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Copolymerization with Depropagation

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Summary

Free-radical copolymerizations of styrene with α-methylstyrene and methyl methacrylate and of acrylonitrile with α-methylstyrene have been carried out in the approximate regions of the ceiling temperatures of α-methylstyrene and methyl methacrylate. A theoretical treatment of copolymerization emphasizing the thermodynamic reversibility of particular propagation reactions has been compared with a kinetic treatment of copolymerization which emphasizes penultimate unit effects on the same propagation reactions. The former is found to adequately describe experimental copolymer composition data over a wide range of temperatures and over the complete range of monomer feed composition.

INTRODUCTION

In the simplest vinyl, free-radical copolymerization there are four and only four propagation steps involved in the formation of a chain and these are irreversible:

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

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

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

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

The resulting kinetics give the usual composition equation

$$m_1/m_2 = ([M_1]/[M_2])(r_1[M_1] + [M_2]/r_2[M_2] + [M_1]) \tag{5}$$

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where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, and m_1 and m_2 denote the concentrations of monomers 1 and 2 in the initial polymer formed from a feed containing the monomer concentrations $[M_1]$ and $[M_2]$. Deviations from Eq. (5) have been ascribed to penultimate unit effects such that the rate constant of reaction (6) differs from that of reaction (7):

$$\sim M_1 - M_1\cdot + M_1 \xrightarrow{k_{111}} \sim M_1M_1M_1\cdot \tag{6}$$

$$\sim M_2 - M_1\cdot + M_1 \xrightarrow{k_{211}} \sim M_2M_1M\cdot \tag{7}$$

The possibility that such effects (and ones further back than penultimate on the chain) are important was explored in a series of papers by Ham (*1–3*). In particular he demonstrated that the copolymerization of acrylonitrile and α-methylstyrene could be described for monomer feeds rich in α-methylstyrene by assuming penultimate effects (*3*).

Deviations from Eq. (5) are also to be expected when one of the copolymerizing monomers is very susceptible to depropagation, as in reaction (8):

$$\sim M_2 - M_2\cdot + M_2 \rightleftharpoons \sim M_2 - M_2 - M_2\cdot \tag{8}$$

A theoretical treatment of various possibilities along these lines has been given by Lowry (*4*). [The only experimental work in vinyl copolymerization with depropagation considered is that of Ivin and co-workers with olefin–sulfur dioxide copolymers. (*5*)] The essential difference between Ham's approach (*3*) and that of Lowry (*4*) is that the former emphasizes the kinetic nature of the chain growth and the impossibility of particular reactions, whereas the latter takes into consideration the thermodynamically reversible nature of the propagation reaction. In doing so, the equations which Lowry has derived make an implicit allowance for the influence of temperature variation on copolymer composition. So, for example, the approach which Ham developed predicts a specific limiting composition for the copolymer from a mixture very rich in the monomer which does not homopolymerize (e.g., α-methylstyrene). This limiting composition is temperature-independent, unlike that which can be predicted from Lowry's equations. The two approaches are similar in that they both assume an explicit model, or set of reactions, which do or do not exhibit penultimate effects. The number of parameters necessary to describe the model is consistently larger in the Ham treatment than in Lowry's. For example, for α-methylstyrene copolymerizations Ham uses three reactivity ratios plus an explicit assumption of zero rate for one reaction (*3*), whereas Lowry's case II (*4*), which we will show is applicable for α-methylstyrene copolymerizations, needs two reactivity ratios and an equilibrium constant.

In this paper we report the results of copolymerizing α-methylstyrene (AMS) with styrene (STY) over a range of temperatures above and below the ceiling temperature of AMS; of copolymerizing AMS with acrylonitrile (AN); and of copolymerizing methyl methacrylate (MMA) with STY above the MMA ceiling temperature. In all cases we have carried out the copolymerizations over a wide range of monomer feeds and have found the Lowry case II to be quite adequate in describing the results.

EXPERIMENTAL

Monomers were all distilled under a reduced pressure of nitrogen immediately prior to polymerizations, which were carried out in ampoules sealed under vacuum after the usual freeze-thaw cycles to remove dissolved gases. Polymerizations were initiated thermally or with benzoyl peroxide, either alone or with freshly distilled dimethylaniline for low-temperature polymerizations.

NMR analyses of α-methylstyrene copolymer compositions were carried out at ambient temperatures on a Varian A-60 using approximately 10% solutions of the copolymers in deuterochloroform. The STY-MMA copolymers were analyzed by the phenyl absorbance at 269 mμ (*6*). Estimated errors for the NMR analyses are ±5%, for the UV analyses, ±2%.

RESULTS

Figures 1 and 2 are typical of the NMR spectra for the copolymers of STY or AN with AMS. In the case of STY-AMS the fractional STY content of the copolymer (m_1) can be calculated from

$$m_1 = [(\mathrm{B} + \mathrm{C}) - \tfrac{2}{3}\mathrm{A}]/[(\mathrm{B} + \mathrm{C}) + \tfrac{1}{3}\mathrm{A}] \qquad (9)$$

where the area of the peaks, denoted A, represents the concentration of —CH_3 hydrogens in the polymer chain, B represents

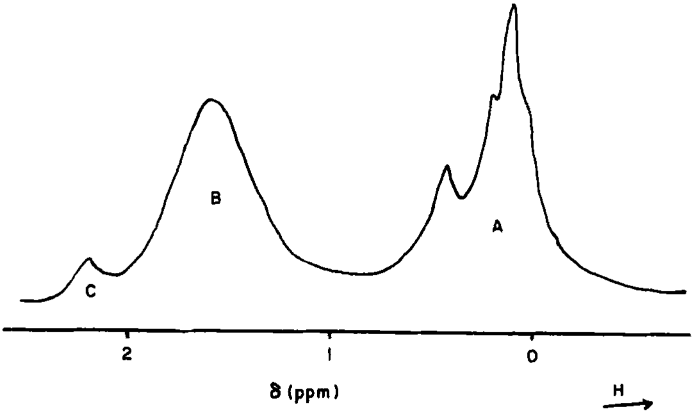

FIG. 1. Portion of the NMR spectrum of copolymer of α-methylstyrene and styrene prepared from a feed containing 5.6% styrene.

—CH_2— hydrogens, and C the α-hydrogens. For AN-AMS copolymers, the phenyl hydrogens of the AMS units provide the basis for calculating the fractional AMS (m_2) content of the copolymer according to

$$m_2 = E/(5D - 4E) \qquad (10)$$

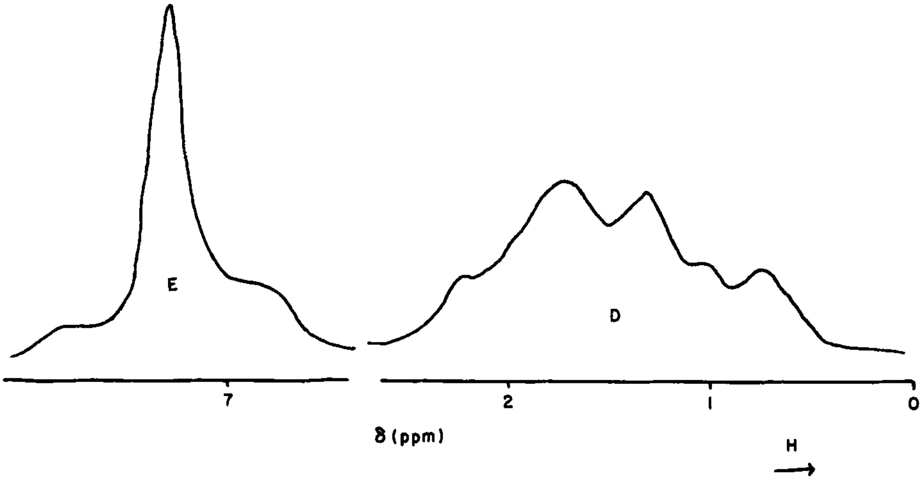

FIG. 2. NMR spectrum of a copolymer of α-methylstyrene and acrylonitrile prepared from a feed containing 32.6% acrylonitrile.

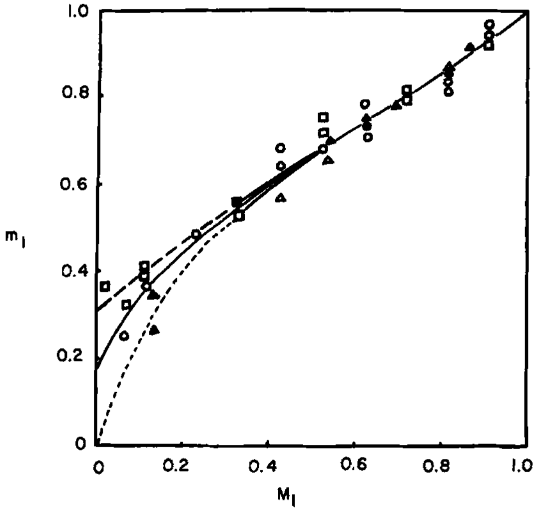

FIG. 3. Variation of copolymer composition with monomer feed in the system styrene (M_1)-α-methylstyrene (M_2) at 0°C: △, 60°C; ○, 100°C; □, Ref. (7) at 0°C; ▲, Ref. (8) at 60°C; ●, curves calculated using Eqs. (13), (14), and (15) and parameters in Table 1 at 0°C (. . .), 60°C (———) and 100°C (---).

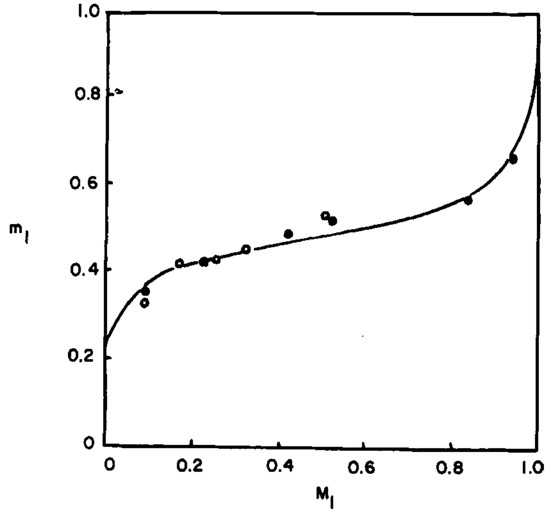

FIG. 4. Variation of copolymer composition with monomer feed in the system acrylonitrile-α-methylstyrene at 75°C: ○, this work; ●, Ref. (3). Curve calculated using Eqs. (13), (14), and (15) and parameters in Table 1.

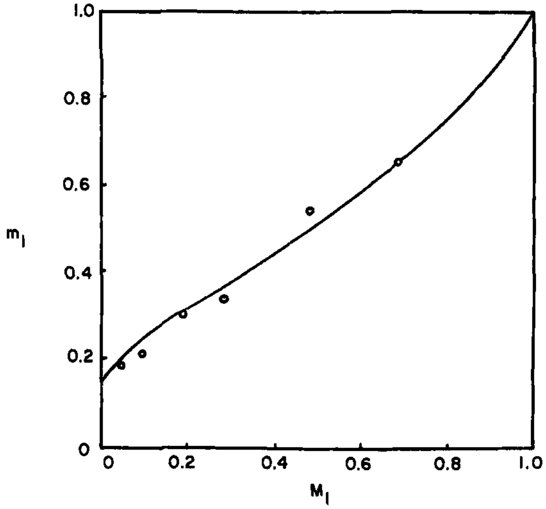

FIG. 5. Variation of copolymer composition with monomer feed in the system styrene (M_1)-methyl methacrylate (M_2) at 250°C. Curve calculated using Eqs. (13), (14), and (15) and parameters in Table 1.

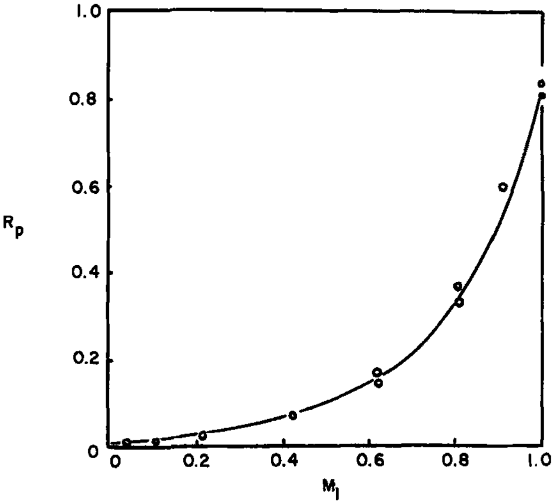

FIG. 6. Per cent conversion per hour for the system styrene (M_1)-α-methylstyrene (M_1) at 60°C using 2.4 × 10^{-3} ml of benzoyl peroxide.

where the area of the peaks denoted D represent —CH_3, —CH_2—, and α-hydrogens and E represents phenyl hydrogens.

The composition data determined in this work for the systems STY-AMS, AN-AMS, and STY-MMA are given in Figs. 3, 4, and 5, respectively, along with pertinent data from the literature (*2*, *7*, *8*). In the systems using AMS it is difficult to obtain data at high-AMS composition because of the apparent retarding effect of AMS on the copolymerization. This is illustrated in Fig. 6, where the rate of copolymerization is seen to approach zero as the AMS mole fraction approaches unity.

DISCUSSION OF RESULTS

The lines drawn through the data presented in Figs. 3, 4, and 5 have been calculated using the equations devised by Lowry for what he termed case II (*4*). In this case it was explicitly assumed that reaction (11) must be considered reversible while reaction (12) need not be.

$$\sim M_2 - M_2\cdot + M_2 \overset{K}{\rightleftharpoons} \sim M_2 - M_2 - M_2\cdot \qquad (11)$$

$$\sim M_2 - M_2\cdot + M_1 \xrightarrow{k_{221}} \sim M_2 - M_2 - M_1\cdot \qquad (12)$$

In his case III Lowry derived equations for those conditions under which reaction (12) must also be considered reversible (*4*). The equations for case III were not tractable for our computer (IBM 1620) and required too many unknown parameters, such as an equilibrium constant for reaction (12). Furthermore, Lowry's hypothetical system (*4*) showed little, if any, difference between the compositions calculated for cases II and III. Therefore, we chose to describe our experimental data by the equations for case II:

$$\frac{m_2}{m_1} = \frac{\beta\gamma - 1 + [1/(1-\beta)]^2}{\{(r_1[M_1]/[M_2]) + 1\}\{\beta\gamma + [\beta/(1-\beta)]\}} \qquad (13)$$

where

$$\beta = (1 + K[M_2] + \frac{K}{r_2}[M_1] - \{1 + K[M_2] + (K/r_2)[M_1]^2 - 4K[M_2]\}^{1/2}/2 \qquad (14)$$

$$\gamma = \{K[M_2] + (K/r_2)[M_1] - \beta\}/K[M_2] \quad (15)$$

To use these equations, which can be seen to give excellent fits for three different systems over a wide temperature range, it is only necessary to know the two usual reactivity ratios r_1 and r_2 and the equilibrium constant K for reaction (11). The latter has been determined for some monomers [including AMS (9) and MMA (*10*)] by measurements of equilibrium monomer concentrations, or may be estimated from heats and entropies of polymerization (*11*). The reactivity ratio r_1 may be determined experimentally in work such as this (where M_2 represents the depropagating monomer) by noting that at small values of M_2 Eq. (5) becomes

$$(m_1/m_2) - 1 = ([M_1]/[M_2])/r_1 \quad (5a)$$

The converse of this, allowing the mole fraction of M_2 to approach unity and thereby determining r_2, is not possible for the kinetic reasons illustrated in Fig. 6 and also because the composition is determined by the thermodynamic reversibility of reaction (11). Therefore the value of r_2 must be estimated by some practicable means. In this work we have used molecular orbital theory (*12*) for a first, close approximation of r_2 followed by curve fitting for a best value. In this fashion only one "adjustable" parameter is necessary to completely describe copolymerization with depropagation over the full range of monomer composition and at a variety of temperatures. The values which have been used are summarized in Table 1.

In the case of the STY-AMS and AN-AMS copolymerizations, estimation of both r_1 and r_2 by molecular orbital calculations proved quite useful, and previously determined values for K were used. However, for the STY-MMA at the elevated temperature of 250°C,

TABLE 1

Values of Reactivity Ratios and Equilibrium Constants

M_1	M_2	T, °C	r_1	r_2	K
STY	AMS	0	1.3	0.3	1.32
	AMS	60	1.3	0.3	0.095
	AMS	100	1.3	0.3	0.015
AN	AMS	75	0.04	0.2	0.061
STY	MMA	250	0.8	0.8	0.105

it was necessary to estimate that both r_1 and r_2 would have approximately the same small activation energy (the values at 60° are both approximately 0.5) and obtain a good fit to the experimental data.

It is also interesting to note that Eqs. (13) to (15) predict that at high relative concentrations of M_2, the limiting polymer composition will be given by

$$\lim_{[M_1]/[M_2] \to 0} m_2 = (2 - K[M_2])/(3 - 2K[M_2])$$

So, if m_2 is measured and extrapolated to zero $[M_1]$, the obtained value plus the concentration of M_2 will yield the equilibrium constant for M_2 homopolymerization.

A comparison of K values obtained in this way with other, existing literature values is given in Table 2.

TABLE 2

Equilibrium Constants Determined from Extrapolation of Copolymer Compositions

M_1	M_2	T, °C	m_1 (extrap.)	K	K (lit.)	Ref.
Styrene	α-Methylstyrene	60	0.18	0.097	0.110	(*9*)
		100	0.31	0.021	0.015	(*9*)
Acrylonitrile	α-Methylstyrene	75	0.23	0.074	0.061	(9)
Styrene	Methyl methacrylate	250	0.16	0.102	0.079	(*10*)

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Zusammenfassung

Radikalpolymerisationen von Styrol mit α-Methylstyrol und Methyl methacrylat und von Acrylnitril mit α-Methylstyrol wurden im Bereich der "ceiling" Temperatur des α-Methylstyrols und Methyl methacrylats durchgeführt. Eine auf theoretischer Basis durchgeführte Behandlung der Kopolymerisation unter Betonung der Reversibilität besonderer Wachstumsreaktionen wurde mit einer auf kinetischer Basis erfolgten Behandlung der Kopolymerisation verglichen wobei im letzteren Falle der Einfluss der vorletzten Einheit auf dieselbe Wachstumsreaktion besonders berücksichtigt wurde. Die erstere Behandlung beschreibt in befriedigender Weise Zusammensetzung des Kopolymeren innerhalb eines weiten Temperaturbereiches und des gesamten Bereiches des angewendeten Monomerengemisches.

Résumé

La copolymérisation radicalaire libre du styrène avec l'α-méthylstyrène et le méthacrylate de méthyle et de l'acrylonitrile avec l'α-méthylstyrène a été effectuée dans les zones de températures maxima de l'α-méthylstyrène et du méthacrylate de méthyle approximativement. Le traitement théorique de la copolymérisation mettant l'accent sur la reversibilité thermodynamique des reactions particuliéres de propagation a été comparé avec le traitement cinétique soulignant l'effet des avant-derniéres unités sur les mèmes réactions de propagation. On trouve que le premier décrit d'une maniére convenable les données experimentales de la composition du copolymère dans un large intervalle de températures et dans une gamme complète de compositions du monomère introduit.