JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 5, (1967)

EDITORIAL

During the past year the *Journal of Polymer Science* was divided into two parts, Part A-1 covering the more organic aspects of macromolecular chemistry with Dr. C. G. Overberger as editor, and Part A-2 dealing with the physical chemistry of polymers under the editorship of Dr. Thomas Fox of Mellon Institute.

A new Advisory Board for Part A-2 has been recently announced and it is now my pleasure to announce the new Advisory Board for Part A-1. This new Advisory Board, we think, represents an excellent cross-section of worldwide active leaders in the polymer field. The editors will rely on the Advisory Board for suggestions of all types, for advice on policy, as well as specific help on controversial manuscripts. We will accelerate our effort to achieve a more rapid publication of manuscripts. It is our purpose to continue to improve Part A-1 and Polymer Letters in every way possible.

The new editorial office for Part A-1, as of February 1, 1967, will be the Department of Chemistry at the University of Michigan. May I convey to the new Advisory Board and Interscience-Wiley Publishers, my sincerest thanks for their excellent cooperation.

C. G. Overberger
Eli Pearce

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Course of the Terpolymerization of Ethylene, Propylene, and Dicyclopentadiene. I. Single Initial Addition of Dicyclopentadiene

ROBERT E. CUNNINGHAM, *Research Division,*
The Goodyear Tire and Rubber Company, Akron, Ohio 44316

Synopsis

Detailed studies were made of the course of the terpolymerization of ethylene, propylene, and dicyclopentadiene to form unsaturated elastomers. All the dicyclopentadiene was added at the start of a polymerization, but the monoolefins were added continuously throughout the run. Under these conditions, unsaturation of the initial polymer is fairly high but decreases steadily as the reaction progresses. From analyses of the initial samples from each run, the catalyst of VCl_4 (with $Al_2Et_3Cl_3$ cocatalyst), with heptane as the polymerization solvent, was most efficient for introducing unsaturation into terpolymer. This system also produces gel in the terpolymer in the latter stages of reaction, however. Catalysts of VCl_4, $VOCl_3$, or $V(C_5H_7O_2)_3$, with $Al_2Et_3Cl_3$ cocatalyst, in benzene solvent gave terpolymers of quite similar unsaturations. With all systems, terpolymer yield increases very rapidly in the first few minutes of reaction, then very slowly for the remainder of the 30-min. reaction time, reflecting the rapid loss of activity of the vanadium catalysts. Molecular weight growth of the terpolymer prepared in heptane was extremely rapid, reaching a high value in a few minutes. When prepared in benzene, the terpolymers showed a steady increase in molecular weight throughout the reaction but reached only a moderate final value (as expressed by inherent viscosity).

The terpolymerization of ethylene, propylene, and dicyclopentadiene by using Ziegler-Natta catalysts, to form an unsaturated, sulfur-curable elastomer has been discussed by various authors.[1-4] These papers, however, described only properties of polymers obtained at the end of a given polymerization time. No details have been published on the course of the terpolymerization reaction or the properties of terpolymers formed in the early stages of the reaction. Hence, experiments were undertaken in these laboratories to follow this particular terpolymerization in detail, especially with regard to the variations of terpolymer yield, molecular weight, and unsaturation with polymerization time.

EXPERIMENTAL

Materials

The sources and purifications of all materials used in these studies are the same as those described in previous papers.[3,4]

Since dicyclopentadiene is a solid at room temperature, it was made up as a 50% solution in heptane for ease of handling. This solution was sparged with nitrogen and stored in a 4-oz. bottle capped with a self-sealing rubber gasket. All transfers from it were made by hypodermic syringe.

Catalyst Solutions

The $Al_2Et_3Cl_3$ was handled as a 1.0M (in Al) solution in heptane (0.50M for a formula weight of $Al_2Et_3Cl_3$). The VCl_4 and $VOCl_3$ were used as 0.10 and 0.323M solutions in heptane, respectively, and the acetylacetonate as 0.10M solution in benzene. All solutions were stored under nitrogen in 4-oz. bottles that were capped with self-sealing rubber gaskets, and were transferred with hypodermic syringes.

Polymerizations

The polymerizations were run by the same techniques that have been detailed in a previous paper.[3] Ethylene and propylene were metered into the system through calibrated flowmeters at 1200 and 800 cc./min., respectively. Mass spectrographic analysis of the feed gas for each run showed it averaged about 58 mole-% ethylene.

The dicyclopentadiene (1.5 g. total) was added all at the start of the run, before catalyst was added. Olefins were fed in continuously throughout the run. Catalysts were formed *in situ* and were added all at once, the $Al_2Et_3Cl_3$ always being introduced first. The vanadium salts were 0.0005M in each run, and the Al/V molar ratio was 10.

Reactions were run for various lengths of time, then terminated, and the polymer was isolated and evaluated by techniques described previously.[3] Thus each point on the curves in the figures represents an individual run, all of which were made under conditions that were as identical as possible. It was decided to use this technique, rather than to carry out a single run for each catalyst–solvent combination and remove samples from it at various times. It becomes difficult to sample these runs as the viscosity of the solution increases; also, by carrying out individual runs for each point, more polymer is obtained for the subsequent analytical investigations.

RESULTS AND DISCUSSION

Four catalyst–solvent combinations (all with $Al_2Et_3Cl_3$ cocatalyst) were studied: VCl_4 with either benzene or heptane, $VOCl_3$ in benzene, and vanadium trisacetylacetonate in benzene. All four of these combinations had been previously shown to form unsaturated terpolymers with ethylene, propylene, and dicyclopentadiene.[3,4] It is well known that *in situ* catalysts of vanadium rapidly lose activity;[5–8] hence it was of interest to determine how this loss of catalyst activity affected the yield of terpolymer with time.

Since all the dicyclopentadiene is added at the start of the reaction, but monoolefins are added continuously throughout the run, terpolymer unsaturation should vary with time of polymerization. Presumably, the initial polymer that forms has the most unsaturation, since dicyclopentadiene concentration is highest at this point. As the polymerization proceeds, dicyclopentadiene concentration diminishes but the olefin concentration should remain essentially constant. Thus unsaturation of the terpolymer should decrease during polymerization.

In addition, the molecular weight growth of the terpolymer could be followed in these studies. No data of this type have been available on this particular terpolymerization system.

Terpolymer Yield

The yield of terpolymer versus polymerization time for the various catalyst–solvent systems is depicted in Figure 1. Because of the exotherm produced by these reactions[1,3,9,10] and the decay in activity of *in situ* catalysts,[5–8] no kinetic data can be obtained for these reactions. The graphs of terpolymer yield versus time are presented only to give a picture of the way these reactions progress, under the conditions used for these studies. Yield increases very rapidly in the first few minutes of reaction as expected, since this is the time at which the catalyst is most active. The rate of polymerization evidently slows very rapidly after 5 min., however, and terpolymer yield increases slowly beyond this time. With VCl_4 in heptane, and vanadium trisacetylacetonate in benzene, yield increases at a slow but linear rate from 5 min. to the final 30-min. sample. With either VCl_4 or $VOCl_3$ in benzene, however, rate of polymerization seems to slow down continually during the entire 30-min. period and in fact almost seems to have stopped by this time. Thus the terpolymer yields reflect the loss of the high initial activity of the catalysts.

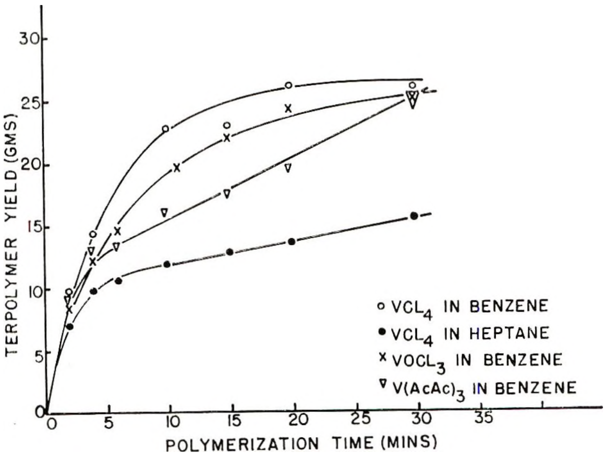

Fig. 1. Variation of terpolymer yield with polymerization time and catalyst–solvent combinations. $V(AcAc)_3$ = vanadium trisacetylacetonate.

It may be noted that, with all four catalyst–solvent combinations, half of the total polymer yield that forms in 30 min. is obtained in the first 3–4 min. of reaction, and about 70–90% of the total yield is obtained in 15 min. These data, together with the data on polymer properties discussed below, show that good yields of terpolymers can be obtained in rather short reaction time.

As shown previously,[3] the reaction in heptane gave the poorest yield. It gave a total of 15 g. of polymer, or 60 g. polymer/mmole of vanadium. For all runs in benzene, about 25 g. of polymer were formed, or 100 g. polymer/mmole of vanadium.

Terpolymer Unsaturation

As discussed above, the terpolymers have a relatively high initial unsaturation which decreases steadily during the run (Fig. 2). At low polymer yields, the system of VCl_4 in heptane produced the terpolymer with the highest unsaturation. Evidently in the initial stages of reaction, this system introduces dicyclopentadiene into the terpolymer very rapidly and reduces the reserve of dicyclopentadiene in the solution. Thus as polymerization continues, polymer that forms in the latter stages of the reaction contains very little unsaturation and the overall unsaturation of the whole polymer falls rapidly. If dicyclopentadiene were metered into the solution at the proper rate, unsaturation could presumably be maintained constant throughout the terpolymer. Under this condition, the VCl_4–heptane combination should be the most efficient of the four catalyst–solvent combinations reported here for introducing unsaturation into the terpolymer.

All three vanadium salts used as catalysts in benzene solvent produced terpolymers with remarkably similar unsaturations (Fig. 2). This indicates that, all other conditions being equal, neither the initial valence of

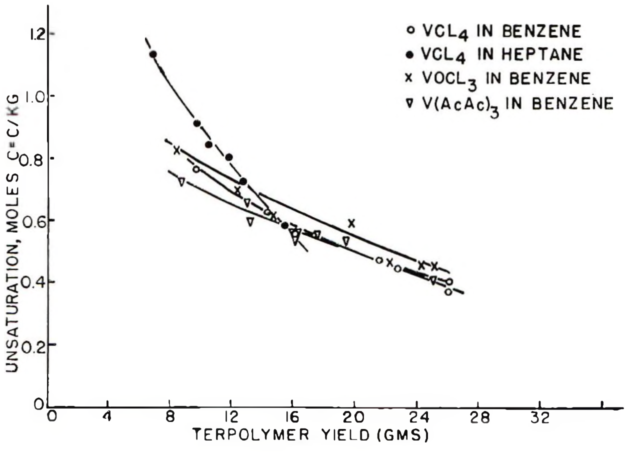

Fig. 2. Terpolymer unsaturation vs. yield for various catalyst–solvent combinations.

the vanadium or the anion of the vanadium salt has any appreciable effect on the introduction of dicyclopentadiene into the terpolymer. Additional studies are needed, however, to establish the universality of this observation. With all three of these systems, terpolymer unsaturation declines steadily as the reaction proceeds, but the decline is not as marked as with the VCl_4–heptane combination.

Terpolymer Molecular Weight

The molecular weight growth of the terpolymers is reported here in terms of their inherent viscosities (Fig. 3); absolute molecular weights of the terpolymers have not been measured. Terpolymer made in heptane had the highest inherent viscosity, as found previously.[3] The growth of inherent viscosity of this terpolymer is extremely rapid, but after the second sample, inherent viscosity began to decrease. At this point, gel was beginning to form in the terpolymer; the last two samples contained about 40 and 70% gel, respectively. This gel is largely true, crosslinked gel, rather than blocks of crystalline polymer which is insoluble at room temperature. Evidently in this system, the second double bond of the dicyclopentadiene is undergoing a slow polymerization also (which would help to account for the rapid decrease in the unsaturation of the terpolymer as shown in Fig. 2). Since inherent viscosity is measured only on polymer soluble in toluene at 30°C., it begins to fall as the gel is formed, presumably because the higher molecular weight fragments are the most easily insolubilized by crosslinking.

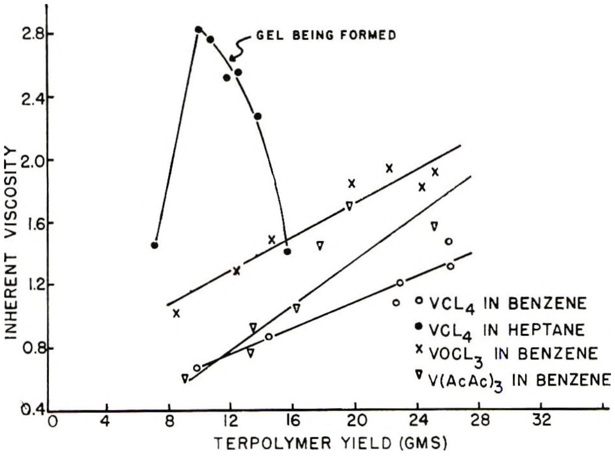

Fig. 3. Inherent viscosity of terpolymer vs. terpolymer yield for various catalyst–solvent combinations.

The three terpolymers made in benzene all have much lower inherent viscosities than the one made in heptane. Their inherent viscosities increase at a steady rate, however, over the range of time reported here. Of the three vanadium salts, $VOCl_3$ gave terpolymer with the highest inherent viscosity, followed by $V(C_5H_7O_2)_3$, with VCl_4 producing the lowest inherent viscosity. All samples made with these catalysts in benzene had low amounts of toluene-insoluble polymer (<10%).

The author wishes to thank the Goodyear Tire and Rubber Company for permission to publish these results. Acknowledgments are due Mrs. V. A. Bittle for determination of the inherent viscosities and percentages of insoluble polymer, Frank Chan for the unsaturation analyses, and J. K. Phillips for the mass spectrographic analyses of the ethylene–propylene mixtures. This is contribution number 351 from the Research Laboratories of The Goodyear Tire & Rubber Co.

References

1. E. K. Gladding, B. S. Fisher, and J. W. Collette, *Ind. Eng. Chem. Prod. Res. Devel.*, **1,** 65 (1962).
2. L. O. Amberg and B. F. Brown, paper presented before the Southern Rubber Group, New Orleans, November 9, 1962.
3. R. E. Cunningham, *J. Polymer Sci. A*, **3,** 3157 (1965).
4. R. E. Cunningham, *J. Polymer Sci. A-1*, **4,** 1203 (1966).
5. W. L. Carrick, A. G. Chasar, and J. J. Smith, *J. Am. Chem. Soc.*, **82,** 5319 (1960).
6. E. Junghanns, A. Gumboldt, and G. Bier, *Makromol. Chem.*, **58,** 18 (1962).
7. G. Bier, A. Gumboldt, and G. Schleitzer, *Makromol. Chem.*, **58,** 43 (1962).
8. G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and D. Fiumani, *J. Polymer Sci.*, **51,** 411 (1961).
9. R. J. Kelly, H. K. Garner, H. E. Haxo, and W. R. Bingham, *Ind. Eng. Chem. Prod. Res. Devel.*, **1,** 210 (1962).
10. F. J. Karol and W. L. Carrick, *J. Am. Chem. Soc.*, **83,** 2654 (1961).

Résumé

Des études détaillées de la terpolymérisation de l'éthylene, propylene et dicyclopentadiene ont été effectuées en vue de former les élastomeres insaturés. Toute la quantité de dicylopentadiene était ajoutée au départ de la polymérisation, mais les monoolefines étaient additionnées continuellement tout au long de l'opération. Dans ces conditions, l'insaturation du polymère initial est assez élevée, mais décroît constamment à mesure que la réaction progresse. De l'analyse des échantillons initiaux pour chaque essai, il s'est averé que le catalysur à base de VCl_4 (avec $Al_2Et_3Cl_3$ comme cocatalyseur) avec l'heptane comme solvant de polymérisation était le plus efficace pour introduire l'insaturation dans le terpolymère. Toutefois, ce système produit également un gel dans les dernières étapes de la réaction. Des catalyseurs à base de VCl_4, $VOCl_3$ ou $V(C_5H_7O_2)_3$, avec $Al_2Et_3Cl_3$ comme cocatalyseur, dans le benzene comme solvant donnaient des terpolymères d'insaturation à peu près similaires. Pour tous ces systèmes le rendement en terpolymères croissait très rapidement au cours des premières minutes de la réaction, ensuite, très lentement pour le restant des trente minutes de réaction, manifestant ainsi une rapide diminution d'activité du catalyseur à base de vanadium. L'accroissement du poids moléculaire des terpolymères préparés dans l'heptane était extrèmement rapide, atteignant une valeur élevée des les premières minutes. Lorsqu'ils étaient préparés dans le benzène, les terpolymères montraient un accorissement constant du poids moléculaire tout au long de la réaction, mais atteignaient seulement une valeur finale modérée. (ainsi qu'il résulte des mesures de viscosité inhérente).

Zusammenfassung

Eine detaillierte Untersuchung des Verlaufs der Terpolymerisation von Äthylen. Propylen und Dicyclopentadien unter Bildung ungesättigter Elastomerer wurde durch-

geführt. Das ganze Dicyclopentadien wurde am Beginn der Polymerisation zugesetzt, die Monoolefine dagegen kontinuierlich während des Versuches. Unter diesen Bedingungen ist die Ungesättigtheit des Anfangspolymeren ziemlich hoch und nimmt mit fortschreitender Reaktion ständig ab. Die Analyse der Anfangsproben der Versuche zeigt, dass der Katalysator aus VCl_4 (mit $Al_2Et_3Cl_3$ als Cokatalysator) mit Heptan als Lösungsmittel für die Polymerisation am wirksamsten Unsättigung in das Terpolymere einführte. Dieses System führt allerdings auch zur Gelbildung im Terpolymeren in den späteren Reaktionsphasen. Katalysatoren aus VCl_4, $VOCl_3$ oder $V(C_5H_7O_2)_3$ mit $Al_2Et_3Cl_3$ als Cokatalysator in Benzol als Lösungsmittel lieferten Terpolymere mit ganz ähnlichem ungesättigten Charakter. Bei allen Systemen nimmt die Ausbeute an Terpolymerem in den ersten Minuten sehr rasch zu und dann sehr langsam für den Rest der Reaktionsdauer von dreissig Minuten, was den raschen Aktivitätsverlust des Vanadinkatalysators erkennen lässt. Der Molekulargewichtsanstieg des in Heptan dargestellten Terpolymeren war äussert rasch und in einigen Minuten wurde ein hoher Wert erreicht. Bei der Darstellung in Benzol zeigte das Terpolymere während der Reaktion eine ständige Molekulargewichtszunahme, erreichte aber, wie die Viskositätszahl zeigt, nur einen mässig hohen Endwert.

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Course of the Terpolymerization of Ethylene, Propylene, and Dicyclopentadiene. II. Two-Step Addition of Dicyclopentadiene

ROBERT E. CUNNINGHAM, *Research Division, The Goodyear Tire and Rubber Company, Akron, Ohio 44316*

Synopsis

Terpolymerizations of ethylene, propylene, and dicyclopentadiene were carried out in which the dicyclopentadiene was added to the reaction system in two equal portions at the beginning and midpoint of each run, while the monoolefins were added continuously. In the resultant elastomers, unsaturation remains much more constant throughout the course of the polymerization than for terpolymers obtained when all dicyclopentadiene is added at the start of the reaction. Yield and molecular weight of the terpolymers produced by either technique are quite comparable, however. With VCl_4 catalyst (with $Al_2Et_3Cl_3$ cocatalyst) in heptane solvent, the two-step addition of the diene gave terpolymers with little gel, in contrast to the high gel in terpolymers formed with the single initial addition of the diene. This system also produced terpolymer with the highest final unsaturation and molecular weight. Catalysts of VCl_4, $VOCl_3$, or $V(C_5H_7O_2)_3$ (with $Al_2Et_3Cl_3$) in benzene gave terpolymers of moderate unsaturations and molecular weights.

The preceding paper[1] described the results of the terpolymerization of ethylene, propylene, and dicyclopentadiene to form unsaturated elastomers, in which all the dicyclopentadiene was added at the start of the reaction. Since the monoolefins were added continuously throughout the reaction, unsaturation of the terpolymer decreased steadily as the polymerization progressed. To provide a constant level of unsaturation throughout the terpolymer, dicyclopentadiene should be metered into the reaction mixture continuously, or at least added in several increments during the course of the polymerization. As the first step toward this goal, polymerizations were run in which the dicyclopentadiene was added to the system in two equal portions during the reaction. Terpolymer yield, unsaturation, and inherent viscosity were then followed throughout the polymerizations, with the use of four catalyst-solvent combinations.

EXPERIMENTAL

Materials

The sources and purifications of all materials used in these studies are the same as described in previous papers.[2,3] Catalyst solutions were also the same as described previously.[1]

Polymerizations

The polymerizations were run by the same techniques that were detailed previously.[1,2] It was observed in the previous paper[1] that, for polymerizations that were run a total of 30 min., about one-half of the polymer is formed in the first 4 min. In the series of polymerizations reported here, one-half of the dicyclopentadiene (0.75 g.) was added at the start of the run, and the remaining half at the end of 4 min. polymerization time. As in the previous study, each point in the figures reproduced below represents an individual run, rather than samples taken from one 30-min. polymerization.

RESULTS AND DISCUSSION

Four catalyst–solvent combinations were used for this study (all with $Al_2Et_3Cl_3$ cocatalyst): VCl_4 in heptane, and VCl_4, $VOCl_3$, or $V(C_5H_7O_2)_3$ in benzene. The main property of the terpolymer that was of interest was unsaturation. By adding the dicyclopentadiene in two equal portions at the beginning and midpoint of each polymerization, unsaturation should be more evenly distributed in the terpolymer than was the case when all dicyclopentadiene was present at the start of the run.

Terpolymer Unsaturation

The unsaturation of the various terpolymers at different stages of the reaction is given in Figure 1. The point at which the second portion of dicyclopentadiene was added is evident for all four systems. As in the previous study, the combination of VCl_4 catalyst in heptane solvent produced terpolymer with the highest unsaturation, for a given yield of terpolymer. The rapid increase in unsaturation after the addition of the

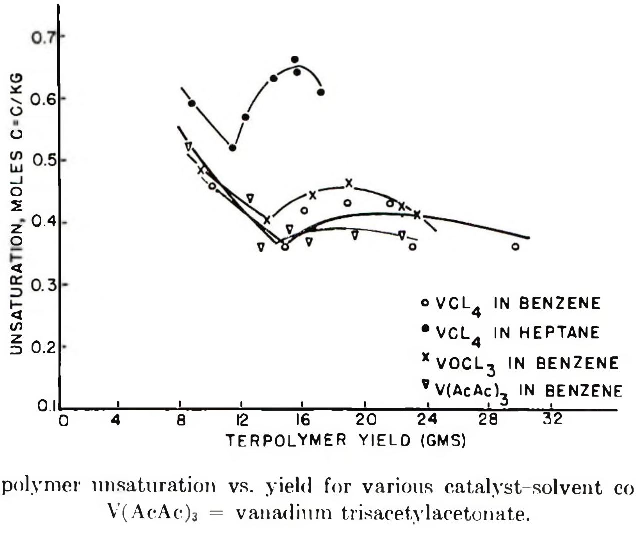

Fig. 1. Terpolymer unsaturation vs. yield for various catalyst–solvent combinations. $V(AcAc)_3$ = vanadium trisacetylacetonate.

second portion of dicyclopentadiene emphasizes this system's ability to incorporate dicyclopentadiene into the terpolymer. The unsaturation of the final polymer is about equal to that of the final polymer obtained from the run in which all dicyclopentadiene was added at the start. Unsaturation of the initial sample is not nearly as high, however, as that for the terpolymer obtained from the former study. Thus unsaturation is more evenly distributed through the polymer obtained by the two-step addition of dicyclopentadiene.

The same conclusion can be drawn for the terpolymers prepared in benzene. All three of these systems produced terpolymers with very similar unsaturations, as was found in the previous study.[1] In contrast to the VCl_4–heptane combination, however, the second addition of dicyclopentadiene to these systems produced only a slight rise in unsaturation of the terpolymer. Rather, unsaturation after this point remained fairly constant for the rest of the run, indicating unsaturation should be even more evenly distributed through these terpolymers than the one made with VCl_4–heptane. Again, the unsaturations of the final terpolymers are comparable to those made with all dicyclopentadiene present at the start, but there is not the great difference between the unsaturations of the initial and final polymer samples.

Terpolymer Yield

Yields of terpolymer versus polymerization time are given in Figure 2. These curves have the same general shape as those obtained from runs in which all dicyclopentadiene was added at the start. There is a rapid increase in yield for the first few minutes of reaction followed by a slow buildup thereafter. Final yields are nearly the same as were obtained in the former experiments. The exception is the VCl_4–benzene system, which

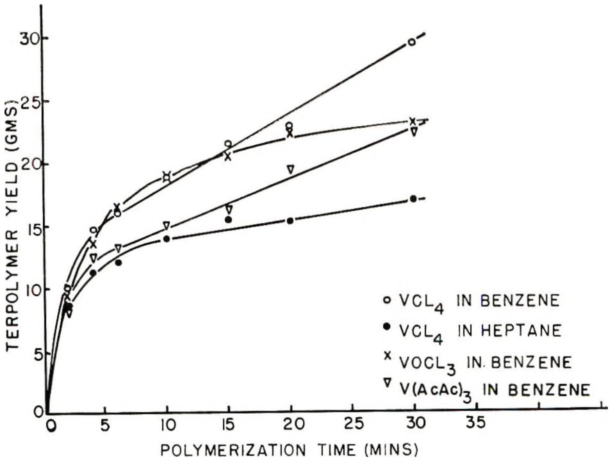

Fig. 2. Variation of terpolymer yield with polymerization time and catalyst–solvent combination.

gave a higher final yield in the study reported here than in the former study.[1]

Terpolymer Molecular Weight

Again, terpolymer molecular weights were not determined, but are compared only as inherent viscosities. These are given for all the polymers in Figure 3. These also show the same general results as were obtained for the runs in which all dicyclopentadiene was added at the start. The combination of VCl_4–heptane gave a very rapid growth of inherent viscosity to a high value. This then remained practically constant for the remaining samples, however, in contrast to the former run in which inherent viscosity fell sharply in the later stages of polymerization.[1] This sharp decrease was attributed to the high gel that formed in the last few samples. With the two-step addition of dicyclopentadiene, however, gel in the terpolymers remained low throughout the run ($< 10\%$). Thus the slower secondary reaction which produces gel in this system (attributed to polymerization of the second double bond in dicyclopentadiene) is suppressed or possibly eliminated by the incremental addition of the diene.

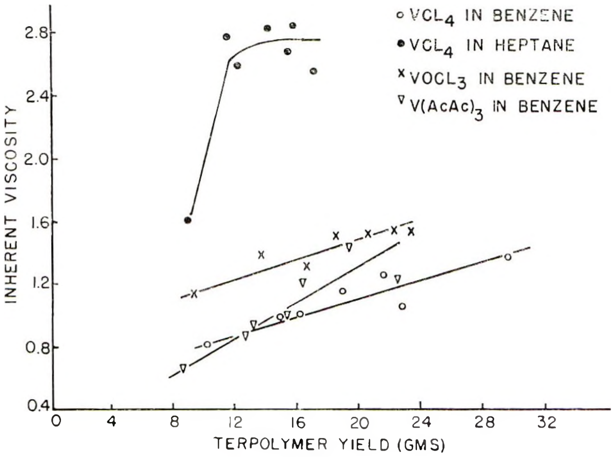

Fig. 3. Inherent viscosity of terpolymer vs. terpolymer yield for various catalyst–solvent combinations.

The inherent viscosities of the polymers produced in benzene increased at a slow but steady rate over the range of time reported here. All three of these terpolymers had comparable inherent viscosities of moderate value, but much lower than that of the terpolymer prepared in heptane. The inherent viscosity of the terpolymer made with VCl_4 in benzene was the same as the corresponding terpolymer obtained when all dicyclopentadiene was added at the start of the run. The terpolymers made with $VOCl_3$ or $V(C_5H_7O_2)_3$ in benzene, however, had slightly lower inherent viscosities than their counterparts from the prior experiments.

CONCLUSIONS

The terpolymerizations of ethylene, propylene, and dicyclopentadiene that are reported in this study produce levels of unsaturation throughout the resultant terpolymers that are more constant than for the cases in which all dicyclopentadiene was present at the start of the reaction. There is considerably less difference between the unsaturations of the initial and final terpolymer samples than was found for those made in the previous study.[1] It can be estimated from the present data that adding the dicyclopentadiene in smaller, more frequent intervals (perhaps only three or four equal portions) at appropriate times during a polymerization should give fairly random distribution of the diene throughout the terpolymer. Such a technique would eliminate the rather difficult laboratory procedure of metering the dicyclopentadiene into the reaction mixture at a constantly changing rate, to correspond with the polymerization rate. An added benefit from this technique is the virtual elimination of gel from terpolymers made in heptane. Polymerizations run in this solvent produce terpolymers with higher unsaturation and much higher molecular weight than those run in benzene. Terpolymer yield and molecular weight by the stepwise addition of dicyclopentadiene are practically unchanged from the values obtained when all the diene is charged initially.

The author wishes to thank The Goodyear Tire & Rubber Company for permission to publish these results. Acknowledgements are due Mrs. V. A. Bittle for determination of the inherent viscosities and percentages of insoluble polymer, Frank Chan for the unsaturation analyses, and J. K. Phillips for the mass spectrographic analyses of the ethylene–propylene mixtures. This is contribution number 352 from the Research Laboratories of The Goodyear Tire & Rubber Co.

References

1. R. E. Cunningham, *J. Polymer Sci. A-1*, **5**, 241 (1967) (Part I).
2. R. E. Cunningham, *J. Polymer Sci. A*, **3**, 3157 (1965).
3. R. E. Cunningham, *J. Polymer Sci. A-1*, **4**, 1203 (1966).

Résumé

Les terpolymérisations d'éthylène, propylène et dicyclopentadiène ont été effectuées; le dicyclopentadiène était additionné au cours de la réaction en deux portions égales au début et à mi-course de chaque opération, tandis que les monooléfines étaient additionnées continuellement. Dans les élastomères en résultant l'insaturation restait beaucoup plus constante tout au long de la polymérisation que dans les terpolymères obtenus et dans lesquels le dicyclopentadiène était ajouté complètement dès le début de la réaction. Le rendement et le poids moléculaire des terpolymères produits par chacune des technique étaient très comparables toutefois. En utilisant un catalyseur àbase de VCl_4 (avec $Al_2Et_3Cl_3$ comme cocatalyseur) dans l'heptane comme solvant, l'addition en deux étapes du diène fournissait des terpolymères avec peu de gel contrairement à la haute tenour en gel formée dans les terpolymères formés lorsqu'on additionnait en une seule fois initialement le diène. Ce système produit également un terpolymère avec une insaturation finale la plus élevée de même qu'un poids moléculaire très élevé. Les catalyseurs à basede VCl_4, $VOCl_3$ ou $V(C_5H_7O_2)_3$ (avec $Al_2Et_3Cl_3$) dans le benzène comme solvant donnaient des terpolymères d'insaturation modérée de même que de poids moléculaire modéré.

Zusammenfassung

Die Terpolymerisation von Äthylene, Propylen und Dicyclopentadien wurde so durchgeführt, dass das Dicyclopentadien dem Reaktionssystem in zwei gleichen Teilen am Beginn und in der Mitte jedes Versuchs, die Monoolefine jedoch kontinuierlich zugesetzt wurden. Bei den gebildeten Elastomeren bleibt die Ungesättigtheit während des Verlaufs der Polymerisation viel konstanter als bei den bei Zusatz des gesamten Dicyclopentadiens am Reaktionsbeginn erhaltenen Terpolymeren. Ausbeute und Molekulargewicht der nach beiden Verfahren erhaltenen Terpolymeren sind aber duchaus vergleichbar. Mit VCl_4-Katalysator (mit $Al_2Et_3Cl_3$ als Cokatalysator) in Heptan als Lösungsmittel, lieferte der Zusatz des Diens in zwei Stufen Terpolymere mit geringem Gelgehalt im Gegensatz zu dem hohen Gelgehalt der bei einfachem Zusatz des Diens am Anfang gebildeten Terpolymeren. Dieses System lieferte auch das Terpolymere mit dem höchsten Endwert der Unsättigung und des Molekulargewichts. Katalysatoren aus VCl_4, $VOCl_3$ oder $V(C_5H_7O_2)_3$ (mit $Al_2Et_3Cl_3$) in Benzol lieferten Terpolymere mit mässigen Werten der Unsättigung und des Molekulargewichts.

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NMR Study of Poly(vinyl Formate)

KERMIT C. RAMEY, DAVID C. LINI, and GARY L. STATTON,
Research and Development Department, The Atlantic Richfield Company, Glenolden, Pennsylvania 19036

Synopsis

The high resolution nuclear magnetic resonance spectrum of poly(vinyl formate), yielded, upon examination at 100 Mc./sec., and under the conditions of decoupling, information on the three tactic forms present. The normal and decoupled spectra indicate that only the CHO resonance is sensitive to the stereochemical configuration. The three components of the CHO resonance are tentatively assigned to isotactic (*i*), heterotactic (*h*), and syndiotactic (*s*) triads with increasing field strength, respectively. This assignment was made on the basis of poly(vinyl alcohol) and poly(vinyl acetate) derived from poly(vinyl formate). The results show that the tacticity is slightly dependent upon the temperature of free-radical polymerization.

Introduction

The use of high resolution nuclear magnetic resonance to determine the stereochemical configuration of polymer chains appears to be well established.[1-5] Recent reports have been concerned with poly(vinyl alcohol) (PVA) and derivatives thereof.[4-7] The spectra clearly show that the tacticity in terms of triads and diads can be obtained from either the normal and/or decoupled spectra of PVA.

Recently, Fujii et al.[8-11] have reported on the polymerization of vinyl formate and on some of the physical properties of the resulting polymers, including tacticity. The tacticity data were obtained from a study of the x-ray diffraction and infrared spectra. This report is concerned with the use of high resolution NMR as a tool to determine the tacticity of PVF and derivatives thereof. The data do not appear to be consistent with the results obtained from the x-ray diffraction and infrared spectra.[8-11] They are, however, consistent with the more recent NMR results reported by Fujii et al.[12] on the derivatives of PVF.

Experimental

The spectra were obtained with a Varian HA-100 spectrometer and decoupling was carried out with a Varian integrator utilizing both field sweep and frequency sweep techniques. The spectra were calibrated by side bands produced by audiofrequency modulation of the magnetic field. A Hewlett-Packard 200J audiofrequency oscillator in conjunction with a

Hewlett-Packard 5512A counter was used. The solutions contained 3–10% (w/v) polymer in $(CD_3)_2CO$ with tetramethylsilane as an internal reference and in D_2O with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as an internal reference. The spectra were run at various temperatures as listed in the respective figures and the conditions for the various polymerizations are described in the following section.

Results and Discussion

Figure 1*A* depicts the 100 Mc./sec. NMR spectrum of sample 1 of PVF in solution in deuterated acetone. The spectrum was run at 60°C., and sample I was prepared from vinyl formate in solution in methyl formate at 30°C., with azobisisobutyronitrile (AIBN) as the initiator. The spectrum consists of three resonances with chemical shifts of τ = 2.00, 4.93, and 8.08 which correspond to the CHO, α, and β protons, respectively.

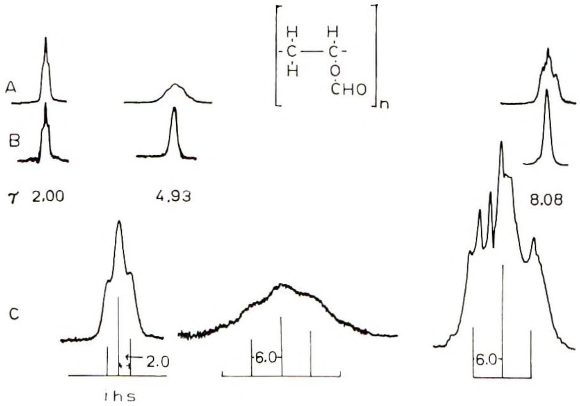

Fig. 1. NMR spectra of poly(vinyl formate) in solution in $(CD_3)_2CO$ as obtained at 100 Mc./sec., and at 60°C.: (*A*) normal; (*B*) decoupled; (*C*) expanded sweep.

A slow sweep of the three resonances is shown in Figure 1*C*. The resonance of the CHO group appears as a distorted triplet which could be due to the overlap of two or more doublets. However, the separation of the three components, τ = 1.98, 2.00, and 2.02 is much larger than that expected for the interaction of protons of this type and a more reasonable explanation would be that the components correspond to the three tactic forms, either *i*, *h*, and *s*, or *s*, *h*, and *i*, with increasing field strength. This assumption appears to be confirmed by the decoupling experiment which shows that the CHO resonance is not appreciably altered by irradiation of the α-protons as shown in Figure 1*B*.

A slow sweep of the resonance of the α-protons appears as a broad five-line pattern ($J_{\alpha\beta}$ = 6.0 cps) which indicates that they are not sensitive to the configuration of the adjacent units, and this appears to be confirmed by the resonance of the α-protons decoupled from the β-protons which yielded only a singlet as shown in Figure 1*B*.

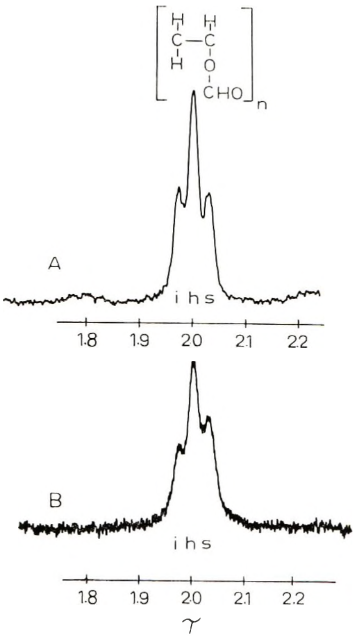

Fig. 2. Expanded sweep of the CHO resonance of poly(vinyl formate): (*A*) sample obtained from the free-radical polymerization at 120°C.; (*B*) sample obtained from the free-radical polymerization at −50°C.

The resonance of the β-protons appears at first to be rather complex. This is, however not the case and the resonance is interpretable in terms of the overlap of a broad triplet ($J_{\alpha\beta} = 6.0$ cps) for the β-protons and a sharp quintuplet which is due to impurities, the partially deuterated species in the solvent $(CD_3)_2CO$. The resonance of the β-protons decoupled from the α-protons appears as a singlet (Fig. 1*B*) which indicates that they are not sensitive to the stereochemical configuration of the backbone chain.

TABLE I

Tacticity of Poly(vinyl Formate)

		Tacticity				
		Triads			Diads[a]	
Sample	Source	*i*	*h*	*s*	*I*	*S*
I	AIBN, vinyl formate, 30°C.	30	40	30	50	50
II	AIBN and UV, vinyl formate and acetaldehyde (50/50), 30°C.	30	40	30	50	50
III	AIBN, and UV, bulk, 60°C.	31	42	27	52	48
IV	AIBN and UV, bulk, 0°C.	26	42	32	47	54
V	$B(CH_2CH_3)_3$, bulk, −50°C.	23	46	31	46	54
VI	AIBN, bulk, 120°C.	27	48	25	51	49

[a] Calculated from triads.

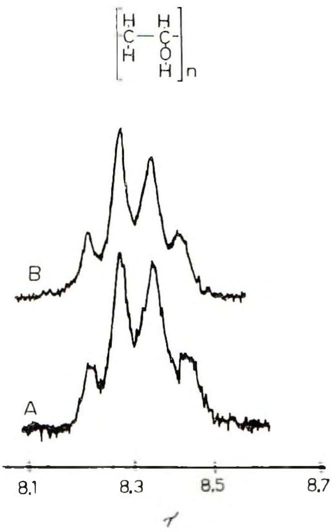

Fig. 3. NMR spectra, upfield portion, of poly(vinyl alcohol): (*A*) sample derived from sample V of PVF; (*B*) sample derived from sample VI of PVF.

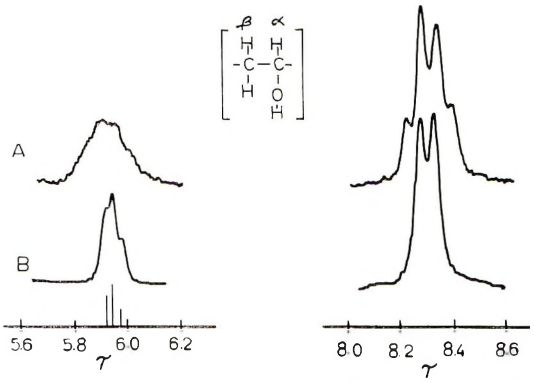

Fig. 4. NMR spectra of poly(vinyl alcohol), commercial sample, in solution in D_2O as obtained at 100 Mc./sec., and at 100°C.; (*A*) normal; (*B*) decoupled.

In Figure 2 are shown a slow sweep of the downfield CHO resonances for two samples. Spectrum *A* corresponds to sample VI, and spectrum *B* corresponds to sample V. The spectra show that the three components vary in intensity with sample, and the tacticity data are listed in Table I. The data were obtained from peak height measurements and the accuracy is estimated to be ±5%.

The assignment of the three components of the CHO resonance of PVF to *i*, *h*, and *s*, triads with increasing field strength, respectively, was based on the spectrum of PVA for which the assignments have been reported,[5-7] and the spectrum of PVAc for which the assignments have also been reported,[4,12,13] both of which were derived from the PVF samples.

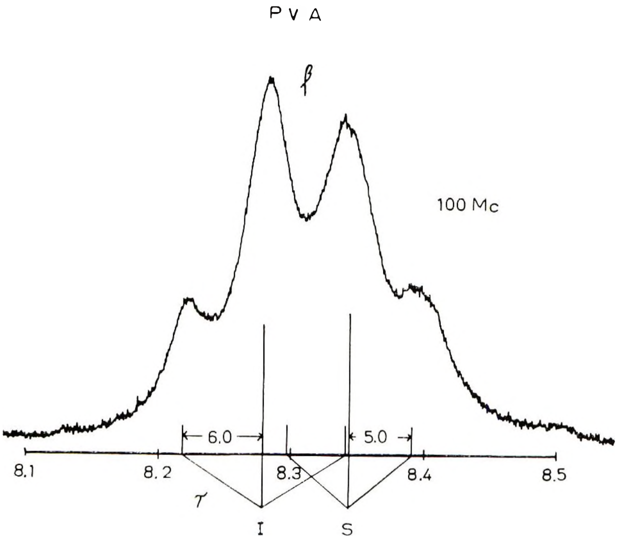

Fig. 5. Expanded sweep of the β-proton resonance of poly(vinyl alcohol).

Some difficulties were, however, experienced in making the assignments as based on the spectra of PVA derived from PVF. In Figure 3, are shown the upfield portions of the spectra of samples A and B of PVA derived from samples V and VI of PVF, respectively. Although the calculated concentration of isotactic diads varies from 46% (sample A) to 51% (sample B) as based on the PVF results, it is difficult to draw significant conclusions as based on the β-proton resonance of the PVA samples alone, and similar results were obtained for the decoupled α-proton resonances. Furthermore, the agreement of data obtained from the normal and decoupled spectra was rather poor.

This lack of agreement of the above results was surprisng and a more detailed study of a commercial sample of PVA was conducted. In Figure 4 is shown the 100 Mc./sec. NMR spectrum of PVA (Vinol, Air Reduction Chemical and Carbide Co.) in solution in D_2O as obtained at 100°C. A small amount of H_2SO_4 was added to shift the OH resonance downfield and an internal standard 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt was used. The resonance of the β-protons consists of two overlapping triplets centered at $\tau = 8.28$ and 8.35, and the α-proton resonance appears as a broad multiplet centered at $\tau = 5.95$. In Figure 4*B*, are shown the resonances of the α-protons decoupled from the β-protons and of the β-protons decoupled from the α-protons. The intensities of the two singlets for the decoupled β-protons are not in agreement with the intensities of the two triplets of the normal spectrum. In fact, the upfield singlet which corresponds to syndiotactic diads appears to be slightly larger than the downfield singlet which corresponds to isotactic diads. The intensities of the decoupled β-proton resonances are, however, in fair agreement with the calculated values as based on the intensities of the decoupled α-proton

TABLE II
Tacticity of Poly(vinyl Formate) and Its Derivatives

		Tacticity				
		Triads			Diads	
No.	Sample and source	*i*	*h*	*s*	*I*	*S*
V	PVF, $B(CH_2CH_3)_3$, bulk −50°C.	23	46	31	46	54[a]
A	PVA, derived from sample V of PVF	—	—	—	49	51[b]
A′	PVAc, derived from sample V of PVF	25	44	31	47	53[a]
VI	PVF, AIBN, bulk, 120°C.	27	48	25	51	49[a]
B	PVA, derived from sample VI of PVF	—	—	—	49	51[b]
B′	PVAc, derived from sample VI of PVF	30	44	26	52	48[a]
C	PVA, (Vinol, Air Reduction Chemical and Carbide Co.)	27	40	33	47	53[a]
					48	52[b]
					48	52[c]
					52	48[d]

[a] Calculated from triads.
[b] From area of β-proton resonances, planimeter.
[c] From peak heights of β-proton resonances, decoupled.
[d] From peak heights of β-proton resonances, normal.

resonances. A slow sweep of the normal β-proton resonance is shown in Figure 5. The spectrum shows that the upfield triplet is slightly more complex as indicated by the width of the lines and has a slightly larger area, as measured by planimeter, than the downfield triplet. These results are similar to those of poly(vinyl chloride) (PVC)[14] and poly(methyl methacrylate) (PMMA).[15] The spectra of the latter polymers seem to indicate that the β-protons corresponding to syndiotactic diads are more

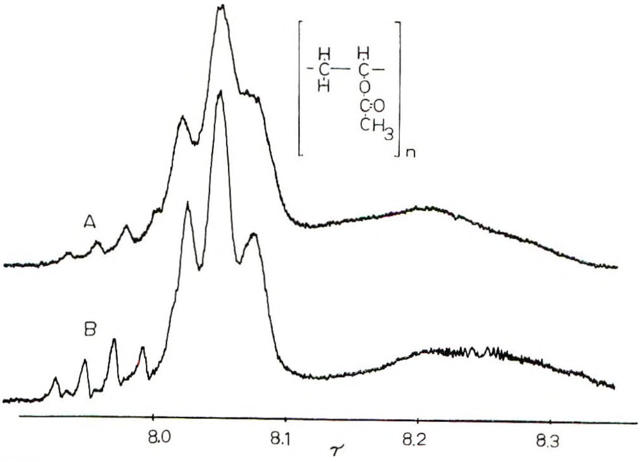

Fig. 6. NMR spectra, upfield portion, of poly(vinyl acetate) in solution in $(CD_3)_2CO$ as obtained at 100 Mc./sec. and 60°C: (*A*) sample derived from sample V of PVF; (*B*) sample derived from sample VI of PVF.

sensitive to tetrad configurations than the corresponding protons in isotactic diads. Therefore, the complexity of the upfield triplet is probably due to the overlap of the various tetrad resonances.

The tacticity data for the commercial sample of PVA as obtained from the normal and decoupled spectra are listed in Table II. The results seem to indicate that the triad values as obtained from peak height measurements of the decoupled spectra are slightly in error. In particular, the syndiotactic content appears to be about 5% high and this is probably due to the smaller spacing between the syndiotactic and deuterotactic resonances, than that between the heterotactic and isotactic resonances.

In Figure 6 are shown the upfield portions of the spectra of samples A and B of poly(vinyl acetate) (PVAc) in solution in $(CD_3)_2CO$ as obtained at 100 Mc./sec. and at 30°C. Samples A and B of PVAc were derived from samples V and VI of PVF, respectively. The small quintuplet is due to the partially deuterated species within the solvent and is indicated by thatched lines. The intensities of the three components of the O—CH_3 resonance are in fair agreement with those reported by Fujii et al.[12] for similar samples and the results as listed in Table II appear to confirm the assignment of the three components of the CHO resonance of PVF to *i*, *h*, and *s* triads with increasing field strength, respectively.

The results indicate that: (*1*) the tacticity of the polymer obtained from the free-radical polymerization of vinyl formate is dependent upon temperature, which is similar to the results for poly(methyl methacrylate); (*2*) the syndiotactic content, in terms of triads and diads, of the polymer obtained from the low temperature polymerization of vinyl formate is slightly higher, than that obtained at higher temperatures, but not nearly as large as that previously reported on the basis of x-ray and infrared studies;[8-11] and (*3*) the free-radical polymerization of vinyl formate in the presence of an aldehyde at 30°C., does not produce a highly syndiotactic polymer as previously reported.[8-11]

References

1. F. A. Bovey, and G. V. D. Tiers, *Fortschr. Hochpolymer. Forsch.*, **3**, 139 (1963).
2. F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).
3. K. C. Ramey and N. D. Field, *J. Polymer Sci. B*, **2**, 865 (1964).
4. K. C. Ramey and N. D. Field, *J. Polymer Sci. B*, **3**, 63 (1965).
5. K. C. Ramey and N. D. Field, *J. Polymer Sci. B*, **3**, 69 (1965).
6. W. C. Tincher, *Makromol. Chem.*, **85**, 46 (1965).
7. V. J. Bargon, K. H. Hellewedge, and U. Johnsen, *Makromol. Chem.*, **85**, 291 (1965).
8. K. Fujii, T. Mochizuki, S. Imoto, J. Ukida, and M. Matsumoto, *Makromol. Chem.*, **51**, 225 (1961).
9. K. Fujii, S. Imoto, J. Ukida, and M. Matsumoto, *J. Polymer Sci. B*, **1**, 497 (1963).
10. K. Fujii, T. Mochizuki, S. Imoto, J. Ukida, and M. Matsumoto, *J. Polymer Sci. A*, **2**, 2327 (1964).
11. K. Fujii, and J. Ukida, *Makromol. Chem.*, **65**, 74 (1963).
12. K. Fujii, Y. Fujiwara, and S. Fujiwara, *Makromol. Chem.*, **89**, 278 (1965).

13. S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *J. Polymer Sci. B*, **4,** 65 (1966).
14. K. C. Ramey, *J. Phys. Chem.*, **70,** 2525 (1966).
15. F. A. Bovey, *Pure Appl. Chem.*, in press.

Résumé

Les spectres de résonance nucléaire magnétique à haute résolution du formiate de polyvinyle fournissaient des informations sur les trois formes tactiques différentes présentes dans le polymère lorsque il était effectué à 100 Mc/sec et dans des conditions de découplage. Les spectres normaux et découplés indiquaient que uniquement la résonance CHO est sensible à la configuration stéréochimique. Les trois composants de la résonance CHO étaient assignés aux triades isotactiques, *i*, hétérotactiques, *h*, et syndiotactiques, *s*, avec des forces de champ croissantes respectivement. Cette attribution a été faite sur la base des alcools polyvinyliques et acétates de polyvinyl dérivés des formiate de polyvinyle. Ces résultats montrent que la tacticité est légérement fonction de la température de la polymérisation radicalaire.

Zusammenfassung

Das bei 100 Mc/sec und unter Entkopplungsbedingungen erhaltene Hochauflösungskernmagnetische Resonanzspektrum von Polyvinylformiat gab Aufschluss über die drei vorhandenen taktischen Formen. Die normalen und entkoppelten Spektren zeigen, dass nur die CHO- Resonanz gegen die stereochemische Konfiguration empfindlich ist. Die drie Komponenten der CHO- Resonanz werden mit steigender Feldstärke versuchsweise isotaktischen, *i*, heterotaktischen, *h*, und syndiotaktischen, *s*, Triaden zugeordnet. Diese Zuordnung wurde auf Grundlage des vom Polyviylformiat abgeleiteten Polyvinylalkohols und Polyvinylacetates durchgeführt. Die Ergebnisse zeigen, dass die Taktizität schwach von der Reaktionstemperatur der radikalischen Polymerisation abhängt.

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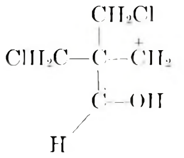
Electron Spin Resonance Study of Irradiated Monomer and Polymer of 3,3-Bis(chloromethyl)oxetane

KOZO TSUJI, TAKEO IWAMOTO, and KOICHIRO HAYASHI, *Department of Polymer Chemistry, Faculty of Engineering*, and HIROSHI YOSHIDA, *Research Reactor Institute, Kyoto University, Kyoto, Japan*

Synopsis

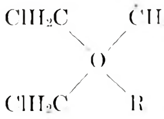
ESR spectra were studied for irradiated 3,3-bis(chloromethyl)oxetane (BCMO) single crystals and poly-BCMO obtained by polymerizing BCMO single crystals in solid state. In both cases, the spectra consist of the superposition of two-line and three-line components at −196°C. On warming the sample, only the former survived. From the examination of hyperfine coupling tensors, it is concluded that the two-line spectrum is due to the free radicals



for the monomer and $-C(CH_2Cl)_2-\dot{C}H-O-$ for the polymer sample, respectively. The orientation of the free radicals gives information about the mode of ring opening in the solid-state polymerization of BCMO.

Introduction

3,3-Bis(chloromethyl)oxetane (BCMO) is polymerized with ionizing radiations by an ionic mechanism. In the course of polymerization, three-line and two-line electron spin resonance (ESR) spectra are observed from BCMO. The former spectrum may be attributed to the free radicals I, II, or III, but structure I is thought to be the most probable in this case.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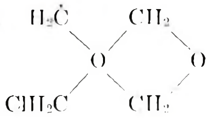
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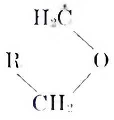
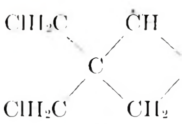
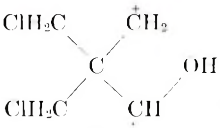

III

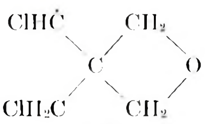
The two-line spectrum may be attributed to free radicals IV, V, or VI, among which the structure V is thought to be the most probable from the viewpoint of polymerization mechanism.[1]



IV



V



VI

Polymer obtained from the radiation-induced solid-state polymerization of BCMO (m.p. 18.6°C.) is crystalline, and the polymer chains are uniaxially oriented and have a planar zigzag conformation.[2,3]

Several workers have reported on the ESR spectra of oriented polymers in relation to the structure of the free radicals as well as of their orientation.[4–11] Kashiwagi discussed molecular orientation in polyethylene from the anisotropy of spectra of the alkyl-type free radicals.[7] One of the present authors (H. Y.) made definite the previous identifications of free radicals in irradiated polyoxymethylene by using stretched polymer samples.[10] Ohnishi et al. concluded from the anisotropy of the spectra that the polymer chains were uniaxially oriented in an irradiated poly-β-propiolactone.[11]

In the present investigation, the ESR spectra from irradiated single crystals of BCMO and those from polymer obtained by polymerizing BCMO single crystals were observed to study the structure of the free radicals and their orientations in connection with polymerization mechanism.

Experimental

Commercial BCMO which was washed with water and distilled twice in the presence of CaH_2 was used for this investigation. Single crystals of rectangular thin plates were grown by allowing molten BCMO to stand at a little below its melting temperature.

The single crystals of BCMO were irradiated with electron beams from a Van de Graaff accelerator to a dose of 3×10^6 rad (1.5×10^5 rad/sec.) at −196°C.

Polymer samples were obtained by irradiating BCMO single crystals at 0°C. with γ-rays from a ^{60}Co source and by extracting the monomer with methanol from thus in-source polymerized BCMO. The polymer samples

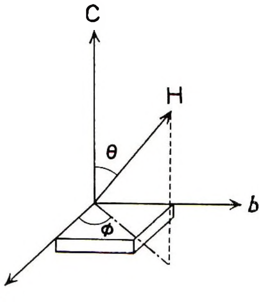


Fig. 1. Relation between an *abc* coordinate system fixed on a sample and direction of the external magnetic field.

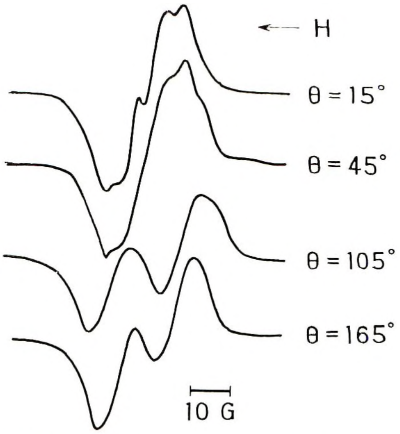


Fig. 2. ESR spectra of BCMO single crystal irradiated with 3 × 10^6 rad at −196°C., kept at −78°C. for 1 hr., and observed at −196°C. at ϕ = 90°.

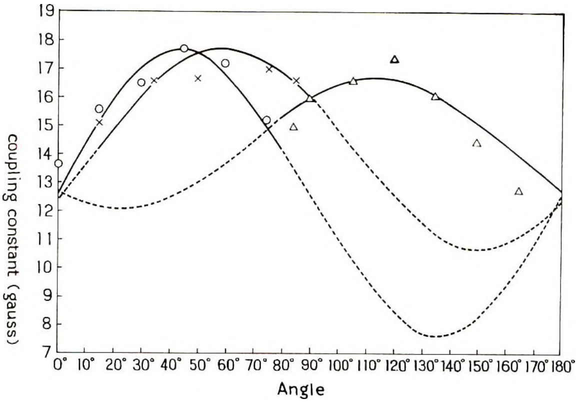


Fig. 3. Anisotropy of the two-line spectrum from the irradiated BCMO single crystal: (○) θ variable, ϕ = 0°; (△) θ variable, ϕ = 90°; (×) θ = 90°, ϕ variable.

were irradiated in the same way as for monomer BCMO samples. No change of the sample shape was observed in the course of the polymerization.

ESR measurements were carried out with a x-band spectrometer at −196°C. in the presence of air for monomer samples, and in vacuum for polymer samples. In order to examine the anisotropy of ESR spectra, the direction of the applied external magnetic field was defined by angles θ and ϕ with respect to the *abc* coordinate axes fixed to the samples as shown in Figure 1.

Results

Immediately after irradiation, the ESR spectrum of the monomer sample consisted of a superposition of two-line and three-line components. After warming the sample to −78°C. for 1 hr., the three-line component disap-

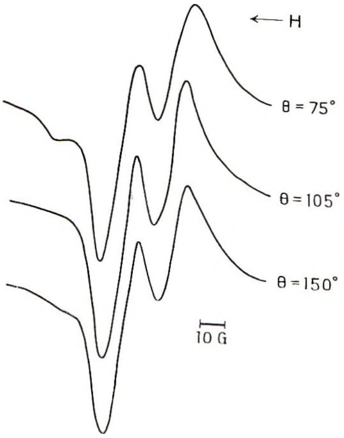


Fig. 4. ESR spectra of poly-BCMO irradiated with 3 × 10^6 rad at −196°C., kept at −78°C. for 1 hr., and observed at −196°C. at ϕ = 0°.

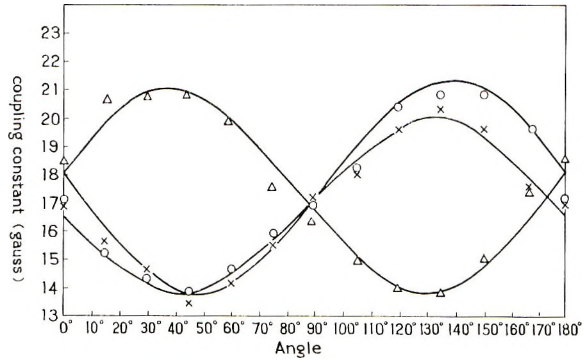


Fig. 5. Anisotropy of the two-line spectrum from the irradiated poly-BCMO (conversion = 59%): (△) θ variable, ϕ = 0°; (○) θ variable, ϕ = 90°; (×) θ = 90°, ϕ variable.

peared and only the two-line component was observed (see Fig. 2). The two-line spectrum was anisotropic, and the dependence of hyperfine coupling constant on the angles θ and ϕ is illustrated in Figure 3. On the other hand, the g value showed little anisotropy. After warming the sample to 0°C. for 1 hr., the intensity of the spectrum became much weaker, but the observed anisotropy was the same as that shown in Figure 3. With this treatment, the polymer yield attained its final value of about 6%.

The ESR spectra from irradiated polymer samples were made up of the superposition of two-line and three-line components. After warming the sample to −78°C. for 1 hr., only the two-line component survived, as shown in Figure 4. The anisotropic character of the two-line spectra was examined for samples with different polymer yield (35%, 59%, 99%), and a representative curve for the sample with the polymer yield of 59% is shown in Figure 5.

Discussion

According to McConnell and Strathdee,[12] the principal values of the hyperfine coupling tensor along the x, y, and z axes (see Fig. 6) due to an α-proton attached to a carbon atom are (in gauss)

$$A_x = -24.6\rho \tag{1}$$

$$A_y = -36.8\rho \tag{2}$$

$$A_z = -7.5\rho \tag{3}$$

where ρ is the spin density on the carbon atom. ρ is in the range of 0.5–0.8 for free radicals with an adjacent oxygen atom.[13]

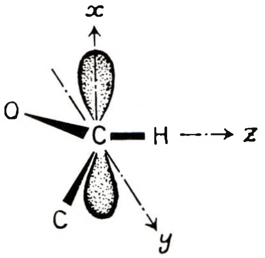


Fig. 6. The xyz coordinate system fixed on the free radical having one α-proton.

The two-line spectrum from monomer single crystal is anisotropic, which indicates that free radicals have the structure, $-\dot{C}H-$. From the result of Figure 3, the principal values of the hyperfine coupling tensor and the direction cosines of the principal axes with respect to the *abc* coordinate calculated for the two-line spectrum of irradiated BCMO single crystal,* are as shown in Table I.

TABLE I

Principal value of hyperfine coupling tensor, gauss		Direction cosine	
−16	0.21	−0.75	0.63
−18	0.68	0.58	0.45
−6	0.70	−0.34	−0.63

The ρ value calculated from the isotropic part of the hyperfine coupling tensor is 0.61. Three principal values of the hyperfine coupling tensor are calculated by using ρ of 0.61 and values for eqs. (1), (2), and (3), of −15, −22, and −5 gauss, respectively. The estimated value of A_x coincides with one of the observed principal values (−16 gauss). These ob-

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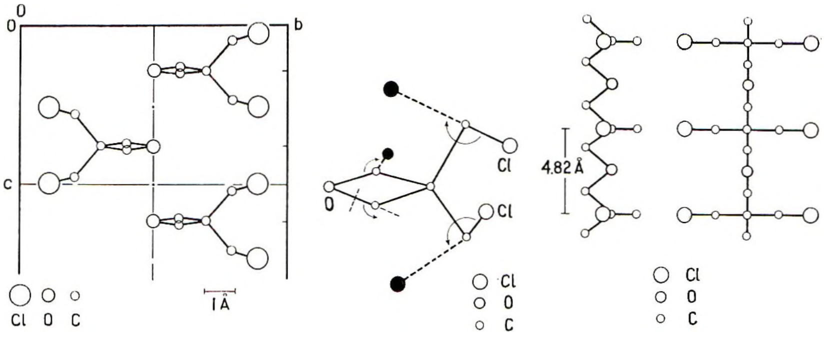
* The hyperfine coupling tensor was calculated from the experimental data in the region where the contribution of the inner doublet was neligible and the observed spectra were simply composed of two-lines due to the outer doublet.[14]



(a) (b) (c)

Fig. 7. Change of crystal structure of 3,3-bis(chloromethyl)oxetane during the polymerization: (*a*) crystal structure of monomer;[15] (*b*) mode of ring opening during the polymerization;[15] (*c*) molecular structure of polymer.[3]

served values are well interpreted by the fact that the x axis coincides with the (0.21, −0.75, 0.63) direction whereas the y and z axes lie on the plane perpendicular to the x axis somewhat at random. A rather small value of ρ (0.61) indicates that the free radicals producing the two-line spectrum have an oxygen atom adjacent to the carbon atom.

The two-line spectrum of irradiated BCMO may be attributed to free radical IV or V, which has the adjacent oxygen atom. The structure of a BCMO single crystal was determined by Nitta et al.[15] (see Fig. 7). Each molecule lies so that the planes of the four-membered rings of the molecules and the lines connecting the oxygen atom and the quaternary carbon atom in the molecules are parallel or antiparallel. Accordingly, the x, y, and z axes of free radical IV may be oriented uniquely with respect to the *abc* coordinate with the assumption that the $\dot{\mathrm{C}}$—H bond bisects the angle of original H—C—H; however, this is not in the case. Free radical V is formed by opening the four-membered ring so that only the x axes of all free radicals lie uniquely in the *abc* coordinate and other two axes do not. This type of free radical agrees rather well with the observed results. The above-mentioned identification of the free radical coincides with the proposed mechanism of the radiation-induced solid-state polymerization of BCMO.[1]

For the two-line spectrum of irradiated polymer sample with a polymer yield of 59%, the principal values of coupling tensor and direction cosines obtained from the experimental results, were as given in Table II. One

TABLE II

Principal value of coupling tensor, gauss	Direction cosine		
−14	0.21	0.80	0.55
−24	0.52	−0.57	0.64
−14	0.84	0.20	−0.51

of the three principal values, 24 gauss, was the same for the other samples with different polymer yields. As the polymer chains are uniaxially oriented, the principal axis corresponding to the principal value of 24 gauss is thought to be the same as the direction of the chains (fiber axis). Other two principal values were almost the same, which indicated that the corresponding two principal axes were distributed at random on one plane. These facts result in a value for A_y of -24 gauss, as the $\dot{C}$—H bond is always perpendicular to the fiber axis. From the isotropic part of the hyperfine coupling tensors, ρ is calculated to be 0.74. On the other hand, 0.65 is observed for the principal value along the y axis which is supposed to orient uniquely. This fact suggests that the A_x and A_z values make a small contribution to the observed value of -24 gauss and that the orientation of polymer axis is not completely uniaxial. The spin density of free radicals in the irradiated polymer is larger than that obtained from monomer sample. One reason why ρ differs between the free radicals of monomer and polymer may be steric distortion in the free radicals of the monomer samples by the four-membered ring. The value of ρ indicates that the two-line spectrum of irradiated poly-BCMO is due to the free radical —C(CH$_2$Cl)$_2$—$\dot{C}$H—O—.

The x axis for the free radical of monomer, and y axis for that of poly-BCMO were almost parallel. This fact indicates that the polymerization of solid BCMO proceeds in a direction perpendicular to the molecular plane of the monomer in opening the oxetane ring. This was also suggested by Nitta et al. from x-ray analysis[15] (see Fig. 7).

The authors wish to express their thanks to Prof. Seizo Okamura of Kyoto University for his continuous encouragement throughout this work and to Prof. Isamu Nitta of Kwansei Gakuin University for his helpful information on x-ray analysis. Thanks are due also to Mr. Koji Matsuda and Mr. Torao Takagaki of the Japanese Association for Radiation Research on Polymers for carrying out the irradiations with the Van de Graaff accelerator, and to Prof. Ff. Williams for reading this manuscript.

References

1. K. Tsuji, K. Hayashi, K. Hayashi, and S. Okamura, *Ann. Repts. Japan. Assoc. Radiation Res. Polymers*, **6**, 155 (1964–1965).

2. K. Hayashi, M. Nishii, and S. Okamura, in *Macromolecular Chemistry* (*J. Polymer Sci. C*, **4**), M. Magat, Ed., Interscience, New York, 1964, p. 839.

3. G. Wasai, T. Saegusa, J. Furukawa, and H. Imai, *Kogyo Kagaku Zasshi*, **67**, 1428 (1964).

4. A. G. Kiselev, M. A. Mokul'skyi, and Yu. S. Lazurkin, *Vysokomolekul. Soedin.*, **2**, 1678 (1960).

5. D. Libby and M. G. Ormerod, *J. Phys. Chem. Solids*, **18**, 316 (1961).

6. S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Chem. Phys.*, **37**, 1283 (1962).

7. M. Kashiwagi, *J. Chem. Phys.*, **36**, 575 (1962).

8. H. Fisher and K. H. Hellwege, *J. Polymer Sci.*, **56**, 33 (1962).

9. D. W. Ovenall, *J. Chem. Phys.*, **38**, 2448 (1963).

10. H. Yoshida and Bengt Rånby, *J. Polymer Sci. A*, **3**, 2289 (1965).

11. S. Ohnishi, S. Sugimoto, K. Hayashi, and I. Nitta, *Bull. Chem. Soc. Japan*, **37**, 524 (1964).

12. H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

13. W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, **1964**, 3625.
14. H. M. McConnell et al., *J. Am. Chem. Soc.*, **82**, 766 (1960).
15. I. Nitta, T. Katayama, and T. Kunizawa, private communication.

Résumé

On a étudié les spectres ESR de monocristaux d'oxétane 3,3-bis-chlorométhylé irradiés (BCMO) et de poly-BCMO obtenu par polymérisation de BCMO sous forme de monocristaux à l'état solide. Dans les deux cas, les spectres consistent dans la superposition des composants de 2 et de 3 lignes à −196°C. En chauffant l'échantillon, uniquement le premier composant reste. A partir de l'examen des tenseurs de couplage hyperfins, on a conclu que le spectre à 2 lignes est dû aux radicaux libres (montré dans le résumé anglais) pour le monomère et pour le polypère $—C(CH_2Cl)_2—CH—O—$ respectivement. L'orientation des radicaux libres donne des informations concernant le mode d'ouverture du cycle dans la polymérisation à l'état solide de BCMO.

Zusammenfassung

ESR-Spektren von bestrahlten 3,3-Bis-(chlormethyl)-oxetan (BCMO)-einkristallen und von bestrahltem, durch Polymerisation von BCMO-Einkristallen in fester Phase erhaltenem Poly-BCMO wurden untersucht. In beiden Fällen bestehen die Spektren bei −196°C aus einer Überlagerung von Zweilinien- und Dreilinienkomponenten. Beim Erwärmen der Proben bleiben nur erstere erhalten. Aus den erhaltenen Hyperfeinkopplungstensoren wird geschlossen, dass das Zweilinienspektrum für das Monomere dem Radikal $\cdot CH(OH)—C(CH_2Cl)_2—\dot{C}H_2$ und für das Polymere dem Radikal $—C(CH_2Cl)_2—\dot{C}H—O—$ zuzuschreiben ist. Die Orientierung der freien Radikale liefert Aufschluss über die Art der Ringöffnung bei der Polymerisation von BCMO in fester Phase.

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Polymerization of Cyclic Sulfides*

J. K. STILLE and J. A. EMPEN, *Department of Chemistry, University of Iowa, Iowa City, Iowa 52240*

Synopsis

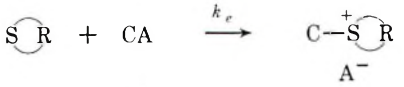
The ring-opening polymerizations of cyclic sulfides containing three-, four-, and five-membered rings were studied. In conjunction with these polymerizations, the relative basicities of the cyclic sulfides employed were also investigated. Polymerizations were effected by the use of phosphorus pentafluoride, boron trifluoride ethyl ether, triethylaluminum, and trimethyloxonium tetrafluoroborate. The resulting polymers were oxidized to the sulfones and differential thermal analyses were obtained on the sulfide polymers as well as the sulfone analogs.

INTRODUCTION

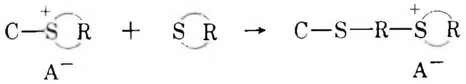
Although the polymerization of cyclic oxides has been investigated extensively and the physical properties of the resulting polymers have been studied, little is known about the polymerization of the corresponding cyclic sulfides. Cationic catalysts, i.e., mineral acids,[1] triethylaluminum,[2] chlorocadmium butyl mercaptide,[3] and boron trifluoride,[1] have been employed for the polymerization of thiiranes. Thiiranes have also been found to polymerize by employing an anionic catalyst, sodium ethoxide.[4] However, certain thietanes were found to polymerize only by the use of cationic catalysts.[5,6] In a preliminary report,[7] the polymerization of cyclic sulfides by triethylaluminum and phosphorus pentafluoride was discussed.

From these reports, it is evident that cyclic sulfides can be polymerized by cationic catalysts, probably proceeding through a sulfonium ion complex, as shown in eqs. (1)-(3), where C denotes a cation and A an anion.

Initiation:



(1)



(2)

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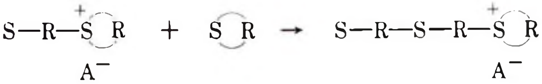
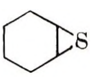
* Presented in part at the Polymer Division, 150th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, and The Princeton University Conference on The Chemistry of Sulfides, June 29-July 1, 1966.

Propagation:



$$\underset{A^-}{S{-}R{-}\overset{+}{S}R} + SR \rightarrow S{-}R{-}S{-}R{-}\underset{A^-}{\overset{+}{S}R} \qquad (3)$$

The polymerization, in which complex formation initially takes place, is thus affected by the base strength of the cyclic sulfide as well as its propensity for ring opening. According to this mechanism, the apparent activation energy for the propagation is a combination of the activation energy for ring opening and the heat of formation of the complex. It was of interest therefore to achieve some knowledge of the realtive base strength of a number of cyclic sulfides (I–VI) and to investigate their ability to polymerize by using a number of cationic catalysts.



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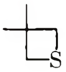


II

III

IV

V

VI

EXPERIMENTAL

Monomers

7-Thiabicyclo[4.1.0]heptane(cyclohexene Sulfide) (I).[8] Cyclohexene sulfide was prepared from cyclohexene oxide and purified by refluxing over calcium hydride and distilling, b.p. 70°C./19 mm. (lit.:[8] 71.5–73.5°C./21 mm.), from fresh calcium hydride under nitrogen. The purified monomer was stored in a glass-stoppered bottle over anhydrous sodium sulfate. Sodium ribbon and molecular sieves were found to polymerize the purified sulfide.

7-Thiabicyclo[2.2.1]heptane (VI) and 6-Thiabicyclo[3.1.1]heptane (IV). An approximately equal molar mixture of 7-thiabicyclo[2.2.1]heptane and 6-thiabicyclo[3.3.1]heptane was prepared as reported.[9] The separation of the isomers was accomplished by the following methods.

Method A. The separation of the bicyclic sulfides was effected by dissolving the isomers in benzene and separating by means of preparative gas chromatography on a column of 5% diisodecyl phthalate on Gas Chrom P. The monomers were sublimed prior to use to give 7-thiabicyclo[2.2.1]-heptane, m.p. 127.0°C., and 6-thiabicyclo[3.1.1]heptane, m.p. 94°C., (lit.[9]: 127.5–128.5°C. and 93.5–95.5°C., respectively).

Method B. The sulfide mixture, 15.2 g., was dissolved in 600 ml. of *n*-nonane. This solution was distilled through a 40-plate column at 88 mm. pressure. About 400 ml. of liquid was collected in seven fractions. The first two fractions contained approximately 90% 7-thiabicyclo[2.2.1] heptane and 10% 6-thiabicyclo[3.1.1]heptane. The other fractions contained only the 7-thiabicyclo[2.2.1]heptane, while the distillation residue was enriched with only 6-thiabicyclo[3.1.1]heptane. The isomers were isolated by separation on a silica gel column. Normal pentane (100 ml.) was employed to displace the nonane and 150 ml. of ethanol was added to elute the sulfide. The bicyclic sulfides could then be isolated by precipitation in water. The monomers were then dissolved in *n*-pentane, dried over molecular sieves, and the solvent was evaporated. The monomers were sublimed and stored in sealed vials in a desiccator.

Thietane (III). Commercial grade thietane (Eastman Organic Chemicals) was purified by first refluxing over calcium hydride followed by distillation from fresh calcium hydride under nitrogen. The purified monomer was stored in a glass-stoppered bottle over molecular sieves. Storing over sodium ribbon was accompanied by polymerization.

3,3-Dimethylthietane (II). 3,3-Dimethylthietane was prepared in a 35% yield by a method previously reported.[10] Final purification was accomplished by refluxing the sulfide over calcium hydride and distilling from fresh calcium hydride under nitrogen. The purified monomer, b.p. 116–118°C./750 mm. (lit.:[10] 120°C./760 mm.) was also stored in a glass-stoppered flask over molecular sieves.

Base Strength Studies

The measurements of the infrared proton shifts of the OH stretching frequency ($\Delta\nu_{,\mathrm{OH}}$) of carbon tetrachloride solutions of phenol (ca. 0.1*M*) and cyclic sulfide base were taken on a Perkin-Elmer Model 421 infrared spectrophotometer. Values for ΔH were obtained from the equation:[11]

$$-\Delta H = 0.016\,\Delta\nu_{\mathrm{OH}} + 0.63.$$

Polymerizations

Triethylaluminum Catalyst.[12–14] A 1*M* mixture of triethylaluminum: water catalyst was prepared under nitrogen in a dry box by adding 0.9 g. (0.05 mole) of water dropwise to 5.7 g. (0.05 mole) of freshly distilled triethylaluminum in 42.3 ml. of dry *n*-heptane at 0°C. A fine suspension in the heptane was obtained. Aliquots of this catalyst suspension (5 mole-% based on monomer) were withdrawn with calibrated hypodermic syringes and added to the polymerization bottle containing 5 ml. of methylene chloride. The bottles were cooled to 0°C. and epichlorohydrin (5 mole-% based on monomer) was added dropwise with occasional shaking. Monomer (1.0 g.) was then added and the bottles were sealed. Polymerization was allowed to proceed for 72 hr.

The catalyst was destroyed by the addition of 1 ml. of methanol. Polymers were isolated by dissolution in benzene or chloroform followed by reprecipitation into methanol. The polymers were lyophylized from benzene.

Phosphorus Pentafluoride.[6,15,16] Phosphorus pentafluoride was obtained by the thermal decomposition of *p*-chlorobenzenediazonium hexafluorophosphate (commercially available as Phosfluorogen A, Ozark Mahoning Company), and from a cylinder of phosphorus pentafluoride gas (Matheson Company), a gas buret being used to measure the volume of catalyst needed (5 mole-% based on monomer). The catalyst was swept into the polymerization flask containing 1.0 g. of monomer in 5 ml. of methylene chloride maintained at −20°C. The solutions were held at −20°C. for 24 hr. and then at 25°C. for 48 hr. The polymers were isolated in the same manner described above.

Boron Trifluoride·Diethyl Ether.[5,6] Reagent-grade boron trifluoride·diethyl ether (Matheson, Coleman and Bell) was distilled under nitrogen prior to use. Monomer (1.0 g.), epichlorohydrin (5 mole-% based on monomer), and methylene chloride, 5 ml., were added to serum bottles which were then flushed with dry nitrogen and capped. The catalyst was added to the polymerization bottle by means of calibrated hypodermic syringes. After 72 hr. of maintaining the polymerizations at room temperature, the polymers were isolated in the manner described above.

Trimethyloxonium Tetrafluoroborate. A 96% yield of trimethyloxonium tetrafluoroborate was prepared as previously reported.[17] Recrystallization was accomplished by suspending the solid nitrobenzene and effecting solution by the addition of liquid sulfur dioxide. As the sulfur dioxide evaporated, the oxonium salt reprecipitated. The precipitate was filtered, washed with anhydrous ethyl ether, and dried under reduced pressure to give 35 g. (75%) of trimethyloxonium tetrafluoroborate, m.p. 165°C. (dec.); lit.:[18] 174–177°C.

The oxonium ion salt (5 mole-% based on monomer) was weighed out in serum bottles in a nitrogen-filled dry box. The bottles were capped and the monomers (1.0 g.) were added through the septum by means of calibrated hypodermic syringes. The solid monomers were first dissolved in a minimum amount of nitromethane and then added to the capped bottles. The polymerizations were run for 3 days at room temperature. The polymers were isolated by pouring the contents of the polymerization bottle into 100 ml. of methanol, filtering the precipitated polymer and drying under reduced pressure.

Molecular Weight Determination

Number-average molecular weights of some of the polymers were obtained on a Mechrolab 301A vapor pressure osmometer. The intrinsic

TABLE I

Number-Average Molecular Weight–Intrinsic Viscosity Relationship[a]

Poly(cyclohexene sulfide)		Polythietane	
$\bar{M}_n$	$[\eta]$, dl./g.	$\bar{M}_n$	$[\eta]$, dl./g.
1970	0.14	1165	0.08
2380	0.19	1875	0.13
5400	0.34	3300	0.17
9700	0.56	5680	0.26

[a] Intrinsic viscosities were obtained in chloroform at concentrations of 0.2–0.5 g./100 ml.

viscosities of the unfractionated polymers were run in chloroform at 25°C. in a Cannon-Ubbelohde semi-micro dilution viscometer. Results are shown in Table I.

Differential Thermal Analysis

Differential thermal analyses were obtained on finely grouped polymer samples by using a DuPont Model 900 differential thermal analyzer. Silicon carbide was employed as a reference material, and the analyses were run from −100 to +300°C. with a heating rate of 20°C./min.

Oxidation to Sulfones

Samples of the sulfide polymers were oxidized to the corresponding sulfones by a method previously reported.[19] The sulfide polymer was suspended in concentrated formic acid and a 4:1 molar excess of 30% hydrogen peroxide was added. The resulting suspension was stirred for 8 hr. to insure complete oxidation (Table II). The initial polymer suspensions become homogeneous approximately $^1/_2$ hr. after the peroxide addition. The resulting polysulfones precipitated from the reaction solution as formed and were isolated by filtering the solution, washing the filtrate with water, and drying under reduced pressure. The infrared spectra of the resulting polymers contained strong sulfone absorption at 1110 and 1280 cm.$^{-1}$.

TABLE II
Conversion to Sulfones

Polymer	Calculated		Found		Sulfone, %[a]
	C, %	H, %	C, %	H, %	
Poly(cyclohexene sulfone) $-\!(C_6H_{10}SO_2)\!-_n$	49.29	6.85	50.50	7.09	90 ± 4.5
Poly(1,3-cyclohexene sulfone) $-\!(C_6H_{10}SO_2)\!-_n$	49.29	6.85	50.75	6.86	87 ± 4.5
Poly(3,3-dimethylthietane-1,1-dioxide) $-\!(C_5H_{10}SO_2)\!-_n$	44.75	7.46	44.69	7.51	95.5–100
Poly(thietane-1,1-dioxide) $-\!(C_3H_6SO_2)\!-_n$	33.98	5.65	35.13	5.39	89 ± 3.4

[a] The per cent of sulfone linkages was calculated from the carbon percentages alone.

DISCUSSION

Several methods have been employed to determine the base strength of cyclic sulfides (Table III). The position of the wavelength of maximum absorption in the ultraviolet has been used as a measure of the electron density of the sulfur atom, with the assumption that the sulfur atom with the highest electron density will have the longest wavelength absorption.[20] However, the actual transition taking place was not clearly defined. Similarly, the chemical shift in the NMR of α- and β-protons in cyclic sulfides has ueen used to measure the electron density on the sulfur atom by assum-

TABLE III

Order of base strength	Method			
	UV spectra[a]	δ, α-CH_2 NMR[b]	K_{eq} for I Complex (UV)[c]	K_{eq} for phenol complex (IR $\Delta\nu OH$)[d]
Strongest	4		5	5
		3 = 4		
	3		6	6
	5	5	4	4
Weakest	6	6	3	3

[a] Method of Davis.[20]
[b] Method of Searles, Gutowsky, Rutledge, and Tamres.[21,22]
[c] Method of Tamres and Searles[22] and McCullough and Mulvey.[23]
[d] Method of Lippert and Prigge.[24,25]

ing that deshielding at the α-proton must be compensated for by a high electron density on the sulfur atom.[21,22]

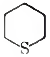
Complex formation with iodine was measured by ultraviolet and visible charge-transfer spectra.[22,23] Complex formation with phenol was also measured in the infrared region by the proton shift upon complexation.[24,25]

It was observed that the order obtained from simple spectral methods was in general the opposite of the order observed from measurement of complex formation equilibria. It seems probable that the latter method is a more reasonable criteria from which to judge relative basicity.

The order of basicity $5 > 6 > 4 > 3$, found for cyclic sulfides is different from that found for cyclic oxides, $4 > 5 > 6 > 3$. This difference has been ascribed to the differences in heteroatom size, differences in ring size (ring strain), and also the differences in polarizability between the oxygen and sulfur atoms. Our work confirms the general trend found for cyclic sulfides (Table IV). The order found for the bridged bicyclic sulfides was consistent with the other cyclic sulfides but a direct comparison could not be made from the chemical shift of the α-protons in NMR because of the inherent differences between the shift of methylene and methine protons. It was also noted that complex formation was nearly the same for all of the cyclic sulfides studied. The heat of formation of the complexes is undoubtedly small compared to the differences in the heat of polymerization of the cyclic sulfides. For example, differences in the heats of polymerization[26] of oxirane (22.6 kcal./mole), and oxetane (19.3 kcal./mole) are large compared to the differences in the heats of complex formation,[27] while the magnitude of the heat of polymerization of tetrahydrofuran (3.5 kcal./mole) is comparable to the heat of complex formation.[27]

It would appear that the conversion of cyclic sulfide to polymer is not affected to any degree by the basicity of heteroatom. Other factors seem to determine whether or not the polymerization will take place; presumably the primary factor is the ring strain. It was observed that tetrahydrothiophene and 7-thiabicyclo[2.2.1]heptane would not polymerize by

TABLE IV. Base Properties of Sulfur Heterocycles[a]

Sulfide no.	Sulfide	Ultraviolet spectra λ, mμ[b]		λ, mμ[c]	NMR spectra δ − 2°, cps		δ − 3°, cps	K_e phenol complex by IR Δν OH[b]		−ΔH, kcal./mole	Δν OH	−ΔH, kcal./mole[e]
			(5)	257							210	2.38
I		261	(4)			(3)	186	237	(6)	4.43		
III		273	(2)	272	[d]			243	(5)	4.52	248	2.91
IV		278	(1)			(2)	200	252	(4)	4.63		
II		265	(3)		172			257	(3)	4.74		
VI		247	(6)			(1)	228	259	(2)	4.78		
V		240	(7)	243	169			277	(1)	5.07	262	3.39
			(8)	233							244	2.99

[a] Numbers in parentheses indicate the order in a given series; [b] this work; [c] data of Gutowsky, Rutledge, Tamres, and Searles;[21] [d] the exact position was not readily observed because of the complex spectrum brought about by proton coupling; [e] data of Lippert and Prigge.[24]

any of the methods employed in this study. On the other hand, the corresponding cyclic oxides were converted to high polymers by the same catalytic systems. An insight into the differences in polymerizability can be gained by a comparison of the strain energies of the cyclic monomers (Table V).[28]

TABLE V
Strain Energy

	Strain energy, kcal./mole			
Ring size	Alkane	Ether	Sulfide	Imine
3	27.43	27.21	19.78	26.87
4	26.04	25.51	19.64	
5	6.05	5.63	1.97	5.80
6	−0.02	1.16	−0.27	−0.15

The calculated strain energy is a composite of angle strain, lone-pair interaction, hydrogen–hydrogen crowding, bond length, and atom size as well as other factors relating to the geometry of the ring system. It can be seen that the strain energy for cyclic alkanes, cyclic ethers, and cyclic imines are nearly the same for similar size ring systems. However, the cyclic sulfides all have considerably lower strain energy which was postulated as arriving in part from the large difference in the bond length of the C—S bond as compared with the other heterocycles listed in Table V. The bond lengths between C—X (where X = C, O, N, and S) are as follows: C—C = 1.54 A., C—O = 1.43 A., C—N = 1.47 A., and C—S = 1.81 A. The longer C—S bond would tend to allow greater C—S—C bond angle distortion in the cyclic sulfide molecule, thus relieving the strain imposed by the small ring system.

It is interesting to note that tetrahydropyran has not been polymerized. This isomer is known to exist in the stable chair form and has a very low strain energy (1.16 kcal./mole). The strain energy of tetrahydrothiophene (1.97 kcal./mole) is only slightly greater than that of tetrahydropyran. Although thermodynamic data has not been reported for the bicyclic isomers, it would seem reasonable to assume that 7-thiabicyclo[2.2.1]-heptane has considerably less strain energy than does 7-oxabicyclo[2.2.1]-heptane.

In the polymerizations with triethylaluminum (Table VI), it was necessary to cool the solution of catalyst in solvent before the addition of epichlorohydrin and monomer. If this was not done, the episulfide would polymerize in an almost explosive manner when added to the catalyst. The polymers obtained from the polymerization where all white solids.

The rate at which phosphorus pentafluoride was introduced into the polymerization system was found to be very critical. The amount of catalyst actually reaching the polymerization vessel was easier to determine by the gas buret method than by the thermal decomposition of a ben-

TABLE VI
Polymerization of Cyclic Sulfides[a]

Monomer	Catalyst	Conversion, %	[η], dl./g.	$T_{g}m$, °C.	T_m, °C.
Cyclohexene sulfide	(1) $AlEt_3$–H_2O	100	0.44	−43	+130
	(2) PF_5	96.9	0.38	−45	+ 86
Thietane	(1) $AlEt_3$–H_2O	52.9	0.30	−56	+ 53
	(2) PF_5	66.7	0.37	−51	+ 55
3,3-Dimethylthietane	(1) $AlEt_3$–H_2O	55.1	0.35	−53	+117
	(2) PF_5	54.7	0.54	−40	+140
6-Thiabicyclo[3.1.1]heptane	(1) $AlEt_3$–H_2O	26.2	0.37	−52	+134
	(2) PF_5	53.5	0.31	−58	+139

[a] Monomer, 1.0 g.; catalyst, 5 mole-% based on monomer; epichlorohydrin, 5 mole-% based on monomer; Solvent, CH_2Cl_2 (5 ml.); polymerization at 25°C. for 3 days.

zenediazonium hexafluorophosphate. Even in this case, however, the actual amount of catalyst actually complexing with the sulfur atom is not known.

It was found that bulk polymerization of the cyclic sulfides using boron trifluoride proceeded to give higher molecular weight polymers than solution polymerization (Table VII). The bulk polymerization of cyclohexene

TABLE VII
Polymerization with Boron Trifluoride[a]

Monomer	Conversion, %	[η], dl./g.
Cyclohexene sulfide	90[b]	0.34
	96[c]	0.33
Thietane	67[b]	0.23
	63[c]	0.64
3,3-Dimethylthietane	80[b]	0.29
	70[c]	0.76
6-Thiabicyclo[3.1.1]heptane	57.5[b]	0.23

[a] Monomer, 1.0 g.; $BF_3 \cdot Et_2O$, 5 mole-% based on monomer.

[b] Solution in 5 ml. of CH_2Cl_2 with 5 mole-% epichlorohydrin co-catalyst. Polymerizations were run for 3 days at 25°C.

[c] Bulk polymerization for 24 hr.

TABLE VIII
Polymerization with Trimethyloxonium Tetrafluoroborate[a]

Monomer	Conversion, %	[η], dl./g.	T_g, °C.	T_m, °C.
Cyclohexene sulfide	47	0.18	−47	+ 85
6-Thiabicyclo[3.1.1]-heptane	20	—	−53	+135
Thietane	41	0.09	−59	+ 49
3,3-Dimethylthietane	55	0.31	−55	+102

[a] Monomer, 1.0 g. (only 0.5 g. of the bicyclic sulfides); $(CH_3)_3OBF_4$, 5 mole-%, bulk polymerization at 25°C. for 5 days. The solid monomers were dissolved in a minimum quantity of nitromethane.

sulfide was very difficult to control. The ring opening was so rapid as to be almost explosive in all bulk polymerization runs. A dark polymeric residue was initially obtained. Dissolution of this residue in benzene or chloroform followed by reprecipitation into methanol gave a white polymer. However, the molecular weight of this polymer was not as high as that of the polymers obtained from the bulk polymerization of thietane and 3,3-dimethylthietane. The polymers from the latter two monomers were tough rubbery solids.

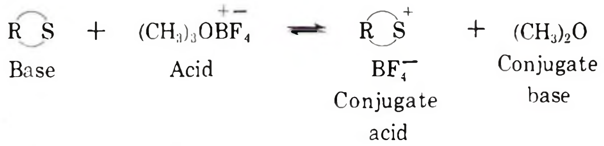
The utilization of trimethyloxonium tetrafluoroborate as a polymerization catalyst (Table VIII) was investigated because this salt is reported to be a good source of methyl carbonium ion [eq. (4)].

$$(CH_3)_3OBF_4 \rightarrow CH_3^+ + (CH_3)_2O + BF_4^- \qquad (4)$$

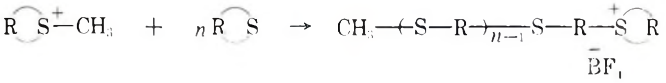
It has been reported that the reaction of diethyl sulfide with triethyloxonium tetrafluoroborate gives a tertiary sulfonium ion salt.[17] A similar reaction of trimethyloxonium tetrafluoroborate [eq. (5)]

$$(CH_3CH_2)_3OBF_4 + (CH_3CH_2)_2S \rightarrow (CH_3CH_2)_3\overset{+-}{S}BF_4 + (CH_3CH_2)_2O \qquad (5)$$

with the cyclic sulfides would lead to a cyclic sulfonium ion which could then polymerize in the presence of monomer to give the growing polymer chain.



(6)



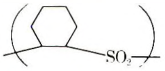
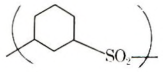
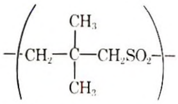
(7)

The one major drawback encountered in the use of this catalyst was its insolubility in most solvents normally chosen for polymerizations. Nitromethane was used to effect solution of the solid bicyclic monomers but the polymer precipitated from this solvent as it formed.

The glass transition (second-order transition) temperature of a number of polymers was obtained. The −40 to −60°C. transition for linear polyethers has been attributed to movement of the —C—O—C— segments of the polymer chain.[29] It seems likely therefore, that the low-temperature transitions that were observed for sulfur polymers were also due to this motion.

It was observed from x-ray powder patterns that the sulfide polymers possessed some degree of crystallinity. A difference in the crystalline transition temperature T_m was noted for the polymers obtained from cyclohexene sulfide. An explanation of this observed difference is not readily available; however, it should be noted that this monomer could polymerize by both a *cis*- and a *trans*- addition to the cyclohexene ring. An increase

TABLE IX
Thermal Properties of Sulfone Polymers

Polymer	T_g, °C.	T_m, °C.
	128	284
$\left(-(CH_2)_3-SO_2-\right)$	—	290
	108	309
 $\left(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2SO_2-\right)$	113	303

in the order polymer segments would tend to lead to an increase in the melting point of the resulting polymer. Another factor that could affect the melting transition is the molecular weight of the polymer. This difference was noted in the polymers obtained from 3,3-dimethylthietane; the highest molecular weight polymer ($[\eta] = 0.54$) recorded in Table VI had a somewhat higher melting transition than the lower molecular weight analogs.

The sulfone polymers (Table IX) obtained from oxidation of the corresponding sulfide polymers had considerably higher glass transition temperatures and all were found to melt with decomposition above 280°C.

A correlation of intrinsic viscosity with molecular weight was obtained for two sulfide polymers from the Mark-Houwink equation.[30,31] Values for K and a for the sulfide polymers in Table I were determined by the intercept and slope, respectively, for a plot of the log of intrinsic viscosity against the log of molecular weight. Unfractionated polymers were employed in this determination; however, nearly straight lines were obtained from this plot. The differences in the K and a values of poly(cyclohexene sulfide) and polythietane (Table X) can be attributed to the differences in polymer structure; the polymer from thietane is very flexible with little restriction of motion in the linear backbone; the polymer from cyclohexene sulfide, on the other hand, has considerably less freedom of motion due to the bulk of the cyclohexane ring.

TABLE X
Intrinsic Viscosity–Molecular Weight Relationship

Polymer	Solvent	Temp., °C.	a	K
Poly(cyclohexene sulfide)	$CHCl_3$	25	0.85	2.34×10^{-4}
Polythietane	$CHCl_3$	25	0.75	3.98×10^{-4}

The DuPont 900 DTA on which the differential thermal analyses were carried out was obtained in part through a gift of the Dunlop Research Center, Sheridan Park, Ontario, Canada. This research was supported in part by a fellowship from the Archer Daniels Midland Corporation, Minneapolis, Minnesota. The x-ray powder patterns were obtained by Dr. N. C. Baenziger of this department.

References

1. J. Lal, *The Chemistry of Cationic Polymerization*, P. H. Plesch, Ed., Macmillan, New York, 1963, p. 487.
2. R. Bacskai, *J. Polymer Sci. A*, **1**, 2777 (1963).
3. A. Noshay and C. C. Price, *J. Polymer Sci.*, **54**, 533 (1961).
4. C. S. Marvel and E. D. Weil, *J. Am. Chem. Soc.*, **76**, 61 (1959).
5. V. S. Foldi and W. Sweeney, *Makromol. Chem.*, **72**, 298 (1964).
6. G. L. Brode, paper presented to the American Chemical Society, 150th Meeting, Atlantic City, N. J., 1965; *Polymer Preprints*, **6**, No. 2, 626 (1965).
7. J. K. Stille and J. A. Empen, paper presented to the American Chemical Society, 150th Meeting, Atlantic City, N. J., 1965; *Polymer Preprints*, **6**, No. 2, 619 (1965).
8. E. E. van Tamelen, in *Organic Synthesis*, Coll. Vol. IV, N. Rabjohn, Ed., Wiley, New York, 1963, p. 232.
9. S. F. Birch, R. A. Dean, and N. J. Hunter, *J. Org. Chem.*, **23**, 1026 (1958).
10. S. Searles, H. R. Hayes, and E. F. Lutz, *J. Org. Chem.*, **27**, 2828 (1962).
11. M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).
12. T. Saegusa, H. Imai, and J. Furukawa, *Makromol. Chem.*, **65**, 60 (1963).
13. T. Saegusa, T. Uishima, H. Imai, and J. Furukawa, *Makromol. Chem.*, **79**, 201 (1965).
14. H. Imai, T. Saegusa, S. Ohsugi, and J. Furukawa, *Makromol. Chem.*, **81**, 119 (1965).
15. D. Sims, *J. Chem. Soc.*, **1964**, 864.
16. E. L. Wittbecker, H. K. Hall, and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 1218 (1960).
17. H. Meerwein, G. Hinz, P. Hoffman, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937).
18. D. J. Pettit and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).
19. H. D. Noether, U.S. Pat. 2,534,366 (1960).
20. R. E. Davis, *J. Org. Chem.*, **23**, 1380 (1958).
21. H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **76**, 4242 (1954).
22. M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).
23. J. D. McCullough and D. Mulvey, *J. Am. Chem. Soc.*, **81**, 1291 (1959).
24. E. Lippert and H. Prigge, *Ann.*, **659**, 81 (1962).
25. E. Lippert and H. Prigge, *Ber. Bunsenges. Phys. Chem.*, **67**, 554 (1963).
26. F. S. Dainton, K. J. Ivin, and D. A. G. Walmsley, *Trans. Faraday Soc.*, **56**, 1784 (1960).
27. S. Searles, M. Tamres, and R. E. Lippencott, *J. Am. Chem. Soc.*, **75**, 2775 (1953).
28. A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, **61**, No. 1, 71 (1965).
29. J. J. Stratta, E. P. Reding, and J. A. Faucher, *J. Polymer Sci. A*, **2**, 5017 (1964).
30. H. Mark, *Der Feste Korper*, Hirzel, Leipzeig, 1938, pp. 65–104.
31. R. Houwink, *J. Prakt. Chem.*, **1957**, 15 (1941).

Résumé

La polymérisation par ouverture de cycle de sulfures cycliques contenant des cycles à 3, 4 et 5 pieces a été étudiée. En rapport avec ces polymérisations, les basicités relatives de ces sulfures cycliques utilisés ont été également étudiées. Les polymérisations ont été effectuées en utilisant du penta-fluorure de phosphore, le complexe trifluoroure bore éther diéthylique, l'aluminium triéthyle et le tétrafluoroborate-triméthyloxonium. Les polymeres résultant ont été oxidés en sulfones et les analyses thermiques différentielles ont été obtenues sur les polymères sulfureux aussi bien que sur les analogous sulfoniques.

Zusammenfassung

Die Ringöffnungspolymerisation cyclischer Sulfide mit 3-, 4- und 5-gliedrigen Ringen wurde untersucht. Im Zusammenhang mit der Polymerisation wurde auch die relative Basizität der verwendeten cyclischen Sulfide bestimmt. Die Polymerisation wurde durch Verwendung von Phosphorpentafluorid, Bortrifluorid-Äthyläther, Triäthylaluminium und Trimethyloxonium-tetrafluoroborat bewirkt. Die erhaltenen Polymeren wurden zum Sulfon oxydiert und Differentialthermoanalysen an den Sulfidpolymeren und den Sulfonanalogen durchgeführt.

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Preparation and Polymerization of Some Vinyl Monomers Containing the 1,3-Dioxolane Group

G. F. D'ALELIO and R. J. CAIOLA,* *Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556*

Synopsis

The synthesis and structure determinations of (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl acrylate, 4-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl itaconate, and [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] methyl fumarate are described. Reactivity ratios in the copolymerization of these monomers with other comonomers are reported and the Alfrey-Price *Q* and *e* values calculated. The post-polymerization study of the effects of ultraviolet light and heat on these polymers and copolymers is presented. The 1,3-dioxolane group when appended to the polymer chain performs as an internal ultraviolet sensitizer. A mechanism is offered to explain the crosslinking behavior of these polymers when treated with ultraviolet light.

INTRODUCTION

Vinyl polymers which possess cyclic functional groups containing oxygen which can undergo post-polymerization reactions have been reported. Among those reported include the glycidyl acrylic esters[1-3] and acrylic esters containing the 2-oxo-1,3-dioxolane group.[4,5] It was considered to be of interest to prepare vinyl polymers with appended cyclic ketal structures. Particularly of interest were the 1,3-dioxolanes. While 1,3-dioxolanes have been useful blocking groups for 1,2-glycols[6] and for ketones,[7] since they are readily hydrolyzed by acids[8] but stable to base,[6] their use as chemical entities in polymers has not been studied. A choice of esters prepared from the known isopropylidene glyceral, 4-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane,[9,10] was made so as to have related olefinic esters whose polymerization tendency varied considerably, and whose copolymerization activities would be expected to differ substantially. The α,β-unsaturated esters selected included an acrylic, itaconic, and fumaric. This paper describes the synthesis and structure elucidation of these new monomers as well as investigations of their polymerizaion reactions. An interesting post-polymerization reaction, crosslinking induced by ultraviolet light, is also described.

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* Present address: The Dow Chemical Company, Midland, Michigan.

EXPERIMENTAL

Monomer Synthesis

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Acrylate. Into a three-necked two-liter flask fitted with stirrer, condenser and drying tube, and addition funnel was placed 50.4 g. (0.38 mole) of isopropylidene glycerol, 38.2 g. (0.38 mole) triethylamine, 950 ml. of benzene, and 0.5 g. anthraquinone. The temperature of the reaction mixture was kept at 0.5°C. by means of a water–ice bath. To the addition funnel 30.6 g. (0.33 mole) of acrylyl chloride dissolved in 50 ml. of benzene was added. The acrylyl chloride solution was added dropwise to the cooled, stirred reaction solution over a 7–8 hr. period. The reaction mixture was allowed to stir at room temperature overnight. The mixture was filtered and 45.5 g. (98%) of triethylamine hydrochloride was collected. The benzene solution was washed two times with 100-ml. portions of distilled water. The benzene solution was dried with anhydrous sodium carbonate, the sodium carbonate was removed by filtration, and the benzene was removed at aspirator pressure.

A vacuum distillation of the yellow liquid yielded 46.8 g. (75.5%) of a colorless liquid, b.p. 59°C./0.8 mm., n_D^{20} 1.4439, d^{20} 1.06783 g./cc., d^{50} 1.0372 g./cc.

ANAL. Calcd. for $C_9H_{14}O_4$: C, 58.05%; H, 7.58%. Found: C, 57.81%; H, 7.67%.

A gas–liquid chromatogram was obtained by using a Tide detergent column with a helium flow rate of 36 ml./min. at a temperature of 169°C. It showed a peak with a retention time of 2 min. and indicated the purity was greater than 99%.

4-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Itaconate. Into a three-necked 500-ml. round-bottomed flask equipped with stirrer, nitrogen inlet tube, and condenser, was placed 61.2 g. (0.545 mole) of itaconic anhydride, 72 g. (0.545 mole) of isopropylidene glycerol, and 250 ml. of benzene which had been dried over sodium. The reagents were allowed to react in a nitrogen atmosphere at 60°C. for 48 hr. The solution was cooled, and *n*-heptane was added until the solution turned slightly turbid. The flask was placed in the refrigerator, and after 3 hr. precipitation of the product occurred. A 66 g. (49.5%) yield of product was obtained. The product was recrystallized from benzene–hexane, m.p. 69–70°C.

ANAL. Calcd. for $C_{11}H_{16}O_6$: C, 54.09%; H, 6.60%. Found: C, 54.05%; H, 6.64%.

[(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]methyl Fumarate. Into a 1000 ml. three-necked flask equipped with stirrer, condenser with drying tube, and addition funnel, 28.5 g. (0.22 mole) of isopropylidene glycerol, 22 g. (0.22 mole) of triethylamine, and 400 ml. of benzene were placed. Into the addition funnel 31 g. (0.21 mole) of methyl fumaryl chloride was placed. The addition was made dropwise over a period of 2.5 hr. to the solution cooled to 5°C., and the reaction mixture was stirred at room temperature overnight. The mixture was filtered, and *n*-hexane was added to the filtrate until it became turbid. A small amount of a sticky material separated after 12 hr. in the refrigerator. The solution was filtered and the solvents were removed at aspirator pressure. The product was distilled, b.p. 122°C./0.08 mm.; 20 g. (39%) of a clear liquid were collected. The product crystallized in the receiving flask. The product was recrystallized from hexane, m.p. 54–55°C.

ANAL. Calcd. for $C_{11}H_{16}O_6$: C, 54.09%; H, 6.60%. Found: C, 54.23%; H, 6.78%.

Homopolymerization

Homopolymers of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate and 4-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl itaconate were prepared by solution polymerization in toluene with 0.1 wt.-% benzoyl peroxide as initiator at 50°C.

Reactivity Ratio Determinations

Solution polymerizations in toluene or dimethylformamide were run under a nitrogen atmosphere in 75 by 20 mm. screw cap vials. Polymerization was initiated by benzoyl peroxide, usually at 0.1 wt.-% based on monomer. Temperatures were kept at 50 ± 0.2°C. Conversions were kept below 13%, generally well below 10%. The polymers were precipitated by pouring the polymerization solution into water–methanol or hexane at room temperature. Purification was affected by reprecipitations. The purified polymers were dried in a vacuum oven at 60°C. to constant weight, and the composition of the copolymers was determined by carbon, hydrogen and oxygen and nitrogen analysis where applicable (performed by Midwest Micro Laboratory, Indianapolis, Indiana).

Reactivity ratios were determined from the differential form of the general copolymerization equation by the method of intercepts.[11]

The comonomers styrene, 2-vinylpyridine, and acrylonitrile used in the copolymerizations were purified before use by distillation. Hexyl methacrylate and butyl acrylate were purified[12] by washing the monomer free of inhibitor with base, drying the monomer over an anhydrous salt, and distilling *in vacuo*.

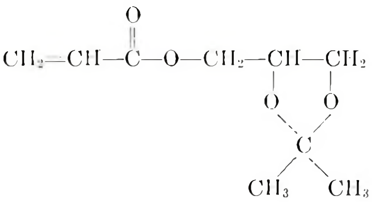
Post-Polymerization Reaction: Crosslinking with Ultraviolet Irradiation

Films of poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate] and selected copolymers were crosslinked by irradiation with ultraviolet light from a 100-w. medium-pressure mercury lamp which emits light from 254 to 365 mμ and from a 450-w. high-pressure mercury Hanovia immersion lamp emitting light at 254, 313, and 365 mμ.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomer (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate (I), was synthesized by the reaction of isopropylidene glycerol and acrylyl chloride in the presence of base.



I

The isopropylidene glycerol was prepared from the acid-catalyzed reaction of glycerol and 2,2-dimethoxypropane. Lorette and Howard[13] have recommended this method of employing dimethoxypropane as a transketalization agent for primary and secondary glycols. Hermans[14] and Smith and Lindberg[15] showed that the 1,3-dioxolane ring, rather than the 1,3-dioxane ring, was the kinetically controlled product in the reaction of glycerol and acetone. Irvine and co-workers[9] proved the structure of isopropylidene glycerol by showing that the methyl ether of their product was identical to the product independently synthesized from allyl iodide. That the dioxolane ring was formed in this study was shown by comparing the refractive indexes of the product and its derivatives with its isomeric dioxane compound and derivatives in Table I.

TABLE I
Refractive Indexes of Glycerol Derivatives

	Refractive index	
Compound	Literature	Found
Isopropylidene glycerol	1.4326 at 25°C.[16]	1.4346 at 20°C.
2,2-Dimethyl-5-hydroxy-1,3-dioxane	1.4427 at 20°C.[17]	
Isopropylidene glycerol α-methyl ether	1.4150 at 20°C.[18]	1.4121 at 20°C.
Glycerol α-methyl ether	1.4463 at 17°C.[16,19]	1.4458 at 16°C.
	1.4450 at 20°C.[18]	
Glycerol β-methyl ether	1.4505 at 17°C.[19]	

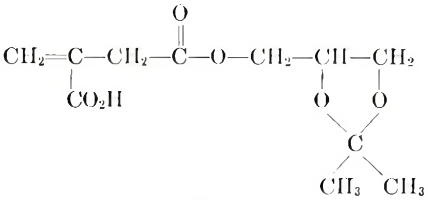
The acrylyl chloride was prepared by the procedure reported by Rehberg[20] whereby phosphorus trichloride is reacted with acrylic acid. The acrylyl chloride boiled at 74–76°C. This compound required distillation before use, as it polymerized to some extent on refrigeration. (If not freshly distilled, a cloudy suspension resulted when added to benzene.)

Monomer characterization was accomplished by its infrared spectrum. The principal characteristics of the spectrum are given in Table II.

TABLE II
Infrared Spectrum Characteristics of Monomer I

Absorption band, μ	Assignment
5.8	C=O
6.15	C=C
7.15	C=C
7.3	CH_3 (from isopropylidene)
8.6	C—O (1,3-dioxolane)
10.2	C=C
10.9	C=C
12.34	Appears to be characteristic of acrylates

Additional structure elucidation of I was obtained by its saponification and gas–liquid chromatographic analysis of the recovered alcohol. The analysis showed that the alcohol was identical with an authentic sample of isopropylidene glycerol. No rearrangement of the isopropylidene glycerol had occurred during esterification. The monomer 4-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl itaconate (II),



II

was prepared from isopropylidene glycerol and itaconic anhydride.

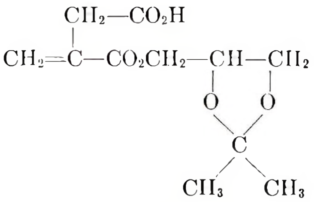
TABLE III
Infrared Spectrum Characteristic of Monomer II

Absorption band, μ	Assignment
3.4–4.4 (broad band)	CO_2H
5.8	C=O
6.0	C=O
6.15	C=C
7.3	CH_3
8.6	C—O
10.2	C=C
10.9	C=C

Itaconic anhydride was prepared from an exchange reaction of itaconic acid and acetic anhydride. This method of preparation has advantages over the conversion of citric acid to itaconic anhydride,[21] as the yields were better and the reaction scale larger.

Monomer II was characterized by its infrared spectrum (Table III) and by its pK_a.

The pK_a was used to differentiate monomer II from its isomer III.[22]



III

In Table IV the pK_a value and the dissociation constant of the product, are compared with the known constants for acrylic and acetic acids.

TABLE IV

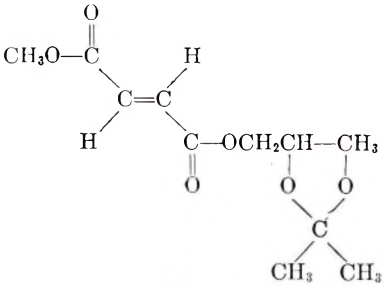
pK_a Values and Dissociation Constants

Compound	Temp., °C.	pK_a	Dissociation constant
4-(2,2-Dimethyl-1,3-dioxolan-4-yl)-methyl itaconate	23	4.19	6.46×10^{-5}
Acrylic acid	25	4.24	5.6×10^{-5}
Acetic acid	25	4.75	1.75×10^{-5}

Clearly, the pK_a is typical of the α,β-unsaturated acid, and the structure of the product corresponded to II.

The alcohol portion of the ester was recovered from the saponification of II and shown to be identical with an authentic sample of isopropylidene glycerol by gas-liquid chromatography.

The monomer [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]methyl fumarate (IV)



IV

was synthesized from isopropylidene glycerol and methyl fumaryl chloride in the presence of base.

The methyl fumaryl chloride was prepared from monomethyl maleate and thionyl chloride. The isomerization of maleates to fumarates is catalyzed by sulfur dioxide and hydrogen chloride.[23] Fumaryl chloride has been prepared from maleic acid and phosphorus pentachloride.[23]

Saponification of IV yielded fumaric acid, m.p. 281°C., isopropylidene glycerol, and methanol. These were shown by mixed melting points and gas–liquid chromatography.

Homopolymerization

The new acrylate and itaconate monomers homopolymerized by free-radical initiators such as benzoyl peroxide and azobisisobutyronitrile. In addition (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate (I) was observed to be particularly sensitive to ultraviolet light. Irradiation of the monomer through Pyrex glass at room temperature with ultraviolet light of wavelength 310–370 mμ for 1 min. resulted in a 50% conversion of monomer to polymer. It was also found that under the same conditions as described above, irradiation for five 3-min. periods of a pure sample of I produced an infusible, insoluble, rubbery polymer. The ultraviolet spectrum of a dilute solution of monomer I in spectral grade tetrahydrofuran showed no maximum above 210 mμ. This is compatible with the findings of Ungnade and Ortega,[25] who showed that other acrylic esters show no maximum above 210 mμ. A spectrum obtained from a concentrated solution of monomer in tetrahydrofuran (25 vol.-% monomer) showed that the monomer absorbed strongly at 370 mμ. This very strong absorption can account for the rapid polymerization of I when irradiated with ultraviolet light for a short time, even through Pyrex glass. The rapid polymerization of I under the conditions described appears to be unique, as no precedent could be found in the literature. In contrast, irradiation of methyl methacrylate and ethyl acrylate through Pyrex glass with a 450-w. high pressure mercury Hanovia immersion lamp at 55°C. for 2 hr. produced little or no polymer.

Solution polymerization of monomers I and II in toluene at 50°C. with benzoyl peroxide as initiator afforded workable polymers. Inherent viscosities in dimethylformamide for poly[(2,2-dimethyl-1,3-dioxolan-4-yl)-methyl acrylate] of 0.48 and for poly[4-(2,2-dimethyl-1,3-dioxolan-4-yl)-methyl itaconate] of 0.43 were obtained.

Copolymerization

These reactive vinyl monomers were copolymerized with a number of comonomers, and the experimental data are shown in Tables V–XVII. The r_1 and r_2 values obtained for these copolymerizations are shown in Tables XVIII–XX. In addition, the Alfrey-Price equations[26] were used to calculate Q and e values.

TABLE V

Copolymerization of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Acrylate with Styrene (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. (C_6H_5-COO)$_2$,	Time,	Conversion			O, %			
no.	g.	mole	g.	mole	(molar)	g.	hr.	g.	%	C, %	(direct)	dM_2	dM_1	dM_2/dM_1
1	1.86	0.01	0.52	0.005	0.5	0.0055	9	0.24	9.9	69.60, 69.32	23.13, 22.95	0.3590	0.3183	1.1278
2	1.86	0.01	1.04	0.010	1.0	0.0073	9	0.35	12.0	71.70, 71.52	20.62, 20.75	0.3222	0.3840	0.8390
3	1.86	0.01	2.08	0.020	2.0	0.0109	9	0.45	11.5	73.95, 73.80	18.16, 18.44	0.2870	0.4469	0.6422
4	1.86	0.01	3.12	0.030	3.0	0.0145	9	0.38	7.6	76.76, 76.58	18.19, 18.26	0.2424	0.5266	0.4603

TABLE VI

Copolymerization of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Acrylate with Hexyl Methacrylate (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. (C_6H_5-COO)$_2$,	Time,	Conversion			O, %			
no.	g.	mole	g.	mole	(molar)	g.	min.	g.	%	C, %	(direct)	dM_2	dM_1	dM_2/dM_1
1	0.931	0.005	0.425	0.0025	0.5	0.0014	80	0.03	2.2	64.22, 64.51	25.96	0.2645	0.2981	0.8872
2	0.931	0.005	0.850	0.0050	1.0	0.0018	120	0.05	2.8	66.42, 66.62	23.87	0.1756	0.3953	0.4442
3	0.931	0.005	1.700	0.0100	2.0	0.0026	110	0.07	2.7	68.17, 67.93	21.52	0.0950	0.4834	0.1965

TABLE VII

Copolymerization of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl acrylate with Butyl Acrylate (M_1)

Expt. no.	M_2 g.	M_2 mole	M_1 g.	M_1 mole	M_1/M_2 (molar)	Wt. $(C_6H_5COO)_2$, g.	Time, min.	Conversion g.	Conversion %	C, %	O, % (direct)	dM_2	dM_1	dM_2/dM_1
1	0.931	0.005	0.64	0.005	1.0	0.0015	60	0.20	12.8	61.81, 62.08	30.49	0.2620	0.3994	0.6559
2	0.931	0.005	1.28	0.010	2.0	0.0221	20	0.19	8.7	63.25, 63.05	27.60	0.1737	0.5278	0.3291
3	0.931	0.005	1.92	0.015	3.0	0.0017	60	0.35	12.3	63.69, 63.53	—	0.1412	0.5750	0.2455
4	0.931	0.005	2.56	0.020	4.0	0.0035	180	0.10	2.9	64.10	—	0.1063	0.6257	0.1698

TABLE VIII

Copolymerization of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Acrylate with 2-Vinylpyridine (M_1)

Expt. no.	M_2 g.	M_2 mole	M_1 g.	M_1 mole	M_1/M_2 (molar)	Wt. azo catalyst, g.	Time, min.	Conversion g.	Conversion %	C, %	N, %	dM_2	dM_1	dM_2/dM_1
1	1.862	0.010	0.526	0.005	0.5	0.0024	240	0.151	6.3	66.26, 66.47	4.93, 5.01	0.3350	0.3578	0.9362
2	1.862	0.010	1.051	0.010	1.0	0.0030	260	0.217	7.1	68.83, 68.87	6.51, 6.44	0.2742	0.4655	0.5890
3	0.931	0.005	1.051	0.010	2.0	0.0020	280	0.101	5.6	70.36, 70.36	7.68, 7.74	0.2296	0.5444	0.4217

TABLE IX

Copolymerization of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Acrylate with Acrylonitrile (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. $(C_6H_5\text{-}COO)_2$,	Time,	Conversion						
no.	g.	mole	g.	mole	(molar)	g.	min.	g.	%	C, %	N, %	dM_2	dM_1	dM_2/dM_1
1	1.860	0.010	0.265	0.005	0.5	0.0021	240	0.146	7.0	59.42	3.89	0.4578	0.2775	1.6490
2	0.931	0.005	0.530	0.010	2.0	0.0036	200	0.032	2.2	60.26	7.93, 7.82	0.3760	0.5619	0.6705
3	0.931	0.005	1.060	0.020	4.0	0.0060	200	0.122	6.1	62.01	14.38, 14.13	0.2470	1.0170	0.2428
4	0.931	0.005	1.590	0.030	6.0	0.0083	200	0.162	6.4	62.28	16.34, 16.11	0.2064	1.1580	0.1780
5	0.931	0.005	2.650	0.040	10.0	0.0133	200	0.212	5.6	63.85	19.21, 19.11	0.1464	1.3700	0.1068

TABLE X

Copolymerization of 4-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Itaconate with Styrene (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. $(C_6H_5\text{-}COO)_2$,	Time,	Conversion			O, % (by differ-			
no.	g.	mole	g.	mole	(molar)	g.	min.	g.	%	C, %	ence)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	0.5207	0.005	1.0	0.0087	90	0.01	0.6	65.78	26.98	0.2861	0.2890	0.9899
2	1.2211	0.005	1.5621	0.015	3.0	0.0139	75	0.01	0.4	67.65	25.01	0.2601	0.3499	0.7433
3	1.2211	0.005	2.0828	0.020	4.0	0.0165	115	0.06	1.8	68.90	23.88	0.2505	0.3725	0.6724
4	1.2211	0.005	2.6035	0.025	5.0	0.0191	105	0.05	1.3	69.45	23.22	0.2419	0.3930	0.6154
5	1.2211	0.005	3.1242	0.030	6.0	0.0217	80	0.09	2.2	70.75	22.10	0.2303	0.4200	0.5483

TABLE XI

Copolymerization of 4-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Itaconate with Hexyl Methacrylate (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. $(C_6H_5\text{-}COO)_2$,	Time,	Conversion			O, %			
no.	g.	mole	g.	mole	(molar)	g.	min.	g.	%	C, %	(by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	0.4256	0.0025	0.5	0.016	75	0.10	6.6	58.11, 58.16	34.15, 33.93	0.3085	0.1447	2.1310
2	1.2211	0.005	0.8512	0.0050	1.0	0.020	80	0.08	4.0	61.45, 61.25	29.68, 29.99	0.2284	0.2596	0.8798
3	1.2211	0.005	1.2768	0.0075	1.5	0.025	65	0.05	2.0	63.01, 62.25	28.03, 28.12	0.1907	0.3136	0.6080
4	1.2211	0.005	2.5536	0.0150	3.0	0.037	70	0.02	0.6	65.32, 65.32	25.31, 25.17	0.1297	0.4011	0.3233
5	1.2211	0.005	3.4048	0.0200	4.0	0.046	80	0.01	0.2	66.55, 66.72	23.62, 23.41	0.0974	0.4475	0.2176

TABLE XII

Copolymerization of 4-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Itaconate with Butyl Acrylate (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. $(C_6H_5\text{-}COO)_2$,	Time,	Conversion			O, %			
no.	g.	mole	g.	mole	(molar)	g.	min.	g.	%	C, %	(by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	1.2816	0.0100	2.00	0.0125	300	0.060	2.4	56.39, 56.55	36.09, 35.97	0.3136	0.1825	1.7180
2	1.2211	0.005	1.6020	0.0125	2.50	0.0141	250	0.025	0.9	57.35, 57.21	34.83, 34.98	0.2839	0.2391	1.1870
3	1.2211	0.005	1.9224	0.0150	3.00	0.0157	210	0.020	0.6	57.45, 57.46	34.72, 34.63	0.2775	0.2512	1.1040
4	1.2211	0.005	2.6032	0.0203	4.07	0.0189	210	0.180	4.8	58.24, 58.46	33.84, 33.64	0.2579	0.2886	0.8936

TABLE XIII

Copolymerization of 4-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Itaconate with 2-Vinylpyridine (M_1)

Expt. no.	M_2 g.	M_2 %	M_1 g.	M_1 %	M_1/M_2 (molar)	Wt. $(C_6H_5COO)_2$, g.	Time, min.	Conversion g.	Conversion %	C, %	N, %	O, % (by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	1.5769	0.015	3.0	0.0180	275	0.050	1.80	68.39	8.44	15.98	0.1502	0.6020	0.2495
2	1.2211	0.005	2.1026	0.020	4.0	0.0166	290	0.025	0.76	71.57	9.51	12.02	0.1293	0.6505	0.1987
3	1.2211	0.005	2.6282	0.025	5.0	0.0192	325	0.015	0.40	71.93	9.98	11.04	0.1146	0.6848	0.1673
4	1.2211	0.005	3.1539	0.030	6.0	0.0217	360	0.025	0.60	72.77	10.48	9.49	0.0990	0.7209	0.1373

TABLE XIV

Copolymerization of [(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]methyl Fumarate with Styrene (M_1)

Expt. no.	M_2 g.	M_2 mole	M_1 g.	M_1 mole	M_1/M_2 (molar)	Wt. $(C_6H_5COO)_2$, g.	Time, min.	Conversion g.	Conversion %	C, %	C, % (by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	0.5207	0.005	1.0	0.0087	110	0.102	5.9	67.10	25.86	0.2696	0.3277	0.8227
2	1.2211	0.005	1.0414	0.010	2.0	0.0113	90	0.105	4.6	67.84	24.97	0.2610	0.3480	0.7500
3	1.2211	0.005	1.5621	0.015	3.0	0.0137	75	0.075	2.8	68.35	24.77	0.2574	0.3565	0.7220
4	1.2211	0.005	2.0828	0.020	4.0	0.0165	60	0.050	1.5	70.37	22.48	0.2341	0.4109	0.5697
5	1.2211	0.005	2.6035	0.025	5.0	0.0217	60	0.153	4.0	71.41	21.23	0.2235	0.4359	0.5127

TABLE XV

Copolymerization of [(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]methyl Fumarate with Hexyl Methacrylate (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. (C_6H_5-COO)$_2$,	Time,	Conversion			O, %			
no.	g.	mole	g.	mole	(molar)	g.	min.	g.	%	C, %	(by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	0.8512	0.005	1.0	0.020	105	0.104	5.0	69.48, 69.26	20.13, 20.18	0.02880	0.5459	0.0527
2	1.2211	0.005	1.7024	0.010	2.0	0.028	30	0.134	4.6	69.50, 69.79	20.41, 19.93	0.01880	0.5603	0.0335
3	1.2211	0.005	2.5536	0.015	3.0	0.037	20	0.196	5.2	70.28, 70.18	19.26, 19.27	0.00941	0.5738	0.0163
4	1.2211	0.005	3.4048	0.020	4.0	0.023	120	0.180	3.9	70.23, 70.43	18.71, 18.73	0.00777	0.5762	0.0134

TABLE XVI

Copolymerization of [(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]methyl Fumarate with Butyl Acrylate (M_1)

Expt.	M_2		M_1		M_1/M_2	Wt. (C_6H_5-COO)$_2$,	Time,	Conversion			O, %			
no.	g.	mole	g.	mole	(molar)	g.	min	g.	%	C, %	(by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	0.6408	0.005	1.0	0.018	60	0.140	7.5	61.54, 61.43	30.01, 29.89	0.1437	0.5063	0.2838
2	1.2211	0.005	1.2816	0.010	2.0	0.025	60	0.178	7.1	62.93, 62.75	28.28, 28.27	0.0945	0.6000	0.1575
3	1.2211	0.005	1.9224	0.015	3.0	0.031	80	0.214	6.8	63.56, 63.56	27.37, 27.41	0.0689	0.6487	0.1062
4	1.2211	0.005	2.5632	0.020	4.0	0.039	80	0.182	4.8	64.44, 64.18	26.25, 26.47	0.0429	0.6983	0.0614
5	1.2211	0.005	3.8448	0.030	6.0	0.025	120	0.289	5.7	64.28, 64.43	26.56, 26.27	0.0372	0.7092	0.0524

TABLE XVII

Copolymerization of [(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]methyl Fumarate with 2-Vinylpyridine (M_1)

Expt. no.	M_2 g.	M_2 mole	M_1 g.	M_1 mole	M_1/M_2 (molar)	Wt. (C_6H_5-$COO)_2$, g.	Time, min.	Conversion g.	Conversion %	C, %	N, %	O, % (by difference)	dM_2	dM_1	dM_2/dM_1
1	1.2211	0.005	0.5256	0.005	1.0	0.0170	285	0.06	3.5	65.57	5.96	21.96	0.2280	0.4213	0.5411
2	1.2211	0.005	1.0513	0.010	2.0	0.0230	300	0.11	5.3	68.79	7.16	17.09	0.1916	0.5060	0.3786
3	1.2211	0.005	1.5769	0.015	3.0	0.0280	285	0.27	9.7	68.19	7.88	17.04	0.1674	0.5621	0.2978
4	1.2211	0.005	2.1026	0.020	4.0	0.0166	275	0.12	3.7	70.73	8.79	13.28	0.1461	0.6116	0.2388
5	1.2211	0.005	2.6282	0.025	5.0	0.0192	265	0.10	2.6	71.43	7.25	14.20	0.1351	0.6372	0.2120
6	0.6106	0.0025	1.5769	0.015	6.0	0.0210	255	0.14	6.4	71.94	9.18	11.95	0.1240	0.6629	0.1870

TABLE XVIII

Reactivity Ratios of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Acrylate (M_2) with Comonomers

Comonomer (M_1)	r_1	r_2	Q_1[a]	e_1[a]		Q_2	e_2
Styrene	0.389 ± 0.04	0.17 ± 0.02	1.00	−0.80		0.69	0.84
2-Vinylpyridine	0.836 ± 0.18	0.12 ± 0.1	1.30	−0.50		0.69	0.73
Hexyl methacrylate	2.37 ± 0.01	0.47 ± 0.06	—	—		—	-
Butyl acrylate	1.32 ± 0.15	0.45 ± 0.15	0.51	1.02		0.63	0.69
Acrylonitrile	0.9 ± 0.09	0.84 ± 0.34	0.60	1.20		0.89	0.82
					Avg.	0.72	0.77

[a] Data of Young.[24]

TABLE XIX
Reactivity Ratios of 4-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Itaconate (M_2) with Comonomers

Comonomer (M_1)	r_1	r_2	Q_1	e_1	Q_2	e_2
Styrene	0.14 ± 0.01	0.18 ± 0.04	1.00	−0.80	1.47	1.13
2-Vinylpyridine	1.06 ± 0.10	0.16 ± 0.11	1.30	−0.50	0.57	1.23
Hexyl methacrylate	1.06 ± 0.12	0.85 ± 0.20	0.70	−0.12	0.61	0.94
Butyl acrylate	0.17 ± 0.07	2.4 ± 1.1	—	—	—	—
				Avg.	0.89	1.1

TABLE XX
Reactivity Ratios of [(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]methyl Fumarate (M_2) with Comonomers

Comonomer (M_1)	r_1	r_2	Q_1	e_1	Q_2	e_2[a]
Styrene	0.17 ± 0.05	0	1.00	−0.80	0.63	2.15
2-Vinylpyridine	0.76 ± 0.06	0	1.30	−0.50	0.47	2.18
Hexyl methacrylate	17.5 ± 2.5	0	—	—	—	—
Butyl acrylate	2.69 ± 0.55	0	—	—	—	—
				Avg.	0.55	2.16

[a] Obtained by assuming that r_2 = 0.001.

The copolymers of monomer I and monomer II were all random copolymers. In the case of monomer II, a large difference is found in the r values with hexyl methacrylate and butyl acrylate, the hexyl methacrylate radical preferring to react with its own monomer whereas the butyl acrylate radical prefers to react with monomer II. The zero value of r_2 for fumarate monomer (IV) showed that this monomer had no tendency to react with itself. In its copolymerization with styrene, where $r_1 = 0.17 \pm 0.05$, the copolymer approached an alternating copolymer. Where r_1 is very large, such as in the copolymerization with hexyl methacrylate, a copolymer enriched with hexyl methacrylate was formed even at low initial hexyl methacrylate concentrations.

The intrinsic viscosity of selected samples of copolymers was determined by using an Ubbelohde dilution viscometer. The usual[27] two-line plot of reduced viscosity and inherent viscosity versus concentration was used. Results are shown in Table XXI.

The intrinsic viscosities indicated that the molecular weights of these copolymers were high.

TABLE XXI
Intrinsic Viscosity [η] of Copolymer Samples

Copolymer composition	Solvent	[η]
Butyl acrylate (73%), 2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate (27%)	DMF	1.53
Hexyl methacrylate (68.3%), 4-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl itaconate (31.7%)	Toluene	0.46
Styrene (47), [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] methyl fumarate	Toluene	0.65

Post-Polymerization Studies

Post-polymerization reactions to obtain crosslinked polymers from linear polymers are well known in the literature. Chemical crosslinking agents are employed when the pendant group contains a related functional group. For example, polyacrylate esters containing hydroxyl groups in the ester portion can be crosslinked[28] with polyepoxides or with polyisocyanates. Light and radiation have also been used to crosslink polymers. Poly-α-olefins have been reported to crosslink by ultraviolet light in the presence of a sensitizer[29] and by neutron radiation.[30]

In this study, ultraviolet light alone was used to crosslink polymers containing the 1,3-dioxolane group. A film of poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate] was crosslinked when irradiated with ultraviolet light from the 100-w. mercury lamp emitting light in the 254–365 mμ region. When a film of the polymer was partially shielded and irradiated, only the exposed portion was crosslinked. The shielded portion was soluble in benzene. The uncrosslinked polymer had been tacky, but this property was lost after irradiation.

Films of copolymers were cast on a flat 2 × 3 in. glass plate, dried, and

TABLE XXII
Irradiation of Copolymer Films

Copolymer	Wt. of copolymer, g.	Duration of irradiation, min.	Wt. of crosslinked copolymer, g.	% crosslinked
Butyl acrylate (73%), (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl acrylate (27%)	0.0096	15	0.0050	52
Hexyl methacrylate (68.3%), 4-(2,2-dimethyl-1,3-dioxolan-4-yl)methyl itaconate (31.7%)	0.0060	20	0.0016	27
Styrene (47%), [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] methyl fumarate (53%)	0.0135	20	0.0092	68
Styrene (47%), [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] methyl fumarate (53%)	0.0108	30	0.0077	71

weighed. The films were irradiated with ultraviolet light from the lamp described above. The plates were then submerged in boiling toluene for 5 min., then in boiling dimethylformamide for 5 min. The plates were then dried and weighed. Nonirradiated films prepared in the same manner were completely dissolved as evidenced by weight measurements of the glass plates. In Table XXII the data from these experiments are shown.

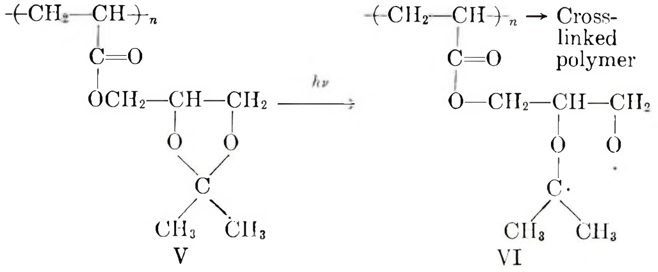
The ultraviolet spectrum of poly[(2,2-dimethyl-1,3-dioxolan-4-yl) methyl acrylate] showed that the polymer began to absorb light at 320 mμ. This is not expected for saturated esters. Closson and Haug[31] showed that saturated esters have weak ultraviolet absorptions with a maximum between 200 and 220 mμ. To demonstrate that there was no monomer contamination in the polymer, an infrared spectrum of the polymer film, was compared to the infrared spectrum of the monomer. The absence of peaks at 6.15, 7.15, 10.15, 10.9, and 12.35 μ in the polymer spectrum clearly showed that no monomer was present. The only possible chromophore which remained in the molecule to account for the ultraviolet absorption was the 1,3-dioxolane group. However Zimkin and Bergmann,[32] in a study of the ultraviolet absorption behavior of 2-alkyl-3-phenyl-1,3-oxazolidines, stated that the compounds have spectra completely analogous to disubstituted anilines and that the oxazolidine ring did not contribute to the absorption of these molecules.

In the experiments described above no effort was made to cool the films during irradiation or to ascertain the wavelength of the light needed to bring about the crosslinking. To separate the effects of heat and ultraviolet light as well as the effect of near and far ultraviolet light, an infrared spectral analysis was performed of thermally treated as well as ultraviolet light treated films. The study was also conducted to obtain some insight into the mechanism of the crosslinking reaction. Films of polymer were cast on three sodium chloride plates used for infrared analysis.

The first plate was placed in an oven at 150°C. for 30 min. It had been previously determined that the polymer crosslinked under these conditions. An infrared spectrum of the crosslinked polymer showed the appearance of hydroxyl absorption, carboxylic absorption as well as a diminishing of the isopropylidene and 1,3-dioxolane absorptions. The second film was irradiated for 30 min. with a 450-w. high-pressure mercury Hanovia immersion lamp emitting light at 254, 313, and 365 mμ. The light was cooled through a water jacket made of quartz. The temperature of the film was about 55°C. The infrared spectrum showed the appearance of hydroxyl absorption. The third film was irradiated for 30 min. under the same conditions, except that a Pyrex plate was used to filter the ultraviolet light below 300 mμ. Only faint hydroxyl absorption was perceptible in the infrared spectrum. However after 5 hr. of irradiation, another infrared spectrum of this film showed strong hydroxyl absorption, and marked decreases in isopropylidene and 1,3-dioxolane absorptions. Each of these treatments crosslinked the polymer. However, different mechanisms appeared to be operating since carboxylic acid absorptions appeared in the spectrum of the thermally crosslinked film, and not at all in the spectrum of the film irradiated with light above 300 mμ.

Jacobs and Steele[33] have reported the crosslinking of poly(ethyl acrylate) by ultraviolet irradiation. After 30 min. they stated that no crosslinking occurred with 254 mμ ultraviolet light, and only 50% of the polymer crosslinked after 1 hr. They[34] proposed a mechanism which involves splitting the ester side chain from the polymer backbone. The infrared spectral study of treated poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate] appeared to exclude this choice of mechanism, since the formation of carboxylic acid and alcohol are not accounted for. Cowley and Melville[35] have found that the chain scission reaction of poly(methyl methacrylate) occurred rapidly upon ultraviolet irradiation at 254 mμ at temperatures of 130°C. or above. This reaction would not be expected to be competitive with the crosslinking reaction at 55°C. of this irradiation. Oster and coworkers[36] have stated that in the presence of ultraviolet sensitizers the crosslinking of poly(methyl methacrylate) is considerably enhanced. It is proposed that, polymers containing the 1,3-dioxolane ring have internal ultraviolet sensitizers, and therefore they crosslinked readily.

A mechanism for the crosslinking reaction under the influence of ultraviolet light is proposed in eq. (1).



(1)

The main facts, hydroxyl formation, crosslinking, and the reduction of the absorption in the infrared spectrum of the 1,3-dioxolane group can be explained by intermediate VI. Hydroxyl formation could have occurred by hydrogen abstraction by the oxygen radical. Crosslinking can be explained by the coupling of the carbon radical of VI with another radical. In addition, the hydrogen abstraction reaction should have produced another carbon radical which was capable of crosslinking. The reduction of the absorption in the infrared spectrum of the isopropylidene can also be explained by the loss of acetone.

The 1,3-dioxolane-containing polymers and copolymers fall into the classification of self-reactive thermosetting acrylic polymers as proposed by Piggott.[37] These polymers require heat alone or trace amounts of catalyst to cause the pendant groups to react.

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This paper is abstracted from a portion of the Ph.D. thesis of R. J. Caiola, Scott Paper Company Research Fellow, University of Notre Dame, 1966.

References

1. J. G. Erickson, U.S. Pat. 2,556,075 (1951).
2. J. G. Erickson, U.S. Pat. 2,567,842 (1951).
3. J. G. Erickson and W. M. Thomas, U.S. Pat. 2,606,810 (1952).
4. J. C. Fang, U.S. Pat. 2,967,173 (1961).
5. J. L. O'Brien and E. M. Beavers, U.S. Pat. 2,979,514 (1961).
6. W. W. Pigman and R. M. Goepp, Jr., *Chemistry of Carbohydrates*, Academic Press, New York, 1948, p. 348.
7. J. Dauben, Jr., B. Löken, and H. J. Ringold, *J. Am. Chem. Soc.*, **76,** 1359 (1954).
8. R. C. Elderfield, *Heterocyclic Compounds*, Wiley, New York, 1957, Vol. 5, p. 16.
9. J. C. Irvine, J. L. A. MacDonald, and C. W. Soutar, *J. Chem. Soc.*, **107,** 343 (1915).
10. J. B. Bell, Jr., V. A. Currier, and J. D. Malkemus, U.S. Pat. 2,915,529 (1959).
11. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **64,** 2356 (1942).
12. E. H. Riddle, *Monomeric Acrylic Esters*, Reinhold, New York, 1954, p. 15.
13. N. B. Lorette and W. L. Howard, *Organic Syntheses*, Vol. 42, Wiley, New York, 1962, p. 1.
14. P. H. Hermans, *Z. Physik. Chem.*, **113,** 337 (1924).
15. L. Smith and J. Lindberg, *Ber.*, **64,** 505 (1931).
16. M. S. Newman and M. Renoll, *J. Am. Chem. Soc.*, **67,** 1621 (1945).
17. N. M. Carter, *Ber.*, **63,** 2399 (1930).
18. H. Hibbert and J. G. Morazain, *Can. J. Res.*, **2,** 1214 (1930).
19. H. Hibbert, M. S. Wheeler, and N. M. Carter, *J. Am. Chem. Soc.*, **51,** 302 (1929).
20. C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Am. Chem. Soc.*, **67,** 1209 (1945).
21. R. L. Shriner, S. G. Ford, and L. J. Roll, in *Organic Syntheses*, Coll. Vol. II, A. H. Blatt, Ed., Wiley, New York, 1943, p. 368.
22. G. F. D'Alelio and L. X. Mallavarapu, *Makromol. Chem.*, **37,** 25 (1960).
23. L. H. Flett and W. H. Gardner, *Maleic Anhydride Derivatives*, Wiley, New York, 1952, p. 48a.
24. L. J. Young, *J. Polymer Sci.*, **54,** 411 (1961).
25. H. E. Ungnade and I. Ortega, *J. Am. Chem. Soc.*, **73,** 1564 (1951).

26. T. Alfrey, Jr. and C. C. Price, *J. Polymer Sci.*, **2,** 101 (1947).
27. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 34.
28. Courtaulds Ltd., Belgium Pat. 615,113 (1962).
29. K. Soumelis and H. Wilski, *Kunststoffe*, **52,** 471 (1962).
30. A. Charlesby, *Proc. Roy. Soc.* (*London*), **A215,** 187 (1952).
31. W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, **86,** 2384 (1964).
32. E. Zimkin and E. D. Bergmann, *Rec. Trav. Chim.*, **71,** 229 (1952).
33. H. Jacobs and R. Steele, *J. Appl. Polymer Sci.*, **3,** 236 (1960).
34. H. Jacobs and R. Steele, *J. Appl. Polymer Sci.*, **3,** 245 (1960).
35. P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A210,** 461 (1952).
36. G. Oster, G. K. Oster and H. Moroson, paper presented at 132nd Meeting, American Chemical Society, New York, September, 1957.
37. K. E. Piggott, *J. Oil Colour Chemists' Assoc.*, **46,** 1009 (1963).

Résumé

La synthèse et les déterminations de structure de l'acrylate de (2,2-diméthyl-1,3-dioxolane-4-yl)méthyle, d'itaconate de (4-2,2-diméthyl-1,3-dioxolane-4-yl)méthyle et fumarate de(2,2-diméthyl-1,3-dioxolane-4-yl)méthyle sont décrites. Les rapports de réactivités au cours de copolymérisation de ces monomeres avec d'autres comonomères sont rapportés et les valeurs d'Alfrey-Price Q et e ont été calculées. Les post-polymérisations résultant des effects de la lumière ultraviolette et de la chaleur sur ces polymères et copolymères sont présentées. Le groupe dioxolane 1,3-lorsqu'il est attaché à une chaîne polymérique agit comme sensibilisateur intramoléculaire dans l'ultraviolet. Un mécanisme est présenté pour expliquerle comportement au pontage de ces polymères lorsqu'ils sont traités a la lumière ultraviolette.

Zusammenfassung

Synthese und Strukturbestimmung von (2,2-Dimethyl-1,3-dioxolan-4-yl)-methylacrylat, 4-(2,2-Dimethyl-1,3-dioxolan-4-yl)-methylitaconat und [(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl]-methylfumarat werden beschrieben. Reaktivitätsverhältnisse bei der Copolymerisation dieser Monomerer mit anderen Comonomeren werden mitgeteilt und die Q- und e-Werte nach Alfrey-Price berechnet. Die Nachpolymerisationseffekte bei der Einwirkung von Ultraviolettlicht und Wärme auf diese Polymeren und Copolymeren werden untersucht. Die an die Polymerkette gebundene 1,3-Dioxolangruppe wirkt als innerer Ultraviolettsensibilisator. Ein Mechanismus zur Erklärung des Vernetzungsverhaltens dieser Polymeren bei Behandlung mit ultraviolettem Licht wird angegeben.

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Preparation and Polymerization of Some Vinyl Monomers Containing the 2-Oxo-1,3-Dioxolane Group

G. F. D'ALELIO and T. HUEMMER, *Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556*

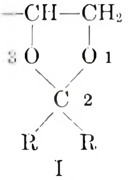
Synopsis

The syntheses and polymerizations of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate, 4-(2-oxo-1,3-dioxolan-4-yl)methyl itaconate, and (2-oxo-1,3-dioxolan-4-yl)methyl maleate are described. Reactivity ratios in the copolymerization of these monomers with other comonomers are reported and the Alfrey-Price Q and e values calculated. The post-polymerization effects of ultraviolet light and heat on these polymers and copolymers are presented and compared to those for similar polymers containing the 2,2-dimethyl-1,3-dixolane groups, which performs as an internal ultraviolet sensitizer. The 2-oxo derivatives are crosslinked thermally but not by ultraviolet light. The crosslinking reaction can be catalyzed by acids, bases, and salts.

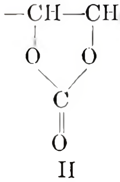
INTRODUCTION

In a previous paper,[1] it was demonstrated that vinyl polymers containing pendant, 2,2-dialkyl-1,3-dioxolane groups (I) crosslinked readily when exposed to ultraviolet light and that this 1,3-dioxolane group acted as an internal ultraviolet sensitizer.

It was considered of interest to compare the behavior of these dioxolanes



I



II

which contain alkyl substitution in the 2-position and which are readily hydrolyzed by acid[2] but stable to base[3] to other 1,3-dioxolanes which do not have hydrocarbon group substitution in the 2-position. Accordingly, the 2-oxo-1,3-dioxolane structure (II) was selected for the comparison. These 2-oxo- derivatives are cyclic carbonates which are hydrolyzed readily by base but less readily by acid, and therefore compliment the 2-alkyldioxolanes, which are cyclic ketals used as blocking groups.[4]

A choice of esters prepared from the known 4-(hydroxymethyl)-1,3-dioxolan-2-one (glyceryl carbonate)[5,6] was made to parallel the corresponding ketals[1] and to have related olefinic esters whose polymerization tendency varied considerably and whose copolymerization activities would be expected to differ substantially. The α,β-unsaturated esters selected included acrylic,[7,8] itaconic, and fumaric derivatives. This paper describes the synthesis of these monomers as well as the investigation of their polymerization reactions. The thermal and ultraviolet post-polymerizations are also studied.

EXPERIMENTAL

Monomer Synthesis

(2-Oxo-1,3-dioxolan-4-yl)methyl Acrylate. (*a*) Into a three-necked two-liter flask fitted with stirrer, nitrogen inlet tube, condenser fitted with an exit drying tube, and two addition funnels was placed 29 g. (0.22 mole) of glyceryl carbonate, 500 ml. of benzene, 50 ml. of dioxane, 0.5 g. 2,6-di-*tert*-butyl-*p*-cresol, and the mixture cooled to −0.5 to 5°C. Then triethylamine, 24.2 g. (0.24 mole), and 20.0 g. (0.22 mole) of acrylyl chloride dissolved in 50 ml. of benzene were added dropwise alternately from the addition funnels to the cooled, vigorously stirred solution over a 6-hr. period. The reaction mixture was allowed to stir at room temperature for 10 hr. The mixture was filtered and 21.9 g. (98.6%) of triethylamine hydrochloride was collected. The benzene–dioxane solution was washed twice with 50 ml. of cold (5°C.) hydrochloric acid solution (5%) and four times with 100-ml. portions of cold (5°C.) distilled water. The benzene solution to which had been added 0.1 g. of *tert*-butyl alcohol was dried with anhydrous magnesium sulfate, filtered, allowed to stand over a mixture of equal parts of sodium bicarbonate and anhydrous sodium sulfate at room temperature for 3 days and then filtered again. The benzene–dioxane solution was cooled to 3–5°C. and stripped of solvent at 0.1 mm. leaving a clear, almost colorless, oil; $n_D^{20} = 1.4471$.

ANAL. Calcd. for $C_7H_8O_5$: C, 48.84%; H, 4.65%. Found: C, 49.30%; H, 4.88%.

Attempts to distil the product even in the presence of additional inhibitor at pressures in the range of 15–10^{-4} mm. resulted in polymerization and decomposition. Boiling points were estimated as 124–126°C./0.9 mm., 100–101°C./0.1 mm. The infrared spectrum of the undistilled product shows the typical vinyl absorptions as well as the acrylate band at 12.35 μ, the carbonate carbonyl at 5.55 μ, and the ester carbonyl at 5.78 μ.

(*b*) Into a three-necked 500-ml. round-bottomed flask equipped with stirrer, nitrogen inlet tube, and condenser fitted with an exit tube were placed 100 ml. of benzene, 11.8 g. (0.1 mole) glyceryl carbonate, 12.6 g. (0.1 mole) acrylic anhydride and 0.3 g. of hydroquinone and mixed thoroughly. Then, 5 ml. tetrahydrofurane containing 0.5 g. triethylamine was added and the mixture refluxed for 36 hr. under nitrogen and allowed to cool. The mixture was washed three times with 100-ml. portions of cold (5°C.) water, then four times with 50-ml. portions of cold 5% sodium bicarbonate solution, then twice with 100-ml. portions of cold water. The benzene solution to which had been added 0.1 g. of *tert*-butyl catechol was dried with anhydrous magnesium sulfate, filtered, allowed to stand over a mixture of equal parts of sodium bicarbonate and anhydrous sodium sulfate for 2 days at room temperature, and filtered again. The benzene solution was cooled to 5–7°C. and stripped of benzene at 0.1–0.2 mm., leaving a clear, colorless oil.

ANAL. Calcd. for $C_7H_8O_6$: C, 48.84%; H, 4.65%. Found: C, 49.32%; H, 4.84%.

Attempts to distil the crude monomer resulted in polymerization and decomposition.

4-(2-Oxo-1,3-dioxolan-4-yl)methyl Itaconate. Into a three-necked 500-ml. round-bottomed flask equipped with stirrer, nitrogen inlet tube, and condenser fitted with an exit drying tube, was placed 55.6 g. (0.5 mole) of itaconic anhydride, 56 g. (0.5 mole) of glyceryl carbonate, and 250 ml. of benzene which had been dried over sodium. The reagents were allowed to react in a nitrogen atmosphere at 60°C. for 48 hr. The solution was cooled and on standing at room temperature or in a refrigerator crystals of the ester product formed which were separated by filtration. A 111 g. (97%) yield of product was obtained. The product was recrystallized from water, m.p. 133–134°C.

ANAL. Calcd. for $C_9H_{10}O_7$: C, 47.00%; H, 4.35%. Found: C, 46.85%; H, 4.47%.

The infrared spectrum shows the expected ester, vinyl, and carbonyl bands as well as the carbonate band at 5.55 μ.

(2-Oxo-1,3-dioxolan-4-yl)methyl Maleate. Into a three-necked 500-ml. round-bottomed flask equipped with stirrer and condenser was placed 49.0 g. (0.5 mole) of maleic anhydride, 59 g. (0.5 mole) of glyceryl carbonate, and 250 ml. of benzene which had been dried over sodium. The reagents were allowed to react at 60°C. for 48 hr. The solution was cooled and on standing at room temperature or in a refrigerator, crystals of the ester product formed which were separated by filtration. A 103.7 (96%) yield of product was obtained. The product was recrystallized from water, m.p. 112–113°C.

ANAL. Calcd. for $C_8H_8O_7$: C, 44.44%; H, 3.70%. Found: C, 44.96%; H, 3.77%.

The infrared spectrum shows the expected ester, vinyl, and carboxyl bands as well as the carbonate band at 5.55 μ.

Itaconic Anhydride. 130-g. portion of itaconic acid (1 mole) was added to a 1000-ml. three-necked flask equipped with a stirrer, thermometer, and a 1-ft. Vigreux column fitted with an adapter and condenser for distillation. Then, 408 g. (4 moles) of acetic anhydride was added and the contents heated with agitation to 60–70°C., at which time a solution resulted. Then, the pressure was lowered to about 30 mm. and approximately 200 ml. of acetic acid distilled over. The temperature of the reaction flask was maintained at 70–74°C. with an electric heating mantle. The solution was filtered hot and cooled overnight in the refrigerator. The product crystallized from the mother liquor and was recrystallized from fresh acetic anhydride, washed with ether to remove the acetic anhydride, and recrystallized from chloroform–ether. The concentration of mother liquor afforded second and third crops of crystals which were purified in the above manner. An 89.7 g. (80%) yield of product, m.p. 67–68°C. was obtained.

ANAL. Calcd. for $C_6H_4O_3$: C, 53.57%; H, 3.57%. Found: C, 53.53%; H, 3.61%.

Homopolymerization

The homopolymer of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate was prepared by polymerizing a 50% toluene solution of the monomer at 40°C. to a 30% conversion, 0.1 wt.-% 2,2′-azobisisobutyronitrile being used as the initiator. The solution was filtered, the polymer precipitated in methanol, isolated, redissolved in dimethylformamide, and reprecipitated in methanol, again redissolved and reprecipitated, isolated, washed with more methanol, and dried in a vacuum oven at 30°C.

The homopolymer of 4-(2-oxo-1,3-dioxolan-4-yl)methyl itaconate was also prepared by polymerizing a 50% toluene solution of the monomer at 40°C. to a 27% conversion, 0.2 wt.-% benzoyl peroxide being used as the initiator. The procedure used for its isolation and purification was similar to that used for the acrylate except that hexane instead of methanol was used as the precipitant.

Reactivity Ratio Determinations

Solution polymerizations in toluene or dimethylformamide were run under a nitrogen atmosphere in 75 by 20 mm. screw-cap vials. Polymerization was initiated by benzoyl peroxide, usually at 0.1 wt.-% based on monomer. Temperatures were kept at 50 ± 0.2°C. Conversions were kept below 10%, generally well below 5%. The polymers were precipitated by pouring the polymer solution into water–methanol or hexane at room temperature. Purification was affected by at least three reprecipitations. The purified polymers were dried in a vacuum oven at 50°C., to constant weight, and the composition of the copolymers was determined by carbon, hydrogen, and oxygen analyses performed by Midwest Micro Laboratory, Indianapolis, Indiana.

Reactivity ratios were determined from the differential form of the general copolymerization equation by the method of intercepts.[9]

The comonomers styrene, vinyl acetate, methyl methacrylate, and methyl acrylate used in the copolymerizations were purified immediately before use by distillation. Hexyl methacrylate was purified[10] by washing the monomer free of inhibitor with base, drying the monomer over anhydrous sodium sulfate, and distilling *in vacuo*.

Post-Polymerization Reactions

Ultraviolet Irradiation. Films of poly-(2-oxo-1,3-dioxolan-4-yl)methyl acrylate, poly-4(2-oxo-1,3-dioxolan-4-yl)methyl itaconate, and selected copolymers were irradiated with ultraviolet light from a 100-w. medium pressure mercury lamp which emits light from 254 to 365 mμ and from a

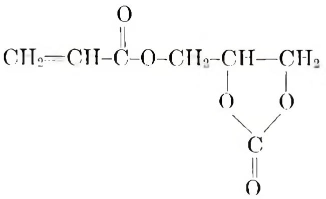
450-w. high-pressure mercury Hanovia immersion lamp emitting light at 254, 313, and 365 mμ.

Thermal Treatment. Films identical to those subjected to radiation were heated at temperatures varying from 50–250°C.

RESULTS AND DISCUSSION

Monomer Syntheses

The monomer (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (III) was synthesized by a modification of the method investigated by Caiola,[11] by the reaction of glyceryl carbonate and acrylyl chloride in the presence of triethylamine as the base.



III

The glyceryl carbonate was prepared from the uncatalyzed reaction of glycerol and propylene carbonate at 110°C. and 35 mm. pressure with propylene glycol distilling as the by-product.[12] To assure that the glyceryl carbonate, which is a clear, water-white, very viscous liquid, was not a linear polycarbonate ester such as $CO(OCH_2CHOHCH_2OH)_2$ and higher members, its molecular weight was determined by the Beckman melting-point depression method with water as the solvent. It was found that glyceryl carbonate is highly associated and that the molecular weight could be obtained only by extrapolation from the ΔT values as $C \rightarrow 0$. The concentrations used were 10, 5, 2, 1, and 0.5 wt.-%. The product had molecular weight 118 ± 2.1 (calculated: 118). The acrylyl chloride was prepared by the procedure reported by Rehberg[13] whereby benzoyl chlo-

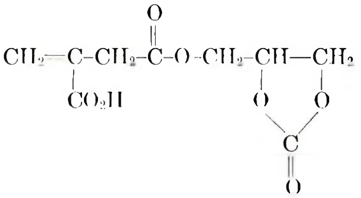
TABLE I
Infrared Spectrum Characteristics of Monomer III

Absorption band, μ	Assignment
5.55	C=O (carbonate)
5.8	C=O
6.15	C=C
7.15	C=C
8.6	C—O (carbonate)
10.2	C=C
10.9	C=C
12.34	Appears to be characteristic of the acrylate structure, —C=C—COO

ride is reacted with acrylic acid. The acrylyl chloride boiled at 75.5–76°C. and was stored under nitrogen in a refrigerator until ready for use. In contrast, when it was prepared from acrylic acid and phosphorus trichloride,[14] the resulting acrylyl chloride was contaminated with phosphorus compounds and polymerized on standing in the cold.

Monomer characterization was accomplished by its infrared spectrum. The principal characteristics of the spectrum are given in Table I.

The monomer 4-(2-oxo-1, 3-dioxolan-4-yl)methyl itaconate (IV), was



IV

prepared from glyceryl carbonate and itaconic anhydride.

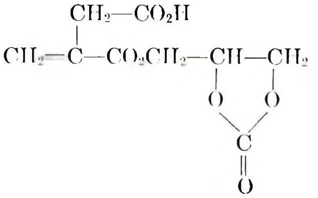
Itaconic anhydride, m.p. 67–68°C., was prepared from an exchange reaction of itaconic acid and acetic anhydride. This method of preparation has advantages over the conversion of citric acid to itaconic anhydride,[15] as the yields and purity were higher and the reaction scale larger.

Monomer IV was characterized by its infrared spectrum (Table II) and by its pK_a.

TABLE II
Infrared Spectrum Characteristic of Monomer IV

Absorption band μ	Assignment
3.4–3.8 (broad band)	COOH
5.55	C=O (carbonate)
5.80	C=O
6.00	C=O
6.15	C=C
8.60	C—O
10.20	C=C
10.90	C=C
12.34	C=C—COO

The pK_a was used to differentiate monomer IV from its isomer (V).[16] In Table III the pK_a value and the dissociation constant of the product are compared with the known constants for acrylic and acetic acids.



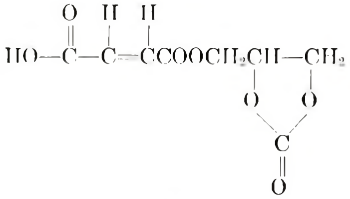
V

TABLE III
pK_a Values and Dissociation Constants at 25°C.

Compound	pK_a	Dissociation constant
4-(2-Oxo-1,3-dioxolan-4-yl)methyl itaconate	4.20	6.48×10^{-5}
Acrylic acid	4.24	5.60×10^{-5}
Acetic acid	4.75	1.75×10^{-5}

Clearly, the pK_a is typical of the α,β-unsaturated acid and the structure of the product corresponds to IV.

The monomer (2-oxo-1,3-dioxolan-4-yl)methyl maleate (VI) was synthesized from glyceryl carbonate and maleic anhydride. Its infrared spectrum was similar to that of IV with characteristic absorption bands at 3.4–3.8, 5.55, 5.8, 6.0, 6.15, 8.6, 10.2, 10.9, and 12.35 μ.



VI

The reaction of glyceryl carbonate, which is a primary alcohol, with the acid anhydrides such as maleic, itaconic, and acrylic anhydrides or with acid chlorides such as acrylyl and methacrylic chlorides was very facile. In the case of the itaconic and maleic anhydrides, the isolation of the resulting hemi-ester was simple since they crystallized easily from the benzene or toluene solution. The purification of these two solid esters was expediently accomplished by recrystallization. The purification of the acrylic ester proved to be difficult. The benzene solvent, in which it was prepared, was removed readily by distillation at reduced pressures leaving the oily ester product. All attempts to purify the crude ester by crystallization techniques were unsuccessful since only glasses were obtained when it was cooled to low temperatures. Also, all attempts to purify the ester by distillation even at pressures as low as 10^{-4} mm. were unsuccessful, since polymerization occurred whenever the ester was heated to temperatures of about 40°C. or higher. This polymerization was experienced whether the esters were prepared from acrylyl chloride or acrylic anhydride. This type of polymerization was not inhibited or retarded by increasing the amount of inhibitors, nor was it experienced when propyl or hexyl acrylates were synthesized by identical procedures. This would indicate that most or all of the polymerization was occurring through the carbonate moiety. This is in contrast to glyceryl carbonate, which can be heated[12] to 100–110°C. without decomposition; at 145°C. it decomposes[17] to carbon dioxide and glycidol. However, its decomposition temperature was lowered greatly and the rate of decomposition accelerated by the deliberate addition of ionic impurities such as sodium carbonate, trimethylamine, trimethylamine hydrochloride, phosphorus, phosphoric and sulfuric acids, and phosphorus trichloride, especially in the presence of water.

Similarly, it was found that the acetate of glyceryl carbonate, (2-oxo-1,3-dioxolan-4-yl)methyl acetate, when free of ionic-type impurities, could be distilled b.p. 122–124°C./0.9 mm. However, the addition of small quantities, less than 1%, of such impurities, caused decomposition with the elimination of carbon dioxide. The carbon dioxide was identified by its conversion to barium carbonate by passing the gas through a clear saturated aqueous solution of barium hydroxide. The acrylic ester was prepared in toluene in about a 10% solution, and no polymerization was observed when the solvent was removed under reduced pressure until a 50–80% concentration of polymer in solvent was reached and the pot temperature reached 40°C. At higher temperatures the polymerization was accelerated and carbon dioxide was identified as the gaseous product. For this reason, the monomer was isolated with a pot temperature fixed at 0–5°C. and a pressure reduced to 0.2 mm. or lower. The monomer thus isolated did not cloud methanol or heptane when added to them. Apparently, the instability of the monomer is due to small amounts of impurities. These can best be removed from the polymers and copolymers by precipitation of the polymers. As shown herein, later, the reprecipitated homopolymers do not crosslink readily below 100°C. unless catalyzed and in this respect are similar to glyceryl carbonate and its acetate. A number of other syntheses for the acrylate monomer were evaluated. The transesterification[8] of methyl or ethyl acrylate with glyceryl carbonate in the presence of sodium methoxide gave a number of products, the major portion of which were substituted propoxy derivatives of the β-propionic ester.

The uncatalyzed or catalyzed reactions of glyceryl monoacrylate with ethyl carbonate, ethylene or propylene carbonate,[12,17] or phosgene were either very poor or gave products of unsatisfactory elemental analyses. The synthesis from acrylyl chloride and glyceryl carbonate with an aliphatic tertiary amine as the hydrohalide acceptor was eventually selected as the most desirable reaction. The use of pyridine or dimethylaniline produced undistilled esters having very yellow and dark-purple colors, respectively. When hydroquinone was used as a polymerization inhibitor in the synthesis, yellow-colored esters were obtained, whereas the use of benzoquinone and naphthoquinone yielded products of brown and dark-red color, respectively. In contrast, an almost colorless monomer was obtained when 2,6-di-*tert*-butyl-*p*-cresol and *tert*-butyl catechol were used. To avoid a high concentration of triethylamine in the reaction system it was added dropwise followed by the addition, dropwise, of the acrylyl chloride. The temperature of the initial addition of the acid chloride was maintained low to avoid the formation of esters containing halogen in the glyceryl moiety.

TABLE IV

Reactivity Ratios of (2-Oxo-1,3-dioxolan-4-yl)methyl Acrylate (M_2) with Comonomers

Comonomer (M_1)	r_1	r_2	Q_1[a]	e_1[a]	Q_2	e_2
Styrene	0.80 ± 0.06	0.20 ± 0.06	1.00	−0.80	0.42	0.60
Vinyl acetate	0.049 ± 0.012	10.20 ± 0.40	0.026	−0.22	0.44	0.61
Hexyl methacrylate	1.50 ± 0.13	0.66 ± 0.08	0.70	−0.12	0.46	0.62
Methyl methacrylate	1.83 ± 0.20	0.521 ± 0.03	0.74	0.40	0.44	0.61
Methyl acrylate	0.965 ± 0.15	1.04 ± 0.10	0.42	0.60	0.44	0.61
				Avg.	0.44	0.61

[a] Data of Young.[20]

Homopolymerization

Free-radical initiators such as benzoyl peroxide and azobisisobutyronitrile caused the homopolymerization of the acrylate (III) and the itaconate (IV) monomers readily, whereas the maleate monomer (VI) was reluctant to do so. Irradiation of the acrylate monomer (III) through Pyrex glass at room temperature with ultraviolet light of wavelength 310–370 mμ for periods of 1–15 min. failed to produce polymer. The irradiation of methyl methacrylate and ethyl acrylate through Pyrex glass with a 450-w. high-pressure mercury Hanovia immersion lamp at 55°C. for 2 hr. produced little or no polymer. This is compatible with the findings of Ungnade and Ortega,[18] who showed that other acrylic esters show no maximum above 210 mμ. In this respect, this acrylic carbonate monomer (III), differs from the acrylic ketal monomer, (2,2-dimethyl-1,3-dioxolan-4-yl)-methyl acrylate[11] which on irradiation under the same conditions described above, underwent in 1 min. a 50% conversion of monomer to polymer and in 15 min. yielded an infusible, insoluble, rubbery polymer. This appears to be a clear indication that the 1,3-dioxolane moiety does not of itself contribute ultraviolet sensitivity and that the nature of the substituent on the 2-carbon of the dioxolane ring, as shown in I and II is a contributing factor. It is of interest to determine whether or not this ultraviolet-induced reactivity is maintained if the 2-methyl groups are replaced by hydrogen, higher alkyl, or aryl structures.

Solution polymerization of monomers III and IV in toluene at 50°C. with azobisisobutyronitrile and benzoyl peroxide, respectively, as initiators afforded workable polymers. Inherent viscosities in dimethylformamide for poly[(2-oxo-1,3-dioxolan-4-yl)methyl acrylate) of 1.04 and for poly[4-(2-oxo-1,3-dioxolan-4-yl)methyl itaconate] of 0.62 were obtained.

Copolymerization

These reactive vinyl monomers were copolymerized with a number of comonomers. The r_1 and r_2 values obtained for these copolymerizations are shown in Tables IV–VI. In addition, the Alfrey-Price equations[19] were used to calculate Q and e values.

The copolymers of monomer III and monomer IV were all random copolymers and in this respect are similar[1] to the corresponding 2,2-dimethyl-

TABLE V
Reactivity Ratios of 4-(2-Oxo-1,3-dioxolan-4-yl)methyl Itaconate (M_2) with Comonomers

Comonomer (M_1)	r_1	r_2	Q_2	e_2
Styrene	0.18 ± 0.05	0.25 ± 0.10	1.36	1.00
Vinyl acetate	0.02 ± 0.01	3.35 ± 0.05	0.91	1.42
Methyl methacrylate	1.38 ± 0.25	0.24 ± 0.15	0.82	1.45
Methyl acrylate	0.45 ± 0.04	1.44 ± 0.40	1.39	1.26
		Avg.	1.12	1.28

TABLE VI
Reactivity Ratios of (2-Oxo-1,3-dioxolan-4-yl)methyl Maleate (M_2) with Comonomers

Comonomer (M_1)	r_1	r_2	Q_2	e_2
Styrene	0.74 ± 0.03	0.10 ± 0.05	0.37	0.82
Vinyl acetate	0.05 ± 0.01	0.09 ± 0.02	0.31	2.11
Methyl methacrylate	7.50 ± 0.50	0[a]	0.24[a]	2.61[a]
Methyl acrylate	9.10 ± 0.40	0.10 ± 0.02	0.08	1.57
		Avg.	0.25	1.78

[a] Calculated by assuming $r_2 = 0.001$.[20]

1,3-dioxolane-containing monomers. The r_2 values for both monomers III and IV are much higher than the r_1 value for vinyl acetate, indicating that their radicals prefer to react with their own monomers than with vinyl acetate. The low and zero r_2 values of monomer VI show that this monomer has little or no tendency to react with itself. In copolymerizations of VI with methyl methacrylate where $r_1 = 7.5 \pm 0.5$ and $r_2 = 0$, a copolymer rich in methyl methacrylate was formed even at low initial methyl methacrylate concentrations. In copolymerization of VI with vinyl acetate, both monomers show a high preference for reaction with the comonomer rather than with itself.

The intrinsic viscosity of selected samples of copolymers was determined by using an Ubbelohde dilution viscometer. The usual[21] two-line plot of reduced viscosity and inherent viscosity versus concentration was used. Results are shown in Table VII.

The intrinsic viscosities indicated that the molecular weights of these copolymers were high.

TABLE VII
Intrinsic Viscosity [η] of Copolymer Samples

Copolymer composition	Solvent	[η]
Methyl methacrylate (89%), (2-oxo-1,3-dioxolan-4-yl)methyl acrylate (11%)	Toluene	1.41
Vinyl acetate (73%), 4-(2-oxo-1,3-dioxolan-4-yl)-methyl itaconate (27%)	Dimethylformamide	1.28
Styrene (68%), (2-oxo-1,3-dioxolan-4-yl)methyl maleate (32%)	Toluene	0.93

Post-Polymerization Reactions

Ultraviolet Irradiation. Post-polymerization reactions to obtain crosslinked polymers from linear polymers are well known in the literature. Chemical crosslinking agents are employed when the pendant group contains a related functional group. For example, polyacrylate esters containing hydroxyl groups in the ester portion can be crosslinked[22] with polyepoxides or with polyisocyanates. Light and radiation have also been used to crosslink polymers. Poly-α-olefins have been reported to crosslink by ultraviolet light in the presence of a sensitizer[23] and by neutron radiation.[24] Recently, poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl acrylate] was shown[11] to crosslink very readily without added sensitizers when irradiated with ultraviolet light from a 100-w. mercury lamp emitting light in the 254–365 mμ region. In contrast, when a film of poly[(2-oxo-1,3-dioxolan-4-yl)methyl acrylate] was irradiated similarly for 1–15 min., the polymer remained soluble and fusible. After 1 hr. of irradiation only 22% of the polymer had crosslinked. These results are comparable to those obtained with other polyacrylates.

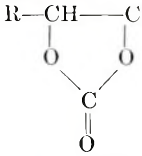
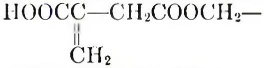
Jacobs and Steel[25] have reported the crosslinking of poly(ethyl acrylate) by ultraviolet irradiation. They found that no crosslinking occurred with 254 mμ ultraviolet light for 30 min., and only 50% of the polymer crosslinked after 1 hr.

Films of representative copolymers were also cast on a flat 2 × 3-in. glass plate, dried, and weighed. The films were irradiated with ultraviolet light from the lamp described above. The plates were then submerged in boiling toluene for 5 min., then in boiling dimethylformamide for 5 min. The plates were then dried and weighed. Both the nonirradiated and the irradiated films prepared in the same manner were completely dissolved as evidenced by weight measurements of the glass plates. Again, this is in contrast to the polymers containing the 2,2-dimethyl-1,3-dioxolane structure, all of which crosslinked when similarly irradiated.[11] As in the case of the corresponding monomers, this is another indication that the 1,3-dioxolane structure does not, of itself, contribute ultraviolet sensitivity to the polymer but that the nature of the substituent on the 2-carbon of the dioxolane ring, as shown in I and II is a contributing factor.

Thermal Treatment. Various samples of the homopolymers and copolymers were immersed in neutral mineral oil in a tube in which was inserted a thermometer; the tube was heated slowly from room temperature at 2°C./min. to the temperature at which CO_2 gas was liberated by the polymer. The acrylic poly(III) which had been thrice reprecipitated showed CO_2 elimination at about 210°C., whereas the same polymer which had not been purified eliminated CO_2 at about 110°C. The acidic itaconyl polymer (IV) eliminated CO_2 at about 135°C. and the acidic 1:1 methyl methacrylate–maleate copolymer (VI) eliminated CO_2 at about 155°C. Films of these same polymers cast on glass plates were heated for 1 hr. at the same temperature at which CO_2 elimination was observed. Foaming occurred in all cases and the resulting films were found to be insoluble in toluene and dimethylformamide, indicating also, that crosslinking had occurred. These results are in agreement with similar studies made on nonpolymeric cyclic carbonates, the results of which are shown in Table VIII.

It is readily observed that those carbonates which contain the free carboxyl group have a CO_2 elimination temperature lower by 50°C. or more than the

TABLE VIII
Temperature of Liberation of CO_2 from Certain Organic Cyclic Carbonates

Structure  where R is	Temperature, °C.	Temperature, °C. with 1 wt.-% of	
		$(C_2H_5)_3N\cdot HCl$	H_3PO_4
H—	208–210	153	170
CH_3—	224–226	160	185
$HOCH_2$—	200	171	168
$ClCH_2$—	220–225	170	189
$HOOCCH_2CH_2COOCH_2$—	140	102	116
HOOCCH=CHCOOCH_2—	150	106	125
 $HOOC\underset{\underset{CH_2}{\parallel}}{C}—CH_2COOCH_2—$	135–140	103	114
o-$HOOCC_6H_4COOCH_2$—	125	105	108
CH_3COOCH_2—	212	132	172

carbonates not containing carboxyl. This indicates that the reaction may be catalyzed by acids and proceeds through an ester exchange mechanism. To confirm this observation the prototype experiments were repeated with the addition of 1 wt.-% of phosphoric acid and triethylamine hydrochloride respectively. In all cases a noticeable drop in the CO_2-elimination temperature was observed, as shown in Table VIII. Salts, other than amine salts, for example, $AlCl_3$, and other acids, such as sulfuric acid, can also catalyze[27] the reaction even in those cyclic compounds which contain a free carboxylic group as shown in Table IX.

TABLE IX
Temperature of Liberation of CO_2 From
 by 1%
of Various Added Substances

Substance	Initial temperature of CO_2 elimination, °C.
$FeSO_4$	112
$NaHSO_4$	112
$CeSO_4$	118
$ZnCl_2$	112
Na_2CO_3	112
None	140

Accordingly, when 0.2% of triethylamine hydrochloride was added to a 45% solution of the acrylate polymer (III) and the mixture heated to 50°C., a crosslinked gel was obtained in 2 hr. Polymer and copolymer films to which catalysts had been added were found similarly to crosslink at lower temperatures than the corresponding films which did not contain these additives.

The mechanism of the CO_2 elimination in the neutral cyclic carbonates and in the reprecipitated acrylic polymer appears to be different than the carboxyl-containing cyclic carbonates and polymers. When heated to above 150°C. glyceryl carbonate yields[17] glycidol, $(\mathrm{HOCH_2}\overline{\mathrm{CH{-}CH_2{-}O}})$, CO_2, and low molecular weight polyethers; when the acrylate polymer (III) was heated, a crosslinked polymer was obtained with the elimination of CO_2. The infrared spectrum of the crosslinked polymer shows a decrease in the carbonate band at 5.55 μ with the appearance of the epoxy bands at 8.02, 11.11, and 11.92 μ and of ether bands at 3.5 and 9.0 μ. The mechanism probably involves the homolytic cleavage of the carbonate ring with the elimination of CO_2 followed by ring closure to the epoxide or by chain extension to polyethers.

In contrast, the infrared spectra of the crosslinked polymers obtained by heating a polymer having carboxyl groups (IV) shows a marked decrease in the carboxyl band at 3.4–3.8 μ, a decrease in the carbonate band at 5.55 μ, and the appearance of hydroxyl bands at 2.77–2.80 μ. These changes in spectra can be explained readily on the basis of an ionic transesterification reaction involving an opening of the carbonate ring followed by the elimination of CO_2. Similar changes in band spectra at 2.77–2.80, 3.4–3.8, and 5.55 μ are found when the succinyl monoester of glyceryl carbonate is heated to 140–150°C.

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References

1. G. F. D'Alelio and R. J. Caiola, *J. Polymer Sci. A-1*, **5**, 285 (1967).
2. R. C. Elderfield, *Heterocyclic Compounds*, Wiley, New York, 1957, Vol. 5, p. 16.
3. W. W. Pigman and R. M. Goepp, Jr., *Chemistry of the Carbohydrates*, Academic Press, New York, 1948, p. 348.
4. H. Hibbert, M. S. Wheeler, and N. M. Carter, *J. Am. Chem. Soc.*, **51**, 302 (1929).
5. J. B. Bell, Jr., V. A. Currier, and J. D. Maldemus, U.S. Pat. 2,915,529 (1959).
6. H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **74**, 2100 (1952).
7. J. L. O'Brien and E. M. Beavers, U.S. Pat. 2,979,514 (April 11, 1961).
8. J. C. Fang, U.S. Pat. 2,967,173 (January 3, 1961).
9. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **64**, 2356 (1942).
10. E. H. Riddle, *Monomeric Acrylic Esters*, Reinhold, New York, 1954, p. 15.
11. R. J. Caiola, Ph.D. Thesis, University of Notre Dame, 1966.
12. *Propylene Carbonate*, Tech. Bull., Jefferson Chemical Company, Inc., July 1952, p. 9.
13. G. H. Stemple, R. P. Cross, and R. P. Mariello, *J. Am. Chem. Soc.*, **72**, 2299 (1950).
14. C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Am. Chem. Soc.*, **67**, 1209 (1945).
15. R. L. Shriner, S. G. Ford, and L. J. Roll, in *Organic Syntheses*, Coll. Vol. II, A. H. Blatt, Ed., Wiley, New York, 1943, p. 368.
16. G. F. D'Alelio and L. X. Mallavarpau, *Makromol. Chem.*, **37**, 25 (1960).
17. H. A. Bruson, U.S. Pat. 2,636,040 (April 21, 1953).

18. H. E. Ungnade and I. Ortega, *J. Am. Chem. Soc.*, **73**, 1564 (1951).
19. T. Alfrey, Jr. and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).
20. L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).
21. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 34.
22. Courtaulds Ltd., Belg. Pat. 615,113 (1962).
23. K. Soumelis and H. Wilski, *Kunststoffe*, **52**, 471 (1962).
24. A. Charlesby, *Proc. Roy. Soc.* (*London*), **A215**, 187 (1952).
25. H. Jacobs and R. Steele, *J. Appl. Polymer Sci.*, **3**, 236 (1960).
26. H. Jacobs and R. Steele, *J. Appl. Polymer Sci.*, **3**, 245 (1960).
27. *Ethylene Carbonate*, Tech. Bull., Jefferson Chemical Company, Inc., November 1952.

Résumé

Les syntheses et polymérisations de l'acrylate de (2-oxo-1,3-dioxolane-4-yl) méthyle et de l'itaconate de (4-2-oxo-1,3-dioxolane-4-yl)méthyle et du maléate de (2-oxo-1,3-dioxolane-4-yl)méthyle ont été décrites. Les rapports de réactivité en cours de copolymérisation de ces monomeres avec d'autres comonmères sont rapportés et les valeurs d'Alfrey-Price Q et e ont été calculées. Les effets de post-polymérisation par la lumiere ultraviolette et la chaleur de ces polymères et copolymères sont présentés et comparés aux polymeres similaires contenant des groupes de 2,2-diméthyl-1,3-dioxolane qui agissent comme un sensibilisateur ultraviolet intramoléculaire. Les dérivés 2-oxo sont pontés thermiquement mais non pas à la lumière ultraviolette. La réaction de pontage peut être catalysée par les acides, les bases et les sels.

Zusammenfassung

Synthese und Polymerisation von (2-Oxo-1,3-dioxolan-4-yl)methylacrylat, 4-(2. Oxo-1,3-dioxolan-4-yl)-methylitaconat und (2-Oxo-1,3-dioxolan-4-yl)-methylmaleat werden beschrieben. Reaktivitätsverhältnisse bei der Copolymerisation dieser Monomeren mit anderen Comonomeren werden angegeben und die Q und e-Werte nach Alfrey-Price berechnet. Die Nachpolymerisationseffekte bei Ultraviolettlichtund Wärmeeinwirkung auf die Polymeren und Copolymeren werden angeführt und mit denjenigen bei ähnlichen Polymeren mit der 2,2-Dimethyl-1,3-dioxolan-gruppe, welche als innerer Ultraviolettsensibilisator wirkt, verglichen. Die 2-Oxoderivate werden zwar thermisch aber nicht durch Ultraviolettlicht vernetzt. Die Vernetzungsreaktion kann mit Säuren, Basen und Salzen katalysiert werden.

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Linear Polymers of Allyl Acrylate and Allyl Methacrylate

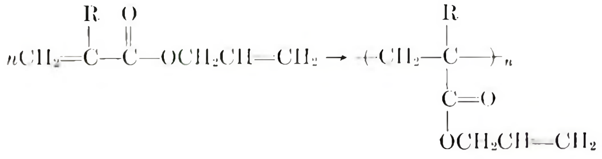
G. F. D'ALELIO and T. R. HOFFEND,*
University of Notre Dame, Notre Dame, Indiana 46556

Synopsis

Allyl acrylate and allyl methacrylate were polymerized by anionic initiators to soluble linear polymers containing allyl groups in the pendant side chains. The pendant unpolymerized allyl groups of the resulting linear poly(allyl acrylates) were shown to be present by: (*1*) the disappearance of the acrylyl and methacrylyl double bond absorptions in the infrared spectra in the conversions of monomers to polymers; (*2*) postbromination of the allyl bonds in the linear polymer; (*3*) the disappearance of the allyl group absorptions in the infrared spectra of the brominated linear polymers; and (*4*) the thermal- and radical-initiated crosslinking of the linear polymers through the allyl groups. Allyl acrylate and allyl methacrylate show great reluctance to copolymerize with styrene under anionic initiation, but copolymerize readily with methyl methacrylate and acrylonitrile. Block copolymers were prepared by reacting allyl methacrylate with preformed polystyrene and poly(methyl methacrylate) anions. The linear polymers and copolymers of allyl acrylate may be classified as "self-reactive" polymers which yield thermosetting polymers. Bromination of the linear polymers offers a convenient method of producing self-extinguishing polymers.

INTRODUCTION

As prototypes for a class of polymers containing acetylenic groups in the pendant side chains,[1] it was deemed advisable first to prepare related prototype polymers containing vinyl groups. This prototype class of polymers can be represented by the general structure II, wherein R = H or CH_3:



$$n\,CH_2{=}\overset{\overset{\displaystyle R}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH{=}CH_2 \rightarrow -\!\!\left(CH_2-\underset{\underset{\displaystyle OCH_2CH{=}CH_2}{\underset{|}{\underset{\displaystyle C{=}O}{|}}}}{\overset{\overset{\displaystyle R}{|}}{C}}\right)\!\!-_n$$

I II

This polymer is a linear polyacrylate containing allyl groups in the pendant side chains.

It can be seen that the repeating unit in the desired polymer is derivable theoretically from an acrylic monomer of the general structure I, which contains two unsaturated and potentially reactive polymerization sites.

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* Present address: Xerox Corporation, Rochester, New York.

In order to use such a monomer to obtain the desired polymer, it is necessary to choose an initiator which will react only with the acrylyl vinyl groups and not with the allyl group.

Since both vinyl and allyl groups are susceptible usually to attack by both radical and cationic initiators, one would expect the radical or cationic polymerization of I to lead to an insoluble, crosslinked product.[2a]

Anionic as well as cationic initiators also polymerize some multivinyl monomers such as ethylene dimethacrylate to insoluble, infusible polymers because both unsaturated moieties react with the initiator.[2b] However, marked differences are found in the reaction of anionic-type initiators on different vinyl moieties.[3-5] Accordingly, it should be possible to prepare linear polymers by the anionic polymerization of monomers containing one vinyl group, for example, $CH_2{=}CH—$ or $CH_2{=}C(CH_3)—$ attached to an electron-withdrawing group, such as $—C(O)O—$ which renders the vinyl group responsive to anionic polymerization, and a second vinyl-type group, such as $—CH_2—CH{=}CH_2$, which is usually nonresponsive to anionic initiation. The linearity of the polymer may then be demonstrated by reacting the unpolymerized vinyl group under other and different conditions after the linear polymer has been produced. Allyl acrylate (AA) and allyl methacrylate (AMA) were chosen as the model monomers for this study.

The purpose of this study is to prepare linear polymers and copolymers of AA and AMA by means of appropriate initiators; this paper describes the polymerization of these two monomers under the influence of various radical, cationic, and anionic initiators. The chemical and spectroscopic methods used in determining the structures of the resulting polymers are given. Also described are the anionic copolymerizations of AA and AMA with various vinyl monomers, and the preparation of block copolymers with polystyrene and poly(methyl methacrylate) anions.

RESULTS AND DISCUSSION

Polymerizations

Allyl acrylate and allyl methacrylate were subjected to radical and cationic polymerizations using benzoyl peroxide and aluminum chloride, respectively, as the initiators. In each case, the expected insoluble, crosslinked polymer was obtained. These results parallel the similar polymerizations of the multivinyl monomers, ethylene diacrylate (EDA) and ethylene dimethacrylate (EDMA). On the other hand, it was believed that the anionic polymerization of EDA and EDMA would lead to insoluble, infusible polymers and that similar polymerizations of AA and AMA would lead to linear, soluble, polymers with pendant allyl groups. The linear polymers would be the result of the polymerization substantially through the acrylic group of the AA and AMA monomers. To demonstrate this point, EDA, EDMA, AA, and AMA were subjected to polymerization reactions using as initiators, *n*-butyllithium and sodium naphthalene; the latter representing the class of radical-anion initiators. With both initiators, the polymerization of EDA and EDMA afforded insoluble, crosslinked polymers. The polymers obtained from AA and AMA with these same initiators were soluble in a number of organic solvents and softened to viscous liquids or masses at higher temperatures. That the allyl group did not react with these initiators was demonstrated by the failure of allyl acetate and diallyl phthalate to yield polymers under identical conditions. The formation of linear, soluble polymers from AA and AMA in contrast to the insoluble, crosslinked polymers obtained from EDA and EDMA points to an essential difference between the two classes of monomers. All of these monomers have two vinyl groups; however, both AA and AMA have only one vinyl group activated by an electron-withdrawing structure whereas EDA and EDMA have two such activated vinyl groups and, therefore, yield crosslinked polymers.

The results of the polymerizations given in Table I indicate that polymerization is occurring only through the acrylyl or methacrylyl moiety. The difference in conversions of AMA and AA to polymers is similar to the differences found in the anionic polymerizations of alkyl methacrylates and acrylates.[6,7] Allyl methacrylate and methyl methacrylate[6,7] (MMA) can be polymerized substantially quantitatively at −70°C. whereas the conversions of AA are not quantitative and are sensitive to temperature. In this respect, AA is similar to isopropyl acrylate.[6,7]

The conversions reported are based on the sum of the amounts of hexane-insoluble polymer precipitated from the reaction solution by addition to hexane and of the hexane-soluble lower molecular weight polymers recovered from the hexane solution by evaporation. In the polymerizations conducted at −70°C., the amount of hexane-insoluble polymer was negligible, while at −40 and −20°C. they averaged about 4 and 7%, respectively. Anionic polymerizations of methyl methacrylate with *n*-butyllithium have been reported to yield appreciable amounts of hexane-soluble polymers[7,8] which were attributable to side reactions involving the attack of butyllithium on the carbonyl of the monomer. The molecular weight distribution of poly(methyl methacrylate) prepared by anionic initiation has been shown to be broad,[7,8] and undoubtedly is also broad in these allyl acrylic ester polymers, as evidenced by the presence of low molecular weight polymers.

The intrinsic viscosities given in Table I are those of the hexane-insoluble polymers and some relative values of their molecular weights may be estimated from other viscosity–molecular weight relationships: $[\eta] = 5.2 \times 10^{-5}M^{0.76}$ in benzene for poly(methyl methacrylate);[7] $[\eta] = 7.15 \times 10^{-5}M^{0.75}$ in acetone for poly(butyl acrylate).[9]

From these equations, it is estimated that for the AA and AMA polymers, the highest molecular weights prepared were of the order of 100,000 and 150,000, respectively, and the lowest molecular weights were of the order of 15,000 and 20,000, respectively.

TABLE I
Anionic Polymerization of Allyl Acrylate and Allyl Methacrylate

Monomer	Monomer concn., %	Solvent	Initiator[a]	Time, min.	Temp., °C.	Conversion, %	$[\eta]$
AMA	25.4	THF	SN	60	−70	97.3	0.574
AMA	25.2	TN	SN	60	−70	96.4	0.531
AMA	10.2	THF	SN	90	−70	97.1	0.433
AMA	10.4	THF	SN	90	−70	95.8	0.410
AMA	10.1	THF	*n*-BuLi	90	−70	90.1	0.387
AMA	10.2	TN	*n*-BuLi	90	−70	93.5	0.399
AMA	10.0	THF	SN	90	−40	89.3	0.262
AMA	10.1	THF	SN	90	−20	70.4	0.118
AA	20.1	THF	SN	120	−70	89.6	0.404
AA	20.3	THF	SN	120	−70	87.2	0.378
AA	20.0	THF	*n*-BuLi	120	−70	84.3	0.355
AA	20.2	THF	SN	120	−40	80.1	0.141
AA	20.0	THF	SN	120	−20	66.2	0.093

[a] SN = sodium naphthalene; THF = tetrahydrofuran; TN = toluene.

Kinetic measurements to determine the effect of monomer and initiator concentrations on rate of polymerization, molecular weight, and microstructure of the polymers are in progress.

The uninhibited linear polymers of AA and AMA are relatively unstable in air, tending to crosslink through the pendant allyl group. The AMA polymers appear to be much more sensitive to crosslinking than the AA polymers. On standing in air for 74 hr. at room temperature, the intrinsic viscosity of a sample of AMA polymer, $[\eta] = 0.574$, increased to 4.40 and became insoluble in seven days. On a similar exposure of a sample of AA polymer, $[\eta] = 0.355$, its intrinsic viscosity increased to 0.474 and was found to be about 80% insoluble after 7 days.

The crosslinking is retarded readily by the presence of inhibitors, and for this reason, an inhibitor was added to the solutions of the polymer after preparation and during purification.

A comparison of the infrared spectra of the monomers AA and AMA with those of the corresponding polymers indicate that the allyl group has not polymerized. In the case of AA, the spectra disclosed the disappearance of the acrylyl $CH_2{=}CH{-}$ bands[10a] at 9.5, 11.9, and 12.3 μ, while in the case of AMA the methacrylyl $CH_2{=}C(CH_3){-}$ bands[10b] at 7.6, 9.85, and 12.3 μ also disappeared. In both cases, the band at 6.95 μ for the $CH_2{=}C{-}$ olefinic structure[11] decreased correspondingly to the loss of the acrylyl and methacrylyl functions; the reduction with retention of the band at 6.95 μ confirms the presence of the allyl, $CH_2{=}CHCH_2{-}$ structure. Both the physical character of the polymers formed and the infrared spectra obtained are strong evidence that polymerization has occurred through the acrylyl double bond without affecting the allyl double bond.

Both anionic and radical polymerizations can proceed simultaneously when an electron-transfer initiator, such as sodium naphthalene, is used under certain conditions.[12] Radical polymerizations of AA and AMA produce crosslinked, insoluble polymers. In contrast, all the polymers and copolymers of AA and AMA prepared with the use of sodium naphthalene initiation were completely soluble in a number of organic solvents. If any radical polymerization of these monomers occurred, it was so slight that the solubility of the polymers was not unduly influenced.

Copolymerizations

Monomers AA and AMA were copolymerized with styrene, acrylonitrile, and methyl methacrylate. The compositions of the styrene copolymers were determined from their elemental analyses for carbon, and the experimental results are shown in Table II.

The AA–styrene and AMA–styrene copolymerizations yielded the expected results. The copolymers consisted almost exclusively of the AA or AMA. These copolymerizations can be compared to the sodium naphthalene copolymerizations of styrene and methyl methacrylate.[13–16] The experimental results for the acrylonitrile polymerizations are shown in Table III. The compositions of the acrylonitrile copolymers were deter-

TABLE II
Copolymerization of Styrene (M_2) and AA or AMA (M_1)

M_1	M_1, mole-%	Styrene (M_2), mole-%	Conversion, %	Carbon in polymer, %	Hydrogen in polymer, %[a]	M_1 in copolymer, mole-%
AA	24.6	75.4	5.9	64.56	7.02	~100
AA	49.3	50.7	7.6	64.08	6.96	~100
AA	73.9	26.1	8.1	64.17	7.10	~100
AMA	25.2	74.8	8.3	66.39	7.89	~100
AMA	50.1	49.9	4.2	66.78	8.02	~100
AMA	75.1	24.9	6.8	67.13	8.08	~100

[a] Calculated for 100% styrene: C, 92.32%; H, 7.68%. Calculated for 100% AA: C, 64.28%; H, 7.14%. Calculated for 100% AMA: C, 66.69%; H, 7.93%.

TABLE III
Copolymerization of Acrylonitrile (M_2) and AA or AMA (M_1)

M_1	M_1, mole-%	Acrylonitrile (M_2), mole-%	Conversion, %	N_2 in copolymer, %[a]	M_2 in copolymer, %[a]
AA	25.1	74.9	4.60	14.55	72.17
AA	48.0	52.0	6.26	7.78	47.06
AA	74.6	26.4	8.15	3.22	23.42
AMA	23.6	76.4	6.28	24.47	96.61
AMA	50.2	49.8	2.49	19.38	87.01
AMA	75.1	24.9	3.93	10.93	60.32
AMA	90.0	10.0	4.38	3.96	27.20

[a] Corrected value.

TABLE IV
Monomer Reactivity Ratios of AA or AMA (r_1) with Acrylonitrile (r_2)

Comonomers	r_1	r_2
AMA, acrylonitrile	0.515 ± 0.10	9.55 ± 0.47
AA, acrylonitrile	1.12 ± 0.21	0.73 ± 0.06

mined from their elemental analyses for nitrogen. The analytical values found for per cent nitrogen were corrected by a factor of 1.15, which was based on the nitrogen combustion analyses of three samples of acrylonitrile homopolymers prepared by anionic polymerization.

In the AMA-acrylonitrile copolymerizations, acrylonitrile is preferentially incorporated into the copolymer. The values obtained are compatible with those obtained in other anionic copolymerizations involving acrylonitrile and methacrylate esters.[17,18] In the AA–acrylonitrile copolymerizations, AA shows a slight tendency to be preferentially incorporated in the copolymers; and thus, it differs from other acrylate copolymerizations.[17,18]

The method of Mayo and Lewis[13,19] was used to determine the reactivity ratios r_1 and r_2 for acrylonitrile–AA and acrylonitrile–AMA monomer pairs and are given in Table IV.

The experimental data for the copolymerization of methyl methacrylate (MMA) with AMA is given in Table V. The composition of the MMA–AMA copolymers could not be determined with reasonable accuracy solely from the elemental analyses for carbon and hydrogen. The infrared spectra of these copolymers show the band for olefinic $CH_2{=}CHCH_2$— structure at 6.95 μ. Bromination of polymers yielded the dibromo derivatives, and the elemental analyses for bromine in conjunction with the carbon values were used to calculate the copolymer compositions. In the MMA–AMA copolymerizations, MMA is preferentially incorporated into the copolymer.

TABLE V
Copolymerization of Methyl Methacrylate (M_2) with AMA (M_1)

M_1, mole-%	MMA (M_2), mole-%	Conversion, %	Br_2, %[a]	M_2 in copolymer, mole-%
50	50	7.18	40.11	52.91
20	80	5.39	11.95	92.10

[a] Calculated for 100% $C_7H_{10}O_2Br_2$: Br = 55.94%.

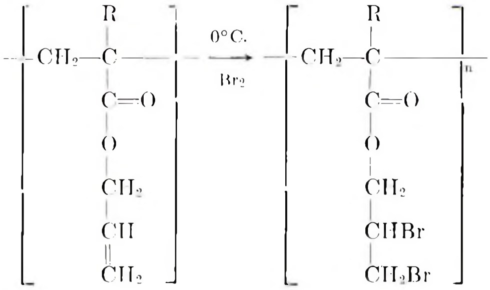
In a similar manner, the bromine content was used to establish the composition of block MMA–AMA (75–25 mole-% feed) copolymer as 81.2–18.8 mole-% MMA–AMA. It is most probable that at least some homopolymer of AMA was formed in this copolymerization, yet the increase in the intrinsic viscosity from 0.350 to 0.402, brought about by the addition of AMA to the poly(methyl methacrylate) anion, is indicative of block formation.

In the case of the block styrene–AMA (80–20 mole-% feed) copolymer elemental analyses for carbon and bromine were used to determine the composition as 83.1 mole-% styrene–16.9 mole-% AMA. Since the polymer was extracted with acetonitrile in which homopoly(allyl methacrylate) is soluble, it can be considered as free of this homopolymer.[18] The infrared spectrum of the residual polymer showed an absorption band at 5.8 μ for the ester and at 6.95 μ for the $CH_2{=}CH{-}CH_2$— group, confirming the presence of the block copolymer. The increase in intrinsic viscosity from 0.387 to 0.413 brought about by the addition of AMA to the polystyrene anion is also indicative of block formation. In the normal anionic copolymerization of a mixture of styrene and AMA, the product consisted almost exclusively of AMA; thus, block polymerization procedure permits, at least, the formation of a styrene–AMA copolymer. Since the styrene block prepared with sodium naphthalene initiation is a "living polymer,"[20] the AMA undoubtedly is attached to the termini of the chains.

Post-Reactions of Linear Polymers

Several of the linear polymers and copolymers prepared from AA and AMA were subjected to various post-reactions of the pendant allyl group. The primary purpose of these post-reactions was to lend support to the proposed linear structures by characterizing the products formed by these reactions. Among the reactions employed were the bromination of the allyl group, as well as the thermal and radical crosslinking of the polymers through the allyl groups.

The linear polymers were subjected to bromination using bromine as the brominating agent. To avoid reactions other than the addition to available double bonds, the reactions were performed at 0°C. and in the dark. To assure a substantial degree of reaction, it was allowed to continue for at least 48 hr. Short bromination times yield polymers which contain residual $CH_2{=}CH{-}CH_2{-}$ groups still available for other reactions. The amount of bromine found in the brominated polymer is in good agreement with the expected values.



R = H, CH_3

A comparison of the infrared spectra of the initial polymers and those of the completely brominated polymer disclosed the disappearance of the carbon–carbon double bond at 6.95 μ.

When ignited in the flame of a bunsen burner and withdrawn from the flame, all of the post-brominated polymers prepared were found to be self-extinguishing. Thus, post-bromination offers a convenient method for preparing self-extinguishing polymers and avoids the problems associated with polymerizing the equivalent monomers, $CH_2{=}C(R){-}COOCH_2\text{-}CHBrCH_2Br$, by ionic or radical initiators.

Further confirmation of the linear structure of these polymers and copolymers and of the reactivity of the free allyl groups was obtained by both the thermal- and radical-induced crosslinking of the polymers through the allyl double bonds. The major portion of the radical-induced post-reactions consisted of casting films of the polymers from solutions containing benzoyl peroxide and heating the solvent-free films at 100°C. to produce insoluble, crosslinked films. The thermal-induced post-reactions were conducted in a similar manner, except that benzoyl peroxide was not included in the polymer solutions and heating was carried out at temperatures in excess of 100°C. Crosslinked films were also obtained in these reactions. The infrared spectra of the crosslinked polymers showed a marked decrease in the band at 6.95 μ, indicating the disappearance of $CH_2{=}CHCH_2\text{-}$ functions.

The partially brominated AMA polymer yielded insoluble, infusible crosslinked polymers which were self-extinguishing when ignited and withdrawn from the flame source.

The thermal- and radical-induced crosslinking of the acrylonitrile–AA and the acrylonitrile–AMA copolymers were also facile. Strips of the films of the acrylonitrile copolymers containing 60 mole-% or more of acrylonitrile could be cold-drawn before crosslinking. The drawn film showed extinction under crossed Nichol prisms. The drawn films also could be crosslinked similarly to the undrawn films.

The MMA–AMA and the styrene–AMA block copolymers also crosslinked readily. Solvent extraction of the crosslinked MMA–AMA film with refluxing acetone for 3 hr., followed by drying of the extracted film to constant weight in a vacuum oven, showed that 98.6% of the polymer was insoluble. The styrene–AMA block copolymer was extracted similarly, and 96.6% of the polymer was found to be insoluble. The infrared spectrum of the soluble portion indicated that it was substantially homopolystyrene.

Post-polymerization reactions to obtain crosslinked polymers from the linear polymers are well known in the literature. Chemical crosslinking agents are employed when the pendant group contains a related functional group. For example, polyacrylic esters containing hydroxyl groups in the ester portion can be crosslinked[21] with polyepoxides or polyisocyanates. The linear polymers and copolymers of allyl acrylate and allyl methacrylate fall in the classification of "self-reactive" thermosetting acrylic polymers as proposed by Piggott.[22]

EXPERIMENTAL

Monomers

Allyl acrylate was synthesized by the method of Fisher,[23] distilled under deoxygenated nitrogen through an 18-in. glass helices-packed column at a reflux ratio of 5:1, the fraction boiling at 121–123°C. collected (lit.:[23] 122°C./760 mm.), redistilled off of calcium hydride, collected in glass receivers which had been flamed, and saturated with helium; b.p. 66.0–66.5°C./100 mm. The product was also identified as allyl acrylate from its infrared spectrum and its refractive index, $n_D^{20} = 1.4308$ (lit.:[23] $n_D^{20} = 1.4295$).

Allyl methacrylate, purchased from the Borden Chemical Company, was purified by the procedure used for allyl acrylate, then saturated with helium. The fraction distilling at 42.5–44.0°C./17 mm. was used.[24]

Acrylonitrile, purchased from American Cyanamid Company, was distilled under deoxygenated nitrogen through an 18-in. glass helices-packed column at a reflux ratio of 15:1, collected, refluxed under deoxygenated nitrogen over calcium hydride, redistilled, collected in flame-dried glass flask, then saturated with helium. The product distilling at 77°C./760 mm. was used.[25]

Commercial styrene, supplied by the Foster Grant Company, was refluxed over calcium hydride under deoxygenated nitrogen, distilled and saturated with helium. The product distilling[26] at 71°C./65 mm., $n_D^{20} = 1.5464$, was used.

Initiators

n-Butyllithium, as a 15.03% solution in hexane, was obtained from the Foote Mineral Company. Only relatively fresh bottles were used.

Sodium naphthalene was prepared according to the method of Scott[27] so that each milliliter of the sodium naphthalene solution contained 23.4×10^{-5} mole of sodium naphthalene.

Tetrahydrofuran, reagent grade, was purified according to the method outlined by Sorenson and Campbell,[28] then distilled from lithium aluminum hydride and saturated with helium.

Toluene, A. R. grade, was purified according to the method of Vogel,[29] then refluxed over calcium hydride, redistilled and saturated with helium.

Elemental analyses for C, H, O, N, and Br were performed by Midwest Microlab, Indianapolis, Indiana and by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Polymerizations

Radical and Cationic

These polymerizations were carried out in rubber-capped serum glass vials with the use of 4 g. of the monomer and 0.02 g. benzoyl peroxide as the radical initiator and 0.02 g. aluminum chloride as the cationic initiator. In addition to AA and AMA, ethylene diacrylate and ethylene dimethacrylate were also polymerized. A typical polymerization was as follows. In a dry-box with a nitrogen atmosphere, into a thoroughly dried 5 ml. serum vial was placed the monomer. The monomer was then saturated with dry deoxygenated nitrogen, the initiator added, the vial sealed and placed in an 80°C. oven. At the end of 34 hr., the contents of all of the vials were tough, infusible masses, insoluble in acetone, toluene, dimethylformamide, and dimethyl sulfoxide.

Anionic

Homopolymerization. A typical anionic polymerization using a modification of a previously described procedure,[7] is given as follows. The reaction vessel attached to a high vacuum manifold consisted of a four-necked glass flask fitted with an externally driven magnetic stirrer, a side-arm to which was attached a 50-ml. round-bottomed flask, a stopcock crowned with a serum cap, and a helium inlet tube.

The solution of monomer was stored over calcium hydride in the round-bottomed flask for at least 8 hr. before use, then degassed twice at 3×10^{-6} mm. Hg and distilled into the reaction vessel, which had been previously flamed while a stream of helium was flowing through it. The system was then pressured with helium to slightly above atmospheric pressure. The reaction vessel was then cooled to the desired temperature. Catalyst solution was then injected volumetrically by means of a hypodermic syringe through the serum cap. The monomer/initiator mole ratio was 300. The polymerization was terminated by the injection of methanol into the reaction mixture.

The polymer was isolated by filtration after pouring the polymer solution slowly into vigorously stirred methanol. The isolated polymer was washed with methanol and dried to constant weight in a vacuum oven at 25°C. The infrared spectra of the monomers and polymers were recorded, and the intrinsic viscosities of representative samples of linear poly(allyl acrylate) and poly(allyl methacrylate) determined.

In addition to AA and AMA, ethylene dimethacrylate and ethylene diacrylate which had been purified and saturated with helium were polymerized at 0°C. as 10% solutions in THF, butyllithium and sodium naphthalene being used as initiators; in all cases insoluble, infusible polymers were obtained. Purified allyl acetate and diallyl phthalate also failed to produce polymers under identical conditions.

Copolymerizations. The general procedure described above for the anionic polymerization was used to prepare the copolymers. The copolymerizations were performed in tetrahydrofuran at −40°C. with *n*-butyllithium as the initiator and at a 10% concentration of monomers. Copolymerizations were generally carried out to under 10% conversion, the time required varying from a few minutes to 1 hr., depending on the composition of the monomer mixture. Generally, the copolymerizations were allowed to proceed until a noticeable increase in viscosity occurred before they were terminated. If the conversion was found to exceed 10%, the reaction was repeated and terminated at a shorter reaction time. The polymers were isolated by precipitation in nonsolvent, redissolved and reprecipitated three times in a suitable solvent–nonsolvent system; the polymer solutions were filtered through sintered glass discs before reprecipitation. For the copolymers of acrylonitrile, dimethylformamide was used as the solvent and methanol as the precipitant. For the remainder of the copolymers, acetone or benzene was used as the solvent and methanol as the precipitant. The isolated copolymers were dried to constant weight in a vacuum oven at 25°C.

Block Copolymerizations. The apparatus described above for the homopolymerization was used for preparing the block copolymers. The procedure described by Baer[30] of polymerizing, at −70°C. with sodium naphthalene as the initiator, first one monomer and then adding the second monomer, was followed. The monomer systems used were styrene–AMA and methyl methacrylate–AMA. Termination, isolation, purification, and drying of the polymer were as described above for the copolymer..

The styrene–AMA block copolymer was prepared by first polymerizing 16.64 g. (0.16 mole) styrene as a 25% solution in tetrahydrofuran for 3 hr., at a sodium naphthalene–styrene mole ratio of 1:300; conversion, 100%; [η] in toluene = 0.387. Then 5.04 g. (0.04 mole) of AMA was injected through the serum cap by means of a hypodermic needle, the reaction allowed to proceed for 1 hr., terminated with methyl alcohol, and the polymer isolated. Then the polymer was treated with refluxing acetonitrile to extract the homopolymer of AMA and dried; yield, 20.7 g. (96%); [η] in toluene = 0.413.

The MMA–AMA block copolymer was prepared similarly by first polymerizing 15 g. (0.15 mole) MMA in 10% solution in tetrahydrofuran at a sodium naphthalene–MMA mole ratio of 1:300; conversion 99.2%; [η] in acetone = 0.350. This was followed by the addition of 6.3 g. (0.05 mole) AMA; yield, 20.2 g. (94.5%); [η] in acetone = 0.402.

Viscosity Determinations

The intrinsic viscosities of representative samples of poly(allyl acrylate) and poly(allyl methacrylate) were determined in acetone solutions in a Canon 25-102 dilution viscometer. The bath temperature was maintained at 20.00 ± 0.02°C., and flow times were determined for at least three solution concentrations.

Post-Reactions

Bromination of Polymers

Bromination of the Linear Polymers of AMA. Into a 125-ml. glass-stoppered flask was placed 0.5 g. of polymer dissolved in 15 ml. of carbon tetrachloride. To this was added 0.5 g. Br_2 as a 20% solution in carbon tetrachloride. The mixture was stirred well, stoppered, and placed in a refrigerator at 0°C. for at least 48 hr. A yellow-orange precipitate which resulted was separated by filtration and washed with carbon tetrachloride, redissolved, and reprecipitated twice using 1:1 acetone–benzene as a solvent and methanol as precipitant, isolated, and dried in a vacuum oven at 25°C. to constant weight.

ANAL. Cald. for the dibromo derivative, $C_7H_{10}O_2Br_2$: C, 29.39%; H, 3.49%; Br, 55.9%. Found: C, 28.90%; H, 3.60%; Br, 54.7%.

Bromination of Linear Polymer of AA. The same procedure was used as in the case of the linear polymer of AMA.

ANAL. Calcd. for the dibromo derivative, $C_6H_8O_2Br_2$: C, 26.48%; H, 2.90%; Br, 58.8%. Found: C, 25.80%; H, 2.76%; Br, 56.6%.

Partial Bromination of Linear AMA Polymer. The procedure described above was used, except that the reaction time was 4 hr.

Anal. Calcd. for 75.8:24.2 mole-% of $C_7H_{10}O_2$:$C_7H_{10}O_2Br_2$: C, 52.88%; H, 6.07%; Br, 23.61%. Found: C, 52.16%; H, 6.04%; Br, 23.31%

Bromination of Methyl Methacrylate–AMA Copolymer (50:50 **mole-% Anal. Feed**). The same procedure used above was also used in this case.

Anal. Calcd. for 52.9:47.1 mole-% $C_7H_{10}O_2$:$C_7H_{10}O_2Br_2$: C, 37.02; H, 4.61; Br, 40.12 Found: C, 37.50; H, 4.69; Br, 40.37.

Bromination of Methyl Methacrylate–AMA Copolymer (80:20 **mole-% Feed**). The same procedure used above was also used in this case.

Anal. Calcd. for 91.2:8.8 mole-% $C_7H_{10}O_2$:$C_7H_{10}O_2Br_2$: C, 51.42%; H, 7.01%; Br, 11.93%. Found: C, 50.91%; H, 6.89%; Br, 11.99%.

Bromination of Methyl Methacrylate–AMA Block Copolymer (75:25 **mole-% Feed**). The procedure described above was used.

Anal. Calcd. for 81:19 mole-% $C_7H_{10}O_2$:$C_7H_{10}O_2Br_2$: C, 47.76%; H, 6.20%; Br, 22.38%. Found: C, 47.12%; H, 6.14%; Br, 21.99%.

Bromination of Styrene–AMA Block Copolymer (80:20 **mole-% Feed**). The procedure described above was used.

Anal. Calcd. for 83.1:16.9 mole-% C_8H_8:$C_7H_{10}O_2Br_2$: C, 64.04%; H, 5.41%; Br, 20.04%. Found: C, 64.53%; H, 5.33%; Br, 19.63%.

Crosslinking of Polymers

Thermal Crosslinking. Approximately 1.0 g. of each of the linear polymers of AMA and AA was dissolved in 10 ml. of benzene. Films were cast on glass plates, the solvent allowed to evaporate at room temperature for 24 hr., and the plates then placed in an oven at 120°C. for 4 hr. The resulting films were found to be insoluble in acetone, carbon tetrachloride, and dimethylformamide.

Approximately 0.25 g. of the linear polymers of AMA and AA were heated at 250°C. for 5 min. on a Fisher-Johns melting point apparatus. The polymers softened and formed films which were found to be insoluble in acetone and dimethylformamide.

Radical Crosslinking. Approximately 0.25 g. of each of the linear polymers of AMA, AA, and the partially brominated polymer of AMA (13.3% Br) were dissolved in 5 ml. of dry benzene, and 0.002 g. of benzoyl peroxide was added. After being thoroughly mixed, the solution was poured onto glass plates, the solvent allowed to evaporate, and the plates placed in a 100°C. oven for 2 hr. The resulting films were found to be insoluble in acetone, benzene, and dimethylformamide.

Similar solutions containing benzoyl peroxide were prepared in benzene of the MMA–AMA copolymers and of the block copolymers of MMA–AMA and styrene–AMA. The films cast from them and treated at 100°C. for 2 hr. were found also to be infusible and insoluble in benzene and dimethylformamide. Similar solutions containing benzoyl peroxide were prepared in dimethylformamide of the acrylonitrile–AA (74.9:26.1) and of acrylonitrile–AMA (87:23) copolymers and films cast and heated at 100°C. These films were insoluble in dimethylformamide.

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References

1. G. F. D'Alelio and R. C. Evers, *J. Polymer Sci. A-1*, in press.
2. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, (a) p. 391; (b) pp. 217–226.
3. E. H. Riddle, *The Monomeric Acrylic Esters*, Reinhold, New York, 1954, p. 29.
4. M. Szwarc, *Makromol. Chem.*, **35**, 132 (1960).
5. A. R. Gantmakher and Y. O. Spirin, *Usp. Khim.*, **29**, 299 (1960).
6. R. K. Graham, J. Panchak, and M. J. Kampf, *J. Polymer Sci.*, **44**, 411 (1960).
7. D. L. Glusker, E. Stiles, and B. Yoncoskie, *J. Polymer Sci.*, **49**, 297, 315 (1961).
8. D. M. Wiles and S. Bywater, *Polymer*, **3**, 175 (1962).
9. G. Meyerhoff, *Fortschr. Hochpolymer. Forsch.*, **3**, 59 (1961).
10. *Sadtler Standard Spectra*, Midget Edition, Sadtler Research Laboratories, Philadelphia, Pa., (a) spectrum No. 1117; (b) spectrum No. 2226.
11. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1960, p. 34.
12. K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **37**, 363 (1959).
13. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
14. H. Ringsdorf, in *Macromolecular Chemistry* (*J. Polymer Sci. C*, **4**), M. Magat, Ed., Interscience, New York, 1964, p. 987.
15. K. F. O'Driscoll, R. J. Boudreau, and A. V. Tobolsky, *J. Polymer Sci.*, **31**, 115, 123 (1958).
16. J. E. Mulvaney, C. G. Overberger, and A. Schiller, *Fortschr. Hochpolymer. Forsch.*, **3**, 130 (1962).
17. Y. Landler, *J. Polymer Sci.*, **8**, 63 (1952).
18. N. L. Zutty and F. J. Welch, *J. Polymer Sci.*, **43**, 445 (1960).
19. C. Walling, E. R. Briggs, W. Cummings, and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 48 (1950).
20. M. Szwarc and A. Rembaum, *J. Polymer Sci.*, **22**, 189 (1956).
21. Courtaulds Ltd., Belg. Pat. 615,113 (1962).
22. K. E. Piggott, *J. Oil Colour Chemists' Assoc.*, **46**, 1009 (1963).
23. C. H. Fisher, C. E. Rehberg, and L. T. Smith, *J. Am. Chem. Soc.*, **65**, 763 (1943).
24. C. E. Rehberg, C. H. Fisher, and L. T. Smith, *J. Am. Chem. Soc.*, **65**, 1003 (1943).
25. E. W. Scott and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 2549 (1932).
26. M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 833 (1937).
27. N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **59**, 2442 (1936).
28. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 255.
29. A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, Green, London, 1960, p. 34.
30. M. J. Baer, *J. Polymer Sci. A*, **2**, 417 (1964).

Résumé

On a polymérisé l'acrylate d'allyle et le méthacrylate d'allyle à l'aide d'un initiateur anionique et l'on a obtenu des polymères linéaires solubles possédant des groupements allyles latéraux. On a montré l'existence des groupements allyliques latéraux non-polymérisés dans les poly-allyle-acrylates résultant de cette polymérisation, par les

tests suivants: (*1*) la disparition des doubles bandes d'absorption acrylyles et méthacrylyles du spectre infra-rouge lors de la conversion des monomères en polymères; (*2*) en bromant après la polymérisation les groupements allyles du polymère linéaire; (*3*) en notant la disparition des absorptions allyles des spectres infra-rouges des polymères linéaires bromés; (*4*) en pontant thermiquement ou à l'aide d'initiateurs radicalaires, les polymères linéaires à l'aide des groupes allyles latéraux. L'acrylate d'allyle et le méthacrylate d'allyle copolymörisent très mal avec le styrène en polymérisation anionique, mais copolymérisent très aisément avec le méthacrylate de méthyle et l'acrylonitile. On a obtenu des copolymères à blocs par réaction du méthacrylate d'allyle avec des polystyrènes, avec des anions polystyréniques et de polyméthacrylate de méthyle préparés au préalable. Les polymères linéaires et d'acrylate d'allyle et ainsi que les copolymères, peuvent être considérés comme des polymères au taux réactionnel qui conduit à des dérivés thermodurcissables. On peut considérer la bromation des polymères linéaires comme une méthode très facile pour produire des polymères non-combustibles.

Zusammenfassung

Allylacrylat und Allylmethacrylat wurden mit anionischen Starten zu löslichen linearen Polymeren mit Allylgruppen in den Seitenketten polymerisiert. Die Anwesenheit der nicht-polymerisierten Allylseitengruppen in den gebildeten linearen Polyallylacrylaten wurde gezeigt durch: (*1*) das Verschwinden der Acrylyl- und Methacrylyldoppelbindungsabsorption in den Infrarotsoektren bei der Umwandlung der Monomeren in die Polymeren, (*2*) Nachbromierung der Allyldoppelbindungen in den linearen Polymeren, (*3*) das Verschwinden der Allylgruppenabsorption im Infrarotspektrum der bromierten linearen Polymeren und (*4*) die thermisch und radikalisch gestartete Vernetzung der linearen Polymeren durch die Allylgruppen. Allylacrylat und Allylmethacrylat zeigen nur geringe Neirung zur Copolymerisation mit Styrol bei anionischem Start, copolymerisieren aber leicht mit Methylmethacrylat und Acrylnitril. Blockcopolymere werden durch Reaktion von Allylmethacrylat mit vorgebildetem Polystyrol- und Polymethylmethacrylatanionen dargestellt. Die linearen Polymeren und Copolymeren von Allylacrylat können als "selbst reaktive" Polymere klassifiziert werden, welche wärmhärtende Polymere ergeben. Die Bromierung der linearen Polymeren bietet eine bequeme Methode zur Herstellung selbstlöschender Polymerer.

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Cationic Graft Copolymerization of Styrene Onto Natural Rubber

YUKIO UENO, TOSHIYUKI KASABO, and
TAKESHI HANADA, *Kyowa Rubber Industry Co., Ltd.,*
Nishinariku, Osaka, Japan, and YUJI MINOURA,
Department of Chemistry, Osaka City University,
Kitaku, Osaka, Japan

Synopsis

The polymerization of styrene was carried out in a cyclohexane solution of natural rubber with stannic chloride. It was found that the grafting copolymerizations of styrene took place as well as the cyclization of rubber. The rate of polymerization of styrene was proportional to the second power of the concentration of styrene and to the concentrations of stannic chloride and natural rubber, respectively. The overall activation energy was about 6 kcal./mole. The percentage grafting increased with increasing concentration of rubber. On the other hand, the grafting efficiency showed the reverse tendency. The percentage grafting could be increased to 150% by the addition of nitrobenzene, a polar solvent.

INTRODUCTION

Little has been reported on cationic graft copolymerization. For example, Plesch[1] reported the graft copolymerization of styrene with poly(vinyl chloride) by use of titanium tetrachloride or aluminum chloride in nitrobenzene.

Kockelbergh and Smets[2] have carried out reactions of isobutylene with chloromethylated or bromomethylated polystyrene using aluminum bromide in CS_2. In these studies, polymers containing halogen, especially chlorine, in their main chain or side chain were used as backbone polymers. Grafted polymers were obtained by grafting of monomers onto the carbonium ions formed by dehalogenation with a Lewis acid. Haas et al.[3] used another method of grafting in which the reactions between the growing polystyryl ions and aromatic substances are used. They obtained graft copolymers of polystyrene with poly-*p*-methoxystyrene, using stannic chloride in nitrobenzene–carbon tetrachloride mixtures.

In this paper, protonation was used as the method for the grafting copolymerization. It is known that cyclization occurs by protonation if a Lewis acid or a protonic acid is added to a solution of natural rubber. Therefore, it may be expected that if a suitable monomer, polymerizable by a cationic mechanism, is added to this system, cyclization and grafting reactions will take place simultaneously.

In this work, reactions between styrene and natural rubber were carried out with the use of stannic chloride in cyclohexane under various conditions, and mixtures of hard, rubbery, grafted copolymer with homopolystyrene were obtained. The effects of the concentrations of styrene, stannic chloride, and rubber and the temperature on the rate of polymerization, the percentage grafting and the grafting efficiency are discussed. It was confirmed that grafting and cyclization had occurred, by carbon-hydrogen analysis and the infrared spectrum of the residue obtained after extraction with boiling acetone.

EXPERIMENTAL

Materials

Natural rubber was dissolved in cyclohexane and reprecipitated with methanol to remove the impurities. The precipitates were filtered off, dried *in vacuo*, and used for the polymerization. Cyclohexane, styrene, and stannic chloride were purified by conventional methods before use.

Fractionation of the Graft Copolymer

Purified and dried rubber was dissolved completely in cyclohexane in a test tube, styrene was added, and the test tube was shaken, cooled, and degassed. The polymerization started when a solution of stannic chloride in cyclohexane was added. The tube was cooled and sealed. The polymerization was carried out at 20°C. for the required length of time. After the reaction, the products were precipitated with methanol, and the precipitates were filtered and dried *in vacuo*.

The styrene conversion was calculated from the increase in weight after drying, and the grafted styrene from the increase in weight of the insoluble portion after extraction with boiling acetone.

Infrared Spectra

The infrared absorption spectra of the natural rubber used, the product of the natural rubber and stannic chloride, and the soluble and insoluble portions of the product of the graft polymerizations were measured.

The spectra were measured on specimens in the form of thin films obtained by casting from chloroform solutions on rock salt plates.

Intrinsic Viscosity

The intrinsic viscosities $[\eta]$ of chloroform solutions of the rubber used, the products obtained on treatment with stannic chloride for a certain length of time, and of the reaction mixtures of rubber with polystyrene obtained were measured at 30°C. with a modified Ubbelohde viscometer.

The percentage grafting is the ratio of the increase in the weight of the acetone-insoluble portions to the weight of rubber used, i.e., the ratio of the grafted polystyrene to the rubber used. The grafting efficiency is the ratio of the grafted polystyrene to the total polymerized styrene.

RESULTS AND DISCUSSION

Confirmation of Cyclization and Grafting

Generally, rubber becomes insoluble in organic solvents when cyclization occurs. The reaction products obtained in these experiments also became powdery and insoluble in either cyclohexane or other solvents, and only swelled in them. The fact that the products were soluble only in chloroform and took a long time to dissolve indicated that the cyclization reaction had occurred; this was confirmed by the infrared spectra of the products.

The formation of graft copolymer was confirmed as follows. The dried reaction mixtures were extracted with boiling acetone. The soluble portion was found to be homopolystyrene. The insoluble portion did not contain homopolystyrene, because polystyrene obtained under the same conditions in the absence of rubber, is soluble in boiling acetone. So the residue was thought to be the grafted copolymer. This was confirmed by its infrared spectrum and carbon–hydrogen analysis.

Figures 1*a* and 1*b* show the infrared spectra of the natural rubber and the product obtained by the reaction between natural rubber and stannic chloride. Figures 1*c* and 1*d* show the infrared spectra of the soluble and insoluble portion, in boiling acetone, of the product in the case in which the polymerization of styrene was carried out in the cyclohexane solution of rubber and stannic chloride.

From Figures 1*a* and 1*b* it was observed that the absorption bands at 1315, 1130, and 1095 cm.$^{-1}$ associated with $=$CH— in the *cis* form of the —C(CH$_3$)$=$CH— group decreased in intensity or disappeared. This suggests the presence of —CH$_2$— adjacent to the —C(CH$_3$)$=$CH— group, i.e., it shows the presence of a —C(CH$_3$)—CH$_2$— group.[4] The small shift of the peak at 1665 cm.$^{-1}$ to 1670 indicates that the natural rubber is partly cyclized. The direction of the shift of the absorption of —CH$_3$ depends on whether —C(CH$_3$)$=$CH— is cyclic or linear.[5]

Table I shows the results of the elemental analysis of natural rubber, polystyrene, and grafted copolymer. The analysis results indicate that styrene is grafted to natural rubber.

The percentage grafting calculated from the increase in the weight of the boiling acetone-insoluble portion (36%) is in agreement with that calculated from the elemental analysis (28%), within the analytical error.

TABLE I

Elemental Analysis of Polymers[a]

Polymer	C, %	H, %
Natural rubber	88.20	11.72
Grafted copolymer[b]	89.48[c]	10.32
Polystyrene	92.16	7.80

[a] [R] = 15 g./l., [M] = 1.75 mole/l., [C] = 4.28×10^{-2} mole/l., 20°C., 120 min.

[b] Grafting percentage is 36%.

[c] This value is equal to a grafting percentage of 28%.

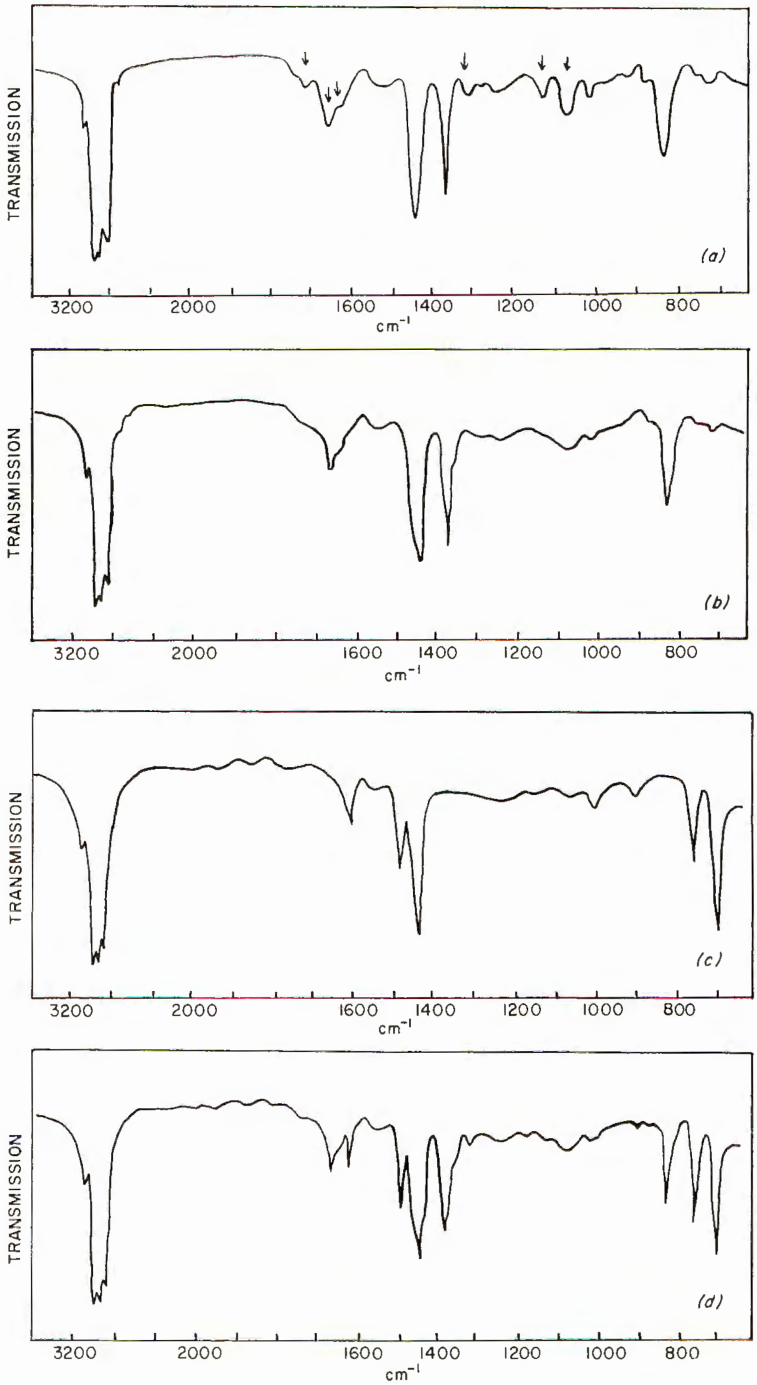


Fig. 1. Infrared spectra of polymers: (*a*) natural rubber; (*b*) cyclized rubber; (*c*) polystyrene; (*d*) graft copolymer. [R] = 15 g./l., [M] = 1.75 mole/l., [C] = 4.28 × 10^{-2} mole/l., 20°C., 120 min.

The effect of reaction time on the bands at 1315, 1130, and 1095 cm.$^{-1}$ is shown in Figure 2. The intensities of the bands decreased with reaction time. Bands associated with styrene at 1603, 1495, 1455, 1028, 765, and 700 cm.$^{-1}$ are not observed in Figure 1*b*, but can be seen in Figure 1*d*. They are the bands of polystyrene as shown in Figure 1*c*.

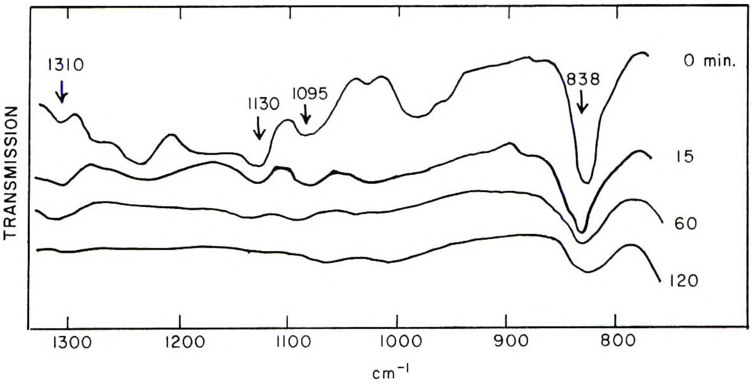


Fig. 2. Effect of reaction time on infrared spectra of graft copolymer. [R] = 15 g./l., [M] = 1.75 mole/l., [C] = 4.28 × 10^{-2} mole/l., 20°C., 120 min.

Consequently it is considered that cyclization of the rubber and the graft polymerization of styrene onto the rubber took place simultaneously.

Rate of Polymerization

Concentration of Styrene. The polymerization was carried out with constant concentrations of rubber and stannic chloride and various concentrations of styrene. The time–conversion curves are shown in Figure 3. The rate of polymerization increased rapidly with the concentration of styrene. Figures 4*a* and 4*b* show the relation between R_p, the apparent rate of polymerization at the early stage, obtained from the time–conversion curves and the concentration of styrene. As this slope is 1.80, it is considered that R_p is proportional to the second power of the concentration of styrene.

Concentration of Stannic Chloride. The polymerization of styrene was carried out at constant concentrations of styrene and rubber and various concentrations of stannic chloride.

The time–conversion curves are shown in Figure 5. R_p increased with the concentration of catalyst. Each rate was obtained at the early stage as mentioned above and was plotted against the concentration of stannic chloride as shown in Figure 6. This slope is 0.98, indicating that R_p is proportional to the concentration of stannic chloride.

Concentration of Rubber. The polymerization of styrene was carried out with various concentrations of rubber and constant concentrations of styrene and stannic chloride. The results, shown in Figures 7 and 8, indicate that R_p is also proportional to the concentration of rubber.

According to these results, the rate of polymerization can be represented as follows:

$$R_p \propto [\mathrm{M}]^2[\mathrm{C}][\mathrm{R}]$$

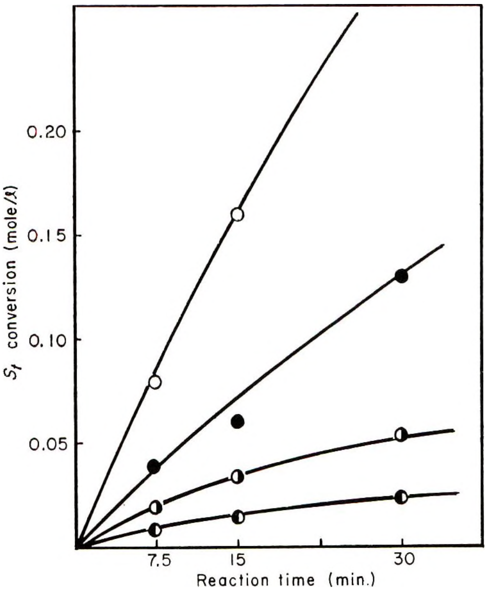
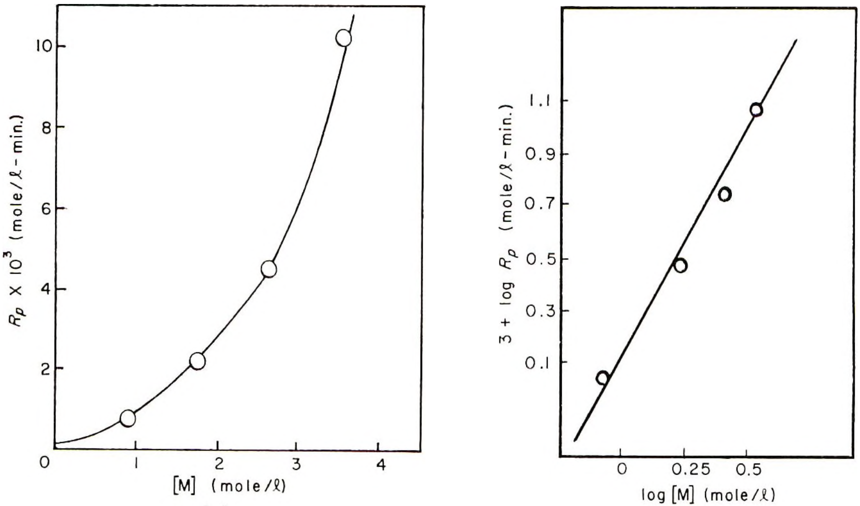


Fig. 3. Effect of monomer concentration on the time–conversion curve: (◐) [M] = 0.875 mole/l.; [M] = (◑) 1.750 mole/l.; (●) [M] = 2.625 mole/l.; (○) [M] = 3.500 mole/l., [R] = 15 g./l., [C] = 4.28 × 10^{-2} mole/l., 20°C.



(a) (b)

Fig. 4. Relationship between monomer concentration and the rate of polymerization. [R] = 15 g./l., [C] = 4.28 × 10^{-2} mole/l., 20°C.

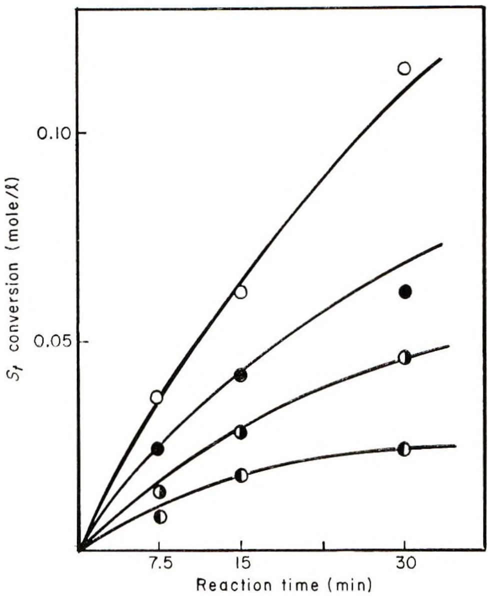


Fig. 5. Effect of catalyst concentration on the time–conversion curve: (◐) [C] = 2.57 × 10^{-2} mole/l.; (◑) [C] = 4.28 × 10^{-2} mole/l.; (●) [C] = 6.00 × 10^{-2} mole/l.; (○) [C] = 7.71 × 10^{-2} mole/l. [M] = 1.75 mole/l., [R] = 15 g./l., 20°C.

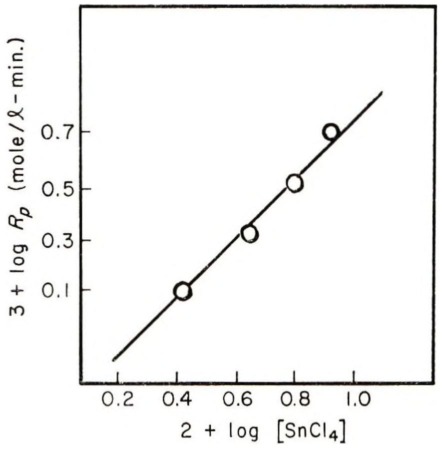


Fig. 6. Relationship between catalyst concentration and the rate of polymerization. [M] = 1.75 mole/l., [R] = 15 g./l., 20°C.

where [M], [C], and [R] represent concentration of monomer, catalyst, and rubber, respectively.

Temperature. The polymerization of styrene was carried out at 10, 20, 30, and 50°C. under constant conditions to investigate the effect of temperature on the rate of polymerization. R_p increased with temperature. The relationship between the rate constant K and the reciprocal of the absolute temperature $1/T$ is shown as Figure 9. The overall activation

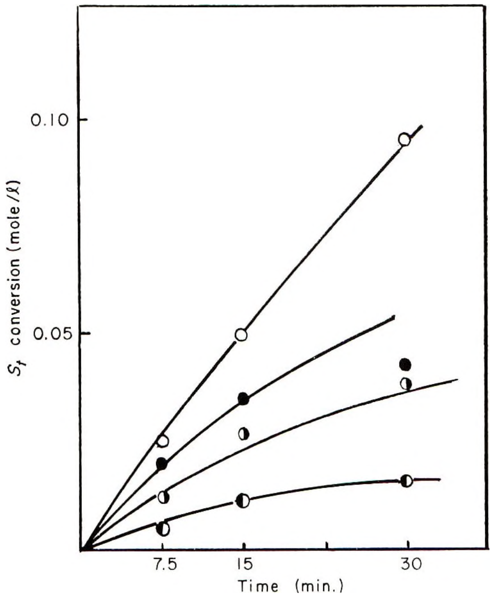


Fig. 7. Effect of rubber concentration on the time–conversion curve: (◐) [R] = 5 g./l.; [◑] [R] 10 g./l.; (●) [R] = 15 g./l.; (○) [R] = 20 g./l. [M] = 1.75 mole/l., [C] = 4.28 × 10^{-2} mole/l., 20°C.

energy calculated from the Arrhenius equation was about 6 kcal./mole. This is a reasonable value for the cationic polymerization of styrene.

Kinetics

The elementary reactions were assumed as shown in eqs. (1)

$$C + M \xrightarrow{k_i} M^+ \tag{1}$$

$$C + R \xrightarrow{k_i'} R^+ \xrightarrow{k_{itr}} R^+ \tag{2}$$

$$R^+ + M \xrightarrow{k_g} M^+ \tag{3}$$

$$M^+ + M \xrightarrow{k_p} M^+ \tag{4}$$

$$M^+ \xrightarrow{k_t} P \tag{5}$$

$$R^+ \xrightarrow{k_t'} R + H^+ \tag{6}$$

$$H^+ + M \xrightarrow{k_h} M^+ \tag{7}$$

$$H^+ + R \xrightarrow{k_h'} R^+ \tag{8}$$

where C represents stannic chloride, possibly in the form of $SnCl_4 \cdot 2H_2O$, M is styrene, and R is rubber or cyclized rubber; k_i and k_i', k_{itr}, k_g, k_p, k_t and k_t' and k_h and k_h' are the rate constants for initiation, proton trans-

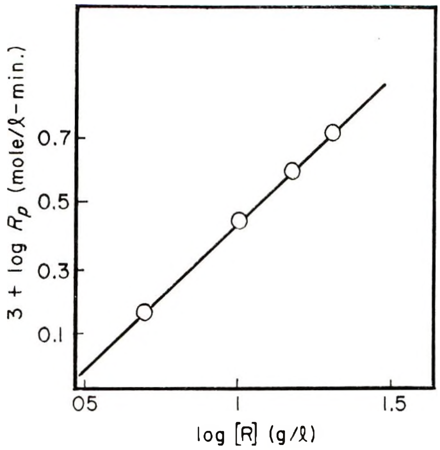


Fig. 8. Relationship between rubber concentration and the rate of polymerization: [M] = 1.75 mole/l., [C] = 4.8×10^{-2} mole/l., 20°C.

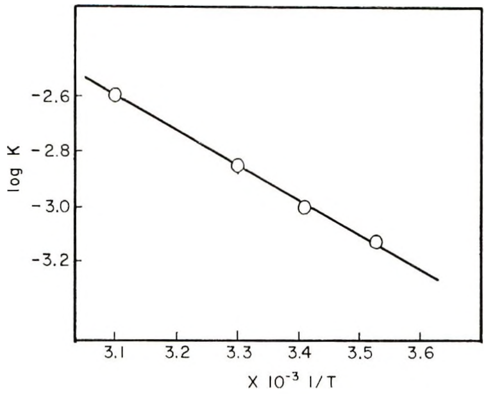
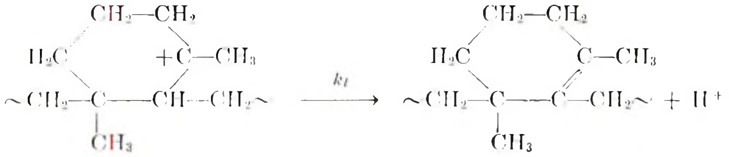


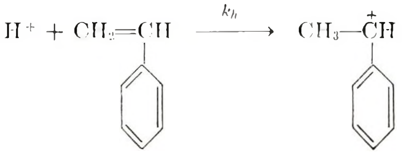
Fig. 9. Relationship between reciprocal of absolute temperature and rate constant. [R] = 15 g./l., [M] = 1.75 mole/l.; [C] = 4.28×10^{-2} mole/l.

fer in a rubber molecule, initiation of grafting, propagation, termination, and reinitiation, respectively.

The mechanisms of termination of R^+ and reinitiation are shown in eqs. (9)–(11).



(9)



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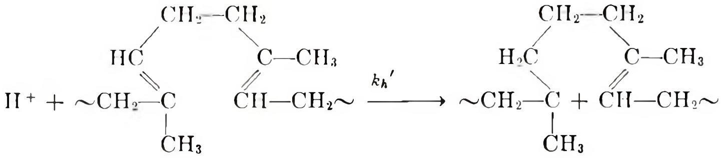
(11)

Assuming steady states for [M$^+$], [R$^+$], and [H$^+$], we have

$$d[\mathrm{M}^+]/dt = k_i[\mathrm{C}][\mathrm{M}] + k_g[\mathrm{M}][\mathrm{R}^+] + k_h[\mathrm{H}^+][\mathrm{M}] - k_t[\mathrm{M}^+] = 0 \quad (12)$$

$$d[\mathrm{R}^+]/dt = k_i'[\mathrm{C}][\mathrm{R}] - k_g[\mathrm{M}][\mathrm{R}^+] + k_h'[\mathrm{H}^+][\mathrm{R}] - k_t[\mathrm{R}^+] = 0 \quad (13)$$

$$d[\mathrm{H}^+]/dt = k_t'[\mathrm{R}^+] - h_h[\mathrm{H}^+][\mathrm{M}] - k_h'[\mathrm{H}^+][\mathrm{R}] = 0 \quad (14)$$

From a summation of eqs. (12)–(14),

$$[\mathrm{M}^+] = (k_i/k_t)[\mathrm{C}][\mathrm{M}] + (k_t'/k_t)[\mathrm{C}][\mathrm{R}] \quad (15)$$

and, as $R_p = k_p[\mathrm{M}^+][\mathrm{M}]$,

$$R_p = (k_pk_i/k_t)[\mathrm{M}]^2[\mathrm{C}] + (k_pk_i'/k_t)[\mathrm{M}][\mathrm{C}][\mathrm{R}] \quad (16)$$

Hence, rewriting k_pk_i/k_t and $k_pk_i'k_t$ in terms of K_1 and K_2, respectively, for convenience, yields eq. (17):

$$R_p = K_1[\mathrm{M}]^2[\mathrm{C}] + K_2[\mathrm{M}][\mathrm{C}][\mathrm{R}] \quad (17)$$

If both sides are divided by [M] we have

$$R_p/[\mathrm{M}] = K_1[\mathrm{M}][\mathrm{C}] + K_2[\mathrm{C}][\mathrm{R}] \quad (18)$$

$R_p/[\mathrm{M}]$ was plotted against [M], with constant [C] and [R], and a straight line having a slight intercept was obtained, as shown in Figure 10. Similarly $R_p/[\mathrm{M}]$ was plotted against [R], with cnstant [C] and [M], and a straight line was obtained, as shown in Figure 11. It also had a slight intercept.

Therefore the equation derived from the elementary reactions is reasonable in explanation of the apparent rate equation. Consequently the apparent rate equation may be written as follows:

$$R_p = K[\mathrm{M}]^2[\mathrm{C}][\mathrm{R}]$$

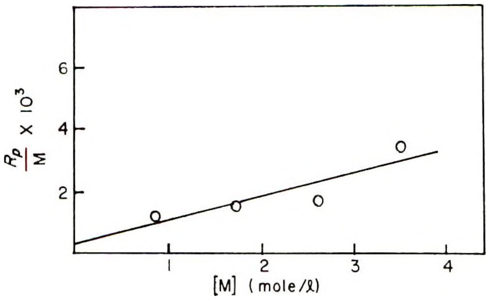

Fig. 10. Relationship between [M] and $R_p/[\mathrm{M}]$. [R] = 15 g./l., [C] = 4.28 × 10^{-2} mole/l.

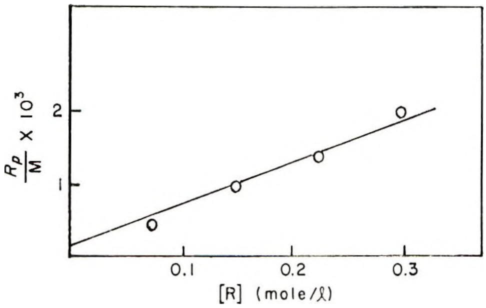

Fig. 11 Relationship between [R] and $R_p/[M]$. [M] = 1.75 mole/l., [C] = 4.28 × 10^{-2} mole/l.

Intrinsic Viscosity

The intrinsic viscosities [η] were obtained for the natural rubber used and the products of the natural rubber and stannic chloride after various time intervals. Measurements were carried out in chloroform, at 30°C. in a modified Ubbelohde viscometer.

As can be seen in Figure 12, [η] decreased with time and became constant after about 30 min. This may be due to the cyclization or scission of the rubber molecules. The influences of the concentrations of styrene, stannic chloride, and rubber on [η] were investigated for products of the copolymerizations after a reaction time of 15 min. [η] decreased slightly with the concentration of styrene or stannic chloride and increased with the concentration of rubber. This results from the low value of [η] of polymerized styrene (the order is of 10^{-2}) in comparison with natural rubber.

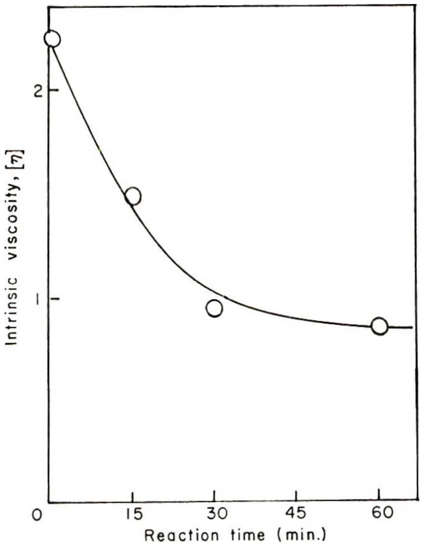

Fig. 12. Intrinsic viscosity of rubber. [R] = 15 g./l., [C] = 4.28 × 10^{-2} mole/l. 20°C.

Grafting Percentage and Efficiency

Reaction Time. The polymerization was carried out at 20°C. for 15, 30, 60, and 120 min. with constant concentrations of styrene, stannic chloride, and rubber. The results are shown in Table II. As can be seen from Table II, the grafting percentage increased with reaction time, while the grafting efficiency decreased with time. This is due to the increase in the ratio of the yield of homopolystyrene to grafted polystyrene.

TABLE II
Effect of Time on Grafting Percentage and Efficiency[a]

Reaction time, min.	Yield, g./l.	Homopoly-styrene, mole/l.	Graft co-polymer, g./l.	Grafted poly-styrene, mole/l.	Grafting per-centage, %	Grafting efficiency, %
15	17.2	0.013	15.8	0.008	5.3	36.3
30	19.7	0.030	16.6	0.015	10.6	34.0
60	26.2	0.082	17.7	0.026	18.0	24.0
120	43.5	0.231	19.5	0.043	30.0	15.8

[a] [R] = 15 g./l., [M] = 1.75 mole/l., [C] = 4.28×10^{-2} mole/l., 20°C.

Concentration of Styrene. The polymerization was carried out with various concentrations of styrene and with constant concentrations of stannic chloride and rubber at 20°C. for 120 min. The grafting percentage and efficiency are listed in Table III.

TABLE III
Effect of Monomer Concentration on Grafting Percentage and Efficiency[a]

Monomer concn., mole/l.	Yield, g./l.	Homopoly-styrene, mole/l.	Graft co-polymer, g./l.	Grafted poly-styrene, mole/l.	Grafting per-centage, %	Grafting efficiency, %
0.875	19.4	0.042	15.0	0	0	0
1.750	43.5	0.105	23.8	0.085	37.0	30.8
2.625	174.6	1.160	34.5	0.187	130.0	13.3
3.500	250.0	1.788	39.5	0.236	163.3	10.4

[a] [R] = 15 g./l., [C] = 4.28×10^{-2} mole/l. 20°C., 120 min.

The grafting percentage increased with increase in the concentration of styrene but the grafting efficiency decreased. This is also due to the same reason mentioned above. The grafting reaction did not occur at 0.875 mole/l. of styrene. The grafting percentage reached 160% at 3.5 mole/l. It was found that the concentration of styrene had a significant effect on the grafting percentage as well as on the rate of polymerization.

Concentration of Stannic Chloride. The polymerization was carried out with various concentrations of stannic chloride at 20°C. for 120 min. The results are shown in Table IV.

TABLE IV
Effect of Catalyst Concentration on Grafting Percentage and Efficiency[a]

Catalyst concn. × 10², mole/l.	Yield, g./l.	Homopolystyrene, mole/l.	Graft copolymer, g./l.	Grafted polystyrene, mole/l.	Grafting percentage, %	Grafting efficiency, %
2.57	28.5	0.167	17.4	0.023	16.0	17.8
4.28	38.7	0.194	18.5	0.034	23.3	14.7
6.00	46.8	0.267	19.0	0.038	26.7	12.5
7.71	99.1	0.744	21.7	0.064	44.7	8.0

[a] [R] = 15 g./l., [M] = 1.75 mole/l., 20°C., 120 min.

The grafting percentage increased with increase in the concentration of stannic chloride, but it was not affected appreciably by the concentration of catalyst, because the increase was only up to 45% under the experimental coditions. The grafting efficiency decreased with increasing the concentration of catalyst.

Concentration of Natural Rubber. The polymerization was carried out with various concentrations of rubber at 20°C. for 120 min. The results are shown in Table V.

TABLE V
Effect of Rubber Concentration on Grafting Percentage and Efficiency[a]

Rubber concn., g./l.	Yield, g./l.	Homopolystyrene, mole/l.	Graft copolymer, g./l.	Grafted polystyrene, mole/l.	Grafting percentage, %	Grafting efficiency, %
5	96.9	0.833	10.2	0.050	104.0	5.6
10	66.7	0.500	14.8	0.046	48.0	8.8
15	58.0	0.376	18.8	0.037	25.3	8.8
20	67.8	0.405	25.7	0.055	28.5	11.9
25	62.8	0.292	32.4	0.071	29.6	19.6

[a] [M] = 1.75 mole/l., [C] = 4.28×10^{-2} mole/l., 20°C., 120 min.

The weight of polymerized styrene and the grafting percentages decreased with increase in the concentration of rubber. This may be explained by the following hypothesis. The influence of the viscosity of the system on the weight of polymerized styrene increases remarkably with increase in the reaction time. Therefore the weight decreased, although the rate of polymerization in the early stages was proportional to the concentration of rubber. The higher the concentration of rubber, the more active centers are formed in the system and thus the lower the degree of polymerization of polystyrene. On the other hand, the lower the concentration of rubber, the less the number of the active centers, and thus the higher the degree of polymerization of polystyrene. Therefore, the grafting efficiency increased, although the grafting percentage decreased.

TABLE VI
Effect of Temperature on Grafting Percentage and Efficiency[a]

Temperature, °C.	Yield, g./l.	Homopolystyrene, mole/l.	Graft copolymer, g./l.	Grafted polystyrene, mole/l.	Grafting percentage, %	Grafting efficiency, %
10	45.0	0.243	19.7	0.045	31.3	15.7
30	109.5	0.862	19.9	0.047	32.7	5.2
50	114.8	0.923	18.8	0.037	25.3	3.8

[a] [R] = 15 g./l., [M] = 1.75 mole/l., [C] = 4.28×10^{-2} mole/l., 120 min.

Influence of Temperature. The polymerization was carried out at 10, 30, and 50°C. for 120 min. in order to investigate the influence of the reaction temperature on the grafting percentage and the efficiency. The results are shown in Table VI.

Temperature did not affect the grafting percentage appreciably, but both grafting percentage and grafting efficiency had a tendency to decrease with increasing temperature. This may be explained by the fact that the rise in temperature promoted the formation of homopolystyrene but restrained the propagation of grafting polystyrene.

Influence of Solvent. The effect of a polar solvent was investigated, as the polymerization proceeds by a cationic mechanism. Various amounts of nitrobenzene as polar solvent were added to cyclohexane (Table VII).

TABLE VII
Effect of Addition of a Polar Solvent on Grafting Percentage and Efficiency[a]

Solvent composition[b]	Yield, g./l.	Homopolystyrene, mole/l.	Graft copolymer, g./l.	Grafted polystyrene, mole/l.	Grafting percentage, %	Grafting efficiency, %
0	67.3	0.474	18.0	0.029	20.0	5.8
0.0625	54.9	0.360	17.5	0.024	16.7	6.3
0.1250	98.5	0.727	22.9	0.076	52.6	9.4
0.1875	107.9	0.753	29.5	0.140	96.7	15.6
0.2500	125.8	0.856	36.7	0.209	145.0	19.6

[a] [R] = 15 g./l., [M] = 1.75 mole/l., [C] = 4.28×10^{-2} mole/l., 20°C., 120 min.

[b] Ratio nitrobenzene/(nitrobenzene + cyclohexane), by volume.

The yield of polystyrene and the grafting percentage increased with increase in the amount of nitrobenzene added. The grafting efficiency also increased. It was therefore concluded that the addition of a polar solvent had a good effect on both the grafting percentage and the efficiency.

Similarly, graft copolymerizations of styrene onto polychloroprene and polybutadiene with the use of stannic chloride were carried out in chloroform, and it was found that graft copolymers could be prepared (Table VIII).

TABLE VIII
Grafting Percentage and Efficiency for Polychloroprene and Polybutadiene[a]

Polymer	Yield, g./l.	Homopolystyrene, mole/l.	Graft copolymer, g./l.	Grafted polystyrene, mole/l.	Grafting percentage, %	Grafting efficiency, %
Polychloroprene	195.0	1.731	28.0	0.125	86.7	7.3
Polybutadiene	128.6	1.090	21.8	0.065	45.3	6.0

[a] $[R] = 15$ g./l., $[M] = 1.75$ mole/l., $[C] = 4.28 \times 10^{-2}$ mole/l., 20°C., 120 min.

References

1. P. H. Plesch, *Chem. Ind.* (*London*), **1958,** 954.
2. G. Kockelbergh and G. Smets, *J. Polymer Sci.*, **33,** 227 (1958).
3. P. M. Kamath and H. C. Haas, *J. Polymer Sci.*, **24,** 143 (1957).
4. M. Štolka, J. Vodehnal, and I. Kössler, *J. Polymer Sci. A*, **2,** 3987 (1964).
5. I. Kössler, J. Vodehnal, and M. Štolka, *J. Polymer Sci. A*, **3,** 2081 (1965).

Résumé

La polymérisation du styrène a été effectuée en solution de cyclohexane du caoutchouc naturel avec le chlorure d'étain. On a trouvé que la copolymérisation greffée du styrène se passe aussi bien que la cyclisation du caoutchouc lui-même. La vitesse de polymérisation du styrène était proportionnelle à la seconde puissance de la concentration en styrène et aux concentrations en chlorure d'étain et de caoutchouc naturel respectivement. L'énergie d'activation globale était d'environ 6 Kcal/mole. Le pourcentage de greffage croissait avec une augmentation de la concentration en caoutchouc. Par ailleurs, l'efficacité de greffage montrait une tendance inverse. Le pourcentage de greffage pouvait augmenter jusque 150% par addition de nitrobenzène, un solvant polaire.

Zusammenfassung

Die Polymerisation von Styrol wurde in einer Cyclohexanlösung von Naturkautschuk mit Zinn-IV-chlorid ausgeführt. Es fand sowohl Propfcopolymerisation von Styrol als auch Cyclisierung von Kautschuk statt. Die Polymerisationsgeschwindigkeit von Styrol war dem Quadrat der Styrolkonzentration sowie der Zinn-IV-chlorid- und Naturkautschukkonzentration proportional. Die Bruttoaktivierungsenergie betrug etwa 6 Kcal./Mol. Die prozentuelle Aufpfropfung nahm mit steigender Kautschukkonzentration zu,die Aufpfropfungsausbeute dagegen zeigte die umgekehrte Tendenz. Die prozentuelle Aufpfropfung konnte durch Zusatz von Nitrobenzol, einem polaren Lösungsmittel auf 150% gesteigert werden.

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Structural Effects in Heteroatom Systems. II. The Calculated Influence of Steric Effects on Polymerization–Depolymerization Equilibria in the Siloxane and Oxymethylene Series. Comparisons with the Phosphazene System.

H. R. ALLCOCK,* *Chemical Department,*
Central Research Division, American Cyanamid Company,
Stamford, Connecticut 06904

Synopsis

The relative stabilities of symmetrically substituted polysiloxanes and polyoxymethylenes are compared in terms of the side-group steric overlap parameters, by means of a semiempirical method described previously. The results provide a qualitative estimate of the relative thermodynamic ease of polymerization of cyclic siloxanes or monomeric methylene oxides or, conversely, of the relative resistance to depolymerization of the polymers. These calculated values are compared with those reported previously for phosphazenes. In general, for polymers of the type, $[R_2Si—O]_n$, $[R_2C—O]_n$, and $[R_2P=N]_n$, if the side group, R, is small (H, halogen or methyl) the inherent steric and bonding characteristics of the chain should cause the polymer stabilities to decrease in the order phosphazenes $\approx$ siloxanes $\gg$ oxymethylenes. If, however, bulkier side groups are present, the order of decreasing stability to depolymerization should be siloxanes $>$ phosphazenes $\gg$ oxymethylenes. In all cases, the depolymerization tendency should increase markedly as the side group overlap parameters increase, and polyoxymethylenes should be the most sensitive to such changes. The calculated results are compared with the limited experimental evidence at present available.

INTRODUCTION

In a previous paper[1] an attempt was made to explain the polymerization and depolymerization behavior of polyphosphazenes, $-[P(R_2)=N]-_n$, in terms of the steric influence of the side groups, R, on the thermodynamics of equilibration. The steric influence of each group was estimated in terms of the maximum rotational van der Waals radii (i.e., the volume swept out when each bond in the side group undergoes 360° rotation). The repulsions between the various units in the polymer were then estimated qualitatively in terms of the area of overlap of these van der Waals boundaries. It was concluded that, for polymers of this type, overlapping of side-group or chain-atom van der Waals radii should generally favor

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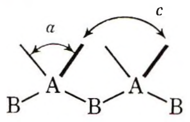
* Present address: Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802.

depolymerization to cyclic oligomers, and the calculated results were found to be reasonably consistent with the known experimental behavior of phosphazenes.

Polysiloxanes, $—[Si(R_2)—O]—_n$, and polyoxymethylenes, $—[C(R_2)—O]—_n$, fall into the same structural category as polyphosphazenes, and the present communication describes an attempt to apply the same approach to these systems also. It was anticipated that the results might allow some conclusions to be drawn about the relative thermodynamic stabilities to depolymerization of siloxanes and phosphazenes and of the relationship between these and oxymethylenes.

As discussed previously,[1] the relative enthalpies of $[—A(R_2)—B—]_n$ type polymers can be compared in terms of three steric interactions, the *a*-type (1:1) repulsion, the *c*-type (1:3) repulsion, and the *d*-type (1:4) repulsion. The latter two represent the principal interactions for the *trans*-planar (I) and *cis-trans*-planar (II) configurations of the chain.



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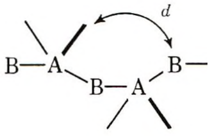

II

For polymer systems in which alternate chain atoms bear no substituents, the *c*-type repulsion is generally significantly greater than the *d*-type. If the side groups are sufficiently large, the *gauche* form will give rise to interactions which are intermediate between the *c*- and *d*-repulsions, and there will be no significant energy wells between the *trans*-planar and *cis-trans*-planar states. The *cis-trans*-planar arrangement of the chain should thus correspond to the lowest energy form if appreciable side group repulsions exist. The *a*- and *d*-type repulsions are, therefore, considered to be more valid measures of chain stability than is the *c*-type repulsion. Each of these repulsions can be estimated by the use of scale graphical representation of the chain, together with the van der Waals radii and side group rotational radii and profiles discussed previously.[1] One significant factor which distinguishes polyoxymethylene derivatives from polysiloxanes and polyphosphazenes is the fact that the depolymerization products of the former are expected to be predominantly monomeric carbonyl compounds rather than cyclic oligomers. Monomeric phosphazine, $R_2P{\equiv}N$, and siloxene, $R_2Si{=}O$, units do not, of course, exist as stable molecules.

EXPERIMENTAL

The atomic and molecular parameters used for the calculations are as follows:* bond angles: R—Si—R, 109.5°; O—Si—O, 109.5°; Si—O—Si,

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* Bond angles and interatomic distances for siloxanes are based on average values for $[Si(CH_3)_2—O]_3$, $[Si(CH_3)_2—O]_4$ and $[Si(CH_3)_2—O]_n$[2–7], while those for oxymethylenes are based on values reported for ethers, trioxane, paraldehyde, metaldehyde, and polyoxymethylene.[8–16]

140°; R—C—R, O—C—O, and C—O—C, 109.5°; covalent atomic radii: Si, 1.02 A.; O—(Si), 0.62 A.; C, 0.77 A.; O—(C), 0.66 A.; van der Waals radii:[17] Si, 2.1 A.; C, 1.7 A.; O, 1.5 A. Side-group parameters are as listed previously.[1]

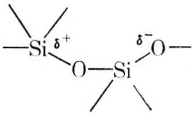
The side-group overlap areas were determined graphically. Those side-group overlaps which occurred within the van der Waals boundary of the supporting heteroatom were excluded. In this respect, it is important to note that an appreciable contribution to the *d*-type repulsion in polyoxymethylenes in the *cis-trans*-planar configuration arises from the overlap of 1:4 carbon and oxygen chain atoms. In Table I, this overlap is separated from that due to the side group–oxygen interaction. The small overlap between 1:4 silicon and oxygen radii in siloxanes is separated similarly.

RESULTS AND DISCUSSION

Calculated *a*-, *c*-, and *d*-side group overlap areas in polysiloxanes, polyoxymethylenes, and polyphosphazenes[1] are listed in Table I. The side groups chosen are for derivatives which have been synthesized or which might conceivably be expected to be synthesized with the use of known techniques. In general, the descending listing of increasing *a*- and *d*-overlap parameters in Table I should reflect an increasing tendency for the polymer to depolymerize.

Polysiloxanes

For each side group listed in Table I, except H, F, Cl, Br, I, and NH_2, there is less *a*- or *d*-overlap in siloxanes than in phosphazenes. This is, of course, principally due to the unusually wide bond angle at oxygen in siloxanes, which can be attributed to the high ionic character of the bond. Siloxanes should thus be somewhat less sensitive to side-group steric effects than phosphazenes. Furthermore, for all except the smallest side-groups, comparisons of the *c*- and *d*-overlap parameters (Table I) show that the *cis-trans*-planar form of the chain (II) is energetically more stable than the *trans*-planar configuration (I). The *gauche* orientation will be of intermediate stability. Even where no *c*- or *d*-overlaps occur (R = H, F, Cl, Br, I, and NH_2), the polar attraction between 1:4 silicon and oxygen atoms



III

(III) would be expected to exert some stabilizing influence on the *cis-trans*-planar form.* There is however, one significant difference between the

* Flory et al.[18] concluded that the *trans*-planar form of polydimethylsiloxane was the most stable configuration in solution because of c-type side group attractions. However, electron and x-ray diffraction measurements of dimethylsiloxane liquid and rubber[6,7] provide evidence for *gauche* conformations.

TABLE I
Steric Overlap Parameters for Polysiloxanes, Polyoxymethylenes, and Polyphosphazenes
Overlap parameters, A.[2]

	$(R_2Si—O)_n$			$(R_2C—O)_n$			$(R_2P{=}N)_n$		
Side group (R)	*a*	*c*	*d*[a]	*a*	*c*	*d*[a]	*a*	*c*	*d*[b]
H	—	—	—	—	—	—	—	—	—
F	—	—	—	—	1.2	0.6	—	—	—
Cl	—	—	—	0.1	3.6	1.2	—	0.2	—
Br	—	—	—	0.1	4.8	1.4	0.1	0.8	—
I	—	—	—	0.1	6.2	1.5	0.1	1.4	—
NH_2	—	—	—	—	5.2	1.5	—	1.5	—
CH_3	—	0.1	—	0.3	7.2	2.3	0.3	3.1	0.1
CF_3	0.8	4.0	0.1	1.6	14.5	4.0	1.5	9.3	1.5
C_6H_5	1.6	8.4	0.8	2.6	29.6	5.1	2.5	19.4	2.4
m-$CH_3C_6H_4$	1.7	24.2	0.8	2.6	57.6	5.1	2.6	43.0	2.5
$NHCH_3$, $N(CH_3)_2$	2.4	9.1	1.4	3.5	23.6	5.9	3.5	15.8	3.5
OCH_3	3.5	10.8	2.6	4.9	25.5	7.4	4.9	18.4	4.6
C_2H_5	3.9	12.5	2.9	5.2	28.7	7.7	5.3	21.0	5.0
o-$CH_3C_6H_4$	10.1	31.0	7.1	12.7	55.5	11.6	12.7	44.0	10.1
n-C_3H_7	12.4	38.8	9.0	15.5	64.7	11.8	15.2	53.4	12.0
OC_2H_5	12.7	38.4	9.3	16.0	64.3	11.8	15.0	53.0	12.2
NHC_6H_5, $N(C_6H_5)_2$	17.5	63.4	9.0	20.8	92.8	11.7	21.5	81.6	12.3
OCH_2CF_3	18.1	55.4	11.0	22.2	85.0	11.8	21.9	72.8	13.9
OC_6H_5	20.1	68.4	10.2	23.5	96.2	11.8	24.2	85.6	13.5
n-C_4H_9	28.1	81.6	14.0	32.8	119.6	11.8	32.3	103.4	14.8

[a] These values exclude the 0.06 A.[2] *d*-type overlap between Si and O chain atoms in siloxanes and the 1.2 A.[2] *d*-type overlap between C and O atoms in polyoxymethylenes.

[b] There is no *d*-type overlap of P and N van der Waals radii in polyphosphazenes.

siloxane and phosphazene chains in the *cis-trans* planar orientation. Whereas in phosphazenes there is no overlap of the van der Waals radii of the 1:4 phosphorus and nitrogen atoms, in siloxanes there is a small (0.06 A.^{2}) overlap between 1:4 silicon and oxygen atoms. This will serve to raise the energy of *cis-trans*-planar siloxane chains relative to phosphazene chains if bulky substituents are absent, particularly when this effect opposes the ionic attraction described above.

Since there is no *a*- or *d*-side group overlap in the dimethylsiloxane model, this system probably reflects a situation in which the thermodynamic stability of the chain is close to a maximum.* The combined effects of 1:4 skeletal steric repulsion, 1:4 skeletal polar attraction and *c*-type side group repulsion may cause the chain to assume a *gauche* orientation.

Polyoxymethylenes

There is a considerable (1.2 A.^{2}) overlap of 1:4 skeletal carbon and oxygen radii in the *cis-trans*-planar form of the polyoxymethylene chain. This is due principally to the relatively narrow angle at oxygen. If, therefore, the *c*-overlap is small (R = H or F), a *gauche* arrangement of the chain may be a more stable state.† Polar attraction of 1:4 carbon and oxygen atoms in the *cis-trans*-planar configuration would be less important for polyoxymethylenes than for siloxanes, because, although the skeletal atoms are closer, there is a smaller electronegativity difference in carbon–oxygen bonds (1.0, 22% ionic character) than in silicon–oxygen bonds (1.7, 51% ionic character) (based on Pauling electronegativity values).[21,22] The ionic character of the —P=N— bond is not known with certainty but it must have appreciable —$\overset{+}{\text{P}}$—$\overset{-}{\text{N}}$— character and may be more ionic than the siloxane bond.

If, however, bulkier side groups are present, (CH_3 groups or larger), the extremely large *c*-type repulsions will force the polyoxymethylene chain to assume or approach a *cis-trans*-planar arrangement in spite of the skeletal hindrance involved. The enthalpy of the molecule will be raised accordingly. Thus, the side group overlaps in polyoxymethylenes will nearly always be much greater than in either polysiloxanes or polyphosphazenes. Polyoxymethylenes should, therefore, have much lower ceiling temperatures than equivalent polyphosphazenes or polysiloxanes with the same side groups and should be more sensitive to minor increases in side-group dimensions than in other systems.

There is an additional factor which serves to enhance the thermodynamic instability of polyoxymethylene chains. While the depolymerization

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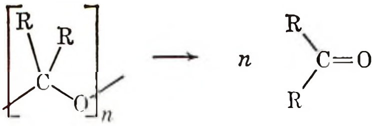
* Lee and Haberland[19] have indicated that $(CH_3HSi—O)_n$ has greater chain flexibility than $[(CH_3)_2Si—O]_n$. However, the onset of chain motions in $(CH_3HSi—O)_n$ (as determined by the same authors from the beginning of NMR line narrowing) occurs only 5° below the equivalent point for $[(CH_3)_2Si—O]_n$, and this implies that side groups smaller than methyl do not influence the rotational barrier height appreciably.

† Flory and Mark[20] concluded that dispersion attractions between O and CH_2 units were mainly responsible for the *gauche* arrangement.

products from polysiloxanes or polyphosphazenes will be cyclic oligomers with bond angles not appreciably different from those in the polymer, the depolymerization products from polyoxymethylenes are expected to be monomeric carbonyl compounds:



Depolymerization of polyoxymethylenes thus involves not only a total elimination of all *c*- and *d*-type strains, but also a considerable release of *a*-type repulsion. Conversion of a polyoxymethylene to a carbonyl compound involves a change from an sp^3 tetrahedral carbon atom to an sp^2p trigonal ($p\pi$) bonded form. The bond angle between the side groups will thus increase from 109.5° to 120° in the depolymerization process, with a concurrent release of all or most of the *a*-type side-group repulsions. Substituted polyoxymethylenes should thus be considerably less thermodynamically stable than equivalent phosphazenes or siloxanes.

COMPARISONS WITH EXPERIMENTAL DATA

Siloxanes

The ability of hexamethylcyclotrisiloxane, $[(CH_3)_2SiO]_3$, or octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, to equilibrate to high molecular weight linear or macrocyclic polymers in the presence of cationic or anionic catalysts is well known. Similarly, the depolymerization of polydimethylsiloxane to cyclic oligomers in the 350–400°C. temperature region has been recognized for many years.[23,24] However, most of the reported depolymerization experiments are for nonequilibrium conditions, in which continuous removal of the more volatile oligomers takes place. If a ceiling temperature exists for polydimethylsiloxanes, it is almost certainly above 400°C. Evidence has been presented that, at least up to 180°C. the ratio of polydimethylsiloxane homologs higher than the trimer is independent of temperature.[25–28] Between 140 and 400°C., the ratio of tetramer in the equilibrium mixture increases only from about 2 to 8%,[29] a result which suggests either that a very high ceiling temperature exists for this system or that there is no ceiling temperature. This behavior is consistent with the absence of *a*- or *d*-overlaps in polydimethylsiloxanes, since conversion of cyclic tetramer to high polymer, for example, should be accompanied by no increase in side-group repulsion. In fact, $\Delta H_{\text{polym.}}$ should be zero or negative. If $\Delta H_{\text{polym.}}$ is zero, the polymer concentration should not change appreciably with temperature.[30] Only a slight shift to favor the depolymerized species might be expected at high temperatures due to the resultant increase in translational entropy, but even this may be counteracted in the dimethylsiloxane system by an increased rotational entropy in the high polymer. If $\Delta H_{\text{polym.}}$ is slightly negative (due to a release of ring strain on polymerization), then a very high ceiling temperature would be expected.

The thermal behavior of dimethylsiloxane should thus represent a maximum degree of thermodynamic stability for polysiloxanes and should also typify the behavior of the (yet unknown) derivatives where R is H, F, Cl, Br, I, or NH_2. In spite of the considerable amount of work which has been reported for dimethylsiloxane systems, there is almost no thermal equilibration data available for compounds in which R is any group other than methyl. Andrianov has indicated that the decreasing activity of cyclosiloxanes to acid-catalyzed polymerization with side-group changes, in the order $CH_3 > C_2H_5 > C_6H_5 > C_6H_4Cl > C_6H_3Cl_2 > O[Si(CH_3)_2O]_4 > OSi(CH_3)_3 > OSi(C_2H_5)_3$, may be attributed to the influence of the side group on the thermodynamics of equilibration.[29] However, kinetic effects almost certainly contribute to this order of reactivities. For phenyl derivatives, $[(C_6H_5)_2SiO]_n$, there is some evidence that the cyclic trimer and tetramer are formed in preference to higher polymers in silanediol cyclization,[31] and equilibration studies with poly(trifluoropropylmethyl)siloxane, $[(CF_3CH_2CH_2)(CH_3)SiO]_n$, showed that the cyclic species are much more strongly favored than in the dimethylsiloxane system.[32] However, larger side groups should cause a marked lowering in the thermodynamic stability of polymers relative to cyclic oligomers in the order of the increasing overlap parameters listed in Table I.

Polyoxymethylenes

Polyformaldehyde and polyacetone are the only symmetrically substituted polyoxymethylenes which have been synthesized. Polyformaldehyde, $[H_2C—O]_n$, depolymerizes near 100°C. Dainton and Ivin calculated the ceiling temperature of polyoxymethylene glycol to be 137°C.[33] The thermal behavior of polyformaldehyde probably represents the maximum thermodynamic stability that can be expected for a symmetrical polyoxymethylene. The rate of depolymerization of a polyoxymethylene may be retarded by a "blocking" of terminal hydroxy groups or by use of a polymer with a molecular weight so high that the concentration of catalytic terminal units is infinitely small, but any side group larger than hydrogen should lower the thermodynamic stability of the polymer appreciably. A measure of the sensitivity of this system to steric repulsions is provided by the fact that polyacetone, $[(CH_3)_2C—O]_n$, depolymerizes rapidly to monomer at room temperature[34] and also by the fact that unsymmetrical polyoxymethylenes, $[HC(R)—O]_n$, where R is C_2H_5, n-C_3H_7, n-C_4H_9, or n-C_6H_{13}, depolymerize readily at room temperature.[35–37]

The fact that no other symmetrical polyoxymethylenes have been prepared is largely explained by the overlap parameters in Table I. Only polycarbonyl fluoride, $[F_2C—O]_n$, would be expected to have a comparable stability to polyformaldehyde. (Similar arguments appear to apply to polythiocarbonyl derivatives.[38]). Polycarbonyl chloride, $[Cl_2C—O]_n$, and polydiaminocarboxane, $[(NH_2)_2C—O]_n$, should in theory be more stable thermodynamically than polyacetone, but all the higher polyketones, substituted polydiaminocarboxanes, and poly(alkoxy and aryloxy carboxanes), $[(RO)_2C{-}O]_n$, should be less stable than polyacetone.

References

1. H. R. Allcock, *Inorg. Chem.*, **5**, 1320 (1966).
2. G. Peyronel, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, **16**, 78 (1954).
3. E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).
4. H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1955).
5. L. K. Frevel, quoted by P. J. Flory et al., *J. Am. Chem. Soc.*, **74**, 3364 (1952).
6. C. W. Lufey, F. S. Palubinskas, and L. R. Maxwell, *J. Chem. Phys.*, **19**, 217 (1951).
7. G. Damaschun, *Kolloid Z.*, **180**, 65 (1962).
8. V. Schomaker, quoted by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).
9. V. Busetti, G. Carazolo, and M. Mammi, *Gazz. Chim. Ital.*, **92**, 1362 (1962).
10. V. Busetti, G. Carazolo, and M. Mammi, *Acta Cryst.*, **16**, A53 (1963).
11. D. C. Carpenter and L. O. Brockway, *J. Am. Chem. Soc.*, **58**, 1270 (1936).
12. P. G. Ackermann and J. E. Mayer, *J. Chem. Phys.*, **4**, 377 (1936).
13. H. M. Powell, G. Huse, and P. W. Cooke, *J. Chem. Soc.*, **1943**, 153.
14. L. Pauling and D. C. Carpenter, *J. Am. Chem. Soc.*, **58**, 1274 (1936).
15. H. Tadokoro, T. Yasumoto, S. Murahashi, and I. Nitta, *J. Polymer Sci.*, **44**, 266 (1960).
16. G. Carazolo and M. Mammi, *J. Polymer Sci. A*, **1**, 965 (1963).
17. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
18. P. J. Flory, V. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 146 (1964).
19. C. L. Lee and G. G. Haberland, *J. Polymer Sci. B*, **3**, 883 (1965).
20. P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964).
21. L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed., Cornell Univ. Press, Ithaca, N. Y., 1960, p. 63.
22. W. Gordy and W. J. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).
23. W. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).
24. M. J. Hunter, J. F. Hyde, E. L. Warrick, and H. J. Fletcher, *J. Am. Chem. Soc.*, **68**, 667 (1946).
25. J. B. Carmichael and R. Winger, *J. Polymer Sci. A*, **3**, 971 (1965).
26. T. Ishzuka and T. Aihara, *Kogyo Kagaku Zasshi*, **59**, 1198 (1956).
27. Z. Laita and M. Jelinek, *Polymer Sci. USSR*, **4**, 535 (1963).
28. M. Morton and E. E. Bostick, *J. Polymer Sci. A*, **2**, 523 (1964).
29. K. A. Andrianov, *Metalorganic Polymers*, Interscience, New York, 1965, pp. 34, 35.
30. G. Gee, *Inorganic Polymers, International Symposium (Nottingham) Chemical Society Special Publication*, No. **15**, 1961, p. 67.
31. C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945).
32. E. D. Brown and J. B. Carmichael, *J. Polymer Sci. B*, **3**, 473 (1965).
33. F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 331 (1950).
34. V. A. Kargin, V. A. Kabanov, V. P. Zubov, and I. M. Papisov, *Dokl. Acad. Nauk. SSSR*, **134**, 1098 (1960).
35. J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Interscience, New York, 1963, p. 112.
36. A. Novak and E. Whalley, *Can. J. Chem.*, **37**, 1710, 1718 (1959).
37. O. Vogl, *J. Polymer Sci. A*, **2**, 4621 (1964).
38. W. J. Middleton, H. W. Jacobson, R. E. Putnam, H. C. Walter, D. G. Pye, and W. H. Sharkey, *J. Polymer Sci. A*, **3**, 4115 (1965).

Résumé

Les stabilités relatives des polysiloxanes substitués symétriquement et des polyoxyméthylènes sont comparées sur la base des paramètres de recouvrement stérique des groupes latéraux au moyen d'une méthode semi-empirique décrite antérieurement. Les résultats permettent d'obtenir une estimation qualitative de la facilité thermodynamique relative de polymerisation des siloxanes cycliques ou des oxydes méthyléniques monomériques ou également de la résistance relative de ces polymères à la dépolymérisation. Les valeurs calculées sont comparées à celles rapportées préalablement pour les phosphazènes. En général, pour les polymères du type $(R_2Si{-}O)_n$, $(R_2C{-}O)_n$ et $(R_2P{=}N)_n$ si le groupe latéral R est petit (H halogène ou méthyle) les caractéristiques inhérentes stériques et liaisons de la chaîne sont responsables de la stabilité des polymères et donnent l'ordre décroissant phosphazènes ≈ siloxanes ≫ polyoxyméthylènes. Si, toutefois, des groupes latéraux plus importants sont présents, l'ordre de stabilité décroissante à la dépolymérisation serait siloxanes > phosphazènes ≫ oxyméthylènes. Dans tous les cas, la tendance à dépolymériser croitrait de facon notoire lorsque le paramètre de recouvrement des groupes latéraux croît et le polyoxyméthylène serait le plus sensible à de telles variations. Les résultats calculés sont comparés avec les données expérimentales limitées disponibles actuellement.

Zusammenfassung

Die relative Stabilität symmetrisch substituierter Polysiloxane und Polyoxymethylene wird mittels einer schon früher beschriebenen semiempirischen Methode bezüglich der Parameter für die sterische Uberlappung der Seitengruppe verglichen. Die Ergebnisse liefern ein qualitatives Mass für die relative thermodynamische Polymerisationswilligkeit der Polymeren. Diese berechneten Werte werden mit den früher für Phosphazene mitgeteilten verglichen. Im allgemeinen sollte für Polymere vom Typ $[R_2Si{-}O]_n$, $[R_2C{-}O]_n$ und $[R_2P{=}N]_n$ bei kleiner Seitengruppe R (H, Halogen oder Methyl) die spezifische sterische und Bindungs-Charakteristik der Kette eine Abnahme der Polymerstabilität in der Reihenfolge Phosphazene ≈ Siloxane ≫ Oxymethylene verursachen. Bei Anwesenheit von Seitengruppen mit grösserer Raumbeanspruchung sollte die Reihe der abnehmenden Polymerstabilität dagegen sein: Siloxane > Phosphazene ≫ Oxymethylene. In allen Fällen sollte die Depolymerisationstendenz mit Anwachsen der Parameter für die Seitengruppenüberlappung merklich ansteigen und Polyoxymethyle sollten dafür am empfindlichsten sein. Die Ergebnisse der Rechnung werden mit demderzeit vorhandenen, beschränkten experimentellen Material verglichen.

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Carborane Polymers. IV. Polysiloxanes

N. MAYES, J. GREEN, and M. S. COHEN, *Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey 07834*

Synopsis

Carboranes attached to silicon through straight-chain alkyl groups were prepared and characterized for thermal stability by TGA and molecular weight change on heating. The monomers for these polymers were prepared generally by platinum-catalyzed addition of a silylhydride to an alkenyl or dialkenyl carborane. Polymerization was effected by hydrolysis-condensation of chlorosilanes, ring opening of cyclosiloxanes, and condensation of alkoxy and chlorosilanes. Two types of polymer structures were prepared, one contained *m*-carborane in the chain backbone, the other contained *o*-carborane as pendant alkylcarborane groups. Both types were obtained as elastomers; however, higher proportions of carborane in the polymers reduced elasticity and finally resulted in nonelastomers. TGA of the backbone carborane siloxane polymer indicated degradation at 370°C. in nitrogen and at 235°C. in air. Chain scission, as determined by molecular weight decrease, was observed on heating in nitrogen at 350°C. TGA of the pendant carborane siloxane polymer indicated that degradation in nitrogen and in air occurred at greater than 400°C. However, chain scission, as determined by molecular weight decrease, was observed upon heating at 300°C. in nitrogen.

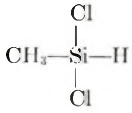
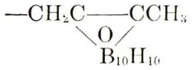
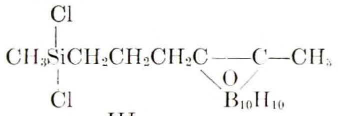
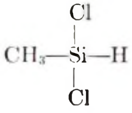
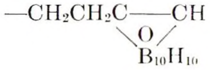
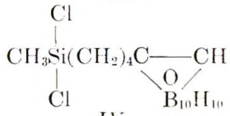
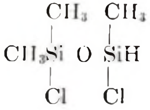
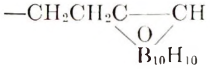
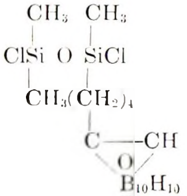
INTRODUCTION

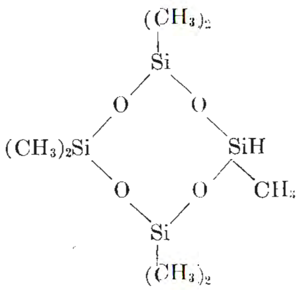
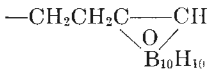
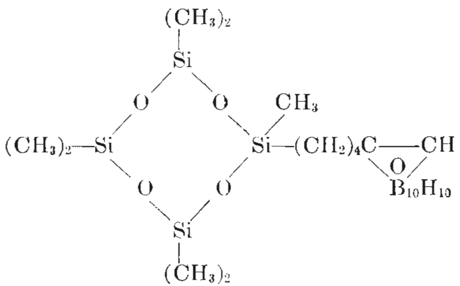
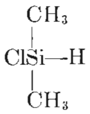
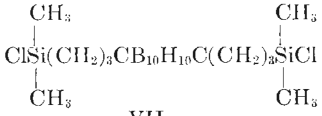
Previous papers in this series[1-3] have described the preparation and properties of carborane polyesters, polyformals, and vinyl polymers. We now report the preparation and properties, particularly the thermal properties, of carborane polysiloxanes.

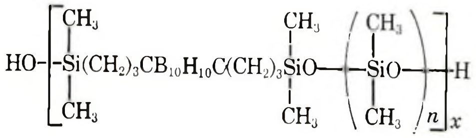
Poly-*m*-carboranylene siloxanes in which carborane is attached directly to silicon have recently been reported.[4] We have prepared carborane siloxane polymers in which carborane is attached to silicon through straight-chain alkyl groups. These polymers are of two types; one contains *m*-carborane in the polymer backbone, the other contains *o*-carborane as pendant groups. We did not attempt to synthesize *o*-carborane backbone polymers because we anticipated difficulties in obtaining linear polymeric products. *o*-Carborane has demonstrated a strong tendency to form cyclic compounds rather than linear products.[5-7] The structures of the two types of polymers that were prepared are illustrated by I and II. These polymers were investigated with the objective of obtaining thermally stable materials, therefore some thermal property determinations were made and are reported here.

TABLE I
Carborane Silane and Siloxane Monomers

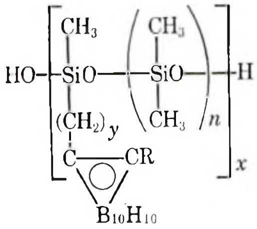
$\equiv SiH + CH_2{=}CHR' \rightarrow \equiv SiCH_2CH_2R'$

$\equiv SiH$	R′	Product
		 III
		 IV
		 V

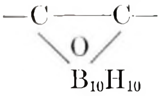
		 VI
 $ClSi(CH_3)_2H$	$—CH_2CB_{10}H_{10}CCH_2CH{=}CH_2$	 $ClSi(CH_3)_2(CH_2)_3CB_{10}H_{10}C(CH_2)_3Si(CH_3)_2Cl$ VII



I



II

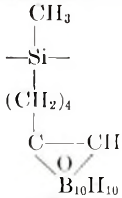
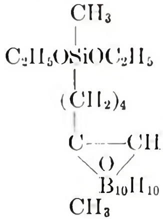
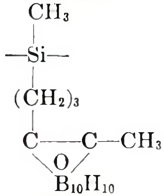
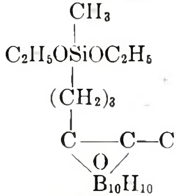
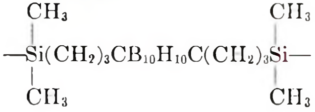
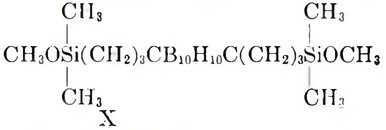
where $n = 0, 1, 3$; $y = 3, 4$; $R = H, CH_3$; $—CB_{10}H_{10}C—$ = *m*-carborane;  = *o*-carborane.

RESULTS

Monomer Synthesis

Some carborane silane and siloxane monomers were prepared utilizing the platinum or chloroplatinic acid-catalyzed addition of hydrosilanes to

TABLE II
Carborane Alkoxy Silane Monomers
$RCl_2 + (C_nH_{2n+1}O)_3CH \rightarrow R(C_nH_{2n+1}O)_2$

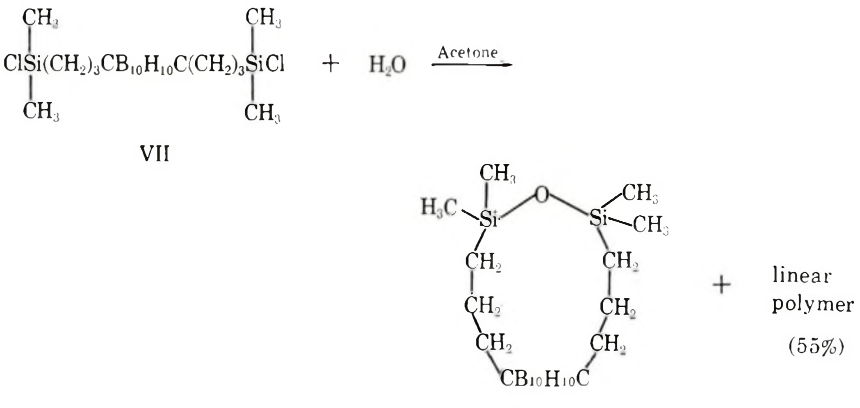
R	Product
	 VIII
	 IX
 $—Si(CH_3)_2(CH_2)_3CB_{10}H_{10}C(CH_2)_3Si(CH_3)_2—$	 $CH_3OSi(CH_3)_2(CH_2)_3CB_{10}H_{10}C(CH_2)_3Si(CH_3)_2OCH_3$ X

alkenyl carboranes.[8] The materials prepared in this manner are given in Table I.

Chlorine substituents on silicon activated the addition of hydrosilanes to the carboranyl alkenes. The addition of dichlorodimethylsilane to butenyl carborane occurred instantaneously and was accompanied by an exotherm. In contrast, alkoxy-substituted silyl hydrides added to carboranyl alkenes with reluctance, and the reaction time was characterized by long reaction time and low conversion.[9a]

To prepare the carborane alkoxy silane monomers necessary for this work, we found it advantageous to conduct the addition reaction with the chloro derivatives and subsequently convert the chloro compounds to alkoxys by reaction with trialkoxymethane. The materials that were prepared in this manner are shown in Table II.

A *m*-carborane cyclosiloxane capable of ring-opening polymerization was also synthesized. This was obtained from the hydrolysis of 1,7-[bis-(3-chlorodimethylsilyl)propyl]-*m*-carborane (VII). The hydrolysis yielded, in addition to the cyclic compound, 55% of the linear polysiloxane.



$ClSi(CH_3)_2(CH_2)_3CB_{10}H_{10}C(CH_2)_3Si(CH_3)_2Cl + H_2O \xrightarrow{\text{Acetone}}$

VII

XI

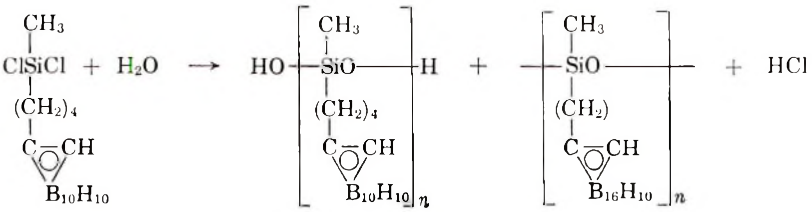
(45%)

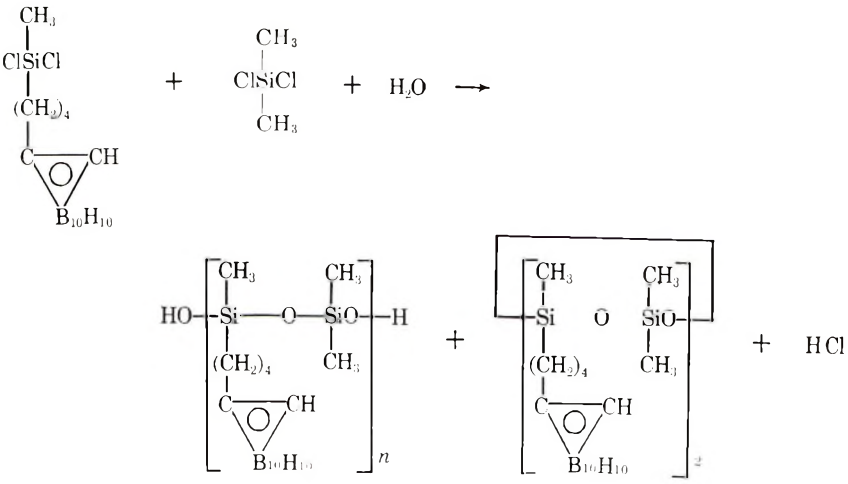
Polymerization

Polymerizations leading to polymers of types I and II were investigated with the objective of obtaining high yields of high molecular weight polymer. The several methods of polymerization that were investigated for each system included: (*1*) hydrolysis–condensation of chloro- and alkoxysilanes, (*2*) ring-opening polymerization of cyclosiloxanes, (*3*) condensation of chloro- and alkoxysilanes with alkyl chloride elimination.

Hydrolysis–Condensation Polymerization. Many silanols are too unstable to exist as such, instead they condense with the elimination of water to form a siloxane. Such silanols, when they are difunctional, condense to polysiloxanes which are either linear, cyclic or a mixture of both. The carborane dichloro- and diethoxysilanes were found to exhibit this behavior and monomers that lead to polymers of types I and II polymerized in this manner.

Monomers III, IV, and V from Table I, and VIII and IX from Table II were found to undergo hydrolysis–condensation to yield polymers of type II along with a mixture of cyclic polysiloxanes. Mixtures of cyclic and linear products were obtained when homopolymers were prepared by hydrolysis of the carborane silane compounds and also when copolymers were prepared by hydrolysis of 1:1 molar ratios of difunctional carboranesilanes and either dichloro- or diethoxydialkylsilanes.



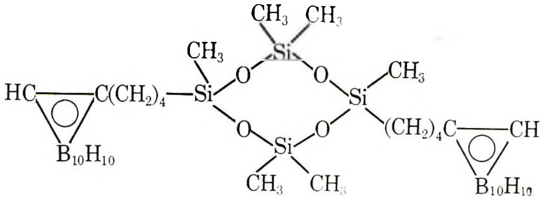


The homopolymer products were brittle, glassy solids that softened at about 70°C. The average molecular weight of such products never exceeded 2200. No serious attempt was made to separate the linear and cyclic products and characterize them individually. However, this was done for the cohydrolysis products, as described below.

The linear and cyclic components of the product from the 1:1 cohydrolysis of methyl-4-(1-*o*-carboranyl)butyldichlorosilane and dimethyldichlorosilane were separated and characterized. Before separation the product is an elastomeric gum of molecular weight 2400. Upon treatment with benzene this product separated to a benzene-soluble portion of molecular weight 890 and a benzene-immiscible portion of molecular weight 14,000.

The latter material is swollen by benzene and dissolved by acetone. It is a tough, flexible thermoplastic material that flows when heated above 100°C. Infrared and elemental analysis indicates it to be essentially a 1:1 copolymer of presumably random structure.

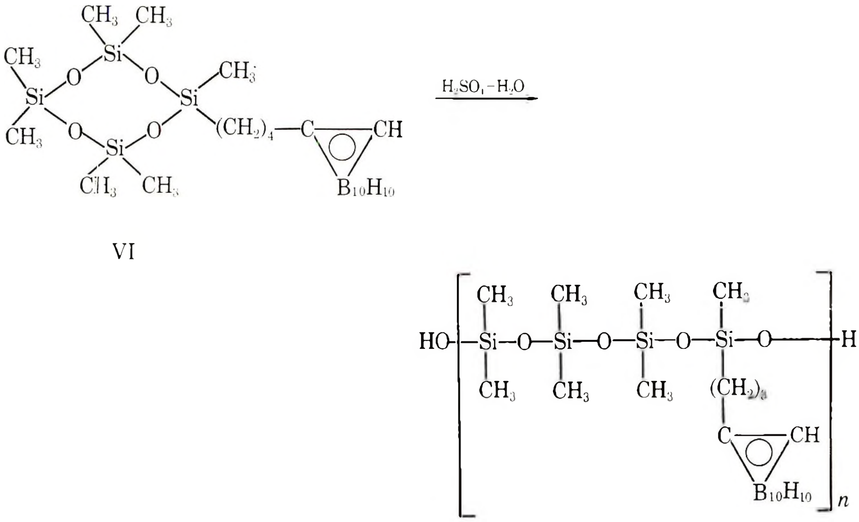
The low molecular weight portion, upon molecular distillation at 200°C./0.4 μ yielded a crystalline product which we believe to be bis-4-(1-*o*-carboranyl)butylhexamethylcyclotetrasiloxane (XII).

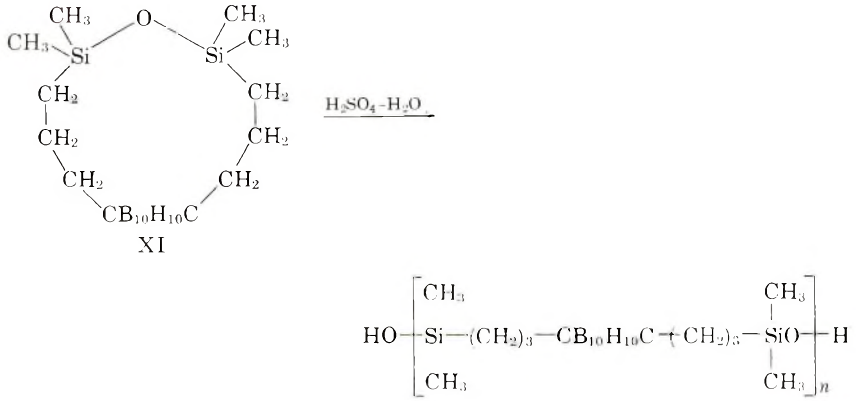

XII

The infrared spectrum supports this structure, as does the molecular weight (calculated 665; found 670).

The hydrolysis–condensation of 1,7-[bis(3-chlorodimethylsilyl)propyl]-carborane was mentioned above. It yields, in addition to the cyclic compound, XI, a linear polymer of type I which is obtained as a tacky gum, soluble in benzene and acetone, and of 6300 molecular weight.

Ring-Opening Polymerization. Polymers of types I and II were obtained by ring-opening polymerization of carborane cyclosiloxanes XI and VI, respectively. These cyclics, upon being heated with acid catalysts, opened to polymers of relatively high molecular weight. They did not respond to base catalysis.


VI

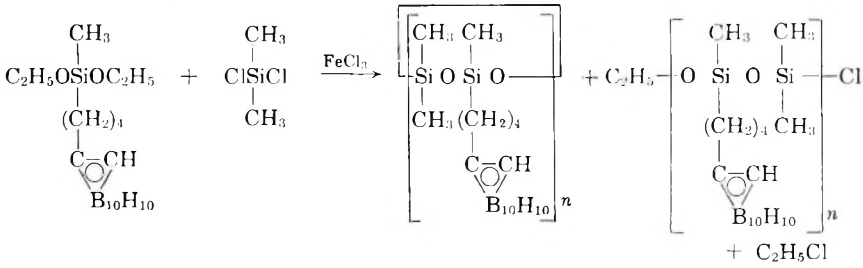


XI

Cyclic VI yielded a tacky, elastomeric gum polymer. In early stages of polymerization the product, a viscous liquid, was soluble in solvents such as benzene and acetone; however, continued reaction led to gum products which swelled in these solvents.

Cyclic XI yielded polymer of molecular weight 8500 when treated with concentrated phosphoric acid and a similar product when treated with concentrated sulfuric acid. These products were elastomeric gums and were completely soluble in aromatic solvents. Product of apparently higher molecular weight was obtained by use of diluted sulfuric acid catalyst. The effect of diluting the catalyst has been discussed by Andrianov.[10] The higher polymer was a considerably tougher and more elastomeric gum; however, it was no longer soluble in aromatic solvents, and the molecular weight is not known.

Condensation Polymerization. Polymers of types I and II were obtained from the ferric chloride-catalyzed reaction of dichloro- and diethoxysilanes. For example, (4-*o*-carboranylbutyl) diethoxymethylsilane and dichlorodimethylsilane reacted to form linear copolymer, cyclic polysiloxane and ethyl chloride.



The polymers that were prepared this way were of relatively low molecular weight and were generally obtained as viscous liquids.

Thermal Stability

Both backbone carborane (type I) and pendant carborane (type II) siloxane polymers exhibited high thermal stability in nitrogen atmosphere.

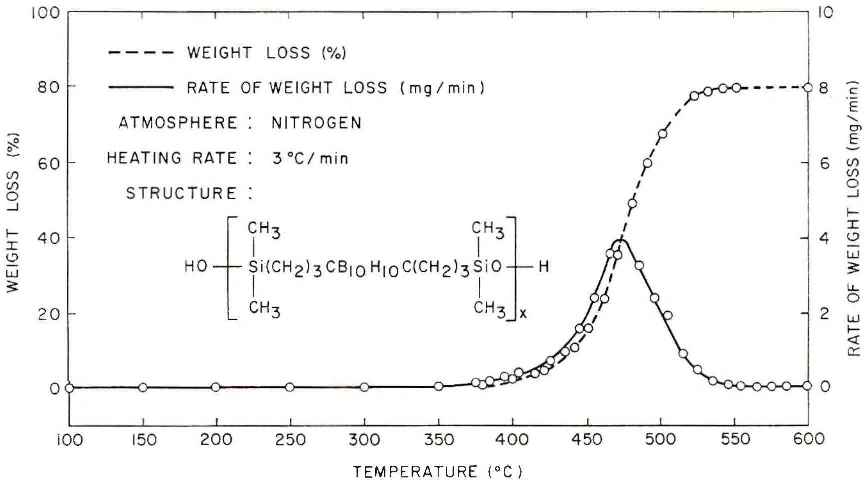


Fig. 1. TGA of type I polymer in nitrogen: (- -) weight loss; (——) rate of weight loss. Heating rate: 3°C./min.

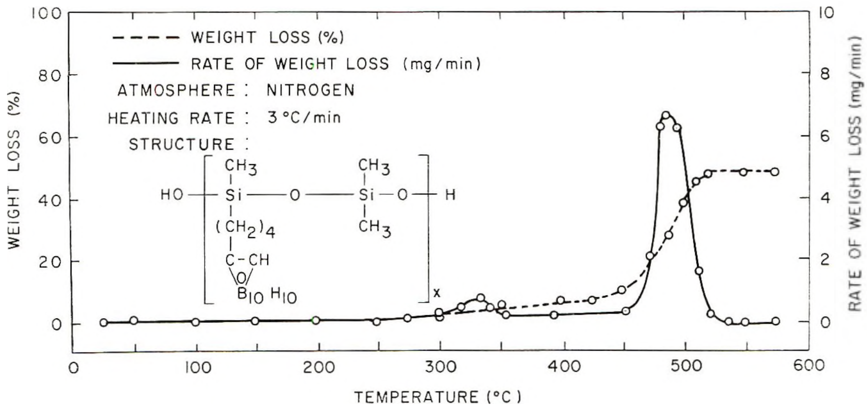


Fig. 2. TGA of type II polymer in nitrogen: (- -) weight loss; (——) rate of weight loss. Heating rate: 3°C./min.

TGA of type I polymer (Fig. 1) shows weight loss beginning at 370°C. with maximum rate of weight loss occurring at 475°C. This polymer has been prepared by ring-opening polymerization and unreacted monomer had been removed by sublimation. Therefore the first weight loss indicated in the TGA is probably due to degradation and not loss of volatile components.

TGA, in nitrogen atmosphere, of type II polymer (Fig. 2), which was not fractionated to remove low molecular weight components, indicates first weight loss at 300°C. This initial weight loss is probably due to volatile components. The major weight loss, which is undoubtedly a result of degradation, occurs above 400°C. with the maximum rate being at 480°C.

Both polymer types exhibited lower thermal stability in air atmosphere. Type I polymer began to lose weight in air at 235°C. and the thermogram

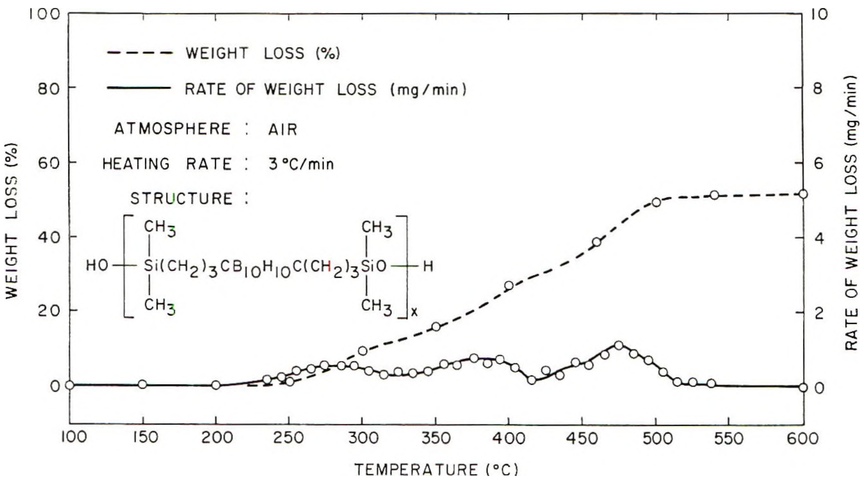


Fig. 3. TGA of type I in polymer in air: (- -) weight loss; (——) rate of weight loss. Heating rate: 3°C./min.

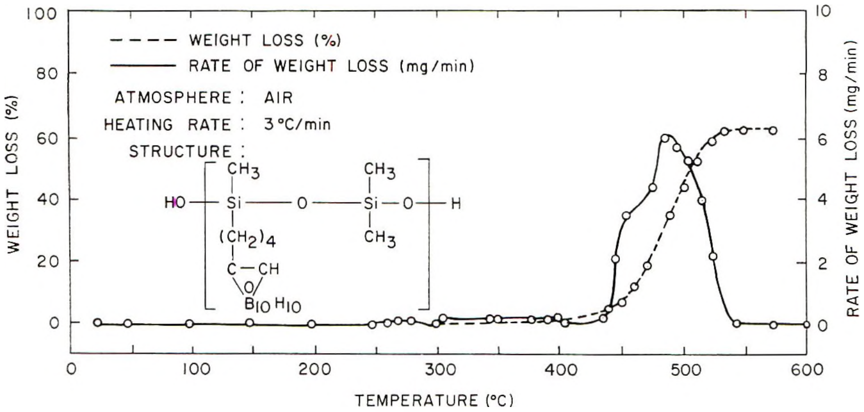


Fig. 4. TGA of type II polymer in air: (- -) weight loss; (——) rate of weight loss. Heating rate: 3°C./min.

(Fig. 3) shows three rate maxima at 280, 375, and 475°C. The type II polymer exhibits a small weight loss in air beginning at 250°C. (Fig. 4) however, the major weight loss begins about 400°C. with the rate maxima occurring at 450 and 480°C. The TGA's indicate both polymers to be of the same order of thermal stability in nitrogen atmosphere. In air atmosphere, however, there is a significant difference. Polymer I degrades extensively below 400°C. Polymer II is apparently stable to this temperature.

Another measure of thermal stability, that of molecular weight change upon thermal aging, indicates that, in nitrogen atmosphere, polymer II actually degrades at lower temperatures than does polymer I. Polymer samples of known molecular weights were heated in sealed glass tubes at

TABLE III
Thermal Degradation of Carborane Siloxane Polymers in Nitrogen

Polymer type	Temperature, °C.	Time, hr.	Molecular weight	
			Original	After heating
I	300	24	6300	7800
I	350	24	6300	6000
II	180	40	4500	8300
II	200	40	4500	5500
II	250	40	4500	4800
II	300	24	7700	4600
II	300	40	4500	4000
II	300	168	7700	1580
II	350	24	7700	2600

several temperatures, and molecular weights were determined after heating. The data, presented in Table III, show that the molecular weight of polymer II samples increased upon being heated at temperatures up to 250°C. evidencing additional reaction of terminal groups. At 300°C. a definite decrease in molecular weight indicated degradation had occurred. Some degradation may have occurred as low as 200°C., since molecular weight after heating at 200°C. was less than after heating at 180°C. Apparently processes of polymerization and degradation were in competition and only at or near 300°C. did degradation become dominant. Similar behavior was observed for polymer I, except that degradation, if any, occurred at or near 350°C. This indicates that the degradation temperature of polymer I is possibly 50°C. higher than that of polymer II.

The degradation observed in both cases is probably thermal rearrangement of linear polymer to more thermodynamically stable cyclic compounds. These cyclic compounds are not volatile, so evidence for their formation is not manifested by weight loss in TGA experiments.

EXPERIMENTAL

Materials

The silanes, dichloromethylsilane, dichlorodimethylsilane, and diethoxydimethylsilane were obtained from Silicones Division, Union Carbide Corporation and used as received.

Chlorodimethylsilane was not commercially available. It was prepared by reduction of dichlorotetramethyldisiloxane (obtained by partial hydrolysis of dichlorodimethylsilane[11]) with lithium aluminum hydride. The reduction, carried out in ether solution, yielded 53% (based on lithium aluminum hydride) chlorodimethylsilane which, because it boils at 36°C., was distilled with ether and used in ether solution. It has been reported that partial reduction of organohalogenosilanes is not possible.[9b] The above-described reduction of dichlorotetramethylsiloxane is a means of doing this indirectly by first partially hydrolyzing dichlorodimethylsilane and then reducing the siloxane bond. That reduction occurs preferentially at the siloxane bond is shown by the 53% yield of chlorodimethylsilane.

1,3-Dichloro-1,1,3-trimethyldisiloxane was prepared by the partial cohydrolysis in ether solution of dichlorodimethylsilane and dichloromethylsilane. Fractional distillation of the resulting mixture yielded 14% of 1,3-dichloro-1,1,3-trimethyldisiloxane, b.p. 120–121°C./756 mm. lit.[12] b.p. 120°/747 mm.).

1,7-Diallyl-*m*-carborane was prepared by the reaction of 1,7-dilithio-*m*-carborane[13] and allyl bromide in ether solution. The distilled product, b.p. 63°C./0.15 mm., n_D^{20} 1.5335, was obtained in 92% yield.

ANAL. Calcd. for $C_8H_{20}B_{10}$: C, 42.82%; H, 8.98%; B, 48.18%. Found: C, 42.72%; H, 8.87%; B, 48.17%.

Dichloro(1-methyl-*o*-carboran-2-yl propyl) methylsilane (III) was obtained upon addition of dichloromethylsilane to 1-allyl-2-methyl-*o*-carborane.[14] The reaction, conducted with a 40% molar excess of silane added carefully to the allyl compound at 90–95°C. in the presence of chloroplatinic acid catalyst, yielded 92% of distilled product, b.p. 135°C./0.02 mm., n_D^{25} 1.5338.

Diethoxy(1-methyl-*o*-carboran-2-yl propyl)methylsilane (IX) resulted from the reaction of dichloro(1-methyl-*o*-carboran-2-yl propyl)methylsilane and triethoxymethane. The reaction, conducted with an excess molar quantity of triethoxymethane, was heated at 80°C. for 3 hr., to yield 82% of distilled product, b.p. 144°C./0.08 mm., n_D^{25} 1.5020.

Dichloro(4-*o*-carboranylbutyl)methylsilane (IV) was prepared by careful addition of dichloromethylsilane to 1-(3-butenyl)-*o*-carborane[14] in the presence of chloroplatinic acid at 40–45°C. Reaction occurred exothermically to yield 92% of distilled product b.p. 165°C./0.05 mm., m.p. 45–47°C.

ANAL. Calcd. for $C_7H_{22}B_{10}Cl_2Si$: C, 26.8%; H, 7.08%; B, 34.5%; Cl, 22.7%. Found: C, 26.5%; H, 7.15%; B, 34.1%; Cl, 22.2%.

Diethoxy(4-*o*-carboranylbutyl)methylsilane[14] (VIII) was prepared by treatment of the dichloro derivative with excess triethoxymethane at 80°C. for 3 hr. The distilled product (b.p. 150°C./0.07 mm., n_D^{25} 1.5007) was collected in 88% yield.

1,3-Dichloro-3(4-*o*-carboranylbutyl)-1,1,3-trimethyldisiloxane (V) resulted from the addition of 1,3-dichloro-1,1,3-trimethyldisiloxane to 1-(3-butenyl)-*o*-carborane at 85°C. in the presence of chloroplatinic acid catalyst. The exothermic reaction yielded 85% of distilled product, b.p. 178°C./0.02 mm., n_D^{25} 1.5082.

ANAL. Calcd. for $C_9H_{28}B_{20}Cl_2OSi_2$: C, 27.89%; H, 7.26%; Cl, 18.25%. Found: C, 27.85%; H, 7.32%; Cl, 18.07%.

Heptamethyl(4-*o*-carboranylbutyl)cyclotetrasiloxane was prepared by addition of heptamethylcyclotetrasiloxane to 1-(3-butenyl)-*o*-carborane at

123°C. in the presence of 5% platinum on carbon catalyst. The reaction yielded 50% of product which distilled from a short path still at 148–156°C./ 5.5 × 10^{-4} mm., n_D^{20} 1.4780, m.p. 35–43°C.

Anal. Calcd. for $C_{13}H_{40}B_{10}Si_4$: C, 32.4%; H, 8.38%; B, 22.5%. Found: C, 29.6%; H, 7.68%; B, 20.59%.

1,7-Bis(chlorodimethylsilylpropyl)-*m*-carborane resulted from addition of excess chlorodimethylsilane to 1,7-diallyl-*m*-carborane in the presence of 5% platinum on carbon catalyst and ether solvent. The reactants were heated at reflux (36–37°C.) overnight and the product collected by distillation (b.p. 175°C./0.07 mm.) in 85% yield.

Anal. Calcd. for $C_{12}H_{34}B_{10}Cl_2Si_2$: C, 34.84%; H, 8.29%; B, 26.16%; Cl, 17.83%; neutralization equivalent, 206.8. Found: C, 34.18%; H, 8.85%; B, 25.94%; Cl, 17.17%; neutralization equivalent 209.8.

1-Oxa-2,12-disila-2,2,12,12-tetramethyl-6,7,8-(1,7-*m*-carboranylene)-cyclododecane (XI) was obtained by hydrolysis of 1,7-bis(chlorodimethylsilylpropyl)-*m*-carborane in acetone solution. An acetone solution of the chlorosilane was added dropwise to excess water in acetone solution at room temperature and stirred overnight. The solvent and excess water were removed by evaporation and the product freed from the gummy residue by sublimation at 200°C./0.025 mm. The crystalline sublimate obtained in 45% yield was recrystallized from a 1:1 mixture of chloroform and acetone to yield needle crystals of m.p. 176.5°C.

Anal. Calcd. for $C_{12}H_{34}B_{10}OSi_{12}$: C, 40.18%; H, 9.55%; B, 30.14%; Si, 15.66%. Found: C, 40.20%; H, 9.89%; B, 30.00%; Si, 16.57%.

The unsublimed residue which accounted for 55% of the product was a benzene-soluble polymer of molecular weight 6300.

1,7-Bis(methoxydimethylsilylpropyl)-*m*-carborane (X) was obtained upon treating 1,7-bis(chlorodimethylsilylpropyl)-*m*-carborane with trimethoxymethane. The product was isolated by distillation at 150°C./0.02 mm. in essentially quantitative yield.

Anal. Calcd. for $C_{14}H_{40}B_{10}Si_2O_2$: C, 41.54%; H, 9.96%; B, 26.71%; Si, 13.88%. Found: C, 41.00%; H, 10.73%; B, 26.4%; Si, 11.11%.

Preparation of Backbone *m*-Carborane Polysiloxane (I)

In addition to preparing this polymer by hydrolysis of 1,7-bis(chlorodimethylsilylpropyl)-*m*-carborane (VII) as described above, it was obtained by ring-opening of 1-oxa-2,12-disila-2,2,12,12-tetramethyl-6,7,8-(1,7-*m*-carboranylene)cyclododecane (XI). A 2-g. portion of the cyclic compound (XI) was mixed with 0.04 g. of 85% phosphoric acid and heated under a nitrogen atmosphere at 190°C. for 24 hr. The product was a clear, colorless, gum that was fully soluble in solvents such as benzene and chloroform. The molecular weight determined by vapor-pressure osmometry was 8500.

A 2-g. portion of cyclic compound (XI) was mixed with 0.062 g. of 65% sulfuric acid and heated at 190°C. overnight. The product was a tough elastomeric solid, light tan in color. It did not dissolve in solvents such as benzene, chloroform, dimethylformamide, or acetonitrile. Polymer similarly prepared with 96% sulfuric acid catalyst was fully soluble in benzene.

Preparation of Pendant *o*-Carborane Polysiloxane (II)

Polymerization by cohydrolysis was accomplished by carefully adding water to an equimolar mixture of dichloro(4-*o*-carboranylbutyl)methylsilane (IV) and dichlorodimethylsilane. For each mole of dichlorosilane 0.5 mole of water was added. After an initial reaction period at ambient temperature to assure reaction with the water, the mixture was carefully heated in stages up to 100°C. and maintained at 100°C. for several hours. Excess water was added at this time to assure complete reaction of the silylchloride. The product, freed of water by heating *in vacuo*, had a molecular weight of 2400.

The reaction product was taken up in benzene to yield a two-phase solution. The lower phase was polymer swollen with benzene. It was freed of benzene by evaporation to leave approximately 60% of tough, elastomeric gum polymer, which was completely soluble in acetone, and of molecular weight 14,000 as determined by vapor-phase osmometry. The upper phase was freed of benzene to leave a viscous liquid residue of molecular weight 890. This accounted for the remaining 40% of the material.

Polymerization of 4-(1-*o*-carboranylbutyl)heptamethylcyclotetrasiloxane (VI)

A 2-g. portion of VI was treated with 0.04 g. of 96% sulfuric acid and heated overnight at 90°C. The product was a viscous liquid of molecular weight 1400. It was completely soluble in solvents such as acetone and benzene. After standing several months at ambient temperature in a closed vessel the polymer became a tacky elastomeric gum which partially dissolved in acetone and partially swelled.

The help of Dr. Eugene O'Brien and Mr. Alan Jackson in some of these preparations is gratefully acknowledged. This work was supported by the Navy under Contracts NObs 84774, NObs 88318, and NObs 90065 and by the Army under Contract DA-11-AMC-852070-(W). The aid of the U. S. Naval Applied Science Laboratory, Brooklyn, N. Y., in obtaining the data is acknowledged.

References

1. J. Green, N. Mayes, and M. S. Cohen, *J. Polymer Sci. A*, **2**, 3113 (1964).

2. J. Green, N. Mayes, A. P. Kotloby, and M. S. Cohen, *J. Polymer Sci. A*, **2**, 3135 (1964).

3. J. Green, N. Mayes, and M. S. Cohen, *J. Polymer Sci. A*, **3**, 3275 (1965).

4. S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, paper presented at 150th American Chemical Society Meeting, New York, September 1965; *Polymer Preprints*, **6**, 1110 (September 1965).

5. S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *Inorg. Chem.*, **3**, 1444 (1964).

6. L. I. Zakharkin, V. I. Bregadze, and O. Yu. Okhlobstin, *J. Organometal. Chem.*, **4**, 211 (1965).

7. N. Mayes and J. Green, *Inorg. Chem.*, **4**, 1082 (1965).

8. N. N. Schwartz, E. O'Brien, S. Karlan, and M. M. Fein, *Inorg. Chem.*, **4**, 661 (1965).

9. D. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, (a) Chap. 2; (b) p. 195.

10. K. A. Andrianov, *Metalorganic Polymers*, Interscience, New York, 1962, p. 255.

11. W. I. Patnode and D. F. Wilcox, *J. Am. Chem. Soc.*, **68**, 358 (1946).

12. N. N. Sokolov and K. A. Andrianov, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim.*, **1957**, 806.

13. D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

14. D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, **2**, 1120–1125 (1963).

Résumé

On a préparé du carborane lié au silicium par des groupes alkyles linéaires et étudié sa stabilité thermique par TGA et par sa variation de poids moléculaire en fonction de la température. Les monomères de ces polymères ont été généralement préparés par addition catalytique au platine d'un hydrure de silicium à un carborane alkényle ou dialkényle. La polymérisation a été effectuée par hydrolyse et condensation de chlorosilanes, ouverture de cyclosiloxanes et condensation des alkoxy- et des chlorosilanes. Deux types de polymères ont été préparés, l'un contenant du *m*-carborane incorporé dans la chaîne, l'autre de l'*o*-carborane comme groupe alkylborane pendant. Les deux types ont été obtenus sous forme d'élastomères; cependant, de fortes proportions de carborane dans les polymères réduisent l'élasticité et finalement aboutissent à des nonélastomères. Le TGA du poly(siloxane-carborane inclus dans la chaîne) indique une dégradation á 370°C dans l'azote et , 235°C dans l'air. En chauffant le polymère à 350°C dans l'azote, on observe des ruptures de chaîne, déterminées par la diminution du poids moléculaire. Le TGA du poly-(siloxane carborane pendant) indique une dégradation en présence d'azote ou d'air au-delà de 400°C seulement. Par contre, des ruptures de chaîne ont déjà pu être observées à 300°C en présence d'azote.

Zusammenfassung

An Silikon durch geradkettige Alkylgruppen gebundene Carborane wurden dargestellt und bezüglich ihrer thermischen Stabilität durch TGA und die Molekulargewichtsänderung beim Erhitzen charakterisiert. Die Monomeren für diese Polymeren wurden i allgemeinen durch platin-katalysierte Addition eines Silylhydrids an ein Alkenyl- oder Dialkenylcarboran dargestellt. Polymerisation wurde durch Hydrolyse-Kondensation von Chlorsilanen, Ringöffnung von Cyclosiloxanen und Kondensation von Alkoxy- und Chlorsilanen bewirkt. Zwei Polymerstrukturtypen wurden dargestellt, eine mit *m*-Carboran in der Hauptkette und die andere mit *o*-Carboran als anhängender Alkylborangruppe. Beide Typen wurden als Elastomere erhalten; höherer Carborananteil in den Polymeren setzte die Elastizität herab und führte schliesslich zu Nicht-Elastomeren. TGA des Hauptketten-Carboran-Siloxanpolymeren zeigte Abbau bei 370°C unter Stickstoff und bei 235°C unter Luft an. Die Molekulargewichtsabnahme liess eine Kettenspaltung beim Erhitzen unter Stickstoff bei 350°C erkennen. TGA des anhängenden Carboran-Siloxanpolymeren zeigt Abbau unter Stickstoff und Luft bei Temperaturen über 400°C an. Die durch die Molekulargewichtsabnahme bestimmte Kettenspaltung war jedoch schon beim Erhitzen unter Stickstoff bei 300°C zuerkennen.

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Synthesis of an Arylene/Alkylene Polyether from Diphenolic Acid and Rosenmund Reduction to the Polyether Aldehyde

ROBERT M. FITCH and CARL DA CHOW,*
Department of Polymers and Coatings, College of Chemistry and Physics,
North Dakota State University, Fargo, North Dakota 58103

Synopsis

The Williamson ether synthesis has been applied to the formation of an arylene/alkylene polyether with pendant carboxyl groups from 4,4-bis(*p*-hydroxyphenyl)pentanoic acid and 1,4-dichlorobutane. The polymer was found to have a viscosity-molecular weight relationship following the equation, $[\eta] = 1.30 \times 10^{-4}M^{0.91}$, in dimethylformamide at 25°C. Hydrogenolysis of the derived polyether acid chloride was found to proceed smoothly at atmospheric pressure in the presence of Pd-$BaSO_4$ catalyst without poisoning of the catalyst by multiple absorption of polymer. The resulting polyether aldehyde undergoes typical aldehyde reactions. The infrared spectra of the polymers are also examined.

INTRODUCTION

As a class of compounds, arylene/alkylene polyethers have been little studied. Even less has been done with such polymers containing pendant functional groups, and yet there is potentially a considerable amount of interesting chemistry associated with them. Diphenolic acid, or 4,4-bis-(*p*-hydroxyphenyl)pentanoic acid, is an ideal starting material for the synthesis of a polyether containing pendant carboxyl groups. From this precursor, derivatives can conceivably be made by means of a variety of well-known reactions.

It was the purpose of this work to undertake the synthesis of a polyether from diphenolic acid (DPA) and 1,4-dichlorobutane via the Williamson ether synthesis [eq. (1)]. Subsequently the acid chloride was to be formed, and from this, by the Rosenmund reduction, the polymeric aldehyde was to be synthesized [eq. (2)]. A further purpose was to characterize the polyether acid with respect to its viscosity-molecular weight relationships.

This synthetic route was of particular interest, since to our knowledge the hydrogenolysis of a polymeric acid chloride has not been reported heretofore. There was some concern that multiple adsorption of the polymer segments on active sites of the catalyst would result in a poisoning effect.

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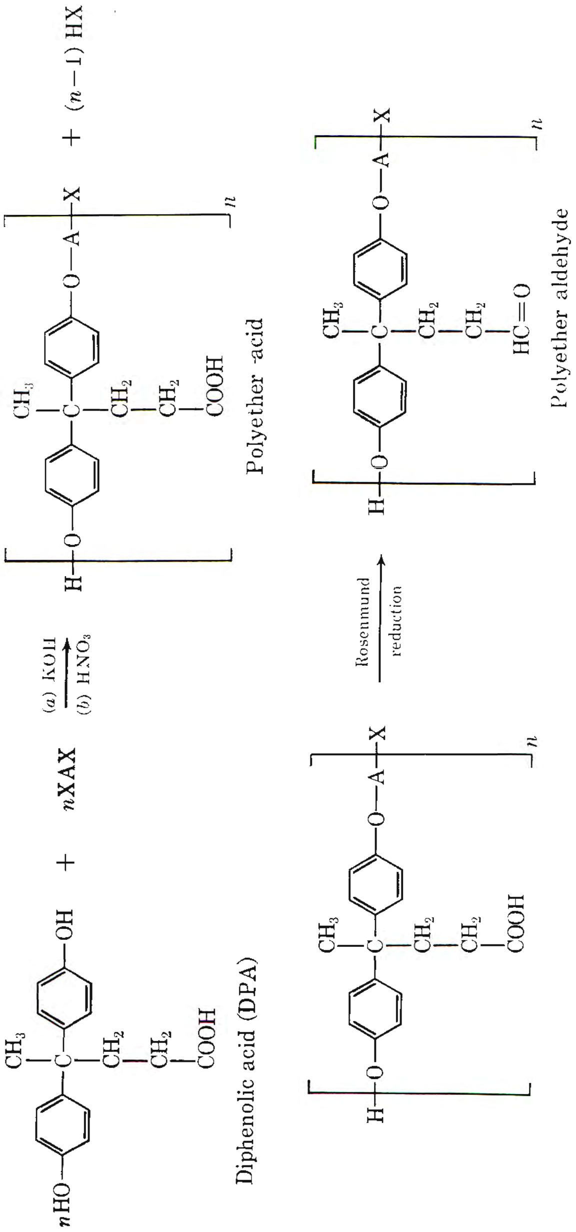
* Present address: Physical Research Laboratory, Dow Chemical Company, Midland, Michigan.


nHO
OH
CH$_3$
C
CH$_2$
CH$_2$
COOH
Diphenolic acid (DPA)
+
nXAX
(a) KOH
(b) HNO$_3$
H
O
A
X
n
+ (n−1) HX
Polyether acid
Rosenmund reduction
HC=O
Polyether aldehyde

(1)

(2)

TABLE I. Effect of Reaction Conditions of Synthesis of Polyether Acid on the Molecular Weight

Expt. no.	Reaction time, days	Reaction medium	Mole ratio alkali/DPA	DPA concn., mole/l. solvent	Temp., °C.	Molecular weight	Side reaction, %	Atmosphere	Excess dichlorobutane, %
2	3	MEK–H_2O (50/50)	4	0.4	Reflux	570[a]		Air	
3	6	MEK–H_2O (37/100)	4	0.25	Reflux	700[a]		Air	
6	3	H_2O	4	1.0	65–70	806[b]	23	Air	
7	3	H_2O	4	1.4	80	832[b]	25.7	Air	
10	3	H_2O	4	0.8	Reflux	1670[b]	20	Air	
11	3	H_2O	4	0.8	Reflux	1320[a]	20	N_2	
13	3	H_2O	4	1.0	Reflux	1400[a]		N_2	20
14[c]	3	H_2O	4	1.0	Reflux	929[a]		N_2	
16	3	H_2O	3.5	1.5	Reflux	1014[a]	0	N_2	
18	3	H_2O	4	0.5	Reflux	1700[d]		N_2	60
21	3	Dioxane–H_2O (4/1)	3.5	0.5	Reflux	450[d]		N_2	
24	3	H_2O	4	0.5	Reflux	1200[d]		N_2	80
25	3	H_2O	4	0.5	Reflux	1100[d]		N_2	80
26	3	H_2O	4	0.5	Reflux	1900[d]		N_2	80
28[e]	$^1/_4$	H_2O	4	0.5	Reflux	1080[d]		N_2	80[e]
29	3	H_2O	4	0.5	Reflux	1750[d]		N_2	80

[a] By vapor-pressure osmometry in methyl ethyl ketone.

[b] By vapor-pressure osmometry in cyclohexanone.

[c] $Br(CH_2)_3Br$ used instead of dichlorobutane.

[d] Intrinsic viscosity in DMF.

[e] 1,4-Dichlorobutene-2 used instead of dichlorobutane.

Experience with the catalytic hydrogenation of unsaturated polymers has shown no retardation in rate due to this effect, however.[1]

The only previous work which is directly related to our polyether-acid synthesis is the condensation of diphenolic acid (DPA) with 1,4-dichloro-2-butene.[2]

EXPERIMENTAL AND RESULTS

Materials

The diphenolic acid (DPA), pure recrystallized grade, provided by S. C. Johnson and Son, Inc., was titrated potentiometrically and was shown to have a purity of 97–98%. 1,4-Dichlorobutane, supplied by du Pont, and the DPA were used as received without further purification.

Polyether Acid

Typical reaction conditions for the synthesis of the polyether acid [eq. (1)] are given below. Modifications of this basic recipe are also described.

To an aqueous KOH solution of diphenolic acid was added an equimolar amount of 1,4-dichlorobutane. The Williamson condensation was allowed to proceed at reflux under nitrogen for 12 hr. If an excess of dihalide was used, it was added in 20% molar excess amounts at 12-hr. intervals until all had been added.

The polyether acid was purified by precipitation with HNO_3 from dilute alkaline solution, filtration, and washing with hot water until the filtrate was halide-free. The polymer was dried *in vacuo* at 55°C. and then placed in a Soxhlet extraction apparatus to isolate the MEK-soluble fraction.

A summary of some of the various reaction conditions used, along with the corresponding molecular weight results is given in Table I. From this it can be seen that the highest molecular weight polymer was obtained (expt. 26) by using a 4/1 mole ratio of NaOH/DPA at 0.5M DPA in water under reflux for 3 days, during which time an 80% excess of dihalide was added to offset side reactions, e.g., dehydrochlorination and hydrolysis. Air must be excluded, as it evidently has a pronounced adverse effect on molecular weight.

Number-average molecular weights were determined in the solvents shown in Table I by means of the Mechrolab 301A vapor-pressure osmometer.

TABLE II
Viscosity–Molecular Weight Relationship for Polyether Acid

$[\eta]$	$\bar{M}_n$
0.0643	570
0.0947	929
0.1043	1035
0.1175	1153
0.1472	1400

Viscosity-average molecular weights were determined by means of a Cannon-Fenske viscometer in dimethylformamide (DMF) at 25 ± 0.01°C. Calibration was accomplished using fractionated polyether acid solutions in methyl ethyl ketone (MEK) by vapor-pressure osmometry. The calibration data are given in Table II and in Figure 1.

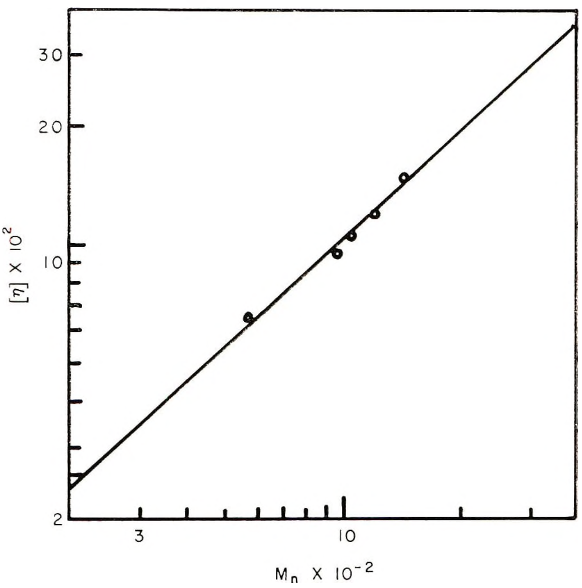


Fig. 1. Log–log plot of intrinsic viscosity vs. molecular weight for polyether acid in DMF at 25°C.

Polyether Acid Chloride

A typical procedure for the synthesis of the polyether acid chloride is given below.

To polyether acid of concentration of 0.04–0.1 mole/l. in THF in a dry flask, 2–3 moles of freshly distilled thionyl chloride per mole of carboxyl group was added. The reaction was conducted at reflux under a N_2 purge until no more hydrogen chloride was produced. After the reaction, a small measured quantity of dry toluene was added, and THF was removed at 40–50°C. under reduced pressure. HCl evolved was absorbed in excess aqueous KOH and back-titrated with standard acid.

This procedure, along with modifications, is summarized in Table III. Oxalyl chloride, a popular reagent for this reaction, was unsatisfactory for our material and, by inference, for polymers generally, since it produced crosslinked products with resulting low conversions (Expts. 5 and 6). Optimum conditions were found to be 67°C. for 21 hr. at a polymer concentration of 0.10*M* in tetrahydrofuran solvent, and a $SOCl_2$/carboxyl ratio of 2.5.

TABLE III
Conversion of Polyether Acid to Acid Chloride

Expt. no.	Molecular weight	Solvent	Moles reagent / Mole carbonyl		Reaction conditions			Results[a]
			$SOCl_2$	$(COCl)_2$	Temp., °C.	Time, hr.	Concn., M	
1	1200	DMF	10		195	12	0.10	+
2	1630	THF	2.0		67	22	0.08	+
3	1700	THF	2.8		67	23	0.05	+
4	1700	THF	2.5		67	24	0.34	+
5	1100	THF		2.0	67	5	0.28	[b]
6	2200	THF		2.5	67	20	0.05	Gel
7	1200	THF	2.5		67	14	0.14	+
8	1725	THF	2.2		67	24	0.04	+
9	1750	THF	2.5		67	12	0.10	+

[a] The polyether acid chlorides produced in Expts. 1, 2, 3, 4, and 9 were converted directly to aldehyde (see Table IV). The plus sign, +, indicates essentially complete conversion with theoretical moles HCl evolved.

[b] Low conversion.

Polyether Aldehyde

To a toluene solution of polyether acid chloride at a concentration of 0.05–0.1 mole/l. of toluene, 1 part of Pd–$BaSO_4$ catalyst, prepared according to Mosettig,[3] for 1–2 parts of polyether acid chloride was added. Hydrogen was passed in at atmospheric pressure. The temperature was kept at 98°C. The reaction was allowed to continue until the evolution of HCl ceased. The solution was cooled to room temperature, cleared with charcoal, all the insoluble materials removed by centrifugation, and finally the polyether aldehyde was obtained by precipitation with *n*-hexane. A summary of the various experimental conditions used is given in Table IV. From this it can be seen that dimethylformamide (DMF) may also be used as a solvent.

TABLE IV
Reduction of Acid Chloride

Expt. no.[a]	Solvent	Wt. Catalyst		Reaction conditions			Tollens' test	Amount of HCl evolved
		g./mole of —COCl	g./g. polymer	Temp., °C.	Time, hr.	Concn., M		
1	DMF	287	0.8	195	12	0.1	+	Theor.
2	ϕCH_3	359	1.0	98	30	0.08	+	$^1/_3$ Theor.
3	ϕCH_3	359	1.0	98	24	0.1	+	Theor.
4	ϕCH_3	180	0.5	98	4	0.1	+	Theor.
9	ϕCH_3	180	0.5	98	12	0.05	+	Theor.

[a] Experiment numbers refer to Table III.

Infrared Spectroscopy

The Beckman IR10 spectrograph was used. The spectrum for DPA was made by KBr disk technique; all others were made by casting from solution a film of the polymer on NaCl plates.

DISCUSSION

Polyether Acid

The polymer is a hard, glassy material soluble in aqueous alkali and insoluble in aqueous acid. It is soluble in DMF, slightly soluble in MEK, insoluble in aromatic and aliphatic hydrocarbons. Potentiometric titration showed the polymer to have 2.84 meq. COOH per gram (theor. 2.92 meq./g.).

A straight-line log–log relationship has been found between molecular weight of the polyether acid, determined by vapor-pressure osmometry and the intrinsic viscosity in DMF. This relationship is shown in Figure 1 and Table II. Fractionation was obtained by extraction with MEK. The derived Mark-Houwink relationship is thus found to be:

$$[\eta]^{25^\circ\text{C.}} = 1.30 \times 10^{-4} M^{0.94}$$

The infrared spectrum of the polyether acid (Fig. 2, No. 51) has several distinguishing features when compared to that of the DPA precursor (Fig. 2, No. 59). The O—H stretching band in the region between 3000 and

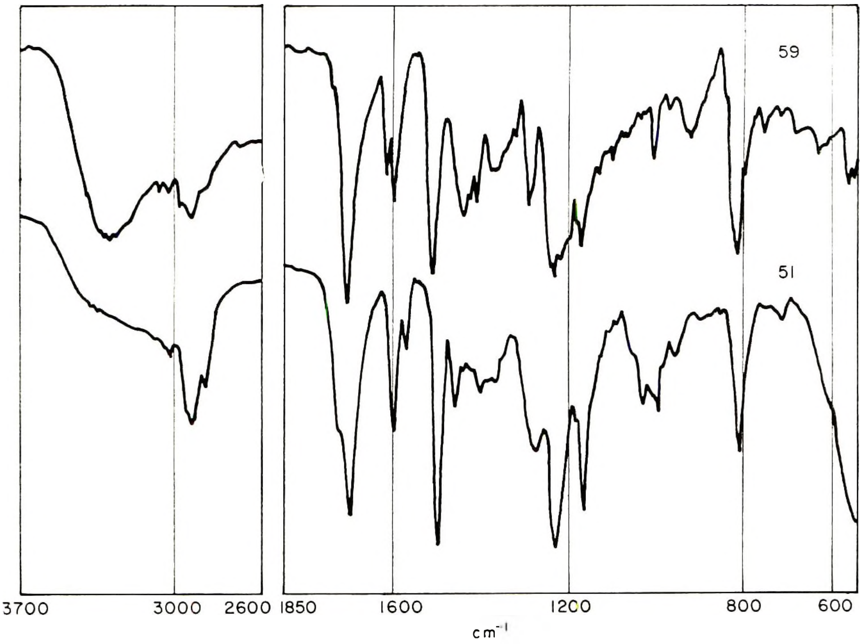


Fig. 2. Infrared spectra: (59) diphenolic acid; (51) polyether acid from DPA + 1,4-dichlorobutane.

3600 cm.$^{-1}$ is typical of RCOOH and exhibits the broadening characteristic of groups in amorphous polymers subject to intermolecular coupling.[4] The absorbance is much less because of consumption of OH in ether formation. Likewise the C=O stretching frequency at 1700 cm.$^{-1}$ is somewhat broadened relative to that in the DPA spectrum. Absorptions due to the benzene rings at 1500 and 1600 cm.$^{-1}$ and to Ar—O stretch at 1235 cm.$^{-1}$ are present in both DPA and polymer acid. However, a pronounced band at 1000 cm.$^{-1}$ due to ArO—CH$_2$ in the polymer indicates the formation of the ether linkage.

Polyether Acid Chloride

Evidence for the replacement of the carboxyl group by acid chloride was immediately apparent in the physical properties of this polymer. It was amorphous, soft and rubbery, and soluble in aromatic hydrocarbons, such as toluene. It reacted vigorously and exothermically with *N*-methylaniline to give the corresponding polymeric amide which was water soluble.

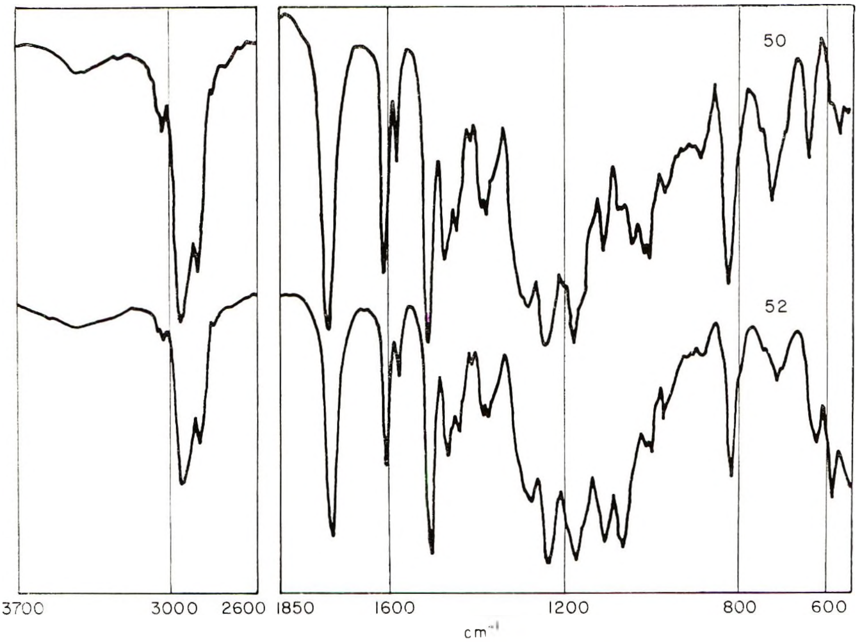


Fig. 3. Infrared spectra: (50) polyether acid chloride; (52) polyether aldehyde.

The infrared spectrum (Fig. 3, No. 50) shows the almost complete disappearance of OH at 3440 cm.$^{-1}$. As a result the Ar—H absorption at 3018 cm.$^{-1}$ is now more clearly defined. The carbonyl absorption has shifted to 1738 cm.$^{-1}$, which is at a lower frequency than predicted for aliphatic acid chlorides[5] but characteristic for aromatic ones.[6] The broadening due to intermolecular coupling (hydrogen bonding) in this band of the amorphous polymeric acid has disappeared in the acid chloride as expected since intermolecular interactions are much weaker in the absence of hydrogen bonding. Undoubtedly strong environmental factors are responsible for this anomalously small shift from carboxyl to acid chloride. The rather strong band at 725 cm.$^{-1}$ can probably be assigned to C—Cl motion.

Polyether Aldehyde

The polyether aldehyde is formed smoothly by the hydrogenolysis of the acid chloride by simply bubbling hydrogen into the solution at atmospheric pressure in the presence of Pd–$BaSO_4$ catalyst. The theoretical amount of HCl is evolved in this process.

The free polymer is soft, rubbery, and soluble in toluene and insoluble in hexane. It exhibits the typical reactions of an aldehyde, including reduction of aqueous silver–ammonia complex (Tollens' reagent) and formation of an adduct with $NaHSO_3$. Completeness of conversion was attested to by the total absence of acidity in potentiometric titration.

The infrared spectrum of this polymer is very similar to that of the corresponding acid chloride. This is to be expected when only one hydrogen is replacing a chlorine atom on a repeating unit with mass of 324 amu. It is distinguished from the acid chloride spectrum, however, by a strong band at 1170 cm.$^{-1}$ and the disappearance of the C—Cl absorption at 725 cm.$^{-1}$.

The polymeric aldehyde can be oxidized back to the corresponding acid using H_2O_2 in aqueous base containing some THF. The oxidation proceeds with difficulty, probably because of the fact that a two-phase system is involved.

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References

1. E. M. Fettes, *Chemical Reactions of Polymers*, Interscience, New York, 1964, pp. 175–193.
2. S. C. Johnson & Son, Inc., Brit. Pat. 811,131 (April 2, 1959).
3. E. Mosettig, *Org. Reactions*, **4**, 363 (1948).
4. R. Zbinden, *Infrared Spectroscopy of High Polymers*, Academic Press, New York, 1964, pp. 4–6.
5. H. A. Szymanski, *Theory and Practice of Infrared Spectroscopy*, Plenum Press, New York, 1964, pp. 279–87.
6. H. A. Szymanski, *Infrared Band Handbook*, Plenum Press, New York (1963).

Résumé

On a appliqué la synthèse de Williamson pour les éthers à la formation d'un polymère arylène/alkylène possédant des groupements carbonyls latéraux. On a effectué cette synthèse en utilisant l'acide 4,4-bis(*p*-hydroxyphényl) pentanique et le 1,4-dichlorobutane. On a trouvé pour ce polymère la relation suivante entre la viscosité et le poids moléculaire: $[\eta]^{25°} = 1.30 \times 10^{-4} M^{0.94}$. Cette équation a été obtenue dans le diméthyl formamide. On a trouvé que l'hydrogénolyse du polyéther dérivé de chlorure acide se déroulait facilement à la pression atmosphérique en présence d'un catalyseur Pd–BaSO$_4$ sans empoisonnement du catalyseur par les multiples adsorptions de polymères. Les polyéthers aldéhydes qui résultent de cette réaction manifestent les propriétés typiques des aldéhydes. On a également examiné le spectre infra-rouge de ces polymères.

Zusammenfassung

Die Äthersynthese nach Williamson wurde auf die Bildung eines Arylene/Alkylenpolyäthers mit anhängenden Carboxylgruppen aus 4,4-Bis-(*p*-hydroxyphenyl)-pentansäure und 1,4-Dichlorbutan angewendet. Die Viskositäts-Molekulargewichts-beziehung für das Polymere war $[\eta]^{25°} = 1{,}30 \times 10^{-4}M^{0.94}$ in Dimethylformamid. Die Hydrogenolyse des abgeleiteten Polyäthersäurechlorides verlief bei Atmosphärendruck in Gegenwart eines Pd–BaSO$_4$-Katalysators glatt ohne Vergiftung des Katalysators durch multiple Polymeradsorption. Der gebildete Polyätheraldehyd zeigt die typischen Aldehydreaktionen. Schliesslich wird das Infrarotspektrum der Polymeren aufgenommen.

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NOTES

Nylon 1313: Synthesis and Polymerization of Monomers

Introduction and Discussion

Interest in *Crambe abyssinica* as an oilseed crop for the United States is based in part on its potential value as a source of polyamide monomers.[1-3] *Crambe abyssinica* is one of the richest known sources of erucic (*cis*-13-docosenoic) acid, which makes up 55–60% of the acids of the seed oil glycerides. Erucic acid may be separated from crambe oil by fractional distillation of the free fatty acids obtained by hydrolysis of the glycerides. Alternatively, the oil may be converted to methyl esters, and the methyl erucate fraction from distillation hydrolyzed to the free acid. This paper describes the synthesis of nylon 1313 from erucic acid.

Brassylic acid (1,13-tridecanedioic acid) was made in 60–70% yields by oxidative ozonolysis[1] of commercial erucic acid (Humko, Memphis, Tenn.). The crude product from the ozonolysis mixture contained about 95% brassylic acid, and the purity was raised to 99%+ by recrystallization. The reaction of brassylic acid with ammonia under conditions described by Sorenson and Campbell[5] for the preparation of azelanitrile gave brassylic acid dinitrile[6-8] (1,11-dicyanoundecane) in better than 90% yield. Catalytic hydrogenation of the dinitrile in the presence of cobalt (Girdler G-67RS catalyst, Chemetron, Louisville, Ky.) and ammonia gave 1,13-diaminotridecane[9] (99%+ by gas–liquid chromatography, GLC) in better than 90% yield. Brassylic acid and 1,13-diaminotridecane were combined in a 1:1 molar ratio to produce the nylon 1313 salt.

Melt polymerization of nylon 1313 salt containing a calculated[10] amount of the diacetate of 1,13-diaminotridecane as a chain terminator produced a nylon 1313 of about 50,000 molecular weight that had an inherent viscosity (0.5% in *m*-cresol at 25°C.) of 0.95. A detailed account of a study of the physical properties of nylon 1313 will be published later.

Experimental

Brassylic Acid (1,13-Tridecanedioic Acid). A solution of erucic acid of about 85% purity (475 g., 1.40 mole) in acetic acid (630 ml.) and water (70 ml.) was maintained at 26 ± 2°C. by external cooling and vigorous stirring while a stream of oxygen containing ozone (3.05 wt.-%) was passed through it at 5.0 l./min. (The ozone was generated in a Welsbach Corporation Model T-816 laboratory ozonator.) When ozone absorption ceased, the mixture had taken up 100.4% of the theoretical amount of ozone necessary to react with the unsaturation present. Production of ozone in the oxygen stream was terminated, and oxygen was passed through the system at 0.2 l./min. while the reaction mixture was heated externally. When the temperature reached 65°C., an exothermic reaction began, and the temperature continued to rise spontaneously to 100°C. Cooling was necessary to maintain this temperature while the exothermic reaction took place over about 15 min. Oxygen flow rate was increased to 1.5 l./min., and the system temperature was maintained at 110–115°C. for an additional hour before the reaction mixture was allowed to stand overnight at room temperature. The crude brassylic acid which crystallized was filtered off and washed first with water and then with cold benzene before being dried at 70°C. *in vacuo*. The yield of crude brassylic acid was 234 g. (68.5% of theory); m.p. 103–107°C.; purity about 96% by GLC. The crude brassylic acid was recrystallized from absolute ethanol (470 ml.) and then from benzene (1000 ml.) to give 188 g. (55% of theory); m.p. 112–114°C.; 99.8% pure brassylic acid by GLC. Fractional distillation of the original filtrate gave pelargonic acid, b.p. 140–143°C./13 mm.; yield 177 g. (80% of theory).

Brassylic Acid Dinitrile (1,11-Dicyanoundecane). Brassylic acid, 96% purity, (500 g., 2.05 mole) and polyphosphoric acid (25 g.) were melted under a slow stream of nitrogen in a three-necked flask equipped with a thermometer, a gas inlet tube, and a simple distilling head, condenser, and receiver. When the melt temperature reached 135°C., the nitrogen was replaced by anhydrous ammonia introduced below the surface of the molten liquid. The temperature rose spontaneously to about 180°C., then was gradually increased to 200°C. and maintained at this point for 2 hr. while ammonia was passed through the system. Water condensed in the receiver without organic material. The flow of ammonia was continued while the reaction temperature was further increased to 300°C. for an additional 7 hr. The small amount of organic matter that condensed in the receiver was returned to the reaction flask. The simple distilling head was replaced by a 15-in. Widmer column, and the reaction product was distilled *in vacuo* to yield brassylic acid dinitrile; 384 g. (91.1% of theory); b.p. 176–180°C./1–2 mm.

ANAL. Calcd. for $C_{13}H_{22}N_2$: C, 75.68%; H, 10.75%; N, 13.58%. Found: C, 75.63%; H, 10.57%; N, 13.38%.

1,13-Diaminotridecane. Brassylic acid dinitrile (52 g., 0.204 mole), *p*-dioxane (160 ml., spectro grade), and Girdler G-67RS cobalt-on-kieselguhr catalyst (10 g.) were placed in a 1170-ml. stainless steel bomb that had been chilled with Dry Ice. The system was flushed with hydrogen, anhydrous ammonia (33 g., 1.94 mole) was added, and the bomb was sealed. The bomb was filled with hydrogen to 1800 psig before shaking and heating were started. The system was heated to 110°C. in 1 hr. and maintained at 110–115°C. for an additional 3 hr. Hydrogen absorption was smooth and rapid, being essentially over after 2 hr. The bomb was cooled, and after the gas was released, the contents of the bomb were removed with the aid of *p*-dioxane. The slurry of products was heated to boiling and filtered to remove the catalyst. Vacuum distillation of the filtrate gave 50 g. (93.5% of theory) of 1,13-diaminotridecane; b.p. 118–119°C./0.4 mm. Purity indicated by GLC was 99.1%.

1,13-Diaminotridecane Diacetic Acid Salt. 1,13-Diaminotridecane (18.19 g., 0.085 mole) was dissolved in absolute ethanol (50 ml.). A solution of acetic acid (0.18 g., 0.170 mole) in absolute ethanol (20 ml.) was added slowly to the diamine solution. There was a slight warming of the mixture, but no crystallization occurred upon prolonged standing. The ethanol was evaporated to leave a clear, viscous oil which crystallized upon cooling *in vacuo* over phosphorus pentoxide. The yield of salt was quantitative, m.p. 79–82°C.

ANAL. Calcd. for $C_{17}H_{38}N_2O_4$: C, 61.04%; H, 11.45%; N, 8.37%. Found: C, 60.95%; H, 11.40%; N, 8.10%.

Nylon 1313 Salt. A solution of 1,13-diaminotridecane (131.2 g., 0.612 mole) in absolute ethanol (225 ml.) was added slowly with vigorous stirring to a solution of brassylic acid (146.5 g., 0.600 mole) in absolute ethanol (1250 ml.). The salt precipitated immediately. Stirring was continued for 0.5 hr. after completion of the addition, and the mixture was allowed to stand overnight. The salt was collected on a filter, washed with two 150-ml. portions of ethanol, and dried in a current of air. The yield was 275 g. (99% of theory); the pH of a saturated aqueous solution of the salt was 7.73 at 25°C.

ANAL. Calcd. for $C_{26}H_{54}N_2O_4$: C, 68.08%; H, 11.87%; N, 6.11%. Found: C, 68.00%; H, 11.95%; N, 6.00%.

Nylon 1313 by Melt Polymerization (Molecular Weight about 50,000). Nylon 1313 salt (500 g., 1.09 mole) and 1,13-diaminotridecane diacetic acid salt (1.540 g.; 0.0046 mole) were placed in a 2-liter round-bottomed flask which had been coated on the inside with a fluorocarbon resin. The system was alternately evacuated and filled with nitrogen three times before it was fitted with a stopper carrying a gas inlet and outlet tube and a stainless-steel stirrer. A slow stream of nitrogen was passed through the flask as it was heated in an oil bath at 225 ± 2°C. After the melt was stirred for 3 hr., the stirrer was raised above the melt and heating continued for an additional hour. The flask was taken out of the bath and allowed to cool under nitrogen before the block of polymer was removed by breaking the flask. The yield of nylon 1313 was 457 g. (99.3%). Overall yield of nylon 1313 from erucic acid was 50.9%.

ANAL. Calcd. for $—NH(CH_2)_{13}—NHCO(CH_2)_{11}—CO—$: C, 73.88%; H, 11.92%; N, 6.63%. Found: C, 73.81%; H, 12.01%; N, 6.46%.

TABLE I

Physical Properties of the Polymer

Molecular weight (expected from stabilizer employed)	50,000
Molecular weight (light scattering) (in 1M sodium acetate in 80% trifluoroacetic acid)[11-14]	47,000
η_{inh} (0.5% in m-cresol at 25°C.)	0.95
$[\eta]$	0.83
Polymer melt temperature, °C.	164–167
T_m (polarizing microscope), °C.	170–172
Specific gravity	1.0245
n_D^{24}	1.536

Physical properties of the polymer are listed in Table I.

We appreciate the excellent technical assistance of Mr. W. L. Mayfield, who performed much of the experimental work, and of Dr. W. J. Barrett and the staff of the Analytical Section, Southern Research Institute, who carried out the analytial determinations.

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Mention in this article of trade names or firms does not constitute an endorsement by the U.S. Department of Agriculture.

References

1. *Agr. Res.*, **11**, No. 5, 6 (Nov. 1962).

2. *Chem. Eng. News*, **42**, No. 9, 50 (Mar. 2, 1964); *ibid.*, **42**, No. 48, 31 (Nov. 30, 1964).

3. G. A. White and I. A. Wolff, *Crops Soils*, **18**, No. 4, 10 (Jan. 1966).

4. H. J. Nieschlag, J. W. Hagemann, I. A. Wolff, W. E. Palm, and L. P. Witnauer, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 146 (1964).

5. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 77.

6. A. J. von Braun and E. Danziger, *Ber.*, **45**, 1970 (1912).

7. V. K. Ziegler and R. Aurnhammer, *Ann.*, **513**, 46 (1934).

8. F. L. Pymon and A. P. T. Easson, Brit. Pat. 500,903 (Dec. 10, 1937); *Chem. Abstr.*, **33**, 11,273 (1939).

9. A. Muller, E. Rolz, and M. Wiener, *Ber.*, **67**, 295 (1934).

10. D. D. Coffman, G. J. Berchet, W. R. Peterson, and E. W. Spanagel, *J. Polymer Sci.*, **2**, 306 (1947).

11. H. C. Beachell and D. W. Carlson, *J. Polymer Sci.*, **40**, 543 (1959).

12. P. R. Saunders, *J. Polymer Sci.*, **43**, 273 (1960).

13. P. R. Saunders, *J. Polymer Sci.*, **57,** 131 (1962).
14. P. R. Saunders, *J. Polymer Sci. A*, **2,** 3755 (1964).

Joseph L. Greene, Jr.
Everett L. Huffman
Robert E. Burks, Jr.
William C. Sheehan*

Southern Research Institute
U.S. Department of Agriculture
Birmingham, Alabama 35205

I. A. Wolff

Northern Regional Research Laboratory
Peoria, Illinois 61604

Received August 9, 1966
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* Present address: Phillips Petroleum Co., Bartlesville, Oklahoma.

Conjugated Double Bonds in Deeply Colored Polymers

It has been shown[1-3] that cyclopentadiene, furan, and pyrrole can be catalytically converted into benzene-soluble polymers, the electronic spectra of which are characterized by peaks in the range 280–360 mμ, owing to the presence of 3–6 conjugated double bonds. We have now found that under the slightly different conditions, specified in Table I (see following page), the three monomers are polymerized to more deeply colored, infusible (up to 360°C.) amorphous powders (yield >80%) which are insoluble in benzene or in the other solvents listed in Table II of reference 3. During the polymerization the reaction mixture, kept under nitrogen, was 10^{-4} *M* with respect to the antioxidant α-tocopherol. Purification of these polymers was carried out by extraction with ethanol in a Soxhlet apparatus. The analytical composition, the infrared spectra (potassium bromide disks), and the unsaturation (determined by shaking the suspensions in a carbon tetrachloride solution of bromine) of the soluble[1-3] and the insoluble polymers were not markedly different, except that the cyclopentadiene polymer was practically free of halogen and did not consume alkali on shaking with an alcoholic solution of potassium hydroxide. The other two polymers contain trichloro- and trifluoroacetic acid residues, as shown by the halogen content and the alkali consumption. The reflectance spectra of these polymers were determined by introducing a finely powdered mixture with magnesium carbonate into the diffuse reflectance attachment (S.P. 540) of a Unicam spectrophotometer. The last two columns of Table I show the results of these measurements. The λ_{max} values in the seventh column were assumed to be identical with the observed maxima of the reflectivity. It will be seen that there are more conjugated double bonds than in the previously described[1-3] polymers, which were prepared under less forcing conditions.

References

1. P. V. French, L. Roubinek, and A. Wassermann, *J. Chem. Soc.*, **1961**, 1953.
2. J. Upadhyay, P. Gaston, A. A. Levy, and A. Wassermann, *J. Chem. Soc.*, **1965**, 3252.
3. M. Armour, A. G. Davies, J. Upadhyay, and A. Wassermann, *J. Polymer Sci.*, in press.

J. Upadhyay
A. Wassermann

William Ramsay and Ralph Forster Laboratories,
University College
London, England

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TABLE I
Polymerization of Cyclopentadiene, Furan, and Pyrrole Without Diluent at 20°C.

Monomer	Catalyst	Initial concn., mole/l.		Time, hr.[a]	Color of polymer	λ_{max}, mμ	No. of conjugated double bonds[b]
		Monomer	Catalyst				
C_5H_6	F_3CCOOH	8.1	2.9	1	Deep red-brown	400[c]	6–7
C_4H_4O	Cl_3CCOOH	8.0	4.0	24		420	7–8
C_4H_5N	F_3CCOOH	7.0	4.0	0.1		480	~12

[a] After completion of mixing of monomer and acid.

[b] Estimated by comparison with the λ_{max} values of polyenes containing a known number of conjugated double bonds.[1]

[c] Shoulder.

NMR Study of α-Methylstyrene–p-Methyl-α-Methylstyrene Copolymers

High-resolution nuclear magnetic resonance spectroscopy is of great importance for the study of styrene polymers in solution. Studies of the NMR spectra of polystyrene and poly-α-methylstyrene have been reported by Bovey et al.[1] The spectra of a number of poly-α-methylstyrene polymers were measured, and relative amounts of the isotactic, syndiotactic, and heterotactic forms discerned by Brownstein et al.[2] A study of the copolymerization of styrene and α-methylstyrene was described by Iino and Tokura.[3]

This note describes an NMR study of cationically prepared[2] copolymers of α-methylstyrene (AMS) and *p*-methyl-α-methylstyrene (PMAMS). Presumably the monomer sequences are nonalternating[3] in these products, and practically all of each polymer unit is in the syndiotactic form.[2]

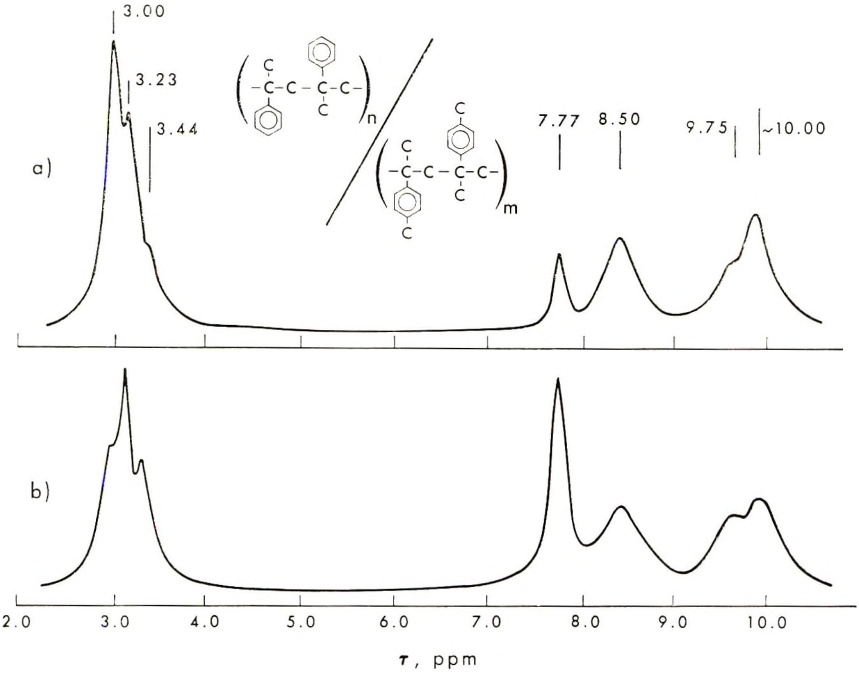

Fig. 1. NMR spectra of 10% solutions of α-methylstyrene (AMS)–*p*-methyl-α-methylstyrene (PMAMS) in CS_2; (*a*) 78.7% AMS–21.3% PMAMS; (*b*) 37.5% AMS–62.5% PMAMS.

The copolymers were dissolved in CS_2, and the spectra were observed on a Varian HR60 instrument at room temperature. The units in the copolymer chain were identified according to the methods of Bovey and Brownstein. The peak positions of the various kinds of protons were measured relative to tetramethylsilane and are shown in Figures 1*a* and 1*b* for the products containing a higher proportion of AMS and of PMAMS, respectively.

The peaks in the region $\tau = 3.0$–3.44 are from protons in an aromatic nucleus. The peak at $\tau = 8.50$ is from chain methylene protons and the peak in the $\tau = 10.0$ region is due to the α-methyl group protons in AMS. We ascribe the peak at $\tau = 7.77$ to the *p*-methyl of PMAMS and the peak at $\tau = 9.75$ to the α-methyl groups in PMAMS. As suggested by Bovey et al.,[1] the α-methyl resonance is shifted to fields higher than that of the methyl groups of small-molecule analogs, because of a diamagnetic shielding effect due to the magnetic anisotropy arising from the phenyl groups of the neighboring styrene units. In the syndiotactic form, this becomes particularly marked when most of the α-methyls are sandwiched between phenyls. The α-methyls in PMAMS experience a lesser diamagnetic shielding effect, evidently because of the presence of the p-methyl substituent.

In spectra 1*a* and 1*b*, changes are observed in the aromatic peaks at $\tau = 3.23$ and 3.44 as compared with the peak at $\tau = 3.00$. When PMAMS is in greater quantity, these peaks increase in intensity, as does the p-methyl peak at $\tau = 7.77$. Since the α-methyl peak at $\tau = 9.75$ also increases, it too apparently belongs to PMAMS. This peak could possibly be due to a heterotactic form of PMAMS, although the method of preparation favors the syndiotactic form.[2]

References

1. F. A. Bovey, G. V. Tiers, and G. J. Fillipovich, *J. Polymer Sci.*, **38,** 73 (1959).
2. S. Brownstein, S. Bywater, and D. J. Worsford, *Makromol. Chem.*, **48,** 127 (1961).
3. M. Iino and N. Tokura, *Bull. Chem. Soc. Japan*, **38,** 1094 (1965).

E. M. BANAS

Research and Development Department
American Oil Company
Whiting, Indiana 46349

O. O. JUVELAND

Research and Development Department
Amoco Chemicals Corporation
Whiting, Indiana 46349

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BOOK REVIEW

Chemistry and Physics of Polycarbonates. Herman Schnell. Interscience, New York, 1964. xi + 225. $12.75.

Since the remarkable, virtually simultaneous discovery and development of bisphenol polycarbonates by Schnell et al. at Bayer and by Fox and Goldberg et al. at General Electric, beginning about thirteen years ago, there has been a great deal of technical and commercial interest in this new family of polyesters. This review of the polycarbonate field to 1962 by Schnell is certainly the best work now available on this subject. Schnell is one of the founding fathers of polycarbonate technology and is thereby extremely well qualified to provide an authoritative picture of this area of polymer chemistry. An earlier book, *Polycarbonates*, by Christopher and Fox was published in 1962, but was much less thorough in its coverage. Although referenced by Schnell in various sections of his book, it would have been appropriate if note had been taken of this first book in the introduction or historical section. Additionally, it seems something of an oversight that no reference is made by Schnell to the first U.S. papers on polycarbonates presented in July 1957 by Fox and Goldberg at the Gordon Polymer Conference.

The main body of this book is devoted to the chemistry and property–structure relationships for aromatic polycarbonates. Schnell's coverage of polycarbonate chemistry is well done and well referenced, providing a good source of information for those interested in this field. The chapter on structure and properties of aromatic polycarbonates is also thorough, covering in some detail various aspects of the behavior of this interesting class of polymers. A brief but informative chapter on raw materials used in polycarbonate synthesis is also provided.

On the negative side, in considering property–structure relationships, one could wish for more detailed comparisons between aromatic polycarbonates and other structurally related condensation polymers. Additionally, more detailed consideration of some facets of the chemical behavior of polycarbonates such as hydrolysis, aminolysis, and thermal oxidative stability would have been desirable.

The section on morphology and crystallinity provides a good, brief summary of the crystallization behavior of polycarbonates, but does not note the crystal melting point for bisphenol-A polycarbonate (~265°). With reference to the crystallinity of aromatic polycarbonates, it is interesting to note that when first discovered, one of the most perplexing questions was the reason for the remarkable toughness displayed by this transparent, high temperature, glassy polymer. Schnell mentions that short-range order has been demonstrated for "amorphous" polycarbonate. However, the point is not made that this short-range order is the logical basis for the unusual strength properties. Indeed, the observation is becoming increasingly general that morphological heterogeneity is a hallmark of tough, strong thermoplastics. This deserves some mention in a consideration of polycarbonate behavior.

Schnell's excellent book covers the literature up to 1962. Since then, much interesting and important work has been published. One of the most useful supplements is a very fine book by Morgan at DuPont, *Condensation Polymers*, published in 1965. This later work contains a great deal of up to date information on polycarbonates and related polyesters and splendidly supplements the Schnell review.

E. P. Goldberg

Research Laboratories
Xerox Corporation
Webster, New York 14580