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Copolymerization with Depropagation. II. Rate of Copolymerization of Styrene - α - Methylstyrene

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SUMMARY

Styrene and α-methylstyrene have been copolymerized at 60°C. At this temperature depropagation of the latter monomer must be considered. The rate of copolymerization and the chain length of the polymer formed are quantitatively interpreted by an extension of the theory previously used to describe the copolymer composition. It is postulated that rapid termination of copolymerization occurs because of the presence in the systems of low molecular weight free radicals of poly(α-methylstyrene) of chain length 3 or less.

INTRODUCTION

For every vinyl monomer there exists a critical temperature above which it is thermodynamically impossible to convert monomer into high polymer. This "ceiling temperature" is a function of pressure and of monomer concentration, but, for a given monomer being converted to a given polymer, the ceiling temperature is not a function of polymerization mechanism. Previous papers, in this series [1] and by Ivin and Spensley [2] and Ivin [3], have explored the experimental applicability of the theoretical models of Lowry [4] for copolymerization of two monomers, one of which was near its ceiling temperature. It was concluded [1, 2] that Lowry's case II was quite adequate for description of copolymer composition data for a variety of systems undergoing free radical or ionic polymerizations where one monomer was capable of depropagating.

Although Lowry's case II is satisfactory for interpretation of composition data in copolymerization with depropagation, it does not describe the rate of copolymerization. In the earlier work it was noted that α-methylstyrene had "an apparent retarding effect" [1] on the rate of copolymerization. In this paper we postulate an interpretation of the kinetics of the copolymerization of styrene with α-methylstyrene which quantitatively accounts for the experimentally determined rate of copolymerization.

THEORETICAL MODEL

Lowry's case II assumes that a penultimate-unit effect operates in the depropagation reaction of monomer such as α-methylstyrene (hereafter designated as M_2), so that reaction (1) exhibits reversibility while reaction (2) may be considered irreversible.

$$\sim\!\sim M_2 - M_2\,\cdot + M_2 \rightleftharpoons \sim\!\sim M_2 - M_2 - M_2\,\cdot \qquad (1)$$

$$\sim\!\sim M_1 - M_2\,\cdot + M_2 \rightarrow \sim\!\sim M_1 - M_2 - M_2\,\cdot \qquad (2)$$

The following conditions are explicitly assumed, as by Lowry [4]:

1. M_1 has a negligible tendency to depolymerize regardless of the nature of the penultimate chain unit.
2. M_2 has a negligible tendency to depolymerize only if it is attached to an M_1 unit or to a single M_2 unit.
3. M_2 has an appreciable tendency to depolymerize whenever it is attached to a sequence of two or more M_2 units.
4. The rate of addition of a particular monomer to any given free radical chain terminus, or the rate of removal of a particular monomer unit from any given free radical chain terminus, is independent of the composition of the remainder of the chain within the above specified limits.

The following additional relationships are defined ($[(m_i)_n^*]$ = concentration of chains ending with n units of M_i):

$$\beta = [(m_2)_{n+1}^*]/[(m_2)_n^*] \qquad \text{where } 1 < n < \infty$$

$$\gamma = [(m_2)_1^*]/[(m_2)_2^*]$$

From Lowry's equations (23) and (24) one obtains

$$R_p = [(m_2)_2^*]\,k_{21}[M_1]\left\{ r_1\,\frac{[M_1]}{[M_2]}\left(\gamma + \frac{1}{1-\beta}\right) + 2\gamma + \frac{3-2\beta}{(1-\beta)^2}\right\} \qquad (3)$$

Both β and γ are functions of $[M_1]$, $[M_2]$, r_2, and the equilibrium constant for reaction (1).

To utilize the rate equation (3) it is only necessary to be able to write a suitable function for $[(m_2)_2^*]$. One possible approach is to define a general termination rate constant, k_t, by the steady-state equation which assumes that the rate of initiation equals that of termination:

$$R_i = R_t = 2k_t\,([(m_1)^*] + [(m_2)^*])^2 \tag{4}$$

This gives

$$[(m_2)_2^*] = \left(\frac{R_i}{2k_t}\right)^{1/2} k_{12}[M_2]\left\{\left\{\gamma + \frac{1}{1-\beta}\right\}^{-1} k_{21}[M_1] + k_{12}[M_2]\right\}^{-1} \tag{5}$$

The rate of copolymerization relative to the rate of homopolymerization of monomer 1 under identical rates of initiation can then be written as

$$R_p^{rel} = \frac{[M_2]}{[M_1]_{bulk}\, r_1 \left(\gamma + \frac{1}{1-\beta}\right)}\left\{ r_1 \frac{[M_1]}{[M_2]}\left(\gamma + \frac{1}{1-\beta}\right) + 2\gamma + \frac{3-2\beta}{(1-\beta)^2}\right\}\left\{1 + \frac{k_{12}[M_2]}{k_{21}[M_1]}\right\}^{-1}\left(\frac{k_{t11}}{k_t}\right)^{1/2}$$

From this expression and experimental data, it is possible to calculate the apparent value of k_t as a function of the monomer feed. Using the experimental data presented in the first paper of this series, [1] the results shown in Fig. 1 were obtained. (The datum at 5% styrene was adjusted down by a factor of 4, calculated so as to account for the greatly reduced rate of initiation due to the length of polymerization time extending over many half-lives of the initiator.)

It can be seen from Fig. 1 that the extrapolated value of k_t at 100% α-methylstyrene is 10^3 greater than that of the homopolymerization termination rate constant of styrene. Since the latter is approximately 10^7, this suggests that the termination rate constant for the free radical derived from a polymerizing pure α-methylstyrene is 10^{10}. This number is about as large as rate constants can be, when one is dealing with a diffusion-controlled reaction between two small molecules in solution [5].

The implication of this is that, in pure α-methylstyrene, attempted initiation of polymerization near the ceiling temperature produces

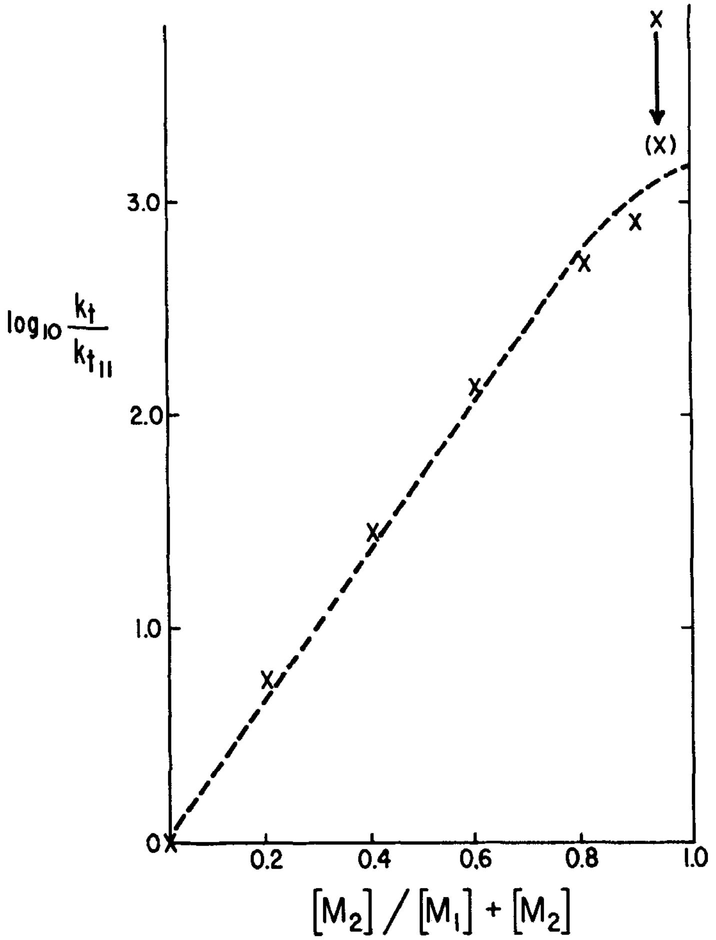

Fig. 1. Variation of apparent termination rate constant with monomer feed in the bulk copolymerization of styrene with α-methylstyrene at 60°C using 2.4×10^{-3} mole/liter of benzoyl peroxide as initiator. (Raw data from [1].)

mostly low molecular weight free radicals, perhaps dimers or trimers, which rapidly diffuse together and terminate. If a comonomer such as styrene is added, then some radical chains may grow to a higher molecular weight and produce polymer. Termination of such chains may occur by reaction either with the very low molecular weight species present or with other high molecular weight chains. It is intuitively obvious that the rate constant for the former process will be greater than for the latter. What is not so obvious, however, is the proper form for a quantitative expression of this which is also mathematically tractable. The most attractive expression from a conceptual point of view would have the termination rate constant, k_t, be a smoothly varying function of the chain lengths of the two mutually terminating radicals: k_t for two very short chains would be 10^{10}, for two very long chains, 10^7. Unfortunately, this is not very tractable at present. Therefore, a simple mathematical model will be used, wherein a step function will be applied to k_t, taking it to be 10^{10} for binary combination of two very small radicals and 10^7 for binary combination of two large radicals. The case of binary combination of a large with a small radical is considered below.

The problem then is to express quantitatively the rates of the three possible modes of termination: (1) small radicals with small radicals, (2) small radicals with large radicals, and (3) large radicals with large radicals.

Let A represent the concentration of all active long chains. Let B represent the concentration of the active short chains, designated as $[(m_2)_n^*]$, where n = 1, 2, 3.

The last statement represents an assumption which is thought to be more valid at high $[M_2]$. It becomes decreasingly valid at high $[M_1]$, since many high molecular weight chains may exist with two or three terminal M_2 units. Unfortunately the expression for $[(m_2)_n^*]$, calculable from Eq. (5), says nothing about what precedes the n terminal M_2 units.

Recognizing the limited validity of this assumption we calculate A and B from previous definitions:

$$A = [(m_2)_2^*]\left(\frac{k_{21}[M_1]}{k_{12}[M_2]}\left(\gamma + \frac{1}{1-\beta}\right) + \frac{\beta^2}{1-\beta}\right) \equiv [(m_2)_2^*]A' \qquad (7)$$

$$B = [(m_2)_2^*]\,(\gamma + 1 + \beta) \equiv [(m_2)_2^*]B' \qquad (8)$$

The termination reaction rate can now be written as

$$R_t = 2k_{t11}\,(A)^2 + 2k_{t12}(A)\,(B) + 2k_{t22}\,(B)^2 \qquad (9)$$

from which we get

$$[(m_2)_2^*] = (R_i/2k_{t11})^{1/2}\Big/\left(A'^2 + \frac{k_{t12}}{k_{t11}}\,A'B' + \frac{k_{t22}}{k_{t11}}\,B'^2\right)^{1/2} \qquad (10)$$

Substitution into Eq. (6) yields

$$R_p^{rel} = \frac{k_{21}[M_1]\left(r_1\dfrac{[M_1]}{[M_2]}\left(\gamma + \dfrac{1}{1-\beta}\right) + 2\gamma + \dfrac{3-2\beta}{(1-\beta)^2}\right)}{k_{11}[M_1]_{bulk}\left(A'^2 + \dfrac{k_{t12}}{k_{t11}}A'B' + \dfrac{k_{t22}}{k_{t11}}B'^2\right)^{1/2}} \qquad (11)$$

APPLICATION OF THE MODEL

If it is assumed that k_{t22} is properly given as 10^{10} by extrapolation of Fig. 1, and reactivity ratios and equilibrium constant are known from the composition studies, then the only experimentally unknown parameters in the last equation are the ratio k_{21}/k_{12} and k_{t12}. The former was calculated from molecular orbital theory [6] to be 3. The latter rate constant should be directly re-

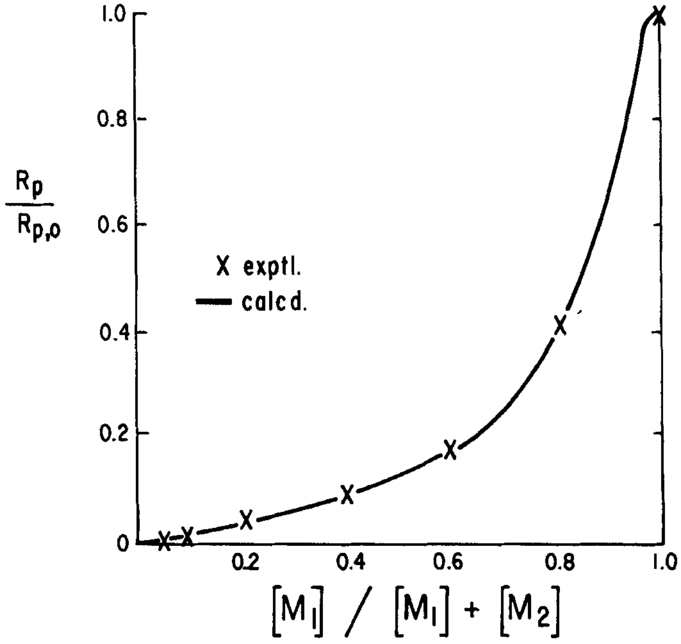

Fig. 2. Rate of copolymerization of styrene-α-methylstyrene relative to rate of homopolymerization of styrene; same conditions as Fig. 1. Solid line is calculated from Eq. (11); points are experimental data from [1].

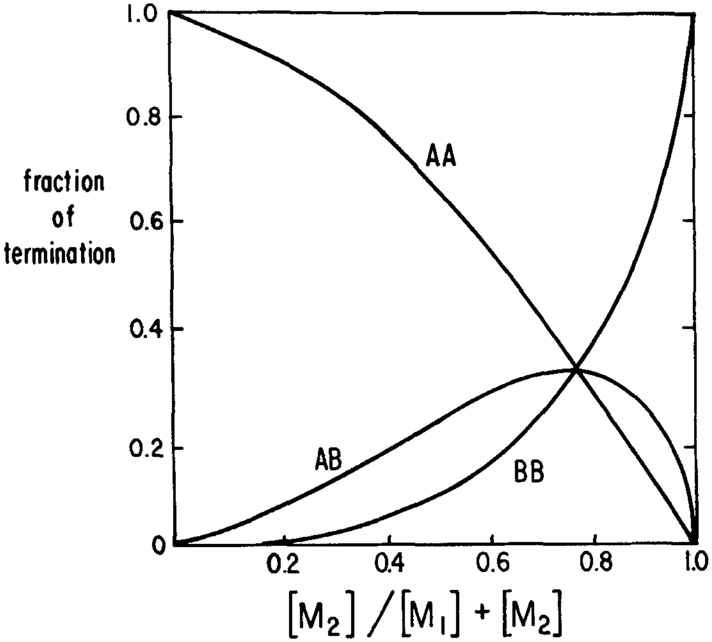

Fig. 3. Relative contribution of three postulated modes to termination of copolymerization of styrene-α-methylstyrene. Curves calculated assuming same parameters as in Fig. 2. AA represents interaction of two large radicals, BB two small radicals, and AB large with small radicals.

lated to a binary diffusion coefficient. Recent work [7] has shown that binary diffusion coefficients can be represented as the general geometric mean of the self-diffusion coefficients of the two diffusing species. In terms of the reactants here:

$$k_{t12} = k_{t11}^{A/A+B}\ k_{t22}^{B/A+B} \tag{12}$$

Equation (11) can now be used to calculate, a priori, the expected rate of copolymerization. Figure 2 shows a comparison between the calculated and experimental values. Figure 3 shows the (calculated) relative contributions of the three termination modes. Although the agreement between the observed and calculated rates is excellent, it must be recognized that no generality for this model has been established. The validity of it is, however, somewhat further substantiated by a consideration of the molecular weights of the copolymers produced. One would expect for a system such as this that the degree of polymerization might be given approximately as

$$\overline{P}_n \simeq R_p/R_t = R_p/R_i \tag{13}$$

where chain transfer has been ignored. Intrinsic viscosity is generally related to degree of polymerization by an equation of the form

$$[\eta] = K(\overline{P}_n)^a \tag{14}$$

where a has a value of approximately 0. 7. These equations can be combined to predict that, with constant R_i,

$$R_p^{copoly}/R_p^{homopoly} = ([\eta]^{copoly}/[\eta]^{homopoly})^{-1/0.7} \tag{15}$$

In Fig. 4 we show a plot of experimental data which conform to this equation. (Reduced, rather than intrinsic, viscosity was used because of small sample sizes.)

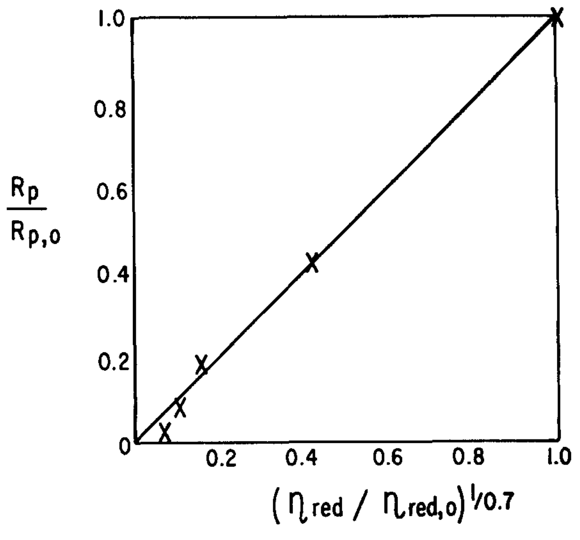

Fig. 4. Variation of reduced viscosity of copolymer of styrene-α-methylstyrene with rate of copolymerization under conditions of Fig. 1.

CONCLUSIONS

In the copolymerization of two monomers, one of which is capable of depropagating, a number of small free radicals are formed. The number of such free radicals increases with the relative concentration of the depropagating monomer and tends to dominate not only the composition of the co-polymer but also the rate of copolymerization and the molecular weight of the polymer formed. In the limit, for the model considered here, the high molecular weight copolymer formed above the ceiling temperature for M_2 will approach a composition consisting of two moles of M_2 for each mole of M_1, as the mole fraction of M_2 is increased in the feed. The copolymer will mostly consist of sequences $-M_2M_2M_1-$. Simultaneously, however, the rate of copolymerization and the average chain length of the copolymer (both high and low molecular weight) will approach zero. Since high molecular weight is assumed in this and Lowry's treatment, the model must fail as the chain length approaches zero.

The technique of copolymerization with depropagation offers a unique way to prepare copolymers of unusual composition and/or sequence distribution. Further work to characterize these systems is underway in this laboratory.

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REFERENCES

[1] K. F. O'Driscoll and F. P. Gasparro, *J. Macromol. Sci.*, **A1**, 643 (1967).
[2] K. J. Ivin and R. H. Spensley, *J. Macromol. Sci.*, **A1**, 653 (1967).
[3] K. J. Ivin, *Pure Appl. Chem.*, **4**, 271 (1962).
[4] G. G. Lowry, *J. Polymer Sci.*, **42**, 463 (1960).
[5] S. Benson, *Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960, p. 503.
[6] K. F. O'Driscoll and T. Yonezawa, *Rev. Macromol. Chem.*, **1**, 1 (1966).
[7] H. T. Cullinan, *Ind. Eng. Chem. Fundamentals*, **5**, 281 (1966).

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