if a penultimate unit effect does exist, its influence on the monomer reactivity ratio is comparatively small.

Rate of Copolymerization and Viscosity of Copolymer

The rates of copolymerization and the viscosity of the copolymers are shown in Figures 8 and 9, respectively.

Figure 8 shows that the rate of copolymerization decreased linearly with increase in the molar ratio of the crotonyl compound to the comonomer for each system. In the case of the viscosity of the copolymer, a similar tendency was also observed, as can be seen in Figure 9. This suggests that

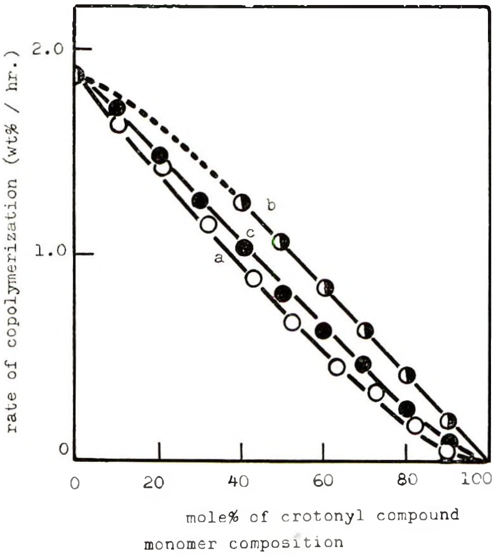

Fig. 8. Relationship between R_p and monomer composition: (*a*) St–MC system; (*b*) St–CN system; (*c*) St–PMK system.

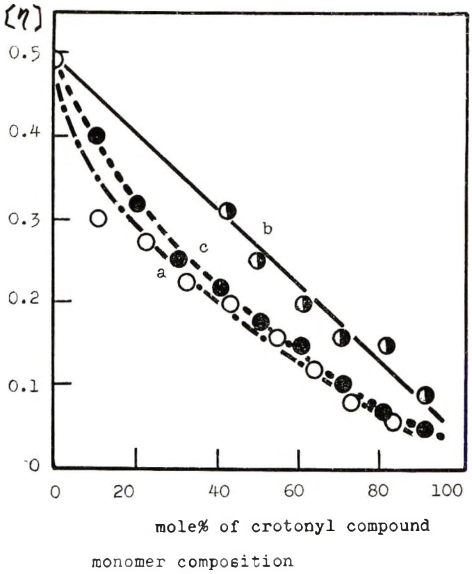

Fig. 9. Relationship between [η] in benzene at 25°C. and monomer composition: (*a*) St–MC system; (*b*) St–CN system; (*c*) St–PMK system.

the rate of propagation decreases with the increase in the molar ratio of the monomer which does not homopolymerize.

Infrared Spectra of Copolymers

The infrared spectra of the copolymers are shown in Figures 10–12.

The infrared spectra of all the copolymers showed the absorption bands characteristic of polystyrene. Bands were observed at 2230 cm.$^{-1}$ for the CN copolymer, at 1735 cm.$^{-1}$ for the MC copolymer and at 1710 cm.$^{-1}$ for the PMK copolymer, due to the C—N, $COOCH_3$ and C═O groups, respectively.

Melting Point of Copolymer

The relationship between the melting point of the copolymer and the copolymer composition is shown in Figure 13.

From the results, in the cases of the St–MC system and the St–PMK system, it was found that the melting point of the copolymer decreased with increasing molar ratio of the MC or PMK to the styrene in the copolymer. It is not clear, however, whether this is due to the essential nature of the copolymer or to the decrease in the molecular weight of the copolymer. On the other hand, in the case of the St–CN system, the melting point of the copolymer increased with increase in the molar ratio of the CN to the styrene in the copolymer, in spite of the decrease in the molecular weight of the copolymer. This suggests that this copolymer has a better heat resistance than polystyrene.

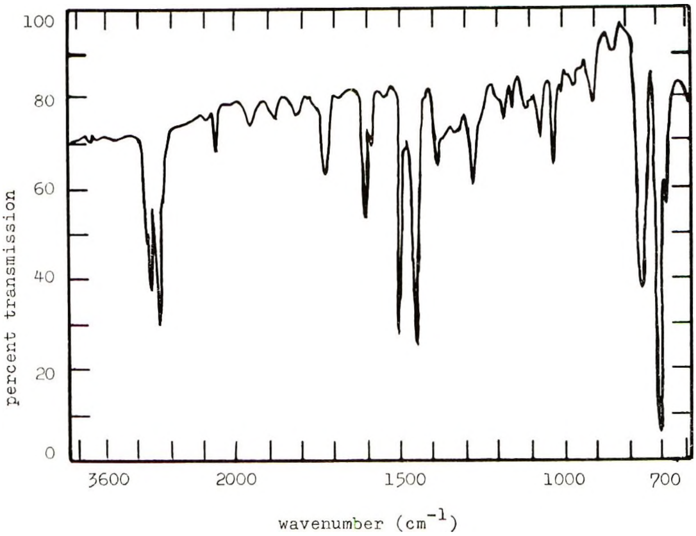

Fig. 10. Infrared spectrum of St–CN copolymer (sample 9).

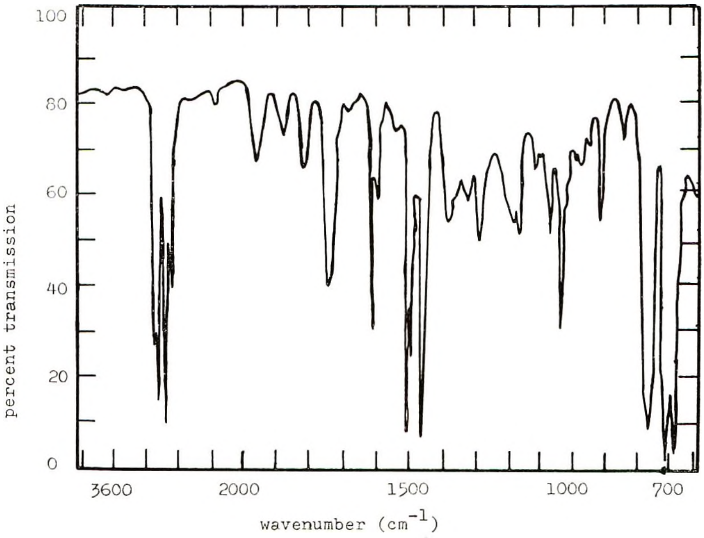

Fig. 11. Infrared spectrum of St–MC copolymer (sample 15).

Q and e Values of Crotonyl Compounds

The Q and e values for the crotonyl compounds were calculated from the r_1 and r_2 values shown in Table IV, by assuming the values for St: $Q = 1.0, e = -0.80$.

In general, both the e value and the Hammett constant σ are terms related to the polarity. Furukawa[13] has found a linear relationship between them using σ_p instead of σ. In order to check this point in this study, the e values

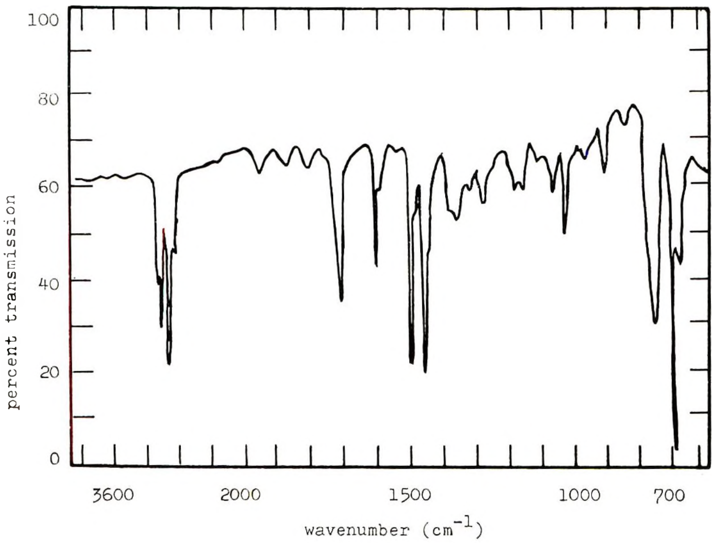

Fig. 12. Infrared spectrum of St–PMK copolymer (sample 25).

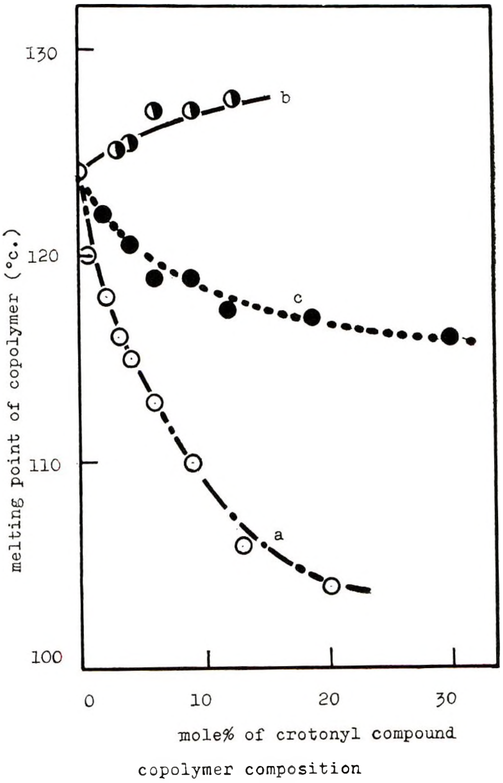

Fig. 13. Relationship between melting point and composition of copolymers: (*a*) St–MC system; (*b*) St–CN system; (*c*) St–PMK system.

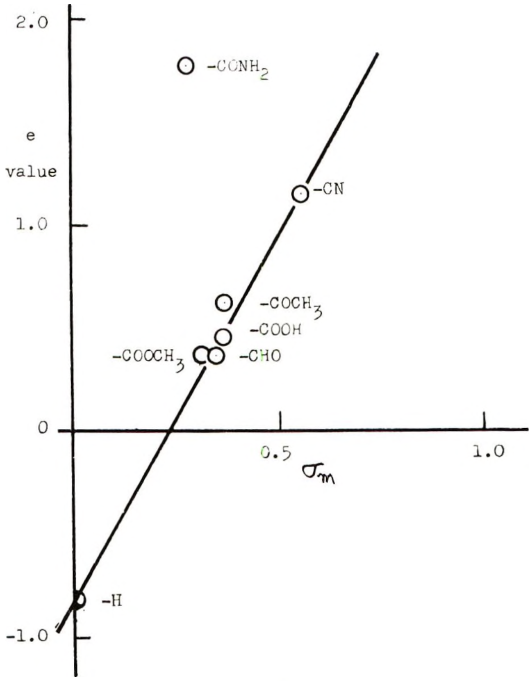

Fig. 14. Relationship between *e* values and Hammett constants σ_m for crotonyl compounds ($CH_3—CH=CHR$).

were plotted against the Hammett constants (σ_m) for the crotonyl compounds, which are shown in Table V, and a linear relationship was confirmed between them, as shown in Figure 14.

This fact suggests that the influence of the substituted group on the double bond is an electroinductive effect rather than a resonance effect, in the case of 1,2-disubstituted olefins. It was found, however, that the *e* values ran parallel to the σ_m of the substituted groups.

TABLE V

Q,e Values and Hammett Constants for Crotonyl Compounds

R in $CH_3—CH=CHR$	*e*	*Q*	σ_m
H[a]	−0.78	0.002	0
CN	1.13	0.009	0.560
$COOCH_3$	0.36	0.015	0.315
$COCH_3$	0.61	0.024	0.376
$CONH_2$[b]	1.76	0.0085	0.280
CHO[a]	0.36	0.013	0.355
COOH[c]	0.45	0.013	0.370

[a] Data of Ham.[5]

[b] Data of Ywakob and Truchmanov.[7]

[c] Data of Mayo and Walling.[1]

It is not yet clear, however, whether the styryl radical of the growing chain end adds to the crotonyl monomer at the position of the methyl group side or at the position of the other group side of the crotonyl monomer. The penultimate unit effects are discussed as follows:

In the systems of St–CN and St–PMK, the following relationship was obtained; r_1 $(= k_{111}/k_{112}) > r'_1$ $(= k_{211}/k_{212})$. If $k_{111} \doteqdot k_{211}$, then $k_{112} < k_{212}$. This may be so because in the case where the penultimate unit is styrene, the resonance energy between the chain terminal radical and the penultimate unit is high, so the reactivity is small compared with that for the case where the penultimate unit is crotononitrile or *n*-propenyl methyl ketone. On the other hand, in the St–MC system, the relationship $r_1 < r'_1$ was obtained. Therefore if $k_{111} \doteqdot k_{211}$, then $k_{112} > k_{212}$. This may follow from the fact that where the penultimate unit is styrene, there is no penultimate unit effect. In the case of methyl crotonate, however, steric hindrance is involved, and the reactivity becomes small.

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Résumé

Les rapports de réactivité monomérique pour la copolymérisation radicalaire du nitrile crotinique (CN), du crotonate de méthyle (MC) et de la *n*-propénylméthylcétone (PMK) avec le styrène (ST) ont été mesurés à 60°C, dans le benzène et l'effet de l'unité pénultième a été trouvé dans ces systèmes: St–CN, $r_1 = 24.0$, $r_2 = 0$; St–MC, $r_1 = 26.0$, $r_2 = 0.01$; St–PMK, $r_1 = 13.7$, $r_2 = 0.01$. La vitesse de copolymérisation et la viscosité du copolymère décroissaient notablement lorsque la fraction molaire du composé crotonique dans le mélange monomérique croissait. Les valeurs Q–e ont également été calculées et trouvées comme suit: CN, $e = 1.13$, $Q = 0.009$; MC, $e = 0.36$, $Q = 0.015$; PMK, $e = 0.61$, $Q = 0.024$. Une relation linéaire a été obtenue entre les valeurs de e des composés crotonques et leur σ_m.

Zusammenfassung

Die Copolymerisationsparameter für die radikalische Polymerisation von Crotonnitril (CN), Methylcrotonat (MC) und *n*-Propenylmethylketon (PMK) mit Styrol (St) wurden bei 60°C in Benzol bestimmt und dabei nachgewiesen, dass der vorletzten Einheit in den wachsenden Ketten in diesen Systemen eine geringe Bedeutung zukommt: St–CN, $r_1 = 24{,}0$, $r_2 = 0$; St–MC, $r_1 = 26{,}0$, $r_2 = 0{,}01$; St–PMK, $r_1 = 13{,}7$, $r_2 = 0{,}01$.

Die Copolymerisationsgeschwindigkeit und die Viskositätszahl der Copolymeren nahm deutlich mit steigendem Molenbruch der Crotonylverbindung in der Monomerenmischung ab. Die Q–e-Werte wurden ebenfalls berechnet. Sie betragen: CN, $e = 1{,}13$, $Q = 0{,}009$; MC, $e = 0{,}36$, $Q = 0{,}015$; PMK, $e = 0{,}61$, $Q = 0{,}024$. Zwischen den e-Werten der Crotonylverbindungen und ihren σ_m-Werten besteht, wie gefunden wurde, ein linearer Zusammenhang.

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Post-Lactonization of Vinyl Polymers Containing Pendent Ester and Hydroxymethyl Groups*

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Synopsis

Copolymers of methyl methacrylate with methyl and ethyl α-hydroxymethylacrylate and with α-hydroxymethylstyrene have been prepared with free-radical initiators at temperatures below 80°C. At higher reaction temperatures or under extrusion conditions, alcohol was eliminated and the free hydroxyl content was greatly decreased. All evidence indicates the formation of six-membered lactone groups in this post-polymerization reaction; direct evidence for their formation is lacking, however, since neither infrared nor nuclear magnetic resonance spectra could be used to detect lactonization in this system. The loss of activity from ^{14}C ester-labeled methyl methacrylate copolymer on heating could be correlated with the extent of lactonization. The degree of lactonization is relatively less with copolymers containing higher amounts of hydroxymethyl groups. The resulting polymers exhibit higher heat distortion temperatures and decreased impact resistance when compared to poly(methyl methacrylate). Attempts were made to incorporate similar lactone structures by cyclocopolymerization with methyl methacrylate of α-methacryloxymethylstyrene or ethyl α-methacryloxymethylacrylate, but only crosslinked polymers or polymers with pendent unsaturation were found.

Many post-polymerization reactions have been reported in which functional groups attached to neighboring, but nonvicinal, chain carbon atoms react to form cyclic structures, generally with the elimination of low molecular weight molecules. Most of the recent literature has been ably summarized by Smets.[1] A recent paper by Zutty and Welch[2] describes the cyclization of uniform vinyl chloride–methyl methacrylate copolymers with the elimination of methyl chloride to form polymers having α-methyl-γ-butyrolactone units in the polymer backbone. They report lactonization to produce polymers of increased rigidity and higher softening point. Lactonization of vinyl chloride–dimethyl itaconate copolymers was reported to form first the six-membered lactone ring, then the five.

This paper reports two approaches to the formation of copolymers containing six-membered (δ) lactone rings in the polymer backbone. The more successful involves the post-reaction of copolymers of methyl methacrylate with α-hydroxymethylstyrene or α-hydroxymethylacrylic esters to form the

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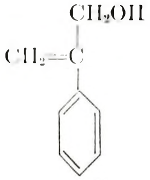
lactone with concurrent elimination of alcohol. Attempts to incorporate similar structures by cyclocopolymerization of appropriate divinyl monomers were generally unsuccessful. Some physical properties of the copolymers containing lactone units are also reported.

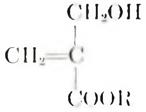
RESULTS AND DISCUSSION

Preparation of Initial Polymers

It is difficult to prepare copolymers of methyl methacrylate (MMA) with α-hydroxymethylstyrene (I) or alkyl esters of α-hydroxymethylacrylic acid (II) with complete avoidance of lactone formation under polymeriza-



I



$$CH_2{=}\overset{\displaystyle CH_2OH}{\underset{\displaystyle COOR}{C}}$$

II

IIa: $R{=}CH_3$
IIb: $R{=}C_2H_5$

tion conditions. To avoid problems with aqueous systems, our studies were confined to bulk or solution copolymers. Temperatures below 80°C. were chosen as conditions to minimize lactonization; for samples in which physical properties were to be investigated, polymerizations were completed at higher temperatures to eliminate as far as possible residual monomer, even though it was recognized that partial lactonization might result. Soluble polymers were found in all cases except where the comonomer was impure.

The rate of polymerization of IIb has been studied by Baldwin and Reed,[3] but no copolymerization data for either type of comonomer have been reported. Our own attempts to determine reactivity ratios for I with MMA were unsuccessful because of lactone formation during preparation and drying of the sample for analysis; no simple system for following relative disappearance of monomers by gas chromatography could be worked out. We did not study the copolymerization of I with a reference monomer such as styrene; unpublished work of Baldwin and Reed[4] has shown that the rates of copolymerization are favorable in that system and that suitable copolymers could probably be prepared. Copolymerization of II with any reference comonomer would give suspect results because of the possibility of lactonization between units of II.

Evidence for Lactone Formation

Satisfactory elemental analyses for high-conversion copolymers were obtained only for samples prepared in solution at 60°C. or in bulk at 60–80°C. Attempts to raise conversions in bulk copolymers by further heat treatment at 120°C. led to significant deviations from the expected analysis, as shown in Table I. At times, marked expansion of the samples was noted, caused by evolution of volatiles at 120°C.

There was a decrease in the hydroxyl absorption in the infrared (ca. 3580 cm.$^{-1}$ for copolymers containing II and ca. 3440 cm.$^{-1}$ for copolymers containing I) for samples in which lactonization occurred. The band is relatively broad and not too intense, and attempts to follow the extent of reaction by quantitative measurement of changes in the hydroxyl absorption did not give consistent results. Unfortunately, formation of the δ-lactone cannot be followed in the infrared, since the carbonyl adsorption of the lactone is indistinguishable from the ester group of the methyl methacrylate always present in high concentration. Nuclear magnetic resonance studies were not fruitful; examination of copolymers of MMA and IIb did not allow resolution of the hydroxyl hydrogen and the methylene hydrogens appeared to be masked by the peak of the methyl ester. Similar problems were encountered with copolymers of MMA and I.

TABLE I
Analysis of Copolymers Before and After Lactonization

Initial polymer, wt.-%	Carbon, %	Hydrogen, %	Oxygen (direct), %
MMA: IIb, 75/25			
Calcd.: original	58.83	7.98	33.2
Found: original[a]	58.67	7.98	33.5
Calcd.: lactonized[b]	—	—	—
Found: lactonized[c]	60.51	8.29	31.1
MMA: I, 75/25			
Calcd.: original	65.13	7.92	27.0
Found: original[a]	65.03	7.61	26.7
Calcd.: lactonized	66.88	7.62	25.5
Found: lactonized[c]	66.33	7.83	25.9

[a] Bulk polymerization, 80°C., portion dissolved, precipitated, washed, dried under vacuum at 60°C.

[b] Cannot be calculated because both methanol and ethanol are lost during lactonization.

[c] Heated 4 hr. at 120°C., then purified by reprecipitation, etc.

Vacuum extrusion of copolymers at 400–500°F., the technique generally used by us to induce lactonization, liberates volatiles which can be trapped and examined. Along with residual monomer, methanol is found in appreciable amounts when copolymers of MMA and I are devolatilized and pelleted. Copolymers of MMA and IIb yield both methanol and ethanol. Polymers are not insolubilized by this treatment, indicating intermolecular reaction to be insignificant. Heating of a solution-prepared copolymer of MMA and IIb (75/25) in chlorobenzene at 130°C. for 4 hr. with a trace of sulfuric acid lowered the free hydroxyl infrared intensity by ca. 90%; by gas chromatography, the solvent was shown to contain methanol and ethanol in a 4/3 ratio, which is lower than statistically expected. Under similar experimental conditions, homopolymer of methyl methacrylate gave no methanol.

A non-aqueous titration of hydroxyl groups was used to follow the loss of hydroxyl functionality as a result of lactonization. This technique is believed not to be interfered with by ester or lactone functionalities. Significant decreases in hydroxyl functionality are found as the reaction proceeds; however, the method was less accurate at low hydroxyl concentrations.

Methyl methacrylate was prepared from ^{14}C-labeled methanol and copolymerized with I at several different monomer ratios. The samples were devolatilized in the usual manner and the loss of activity compared with that calculated for complete lactonization (Table II). At low levels (5–15%) of copolymerized I, the loss of activity is very close to the calculated amount, indicating essentially complete lactonization; with copolymers containing 25–30% of copolymerized I, the reaction is not complete. The data also indicate a substantial loss of activity (equated with lactone formation) upon heating the samples to raise conversion to polymer.

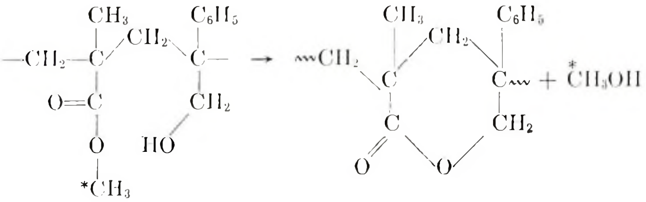


TABLE II
Lactonization of α-Hydroxymethylstyrene–Methyl (^{14}C Ester Labeled) Methacrylate Copolymers

	Monomer weight ration, MMA/I			
	90/10	85/15	75/25	70/30
Activity of monomer, dpm/g.	8491	8025	7230	6664
MMA, mole-%				
From feed	85.3	80.3	72.5	67.0
From activity	85.3	80.8	72.5	67.0
Activity of polymer, calcd. for complete lactonization, dpm	8010	7150	5780	4780
Activity of original polymer, (% reaction)[a]	8442(53%)	7995(30)	7052(29)	6227(19)
Activity after one extrusion[b]	7937(≥100%)	7119(100)	6324(71)	5733(59)
Activity after two extrusions	—	—	6154(80)	5585(65)
Activity after molding	7700(>100)	7208(100)	6113(82)	5521(68)

[a] Polymerized in bulk at 80°C., followed by 4 hr. at 120°C.

[b] In a 1-in. Killion extruder, vacuum vented.

We briefly examined 1:1 copolymers of I with acrylonitrile, prepared in bulk at 70°C. Samples reprecipitated from dimethylformamide solution appeared to have undergone δ-iminolactone (or δ-lactam) formation; examination of the infrared spectra showed a very weak nitrile band at 2270 cm.$^{-1}$ and a strong band at 1665 cm.$^{-1}$. Similarly, 1:1 copolymers of I with methacrylic acid (prepared in bulk at 80°C.) were soluble and were found to contain only ca. 60% of the expected acid functionality. Thus, a similar uncatalyzed reaction is found in several systems; the driving force is probably the ring closure, since these reactions do not readily occur in uncatalyzed open-chain systems.

In summary, there is substantial evidence that the free hydroxyl content is greatly decreased and that the corresponding alcohols are eliminated under several types of post-treatment conditions. There is evidence that the post-reaction is complete only for low levels of hydroxyl-containing comonomer. There is no direct evidence to support the internal δ-lactone structure, but such a postulate is consistent with the data presented.

Physical Properties of Lactonized Copolymers

It is impossible to separate the effect on physical properties of the lactone group from the effect caused simply by the introduction of an appreciable amount of an hydroxyl-containing comonomer, since the properties reported are measured on molded pieces and no nonlactonized controls are available. Moreover, the polymerization and extrusion conditions, especially at higher comonomer levels, did not generally lead to complete lactonization. Some typical properties are shown in Table III. The incorporation of lactone groups appears to increase the heat distortion temperature of the copolymers somewhat more than might be expected for the incorporation of another bulky comonomer. [This observation is based on Vicat heat distortion temperatures obtained by us for copolymers

TABLE III

Physical Properties of Lactonized Copolymers

	MMA/IIb		MMA/I		PMMA
	85/15	75/25	85/15	75/25	(100%)[a]
Heat distortion temperature, °C.[b]	—	95	111	116	90
Charpy impact, ft.-lb.[c]	4.5	3.1	3.1	3.7	7.0
Flexural strength × 10^{-3}, psi[d]	10.3	10.5	9.9	14.1	12.9
Modulus in flexure × 10^{-5}, psi	4.60	4.80	5.37	5.65	4.95
Deflection at break, in.	0.27	0.26	0.21	0.33	0.36
Water absorption, %					
1 day	—	0.38	—	0.20	0.29
7 days	0.40	0.44	—	0.45	0.59

[a] $\bar{M}_v = 120{,}000$.

[b] Values at 264 psi, ASTM-D-648-56.

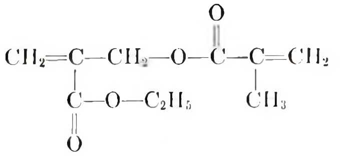
[c] Unnotched values, ASTM 256-56.

[d] ASTM D-790-49T.

of MMA with comonomers of the type $CH_2{=}C(C_6H_5)CH_2X$, where X is H, F, OR, and OOCR, as well as comonomers of the type $CH_2{=}C(COOR)$-CH_2Y, where Y is F,[5] OR, and COOR; in no case were the softening temperatures as high as those reported here.] However, the lactone formation in both systems studied decreases the impact resistance of the polymers. Both changes are probably reflections of the increased chain stiffness contributed by the internal six-membered ring, especially as the ring contains two substituents (an α-methyl and a γ-phenyl or carboalkoxy) attached to the same carbon atoms which join the ring to the chain.

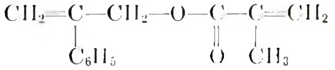
Cyclopolymers

It was hoped that copolymers of structure equivalent to those prepared by post-lactonization could be prepared by incorporation of a suitable difunctional monomer. To this end, ethyl α-methacryloxymethylacrylate (III) and α-methacryloxymethylstyrene (IV) were prepared. Under a variety of copolymerization conditions with MMA or with styrene, either crosslinked copolymers or copolymers with pendent unsaturation (determined by infrared absorption) were formed, with little evidence for appreciable formation of cyclic structures. Apparently the cross-reactivity with the MMA or styrene comonomer was so high that immediate cyclization was prevented, and that the unreacted moiety was then left to function as a crosslinking site or to remain as pendent unsaturation. Parenthetically, lactone formation and absence of pendent unsaturation was noted with copolymers of MMA and vinyl 3-butenoate (V) prepared in benzene solution.



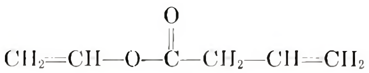
$CH_2{=}C(COOC_2H_5){-}CH_2{-}O{-}C({=}O){-}C(CH_3){=}CH_2$

III



$CH_2{=}C(C_6H_5){-}CH_2{-}O{-}C({=}O){-}C(CH_3){=}CH_2$

IV



$CH_2{=}CH{-}O{-}C({=}O){-}CH_2{-}CH{=}CH_2$

V

Possibly the less resonance-stabilized vinyl ester radical is more prone to cyclize than the methacryl radical from monomers III and IV. In no case did we obtain sufficient data to treat these systems by cyclocopolymerization kinetics.[6]

EXPERIMENTAL

Monomers

Ethyl α-hydroxymethylacrylate was purchased from the Koppers Company and was freed of excess inhibitor by passage through a column of Amberlite XE-208 ion-exchange resin. Methyl α-hydroxymethylacrylate was synthesized by Dr. J. B. Mettalia by the method of Rosenthal et al.;[7] careful redistillation was necessary to remove small amounts of impurities which caused the formation of crosslinked copolymer under very mild reaction conditions. Methyl methacrylate was used directly as received from the Rohm and Haas Company; methacrylic acid and acrylonitrile were commercial materials of low inhibitor content.

α-Hydroxymethylstyrene was purchased from the Sinclair Petrochemicals Company. Careful redistillation from sodium carbonate was required to remove chlorine-containing impurities which depressed the rate of copolymerization, lowered the molecular rate, and contributed to color formation. Distillation without use of sodium carbonate leads to extensive rearrangement of I to 2-phenylacetaldehyde.

Methyl methacrylate labeled in the ester position was prepared by Dr. W. R. Lyman from radioactive methanol; the specific activity of the ester was 4.68×10^{-3} μc./g. (10,400 dpm/g.). The level of activity was such that the standard polymerization and processing conditions used throughout this work could be employed as long as reasonable caution was employed.

α-Methacryloxymethylstyrene (2-phenylallyl methacrylate) was prepared from α-hydroxymethylstyrene and methacryloyl chloride. A solution of 134 g. of 2-phenylallyl alcohol, 135 ml. of *N,N*-dimethylaniline, and 200 ml. of ether was stirred and heated at reflux, and 105 g. of methacryl chloride (obtained from the J. T. Baker Chemical Co.) was added dropwise during a 2.5 hr. period, whereupon the mixture was heated and stirred an additional 4 hr. The mixture was cooled, and 300 ml. of water was added to dissolve the precipitated amine hydrochloride. The ethereal layer was separated, and the aqueous portion was extracted with four 500-ml. portions of ether. The combined ether layers were washed with three 500-ml. portions of 20% aqueous hydrochloric acid, one 500-ml. portion of water, three 500-ml. portions of 10% aqueous sodium carbonate solution, and one 500-ml. portion of water. The organic solution was dried over anhydrous magnesium sulfate, and the ether was removed *in vacuo*. Distillation of the residue through a 6-in. Vigreaux column gave 54.6 g. of material boiling at 81°C./0.3 mm.–84°C./0.6 mm.

ANAL. Calcd. for $C_{13}H_{14}O_2$: C, 77.20%; H, 6.98%. Found: C, 77.00%; H, 7.10%.

Ethyl α-methacryloxymethylacrylate was prepared similarly from ethyl α-hydroxymethylacrylate. A solution of 195 g. of ethyl α-hydroxymethylacrylate, 212 ml. of *N,N*-dimethylaniline, and 200 ml. of dry ether was heated at reflux, and 165 g. of methacryl chloride (obtained from the J. T. Baker Chemical Co.) was added dropwise during a 3.5 hr. period. The heating and stirring were continued for 3.5 hr. during which time the amine hydrochloride precipitated. The mixture was cooled, and 250 ml. of water was added to dissolve the amine hydrochloride. The ether layer was separated and was extracted with five 50-ml. portions of cold 10% aqueous sulfuric acid. The ethereal layer was then washed with 25 ml. of a saturated aqueous sodium bicarbonate solution and was dried with anhydrous magnesium sulfate. The ether was removed *in vacuo*, and the monomer was distilled through a 6-in. Vigreaux column; there was obtained 102.5 g. of material boiling at 65°C./0.1 mm.–68°C./0.2 mm. A large amount of polymerized residue remained in the distillation flask.

Vinyl 3-butenoate was prepared by the transvinylation of vinyl acetate and 3-butenoic acid catalyzed by a mercury derivate of a macroreticular sulfonic acid cation exchange resin.[8] A 250-ml. reaction flask is charged with 8.6 g. 3-butenoic acid and 86 g. vinyl acetate. As the temperature was raised to 45°C., 6 g. of catalyst resin was added and the mixture stirred for 16 hr. The resin was prepared by treating 40 g. of Amberlite XE-205 cation exchange resin with 61.6 g. of mercuric acetate in 500 ml. acetic acid at 60°C. for 16 hr. The reaction mixture was separated from the resin, washed with water and dilute base, and stripped to remove excess vinyl acetate. The product was then flash-distilled.

ANAL. Calcd. for $C_6H_8O_2$: C, 64.30%; H, 7.14%. Found: C, 64.63%; H, 7.20%.

Polymerization

Solution polymerizations were generally conducted at 60°C. in toluene solution under helium or pre-purified nitrogen with azobisisobutyronitrile as initiator and *n*-dodecyl mercaptan as chain transfer agent. In a typical polymerization, a mixture of reagent toluene (69 ml.), 0.164 g. azobisisobutyronitrile, and 0.088 ml. *n*-dodecyl mercaptan was charged to a 200-ml. round-bottomed flask and degassed with helium for 30 min. To the flask was then charged a mixture of methyl methacrylate (22.5 g.) and ethyl α-hydroxymethylacrylate (7.5 g.). The flask was stoppered and heated for 48 hr. at 60°C. The polymer was precipitated by addition of a large excess of petroleum ether; the yield of polymer was precipitated by addition of a large excess of petroleum ether; the yield of polymer was 26.5 g. (90%). The polymer had a reduced specific viscosity (RSV) in ethylene dichloride at 30°C. of 0.32 dl./g.

Bulk polymerizations were carried out in glass or in cellophane bags after degassing of the monomers. In a typical polymerization, a mixture of methyl methacrylate (37.5 g.), methyl α-hydroxymethylacrylate (12.5 g.), 0.05 g. *tert*-butyl peracetate, and 0.29 ml. of *n*-dodecyl mercaptan was polymerized at 80°C. for 24 hr. The polymer had an RSV of 0.36 dl./g. In some cases, the polymer was heated at 120°C. for 4 hr. or longer in an attempt to obtain higher conversions. Noticeable expansion of the polymer generally occurred.

Analysis

Nuclear magnetic resonance measurements were carried out on chloroform solutions on a Varian HR-60 instrument. Hydroxyl titrations were carried out by Dr. G. V. Foster as follows. The polymer sample was dissolved in pyridine, excess phthalic anhydride added, the mixture heated on a water bath for 2 hr., excess water added, and the sample heated for 10 min. to convert excess anhydride into phthalic acid. The samples were then titrated potentiometrically in pyridine with $0.01N$ tetrabutylammonium hydroxide. The half acid ester formed by reaction with the polymeric hydroxyl groups shows a break in the curve which differs from the two found for phthalic acid.

The radioactive samples were analyzed by Dr. W. R. Lyman by solution of 0.1 g. of polymer in 15 ml. of D-169 solvent,[9] which is dioxane containing scintillators. Determination of activity was measured in a Packard Tri-Carb liquid scintillation spectrometer, Model 3314.

Extrusion and Fabrication

Polymers were granulated (if prepared in bulk) and extruded in a 1-in. Killion extruder with full vacuum applied at the vent. In some experiments traps cooled with Dry Ice were placed in the vacuum system to trap and identify the volatiles. Typical extrusion heater settings (for the experiments described in Table II) were: zone 1, 400°F.; zone 2, 460°F.; zone 3, 495°F.; zone 4, 435°F.

Pellets from the extruder were molded on a 1-oz. Watson Stillman machine. Cylinder settings were generally from 480 to 520°F. Physical tests on molded bars followed American Society for Testing Materials (ASTM) procedures.

We are grateful to many members of the Research Division for synthesis and application support. Mr. R. L. Kelso directed the devolatilization and fabrication studies. The able technical assistance of L. W. Cox, J. J. Mullen, E. J. Tanck, and F. E. Zimmerman was most appreciated.

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Résumé

Des copolymères de méthacrylate de méthyle avec les α-hydroxyméthyl-acrylate de méthyle et d'éthyle et avec l'α-hydroxyméthyl-styrène ont été préparés au moyen de radicaux initiateurs à des températures inférieures à 80°C. A température de réaction plus élevée ou dans les conditions d'extrusion, l'alcool était éliminé et la teneur en groupes hydroxyles étaient grandement diminuées. Ceci indique la formation de groupes lactoniques à six membres en cours de cette post-polymérisation; une preuve directe de leur formation fait défaut toutefois, parce que ni les spectres infrarouge, ni ceux de résonance nucléaire magnétique ne peuvent être utilisés pour détecter de la lactonisation dans ce système. La parte d'activité au départ du copolymère méthacrylique avec groupes esters méthyliques marquées au carbone-14, par chauffage peut être reliée au dégré de lactonisation. Le degré de lactonisation est relativement plus faible pour les copolymères contenant des quantités élevées des groupes hydroxyméthylés. Les polymères résultants montrent des températures de distordion thermique plus élevées et une résistance à l'impact diminuée lorsqu'on la compare au polyméthacrylate de méthyle. Des essais ont été faits pour incorporer des structures lactoniques semblables par cyclo-co-polymérisation avec le méthacrylate de méthyle de l'α-méthacryloxyméthylstyrène ou de l'acrylate d'éthyl-α-méthacryloxyméthylé, mais uniquement des polymères pontés ou des polymères avec des insaturations latérales ont été obtenus.

Zusammenfassung

Copolymere von Methylmethacrylat mit Methyl- und Äthyl-α-hydroxymethylacrylat und mit α-Hydroxymethylstyrol wurden bei Temperaturen unter 80°C mittels radikalischer Starter hergestellt. Bei höheren Reaktionstemperaturen oder unter Extrusionsbedingungen wurde Alkohol abgespalten und der Gehalt an freiem Hydroxyl beträchtlich verringert. Alle Befunde weisen auf die Bildung einer sechsgliedrigen Laktongruppe in dieser Nachpolymerisationsreaktion hin; ein direkter Beweis dafür fehlt jedoch, da weder Infrarotnoch Kernresonanzspektren zum Nachweis der Laktonisierung in diesem System verwendet werden konnten. Der während des Erhitzens auftretende Aktivitätsverlust eines in der Estergruppe mit C^{14} markierten Methylmethacrylat-Copolymeren konnte mit dem Ausmass der Laktonisierung korreliert werden. Der Grad der Laktionsierung ist bei Copolymeren mit höherem Gehalt an Hydroxymethylgruppen relativ niedrig. Die entstehenden Polymeren zeigen im Vergleich mit Polymethylmethacrylat höhere Hitzeverformungstemperaturen und eine verminderte Schlagfestigkeit. Versuche wurden unternommen, um durch Cyclocopolymerisation von α-Methacryloxymethylstyrol oder Äthyl-α-methacryloxymethylacrylat mit Methylmethacrylat ähnliche Laktonstrukturen in das Polymere einzubauen, doch wurden lediglich vernetzte Polymere oder Polymere mit anhängenden Doppelbindungen gefunden.

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Emulsion Polymerization of Vinyl Stearate

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Synopsis

The polymerization of vinyl stearate in aqueous emulsions with a non-ionic emulsifying agent and potassium peroxydisulfate as initiator has been investigated by use of a dilatometric method to follow the reaction. In general, the reaction kinetics do not follow the pattern established for styrene. Variation of initiator concentration produced latices containing approximately equal numbers of latex particles, even though the rate of reaction was almost directly proportional to the peroxydisulfate concentration. For a given initiator and monomer concentration polymerization occurs very slowly when the monomer is completely solubilized but as the number of micelles is reduced and the number of emulsion droplets increased, the rate increases to an optimum value, whereafter it decreases. A mechanism is proposed by which the sparsely soluble vinyl stearate reacts and redistributes itself into latex particles of a different size range from the micelles and emulsion droplets originally present.

INTRODUCTION

Many vinyl monomers, e.g., styrene, although sparingly soluble in water, may be polymerized by dispersing them in an aqueous solution of an emulsifying agent, with the addition of a water-soluble initiator. The advantage of such a system is the production of a high molecular weight polymer at a rapid rate of reaction, with isothermal conditions easily maintained.

According to Harkins,[1,2] the mechanism of the reaction involves the transfer of monomer molecules from emulsion droplets through the aqueous phase to the reacting site in the latex particles. This requires that the monomer must be sufficiently soluble in water, if this is not to be the rate-determining part of the process.

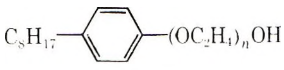
The work presented in this paper represents an attempt to examine the mechanism of emulsion polymerization in an extreme situation of very low aqueous solubility of monomer. The monomer chosen was vinyl stearate which has been shown by surface film measurements,[3] to have a solubility of 7×10^{-7} mole/l. (cf. styrene,[4] 3.68×10^{-3} mole/l.).

EXPERIMENTAL

Materials

Monomer. Vinyl stearate was kindly supplied by Air Reduction Chemical Co. (New York) as a commercial product which was purified as described by Fort and Alexander,[5] yielding a waxy, crystalline substance with melting point 34–35°C.

Emulsifier. Previous investigations[6,7] have indicated that the most stable emulsions of vinyl stearate are obtained with a mixture of a non-ionic emulsifier, such as fatty acid esters of anhydrosorbitol or anhydromannitol, and an ionic emulsifier, such as branched-chain alcohol sulfates. Usual emulsifiers, cationic and anionic, by themselves, were unsatisfactory. Experiments in this laboratory have confirmed the latter viewpoint, but it has been found that solutions of long-chain non-ionic detergents produce very stable emulsions without the help of any additives. A poly(ethylene oxide) adduct of isooctyl phenol, having the structure I,



I

where *n* has the average value of 10, as shown by microanalysis, was used without further purification.

Initiator. Potassium peroxydisulfate was twice recrystallized from hot water (80°C.) to yield a product containing 99.0% peroxydisulfate by analysis.

Polymer Solvent. Toluene was twice distilled at atmospheric pressure, the 110–111°C. fraction being collected. All other chemicals were of analytical reagent grade.

Procedure

The dilatometric apparatus used to measure the rate of polymerization of vinyl stearate has been described previously.[8] By weighing the polymer formed in a series of experiments with various initial monomer concentrations, it was found that the volume contraction was linearly dependent on the amount of formed polymer. The specific contraction of 0.070 cc./g. of polymer was in good agreement with the value of 0.065–0.088 cc./g. calculated from the densities of monomer and polymer (0.9037 and 0.960–0.982 g./cc., respectively[9]).

The emulsion was prepared at 56°C. in a modified separating flask from the required amounts of emulsifier solution and solid vinyl stearate. A high-speed homogenizer was operated at high speed for 5 min., then at its lowest speed for an equal time, so that air bubbles were expelled. A 5 ml. portion of a potassium peroxydisulfate solution was pipetted into the dilatometer, which stood in a thermostat at 50.0°C., followed by the emulsion until the apparatus was completely filled. Most of the entrapped air bubbles were expelled with the aid of the magnetic stirrer. Any that remained dissolved in the aqueous phase on cooling from 56 to 50°C. No measures were taken to deaerate the system; the consequent occurrence of an induction period was considered an advantage in providing ample time for temperature equilibration of the mixture.

After a particular reaction had been followed to the desired extent with the aid of a cathetometer, the latex was collected for examination by electron microscopy, light scattering, or ultracentrifugation. Alternatively, the formed polymer was precipitated, by pouring into four volumes of acetone, collected, washed thoroughly with acetone, and dried under vacuum. The molecular weight of the product was determined from viscosity measurements of toluene solutions at 25°C. and calculated according to the data of Burlant and Adicoff.[10]

$$[\eta] = 1.0 \times 10^{-3} \bar{M}_n^{0.65}$$

For determination of the size and number of particules in a latex sample, a drop of diluted latex was dried down on a nitrocellulose-covered electron microscope grid, which was subsequently viewed in an electron microscope at a linear magnification of 10,000. In latices prepared with emulsifier/monomer ratio greater than equimolar, the resulting particles were small ($d < 40$ mμ) and when subsequently viewed in the electron microscope were covered with a diffuse layer of material, apparently due to the emulsifier. Both factors contributed to a loss of contrast in the electron microscope. This method of determination of particle numbers was therefore supported by ultracentrifugation and light-scattering measurements.

Of the difficulties encountered in this section of the work, the following should be mentioned briefly. In ultracentrifugation, the rate of sedimentation depends, among other variables, on the density difference between the medium and the sedimenting particles. Poly(vinyl stearate) is less dense than water, while the emulsifier is more dense. A latex particle of a certain size formed from poly(vinyl stearate) and an absorbed layer of emulsifier can have a density equal to that of the medium and thus may not sediment at all. With increasing size of latex particles and decreasing concentrations of emulsifier the latex should "cream" and move towards the rotational axis of the ultracentrifuge. In the case of light-scattering measurements, the whole latex particle, together with its adsorbed layer of emulsifier, contributes to the scattering. The elucidation of the "true" size of latex particles from such measurements is not a simple matter.

Information concerning the extent of solubilization of vinyl stearate in solutions of the emulsifier was obtained by stirring various amounts of monomer with a fixed amount of emulsifier solution. The resulting mixture was viewed in a optical microscope, emulsion droplets being clearly visible if present.

The size and number of emulsion droplets for each of the various reaction mixtures was determined by comparison with the Dow standard latex LS-066-A (diameter 0.814 μ). The emulsion and latex were fixed on a slide in gelatin and observed in the microscope.

RESULTS

Figure 1 is a plot of the logarithm of instantaneous rate versus time for the system consisting of 0.102M vinyl stearate (VS), 0.0458M emulsifier

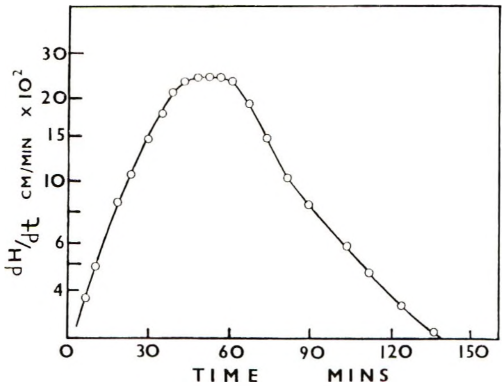


Fig. 1. Plot of log (instantaneous rate) vs. time for the system (VS 0.102*M*, E 0.0458*M*, PP 10 *mM*).

(E), and 10*mM* potassium peroxydisulfate (PP) at pH 3.8, 50.0°C. (denoted in shorthand as VS 0.102*M*, E 0.0458*M*, PP 10*mM*).

The structure of the curve is very similar to that observed in the emulsion polymerization of styrene,[11] except that no Trommsdorff effect is evident in the latter stages of the reaction. Thus it would appear possible to compare kinetics of vinyl stearate polymerization with those of styrene. For example, the attainment of a constant rate might signify the disappearance of micelles and no new latex particle formation thereafter. Also the commencement of the more or less first-order part of the reaction might indicate the exhaustion of monomer supply from the emulsion droplets.

The polymerization has been studied as a function of each component, by varying in turn the monomer, initiator, and emulsifier concentrations.

In the results given below, V_p is the rate of polymerization when its value is at a maximum, taken from the dilatometric measurement. The number of latex particles, N, was measured for latex samples polymerized to at least 80% conversion. C_M, the concentration of monomer in the latex particles, expressed as moles of monomer per liter of latex particle, was determined by assuming that the point at which the rate begins to fall represents the disappearance of monomer droplets. All the monomer is then in the latex particles, and from the amount of conversion that has already occurred, the monomer concentration in the latex particles is calculated (a constant monomer:polymer ratio is assumed over all the particles). P is the integral average degree of polymerization of the formed polymer at $\geqslant 80\%$ conversion.

Variation of Monomer Concentration

The rate of polymerization of vinyl stearate was measured for varying initial amounts of monomer at constant emulsifier and initiator concentrations. The amount of monomer is expressed as moles per liter of emulsion and is represented by simple molar notation. In Figure 2 the reaction curves are shown in terms of volume contraction versus time for each of

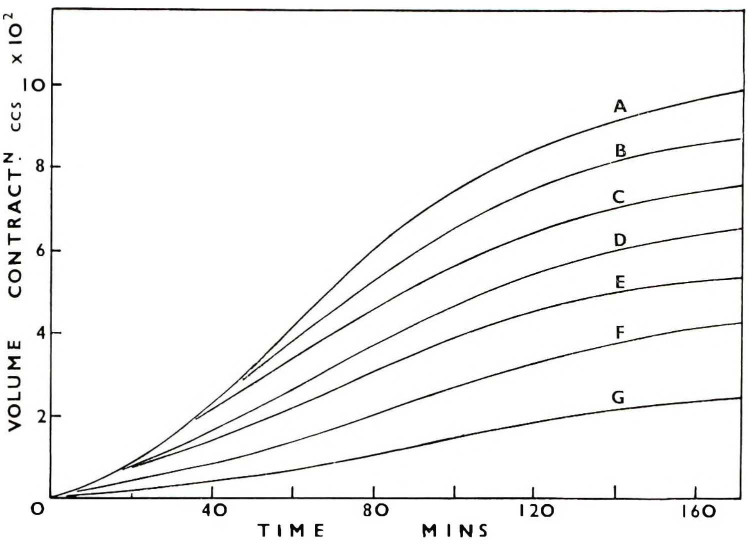


Fig. 2. Volume contraction vs. time curves for seven initial monomer concentrations: (*A*) 0.1021*M*; (*B*) 0.0892*M*; (*C*) 0.0750*M*; (*D*) 0.0633*M*; (*E*) 0.0519*M*; (*F*) 0.0390*M*; (*G*) 0.0261*M*.

seven initial amounts of monomer. Table I gives the values of V_p, C_M, N, and $\bar{P}$ determined for these systems. Also given is k_1, the rate constant for the stage where the reaction follows more or less a first-order relationship. The values of N have been determined by ultracentrifugation in the systems of 0.0519*M* and 0.0261*M* monomer. In these cases the particle size distribution was very narrow and it was assumed that the weight-average and volume-average diameters were equal. The system of 0.1021*M* monomer was studied by electron miscroscopy, 200 particles being counted.

In these results we see a regular decrease in V_p and $\bar{P}$ with decrease in monomer amount accompanied by an increase in the number of latex particles, while C_M and k_1 remain constant within experimental error.

TABLE I

Variation of Monomer Concentration[a]

Monomer amount, moles/l. emulsion	$V_p \times 10^6$, mole/l.-sec.	$k_1 \times 10^4$, sec.$^{-1}$	C_M, mole/l. latex particles	d_v, mμ	N, ml.$^{-1}$	$[\eta]$, dl./g.	$\bar{P}$
0.1021	13.2	1.3	1.9	57 ± 2	$(9.5 \pm 1.0) \times 10^{14}$	0.262	17.0
0.0892	11.4	1.5	1.8	—	—	0.257	16.5
0.0750	8.77	1.3	1.7	—	—	0.236	14.5
0.0644	6.94	1.6	1.6	—	—	0.235	14.4
0.0519	5.49	1.4	1.5	22.0	1.36×10^{16}	0.216	12.5
0.0390	4.25	—	1.6	—	—	0.202	11.4
0.0261	2.85	—	1.7	7.2	3.47×10^{17}	0.173	9.0

[a] Emulsifier, 0.0915*M*; potassium peroxydisulfate, 10*mM* (unbuffered); *T*, 50.0°C.

Variation of Initiator Concentration

In Table II are the results of experiments in which the initiator concentration, C_I, was varied over a 20-fold range while the other constituent concentrations (VS 0.102M, E 0.0915M) were kept constant. A double logarithmic plot is given in Figure 3 to show the relationship between V_p and C_I. For comparison the line representing 0.4 power dependence (as for styrene) is also shown. It is found that V_p varies as $C_I^{0.8}$.

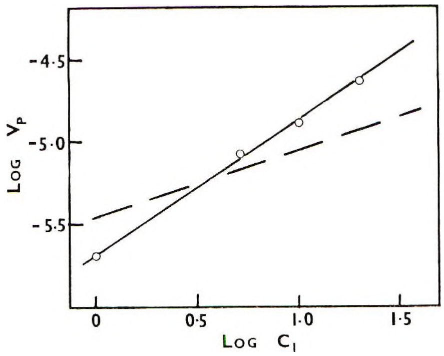


Fig. 3. Variation of initiator concentration, log V_p vs. log C_I. (O) vinyl stearate; (– – styrene (data of Bartholomé et al.[11]).

The values quoted for N were determined by electron microscopy supported by light-scattering measurements. N is independent of initiator concentration within experimental error.

TABLE II
Variation of Initiator Concentration[a]

C_I, mM	V_p × 10^6, mole/l.-sec.	C_M, mole/l. latex particles	d_v, mμ	N × 10^{-14}, ml.$^{-1}$	$\frac{V_p}{NC_M}$ × 10^{21}	[η], dl./g.	$\bar{P}$
20	23.6	1.9_0	57 ± 2	9.5 ± 1.0	12.9	0.275	18.3
10	13.4	1.9_4			7.3	0.269	17.6
5	8.4	1.9_2			4.6	0.252	15.9
1	2.0	1.9_6			1.1	0.277	18.5

[a] Vinyl stearate, 0.102M; emulsifier, 0.0915M; pH 3.8 (acetate buffer); T, 50.0°C.

Variation of Emulsifier Concentration

The results of experiments covering a 32-fold range of emulsifier concentration are given in Table III and Figure 4. The outstanding feature is that V_p has its greatest value at an emulsifier concentration about 0.03–0.04M, while at both higher and lower emulsifier concentrations the value of V_p is less.

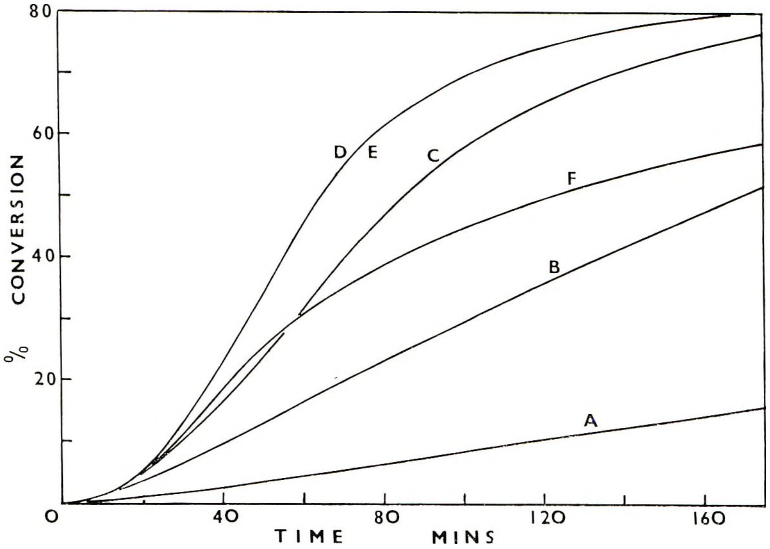


Fig. 4. Variation of emulsifier concentration, percentage conversion vs. time curves: (*A*) $0.366M$; (*B*) $0.183M$; (*C*) $0.0915M$; (*D*) $0.0458M$; (*E*) $0.0229M$; (*F*) $0.0114M$.

The number of latex particles N per cubic centimeter of latex decreases with decreasing emulsifier concentration, an expected trend. However a double logarithmic plot shows no possible linear relationship.

The number of particles was determined by ultracentrifugation in the systems with $0.366M$ and $0.183M$ emulsifier, and it was assumed that the particle size distribution was so narrow that $d_w \sim d_v$.

TABLE III
Variation of Emulsifier Concentration[a]

C_E, mole/l.	$V_p \times 10^6$, mole./l.-sec.	C_M, mole/l. latex particles	d_v, mμ	N, ml.$^{-1}$	$[\eta]$, dl./g.	$\bar{P}$
0.366	2.44	1.8	7.34	1.36×10^{18}	0.167	8.5
0.183	5.76	1.6	22.0	2.70×10^{16}	0.225	13.4
0.0915	13.4	1.9	57	9.5×10^{14}	0.269	17.6
0.0458	21.8	1.7	77.6	2.51×10^{14}	0.302	21.0
0.0229	21.0	1.8	86.8	1.36×10^{14}	0.307	21.6
0.0144	13.1	1.9	328	2×10^{11}	0.328	23.9

[a] Vinyl stearate, $0.102M$; potassium peroxydisulfate, $10mM$; pH 3.8 (acetate buffer); T, 50.0°C.

As the emulsifier concentration was decreased below $0.0458M$, increasing amounts of latex creamed. This factor, coupled with increasing breadth of size distribution contributed considerably to the uncertainty of N as determined by electron microscopy.

Emulsion Droplets

It was found in all emulsions prepared that the droplets were monodisperse and of the same size as the Dow latex (LS-066-A), i.e., diameter = 0.80 ± 0.05 μ.

With the information on size of emulsion droplets and the extent of solubilization of monomer in micelles, it was possible to calculate the number of emulsion droplets as shown in Table IV. The surface area of an emulsion droplet is 2×10^{-8} cm.^{2}, while that of a micelle is 1.20×10^{-12} cm.^{2} The saturation solubilization corresponds to about 45 monomer molecules per micelle of 100 emulsifier molecules (verified by ultracentrifugation).

TABLE IV
Numbers of Emulsion Droplets and Micelles and Amount of Contained Monomer

		Micelles		Emulsion droplets	
Monomer concn., M	Emulsifier concn., M	Number $\times 10^{-17}$, ml.$^{-1}$	Solubilized monomer, mole/l.	Number $\times 10^{-10}$, ml.$^{-1}$	Emulsified monomer, mole/l.
0.102	0.366	22.0	0.102	—	—
0.102	0.183	11.0	0.078	3.1	0.024
0.102	0.0915	5.45	0.036	8.7	0.066
0.102	0.0458	2.64	0.014	11.6	0.088
0.102	0.0229	1.28	0.003	13.0	0.099
0.102	0.0114	0.61	0.001	13.3	0.101
0.102	0.0915			8.7	0.066
0.089	0.0915			7.0	0.053
0.075	0.0915			5.15	0.039
0.064	0.0915			3.70	0.028
0.052	0.0915			2.11	0.016
0.039	0.0915			0.40	0.003
0.026	0.0915			—	—

DISCUSSION

In the first place let us compare the above kinetic results with those obtained with styrene in similar experiments performed by Bartholomé et al.[11] In summary the styrene behavior is as follows.

In systems of constant emulsifier and initiator, but varying monomer: water phase ratios, the quantities, V_p, C_M, N, and $\bar{P}$ remain the same, while K_1 diminishes by one half when the initial monomer concentration is doubled, and so on.

For varying initiator concentrations both V_p and N are approximately proportional to $C_I^{0.4}$. The expression V_p/NC_M yields a constant value, indicating a constant number of free radicals in each particles. P increases with decreasing C_I.

For varying emulsifier concentrations V_p and N are both approximately proportional to $C_E^{0.6}$. P increases slightly with increase in C_E.

An explanation of the above behavior of styrene in terms of the Smith-Ewart theory[12] is given by Bartholomé et al. and will not be discussed here.

It is immediately obvious that the vinyl stearate kinetics are completely different from those of styrene.

The most noteworthy points of the vinyl stearate results are as follows.

The number of latex particles is independent of the initiator concentration, while the rate of polymerization is almost directly proportional to it. (Table II, Fig. 3).

There is an unusual variation of rate of polymerization with emulsifier concentration; polymerization occurs very slowly when the monomer is completely solubilized, but as the number of micelles is reduced and the number of emulsion droplets increased, the rate increases to an optimum value whereafter it decreases (Table III, Fig. 4).

An interesting comparison can be made between results with the systems (VS $0.102M$, E $0.366M$, PP $10mM$) of Table III and (VS $0.026M$, E $0.0915M$, PP $10mM$) of Table I. The monomer and emulsifier concentrations of the former are four times those of the latter, and it is noted that this factor is repeated approximately in values of N, and the length of the period of constant rate. Other quantities V_p, C_{M}, and P are approximately the same for both. A similar comparison can be made between the systems (VS $0.102M$, E $0.183M$, PP $10mM$) and (VS $0.052M$, E $0.0915M$, PP $10mM$) where the factor is two in concentration and number of particles. It would appear that the ratio of monomer to emulsifier (below a certain level), at a constant initiator concentration, determines the rate of reaction.

Other workers have observed that the features of the Harkins-Smith-Ewart scheme are completely applicable only to styrene monomer, under quite specific conditions. Extension of the theory is invariably necessary when considering other monomers with different chemical and physical properties. For example, in the emulsion polymerization of vinyl acetate (ca. 3% soluble in water), it is suggested that the monomer diffuses completely into the polymer particles very early in the reaction[13] and also that some polymer chains grow in the aqueous phase.[14] Methyl methacrylate, which is subject to a strong gel effect in bulk,[15] also exhibits some anomalies in emulsion polymerization, presumably arising from the same considerations.[16] Styrenes which have been methylated in the benzene nucleus, show a steric hindrance of the termination reaction which also leads to an increase in the average number of free radicals per particle, according to Gerrens and Kohnlein.[17]

This last-mentioned study is the one having most bearing on the vinyl stearate behavior, as the solubility in water of 2,4-dimethylstyrene would be expected to be somewhat less than that of styrene.

The relevent data from the emulsion polymerization of 2,4-dimethylstyrene are that the number of latex particles is found to be proportional to $C_{\mathrm{I}}^{0.08}$ and $C_{\mathrm{E}}^{1.0}$, while the rate of polymerization is proportional to $C_{\mathrm{I}}^{0.4}$ and $C_{\mathrm{E}}^{0.6}$. We see this pattern of behavior as being intermediate between styrene and vinyl stearate.

In attempting to relate the observed behavior of vinyl stearate to the Harkins-Smith-Ewart scheme, we find there are two questions arising from the sparse solubility of vinyl stearate in water.

First, is the solubility sufficient to maintain the supply of monomer to the reacting polymer particles (assuming the mechanism to be diffusion of monomer from the emulsion droplets via the aqueous phase)? From the fundamental diffusion equation,[18] it can be shown that the diffusion current I of molecules of a substance diffusing into a spherical particle of radius r is

$$I = 4\pi r D \Delta C \tag{1}$$

where D is the diffusion coefficient and ΔC is the difference in concentration of the diffusing substance far from the particle and at its surface. For the system (VS $0.102M$, E $0.0458M$, PP $10mM$), by assuming a free radical in each alternate latex particle, one can calculate that 105 monomer molecules per second are adding to each radical. If the monomer:polymer ratio within the particle is to be maintained (normally 1:1 for styrene[1]) 210 molecules of monomer must enter a growing latex particle every second. Presuming the concentration of monomer to be zero at the surface of a particle of radius 30 mμ, we can calculate, by eq. (1) the concentration of monomer in solution $[\mathrm{M}]_{\mathrm{aq}}$ required to maintain a diffusion current of 210 molecules per second. Taking D as 5×10^{-6} cm.^{2}/sec. (approximate value for a molecule of this size), we find $[\mathrm{M}]_{\mathrm{aq}}$ to be 1.1×10^{12} molecules/ml., considerably less than the measured solubility of vinyl stearate in water of 4.2×10^{14} molecules/ml., even allowing for variation in the quantities in eq. (1).

The second question concerns the rate of dissolution of vinyl stearate from the emulsion droplets. Comparison with results of dissolution kinetics studies[19,20] indicates that the rate of dissolution of vinyl stearate might be sufficient to replace the monomer removed from the aqueous phase into reacting latex particles. However, the vinyl stearate emulsion presents a physical picture completely different from the systems generally studied in dissolution kinetics. More to the point is the work of Nakagawa and Tori,[21] who used nuclear magnetic resonance to study the exchange of benzene molecules between emulsifier micelles and the aqueous phase. They interpret the signal shape obtained as representing a lifetime of 10^{-4} sec. or less for benzene molecules in sodium dodecyl sulfate micelles. Assuming the lifetime to be inversely proportional to the molecular weight and the aqueous solubility of the molecule, a vinyl stearate molecule might be expected to have a lifetime of about 4 sec., i.e., in the space of 4 sec. all the monomer can exchange between the aqueous phase and the micelles and emulsion droplets.

On the above reasoning there is no evidence that the emulsion polymerization of vinyl stearate might be very much different from that of styrene. The experiments of course, contradict this, and therefore we suggest that the mechanism described by Harkins must be considerably modified to apply to vinyl stearate.

From the solubility measurements,[3] 1 ml. of aqueous phase contains 4.2×10^{14} dissolved monomer molecules, while free radicals are generated at the rate of 1.2×10^{13}/sec. (10*mM* potassium peroxydisulfate solution at 50°C., $k = 1.0 \times 10^{-6}$ sec.$^{-1}$;[22]) i.e., one radical per 35 dissolved monomer molecules under static conditions. Initiation in the aqueous phase is therefore feasible and is evidenced by the observation that the reaction rate is slower in systems where the monomer is completely solubilized by emulsifier (i.e., more stable with respect to monomer). Two alternative descriptions of the creation of a latex particle are as follows: (*a*) the free radical from the initiator enters a micelle directly, whereupon reaction with the solubilized monomer can occur; or (*b*) the initiator radical reacts with monomer molecules in the aqueous phase. Free emulsifier molecules surround the polymer radical to stabilize it, perhaps incorporating some more monomer molecules in doing so. Of these the latter mechanism seems more logical, there being no apparent driving force for the initiator radicals to enter a micelle.

Concerning the propagation of the reaction it is obvious that transfer of monomer must take place since the final number of latex particles is less than the original number of micelles in all systems, and only at the lowest soap concentrations does reaction appear to occur in emulsion droplets (Table III, small number of latex particles). Transfer is most apparent in systems where all the monomer is solubilized. One might expect that the monomer in a micelle is in a stable state and loath to transfer to the extent of 50% which is the extent to which the total number of particles is reduced. (Cf. Table III and Table IV.) In agreement is the observation that the reaction is complete in about 24 hr. or half the time necessary for one radical to be created per micelle, although any possible acceleration in the production of free radicals by the emulsifier is not taken into account.

Other than by diffusion through the aqueous phase, the transfer of monomer might be achieved on collision of the particles. In the system the latex particles, monomer droplets, and micelles are undergoing considerable Brownian motion, and only a small fraction of the collisions need result in coalescence to account for increased rates of reaction.

While it is reasonable to assume that two micelles after collision emerge again as two micelles of the same size as before the collision, this need not be the case on collision of a latex particle with a micelle containing solubilized monomer. Poly(vinyl stearate) is soluble in its monomer, so that on energetic grounds coalescence is possible, even if the latex particle is dead. If the latex particle is not dead, the free radical in it will start the polymerization of monomer, if the micelle remains in contact for a long enough time. The collision of two latex particles both undergoing polymerization could result in the formation of a dead latex particle. The probability of this reaction is higher, the higher the percentage of latex particles with respect to the total number of particles present in the system.

Most profitable would be collision of a growing latex particle with an emulsion droplet. In such a collision it is envisaged that the latex particle would maintain its separate identity, but now the separation of reacting polymer radical and unreacted monomer is reduced to a layer of emulsifier molecules through which monomer might diffuse rapidly. The length of time the two particles remain in contact would determine the amount of monomer transferred. The collisions are necessarily "sticky," i.e., much longer than a perfectly elastic collision; perhaps the force of impact of the relatively faster-moving latex particle causes a temporary crater in the emulsion droplet, thus further lengthening the time of contact. With its very large size, an emulsion droplet ($d \sim 0.8\ \mu$) would be taking part in a large number of collisions with latex particles ($d \sim 0.04\ \mu$) at any particular instant.

The observed fact is that a system containing emulsion droplets initially has no latex particles approaching that size at the completion of the reaction (except where the soap concentration is very low). This is seen in the emulsion polymerizations of both styrene and vinyl stearate which have considerable differences in solubility in water.

The series of experiments using the same emulsion with different initiator concentrations (Table II) serves to illustrate our postulated mechanism. The rate of reaction is almost directly proportional to the initiator concentration. In these systems the number of latex particles created in unit time depends directly on the number of free radicals generated in unit time. For the higher initiator concentrations, the larger number of active polymer particles results in a correspondingly larger number of successful collisions in a given time interval. Given the time however, the systems of lower initiator concentration "catch up" with the others, as indicated by the fact that the final number of latex particles in each system is the same. If the latex samples for particle number determination were taken after a given time, not conversion, a dependence on the initiator concentration would be expected. The fact that V_p varies as $C_I^{0.8}$ and not $C_I^{1.0}$ indicates that a limited amount of monomer diffuses through the aqueous phase.

The variation of monomer concentration (Table I) varies the number of effective collisions by varying the number of emulsion droplets.

The situation is that the same number of latex particles is created in unit time in each system. Reaction begins in micelles and supply of monomer is very slow. Thus the reaction curves all follow approximately the same path initially, i.e., the same amount of monomer is converted to polymer in unit time. Then the collisions with the emulsified monomer begin to bear notice. The number of collisions of emulsion droplets and latex particles simply depends on the number of the droplets and particles, and thus the rate of reaction is almost directly proportional to the number of emulsified monomer droplets. The same percentage of monomer is therefore converted in unit time at each monomer concentration. The final number of latex particles should be about the same in each case, but this is not observed probably because the particles are of larger sizes at higher monomer concentration and, supported by the same amount of emulsifier, are less stable, so that coalescence occurs to a greater extent.

The system of highest emulsifier concentration and completely solubilized monomer displays a continuous increase in rate for a considerable time (1 hr.) before a constant value is attained (Fig. 4). If the reaction was proceeding solely in micelles with no transfer of monomer, a constant and slower rate would be expected very early in the reaction. The rate-determining step is the entry of radicals, not the reaction of monomer contained within them. In the initial stages of the rection, micelle–micelle collisions represent almost all of the collisions which occur. These collisions are ineffectual as regards the reaction. As time increases, so also does the number of growing latex particles, which are identical with the micellar particles, except that polymer is contained. Thus the percentage of micelle–latex particle collisions increases. A fraction of these collisions results in transfer of monomer from micelle to latex particle, thus increasing the amount of monomer reacting with the one radical. The gradual increase in overall rate is therefore observed. The later stages of the reaction have increasingly more and more latex–latex particle collisions, and the overall rate of reaction diminishes.

Considering the remaining systems of Figure 4 we can see that all follow approximately the same rate for the first 15–20 min., a rate which is appreciably greater than the initial rate for the system with 0.366*M* emulsifier. The difference is attributed to the micelles being saturated with monomer (45 monomer molecules per micelle compared to 28 for 0.366*M* emulsifier), and the initial reaction depending principally on the micelles. Monomer is also present in the form of emulsified droplets, the number of which increases with decreasing emulsifier concentration while the number of micelles correspondingly decreases (Table IV). Collision of latex particles with monomer droplets becomes more probable if, as appears from the initial rate of reaction, the latex particles are formed at approximately the same rate.

On maintaining the premise that latex particles can successfully withdraw monomer from the emulsion droplets and then break away, the acceleration in rate of reaction as the initial emulsifier concentration is reduced from 0.366 to 0.0458*M* can be accounted for. Eventually, however, a stalemate is reached where the decrease in the number of micelles becomes a more dominant influence than the increase in emulsion droplets, and the faster rates of reaction can no longer be achieved.

It is worth noting that the formed latices were stable with the exception of that prepared using 0.0114*M* emulsifier. In this case the latex particles were found to cover a broad range of sizes up to 1 μ, and creaming of the latex occurred on standing [poly(vinyl stearate) is less dense than water]. This we attribute to polymerization occurring within the emulsion droplets, possibly initiated by colliding latex particles which do not detach themselves because of the deficiency of emulsifier in the system.

In general the measured average degrees of polymerization appear to conform to the pattern expected from our postulated mechanism. For example, variation of initiator concentration (Table II) produced no significant variation in degree of polymerization. In other systems, an increase in emulsion droplets generally produced an increased P. It must, however, be pointed out that transfer reactions occur in all cases varying to extents, e.g., in Table III, line 1, six polymer molecules are formed per initiator radical; in lines 4 and 5, the figure is 20. Overall, the extent of transfer reactions depends directly on the rate of reaction.

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Résumé

La polymérisation en émulsion aqueuse du stéarate de vinyle avec un agent émulsifiant non-ionique et du peroxydisulfate de potassium comme initiateur, a été étudiée en utilisant une méthode dilatométrique pour suivre la réaction. En général, les cinétiques de réaction ne suivent pas les diagrammes prévus pour le styrène. La variation de la concentration en initiateur produisait des latex contenant environ un nombre égal de particules de latex bien que la vitesse de réaction était généralement directement proportionnelle à la concentration en peroxyde de sulfate. Pour un initiateur déterminé et une concentration en monomère déterminée, la polymérisation était très lente lorsque le monomère était complètement solubilisé mais lorsque le nombre de micelles était réduit et que le nombre d'émulsions croissait, la vitesse croît à une valeur optimum après laquelle elle diminue. Un mécanisme est proposé suivant lequel le stéarate de vinyle faiblement soluble réagit et se redistribue dans des particules de latex de grandeur différente au départ des micelles et des gouttes d'émulsion originellement présentes.

Zusammenfassung

Die Polymerisation von Vinylstearat in wässrigen Emulsionen mit nichtionischen Emulgatoren und Kaliumperoxydisulfat als Starter wurde unter Verwendung einer dilatometrischen Methode zur Verfolgung der Reaktion untersucht. Die Reaktionskinetik folgt im allgemeinen nicht dem für Styrol gültigen Schema. Bei variierter Starterkonzentration ergaben sich Latices, die eine ungefähr gleiche Anzahl von Latexpartikeln enthielten, obwohl die Reaktionsgeschwindigkeit der Peroxydisulfatkonzentration sogar fast direkt proportional war. Bei vorgegebener Starter- und Monomerenkonzentration geht die Polymerisation nur sehr langsam vor sich, solange das Monomere vollständig solubilisiert ist; wenn die Zahl der Mizellen aber zurückgeht und die Anzahl der Emulsionströpfchen zunimmt, steigt die Geschwindigkeit bis zu einem Optimalwert an und nimmt danach wieder ab. Ein Mechanismus wird vorgeschlagen, nach dem das wenig lösliche Vivylstearat reagiert und sich aus den ursprünglich vorhandenen Mizellen und Emulsionströpfchen neu auf die Latexpartikel unterschiedlicher Grössenbereiche verteilt.

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Graft Polymers: Chain Transfer and Branching

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Synopsis

The vinyl monomers, methyl methacrylate, ethyl methacrylate, and methyl acrylate were polymerized in the presence of chlorinated rubber or poly(vinyl chloride) in homogeneous solution with benzoyl peroxide as catalyst. A graft polymer was formed by a chain-transfer reaction involving the growing polymer radicals to the backbone of chlorinated rubber or poly(vinyl chloride), in addition to homopolymer from the monomer. The homopolymer was isolated from the polymer mixture by fractional precipitation from methyl ethyl ketone solution with methanol as precipitant. The chain-transfer constants for the branching reactions were evaluated. The ratios $k_p/(k_t)^{1/2}$ for the grafting reactions were obtained by a correlation of chain-transfer constants with the extent of branching. The chain-transfer data were correlated on the basis of an extension of the *Q–e* scheme of Alfrey and Price to polymer–polymer transfer reactions. Specific effects due to the backbone are found to have considerable influence on the course of the chain-transfer reactions and $k_p/(k_t)^{1/2}$ of the grafting reactions.

INTRODUCTION

The action of regulators in controlling the degree of polymerization of a vinyl polymer is widely recognized.[1-7] The possibility of a "pre-existent (dead)" polymer acting as chain transfer agent leading to self-branching was discussed by Flory[8] and experimental evidence for such polymer–polymer transfer was presented.[9-20] The greater susceptibility of halogen atoms to chain-transfer reactions was obvious from an examination of chain-transfer data[4,21] and the possibility of formation of branched polymers with greater ease by chain transfer at Cl in the polymer (as in vinylidene chloride–styrene copolymer) as branching sites was pointed out by Mark and Alfrey.[22] The investigations by Smets[14,15] and Schulz[11,12] and others[13,16-20] involved such transfer reactions leading to branched polymers. We studied the branching reactions from a somewhat different approach. Poly(vinyl chloride) (PVC) and chlorinated rubber (ClR) were used as the backbones and methyl methacrylate (MMA) ethyl methacrylate (EMA) and methyl acrylate (MA) as monomers for the side chains (grafts). The chain-transfer constants and the rate constants for the grafting reactions were evaluated by correlation with the extent of branching. The *Q–e* scheme of Alfrey and Price was applied to our chain-transfer data in order to get an insight into the reactivity of the polymer radicals. The results indicated the specific influence of the backbone on $k_p/(k_t)^{1/2}$ for the grafting reaction. The chain-transfer constant as well as the extent of branching were governed not only by the radical reactivities but also by the mutual compatibility of the backbone and side chains. The correlations on the basis of the Q–e scheme indicated highly polar character and higher reactivities of the radicals of PVC and ClR compared to simple hydrocarbon radicals.

EXPERIMENTAL

Materials

The ClR polymers (~65% Cl, no unsaturation; supplied by Tata Chemicals Ltd., Mithapur, India), and PVC (supplied by Rajasthan Vinyl and Chemicals, New Delhi; Calico Chemicals and Plastics Division, Bombay, India) were purified by repeated reprecipitation from methyl ethyl ketone (MEK) and tetrahydrofuran (THF) solution, respectively, by addition of water. The monomers MMA, EMA, and MA (all Rohm and Haas products) were chemically purified from inhibitors and distilled under reduced nitrogen pressure. The solvents (benzene, toluene, cyclohexanone, methyl ethyl ketone, and methanol) were purified by standard procedures. Benzoyl peroxide was purified by recrystallization from cold chloroform.

Graft Copolymerization

The polymerization recipe consisted of monomer (1.5 mole/l.), benzoyl peroxide (5×10^{-3} mole/l.) the backbone polymer P (ClR or PVC, 0–0.4 mole/l.), and a solvent (benzene or toluene in case of ClR and cyclohexanone for PVC) to provide a homogeneous phase as well as to reduce the viscosity of the medium. The polymerizations were conducted at 70–80°C. for 3 hr. in sealed glass ampules (20 ml. capacity) after flushing of the system with nitrogen. The homopolymers poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), or poly(ethyl methacrylate) (PEMA) were isolated quantitatively from the accompanying graft polymer and the unreacted backbone polymers by fractional precipitation from methyl ethyl ketone–methanol mixtures according to the procedure described by Smets.[14,15]

Degree of Polymerization

The degree of polymerization P_n of the homopolymers recovered after removal of unreacted backbone polymers and the graft polymers by fractionation[23–24] was determined by viscometry in an Ubbelohde suspended-level dilution viscometer (ASTM specification D446-46 T) with solutions of polymer concentrations of 0.1–0.5 g./dl. The intrinsic viscosities were computed by graphical extrapolation by employing Huggins' relation[25]

$$(\eta_{sp}/c)_{c=0} = [\eta] + K'[\eta]^2c$$

where η_{sp}, $[\eta]$, and c refer to the specific viscosity, intrinsic viscosity, and concentration grams per deciliter, respectively. The relationships used for the system PMMA–benzene at 30°C.,[26] for the system PEMA–MEK at 25°C.,[27] and for the system PMA–acetone at 20°C.[28] are as follows, respectively,

$$P_n = 2.22 \times 10^3 [\eta]^{1.32}$$

$$[\eta] = 1.44 \times 10^{-5} \bar{M}_n{}^{0.88}$$

$$P_n = 11.2\ [\eta]^{1.22}$$

where $[\eta]$, P_n, and $\bar{M}_n$ refer to the intrinsic viscosity (in deciliters per gram), degree of polymerization, and number-average molecular weight, respectively.

RESULTS AND DISCUSSION

The results of the fractionation experiments were expressed by the following quantities: grafting efficiency (GE) = weight of new polymer bound to the backbone/weight of total polymer formed (as grafts + homopolymer); R_g = rate of graft polymerization; R_h = rate of homopolymerization; and $R_p = (R_g + R_h)$ = rate of total polymerization, all the quantities being evaluated from the weights of polymers. The grafting efficiencies were 0.1–0.5, depending on the backbone concentration. As expected, grafting efficiencies increased with increase in backbone concentration.[23,24]

The degree of polymerization of a vinyl polymer obtained from the system backbone polymer (chain-transfer agent)–monomer–catalyst–solvent is given by

$$\frac{1}{(P_n)} = C_{\mathrm{M}} + \frac{k_t R_p}{k_p{}^2[\mathrm{M}]^2} + \frac{C_{\mathrm{cat}} k_t R_p{}^2}{k_d f k_p{}^2 [\mathrm{M}]^3} + C_{\mathrm{s}} \frac{[\mathrm{S}]}{[\mathrm{M}]} + C_{\mathrm{p}} \frac{[\mathrm{P}]}{[\mathrm{M}]} \qquad (1)$$

where C_{M}, C_{cat}, C_{s}, and C_{p} refer to chain-transfer constants of polymer radicals to monomer, catalyst, solvent, and the backbone polymer respectively; k_t and k_p are the termination and propagation rate constants, respectively; [M], [S], and [P] refer to initial concentrations of monomer, solvent, and backbone polymer respectively; and (P_n), $(P_n)_0$ are the degrees of polymerization of the homopolymer formed in the presence and absence of the backbone polymer. In the latter case $(P_n)_0$ is represented by eq. (1) except that the term $C_p[\mathrm{P}]/[\mathrm{M}]$ does not appear on the right-hand side, i.e.,

$$[1/(P_n)] - [1/(P_n)_0] = C_{\mathrm{p}}[\mathrm{P}]/[\mathrm{M}] \qquad (2)$$

Plots of $1/(P_n) - 1/(P_n)_0$ against [P]/[M] for various transfer reactions are shown in Figure 1 and chain-transfer constants C_{p} are evaluated from slopes (Table I). The chain-transfer constants obtained refer to the middle groups only and not to the endgroups in the backbone polymer, since

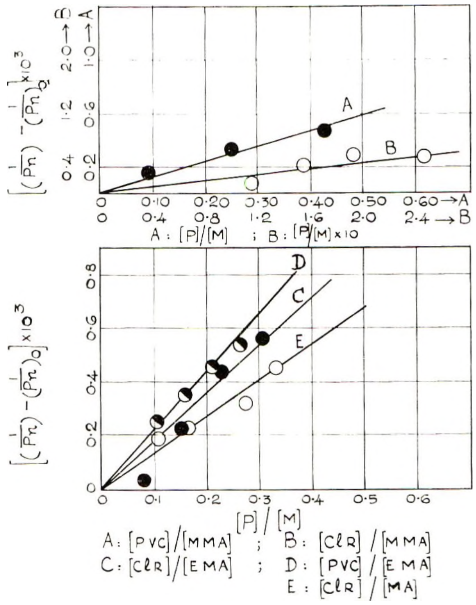

Fig. 1. Evaluation of chain transfer constants [plots of eq. (2)].

by the very method of preparation of PVC[33] and ClR, the endgroup unsaturation was eliminated. Furthermore, endgroup activity, if present, becomes insignificant at the high molecular weights of ClR (4×10^6) and PVC (10^5) used for our experiments.[23,24] The scatter observed in the plots of C of Figure 1 at low value of $[P]/[M]$ may be attributed to possible errors in $1/(P_n) - 1/(P_n)_0$ at very high value of P_n.

TABLE I
Chain Transfer Constants and $k_p/(k_t)^{1/2}$ Values

Polymer P	Monomer M (side chain)	Temp., °C.	$C_p = k_3/k_4 \times 10^3$	$k_5/(k_6)^{1/2} = k_p/(k_t)^{1/2}$ for grafting reaction[a]	$k_p/(k_t)^{1/2}$ for homopolymerization[b]
ClR	MMA	80	2.33	0.03	0.112
ClR	MA	75	1.26	1.87	0.964
ClR	EMA	70	1.83	0.20	—
PVC	MMA	70	1.00 1.10[d]	0.67	0.190[c]
PVC	EMA	70	2.10	0.72	—

[a] Calculated from the slopes of plots of eq. (23) (Fig. 2) with $f = 0.72$; $k_d = 1.41 \times 10^{-4}$ sec.$^{-1}$.[29–30]

[b] $k_p/(k_t)^{1/2}$ calculated from the data of Matheson et al.[31] at 60°C. except as otherwise noted.

[c] Values determined by the authors at 70°C. in cyclohexanone.[23,24]

[d] C_p value for PMMA radicals to PVC reported by Minoura et al.[32]

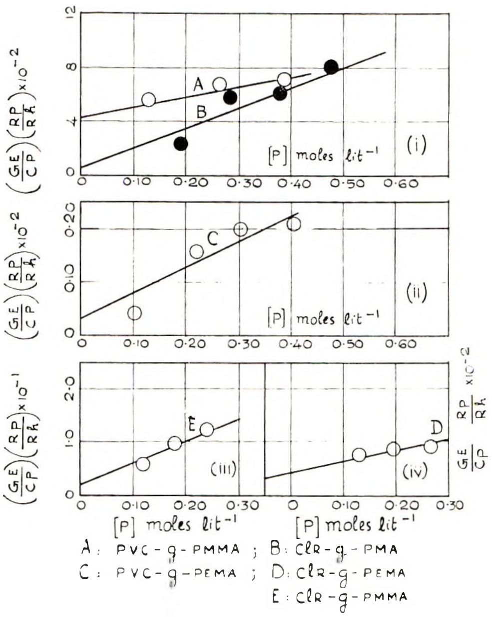

Fig. 2. Evaluation of $k_5/(k_6)^{1/2}$ [plots of eq. (23)].

Mechanism of Grafting Reaction

The sequence of reactions given in eqs. (3)–(11) leading to the formation of graft and homopolymers appears to be important.

Production of radicals:

$$\text{Catalyst (benzoyl peroxide)} \xrightarrow{k_d f} 2\text{C}\bullet \tag{3}$$

Initiation:

$$\text{C}\bullet + \text{M} \xrightarrow{k_1} \text{R}\bullet \tag{4}$$

$$\text{C}\bullet + \text{P} \xrightarrow{k_2} \text{P}\bullet \tag{5}$$

Chain transfer:

$$\text{R}\bullet + \text{P} \xrightarrow[\substack{\text{(termination of} \\ \text{homopolymer radicals)}}]{k_3} \text{P}\bullet + \text{RH} \tag{6}$$

Propagation:

Homopolymer:

$$\text{R}\bullet + \text{M} \xrightarrow{k_4} \text{R}\bullet \tag{7}$$

Graft Polymer:

$$\text{P}\bullet + \text{M} \xrightarrow{k_5} \text{P}\bullet \tag{8}$$

Terminations:

Graft + graft:

$$P^\bullet + P^\bullet \xrightarrow{k_6} \text{Nonradical products} \qquad (9)$$

Graft + homo:

$$P^\bullet + R^\bullet \xrightarrow{k_7} \text{Nonradical products} \qquad (10)$$

Homo + homo:

$$R^\bullet + R^\bullet \xrightarrow{k_8} \text{Homopolymer} \qquad (11)$$

$C^\bullet$ and $R^\bullet$ refer to the catalyst radicals and homopolymer radicals, respectively, and $P^\bullet$ refers to the reactivity of backbone radicals as well as graft polymer radicals, both the reactivities being assumed to be the same while the reactivity of homopolymer radicals, $R^\bullet$ was different from $P^\bullet$. A different reactivity was assigned to the backbone and graft polymer radicals ($P^\bullet$) on one side as distinct from homopolymer radicals ($R^\bullet$) on the other, especially because of certain possible side reactions involving graft removal, etc., arising from incompatibility. In fact, PVC and PMMA were shown to be incompatible by Kern.[34] This type of graft removal is likely to occur in the presence of a poor solvent for the backbone and good solvent for the side chains and at high temperatures,[35,36] as in the case of the systems under consideration. Termination reactions involving primary radicals are unimportant under high monomer concentrations ($1.5M$) and low catalyst concentrations[37–39] used in this investigation.

Applying steady-state conditions, we have

$$d[C^\bullet]/dt = 2k_df[\text{cat}] - k_1[C^\bullet][M] - k_2[C^\bullet][P] = 0 \qquad (12)$$

$$d[P^\bullet]/dt = k_2[C^\bullet][P] + k_3[R^\bullet][P] - k_6[P^\bullet]^2 - k_7[P^\bullet][R^\bullet] = 0 \qquad (13)$$

$$d[R^\bullet]/dt = k_1[C^\bullet][M] - k_3[R^\bullet][P] - k_7[P^\bullet][R^\bullet] - k_8[R^\bullet]^2 = 0 \qquad (14)$$

Under the conditions of the experiment, $[M] \gg [P]$.

The following conditions are therefore applicable: $k_1[M] \gg k_2[P]$ and $k_8[R^\bullet] \gg k_7[P^\bullet]$. From eq. (12),

$$[C^\bullet] = 2k_df[\text{cat}]/(k_1[M] + k_2[P]) \qquad (15)$$

Adding eqs. (13) and (14), we have

$$[C^\bullet](k_1[M] + k_2[P]) - 2k_7[P^\bullet][R^\bullet] - k_6[P^\bullet]^2 - k_8[R^\bullet]^2 = 0 \qquad (16)$$

From eqs. (14) and (15)

$$[R^\bullet] = 2k_df[\text{cat}]/(k_3[P] + k_7[P^\bullet] + k_8[R^\bullet]) \qquad (17)$$

It is possible to obtain from eqs. (15)–(17), after neglecting terms of smaller magnitude,

$$[P^\bullet]^2 = (2k_df[\text{cat}]/k_6)\left\{1 - 2k_7[P^\bullet]/(k_3[P] + k_7[P^\bullet] + k_8[R^\bullet])\right\} \qquad (18)$$

According to the condition, $k_8[\mathrm{R}^\bullet] \gg k_7[\mathrm{P}^\bullet]$, the term in the braces on the right-hand side of eq. (18) becomes nearly equal to unity; therefore

$$[\mathrm{P}^\bullet] = (2k_d f[\mathrm{cat}]/k_6)^{1/2} \tag{19}$$

Dividing eq. (19) by eq. (17) and neglecting terms of smaller magnitude, we have

$$\frac{[\mathrm{P}^\bullet]}{[\mathrm{R}^\bullet]} = \frac{k_3[\mathrm{P}]}{(k_6)^{1/2}\,(2k_d f[\mathrm{cat}])^{1/2}} + \frac{k_7}{k_6} \tag{20}$$

Taking $[\mathrm{P}^\bullet]$ and $[\mathrm{R}^\bullet]$ proportional to the respective rates of polymerization R_g and R_h, we have

$$R_g/R_h = k_5[\mathrm{P}^\bullet]/k_4[\mathrm{R}^\bullet] \tag{21}$$

Substituting eq. (20) for $[\mathrm{P}^\bullet]/[\mathrm{R}^\bullet]$ yields

$$\frac{R_g}{R_h} = \frac{k_5k_3[\mathrm{P}]}{(k_6)^{1/2}k_4(2k_d f[\mathrm{cat}])^{1/2}} + \frac{k_5k_7}{k_4k_6} \tag{22}$$

By definition, the rate of graft polymerization equals the product of rate of total polymerization times grafting efficiency, $R_g = R_p(\mathrm{GE})$, and chain transfer constant $C_\mathrm{p} = k_3/k_4$.

Therefore, eq. (22) becomes

$$\frac{GE}{C_\mathrm{p}}\left(\frac{R_p}{R_h}\right) = \frac{k_5[\mathrm{P}]}{(k_6)^{1/2}\,(2k_d f[\mathrm{cat}])^{1/2}} + \frac{k_5k_7}{k_3k_6} \tag{23}$$

Plots of $\mathrm{GE}R_p/C_\mathrm{p}R_h$ versus [P] are shown in Figure 2 for various grafting reactions studied. These plots are linear initially with upward curvatures at high backbone concentrations. Only plots at low [P] are shown in Figure 2. This may be understood in terms of the termination becoming increasingly diffusion-controlled due to the increased viscosity of the medium as is the case in the methyl methacrylate polymerizations.[40] The importance of the viscosity of the medium in graft polymerizations was discussed by Lazâr,[41] Smets,[42] and others. From the initial slopes of the plots (Fig. 2) the ratio $k_5/(k_6)^{1/2}$ was obtained (Table I). The small magnitude of the intercepts in the plots (Fig. 2) is probably due to predominance of termination involving two graft polymer chains over terminations involving homopolymer radicals. Besides termination of homopolymer radicals by chain-transfer reaction [eq. (6)] which determines the value of C_p and termination reactions [eqs. (10) and (11)] which govern the value of R_h, the mutual termination reaction [eq. (9)] involving two graft polymer radicals seems to be important.

The values of $k_5/(k_6)^{1/2}$ for the graft polymerization are of comparable in magnitude with $k_p/(k_t)^{1/2}$ values for homopolymerization reactions (Table I), slight variations being obviously due to the extent of possible specific effects, e.g., graft removal (which decreases GE and increases R_h) arising out of the incompatibility[34,41] between backbone and graft side chains as well as specific configurational effects of the backbone on the grafting reactions, all of which are absent in the homopolymerization reactions. The slightly higher value of $k_5/(k_6)^{1/2}$ in comparison with $k_p/(k_t)^{1/2}$ (Table I) is attributable to decrease in termination rate constant (k_6) due to high viscosity of the reaction medium caused by the presence of added polymer (backbone).

It may be mentioned that the numerical value of the term GER_p/C_pR_h [eq. (23)] was determined by experiment and therefore the lines drawn through the experimental data (Fig. 2) are subject to errors, though of small magnitude, encountered during fractionation and isolation of the homopolymer (PMMA, PMA, PEMA etc.), from the polymer mixture. In other words, the terms GE and R_h may be in slight error because they are computed from the weight of the free homopolymer recovered after the fractionation procedure. The slight discrepancies between $k_5/(k_6)^{1/2}$ and $k_p/(k_t)^{1/2}$ (Table I) values may also partly be attributed to the errors encountered during fractionation.

Q–e Scheme

It was suggested by Fuhrman and Mesrobian[28] that chain transfer data for polymer–solvent systems might be correlated with the *Q–e* scheme of Alfrey and Price.[22,43] This was extended by Voeks[19] to polymer–polymer transfer reactions. The chain-transfer constant is given by:

$$C_p = (Q_p/Q_m) \exp \{e_M(e_M - e_p)\} \qquad (15)$$

where Q_p and Q_M are the Q values (specific reactivity), e_p and e_M the e values (polarity) for the backbone polymer and grafting monomer, respectively, as in copolymerization. Making use of the values Q_M and e_M for MMA, MA, and EMA published for the copolymerization data[44] and C_p values for various grafting reactions determined experimentally by us (Table I), Q_p and e_p were evaluated for chlorinated rubber and poly(vinyl chloride) and compared (Table II) with those for hydrocarbon solvents tabulated by Voeks[19] and Katagiri et al.[45] As expected, the Q_p and e_p

TABLE II

Q–e Values for Polymers[a]

Polymer	$Q_p \times 10^3$	e_p
ClR	1.47	+2.29
ClR	8.53	+4.29
PVC	1.80	+2.61
Carbon tetrachloride[b]	0.538	+3.21
Chloroform[b]	0.015	+0.72
Trichlorobromomethane[b]	38.9	+3.19

[a] Calculated from $C_p = (Q_p/Q_M)\exp\{e_M(e_M - e_p)\}$ with C_p values from Table I and Q_M and e_M from published data.[44]

[b] Data of Katagiri et al.[45]

values are higher for ClR and PVC than the corresponding values for the hydrocarbon solvents like CCl_4, etc. The high and fluctuating values of Q_p and e_p for ClR and PVC may be attributed to the Q–e scheme being highly empirical, as also discussed by Alfrey and Price[22] in connection with copolymerization. Nevertheless the Q_p and e_p values serve as a useful guide for calculating the chain transfer constant for any branching reaction, with a knowledge of Q and e for the grafting monomer.

CONCLUSION

The chain transfer reactions in graft polymerization were considerably influenced by the effects arising out of the incompatibility of the side chains to the backbone. The $k_p/(k_t)^{1/2}$ values for the grafting reactions were of comparable magnitude to homopolymerization reactions, slight variations being traced to the increased viscosity of reaction medium, specific nature of the backbone, as well as the backbone–monomer combinations, etc., the latter effects possibly being eliminated in the case of self-branching reactions where the backbone and side chains are composed of the same monomer units.

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Résumé

Des monomères vinyliques tel que le méthacrylate de méthyle, le méthacrylate d'éthyle et l'acrylate de méthyle ont été polymérisés en présence de caoutchouc chloré ou de chlorure de polyvinyle en solution homogène en présence de péroxyde de benzoyle comme catalyseur. Outre la formation d'homopolymère au départ du monomère un polymère greffé a été obtenu par réaction de transfert de chaîne comportant des radicaux polymériques de chaînes en croissance sur la chaîne principale du caoutchouc chloré ou du chlorure de polyvinyle. L'homopolymère a été isolé au départ du mélange de polymère par précipitation fractionnée au départ de la méthyl éthyl cétone par addition de méthanol comme précipitant. Les constantes de transfert de chaîne pour les réactions de ramification ont été évaluées; les rapports de $k_p/(k_t)^{1/2}$ pour les réactions de greffage ont été obtenues en correlant les constantes de transfert de chaîne au taux de ramification. Les résultats du transfert de chaîne ont été reliées sur la base, de l'extension du schéma *Q–e* de Alfrey et Price aux réactions de transfert polymère–polymère. Des effets spécifique dûs à la chaîne principale ont une influence considérable sur le cours des réactions de transfert de chaînes et sur les valeurs de $k_p/(k_t)^{1/2}$ des réactions de greffage.

Zusammenfassung

Vinylmonomere wie Methylmethacrylat, Äthylmethacrylat und Methylacrylat wurden in Gegenwart von chloriertem Kautschuk oder von Polyvinylchlorid in homogener Lösung mit Benzoylperoxyd als Starter polymerisiert. Durch eine Kettenübertragungsreaktion zwischen den wachsenden Polymerradikalen und der Hauptkette des chlorierten Kautschuks oder des Polyvinylchlorids bildete sich neben dem Homopolymeren aus dem Monomeren ein Pfropfpolymeres. Das Homopolymere wurde aus der Polymermischung durch fraktionierte Fällung aus Methyläthylketonlösung mit Methanol als Fällungsmittel isoliert. Die Übertragungskonstanten für die Verzweigungsreaktionen wurden ermittelt und die Quotienten $k_p/(k_t)^{1/2}$ für die Pfropfungsreaktion wurden durch eine Korrelation der Übertragungskonstanten mit dem Ausmass der Verzweigung erhalten. Die Daten für die Kettenübertragung wurden auf der Basis des auf Polymer–Polymer-Übertragungsreaktionen ausgedehnten *Q*–*e*-Schemas von Alfrey und Price korreliert. Spezifische Effekte der Hauptkette besitzen, wie gefunden wurde, einen beträchtlichen Einfluss auf den Verlauf von Kettenübertragungsreaktionen und den $k_p/(k_t)^{1/2}$-Wert der Pfropfungsreaktionen.

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α,ω-Diols from Polymerization of Ethylene

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Synopsis

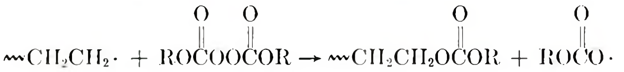
Polyethylene is prepared in silver perchlorate solution by initiation with dialkyl peroxydicarbonates at 0–40°C. Saponification of the polymer endgroups yields a product rich in α,ω-diols. Well-known reactions convert the hydroxyl groups to other functional groups. The diol may be condensed with phosgene so as to increase its molecular weight severalfold or crosslinked with silicon tetrachloride to form a network.

Introduction

The more familiar types of linear polyethylene contain no more than one functional group per chain.[1,2] In this paper we describe low-temperature, free-radical polymerization conditions for preparing an essentially difunctional, nearly linear polyethylene.

Polymerization Conditions

Bier et al.[3] reported that ethylene polymerized at useful rates at 30°C. in aqueous silver perchlorate solution. We have conducted polymerizations in this solvent at 0–40°C. using large concentrations of diisopropyl, diethyl, and dimethyl peroxydicarbonates as initiators. Under the conditions in Table I, ethylene polymerizes without an induction period, and rates decrease with choice of initiator in the order dimethyl > diethyl > diisopropyl peroxydicarbonate. Polyethylene precipitates from the start as irregular particles 1–100 μ in diameter, but rate decreases smoothly without the apparent acceleration (Fig. 1) expected from radical encapsulation.[4,5] Chain transfer to initiator [eq. (1)] is a possible explanation of the short chain lifetime and low molecular weights of Table I.



$$\sim\!CH_2CH_2\cdot + RO\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}OR \rightarrow \sim\!CH_2CH_2O\overset{\overset{O}{\|}}{C}OR + RO\overset{\overset{O}{\|}}{C}O\cdot \qquad (1)$$

Polymer Structure and Reactions

Carbonate groups, ROC(O)O—, are the principal endgroups expected from peroxydicarbonate initiation in dry systems.[6] In the polymers of Table I, both carbonate and hydroxyl infrared bands are evident. As calculated from the absorptivity of diethylcarbonate in cetane at 5.72 μ, the polymer contains only 0.2–1 carbonate groups per chain. The high

TABLE I

Sample	Initiator	Wt. initiator, g.	Silver perchlorate wt.-%	Silver perchlorate g. of soln.	Temperature, °C.	Pressure, psig	Reaction time, hr.	Yield, g.	Melting point, °C.[d]	Molecular weight (ebullioscopic)	Intrinsic viscosity, dl./g.[e]	Density, g./ml.[f]
A	*i*-Pr[a]	2.2	30	500	30–38	750–850	23	92	128	16,000 ± 3,000	0.93	0.948
B	Et[b]	2.2	20	500	26–34	280–300	6.5	6.6	123	3,300 ± 200	0.23	0.961
C	Et	0.79	20	59	10	78–105	6	0.55	121	3,300 ± 500	—	—
D	Me[c]	1.1	30	500	12–19	270–325	6	40.2	128	—	1.2	0.966
E	Et	4.8	30	500	8–13	240–315	6	13.5	128	3,200 ± 160	0.45	0.965
F	Et	0.1	50	60	0	75–105	6	2.3	133	15,000 ± 2,500	1.9	0.933
G	*i*-Pr	2.2	20	500	18–22	290–310	48	32.5	125	16,000 ± 2,000[g]	0.76	0.960
H	Me	2.2	20	500	11–14	273–295	6	19.5	113	9,400 ± 600[h]	—	0.962

[a] Diisopropyl peroxydicarbonate.

[b] Diethyl peroxydicarbonate.

[c] Dimethyl peroxydicarbonate.

[d] DTA peak on quenched samples. Heating rate 30°C./min. Linear polyethylene (chromium oxide process) peak 135°C., density 0.963 g./ml.

[e] In decalin, 150°C.

[f] Precipitated in acetone, not annealed.

[g] Light-scattering molecular weight = 39,000 ± 3,900. $\bar{M}_w/\bar{M}_n = 2.5 \pm 0.6$.

[h] Light-scattering molecular weight-26,000 ± 1,300. $\bar{M}_w/\bar{M}_n = 2.8 \pm 0.3$.

concentration of perchlorate and silver ions perhaps catalyzes the hydrolysis of carbonate groups. Total double bond content (vinyl, vinylidene, and *trans*-vinylene) amounts to <0.1 per chain as measured by the usual infrared procedure.[7a]

The carbonate groups are removed (with no measurable change in polymer molecular weight) by refluxing the polymer under nitrogen in potassium hydroxide–1-butanol–xylene–triethylene glycol–water.[8] The saponified polymer undergoes several reactions (Table II) typical of primary alcohols. The transparency of the polyethylene backbone through most of the infrared facilitates detection and monitoring of these reactions.

Treatment of the fully saponified polymer with excess phenylisocyanate yielded phenylurethans which were purified by repeated precipitations in acetone. Ultraviolet spectra and nitrogen analyses (Table III) of the phenylurethans correspond to two functional groups per number-average chain.

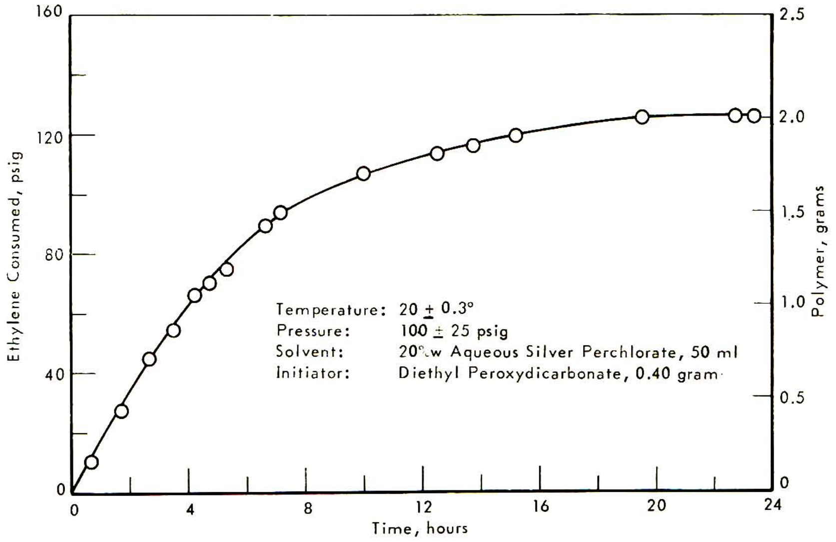


Fig. 1. Polymerization of ethylene in silver perchlorate.

The course of a polycondensation reaction verified the high diol content of the polymer. Half of a saponified sample (Table I, sample E, <0.05 double bonds per chain) was treated with phosgene and pyridine in hydrocarbon solution. The excess phosgene was removed with a nitrogen stream and the other half of the polymer sample was then added. The viscosity of the system increased sharply. The final polymer was a polycarbonate (absorption at 5.73 μ) having five to six times the molecular weight of the initial sample: original molecular weight 3200 ± 160, final molecular weight 20,000 ± 4,000. By classical condensation theory, the initial polymer must have contained at least 80 mole-% diol to increase fivefold in molecular weight.

By treating the polymer with a tetrafunctional agent, gelation was effected. Slow addition of excess silicon tetrachloride to a solution of polymer in xylene precipitated 24% of gel. A difunctional analog, dimethyldichlorosilane, increased the molecular weight of the sample by a small percentage but precipitated no gel.

TABLE II
Reactions of Hydroxyl-Bearing Polyethylene

Reagent[a]	Product	Infrared maxima, μ
Acetic anhydride, pyridine	Acetate	5.73, 8.07
Adipoyl chloride, pyridine, then water	Hydrogen adipate	2.95, 5.70, 5.80, 3.95, 4.05
Phenylisocyanate, pyridine,	Phenylurethan	3.0, 5.75, 6.25, 6.6, 7.65, 8.3
Phosgene, pyridine	Chloroformate	5.62
Phosgene, pyridine, then isopropyl alcohol	Isopropyl carbonate	5.73
Phosphorus oxychloride	Phosphate	4.15, 4.35, 8.3, 9.7
Thionyl chloride	Chlorosulfite	8.2, 8.4
Triphenylphosphine + bromine	Bromide	15.35
Trityl chloride	Trityl ether	11.15, 13.0, 13.2, 14.25

[a] Polymer dissolved in hot hydrocarbon or chlorobenzene and treated with the indicated reagent.

TABLE III
Phenylurethans of Hydroxyl-Bearing Polymers

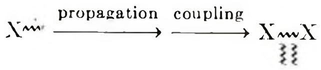
Starting alcohol	Nitrogen content, wt.-%		Absorptivity,[b] l./mole-cm.
	Theoretical	Found	
1,10-Decanediol	6.79[a]	6.77	1637 ± 80
1-Hexanol	6.33	6.27	842 ± 40
Polyethylene, sample A	0.18[a]	0.17	1416 ± 260
Polyethylene, sample B	0.85[a]	0.73	1589 ± 100
Polyethylene, sample C	0.85[a]	0.8	1757 ± 270

[a] Assuming two nitrogen atoms per number average chain.

[b] At 274 mμ, in decane, 110°C., nitrogen atmosphere. Absorptivity errors calculated assuming 10–20% error in ebullioscopic molecular weight.

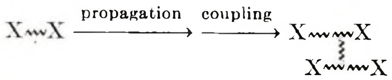
The infrared spectra of polymer samples[7b] of Table I indicate the presence of 5–10 methyl groups per thousand carbon atoms. Melting points of the high molecular weight samples (133°C., sample F, Table I, compared to 135°C. for linear polyethylene in the same apparatus) confirm the presence of branching. This branching must be produced chiefly by backbiting [eq. (2), (3)] to account for the difunctionality of the polymer; intermolecular reactions [eqs. (4), (5)] should increase functionality above two. $\overline{M}_w/\overline{M}_n$ ratios for two samples (Table I) also suggested a rather low level of long-chain branching.

$$\mathrm{X}{\sim\sim}\cdot \rightarrow \mathrm{X}\overset{\cdot}{\sim\sim} \qquad (2)$$



$$\mathrm{X}\overset{\cdot}{\sim\sim} \xrightarrow{\text{propagation}} \xrightarrow{\text{coupling}} \mathrm{X}\underset{\wr\wr}{\sim\sim}\mathrm{X} \qquad (3)$$

$$\mathrm{X}{\sim\sim}\cdot + \mathrm{X}{\sim\sim}\mathrm{X} \rightarrow \mathrm{X}{\sim\sim} + \mathrm{X}\underset{\cdot}{\sim\sim}\mathrm{X} \qquad (4)$$



$$\mathrm{X}\underset{\cdot}{\sim\sim}\mathrm{X} \xrightarrow{\text{propagation}} \xrightarrow{\text{coupling}} \begin{array}{l}\mathrm{X}{\sim\sim\sim\sim}\mathrm{X}\\ \quad\ \ \wr \\ \quad \mathrm{X}{\sim\sim\sim\sim}\mathrm{X}\end{array} \qquad (5)$$

Polymerization By-Products

When potassium peroxydisulfate is used to initiate polymerization,[3] hydroxyl (3.0 μ) and ether groups (9.6 μ) are observed in the polymer. Traces of tetrahydrofuran are observed as by-product. If peroxydisulfate is added fast enough, no polyethylene is obtained, and tetrahydrofuran (1% conversion) is the major organic product. The ratio of tetrahydrofuran to ethanol is at least 10/1 by gas–liquid chromatography (GLC).

The presence of ether units in the polymer chain can be rationalized as etherification by sulfate endgroups [eqs. (6), (7)] while tetrahydrofuran is probably the product of radical coupling and etherification [eqs. (8), (9)].

$$\mathrm{Ag^+ + {\sim\sim}OSO_3^- + H_2O \rightarrow {\sim\sim}OH + AgHSO_4} \qquad (6)$$

$$\mathrm{Ag^+ + {\sim\sim}OSO_3^- + {\sim\sim}OH \rightarrow {\sim\sim}O{\sim\sim} + AgHSO_4} \qquad (7)$$

$$\mathrm{2\overset{\ominus}{O}_3SOCH_2CH_2\cdot \rightarrow \overset{\ominus}{O}_3SOCH_2CH_2CH_2CH_2OSO_3^{\ominus}} \qquad (8)$$

$$\mathrm{2Ag^+ + \bar{O}_3SOCH_2CH_2CH_2CH_2OS\bar{O}_3 + H_2O \rightarrow}$$

$$\mathrm{\overline{O{-}CH_2CH_2CH_2C}H_2 + 2AgHSO_4} \qquad (9)$$

A high coupling/disproportionation ratio would also explain the reported[9] high yields of α,ω-dichlorides formed by treating ethylene in aqueous sodium chloride with peroxydisulfate.

When peroxydicarbonates are used for initiation, no tetrahydrofuran is detected among the products. The saponified polymer absorbs much more weakly in the ether C–O stretch region than does peroxydisulfate-initiated polymer, and it is not reduced in molecular weight when treated with triphenylphosphine dibromide, a powerful ether-cleaving reagent.[10] The hydroxyl groups of the polymer are evidently not etherified by the carbonate groups, as they are when peroxydisulfate is the initiator. Carbon dioxide, isopropanol, and acetone were the only by-products observed in the diisopropyl peroxydicarbonate-initiated reaction.

Experimental

Peroxydicarbonates were prepared by the method of Strain et al.[11] and analyzed by iodometry. Assays showed diisopropyl peroxydicarbonate, 98.0%; diethyl peroxydicarbonate, 98.0%; dimethyl peroxydicarbonate, 98.5%.

Caution: Dimethyl peroxydicarbonate detonates with great destructive power when struck or heated. No explosions occurred during polymerizations but heavy barricades are recommended.

A 1-liter stainless steel Magnedrive reactor (Autoclave Engineers, Inc., Erie, Pennsylvania) equipped with an internal cooling coil was charged with 500 g. of 20–30% silver perchlorate (G. Fredrick Smith Co.). This solution was heated to 70–80°C. and purged several times with 400 psi nitrogen. The solution was then cooled to polymerization temperature, initiator was added and the mixture was purged several times and charged with ethylene (Phillips 99%), 6 ppm oxygen). The consumed ethylene was replaced after pressure decrements of 50–100 psi. At the end of the reaction period, polymer was removed, immediately filtered, washed with ice water, then with ice cold acetone, and dried under vacuum at room temperature.

To prepare samples for spectroscopic measurements polymer was saponified under nitrogen,[8] reprecipitated three times in acetone from hot xylene or toluene, then vacuum-dried at 50°C. Exposure of the polymer to light and oxygen was minimized.

The silver content of the polymer was reduced to 0.2–0.4% by three water washes. Saponification of the polymer causes precipitation of this remaining silver as large particles of metal in yield >97%. Neutron activation analysis on a saponified, reprecipitated sample showed silver content to be below 40 ppm.

Before ebullioscopic molecular weights were measured, the reprecipitated polymer was dissolved in hot toluene, and the toluene was evaporated in vacuum. Molecular weights were then measured in toluene in microebulliometers.[12]

Tetrahydrofuran as a by-product of polymerization was identified by its emergence time on three different GLC columns and by the mass spectrum of the trapped material.

Weight-average molecular weights were obtained by light scattering in α-chloronaphthalene.

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Résumé

Un polyéthylène a été préparé en solution dans le perchlorate d'argent par initiation avec les peroxydicarbonates de dialcoyles de 0 à 40°C. La saponification des groupes terminaux du polymère fournit un produit riche en α,ω-diols. Des réactions bien connues transforment ces groupes hydroxyles en autres groupes fonctionnels. Le diol peut être condensé avec le phosgène de façon à augmenter son poids moléculaire de nombreuses fois, ou ponté au moyen de tétrachlorure de silicium avec formation de réseaux.

Zusammenfassung

Polyäthylen wurde in einer Silberperchloratlösung durch Anregung mit Dialkylperoxydicarbonaten bei 0–40° hergestellt. Die Verseifung der Endgruppen des Polymeren ergibt ein Produkt, das reich an α,ω-Diolen ist. Die Hydroxylgruppen lassen sich durch bekannte Reaktionen in andere funktionelle Gruppen überführen. Das Diol kann mit Phosgen kondensiert werden, wobei sein Molekulargewicht um ein Mehrfaches vergrössert wird, oder mit Siliciumtetrachlorid unter Bildung eines Netzwerks verknüpft werden.

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NOTES

Relative Reactivities of the cis *and* trans *Crotonic Compounds in Anionic Polymerization*

We have examined relative polymerizabilities of the *cis* and *trans* isomers of crotononitrile and *sec*-butyl crotonate by some anionic catalysts in both polar and nonpolar solvents. It has been found that, although in general, the *trans* compounds are more reactive than the *cis* isomers, their relative reactivities are more or less dependent on the types of catalysts and solvents used.

Experimental

The *cis*- and *trans-sec*-butyl crotonates were synthesized separately by the methods used for the preparation of their alkyl homologs.[1] The *trans*-crotonate was prepared by the esterification of *trans*-crotonic acid with *sec*-butyl alcohol in the presence of sulfuric acid, while the *cis* isomer was synthesized through the reaction between the silver salt of the *cis*-crotonic acid[2] and *sec*-butyl iodide; *trans*, b.p. 165–166°C., *cis*, b.p. 64–65°C./20 mm. *trans*-Crotononitrile was prepared by the dehydration of the corresponding crotonic amide in the presence of phosphorus pentoxide,[3] and the *cis* isomer was separated from a commercial *cis–trans* mixture of crotononitrile, a product of the Tokyo Kasei Co., by fractional distillation through a packed column; *trans*, b.p. 120–121°C. (lit.[3] b.p., 118–119°C.), *cis*, b.p. 110–112°C. (lit.[4] b.p. 108°C.). The isomer purity of this last monomer was 85.0%, whereas the three other compounds were 99.8–100.0% pure.

Solvents were distilled over sodium benzophenone ketyl under a nitrogen atmosphere. All chemicals used were checked for purity by vapor-phase chromatography. Polymerizations were conducted under dry, oxygen-free nitrogen.

Mixtures of *cis*- and *trans*-crotononitriles were subjected to copolymerization at −78°C. by adding a specified amount of catalyst solution. The catalysts used in this study included the alkali metal naphthalenes, phenylmagnesium bromide and lithium aluminum hydride. Various solvents were used for the sake of comparison. After an appropriate reaction time, usually 30–60 min., an aliquot of the reaction mixture was taken and poured into petroleum ether to precipitate the copolymer formed. The two monomeric isomers that remained unreacted were determined by vapor-phase chromatography. The isomer reactivity ratios, r_{cis} and r_{trans}, were evaluated according to the method of Finemann and Ross.[5]

In the case of *sec*-butyl crotonate, only the *trans* isomer was polymerizable by the catalysts used here. The polymer formed was treated in a manner analogous to that adopted for the nitrile.

Results and Discussion

Typical copolymerization data for *cis*- and *trans*-crotononitriles are shown in Table I, for experiments carried out in the presence of lithium aluminum hydride in tetrahydrofuran at −78°C. The extent of polymerization was kept below 12.0% in all runs.

In Table II, the reactivity ratios of *cis*- and *trans*-crotononitriles obtained under various conditions are compared. It may be noticed there that the *trans* isomer is somewhat more reactive than the *cis* isomer.

Illustrated in Figure 1 are two contrasting examples of the *cis–trans* copolymerization curves for crotononitrile. It may be seen in both Table I and Figure 1 that the *trans*-

TABLE I
cis–trans Copolymerization of Crotononitrile Catalyzed by $LiAlH_4$ in THF at −78°C.[a]

cis Isomer in monomer feed, mole-%	Reaction time, min.	Conversion, %	*cis* Isomer in monomer mixture consumed, mole-%
18.9	30	10.8	4.3
31.5	30	11.1	16.2
39.8	50	10.2	23.9
58.4	40	9.4	48.7
63.8	60	10.4	51.1
69.3	40	6.6	59.6
85.2	60	11.8	84.5

[a] Initial total monomer concentration, 3.3×10^{-1} mole/l.; catalyst concentration, 6.6×10^{-3} mole/l.; reaction temperature, −78°C.

crotononitrile is somewhat more reactive than the *cis* isomer and that this difference is dependent upon the catalysts as well as the solvents used.

The catalysts used in this study may conveniently be divided into two classes; one is the family of alkali metal naphthalenes and the other includes phenylmagnesium bromide and lithium aluminum hydride. The former group is known to polymerize methyl methacrylate into an atactic polymer when used in tetrahydrofuran, while the latter are stereospecific catalysts giving highly isotactic or syndiotactic poly(methyl methacrylate).[6] The results given in Table I may then be stated as follows.

The *cis* and *trans* isomers of crotononitrile show approximately the same reactivities in those catalyst–solvent systems that are nonstereospecific for the methyl methacrylate polymerization, whereas, in the case of stereospecific catalysts, the *trans* monomer shows greater reactivity than the *cis* isomer.

In the case of *sec*-butyl crotonates, only the *trans* monomer was polymerizable by the stereospecific catalysts, as is seen in Table III. Anionic polymerization of crotonic esters has already been reported by Miller and Skogman[7] and by Tsuruta et al.[8,9] without

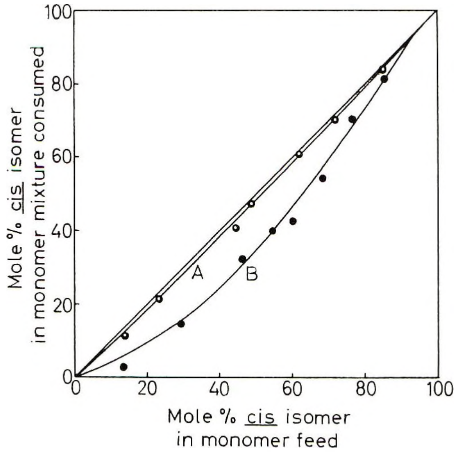

Fig. 1. Copolymerization of *cis*- and *trans*-crotononitriles catalyzed by (*A*) Na naphthalene in THF; (*B*) $LiAlH_4$ in ether.

TABLE II
Copolymerization Reactivity Ratios of *cis*- and *trans*-Crotononitriles[a]

Catalyst	Solvent	Temperature, °C.	r_{cis}	r_{trans}
Li naphthalene	THF	−78	0.98 ± 0.10	0.96 ± 0.04
Na naphthalene	THF	−78	0.97 ± 0.04	1.13 ± 0.02
K naphthalene	THF	−78	0.94 ± 0.04	1.05 ± 0.02
C_6H_5MgBr	*n*-Hexane	0	0.79 ± 0.31	1.55 ± 0.11
$LiAlH_4$	Ether	−78	0.92 ± 0.21	2.64 ± 0.06
$LiAlH_4$	THF	−78	1.48 ± 0.54	4.09 ± 0.18

[a] Initial total monomer concentration, 3.3×10^{-1} mole/l.; catalyst concentration, 6.6×10^{-3} mole/l.

any comment on the relative reactivities of the *cis* and *trans* isomers. Under our experimental conditions *cis*-*sec*-butyl crotonate did not polymerize at all, nor did it enter into copolymerization with its *trans* isomer.

The origin of the stereospecificity to be introduced into linear polymers is generally attributed to the regular orientation of the adding monomer and/or the polymer end by virtue of their coordination with catalysts. If this is true in our present case, the experimental results described above may be taken as an implication that, in the cases of crotonic compounds, the coordination is more favorable for the polymerization of the *trans* monomers than for that of the *cis* isomers.

TABLE III
Polymerization of *cis*- and *trans*-*sec*-Butyl Crotonates[a]

		Polymer yield, %[b]	
Catalyst	Solvent	*cis*	*trans*
$CaZnEt_4$	Toluene	0.0 (4 days)	93.8 (2 days)
$LiAlH_4$	Ether	0.0 (12 days)	34.7 (4 days)
$LiAlH_4$	THF	0.0 (12 days)	55.2 (4 days)

[a] Monomer concentration, 1.0 mole/l.; catalyst concentration, 5.0×10^{-2} mole/l.; reaction temperature, −78°C.

[b] Percentage of the methanol-insoluble polymer formed with respect to feed monomer.

Studies of the correspondence between the polymerizability and stereospecificity are under way.

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Redox Behavior in Photosensitized Crosslinking of Vinyl Polymers Containing N-Hydroxymethylacrylamide as a Component

It is well known that *N*-hydroxymethylacrylamide is useful as a crosslinker[1] when incorporated into a vinyl polymer either by homo- or copolymerization or by methylolation of the acrylamide component in the polymer. The crosslinking effect of *N*-hydroxymethylacrylamide is much improved by the presence of either an acid catalyst such as ammonium chloride or a free-radical-liberating catalyst such as potassium persulfate.[2]

Nevertheless, the application of heat is usually required if satisfactory results are to be obtained.

In a search for catalysts which would operate at lower temperatures we have found that such inorganic salts as ferric chloride, which are composed of metallic cations susceptible to redox reactions and acid anions, are particularly effective under irradiation of near ultraviolet light. Thus, when a slightly yellow film made of an acrylic polymer copolymerized with *N*-hydroxymethylacrylamide such as the methyl methacrylate–butyl acrylate–*N*-hydroxymethylacrylamide terpolymer (10/10/5 by weight) and containing a few per cent of ferric chloride is exposed to a radiation from a 75-w. mercury lamp (minimum wavelength, 250 mμ), the exposed region becomes colorless, denoting the reduction of ferric to ferrous ions, and insoluble in a few minutes.

The effects of various inorganic salts, together with the result with β-methylanthraquinone as the standard,[3] are indicated in Table I. It is interesting to note that effective compounds are all those which are susceptible to redox reactions under irradiation of light, including β-methylanthraquinone, and their crosslinking mechanisms might involve the intermediate generation of free radicals resulting from the redox interactions of the hydroxymethylacrylamide group in the polymer with salts, although at this stage no definite discussions of the mechanisms can be made.

TABLE I
Effect of the Kind of Catalyst on the Photosensitized Crosslinking of Methyl Methacrylate–Butyl Acrylate–*N*-Hydroxymethylacrylamide Terpolymer (10/10/5 by Weight)

Catalyst (1% based on polymer)	Color change during exposure[a]	Exposure time required for insolubilization, min.	Oxidation potential[b] E°_{ox}
None	—	Soluble	—
Ceric ammonium nitrate	Yellow to colorless	3	+1.45 ($Ce^{+4} \rightleftharpoons Ce^{+3}$)
Ferric chloride	Light yellow to colorless	4	+0.75 ($Fe^{+3} \rightleftharpoons Fe^{+2}$)
Silver nitrate	—	Soluble[c]	+0.80 ($Ag^{+1} \rightleftharpoons Ag$)
Stannous chloride	—	5	+0.14 ($Sn^{+4} \rightleftharpoons Sn^{+2}$)
Zinc chloride	—	Soluble[c]	—
Ammonium chloride	—	Soluble[c]	—
β-Methylanthraquinone	Yellow fluorescence	5(partly insoluble)	—

[a] 75-w. mercury lamp.

[b] At 30°C.

[c] After prolonged exposure (more than 30 min.).

Since a *N*-hydroxymethylacrylamide copolymer in solution is crosslinked and insolubilized even at room temperature when left in a strongly acidic medium for a long time, strong Lewis acids, such as stannic chloride, are not desirable for this study. Although ceric ammonium nitrate, ferric chloride, and stannous chloride, as listed in Table I, are all acidic substances, the polymer solutions containing these salts are fairly stable over a long period of time at room temperature; the polymer films containing these compounds in absence of light were also stable for at least 24 hr.

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Dissociation Constants of Onuphic Acid

Onuphic acid, a polysaccharide extracted from the tube of the polychaete *Hyalinoecia tubicola*, contains 14.4% phosphorus.[1] Approximately 90% of the phosphorus is in the form of phosphomonoester and the remaining 10% is present as diester.[2] This polydibasic, strong acid provides an unusual material for testing existing theories which relate the dissociation constants of polymers with those of their monomers.[3-5]

Experimental

Onuphic acid was extracted (with EDTA), purified, and decationized as described elsewhere.[1] Potentiometric titrations were carried out in $1M$ potassium chloride by using a Radiometer TTT1 titrator with glass and calomel electrodes. Carbon dioxide was excluded from the system, and the solutions and procedures outlined previously[2] were used.

Results

The titration curve (a typical example is shown in Fig. 1) is reproducible on back-titration and on subsequent retitration. Minor variations in the curve may be attributed to concentration effects. By using a treatment similar to that of Speiser et al.[4] the apparent first dissociation constant G_1 is defined by the equation:

$$G_1 = a_{\mathrm{H}^+}[\mathrm{P}^-]/([P_t] - [\mathrm{P}^-]) \tag{1}$$

where a_{H^+} is the activity of hydrogen ions, and $[\mathrm{P}^-]$ and $[\mathrm{P}_t]$ are the molarities of phosphate in the once-ionized form and total phosphate, respectively. The titration constant G is thus neither the thermodynamic equilibrium constant (relating activities) nor the concentration equilibrium constant (relating concentrations), but a hybrid constant. This titration constant is nevertheless significant and avoids the use of activity coeffi-

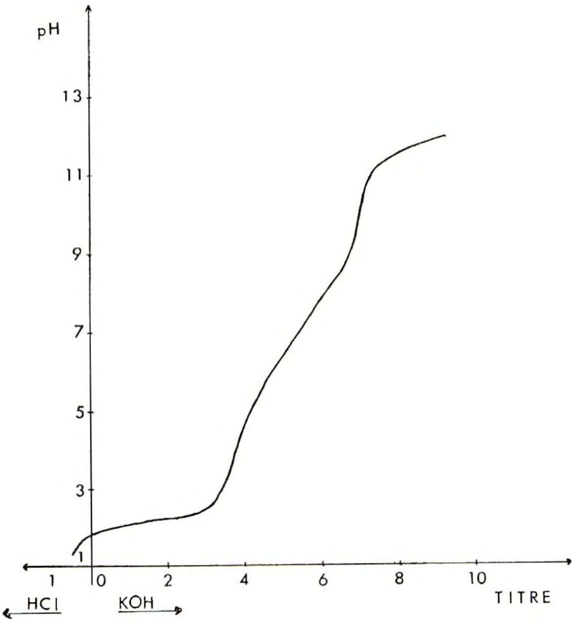

Fig. 1. Typical titration curve for onuphic acid. Plot of pH against titre in milliliters of $0.1N$ KOH and HCl, each $1M$ with respect to KCl, for a solution containing 3.72×10^{-4} g.-atom of phosphorus as onuphic acid.

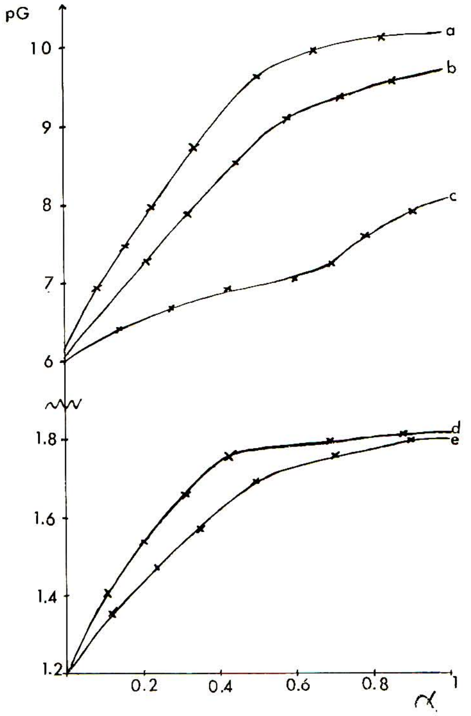

Fig. 2. Graphs of pG_1 against α_1 and pG_2 against α_2 at different initial concentrations: (*a*) $[P_t]$ initial = 0.00417; (*b*) $[P_t]$ initial = 0.01316; (*c*) $[P_t]$ initial = 0.01834; (*d*) $[P_t]$ initial = 0.07790; (*e*) $[P_t]$ initial = 0.03496.

cients, which could not readily be measured in the presence of the polyelectrolyte. pG_1 was calculated directly from eq. (1), without introducing the Henderson-Hasselbach equation, which is not a valid approximation of eq. (1) for a strong acid dissociation.

The degree of dissociation α_1 is equal to $[P^-]/[P_t]$.

Similarly, G_2 is defined by eq. (2):

$$G_2 = a_{H^+}[P^{2-}]/[P^-] \tag{2}$$

where $[P^{2-}]$ is the concentration of twice-ionized phosphate groups. The degree of dissociation is given by:

$$\alpha_2 = [P^{2-}]/(2[P_t] - [P_d]) \tag{3}$$

where $[P_d]$ is the molarity of phosphodiester groups, which have only one ionization. By using the principle of electroneutrality and the known value for the proportion of diester (10% of the phosphate groups[2]), values of α_2 were calculated.

pG_2 was calculated by using the Henderson-Hasselbach equation, which is valid for the weaker acid dissociation:

$$pG_2 = pH + \log[(1 - \alpha_2)/\alpha_2] \tag{4}$$

Graphs of pG against α are shown in Figure 2 for both dissociations.

An alternative method of expressing the results, by plotting pH against $\log[(1 - \alpha)/\alpha]$ is shown in Figure 3. The equations of the linear plots were obtained by using the least-squares method with the aid of a computer. The values of the gradients and intercepts obtained in this way are set out in Table I, together with the intercepts from Figure 2.

TABLE I

Constants in the Equations: pH = $pK - n \log [(1 - \alpha)/\alpha]$ and $pG = pK_0 + f(\alpha)$ for Several Concentrations

$pK_{0,1}$	$pK_{0,2}$	pK_1	pK_2	n	Initial $[P_t]$
1.20		1.70		1.08	0.03496
1.20		1.75		1.11	0.07790
	6.09		9.66	4.92	0.00417
	6.00		8.63	4.90	0.01316
	5.92		6.89	2.34	0.01834

Discussion

As is to be expected for polyelectrolytes,[3,4] the titration curve of onuphic acid is not as sharp as the curve of a monomeric phosphate under similar conditions.

The increase of the apparent dissociation constant pG with the degree of dissociation is in agreement with theory[4-6] and with the behavior of other polyelectrolytes.[4-6] The shapes of the plots in Figure 2 resemble those obtained for polycarboxylic acids.[4,6] The slope of the plot of pG_2 against α_2 is higher at lower concentration, in accord with other observations, but the plot of pG_1 against α_1 is anomalous in this respect. The constant value of pG extrapolated to $\alpha = 0$ supports the view[4,6] that this extrapolated quantity may be regarded as pK_0, where K_0 is the intrinsic dissociation constant of the ionizing group. The values of pK_0 for both dissociations of onuphic acid are within the range of values expected for phosphate compounds (see Table II). Since the extrapolation re-

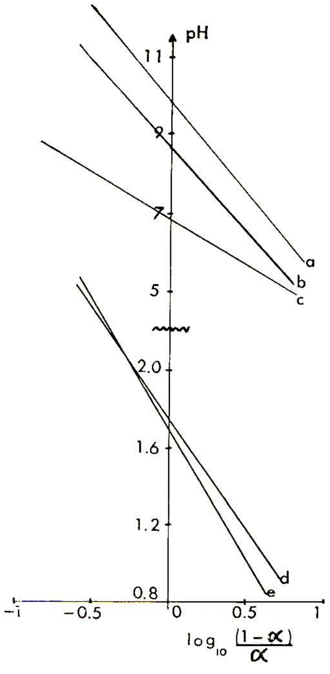

Fig. 3. Graphs of pH against $\log [(1 - \alpha_1)/\alpha_1]$ and $\log [(1 - \alpha_2)/\alpha_2]$ at different initial concentrations: (*a*) $[P_t]$ initial = 0.00417; (*b*) $[P_t]$ initial = 0.01316; (*c*) $[P_t]$ initial = 0.01834; (*d*) $[P_t]$ initial = 0.07790; (*e*) $[P_t]$ initial = 0.03496.

moves electrostatic effects due to the polymeric nature of the acid but does not allow for the inductive and similar effects found in monomeric acids, close agreement with the constants for inorganic orthophosphate is not to be expected.

The linear dependence of log $[(1 - \alpha)/\alpha]$ shown in Figure 3 and the concentration dependence of the gradient and intercept are in agreement with the results of Katchalsky and Spitnik[3] for polycarboxylates. The magnitude of the empirical constant n is unusually large for the second dissociation of onuphic acid when compared to the values between 1 and 2 obtained for poly(carboxylic acids).[3] In the absence of activity corrections, the value of pK obtained from the modified Henderson-Hasselbach equation is considerably concentration-dependent, and pK_0 obtained by extrapolation of the graphs in Figure 2 provides a better constant characteristic of the polymer.

In order to minimize the effects of rapid change of ionic strength, all the titrations described here were carried out at concentrations of 1M with respect to KCl. In agreement with expectations,[3] the pH of solutions of free onuphic acid in deionized water was lowered considerably by the addition of salt.

TABLE II
Dissociation Constants of Some Phosphate Compounds

Compound	pK_1	pK_2	Reference
H_3PO_4	1.97	6.82	Kumler and Eiler[7]
Inorganic polyphosphates	1–3	7–9	Van Wazer[8]
Alkyl monoesters	1.5–1.9	6.3–6.8	Kumler and Eiler[7]
Alkyl diesters	1.2–1.8	—	"
Glycerol and sugar monoesters	0.8–2.1	5.6–6.8	"
Nucleotides and nucleic acids	0.7–2.5	5.5–7	Peacocke[9]
Onuphic acid	1.2	6.0	This work

Although the results of onuphic acid have been shown to fit the qualitative picture developed for polycarboxylic acids,[3–6] the predictions of the corresponding equation of Katchalsky and Gillis,[5] derived from theory, are not borne out quantitatively. Since the theoretical equation[5] was developed for polymeric weak acids, the strong acid nature of onuphic acid may be responsible for the differences. The behavior of onuphic acid is also qualitatively similar to that of the nucleic acids (see for instance Jordan[10]), but electrostatic effects are not so pronounced in the nucleic acids and additional complications are present due to their ampholytic nature.

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Effect of Temperature on Diene Incorporation into Isobutylene–Diene Copolymers

During the course of our fundamental studies in cationic polymerization, we investigated some aspects of the effect of temperature on the copolymerization of isobutylene ($iC_4^{=}$) with conjugated dienes [butadiene ($C_4{}^{=}_{=}$) and isoprene ($iC_5{}^{=}_{=}$)]. In a series of experiments we used an $AlEtCl_2$ catalyst and methyl chloride diluent at −30, −78, −100, and −125°C. Initial monomer concentrations (in volume per cent) were $[iC_4^{=}]_0/[C_4{}^{=}_{=}]_0 = 30/70$ and $[iC_4^{=}]_0/[iC_5{}^{=}_{=}]_0 = 92/8$. Care was taken to terminate the polymerizations at low conversions (less than 15%). Total butadiene incorporation was calculated from the unsaturation level of the polymer by using the drastic iodine–mercuric acetate method[1] and infrared spectroscopy. Infrared spectroscopy was also used to calculate the amounts of 1,4 and 1,2 incorporation of butadiene. The results are shown in Table I. For isobutylene–isoprene polymers we obtained the total amount of isoprene incorporation only from iodine numbers, since no reliable infrared method is available for these systems.

Apparently, overall butadiene incorporation is greatly affected by the polymerization temperature whereas isoprene incorporation is not. Evidently, the overall activation energy for isoprene incorporation is similar to that for isobutylene incorporation, whereas the energy for butadiene entry is somewhat higher. It could be that the electron-releasing methyl group in the isoprene "activates" this molecule and, thus, is responsible for the lower activation energy of isoprene entry compared to butadiene entry.

TABLE I

Diene Incorporation as a Function of Temperature with $AlEtCl_2$ Catalyst[a]

	Unsaturation, mole-%				
	Total			Structures	
Temp., °C.	By I_2 method ($iC_5{}^{=}_{=}$)	By I_2 method ($C_4{}^{=}_{=}$)	By infrared ($C_4{}^{=}_{=}$)[b]	1,4 ($C_4{}^{=}_{=}$ by infrared)[c]	1,2 ($C_4{}^{=}_{=}$ by infrared)[d]
−30	3.28	19.56	15.6, 15.9	12.54, 12.79	3.06, 3.11
−78	3.47	10.65	12.6, 12.6	10.21, 9.81	2.39, 2.79
−100	3.38	7.83	9.25, 9.53	7.04, 7.09	2.21, 2.44
−125	—	8.32	6.04, 6.38	4.41, 4.40	1.63, 1.98

[a] Duplicate determinations of sample for all infrared data.

[b] Determined by analysis of 1225, 980, and 965 cm.$^{-1}$ bands.

[c] Determined by analysis of 965 cm.$^{-1}$ band. There is no evidence for absorption at 725 cm.$^{-1}$ indicating the virtual absence of internal *cis* unsaturation, i.e., *cis*-1,4 diene incorporation.

[d] Determined by analysis of 908 cm.$^{-1}$ band.

We find (from Table I) that the amount of butadiene present as the 1,4 structure in the copolymer is about two to four times that amount incorporated as the 1,2 structure at the temperatures investigated. Also, the effect of polymerization temperatures on the amount of 1,4 entry is more pronounced than that on the amount of 1,2 entry of butadiene.

We analyze the findings in the following manner. The total of butadiene incorporation (U_T) (in mole per cent) is the sum of the butadiene present as the 1,4 structures ($U_{1,4}$) and the 1,2 structures ($U_{1,2}$).

$$U_T = U_{1,4} = U_{1,2} \tag{1}$$

The individual unsaturation values are described by eqs. (2).*

$$U_{1,4} \cong \frac{\{k_{12}{}^{1,4}[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] + k_{22}{}^{1,4}[\sim\!\sim\mathrm{C}_4{}^{\oplus}]\}[\mathrm{C}_4{}^{=}_{=}]_0}{\{(k_{12}{}^{1,4} + k_{12}{}^{1,2})[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] + (k_{22}{}^{1,4} + k_{22}{}^{1,2})[\sim\!\sim\mathrm{C}_4{}^{\oplus}]\}[\mathrm{C}_4{}^{=}_{=}]_0 + \{k_{11}[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] + k_{21}[\sim\!\sim\mathrm{C}_4{}^{\oplus}]\}[\mathrm{iC}_4{}^{=}]_0} \tag{2a}$$

$$U_{1,2} \cong \frac{\{k_{12}{}^{1,2}[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] + k_{22}{}^{1,2}[\sim\!\sim\mathrm{C}_4{}^{\oplus}]\}[\mathrm{C}_4{}^{=}_{=}]_0}{\{(k_{12}{}^{1,4} + k_{12}{}^{1,2})[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] + (k_{22}{}^{1,4} + k_{22}{}^{1,2})[\sim\!\sim\mathrm{C}_4{}^{\oplus}]\}[\mathrm{C}_4{}^{=}_{=}]_0 + \{k_{11}[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] + k_{21}[\sim\!\sim\mathrm{C}_4{}^{\oplus}]\}[\mathrm{iC}_4{}^{=}]_0} \tag{2b}$$

Here, the use of initial concentrations of reactants (as indicated by the subscript zero) is a good approximation, because the polymerizations are terminated at low conversions. In eqs. (2), we represent the total rate constants for diene incorporation (k_{12} for copolymer formation; k_{22} for butadiene homopolymer formation) as the respective sums of those rate constants for 1,2 entry ($k_{12}{}^{1,2}$ and $k_{22}{}^{1,2}$) and 1,4 entry ($k_{12}{}^{1,4}$ and $k_{22}{}^{1,4}$) of the diene. That is,

$$k_{12} = k_{12}{}^{1,4} + k_{12}{}^{1,2} \tag{3a}$$

$$k_{22} = k_{22}{}^{1,4} + k_{22}{}^{1,2} \tag{3b}$$

An analysis of diene incorporation in terms of eqs. (2) assumes that the modes of structure formation of the diene proceed via distinct activational paths.

Appearing also in eqs. (2) are the (steady-state) concentrations of the growing isobutylene ion $[\sim\!\sim\mathrm{iC}_4{}^{\oplus}]$ and butadiene ion $[\sim\!\sim\mathrm{C}_4{}^{\oplus}]$. The detailed structure of the butadiene ion is not further specified in eqs. (2).

Equations (2) can be simplified by a knowledge of the reactivity ratios. The reactivity ratios for the $\mathrm{AlEtCl_2}$ catalyst at -100°C. are $r_1 = k_{11}/k_{12} = 43$ and $r_2 = k_{22}/k_{21} \cong 0$.[2] Using the steady-state assumption

$$k_{12}[\sim\!\sim\mathrm{iC}_4{}^{\oplus}][\mathrm{C}_4{}^{=}_{=}]_0 = k_{21}[\sim\!\sim\mathrm{C}_4{}^{\oplus}][\mathrm{iC}_4{}^{=}]_0$$

we may show that $k_{11}[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] > k_{21}[\sim\!\sim\mathrm{C}_4{}^{\oplus}]$ as follows.

Assume

$$k_{11} > k_{21}[\sim\!\sim\mathrm{C}_4{}^{\oplus}]/[\sim\!\sim\mathrm{iC}_4{}^{\oplus}] = k_{21}[\mathrm{C}_4{}^{=}_{=}]_0/[\mathrm{iC}_4{}^{=}]_0$$

Inserting the proper quantities for the isobutylene–butadiene case we find

$$k_{11} > (k_{11}/43)(70/30) = 0.054k_{11}$$

which substantiates our assumption. Furthermore, in view of the reactivity ratios we may say that $k_{22} \sim 0$, or $k_{22}{}^{1,2} \sim k_{22}{}^{1,4} \sim 0$. With these considerations, eqs. (2) simplify to become eqs. (4).

$$U_{1,4} \cong \frac{k_{12}{}^{1,4}[\mathrm{C}_4{}^{=}_{=}]_0}{(k_{12}{}^{1,4} + k_{12}{}^{1,2})[\mathrm{C}_4{}^{=}_{=}]_0 + k_{11}[\mathrm{iC}_4{}^{=}]_0} \tag{4a}$$

$$U_{1,2} \cong \frac{k_{12}{}^{1,2}[\mathrm{C}_4{}^{=}_{=}]_0}{(k_{12}{}^{1,4} + k_{12}{}^{1,2})[\mathrm{C}_4{}^{=}_{=}]_0 + k_{11}[\mathrm{iC}^{=}]_0} \tag{4b}$$

The rate constants governing homopolymer formation (k_{11}) and the separate processes for 1,4 entry of diene ($k_{12}{}^{1,4}$) and 1,2 entry of diene ($k_{12}{}^{1,2}$) are expressed in eqs. (5).

$$\begin{aligned} k_{11} &= A \exp\{S_{11}{}^*/R\} \exp\{-E_{11}{}^*/RT\} \\ k_{12}{}^{1,4} &= A \exp\{S_{12}{}^{1,4*}/R\} \exp\{-E_{12}{}^{1,4*}/RT\} \\ k_{12}{}^{1,2} &= A \exp\{S_{12}{}^{1,2*}/R\} \exp\{-E_{12}{}^{1,2*}/RT\} \end{aligned} \tag{5}$$

---

* In chain (1,4) or pendant (1,2) structure formation of the diene may occur conceivably in either the 12 or 21 propagation steps. Straightforward calculations show that eqs. (2) describe both situations.

Here, S_{11}^* is the activation entropy for the transition state leading to isobutylene incorporation; $S_{12}^{1,2*}$ is the activation entropy for incorporation of diene as the 1,2 structure; $S_{12}^{1,4*}$ is the activation entropy for 1,4 entry of diene; and E_{11}^*, $E_{12}^{1,2*}$, and $E_{12}^{1,4*}$ are the activation energies for attainment of the transition states, respectively. In eqs. (5), A is a pre-exponential factor which is assumed to be constant.

We may divide eq. (4b) into eq. (4a) to obtain eq. 6. Furthermore, by using eqs. (1), (5), and (6) in eqs. (4) and rearranging, we arrive at eqs. (7).

$$\frac{U_{1,4}}{U_{1,2}} = \frac{k_{12}^{1,4}}{k_{12}^{1,2}} = \frac{\exp\{\Delta S_{12}^{1,4*}/R\}\exp\{-\Delta E_{12}^{1,4*}/RT\}}{\exp\{\Delta S_{12}^{1,2*}/R\}\exp\{-\Delta E_{12}^{1,2*}/RT\}} \tag{6}$$

$$\frac{k_{11}}{k_{12}^{1,4}} = \frac{1 - U_{\mathrm{T}}}{FU_{1,4}} = \exp\{-\Delta S_{12}^{1,4*}/R\}\exp\{\Delta E_{12}^{1,4*}/RT\} \tag{7a}$$

$$\frac{k_{11}}{k_{12}^{1,2}} = \frac{1 - U_{\mathrm{T}}}{FU_{1,2}} = \exp\{-\Delta S_{12}^{1,2*}/R\}\exp\{\Delta E_{12}^{1,2*}/RT\} \tag{7b}$$

where F is the charge concentration $([\mathrm{iC}_4{}^{=}]_0/[\mathrm{C}_4{}^{=}_{=}]_0)$.

The values of the activation parameters for 1,4 and 1,2 entry of diene are given relative to those for isobutylene incorporation in the manner of eqs. 8.

$$\begin{aligned}\Delta S_{12}^{1,4*} &= S_{12}^{1,4*} - S_{11}^*\\ \Delta E_{12}^{1,4*} &= E_{12}^{1,4*} - E_{11}^*\\ \Delta S_{12}^{1,2*} &= S_{12}^{1,2*} - S_{11}^*\\ \Delta E_{12}^{1,2*} &= E_{12}^{1,2*} - E_{11}^*\end{aligned} \tag{8}$$

Equations (7) indicate that a plot of log $[(1 - U_{\mathrm{T}})/FU_{1,4}]$ versus $1/T$ should yield $\Delta E_{12}^{1,4*}$ from the slope and $\Delta S_{12}^{1,4*}$ from the intercept. Similarly, a plot of log $[(1 - U_{\mathrm{T}})/FU_{1,2}]$ versus $1/T$ should give $\Delta E_{12}^{1,2*}$ from the slope and $\Delta S_{12}^{1,2*}$ from the intercept. These plots are shown in Figure 1*A*. Calculated values of the relative activation constants are displayed in Table II.

The internal consistency of the activation values can be checked readily. From eq. (6) it is apparent that a plot of log $U_{1,4}/U_{1,2}$ versus $1/T$ gives the relative quantities $(\Delta E_{12}^{1,4*} - \Delta E_{12}^{1,2*})$ from the slope and $(\Delta S_{12}^{1,4*} - \Delta S_{12}^{1,2*})$ from the intercept. Such a plot is shown in Figure 1*B*, and the resulting differences of activation constants are listed in Table II. Evidently, the values of the relative activation constants as calculated from eqs. (6) and (7) are generally consistent.

According to these findings the activation energy for incorporation of butadiene as the 1,2 structure is higher than that for isobutylene incorporation, while the activation energy

TABLE II

Activation Constants for Butadiene Incorporation Relative to that for Isobutylene Incorporation in Isobutylene–Butadiene Copolymers ($\mathrm{AlEtCl_2}$ Catalysts)

	Activation entropy, cal./mole-deg.		Activation energy	
Equation	Parameter	Value, kcal./mole	Parameter	Value, kcal./mole
7a (Fig. 1*A*)	$\Delta S_{12}^{1,4*}$	−1.7	$\Delta E_{12}^{1,4*}$	0.88
7b (Fig. 1*A*)	$\Delta S_{12}^{1,2*}$	−5.9	$\Delta E_{12}^{1,2*}$	0.54
7a-b (Fig. 1*A*)	$\Delta S_{12}^{1,4*} - \Delta S_{12}^{1,2*}$	4.2	$\Delta E_{12}^{1,4*} - \Delta E_{12}^{1,2*}$	0.34
6 (Fig. 1*B*)	$\Delta S_{12}^{1,4*} - \Delta S_{12}^{1,2*}$	5.0	$\Delta E_{12}^{1,4*} - \Delta E_{12}^{1,2*}$	0.50

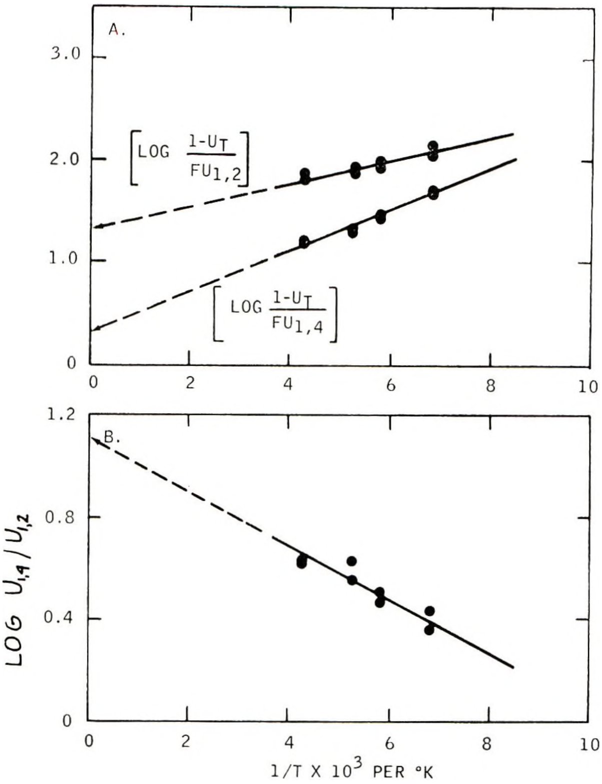

Fig. 1. Determination of activation constants for isobutylene–butadiene polymerization ($AlEtCl_2$ catalyst).

for 1,4 entry of butadiene is still higher. Furthermore, we conclude from the entropy values that the transition state for 1,2 entry of butadiene is more ordered than that for 1,4 entry of the diene. Also, both of these transition states are more ordered than that for isobutylene incorporation.

From our entropy values we calculate (using Boltzmann's formula) that the number of allowed configurations in the transition state for 1,4 entry of diene is about 10 times that for 1,2 entry of diene. This indicates that much more steric hindrance operates in the transition state leading to 1,2 diene structures than in the transition state leading to 1,4 diene structures. At present we do not have sufficient information to elucidate further the nature of the transition states.

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The Chemistry of Organic Film Formers. D. H. SOLOMON, Ed. Wiley, New York, 1967. xi + 369. $14.95.

This is a useful book covering the chemistry of organic film formers. Dr. D. H. Solomon's main objectives were to provide the basic chemistry necessary to approach coating technology from a scientific point of view and to compile in a single volume the chemistry of surface coatings which has appeared in the technical literature of the leading industrial nations. He has succeeded in meeting his objectives and at the same time fills the need of readers for a comprehensive, up-to-date reference text dealing with the basic organic chemistry of surface coatings. Dr. Solomon, as an active research worker and contributor to the field of surface coatings, brings experience and knowledge to his account.

The first chapter gives an introduction to basic polymer chemistry. This chapter contains a lucid discussion of polymer synthesis, copolymers, polymer characterization, polymer glass transition, and solubility parameters, with emphasis being placed on the pertinence of these topics to surface coatings.

The following chapters discuss virtually every class of polymer used in surface coating technology, including glyceride oils, varnishes and alkyds, vinyl and acrylic modified oils and alkyds, unsaturated polyesters and high solids coating systems, thermoplastic cellulose, acrylic and vinyl coatings, epoxy resins, polyurethanes and related polymers derived from isocyanates, amine- and phenol-formaldehyde resins, thermosetting vinyl and acrylic copolymers, water-dilutable polymer systems, and rubber and silicone resins. An appendix is included containing sixteen samples of typical coating preparations.

Ample references have been provided for those who want to further explore the discussed topics in greater detail. Polymer scientists engaged in fields other than surface coatings will also find this a useful text.

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