mixtures. Attempts to cross-link films immersed in benzene with bis(4-isocyanatophenyl)methane failed.

Evaluation of the alternative cross-linking agents was carried out in pyridine solutions at 75° using 0.15 mol of cross-linking agent per mol equiv of cellulose. The gelation time was considered to be a measure of the reactivity; the following results were obtained [cross-linking agent, time (hr)]: *p*-isocyanatophenylsulfonyl isocyanate, 0.25; chlorosulfonyl isocyanate, 8; dichloroacetic acid, 8; bis(4-chlorosulfonyl phenyl) ether, >48. The cross-links produced by dichloroacetic acid were not stable to alkaline hydrolysis as evidenced by dissolution of 1 g of gel in 2% NaOH after 48 hr at room temperature.

Characterization of the Ion-Exchange Resins. The ion-exchange capacity of these materials was determined by slurrying 1.0 g of the dry polymer in 50 ml of 1.0 *M* NaCl. A known volume of standard NaOH was added. Enough NaOH was added to assure that the pH of the mixture was in the 8–10 range. Finally, the total solution volume was made up to 100 ml with distilled water and the mixture was shaken frequently at room temperature for 48 hr. Aliquots of the supernatant liquid were titrated with standard HCl to the phenolphthalein end point and capacities determined in milliequivalents per gram of dry polymer.

The titration curve was determined by slurrying 1.0 g of dry resin in a mixture of 45 ml of 1 *M* sodium chloride and 45 ml of distilled water and measuring the pH of the mixture until a constant pH value was obtained. Although constant pH values were usually obtained within 0.5 hr, the mixture was stored 4 hr to assure that equilibrium had been established. An aliquot of standard base was then added: the mixture was allowed to equilibrate 1 hr and the new pH recorded. This process was repeated until the addition of base did not change the pH of the mixture. A plot of pH *vs.* milliequivalents of base added per gram of sample was considered the titration curve. The average pK_a, estimated from the pH at half-capacity, was 4.5.

Acknowledgment. The authors would like to acknowledge the assistance of F. A. Iddings and E. L. Steele of the Nuclear Science Center, L.S.U., in the analysis of the cellulose derivatives by neutron activation.

Multicomponent Polymerization. II. The Effect of Mixing on Copolymerization in Continuous Stirred Tank Reactors[1]

K. F. O'Driscoll and R. Knorr

Department of Chemical Engineering, State University of New York, Buffalo, New York 14214. *Received June 18, 1969*

ABSTRACT: Calculations have been carried out to describe the course of three vinyl copolymerizations which typify free-radical copolymerizations. Conversion of monomer to polymer, and copolymer average composition, as well as copolymer composition distribution (CCD), have been calculated for these three systems in batch reactors (BR) and in continuous stirred tank reactors which have perfect, homogeneous micromixing (HCSTR) or imperfect mixing which leads to segregation on the microscopic scale (SCSTR). The results of the calculations indicate that conversion and *average* composition behavior are not necessarily strongly dependent on mixing in a CSTR, although they are in some systems. However, the CCD is strongly affected by mixing in all systems where the composition drifts with conversion. The magnitude of the effect of mixing on CCD increases with conversion. In the limit a SCSTR gives at high conversion the same CCD as a BR. A HCSTR always gives a monodisperse CCD. Limitations and applications of the calculations are discussed.

1. Polymerization in a CSTR

The use of a continuous stirred tank reactor (CSTR) for linear chain-growth polymerization reactions has much to offer with respect to control of product properties. Denbigh,[2] for example, has shown that in vinyl polymerizations a molecular weight distribution (MWD) can be achieved with a CSTR which is much narrower than that with a comparable batch reactor (BR). In addition it has been shown that molecular weight can be readily modified by appropriate changes in feed rate and composition.

Other advantages are apparent when one considers multicomponent polymerizations. As an example, consider the copolymerization of a mixture of two monomers of unequal reactivity. In a BR the relative supply of the more reactive monomer becomes depleted and the copolymer composition drifts in response to this change. This drift gives rise to a copolymer composition distribution (CCD) ranging from that copolymer composition formed from the initial mixture to those compositions formed in the final stages of reaction. The situation is quite different when the same reaction takes place in an ideal (or homogeneous) CSTR (HCSTR). In this case the depletion of the monomers is compensated for by the feed stream so that a steady-state reaction mixture composition is realized. Aside from statistical variations in copolymer composition, which as shown by Stockmayer[3] become insignificant at high degrees of polymerization, the resulting copolymer is homogeneous in composition.

In many cases this homogeneity or the lack of it can be of great importance. An example is the situation where two pure homopolymers, such as polystyrene and polyacrylonitrile, are incompatible. A physical

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[1] Preceding paper: K. F. O'Driscoll and R. S. Knorr, *Macromolecules*, **1**, 367 (1968).

[2] K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).

[3] W. H. Stockmayer, *J. Chem. Phys.*, **13**, 199 (1945).

mixture of the two homopolymers is likely to be brittle or opaque while a homogeneous copolymer of the same composition, due to enforced compatibility, may be tough and transparent. A heterogeneous copolymer of the same composition is likely to have properties somewhere between the two extremes depending on the degree of heterogeneity.

In cases where heterogeneity is undesirable it is common to reduce the degree of heterogeneity in batch copolymerizations by adding amounts of the more reactive monomer as the reaction proceeds to compensate for the drift in monomer composition. In many systems, however, the drift is so great that the CSTR may be the only practical method of producing homogeneous copolymer of desired composition. This point is illustrated later in this paper by considering the copolymerization of methyl methacrylate (MMA) and vinyl acetate (VAC).

These factors coupled with the impetus provided by recent advances in high-speed digital computation and analytical techniques such as gel permeation chromatography (gpc) are responsible for the intense interest currently focused on theoretical and experimental analysis of the kinetics and reactor dynamics of polymerization in CSTR's.[4,5] Of prime importance in much of this recent work has been the assumption of perfect mixing. For many reactions, conducted at low viscosities, this is an excellent approximation but in view of the fact that polymerization mixtures tend to become increasingly viscous with higher conversion it is especially important to investigate the effect of nonideal mixing on polymerization in CSTR. Not only is it important to know when nonideal mixing is likely to become important but it is also important to understand what is likely to occur in relation to the ideal situation. It is this latter problem that is taken up in this work.

Because this paper attempts a synthesis of two areas which have been thoroughly, but separately developed, brief backgrounds are presented for copolymerization and for mixing. A reader familiar with one, but not the other, is referred to the references for more complete treatments.

2. Background. Copolymerization

In the simplest free-radical copolymerization of two vinyl monomers, M_1 and M_2, there are four and only four propagation steps involved in the formation of a chain.[6]

$$\sim\!\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim\!\sim M_1 - M_1\cdot \tag{1}$$

$$\sim\!\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim\!\sim M_1 - M_2\cdot \tag{2}$$

$$\sim\!\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim\!\sim M_2 - M_1\cdot \tag{3}$$

$$\sim\!\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim\!\sim M_2 - M_2\cdot \tag{4}$$

Copolymer and monomer feed composition are related by the well-known copolymer composition equation

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{5}$$

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, and the mole fractions of monomer i in the feed and instantaneous copolymer are f_i and F_i, respectively. The variation of composition f_i, with conversion, m, is governed, in turn, by a simple material balance. This relationship, known widely as the Skeist equation, has been successfully integrated by Meyer and Lowry

$$\mathrm{d}m = \frac{\mathrm{d}f_1}{f_1 - F_1} \tag{6a}$$

$$m = 1 - \left(\frac{f_1}{f_1^0}\right)^{\alpha}\left(\frac{1 - f_1}{1 - f_1^0}\right)^{\beta}\left(\frac{f_1^0 - \delta}{f_1 - \delta}\right)^{\gamma} \tag{6b}$$

where $\alpha = r_2/(1 - r_2)$, $\beta = r_1/(1 - r_1)$, $\gamma = (1 - r_1 r_2)/[(1 - r_1)(1 - r_2)]$, $\delta = (1 - r_2)/(2 - r_1 - r_2)$. The previous paper in this series[1] showed that free-radical copolymerization using an initiator with a first-order decay could be described as following a time course as given by

$$\ln\left[\left(\frac{f_1}{f_1^0}\right)^{a}\left(\frac{1 - f_1}{1 - f_1^0}\right)^{b}\left(\frac{f_1^0 - \delta}{f_1 - \delta}\right)^{c}\right] = 2(k_{21} - Xk_{22})\left(\frac{e[\mathrm{I}]_0}{k_{\mathrm{d}}k_{\mathrm{t}}}\right)^{1/2}\left(\exp\left(\frac{-k_{\mathrm{d}}t}{2}\right) - 1\right) \tag{7}$$

where $a = \alpha(1 - X) + 1$, $b = \beta(1 - X) - X$, $c = \gamma(1 - X)$, $X = (k_{11} - k_{21})/(k_{12} - k_{22})$, and e and k_{d} are the efficiency and decomposition rate constant, respectively, of the initiator, I. An important assumption made in deriving eq 7 was the time independence of k_{t}, the bimolecular termination rate constant. Since k_{t} is diffusion controlled in most free-radical polymerizations,[8] this assumption seriously limits the quantitative applicability of eq 7. In addition, k_{t} is to some extent dependent on the composition of the polymer chain. Therefore, if the polymer composition drifts with conversion, this may also render eq 7 invalid. In spite of these limitations, eq 7 has been experimentally verified.[1]

Figure 1 shows the instantaneous composition of the copolymer formed from a given monomer feed for two systems which between them have the characteristics which are typical of practically all the copolymerizations conforming to the reaction sequence shown in eq 1–4.

It is to be noted that in the system with $r_1 = 0.5$, $r_2 = 0.1$, there is a particular feed composition ($f_1 = 0.643$) which gives copolymer having the same composition. By analogy with distillation this is called an azeotropic composition. The necessary and sufficient condition for azeotropy is that both reactivity ratios must be greater than or both must be less than unity. For this reason, the system in Figure 1 with $r_1 = 20$, $r_2 = 0.015$ does not possess an azeotrope. In free-

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(4) (a) Z. Tadmor and J. A. Biesenberger, *Ind. Eng. Chem. Fundam.*, **5**, 336 (1966); (b) J. Duerksen and A. Hamielec, *J. Polym. Sci., Part C*, **25**, 155 (1968).

(5) D. Chappelear and R. Simon, review paper presented at the Meeting of the American Chemical Society, San Francisco, Calif., April 1968; Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

(6) G. Ham, Ed., "Copolymerization," Interscience Publishers, New York, N. Y., 1964.

(7) V. E. Meyer and G. G. Lowry, *J. Polym. Sci., Part A*, **3**, 2843 (1965).

(8) A. M. North, *Polymer*, **4**, 134 (1963).

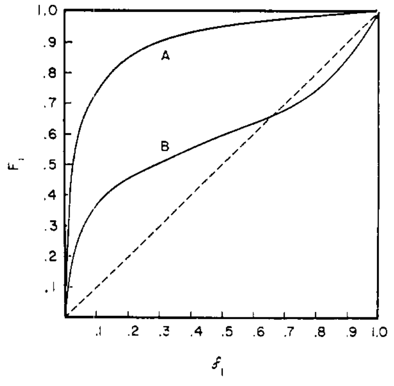

Figure 1. Instantaneous copolymer composition as a function of monomer feed: curve A, r_1 = 20, r_2 = 0.015; curve B, r_1 = 0.5, r_2 = 0.1.

radical copolymerization r_1 and r_2 are rarely both greater than unity. A system with r_1 and r_2 both less than unity which is near, but not at an azeotrope, always drifts away from the azeotrope with increasing conversion.

When both reactivity ratios are less than unity, the copolymer formed tends to have the two monomers alternating along the chain in a random fashion. However, when r_1 is very much greater than unity and r_2 very much less, the copolymer formed tends to be relatively rich in monomer 1 at first and, as conversion proceeds, it becomes rich in monomer 2. The result is not a random copolymer, but rather a product that more closely approximates a mixture of homopolymers.

Although the copolymerization kinetics have been very well described and used from the standpoint of monomer reactivity and instantaneous copolymer composition, there has been little information published on copolymerization to high conversions, copolymer composition distributions, or continuous copolymerizations. Most of the published work on rate of copolymerization, until recently, dwelt on the concept of the "ϕ-factor," which is supposed to describe the enhanced reactivity in the termination reaction for two free-radical chain ends of dissimilar polarity. In a number of experimental and theoretical papers, North and coworkers have shown this concept to be of limited use, if not totally invalid, for the simple reason that the termination reaction is usually diffusion controlled.[8]

3. Incomplete Mixing

If a specific kinetic model, such as eq 1–7, is assumed in order to represent the chemical nature of a given copolymerization then the influence of incomplete mixing in CSTR may be attributed to two factors, namely, variation of the residence time distribution (RTD) and concentration history.

The measurement and description of RTD is a relatively simple matter. Concentration history in comparison presents a difficult problem. This is due in part to its extreme variability and resistance to measurement, but the main difficulty lies in establishing a suitable mathematical representation and applying it to an assumed kinetic model. Normally one might use some sort of visual aid, such as an inert dye, to obtain qualitative data on flow patterns. Next some quantitative judgment is necessary regarding the relative importance of the various flow regimes observed. The product of this endeavor would take the form of an analog reactor system composed of appropriate basic models (*e.g.*, BR, HCSTR) in a suitable arrangement, with the complexity depending on the degree of accuracy desired and justifiable.

Considering the subjective nature of this sort of treatment it seems appropriate in dealing with the basic principles of the effect of mixing on copolymerization to consider only limiting cases of reactor dynamics and to concentrate on the effect of these limiting cases on kinetic behavior commonly found in copolymerization. The result sought is the beginning of an understanding of the problem rather than a detailed description of copolymerization reactor dynamics.

The concept of a segregated CSTR (SCSTR) is useful as a limiting case which illustrates the effect of concentration history on a reaction. As first outlined by Danckwerts[9] the relationship between a HCSTR and a SCSTR is defined.

(1) Complete Segregation (SCSTR). The incoming fluid is broken up into fragments of undefined size and shape but which are small compared to the reaction volume. These fragments are uniformly dispersed so that the distribution of their reaction times is the same as that of a well-stirred (mixed) CSTR. In effect it is a collection of batch reactors in parallel with ideal RTD. Macromixing is identified with the SCSTR concept.

(2) Perfect Mixing (HCSTR). The incoming fluid is dispersed on a microscopic scale as outlined in the definition of a well-stirred CSTR. Micromixing is identified with the HCSTR concept.

The concepts proposed by Danckwerts were generalized by Zwietering[10] to include variation of RTD as well as concentration history. Zwietering's concept of maximum mixedness as a limiting degree of mixing was defined as the maximum amount of mixing occurring as early as possible and consistent with observed RTD. The concept of complete segregation was generalized to conform to any RTD. Segregation becomes in effect a parallel set of BR's with observed RTD. With ideal RTD Zwietering's definition reduces to the HCSTR and SCSTR.

The concept of micro- and macromixing was utilized by Biesenberger and Tadmor[4a] to study the effect of incomplete mixing on MWD in continuous homopolymerization. Their results indicate that within the scope of the mathematical model chosen the effect of segregation is to produce MWD's which are broader than those characteristic of both BR and HCSTR. Their results show little effect of mixing on conversion where the pseudo-steady-state assumption is valid. This is because a constant chain end concentration will give to a polymerization reaction a quasi-first order character. In real polymerizations where the chain end concentration may be variable, as in free-radical polymerizations at high conversions, the effects of mixing may be at variance with the results predicted by their model.

In a paper dealing with influence of incomplete mixing in continuous reactors Szabo and Naumann[11]

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(9) P. V. Danckwerts, *Chem. Eng. Sci.*, **8**, 93 (1958).

(10) Th. N. Zwietering, *ibid.*, **11**, 1 (1959).

(11) T. Szabo and E. Naumann, paper presented at AIChE Meeting, St. Louis, Mo., Feb 1968.

calculated cumulative composition distributions for styrene–acrylonitrile copolymerization in various nonideal mixing situations. The limiting cases of maximum mixedness and complete segregation were investigated for RTD's corresponding to combinations of BR and CSTR in series. In carrying out the necessary calculations the authors assume a pseudo-first-order reaction scheme which they assert is justifiable at low conversion and yields valuable qualitative results at higher conversions. This appears to be useful only in situations of little practical interest, *i.e.*, monomer pairs which give little drift in reaction composition with conversion.

Although the monomer pair chosen for study by Szabo and Naumann was of necessity such that only a small quantitative effect of mixing on CCD could be expected, their calculations are sufficient to show the broadening effect on CCD with variation of RTD and concentration history. In a paper by Mecklenburgh[12] the possibility of using copolymerization as a tracer technique in the study of mixing is suggested. Calculations are carried out for a number of nonideal continuous reactor models using an analytical relation between conversion, composition, and time. This relation, though based on a chemically controlled termination mechanism, could be adaptable to a diffusion-controlled termination mechanism. Mecklenburgh shows that a broadening of CCD is to be expected with segregation in CSTR and a narrowing effect is expected with back-mixing in tubular reactors. The author stresses the fact that, in theory, since a CCD is almost uniquely determined by mixing patterns, the former could serve as a descriptor of the latter. In contrast, inert tracer techniques are largely limited to determination of RTD only.

4. Kinetic Systems for Calculations

The work of Biesenberger and Tadmor[4a] has shown that segregation in a CSTR will have no effect on conversion for a homopolymerization for which a pseudo-steady-state assumption is valid. A similar situation obtains in a copolymerization with respect to both conversion and *average* composition of the copolymer. However, the CCD in a copolymerization will always be affected by segregation. A copolymerization can achieve a pseudo-steady-state condition either because composition drifts little with conversion, or because the rate constants k_{ii} and k_{ij} (i and j are 1 or 2) are equal to within an order of magnitude or less. This can be seen by inspection of the rate equation for the consumption of monomer i

$$\frac{-\mathrm{dM}_i}{\mathrm{d}t} = k_{ii}\mathrm{M}_i\cdot\mathrm{M}_i + k_{ji}\mathrm{M}_j\cdot\mathrm{M}_i \tag{8}$$

which can be rewritten as

$$\frac{-\mathrm{dM}_i}{\mathrm{d}t} = (k_{ii}\mathrm{M}_i\cdot + k_{ji}\mathrm{M}_j\cdot)\mathrm{M}_i \tag{9}$$

or

$$\frac{-\mathrm{dM}_i}{\mathrm{d}t} = K\mathrm{M}_i \tag{10}$$

Table I

KINETIC PARAMETERS FOR CALCULATIONS[a]

System	r_1	r_2	k_{11}	k_{22}	k_t	ek_d	$[\mathrm{I}]_0$
I	20	0.015	350	1150	10^7	6×10^{-6}	0.05
II	20	0.015	5000	300	10^7	6×10^{-6}	0.05
III	0.5	0.1	300	1500	10^8	6×10^{-6}	0.05

[a] All units are moles, liters, and seconds.

where K is a pseudo-first-order rate constant which will change only slightly if the active chain end concentrations change only slightly, or if k_{ii} approximately equals k_{ji}. As a consequence of this, segregation will have little effect on conversion or average copolymer composition. In addition, one could also expect the effect of segregation on the CCD to be small when composition drift is small, but not necessarily when k_{ii} is of the same magnitude as k_{ji}.

The magnitude of composition drift is governed by the quantity $|F_1 - f_1|$, the denominator of eq 6a. The larger this term is, the more rapid will be the drift in composition with conversion. When this term is small for a given monomer pair, their copolymerization can almost be treated as a homopolymerization, with the MWD described in a manner similar to that of Biesenberger and Tadmor,[4a] and the effect of mixing on CCD, composition and conversion ignored. However, when the term $|F_1 - f_1|$ is large or k_{ii} is not similar to k_{ji}, mixing effects must be considered to be important for conversion and average composition as well as for CCD. For purposes of discussion we define three systems, two of which conform to curve A of Figure 1, the third to curve B of Figure 1. Kinetic parameters of these systems are listed in Table I. The equations used to calculate conversions, average compositions and CCD are eq 5, 6, and 7 and those summarized in the Appendix. A computer program and flow diagram for the detailed calculations is available on request.

All calculations were carried out with the somewhat unrealistic assumption that reaction rate constants were independent of conversion, reactor viscosity, composition, or other conceivable variables. The implications of this are discussed in the Conclusions.

5. Results of Calculations

System I. This system, whose kinetic constants approximate those of methyl methacrylate (M_1)–vinyl acetate (M_2), was originally chosen to test the experimental validity of eq 7 in a BR. Conversion–time curves such as those shown in Figure 2 were experimentally observed. The sudden increase in rate of polymerization in a BR can be attributed to the depletion of the more reactive monomer which paradoxically homopolymerizes at a slower rate. The nonlinear character of the conversion–time curve in a BR is the cause of the large effect of mixing in a CSTR, whether conversion or *average* composition is considered.

System II. This system has approximately the same kinetic constants as system I, except that the propagation rate constants have been chosen so as to make the more reactive monomer homopolymerize faster. It approximates the real system methyl acrylate (M_1)–vinyl acetate (M_2). The monotonic change in the rate of consumption of monomer in a BR copolymeri-

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[12] J. C. Mecklenburgh, paper presented at Tripartite Chemical Engineering Conference, Montreal, Sept 1968.

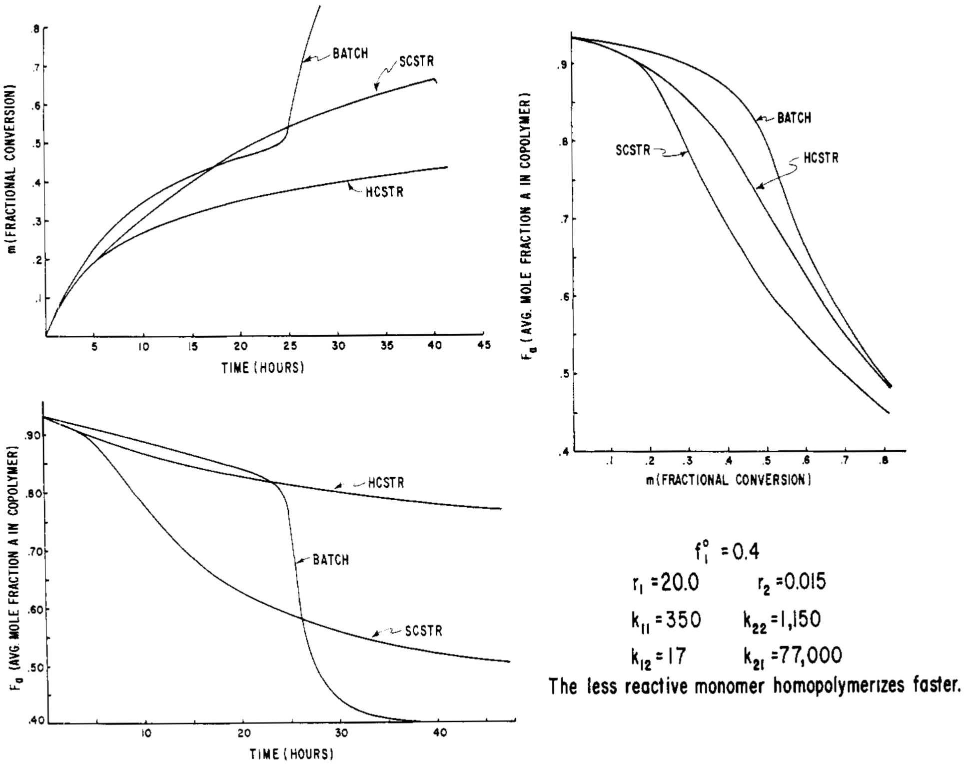

Figure 2. Time–conversion–average composition behavior for system I at an initial feed of $f_1^0 = 0.4$. The time axis is reaction time for the BR, average holding time for CSTR.

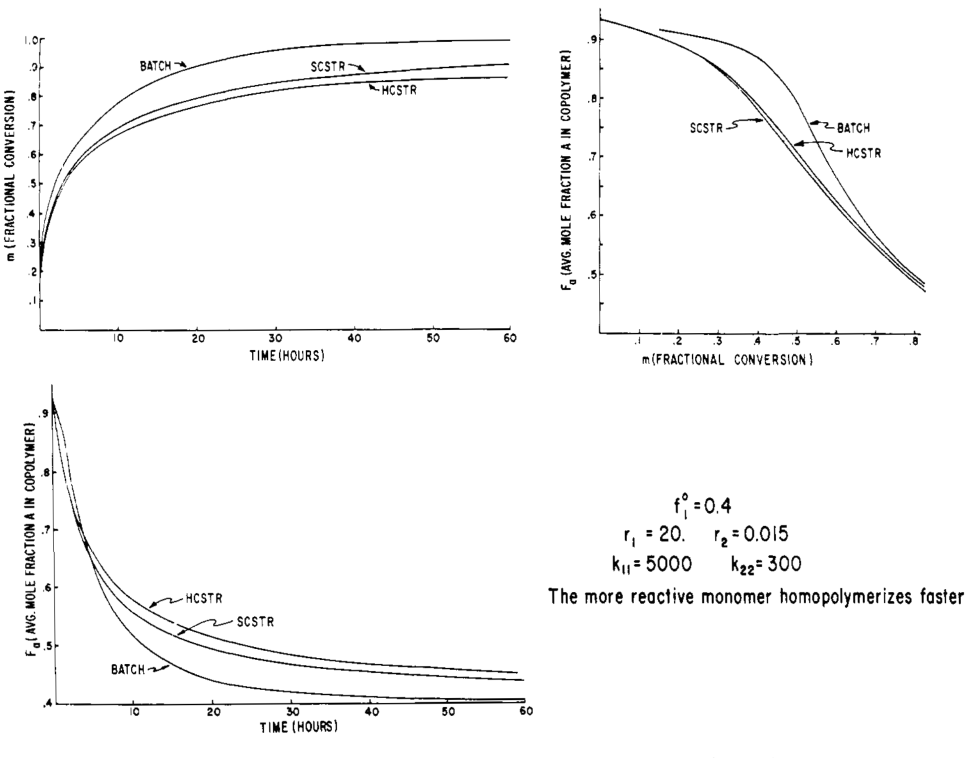

Figure 3. Time–conversion–average composition behavior for system II at an initial feed of $f_1^0 = 0.4$. The time axis is reaction time for the BR, average holding time for the CSTR.

zation of this monomer pair arises from the similarity of k_{11} and k_{21}. This causes the smallness of the difference between the HCSTR and SCSTR behavior shown in Figure 3 for average composition and conversion. Figure 3 is, however, quite misleading with respect to CCD behavior in this system. As shown in Figure 4, there is a strong effect of the concentration history on the CCD. The broad distribution expected in a BR is almost matched at equivalent average copolymer composition by the SCSTR at fairly high conversions in system II. (Similar behavior is found in system I.) In contrast the HCSTR yields, for high

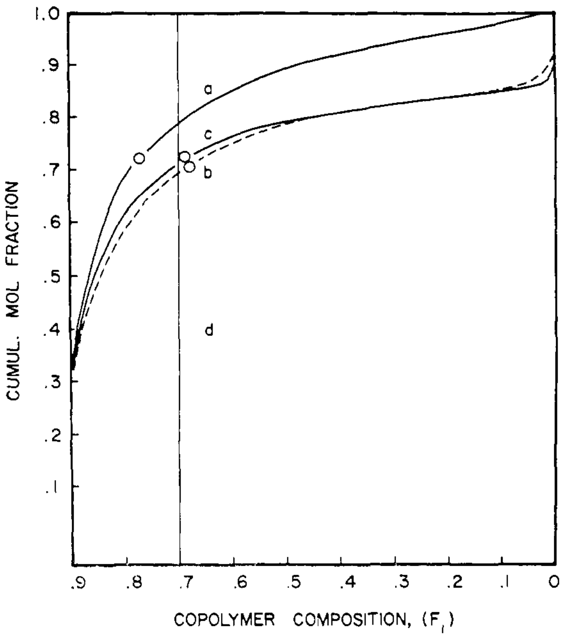

Figure 4. Comparison of CCD obtained in different reactors for system II with $f_1{}^0 = 0.4$; open circles are average values of copolymer composition ($\bar{F}_1$): curve a, BR at 51.4% conversion with $\bar{F}_1 = 0.77$; curve b, BR at 58.5% conversion with $\bar{F}_1 = 0.69$; curve c, SCSTR at 51.4% conversion with $\bar{F}_1 = 0.69$; curve d, HCSTR at 51.4% conversion with $\bar{F}_1 = 0.70$.

chain length polymer in all systems, a spikelike monodisperse distribution of composition. Figure 5 demonstrates that the similarity between BR and SCSTR distributions increases with increasing conversion.

System III. Unlike systems I and II, this system displays an azeotrope. Its rate constants are similar to styrene (M_1)-acrylonitrile (M_2). The magnitude of the term $|F_1 - f_1|$ is greater at f_1 values lower than the azeotrope, and it is in this region that mixing effects would be expected to be stronger. Figure 6 shows that in a system whose feed composition is in this region, the CCD becomes increasingly broad as the conversion at which the CSTR is operated is made greater. It is also to be noted in Figure 6 that the discrepancy between the *average* composition obtained in a SCSTR and a HCSTR is small at all conversions, but the heterogeneity of the composition distribution in the SCSTR is so large as to include even large amounts of homopolymer at advanced conversions.

Having seen in Figure 6 the broadening of the CCD with increasing conversion in a SCSTR, it is instructive to see how the CCD at 100% conversion compares for different initial concentrations in the monomer feed. Figure 7 shows this for system III, where the effect of moving away from the azeotrope is quite obvious. Any of the individual curves in Figure 7, together with a vertical line drawn through its intercept on the abscissa, forms an envelope of the possible CCD's obtained between zero and 100% conversion.

Finally, Figure 8 shows that, even when operating under near-azeotropic conditions, it is possible in a SCSTR to generate a CCD which is quite heterogeneous, much more so than a comparable BR.

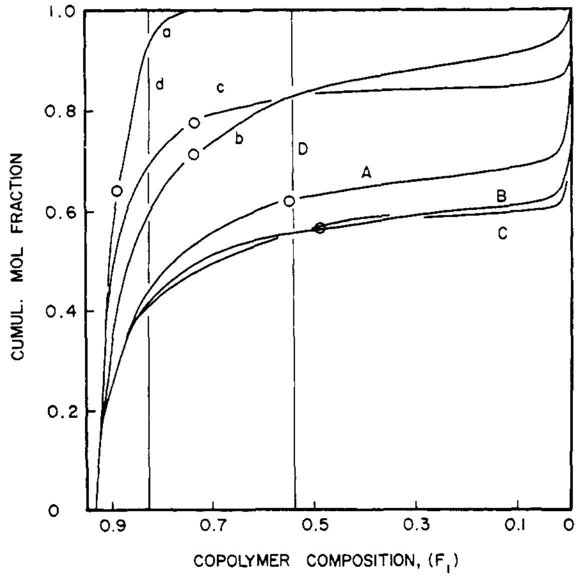

Figure 5. Comparison of CCD obtained with system I at two conversion levels in various reactors; open circles are average values of copolymer composition ($\bar{F}_1$): curve a, BR at 35% conversion with $\bar{F}_1 = 0.89$; curve b, BR at 54% conversion with $\bar{F}_1 = 0.74$; curve c, SCSTR at 35% conversion with $\bar{F}_1 = 0.74$; curve d, HCSTR at 35% conversion with $\bar{F}_1 = 0.83$; curve A, BR at 73% conversion with $\bar{F}_1 = 0.55$; curve B, BR at 82% conversion with $\bar{F}_1 = 0.49$; curve C, SCSTR at 73% conversion with $\bar{F}_1 = 0.49$; curve D, HCSTR at 73% conversion with $\bar{F}_1 = 0.54$.

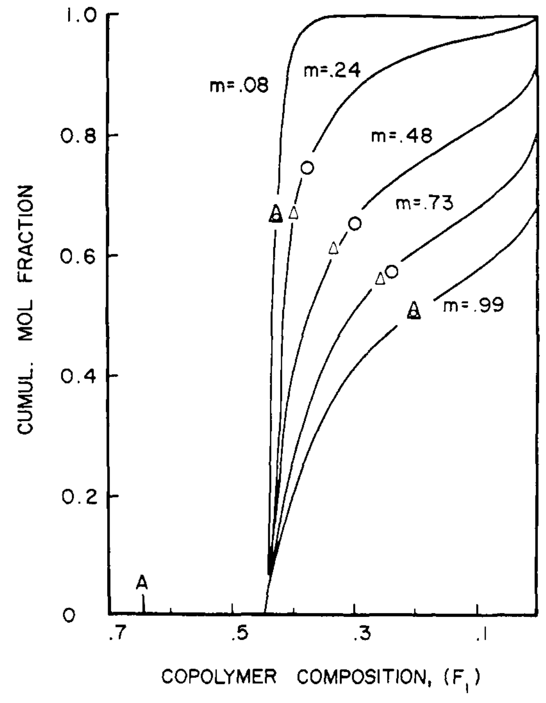

Figure 6. Change of CCD from SCSTR with conversion (m) for system III with $f_1{}^0 = 0.2$; ○, $\bar{F}_1$ in SCSTR; △, $\bar{F}_1$ in HCSTR. Point A on abscissa is azeotrope.

6. Conclusions

The effect of mixing on MWD has not been discussed, since the results would, qualitatively, be the same as those of Biesenberger and Tadmor,[4a] with

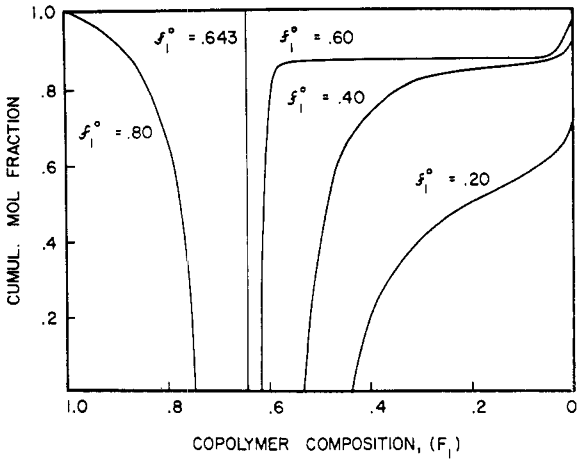

Figure 7. CCD at 100% conversion in SCSTR (and BR) for various initial feeds (f_1^0) of system III.

the added complexity of the effective change in the propagation rate as monomer composition drifts.

The effect of mixing on CCD can be seen to be a strong function of the term $|F_1 - f_1|$. In systems having an azeotrope, this is a measure of the difference between the monomer feed and the azeotrope. In systems not having an azeotrope, it has been demonstrated that those systems in which the less reactive monomer homopolymerizes faster exhibit strong dependence of conversion, average copolymer composition and CCD. If the less reactive monomer homopolymerizes more slowly, the CCD is strongly influenced by mixing even though the average composition and conversion show little effect.

Throughout these calculations, as mentioned above, the influence of increasing conversion on rate constants, particularly the termination rate constant k_t, has been ignored. This has the result of rendering the calculations inaccurate with respect to time. Although this affects the results quantitatively, it does not alter the qualitative conclusions which can be drawn.

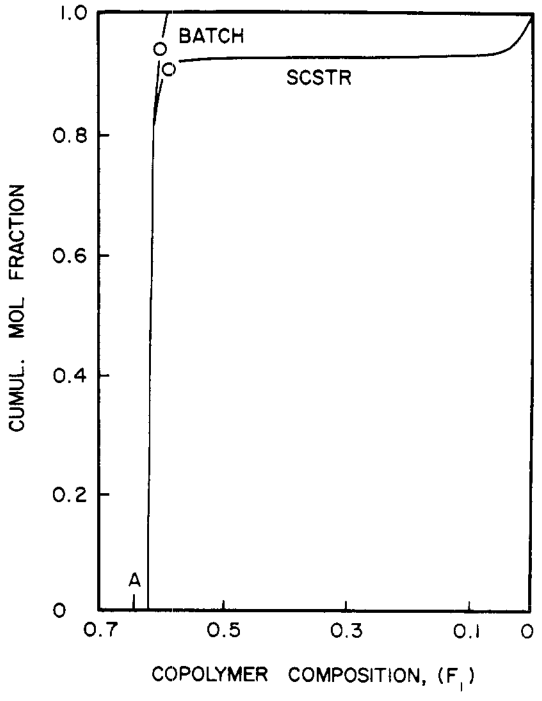

Figure 8. Comparison of CCD in BR and SCSTR near azeotropic composition (A) for system III at 82.3% conversion with f_1^0 = 0.6; open circles are $\bar{F}_1$.

The heterogeneous CCD which may be expected from a copolymerization conducted in a BR or CSTR operated with poor mixing should have important effects on copolymer properties. If these effects are undesirable they can be minimized by improving the mixing in the CSTR and by carrying out the reaction in the BR or CSTR to a lower degree of conversion.[13]

The present practice of operating a BR with intermittent additions of the more reactive monomer to maintain a fairly stable monomer feed level is an unhappy compromise between a true BR and a well-stirred CSTR. Although it reduces the composition broadening expected in a BR, it does not approach the narrow CCD which is to be expected in a HCSTR.

Experimental verification of the calculations presented in this paper ought to be a very difficult task. In the first place, the calculations, as emphasized, ignore the effect of viscosity on rate constants. Second, and even more important for experimental verification, there existed until recently no simple method for fractionating copolymer on the basis of composition which did not also fractionate on the basis of molecular weight. Such a technique is necessary to construct, from experimental data, curves such as Figures 4–8. Using the thin layer chromatographic technique recently applied by Inagaki, *et al.*, to styrene–methylacrylate copolymers,[14] it may prove possible to verify some of the quantitative predictions of this paper relative to CCD broadening brought on by poor mixing. Experimental work to this end is now underway in this laboratory.

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Appendix

The appendix is divided into three separate parts covering BR, HCSTR, and SCSTR. In each part the principle equations used to calculate the results for that particular reactor are summarized.

1. Batch Reactor. The mathematical relations presented in this section are used not only in application to BR analysis, but also in numerical integrations necessary for analysis of the SCSTR.

Fractional conversion, m, and monomer composition, f_1, are related by eq 6b presented in the main body of this paper. The instantaneous copolymer composition, F_1, at given values of m or f_1 is obtained from the copolymer composition eq 5. The time at

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(13) It may be worth noting that, for a fixed conversion, the operation of an SCSTR at shorter holding times and higher $[P_T]$ will tend to narrow the CCD; in the limit that of the BR operated at the same conversion will be approached. Safety considerations might make this a poor approach to narrowing the CCD.

(14) H. Inagaki, H. Matsuda, and F. Kamiyama, *Macromolecules*, 1, 520 (1968).

which these variables will simultaneously occur is then calculated from eq 7.

The average copolymer composition, $\bar{F}_1$, is obtained from a material balance

$$\bar{F}_1 = \frac{f_1^0 - f_1(1 - m)}{m} \qquad (11)$$

Copolymer composition distributions (CCD) are calculated by neglecting statistical variations in instantaneous copolymer composition. (This neglect is justified for high molecular weight copolymer.) The CCD for any total conversion m^* is obtained by a plot of

$$m/m^* \textit{ vs. } F_1 \qquad (12)$$

where, it is emphasized, F_1 is the instantaneous composition of copolymer being produced at conversion m.

The differential copolymer composition equation is calculated by differentiating eq 5 and 6b and combining the results as indicated below

$$\frac{1}{m^*}\frac{\mathrm{d}m}{\mathrm{d}F_1} = \frac{1}{m^*}\frac{\mathrm{d}m}{\mathrm{d}f_1}\frac{\mathrm{d}f_1}{\mathrm{d}F_1} =$$

$$(1 - m)\left(\frac{\alpha}{f_1} - \frac{\beta}{1 - f_1} - \frac{\gamma}{f_1 - \delta}\right) \times \frac{[(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2]}{[(r_1 + r_2 - 2r_1r_2)f_1^2 + 2r_2(r_1 - 1)f_1 + r_2]} \qquad (13)$$

Two special cases, which prove to be of particular importance in the SCSTR, are complete consumption of one component to give homopolymerization in the final stages of the reaction, and complete consumption of initiator to give a "dead end" condition. The former is dealt with in these computations by using homopolymerization kinetics when f_1 becomes less than 10^{-10}. If time is set equal to infinity in eq 7, the "dead end" value of f_1 is calculated from

$$\ln\left[\left(\frac{f_1}{f_1^0}\right)^a\left(\frac{1 - f_1}{1 - f_1^0}\right)^b\left(\frac{f_1^0 - \delta}{f_1 - \delta}\right)^c\right] = - 2(k_{21} - Xk_{22})\left(\frac{e[\mathrm{I}]_0}{k_\mathrm{d}k_\mathrm{t}}\right)^{1/2} \qquad (14)$$

2. HCSTR. To obtain m as a function of f_1 in the HCSTR, it is assumed that the BR relations for the instantaneous copolymer composition and for the average copolymer composition (eq 5 and 11, respectively) hold also for the HCSTR. Owing to the steady-state nature of the HCSTR, it is further assumed that these equations give equivalent results.

To actually carry out the calculations, it is necessary to assume a value of f_1^0 and of f_1, calculate the corresponding F_1 from eq 5, and then, to determine m, substitute the results into the following form of eq 11

$$m = \frac{(f_1^0 - f_1)}{(F_1 - f_1)} \qquad (15)$$

The next step is to determine the time of reaction, or more properly the holding time of the reactor, which will yield the calculated values of m and F_1. In such a calculation, it is necessary to assume a particular rate of initiation and its time dependency.

The equation relating the reactor holding time, θ, to m and f_1 is derived by starting with material balances on the two monomeric components

$$-(\mathrm{M}_1 - \mathrm{M}_1^0) = \theta(k_{11}\mathrm{M}_i\mathrm{M}_1 + k_{21}\mathrm{M}_2\cdot\mathrm{M}_1) \qquad (16$$

and

$$-(\mathrm{M}_2 - \mathrm{M}_2^0) = \theta(k_{22}\mathrm{M}_2\cdot\mathrm{M}_2 + k_{12}\mathrm{M}_1\cdot\mathrm{M}_2) \qquad (17)$$

Equations 16 and 17 can be rearranged to

$$\left(\frac{\mathrm{M}_1^0 - \mathrm{M}_1}{\mathrm{M}_1}\right) - X\left(\frac{\mathrm{M}_2^0 - \mathrm{M}_2}{\mathrm{M}_2}\right) = \theta(\mathrm{M}_1\cdot + \mathrm{M}_2\cdot)(k_{21} - Xk_{22}) \qquad (18)$$

where X is as defined in eq 7.

If we ignore the small concentration of active chain ends flowing out of the CSTR, a material balance on total radical concentration will give the steady-state condition

$$\mathrm{M}_1\cdot + \mathrm{M}_2\cdot \sim (R_\mathrm{i}/2k_\mathrm{t})^{1/2} \qquad (19)$$

where R_i is the rate of initiation. In this work a first-order decay of initiator has been assumed so that $R_\mathrm{i} = 2ek_\mathrm{d}[\mathrm{I}]$. The steady-state value of the initiator concentration, [I], is obtained from another material balance, giving then for R_i

$$R_\mathrm{i} = \frac{2ek_\mathrm{t}[\mathrm{I}]_0}{(1 + \theta k_\mathrm{d})} \qquad (20)$$

Substitution of these results in eq 18 gives

$$\left(\frac{\mathrm{M}_1^0 - \mathrm{M}_1}{\mathrm{M}_1}\right) - X\left(\frac{\mathrm{M}_2^0 - \mathrm{M}_2}{\mathrm{M}_2}\right) = \theta\left(\frac{ek_\mathrm{d}[\mathrm{I}]_0}{(1 + \theta k_\mathrm{d})k_\mathrm{t}}\right)^{1/2}(k_{21} - Xk_{22}) \qquad (21)$$

Using the relations

$$\mathrm{M}_1 = (\mathrm{M}_1^0 + \mathrm{M}_2^0)f_1(1 - m) \qquad (22)$$

and

$$\mathrm{M}_1^0 = (\mathrm{M}_1^0 + \mathrm{M}_2^0)f_1^0 \qquad (23)$$

it is possible to reduce eq 21 to the desired form

$$\frac{f_1^0}{f_1(1 - m)} - X\frac{(1 - f_1^0)}{(1 - f_1)(1 - m)} - (1 - X) = \theta\left(\frac{R_\mathrm{i}}{2k_\mathrm{t}}\right)^{1/2}(k_{21} - Xk_{22}) \qquad (24)$$

which is a simple quadratic in θ since R_i is a linear function of θ.

If it can be assumed that the chain length is long enough for statistical variations in copolymer composition to be negligible, then, due to the steady-state nature of monomer concentrations in the HCSTR, there will be no spread in copolymer composition. Therefore the CCD will be a step function as shown, for example, in Figures 4d, 5d, and 5D.

3. SCSTR. The segregated CSTR has been treated as a set of batch reactors, operating in parallel, with a distribution of reaction times given by the ideal residence time distribution

$$\frac{1}{\theta}\exp(-t/\theta) \qquad (25)$$

The average fractional conversion, $\bar{m}$, for a given SCSTR holding time, θ, is obtained by summing the contributions of each hypothetical BR by integration

$$\bar{m} = \frac{1}{\theta}\int_0^\infty m \exp(-t/\theta)\, \mathrm{d}t \qquad (26)$$

Since it is not possible to express m analytically in terms of time, this equation is integrated numerically up to the point where f_1 is reduced to a value of 10^{-10}. Beyond this point an integration using equations for homopolymerization is employed as done previously in ref 4a.

The average monomer composition in the product stream, $\bar{f}_1$, is calculated by summing the residual monomer from each hypothetical BR

$$\bar{f}_1 = \frac{\bar{M}_1}{\bar{M}} = \frac{1}{\theta}\,\frac{\int_0^\infty f_1(1 - m)\exp(-t/\theta)\,\mathrm{d}t}{(1 - \bar{m})} \qquad (27)$$

The average copolymer composition is then calculated from this result as

$$\bar{F}_1 = \frac{f_1{}^0 - \bar{f}_1(1 - \bar{m})}{\bar{m}} \qquad (28)$$

The CCD represents the fraction of copolymer molecules having compositions ranging from that formed instantaneously at zero conversion, $F_1{}^0$, to that value of F_1 obtained at some advanced conversion. This is equivalent to saying that the CCD represents the fraction of the copolymer product formed between time zero and time t_{F_1} at which the instantaneous composition being formed is F_1. Since, in the SCSTR, the fraction of molecules retained for t_{F_1} or greater is

$$\frac{1}{\theta}\int_{t_{F_1}}^\infty \exp(-t/\theta)\,\mathrm{d}t = \exp(-t_{F_1}/\theta) \qquad (29)$$

then, on a basis of 1 mol of reaction mixture, the number of moles of copolymer formed in this time period with composition between F_1 and $F_1{}^0$ is

$$m_{F_1}\exp(-t_{F_1}/\theta)$$

Similarly

$$\frac{1}{\theta}\int_0^{t_{F_1}} m\exp(-t/\theta)\,\mathrm{d}t$$

moles of copolymer are contributed from molecules spending less than t_{F_1} units of time in the reactor. Normalizing by dividing by the total moles formed, the CCD becomes

$$\frac{1}{\bar{m}}\left(\frac{1}{\theta}\int_0^{t_{F_1}} m\exp(-t/\theta)\mathrm{d}t + m_{F_1}\exp(-t_{F_1}/\theta)\right) \qquad (30)$$

The differential distribution can be obtained by differentiating the CCD giving

$$\frac{1}{\bar{m}}\frac{\mathrm{d}m}{\mathrm{d}F_1}\exp(-t_{F_1}/\theta) \qquad (31)$$

The quantity $\mathrm{d}m/\mathrm{d}F_1$ can be obtained from the differential copolymer composition equation for BR, eq 13.

Structural Studies of the Optically Active and Racemic Poly(propylene sulfides)

Hideko Sakakihara,[1a] **Yasuhiro Takahashi,**[1a] **Hiroyuki Tadokoro,**[1a] **Pierre Sigwalt,**[1b] **and Nicolas Spassky**[1b]

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, Japan, and Faculté des Sciences, Laboratoire de Chimie Macromoléculaire, Paris, 5e, France.
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ABSTRACT: The crystal structure of optically active poly(propylene sulfide) and racemic poly(propylene sulfide) were studied by X-ray diffraction. All reflections of X-ray fiber photographs of the optically active polymer were indexed by the orthorhombic unit cell; the cell dimensions are a = 9.95 Å, b = 4.89 Å, and c (fiber axis) = 8.20 Å, and the space group is $P2_12_12_1\text{-}D_2{}^4$. Two molecular chains characterized by a twofold screw axis pass through the unit cell. The crystal structure of the optically active polymer is very similar to that of racemic poly(propylene oxide). The fact that the fiber photograph of the racemic polymer gives the same X-ray pattern as the optically active polymer suggests that the both polymers have the same crystal structure. Namely, it may be concluded that the racemic polymer sample consists of the two kinds of optically active crystallites, R (rectus) and S (sinister).

Several authors have investigated the crystal structure of racemic poly(propylene oxide) by X-ray diffraction since the report of Natta, Corradini, and Dall'Asta[2a] in 1956. Stanley and Litt[2b] have considered that the oxygen atoms and methylene groups are almost interchangeable and it is possible that optically active and *dl* unit cells are present at the same time. But in the recent report by Cesari, Perego, and Marconi,[3] no attention is paid to this question. In order to justify the conclusion of Stanley and Litt, two problems should be cleared up: one is the crystal structure of optically active poly(propylene oxide) and the other is the differ-

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