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Copolymerization Systems Involving Reversible Propagation Steps

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Summary

The influence of reversal of propagation reactions on copolymer composition has been studied for three systems: (1) anionic copolymerization of vinyl mesitylene (M_1) and α -methylstyrene (M_2) in tetrahydrofuran (THF), (2) radical copolymerization of styrene (M_1) and methyl methacrylate (M_2) in *o*-dichlorobenzene (ODCB), and (3) cationic copolymerization of styrene (M_1) and α -methylstyrene (M_2) in methylene chloride and in bulk. ^{14}C -labeled M_2 was used in systems (1) and (3).

In each case a transition from "normal" behavior to "abnormal" behavior was observed as the conditions were adjusted to favor depropagation reactions involving the shedding of M_2 units. For systems (1) and (2), Lowry's mechanism II, in which only active species terminating in *three* M_2 units are assumed to depropagate, provides a reasonably satisfactory interpretation of the variation of copolymer composition with $[M_2]$ at constant feed composition.

The following reactivity ratios were determined:

System (1) at -78°C in THF: $r_1 = 0.29 \pm 0.03$, $r_2 = 0.49 \pm 0.02$; at 0°C :
 $r_1 = 0.2 \pm 0.1$, $r_2 = 0.72 \pm 0.07$.

System (2) at 132°C in ODCB: $r_1 = 0.545 \pm 0.006$, $r_2 = 0.588 \pm 0.007$.

System (3) at -20°C in bulk: $r_1 = 0.14 \pm 0.06$, $r_2 = 10.1 \pm 1.5$.

INTRODUCTION

For the copolymerization of two monomers the copolymer composition can usually be related to the monomer feed composition

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by the Lewis-Mayo (1) equation. This equation rests on the assumptions of (1) long chains, (2) no effect of medium on the reactivity ratios, (3) no penultimate unit effects, and (4) no reversibility of the propagation reactions. With these assumptions the results may be analyzed in terms of four propagation rate constants.

Deviations from the Lewis-Mayo equation have sometimes been interpreted (2) in terms of a failure of assumption (3). However, under certain conditions reversible propagation reactions are bound to be involved, especially with monomers such as α -methylstyrene, acetaldehyde, and some 5-, 6-, 7-ring compounds, and it is essential that these should be taken into account in interpreting the copolymer composition data.

The basic theory for copolymerization with reversible propagation was worked out by Lowry (3) and extended by Hazell and Ivin (4). Several possible mechanisms were considered, with various reversible propagation steps. Recently a completely general mechanism was published by Durgaryan (5).

The monomers showing the greatest tendency toward reversible propagation are those with the lowest heats of polymerization (0 to 10 kcal/mole). Two cases may be distinguished: that in which the low heat is a natural consequence of the normal bond strengths (as in the formation of polysulphones or the polymerization of 6-ring monomers), and that in which it is the result of strain in the polymer (as in the polymerization of α -methylstyrene or methyl methacrylate).

The consequences of this for copolymerization under conditions where the concentration of monomer M_2 is close to its equilibrium value, $[M_2]_e$, are as follows (6). In the first case all active polymer species with a terminal M_2 group will be liable to depropagate (mechanism IV) (4), while in the second the active species with a terminal M_2 group will not depropagate so long as the adjacent monomer units are such that there is no strain in the polymer (mechanism I, II, or III) (3).

The only previous experimental investigation of these effects is that of Hazell and Ivin (4). They examined various systems in which two olefins were copolymerized with sulfur dioxide. These systems are examples of the first case above and fit mechanism IV. The present work describes an investigation of three systems expected to be examples of the second case and therefore expected to fit mechanism I, II, or III.

Throughout this paper f_2 denotes the feed composition in terms of the two monomer concentrations, i.e., $f_2 = [M_2]/([M_1] + [M_2])$, while F_2 is the mole fraction of M_2 in the copolymer.

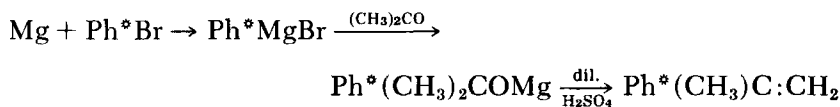
**SYSTEM (1): ANIONIC COPOLYMERIZATION OF VINYL
MESITYLENE (M_1) AND α -METHYLSTYRENE
(M_2) IN THF**

This system has the advantages (1) that the equilibrium concentrations of M_2 in tetrahydrofuran (THF) are known (7,8), (2) that vinyl mesitylene is comparable in reactivity with α -methylstyrene at low temperatures (styrene is unsuitable since it is much too reactive), and (3) that vinyl mesitylene has a much larger heat of polymerization (9) than α -methylstyrene so that its homopolymerization is irreversible under the conditions of the experiments.

Anionic polymerization of vinyl monomers demands the rigorous exclusion of terminating impurities such as oxygen and water. The preparation of initiator solution (sodium naphthalide/THF), the final purification of monomers and solvent, and the polymerization reactions themselves were therefore performed in a vacuum system using scrupulously clean glassware. Since the changes in copolymer composition to be investigated were relatively small, it was essential to use a sensitive method of analysis. This was achieved by ^{14}C -labeling of M_2 .

Experimental

Purification of Monomers. α -Methylstyrene- ^{14}C , uniformly labeled in the ring, was prepared from $\text{PhBr-}^{14}\text{C}$. Then 5.8 mg (17.4 $\mu\text{C}/\text{mg}$) was diluted with 23 ml of PhBr and submitted to the Grignard reaction:



After reaction 30 ml of M_2 was added as carrier. VPC showed that the final distillate contained 2% PhBr and 1% cumene. To remove traces of $\text{PhBr-}^{14}\text{C}$ an equal volume of PhBr was added and the mixture subjected to a further Grignard reaction:



The unreacted M_2 was recovered by fractional distillation under oxygen-free nitrogen and further diluted with inactive M_2 to give a specific activity of about 200,000 dis./min/g (impurity content less than 0.5% by VPC).

Vinyl mesitylene (Koch Laboratories Ltd.) contained less than 1% impurities (VPC).

Each monomer was degassed over powdered CaH_2 on a vacuum line and then distilled onto Na film or liquid K-Na alloy. The monomer was allowed to prepolymerize to some extent before being distilled into weighed tubes fitted with break seals. The filled ampoules were reweighed after sealing and stored at $-78^\circ C$ until required.

Preparation of Initiator Solutions. THF was distilled under vacuum from a vessel containing K-Na alloy onto a mixture of naphthalene and sodium tetraphenylboron, the latter being present to suppress ionization of the ion pairs (10). The solution was then placed in contact with a sodium film and after a sufficiently intense green color (due to naphthalide) had developed, corresponding to about 10^{-3} to 10^{-2} mole/liter, the solution was divided between a number of cooled ampoules which were then sealed off.

Polymerization Procedure. An ampoule of each monomer and one of initiator solution were joined to a tube containing a glass breaker. The polymerization vessel so formed was fitted with a standard joint, cleaned, and evacuated. For copolymerizations at $0^\circ C$ the vessel was then sealed off. For copolymerizations at $-78^\circ C$ pure THF was distilled into the vessel before sealing off; the purpose of the THF was to enable the otherwise solid monomers to be brought into solution at $-78^\circ C$ before initiating the copolymerization. The seals on the monomer ampoules were broken, the monomers thoroughly mixed, and the vessel totally immersed in a bath at the required temperature. Copolymerization was initiated by breaking the seal to the initiator solution and thoroughly mixing the contents of the vessel as rapidly as possible. Successful initiation was indicated by the appearance of the orange-red color of the "living ends."

The reaction was allowed to proceed to low conversion, usually less than 5% (determined by trial and error) and was then terminated by raising the side arm out of the bath and breaking off its tip. The total volume of the reaction mixture was determined from the levels of solution at the temperature of the bath.

The reaction products were poured into a tenfold excess of methanol and the mixture allowed to stand at -10°C . The polymer was then filtered off washed, dried, and reprecipitated from benzene solution in excess methanol. The polymer was finally dried to constant weight at 60°C under vacuum. Tests showed that this procedure was adequate to remove all traces of adsorbed radioactive monomer. The amount of methanol-soluble copolymer (checked by steam distilling the methanolic filtrates) was negligible in all experiments.

^{14}C Analysis of the Copolymers. A liquid scintillation counting technique was employed. First, 10 to 20 mg of polymer was accurately weighed into a counting phial, 4.00 ml of scintillator solution (5.5 g/liter DPO in sulfur-free toluene) pipeted in, and the phial closed with a polythene cap. After a few hours the polymer had dissolved and the phial was gently shaken to obtain a homogeneous solution before measuring the count rate on a coincidence counter. A standard, sealed-off, tube containing *n*-hexadecane- ^{14}C was counted before and after each measurement as a check on instrument efficiency and the usual correction for background was applied. Addition of 10 to 20 mg of nonradioactive polymer of M_1 or M_2 to a ^{14}C -active sample had a negligible effect on the count rate, showing that quenching by the solute was unimportant.

The weight fraction of α -methylstyrene units in a copolymer was calculated from the ratio of the specific activities of the copolymer and a sample of poly(α -methylstyrene- ^{14}C) prepared from the same batch of monomer.

Results and Discussion

Three sets of experiments were performed: the first at -78°C to determine the reactivity ratios under conditions where no depropagation reactions occurred; the second at 0°C at sufficiently high concentrations of M_2 that depropagation reactions were unimportant; and the third at 0°C at progressively lower concentrations of M_2 , keeping $[M_2]/[M_1]$ approximately constant, such that depropagation reactions played an increasing role.

Copolymerization at -78°C . The copolymer composition curve is shown in Fig. 1, where f_2 is the average composition of the feed during polymerization. Experiments without added sodium tetraphenylboron gave the same results, indicating that the reactivity

ratios for the reaction of the ion pairs are the same as for the free ions.

The Fineman-Ross (11) plots of the results were good straight lines giving $r_1 = 0.29 \pm 0.03$ and $r_2 = 0.49 \pm 0.02$ at -78°C . The system is thus one which shows a tendency toward alternating copolymerization.

Copolymerization at 0°C at Relatively High $[M_2]$. At 0°C $[M_2]_e = 0.75$ mole/liter. The results of experiments covering the range of composition $f_2 = 0.31$ to 0.94 and $[M_2] = 1.7$ to 4.1 mole/liter are shown in Fig. 2. In one experiment the ionization was not repressed, without significant effect on the composition. The apparent reactivity ratios derived from these data are $r_1 = 0.2 \pm 0.1$ and $r_2 = 0.72 \pm 0.07$. In view of the fact that $[M_2]$ was considerably in excess of $[M_2]_e$, these should be close to the true values. The larger uncertainty in r_1 at 0°C compared with the value at -78°C arises from a large scatter in the points at high f_1 . This may be due to the prevalence of chain transfer to M_1 , which is known to occur to a greater extent at 0°C than at lower temperatures (12).

The values of r_2 at 0 and -78°C give $E_{22} - E_{21} = 0.5 \pm 0.15$ kcal/mole and $\Delta S_{22}^\ddagger - \Delta S_{21}^\ddagger = 1.25 \pm 0.7$ cal/deg/mole.

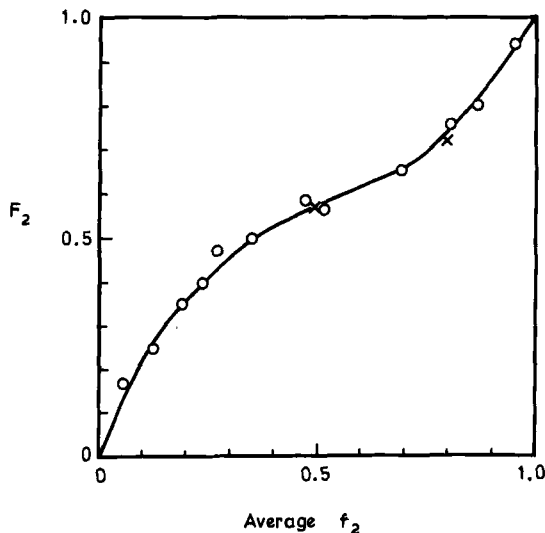


FIG. 1. Copolymer composition curve for the anionic copolymerization of vinyl mesitylene (M_1) with α -methylstyrene (M_2) in THF at -78°C . Crosses indicate experiments in which no sodium tetraphenylboron was added.

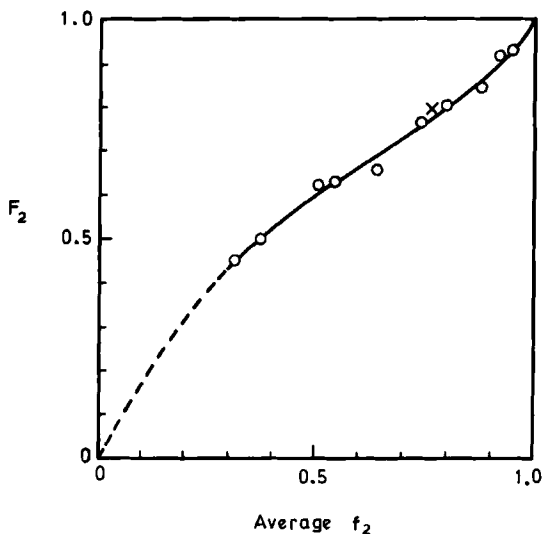


FIG. 2. Copolymer composition curve at 0°C (cf. Fig. 1).

Copolymerization at 0°C at Lower Concentrations of M_2 . A series of runs were performed keeping the average f_2 as close to 0.91 as possible and decreasing $[M_2]$ from 3.90 to 0.054 mole/liter. The results are shown in Table I and plotted in Fig. 3. This graph shows the expected falloff in F_2 as $[M_2]$ falls below $[M_2]_e$. It also shows that the composition tends to a limiting value of F_2 of about 0.65 as $[M_2]$ decreases toward zero. This means that at 0°C the polymer anions of structure $\sim M_1M_2^-$ and $\sim M_1M_2M_2^-$ do not readily depropagate and that Lowry's mechanism II or III (but not I) should apply (3).

From Lowry's equations it is possible to calculate F_2 as a function of $[M_2]$ for mechanisms I and II, knowing f_2 , $[M_2]_e$, r_1 , and r_2 . The curves predicted for $f_2 = 0.91$ are shown in Fig. 3, and a point-by-point comparison (taking the individual values of f_2) is shown in Table 1. Two sets of values of r_1 and r_2 were tried, one corresponding to the "best" values 0.2 and 0.72, respectively (see above), the other with r_1 and r_2 at the limits of error, taken in such a direction as to improve the agreement between theory and experiment. It may be seen that mechanism II predicts a curve which comes fairly close to the experimental points.

Mechanism III, in which anions of structure $\sim M_2M_2M_2^-$ as

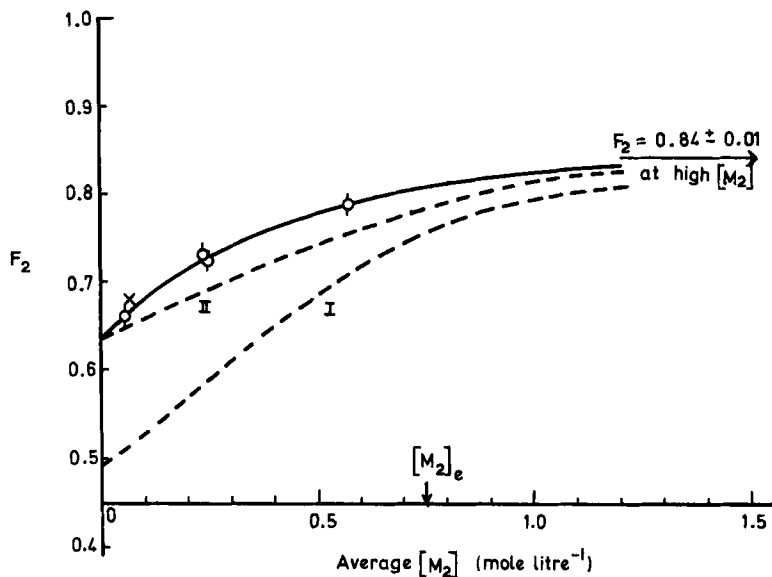


FIG. 3. Effect of depropagation on copolymer composition at 0°C. The dashed lines are calculated for Lowry's mechanisms I and II taking $f_2 = 0.91$, $r_1 = 0.2$, $r_2 = 0.72$, $[M_2]_e = 0.75$.

TABLE I
Sodium Naphthalide-Initiated Copolymerization of Vinyl Mesitylene (M_1) with α -Methylstyrene (M_2) in THF at 0°C^a

| Exptl. results | | Calcd. values of F_2 | | | | | |
|--------------------|-----------------------------|------------------------|-------------------|-------------------------|-------------|-------------|-------------|
| Av. f_2 | Av. $[M_2]$, mole/liter | Wt. % conversion | F_2 | Lowry II | | Lowry I | |
| | | | | r_1 0.2 r_2 0.72 | 0.1 0.79 | 0.2 0.72 | 0.1 0.79 |
| 0.875 | 3.90 | 2.0 | 0.841 ± 0.013 | 0.840 | 0.851 | 0.837 | 0.848 |
| 0.892 | 0.575 | 4.4 | 0.790 ± 0.012 | 0.750 | 0.761 | 0.703 | 0.715 |
| 0.917 | 0.250 | 6.9 | 0.730 ± 0.011 | 0.696 | 0.698 | 0.588 | 0.590 |
| 0.935 | 0.240 | 3.3 | 0.723 ± 0.011 | 0.693 | 0.696 | 0.589 | 0.592 |
| 0.924 ^b | 0.0622 | 5.0 | 0.675 ± 0.010 | | | | |
| 0.920 | 0.0539 | 7.6 | 0.660 ± 0.010 | 0.659 | 0.662 | 0.514 | 0.517 |

^a Effect of $[M_2]$ on F_2 at approximately constant f_2 , $[\text{Na} \cdot \text{Naph}] = 10^{-3}$ to 10^{-2} , $[\text{NaBPh}_4] \approx 0.1$, reaction time 10 to 45 min, $[M_2]_e = 0.75$.

^b In this experiment the cation was potassium and no salt was added.

well as $\sim M_2M_2M_2^-$ are assumed to depropagate, unfortunately cannot be used to make quantitative predictions because it involves too many parameters, but it is interesting to note that for a given set of conditions it predicts higher values of F_2 than those given by mechanism II (except at the extremes of $[M_2]$ where the values are the same), and would therefore lead to better agreement with experiment.

We may therefore conclude that for this system the experimental results are in accord with either mechanism II or III.

SYSTEM (2): RADICAL COPOLYMERIZATION OF STYRENE (M_1) AND METHYL METHACRYLATE (M_2) IN ODCB

This system has previously been investigated in bulk up to 132°C. Under these conditions depropagation effects are negligible. In *o*-dichlorobenzene (ODCB), Bywater (13) found $[M_2]_e = 0.339$ mole/liter at 132°C, so that it should be possible to detect depropagation effects at this temperature by working in ODCB solution.

Experimental

Purification of Monomers and Solvent. The *monomers* were freed of inhibitors by shaking with dilute aqueous sodium hydroxide, washed, dried, fractionally distilled under oxygen-free nitrogen, and stored at -10°C in the dark until required.

ODCB was fractionally distilled under reduced pressure of nitrogen and stored in the dark.

Polymerization Procedure. Reactions were performed in a vessel which was heated by a lagged chlorobenzene vapor bath (132°C). A measured volume of ODCB (10 to 100 ml) was pipeted into the vessel and flushed at room temperature with oxygen-free nitrogen. Flushing was continued at a slow rate while the vapor bath was brought to its working temperature. The flow was then stopped and a known volume (0.8 to 2.2 ml) of a mixture of monomers of known composition was injected into the preheated solvent. The flow of nitrogen was restored for a short time to expel oxygen and to ensure thorough mixing. Loss of monomer by evaporation in the nitrogen stream was reduced by means of a water-cooled condenser situated just above the reaction vessel. Tests with materials of similar volatility showed that there was a negligible change in concentration under the conditions used.

"Thermal" initiation was found sufficient to induce a convenient rate of copolymerization when high monomer concentrations were employed. For lower monomer concentrations, initiation was assisted by ultraviolet radiation from a Mazda mercury lamp situated about 10 cm from the vapor jacket (from which part of the lagging was removed). However, at very high dilution this method proved unsuitable because of the formation of tars from ODCB; thermal initiation with long reaction times (3 hr) was used instead.

The copolymerizations were terminated after 1 to 5% conversion (determined by trial and error), by reversing the earlier direction of flow of nitrogen and forcing the mixture out of the reaction vessel into excess methanol. Polymer made from dilute solutions of monomer was partially soluble in methanol and was recovered by steam distillation of the methanolic mixture. The polymer deposited on the sides of the flask used for steam distillation. It was dissolved in acetone and reprecipitated in water, coagulation being facilitated by the addition of hydrochloric acid. The polymer was filtered and dried to constant weight under vacuum at 60°C.

For reactions at higher monomer concentrations the polymer was completely precipitated by an excess of 3:1 methanol-water mixture and the steam distillation process was unnecessary.

Analysis of the Copolymers. The composition of the copolymer was determined by carbon analysis. The homopolymers gave the following results.

Polystyrene: 92.15, 91.85, 92.3%; average 92.1%; theoret. 92.27%

Poly-MMA: 60.25, 60.1, 59.9%; average 60.1%; theoret. 60.0%

The steam distillation process had no effect on the results of the analysis. The chlorine content of the polymers was less than 0.3%, indicating the absence of ODCB tar in the recovered polymers as well as the absence of appreciable chain transfer to solvent.

The infrared spectra of the copolymers prepared at 132°C in ODCB showed the same qualitative features as those of polymers prepared by benzoyl peroxide-initiated bulk copolymerization at 60°C.

Results and Discussion

Copolymerization at 132°C at Relatively High $[M_2]$. The results under these conditions are summarized in the first half of Table 2. Concentrations were corrected from room temperature to 132°C by

TABLE 2
 Radical-Initiated Copolymerization of Styrene (M_1) and Methyl
 Methacrylate (M_2) in *o*-Dichlorobenzene at 132°C

| Exptl. results | | | | | | |
|-------------------------------------|-----------------------------|-----------------------------|---------------------|----------|---------|-------|
| Av. f_2 | Av. $[M_1]$, mole/liter | Av. $[M_2]$, mole/liter | Wt. % conversion | F_2 | | |
| 0.177 | 3.85 | 0.83 | 1.9 | 0.244 | | |
| 0.305 | 3.23 | 1.42 | 1.5 | 0.360 | | |
| 0.419 | 2.31 | 1.66 | 1.5 | 0.443 | | |
| 0.520 | 1.91 | 2.07 | 2.4 | 0.521 | | |
| 0.621 | 1.51 | 2.47 | 3.2 | 0.590 | | |
| 0.740 | 0.96 | 2.73 | 3.0 | 0.688 | | |
| 0.845 | 0.56 | 3.04 | 3.7 | 0.792 | | |
| 0.916 | 0.17 | 1.82 | 1.5 | 0.876 | | |
| Calcd. values ^a of F_2 | | | | | | |
| | | | | Lowry II | Lowry I | |
| 0.916 | 0.127 | 1.376 | 1.04 | 0.860 | 0.856 | 0.853 |
| 0.916 | 0.126 | 1.380 | 2.06 | 0.856 | 0.857 | 0.853 |
| 0.917 | 0.0151 | 0.166 | 1.68 | 0.760 | 0.706 | 0.626 |
| 0.919 ^b | 0.0145 | 0.165 | 4.25 | 0.740 | 0.707 | 0.626 |
| 0.918 | 0.0111 | 0.125 | 0.98 | 0.704 | 0.688 | 0.591 |
| 0.921 ^c | 0.0135 | 0.159 | 7.2 | 0.695 | 0.664 | 0.539 |

^a Taking $[M_2]_e = 0.339$ at 132°C, $r_1 = 0.545$, $r_2 = 0.588$; and $[M_2]_e = 0.83$ at 155.5°C and same r_1 and r_2 as at 132°C.

^b $[\eta]$ of polymer = 5.5 ml/g, giving $\bar{M}_w \sim 6000$ assuming Stockmayer's relation (14).

^c At 155.5°C.

using reported data on the densities of the components of the reaction mixture and assuming no volume change on mixing (15-17). The Fineman-Ross plot is shown in Fig. 4. The slope gives $r_1 = 0.545 \pm 0.006$, and the intercept on the y_1 axis gives $r_2 = 0.588 \pm 0.007$. These reactivity ratios are close to those which have been reported for the *bulk* copolymerization: $r_1 = 0.590 \pm 0.026$, $r_2 = 0.536 \pm 0.026$ (131°C) (18); $r_1 = 0.60$, $r_2 = 0.55$ (132°C), although the presence of the solvent has caused a reversal in the relative magnitudes.

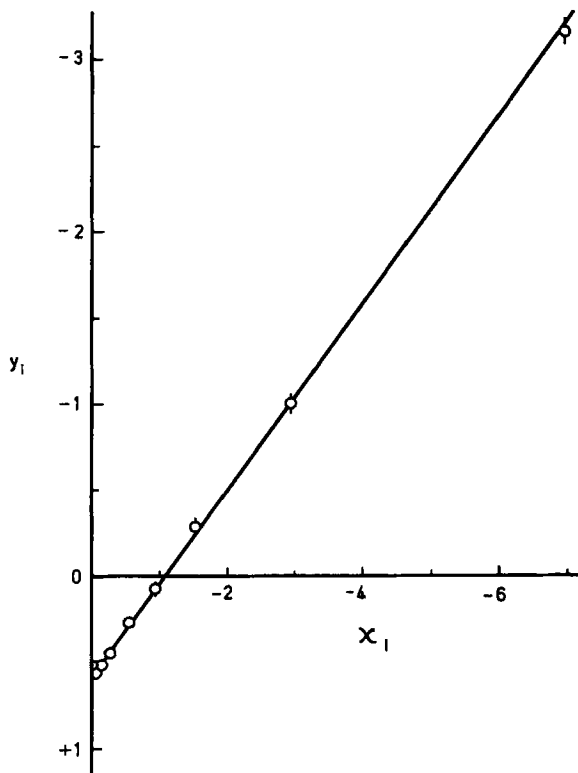


FIG 4. Fineman-Ross plot for radical-initiated copolymerization of styrene (M_1) and methyl methacrylate (M_2) in *o*-dichlorobenzene at 132°C and at relatively high concentrations of monomer. $y_1 = f_1(1 - 2F_1)/(1 - f_1)F_1$; $x_1 = f_1^2(F_1 - 1)/(1 - f_1)^2F_1$.

Copolymerization at 132°C at Lower Concentrations. The results at lower concentrations, keeping f_2 approximately constant at 0.917, are shown in the lower half of Table 2. The experimental values of F_2 are compared with those calculated from Lowry's first and second mechanisms. As with the first system, the results conform much more closely to mechanism II than to mechanism I for the region where there is marked depropagation ($[M_2] < 0.3$). Even better predictions would be obtained by modifying mechanism II in the direction of mechanism III. The single experiment at 155.5°C (last line of Table 2), where depropagation effects are even more pronounced, confirms these conclusions. Measurement of $[\eta]$ for

one of the copolymers (see Table 2) showed that the chains were reasonably long in spite of the extreme conditions.

SYSTEM (3): CATIONIC COPOLYMERIZATION OF STYRENE (M_1) AND α -METHYLSTYRENE (M_2) IN CH_2CL_2 AND IN BULK

This system is at first sight an attractive one, since α -methylstyrene is considerably more reactive than styrene under "normal" conditions. A relatively large change in composition should therefore occur as depropagation becomes more important. Unfortunately it turned out that when the conditions were adjusted to favor depropagation, either by raising the temperature from -20°C to above 0°C (stannic chloride-initiated bulk polymerization) or by lowering $[M_2]$ from 1.5 to 0.1 mole/liter (stannic chloride-initiated polymerization in methylene chloride at 0°C), considerable amounts of methanol-soluble material were produced. Furthermore the methanol-soluble fraction contained rather more α -methylstyrene units than the methanol-insoluble fraction; for example, in one experiment the F_2 values were 0.920 and 0.805, respectively. This difference could be due to preferential initiation through α -methylstyrene or to the higher solubility of α -methylstyrene-rich polymer. Because of these difficulties this system was not investigated in detail. ^{14}C -labeled α -methylstyrene was again used.

Results and Discussion

The reactivity ratios for bulk polymerization at -20°C were found to be $r_1 = 0.14 \pm 0.06$ and $r_2 = 10.1 \pm 1.5$ (see Fig. 5). The two lowest points in this plot refer to values of f_2 below 0.2 and the F_2 values are likely to be low because of the occurrence of depropagation reactions. For this reason they were ignored when drawing the straight line. The reactivity ratios for polymerization in ethyl chloride solution at 0°C , determined by Ludwig et al. (20) ($r_1 = 0.05$, $r_2 = 2.90$) are likely to be in error for the same reason.

In a series of measurements on the bulk copolymerization with $f_2 = 0.90$, F_2 fell off as the temperature was raised above 40°C . This accords with the general observation on other systems, including the polysulfones, that depropagation effects come into play when the temperature is above a point 20°C below the ceiling temperature for M_2 at the prevailing concentration.

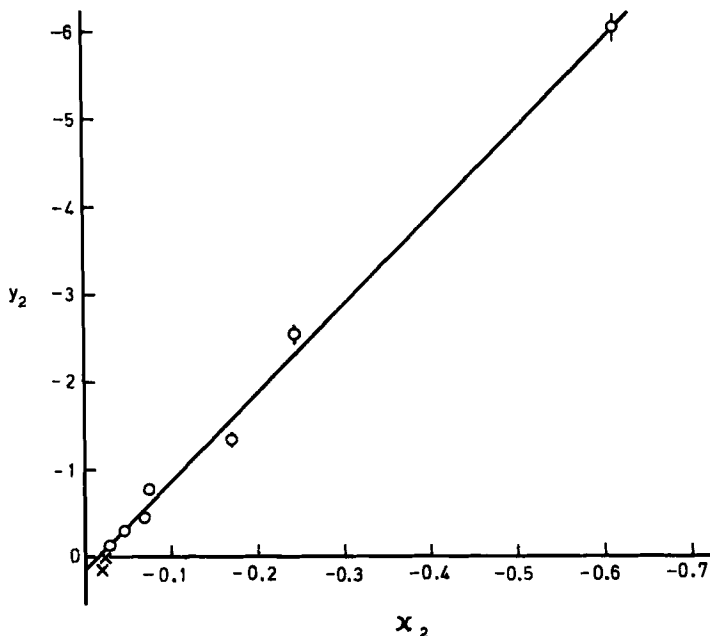


FIG. 5. Fineman-Ross plot for SnCl_4 -initiated bulk copolymerization of styrene (M_1) and α -methylstyrene (M_2) at -20°C .

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Zusammenfassung

Der Einfluss der Umkehr der Fortpflanzungsgeschwindigkeit auf die Copolymerenzusammensetzung wurde in drei Systemen untersucht: (1) Anionische Copolymerisation von Vinylmesitylen (M_1) und α -Methylstyrol (M_2) in Tetrahydrofuran (THF); (2) Radikalcopolymerisation von Styrol (M_1) und Methyl methacrylat (M_2) in *o*-Dichlorbenzol (ODCB); (3) Kationische Copolymerisation von Styrol (M_1) und α -Methylstyrol (M_2) in Methylenchlorid und ohne Lösungsmittel. ^{14}C markiertes M_2 wurde in den Systemen (1) und (3) verwendet.

In jedem Falle wurde ein Übergang von "normalem" zu "abnormalem" Verhalten beobachtet wenn die Bedingungen so gewählt waren, dass Depropagationsreaktionen begünstigt wurden, die auf einer Abgabe von M_2 Einheiten beruhen. In den Systemen (1) und (2), in welchen angenommen wurde, dass nur solche Anteile depropagieren, die von drei M_2 Einheiten abgesättigt werden, ergibt Lowry's Mechanismus II eine sinnvolle und zufriedenstellende Interpretation der Änderung der Copolymerenzusammensetzung mit (M_2) bei konstanter Totalzusammensetzung.

Die folgenden Reaktivitätsverhältnisse wurden bestimmt:

System (1) bei -78° in THF: $r_1 = 0.29 \pm 0.03$, $r_2 = 0.49 \pm 0.02$; bei 0° : $r_1 = 0.2 \pm 0.1$, $r_2 = 0.72 \pm 0.07$.

System (2) bei 132° in ODCB: $r_1 = 0.545 \pm 0.006$, $r_2 = 0.588 \pm 0.007$.

System (3) bei -20° in unverdünntem Zustand: $r_1 = 0.14 \pm 0.06$, $r_2 = 10.1 \pm 1.5$.

Résumé

L'influence de la réversibilité des réactions de propagation sur la composition du copolymère a été étudiée dans trois systèmes: (1) copolymérisation anionique du vinyl mésitylène (M_1) avec l' α -méthylstyrène (M_2) dans le tétrahydrofurane (THF); (2) copolymérisation radicalaire du styrène (M_1) et du méthacrylate de méthyle (M_2) dans l'*o*-dichlorobenzène (ODCB);

(3) copolymérisation cationique du styrène (M_1) et de l' α -méthylstyrène (M_2) dans le chlorure de méthylène et en bloc. M_2 ^{14}C -marqué a été employé dans (1) et (3).

Dans chaque cas une transition d'un comportement "normal" en "anormal" a été observée au fur et à mesure de l'ajustage des conditions favorisant la réaction de dépropagation avec perte d'unités M_2 . Pour les systèmes (1) et (2) le mécanisme II de Lowry, selon lequel on assume qu'uniquement les espèces actives se terminant en trois unités M_2 se dépropagent, fournit une interprétation satisfaisante raisonnable des variations de la composition du copolymère à composition constante d'alimentation.

Les rapports suivants de réactivités ont été déterminés:

Système (1) à -78°C en THF: $r_1 = 0.29 \pm 0.03$, $r_2 = 0.49 \pm 0.02$; à 0°C :
 $r_1 = 0.2 \pm 0.1$, $r_2 = 0.72 \pm 0.07$.

Système (2) à 132°C en ODCB: $r_1 = 0.545 \pm 0.006$, $r_2 = 0.588 \pm 0.007$.

Système (3) à -20°C en bloc: $r_1 = 0.14 \pm 0.06$, $r_2 = 10.1 \pm 1.5$.