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Effects of Depropagation on Free Radical Copolymerization Kinetics†

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Received November 9, 1982

ABSTRACT: Three methods for calculating the effects of depropagation on free radical polymerization processes are described and compared. For the case of one depropagating monomer, all three methods (Monte Carlo simulation, "brute force" numerical integration, and a simple analytical expression for the effects of depropagation) are practical under a wide range of polymerization conditions. In this case, the analytical method is the most accurate and efficient. In the case of two (or more) depropagating monomers, we have not yet employed an analytical method, and the "brute force" method is not as broadly applicable as in the case of one depropagating monomer. However, the Monte Carlo method provides a feasible and practical way of simulating the effects of depropagation of more than one monomer on free radical polymerization, including the effects of cross-depropagation.

Introduction

Apart from a series of publications by O'Driscoll et al.[1] and an important paper by Wittmer,[2] relatively little attention has been given to the effects of depropagation reactions on free radical copolymerization processes since the early work of Lowry.[3] Most published work in this area has been concerned with the effects of depropagation on copolymer composition and sequence distribution. In this paper, three different approaches to the computer simulation of free radical copolymerization with depropagation are described and compared for the case where one monomer can undergo depropagation. These methods are (1) application of Monte Carlo methods in conjunction with numerical integration of the free radical polymerization kinetics, (2) "brute force" integration of the polymerization kinetics equations, including all free radical species of the type $R(M_1)_n\dot{M}_1$ (where M_1 is the monomer capable of depropagation) present in significant concentration, (3) numerical integration of the free radical polymerization kinetics, including a simple analytical expression for the effects of depropagation. We confine our attention to the case where the monomer(s) capable of undergoing depropagation can depropagate only if the resulting polymer radical is terminated by a monomer capable of undergoing depropagation. For example, in the case where only monomer M_1 can depropagate, the reaction $RM_2M_1\dot{M}_1 \rightarrow RM_2\dot{M}_1 + M_1$ is included, but the reaction $RM_2\dot{M}_1 \rightarrow R\dot{M}_2 + M_1$ is not permitted. For one depropagating monomer this corresponds to Lowry's case I. However, it should be noted that the approaches discussed in this paper could easily be applied in other cases.

Under the assumptions outlined above, the case of one depropagating monomer species is particularly simple since the depropagation reaction does not change the nature of the reactive free radical end group on the polymer radical. Consequently, we will first discuss the analysis of free radical polymerization kinetics with one depropagating monomer and then go on to the more general case of two or more depropagating monomers. If two or more monomers are capable of depropagation, the "brute force" integration approach is unsatisfactory under many conditions, and we have not developed a general analytical solution for the effects of depropagation. Consequently, only the Monte Carlo approach has been implemented.

One feature of our simulations is the explicit inclusion of radical–radical recombination and disproportionation reactions. This enables us to calculate monomer consumption, polymer composition, etc. under conditions where very low molecular weight polymer is being produced.

All three of our methods for simulating the effects of depropagation on free radical polymerization rely on the use of numerical methods to integrate a differential equation for the species concentrations. For this step we use a Gear algorithm.[4] In all cases, we also used standard Monte Carlo methods[5,6] to obtain monomer sequence distributions.

The basic model used in our work is one that includes initiator and monomer feed rates and initiation, propagation, depropagation, and termination reactions. The effects of other reactions such as chain transfer, thermal initiation, reaction with impurities, etc. are not considered in this paper. The specific situation simulated in the examples used in this paper is one in which initiator and monomer are fed at constant rate into a reaction vessel. The increase in volume due to addition of monomer and initiator is not taken into account. However, it would be easy to modify our computer programs to include this effect. It should also be noted that while only one po-

† Contribution No. 3121.

0024-9297/83/2216-1661$01.50/0

lymerization process (constant monomer and initiator feed) has been explicitly simulated, the methods presented in this paper are quite general and could be applied to many situations such as a pure "batch" process, staged feed, continuous processes, etc.

Effect of One Depropagating Monomer on Free Radical Copolymerization

Since our main concern is with the effects of depropagation on free radical polymerization, a simple initiation/propagation/depropagation/termination model is used. The basic reaction scheme is given below.

Initiation. To represent the initiation reaction without unnecessary complications, we assume that initiator is fed at a constant rate into the reaction vessel and that the initiator undergoes first-order decomposition to give 2 initiator radicals ($\dot{R}$) with an efficiency E_I; i.e.

$$(d[I]/dt)_{feed} = F_I \tag{1}$$

where F_I is the initiator feed rate and

$$I \xrightarrow{k_I} 2E_I\dot{R} \tag{2}$$

where k_I is the first-order decay constant for the initiator, and E_I is the intitiator efficiency.

Propagation. The propagation reactions can be represented as

$$\dot{R} + M_i \rightarrow R\dot{M}_i \tag{3}$$

$$R\dot{M}_i + M_j \rightarrow R\dot{M}_j \tag{3a}$$

where $R\dot{M}_i$ represents any radical species in which the terminal free radical group is derived from monomer M_i, and $\dot{R}$ represents a radical species resulting from initiator decomposition. We assume that all species of the type $R\dot{M}_i$ have equal reactivity irrespective of the nature of R.

Termination. The termination reactions included in our model may be written as

$$R\dot{M}_i + R\dot{M}_j \rightarrow RM_iM_jR \tag{4}$$

$$R\dot{M}_i + R\dot{M}_j \rightarrow RM_i(S) + RM_j(U) \tag{5}$$

$$R\dot{M}_i + R\dot{M}_j \rightarrow RM_i(U) + RM_j(S) \tag{5a}$$

Equation 4 represents the effects of polymer radical–radical recombination, and eq 5 and 5a represent termination via disproportionation reactions. $RM_i(S)$ represents a product polymer molecule with a saturated end group, and $RM_i(U)$ represents a polymer with an unsaturated end group produced by disproportionation.

Using eq 1–5a, one can write a set of coupled differential equations that can be solved by standard (numerical) methods. The quantities obtained in this manner are the initiator concentration [I], the initiator radical concentration [$\dot{R}$], the concentration of polymer radicals [$R\dot{M}_i$] (i = 1, n, where n is the number of monomers), and the concentration of product polymer molecules [RM_iM_jR] (i = 1, n; j = 1, n), [$RM_i(U)$] (i = 1, n), and [$RM_i(S)$] (i = 1, n). In addition, the monomer concentrations [M_i] (i = 1, n) can also be calculated at any time during the course of the reaction. For the purpose of illustration, attention is focused on the monomer concentrations [M_i] in this paper. However, the computer programs developed in conjunction with this work calculate the concentration of all these species at any chosen time(s) during the reaction.

Depropagation. If one of the monomers (X) can undergo depropagation if (and only if) the depropagation product is a radical species in which the terminal radical group is also derived from X, eq 1–5a must be supplemented by the reactions

$$R\dot{X} + X \rightarrow RX\dot{X} \tag{6}$$

$$RX\dot{X} \rightarrow R\dot{X} + X \tag{6a}$$

$$RX\dot{X} + X \rightarrow RXX\dot{X} \tag{6b}$$

$$R(X_n)\dot{X} + X \rightarrow R(X_{n+1})\dot{X} \tag{7a}$$

$$R(X_{n+1})\dot{X} \rightarrow R(X_n)\dot{X} + X \tag{7b}$$

In these equations, R represents a group that is not terminated by monomer X. We assume that species of the type $R\dot{X}$ cannot depropagate. The addition of these reactions can add considerable complications to the simulation of free radical polymerization kinetics since the concentration of $R(X_{n+1})\dot{X}$ is needed to calculate the concentration of $R(X_n)\dot{X}$ and the concentration of $R(X_{n+2})\dot{X}$ is needed to calculate the concentration of $R(X_{n+1})\dot{X}$, etc. Three approaches to the computer modeling of free radical polymerization kinetics are described below.

Computation Methods

Method I. Monte Carlo Calculation of the Effects of Depropagation. Our Monte Carlo method for the simulation of the effects of depropagation on free radical polymerization is based on the observation that the reactions

$$R(X_n)\dot{X} + X \rightarrow R(X_{n+1})\dot{X} \tag{7a}$$

and

$$R(X_n)\dot{X} \rightarrow R(X_{n-1})\dot{X} + X \tag{7b}$$

change the concentration of monomer X but do not change the total concentration of all polymer radicals terminated in a radical group derived from monomer X. Consequently, free radical polymerization kinetics, including the effects of one depropagating monomer, can be analyzed by using eq 1–5a provided appropriate modifications are included to account for the effects of depropagation on monomer consumption. This can be accomplished by replacing equations of the type

$$R\dot{M}_i\ (M_i \neq X) + X \rightarrow R\dot{X} \tag{8}$$

by

$$R\dot{M}_i\ (M_i \neq X) + \alpha X \rightarrow R\dot{X} \tag{8a}$$

and by replacing

$$\dot{R} + X \rightarrow R\dot{X} \tag{9}$$

by

$$\dot{R} + \alpha X \rightarrow R\dot{X} \tag{9a}$$

In eq 8a and 9a, α represents the average number of X monomers added to a radical species not terminated in a radical group derived from the reversible monomer (X) before reaction with a monomer other than X or a termination reaction "caps" the $R(X_n)\dot{X}$ radical, preventing further addition or removal of X. In general, α is a complex function of the concentrations of all of the species that can react with $R\dot{X}$, the corresponding rate constants, and the rate constant for the depropagation reaction. Clearly, α changes throughout the course of the polymerization reaction. Monte Carlo methods have been used to calculate α during the course of the numerical integration of the polymerization kinetics equations. It is also necessary to eliminate the reaction

$$R\dot{X} + X \rightarrow R\dot{X} \tag{10}$$

from eq 3a. The overall effect of this reaction is to con-

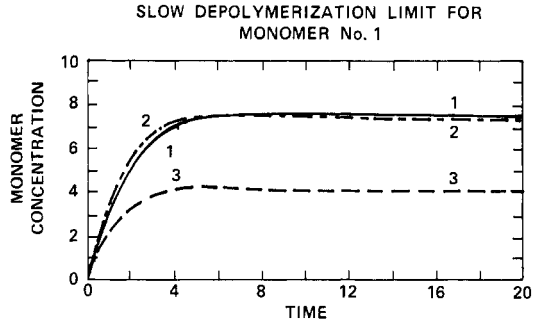

Figure 1. Some results obtained from a simulation of the copolymerization of three monomers with one depropagating monomer (monomer 1) using the Monte Carlo method described in the text. The parameters used in this simulation are given in Appendix I. In this case, the depropagation rate constant was set to "zero" (10^{-5}). Though only monomer concentrations are shown in this figure, our computer programs calculate the concentrations of all species present as well as sequence distributions and molecular weight distributions.

sume X, and the effect of this reaction on the concentration of X is included in the quantity α. α is calculated by simulating, on the computer, the propagation/depropagation/capping reactions for monomer X

$$\dot{R} + X \longrightarrow R\dot{X} \underset{P_1}{\overset{P_3}{\rightleftharpoons}} RX\dot{X} \underset{P_5}{\overset{P_3}{\rightleftharpoons}} RXX\dot{X} \underset{P_5}{\rightleftharpoons} \text{etc.} \qquad (11)$$

P_2 | P_4 | P_4

capping reaction | capping reaction | capping reaction

$$P_1 + P_2 = 1 \qquad (11a)$$

$$P_3 + P_4 + P_5 = 1 \qquad (11b)$$

The probabilities P_1 to P_5 are calculated from the appropriate concentrations and rate constants. The Monte Carlo analysis starts with the addition of X to $\dot{R}$ and selects the various branches in the reaction scheme shown in eq 11 based on the generation of a random number (r) evenly distributed over the range 0–1. For example, if the species $R(X_5)\dot{X}$ has been generated in the simulation, the next step will be removal of X to form $R(X_4)\dot{X}$ if $r \leq P_3$, capping of $R(X_5)\dot{X}$ if $P_3 < r \leq P_3 + P_4$, and addition of X to form $R(X_6)\dot{X}$ if $r > P_3 + P_4$. The processes are continued until a capping event occurs, and the total number of X molecules consumed is recorded. The whole process is repeated many times, and the number of X monomers consumed is averaged to obtain an accurate value for α.

Since the overall effect of depropagation is to change the rate of monomer consumption, the initiation/propagation/depropagation/termination reaction scheme (eq 1–7b) is replaced by the modified initiation/propagation/termination reaction scheme discussed above (eq 1–5a) modified by the substitution of eq 8a for eq 8, the substitution of eq 9a for eq 9, and the elimination of eq 10). The quantity α is recomputed frequently with the Monte Carlo procedure outlined above. α can be updated at regular intervals during the numerical interaction of the modified initiation/propagation/termination reactions or whenever the concentrations of species controlling the numerical value of α have changed significantly. An arbitrary set of monomer and initiator feed rates and reaction rate constants were used in these calculations. The values for these parameters are given in Appendix I. The calculations described in this paper were carried out without the use of specific units for concentrations, reaction rate constants, etc. The reader can insert any self-consistent set of units if desired. The only parameter that

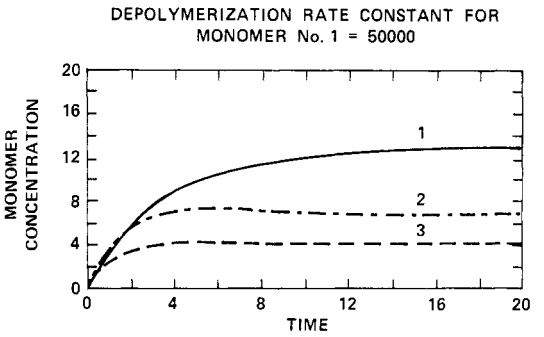

Figure 2. The parameters used to obtain this figure are the same as those used in Figure 1 except that a depropagation rate constant of 50 000 has been used for monomer 1.

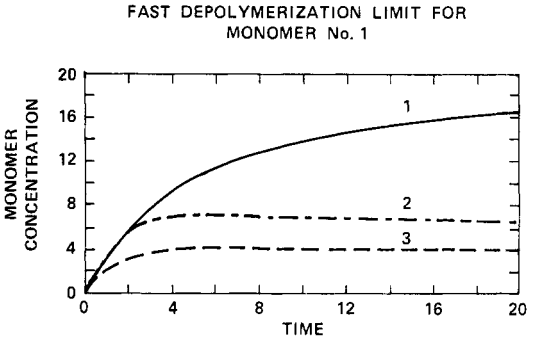

Figure 3. In this figure, the depropagation rate constant has been increased to 10^8. All the other parameters (which are the same as those used in Figures 1 and 2) are given in Appendix I.

is changed is the depropagation rate constant for X (monomer 1). In Figure 1, the depropagation rate constant is zero. The results shown in Figure 1 and those obtained without using the Monte Carlo method (i.e., numerical integration of eq 1–5a without modification) are in excellent agreement. In Figure 2, the depropagation rate constant has been increased to an intermediate value (50 000). The main effect is to increase the concentration of monomer 1. However, there are also more subtle changes in the concentrations of the other two monomers used in this simulation as a function of time. There are, of course, important changes in the monomer sequence distributions in the polymer produced. These effects are analyzed by a second Monte Carlo calculation in our programs. However, those results are not presented in this paper. In Figure 3, the depropagation rate constant was set to a very high value (10^8). In this case, the results can be checked with eq 1–5a by setting the rate of the "reaction"

$$R\dot{X} + X \rightarrow R\dot{X} \qquad (10)$$

to zero. Again the results obtained by both methods are in very good agreement. The molecular weight of the polymers obtained in these simulations are quite low. For example, the number-average degree of polymerization associated with the simulation in Figure 2 is ~74. Consequently, the contribution of termination reactions to the "capping" processes in eq 11 are quite important and must be carefully included in the Monte Carlo calculation of α.

Method II. "Brute Force" Integration of Polymerization Kinetics Including Depropagation Reactions. An alternative approach to the simulation of free radical polymerization kinetics with one depropagating monomer ($X = M_1$) is to explicitly include a sufficiently large number of species of the type $R(X_n)\dot{X}$ in the polymerization kinetics and numerically integrate the corresponding coupled differential equations using numerical methods.

Table I
Comparison of the Calculated Concentrations of Reactive Species Obtained Using Different Simulation Methods with a Depropagation Rate Constant of 0.0 at Time $t = 200$

species	simulation method				
	D	E (Monte Carlo)	F(5)	F(10)	F(15)
I	0.18182	0.18182	0.18182	0.18182	0.18182
$\dot{R}$	0.29964×10^{-5}	0.30009×10^{-5}	0.28629×10^{-5}	0.30000×10^{-5}	0.30022×10^{-5}
M_1	7.3839	7.3337	7.7325	7.3749	7.3695
M_2	7.3937	7.3995	7.7385	7.3848	7.3795
M_3	4.1119	4.1128	4.3017	4.1070	4.1040
RM_1	0.29734×10^{-3}	0.29562×10^{-3}	0.15982×10^{-3}	0.16700×10^{-3}	0.16711×10^{-3}
RM_2	0.48318×10^{-3}	0.48398×10^{-3}	0.46215×10^{-3}	0.48375×10^{-3}	0.48409×10^{-3}
RM_3	0.45404×10^{-3}	0.45469×10^{-3}	0.43495×10^{-3}	0.45455×10^{-3}	0.45486×10^{-3}
$RM_1 + \sum_n R(M_1)_n M_1$	0.19562×10^{-3}	0.29562×10^{-3}	0.28318×10^{-3}	0.29773×10^{-3}	0.29795×10^{-3}

Table II
Comparison of the Calculated Concentrations of Reactive Species Obtained Using Different Simulation Methods with a Depropagation Rate Constant of 50 000 at Time $t = 20.0$

species	simulation method		
	E (Monte Carlo)	F(5)	F(10)
I	0.18182	0.18182	0.18182
$\dot{R}$	0.25399×10^{-5}	0.25401×10^{-5}	0.25420×10^{-5}
M_1	13.078	13.098	13.093
M_2	6.8762	6.8674	6.8601
M_3	4.0518	4.0476	4.0437
RM_1	0.46388×10^{-3}	0.39094×10^{-3}	0.39152×10^{-3}
RM_2	0.40031×10^{-3}	0.40030×10^{-3}	0.40059×10^{-3}
RM_3	0.38695×10^{-3}	0.38697×10^{-3}	0.38725×10^{-3}
$RM_1 + \sum_n R(M_1)_n M_1$	0.46388×10^{-3}	0.46514×10^{-3}	0.46584×10^{-3}

In addition to propagation/depropagation reactions (eq 7a,b), radicals of the type $R(X_n)\dot{X}$ can also react with nondepropagating monomers (M_i, $i \neq 1$) and participate in termination reactions. Under these conditions, $[R(X_n)\dot{X}]/[R(X_{n-1})\dot{X}] < 1$. For sufficiently large n the concentration of $R(X_n)\dot{X}$ ($[R(X_n)\dot{X}]$) becomes negligibly small. It can also be shown (see below) that $\sum_{m=1}^{\infty}[R(X_{n+m})\dot{X}]$ is also arbitrarily small for sufficiently large n. Consequently, free radical polymerization can be simulated in the presence of one depropagating monomer by including a finite number of species of the type $R(X_n)\dot{X}$ explicitly in a set of reactions that is solved numerically. For a wide range of practical conditions, only a relatively small number (N) of species of the type $R(X_n)\dot{X}$ need to be included to obtain results of adequate accuracy.

This method has been implemented and gives results in good agreement with the Monte Carlo method described above. Table I shows some of the results obtained with the parameters given in Appendix I in conjunction with a depropagation rate constant of 0. In this case the polymerization can also be simulated by integrating the initiation/propagation/termination equation numerically. In Table I, this approach is called method "D", and the results obtained with this method can be considered to be "exact". In Tables I and II, method "E" refers to the Monte Carlo method and method "F(N)" indicates numerical integration including species of the type $R(X_n)\dot{X}$, where N is the maximum value of n.

Methods E and F(N) were developed to simulate polymerization kinetics under conditions where depropagation can occur. However, they can also be used (inefficiently) in cases where depropagation does not occur. Table I compares the results obtained with methods D, E, and F(N) (N = 5, 10, and 15) and the parameters given in Appendix I to the results discussed earlier in this paper. The results shown in Table I indicate that in this case it is sufficient to include species of the type $R(X_n)\dot{X}_n$, up to $n \simeq 10$, to obtain the concentrations of all species with an error of less than 1%.

In Table II methods E (the Monte Carlo method), F(5), and F(10) are compared for a depropagation rate constant of 50 000. Since depropagation decreases the average length of (X_n) sequences, very good results are now obtained for method F(N) with $N \gtrsim 5$. Because depropagation reduces the number of species of the type $R(X_n)\dot{X}$ needed to obtain accurate results, this method is practical as well as feasible in most cases where depropagation is important.

It might be expected "intuitively" that $[R(X_{n+1})\dot{X}]/[R(X_n)\dot{X}]$ should have the same value (C) for all n at any particular time during the polymerization process. This relationship was established numerically by using the "brute force" integration method and motivated the simple analytic expression for the quantity α (see above) needed to calculate the effects of depropagation on free radical polymerization.

Method III. "Analytic" Method. Despite the intuitive appeal and the apparent simplicity of the relationship

$$[R(X_n)\dot{X}]/[R(X_{n-1})\dot{X}] = C \qquad (12)$$

our proof for this relationship is somewhat involved and is discussed in Appendix II. In this section, we assume the result given in eq 12 and use it to derive a simple analytical expression for α.

Since the free radical species formed during the course of a polymerization reaction are much more reactive than the nonradical species, their concentrations relax much more rapidly than the monomer concentrations. Consequently, it is a very good approximation to assume that the polymer radical concentrations are in a steady state

determined by the much more slowly relaxing monomer concentrations. Using the steady-state approximation, one can show that

$$[R(X_n)\dot{X}] = \frac{A[R(X_{n-1})\dot{X}] + k_d[R(X_{n+1})\dot{X}]}{A + k_d + k_c} \quad (13)$$

For this equation, A is given by

$$A = k_p[X] \quad (14)$$

where k_p is the propagation rate constant for addition of the monomer X to a polymer radical derived from X ($R\dot{X}$ etc.). k_d is the depropagation rate constant for monomer X, and k_c is the pseudo-first-order rate constant for the rate of "capping" of radicals of the type $R(X_n)\dot{X}$ by reaction with polymer radicals and reaction with monomers that cannot depropagate.

If we assume that eq 12 is correct and substitute into eq 13, we find that

$$[R(X_n)\dot{X}] = \left[\frac{A/C + k_dC}{A + k_d + k_c}\right][R(X_n)\dot{X}] \quad (15)$$

or

$$k_dC^2 - (A + k_d + k_c)C + A = 0 \quad (16)$$

Solving eq 16 for C gives

$$C = \frac{(A + k_d + k_c) \pm [(A + k_d + k_c)^2 - 4Ak_d]^{1/2}}{2k_d} \quad (17)$$

For our system, one of the solutions has a value >1, which can be rejected on physical grounds. The other solution lies in the range $0 < C < 1$. Using this value of C, we can obtain the concentrations of species of the type $R(X_n)\dot{X}$ from the concentration of $R\dot{X}$ from the relationship

$$[R(X_n)\dot{X}] = C^n[R\dot{X}] \quad (18)$$

The average number of X monomers consumed each time monomer X reacts with a radical species in which the radical group is not derived from X is given by

$$\alpha = \frac{\sum_{n=0}^{\infty}(n + 1)[R(X_n)\dot{X}]}{\sum_{n=0}^{\infty}[R(X_n)\dot{X}]} \quad (19)$$

From eq 19, we have

$$\alpha = \frac{1 + 2C + 3C^2 + 4C^3 + ...}{1 + C + C^2 + C^3 + ...} \quad (20)$$

or

$$\alpha = 1/(1 - C) \quad (21)$$

The quantity α is the same quantity (α) that was calculated in our Monte Carlo simulations (see above). Consequently, free radical polymerization kinetics with one depropagating monomer ($X = M_1$) can be analyzed using the same set of modified initiation/propagation/termination reactions as was used in the Monte Carlo method. An expression very similar to eq 17 has been obtained by Wittmer[2] for the case of two copolymerizing monomers. Wittmer does not explicitly include the effects of termination reactions in his analysis. However, he does give analytic results for the case where both monomers can undergo depropagation as well as propagation reactions.

Figure 4 shows some results (monomer concentrations as a function of time) using the same set of parameters that were used to obtain Figure 2, except that the initiator feed rate was increased fivefold. Because of the higher initiator feed rate, the average degree of polymerization (at steady state) is now very low (~15). Figure 5 shows the results obtained when the same calculation was repeated using the Monte Carlo method. This calculation has also been carried out with the "brute force" numerical integration procedure described above. The results obtained with this method are indistinguishable from those shown in Figures 4 and 5 on the scale of these two figures. Numerical comparisons indicate that the concentrations of all species obtained from the three different methods agree to within 0.2%.

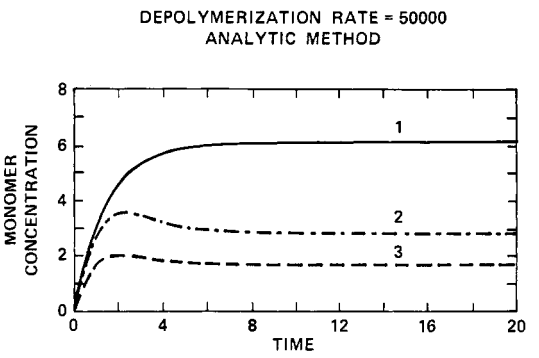

Figure 4. Calculated concentrations of the three monomers in a copolymerization reaction obtained by using the analytical method for including the effects of depropagation. The parameters are the same as those used in Figure 2 except that the initiator feed rate has been increased by a factor of 5. The average degree of polymerization (at steady state) is now only ~15.

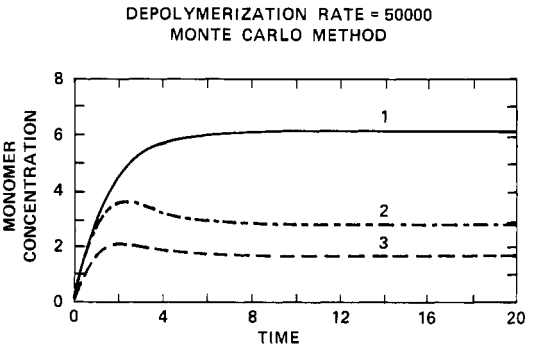

Figure 5. Results obtained when the calculation shown in Figure 4 is repeated using the Monte Carlo method. The good agreement between the results shown in Figure 4 and this figure indicates that both the Monte Carlo and analytic methods give the same value for the parameter α, which is a measure of the effects of depropagation on monomer concentration.

Free Radical Polymerization with Two (or More) Depropagating Monomers

The simulation of free radical polymerization kinetics with more than one depropagating monomer is considerably more complicated than similar calculations with one depropagating monomer. Not only do the depropagation reactions influence monomer concentrations but the depropagation reactions also change the nature of the reactive end group of the polymer radical molecules if cross-depropagation is allowed. The "brute force" numerical integration procedure becomes increasingly inefficient and, for the case of three or more depropagating monomers, almost totally impractical under a wide range of conditions. Similarly, the analytical method becomes increasingly complex, and we have not yet found a general solution for the case of two or more monomers if the effects of cross-depropagation are included. It should be possible to develop general analytic expressions based on an extension of the results of Wittmer[2] to include the effects of additional monomers, the effects of cross-depropagation on

polymer radical end group concentrations, and explicitly the effects of termination reactions. If cross-depropagation is not included, the methods discussed in the earlier sections of this paper can be applied.

Fortunately, the Monte Carlo method can be used even in cases where cross-depropagation is included at relatively little additional cost in terms of computer time. The general approach is similar to the Monte Carlo method described above. In this section, we discuss the specific case of two depropagating monomers, but no new features are introduced on going from two or more than two depropagating monomers. Our first step is to modify the normal initiation/propagation/termination kinetics equations to account for the effects of depropagation on monomer concentrations. This can be accomplished by replacing the normal propagation reactions involving the monomers capable of depropagation (monomers M_1 and M_2) by

$$\dot{S} + \alpha_{11}M_1 \rightarrow \quad (22a)$$

$$\dot{S} + \alpha_{12}M_2 \rightarrow \quad (22b)$$

$$\dot{S} + \alpha_{21}M_1 \rightarrow \quad (22c)$$

$$\dot{S} + \alpha_{22}M_2 \rightarrow \quad (22d)$$

Equations 22a–d are intended to express the effects of depropagation on monomer *consumption*. In these equations, α_{ij} is the average number of M_j monomers added to a radical $\dot{S}$ before the "growing" radical chain is capped by addition of a nondepropagating monomer or by a termination reaction if the first monomer (capable of depropagation) to add to $\dot{S}$ is M_i. $\dot{S}$ is a radical species terminated in a radical group derived from a nondepropagating radical ($R\dot{M}_i$, $i > 2$) or an initiator radical. As in the case of one depropagating monomer, the quantities α_{ij} are complex functions of the concentrations and rate constants. These quantities are calculated in a Monte Carlo simulation very similar to that used to calculate α in the one monomer case and are frequently updated during the course of the simulation (reaction).

It is also necessary to account for the fact that depropagation of one monomer (M_i) from another monomer (M_j) converts a radical of type $R\dot{M}_i$ to one of type $R\dot{M}_j$, thus changing the total concentrations of the polymer radical end groups. This effect can be accounted for by including the "reactions"

$$\dot{R} + M_1 + \beta_1(R\dot{M}_1\text{–}R\dot{M}_2) \rightarrow R\dot{M}_1 \quad (23a)$$

$$\dot{R} + M_2 + \beta_2(R\dot{M}_1\text{–}R\dot{M}_2) \rightarrow R\dot{M}_2 \quad (23b)$$

and

$$R\dot{M}_i\ (i > 2) + M_1 + \beta_1(R\dot{M}_1\text{–}R\dot{M}_2) \rightarrow R\dot{M}_1 \quad (24a)$$

$$R\dot{M}_i\ (i > 2) + M_2 + \beta_2(R\dot{M}_1\text{–}R\dot{M}_2) \rightarrow R\dot{M}_2 \quad (24b)$$

to account for the effects of "cross-depropagation" on the exchange of $R\dot{M}_1$ and $R\dot{M}_2$. The quantities β_1 and β_2 are easily obtained during the same Monte Carlo simulation that is used to calculate the quantities α_{ij}.

The overall modification to the propagation equations including the effects of depropagation on both monomer consumption and polymer radical concentration becomes

$$\dot{S} + M_1 + \alpha_{11}M_1 + \alpha_{12}M_2 \rightarrow \beta_1(R\dot{M}_2\text{–}R\dot{M}_1) + R\dot{M}_1, \text{ etc.} \quad (25)$$

The effects of all of the reactions

$$R\dot{M}_i\ (i \leq 2) + M_j\ (j \leq 2) \rightarrow R\dot{M}_j \quad (26)$$

as well as the reactions

$$R\dot{M}_i + M_j\ (j > 2) \rightarrow R\dot{M}_j \quad (27)$$

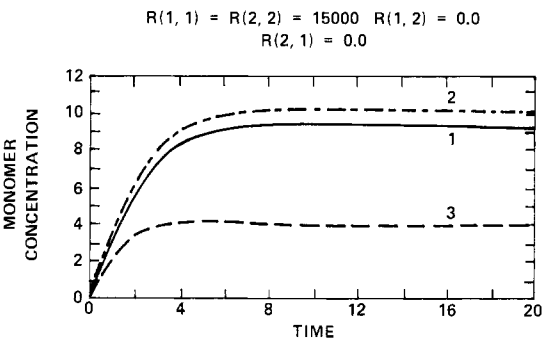

Figure 6. Simulation of free radical polymerization with two depropagating monomers without cross-depropagation. The parameters used in this calculation are given in Appendix I. The self-depropagation rate constant is 15 000 for both monomers.

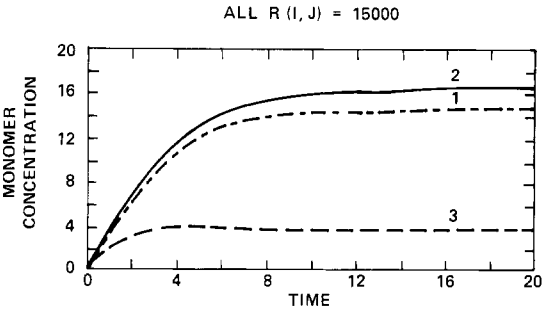

Figure 7. In this calculation, all of the parameters are the same as those used in Figure 6 except that the cross-depropagation rate constants are also set to a value of 15 000.

on the concentrations of the polymer radicals ($R\dot{M}_i$) must also be retained to account for the effects of forward propagation.

Figure 6 shows some of the results of a simulation using our standard set of parameters (Appendix I) and self-depropagation rate constants of 15 000 for both monomer 1 and monomer 2 (M_1 and M_2). There is no "cross-depropagation" in this calculation. In Figure 7, the calculation shown in Figure 6 is repeated with the inclusion of cross-depropagation of monomer 2 from monomer 1 and monomer 1 from monomer 2 (also with a rate constant of 15 000).

Discussion

Three methods have been developed to simulate free radical copolymerization kinetics, including the effects of depropagation of one of the monomers. All three methods are practical in the sense that results of reasonably good accuracy can be obtained by using relatively small amounts of computer time. The analytical method is to be preferred in that it gives the most accurate answers and also requires the least amount of computer time. However, the "brute force" integration method and (particularly) the Monte Carlo method are easier to extend to other (more complex) problems. In the case of two or more depropagating monomers, we have not yet developed an analytical expression for the effects of depropagation on monomer consumption in the general case where "cross-depropagation" is included. However, the Monte Carlo method provides an attractive way of simulating copolymerization kinetics under these conditions. Fortunately, the amount of computer time required to get results of reasonable accuracy increases only slowly with the number of depropagating monomers. By contrast, the "brute force" integration method soon becomes impractical as the number of depropagating monomers increases.

One interesting feature that can be seen in several of our calculations is a maximum in the concentrations of some

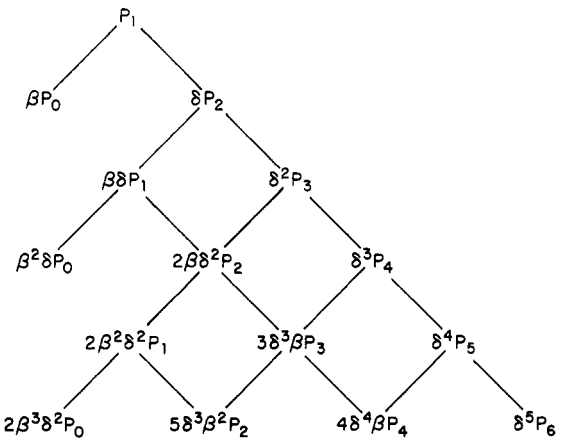

Figure 8.

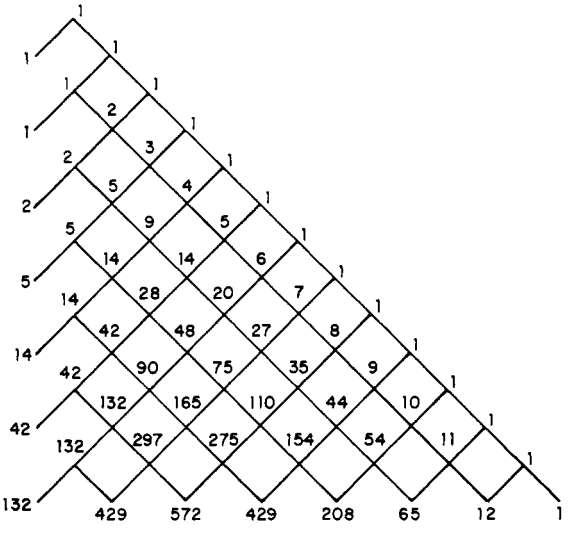

Figure 9.

of the monomers. This effect is particularly pronounced in cases where one of the monomers (M_1) is undergoing depropagation. While there can be no simple explanation for such behavior in a complex kinetic system, the following comments are tendered.

In those cases where a maximum is seen in the concentrations of monomers 2 and 3 (e.g., Figures 2 and 4), the relaxation times for these monomers are shorter than the relaxation time for monomer 1. Consequently, the concentrations of monomers 2 and 3 tend toward a steady state determined by the concentration of monomer 1. If the effect of increasing monomer 1 concentration is to decrease the steady-state concentrations of monomers 2 and 3, a peak may be observed in the concentrations of monomers 2 and 3. For the parameters used in our simulations, polymer radicals of the type $R\dot{M}_1$ are more reactive toward monomers M_2 and M_3 than polymer radicals terminated in radical groups derived from M_2 and M_3. Consequently, an increase in monomer M_1 concentration will increase the concentration of $R\dot{M}_1$, which in turn decreases the concentration of M_2 and M_3. Since depropagation of M_1 increases the M_2 concentration, the concentration of radicals terminated in M_1 is increased, and the other monomer concentrations fall as the M_1 concentration increases. As expected, the steady-state monomer concentrations are reduced on increasing the initiator feed rate, and the steady state is approached more rapidly. The overshoot in the concentrations of monomers M_2 and M_3 is also increased. We have no simple explanation for this increase. However, part of this effect may result from the fact that the initiator concentration has not reached steady state by the time the peaks in the concentrations of monomer 2 and monomer 3 are reached.

Acknowledgment. I thank an anonymous reviewer for bringing the work of Wittmer (ref 2) to my attention.

Appendix I. Kinetic Parameters for Calculations Used To Obtain Figures

Feed Rates	
initiator	0.1
monomer 1	3.5
monomer 2	4.0
monomer 3	2.5
Initiator Decomposition	
efficiency	0.8
rate constant	0.5

Rate Constants for $\dot{R} + M_i \rightarrow R\dot{M}_i$

$i = 1$	2000
$i = 2$	3000
$i = 3$	4000

Rate Constants for $R\dot{M}_i + M_j \rightarrow R\dot{M}_j$

$i = 1, j = 1$	700
$i = 1, j = 2$	600
$i = 1, j = 3$	500
$i = 2, j = 1$	350
$i = 2, j = 2$	450
$i = 2, j = 3$	550
$i = 3, j = 1$	200
$i = 3, j = 2$	300
$i = 3, j = o$	400

Rate Constants for $R\dot{M}_i + RM_iM_jR$

$i = 1, j = 1$	10 000
$i = 1, j = 2$ (and $i = 2, j = 1$)	20 000
$i = 1, j = 3$ (and $i = 3, j = 1$)	30 000
$i = 2, j = 2$	25 000
$i = 2, j = 3$ (and $i = 3, j = 2$)	25 000
$i = 3, j = 3$	30 000

Rate Constants for $R\dot{M}_i + R\dot{M}_j \rightarrow RM_i(S) + RM_j(U)$

$i = 1, j = 1$	60 000
$i = 1, j = 2$	20 000
$i = 1, j = 3$	30 000
$i = 2, j = 1$	10 000
$i = 2, j = 2$	20 000
$i = 2, j = 3$	30 000
$i = 3, j = 1$	40 000
$i = 3, j = 2$	50 000
$i = 3, j = 3$	60 000

Appendix II

In this appendix a simple analytic expression for the effects of depropagation of one monomer on free radical copolymerization kinetics is derived.

Using the steady-state approximation for short-lived radical species, one can show that

$$[R(X_n)\dot{X}] = \frac{A[R(X_{n-1})\dot{X}] + k_d[R(X_{n+1})\dot{X}]}{A + k_d + k_c} \quad \text{(A1)}$$

where X is the depropagating monomer. To obtain a simple analytic solution for the effects of depropagation, we need to establish a relationship between $[R(X_{n+1})\dot{X}]$ and $[R(X_n)\dot{X}]$ alone. Here, we show that

$$[R(X_{n+1})\dot{X}] = C[R(X_n)\dot{X}] \quad \text{(A2)}$$

where C is a constant independent of n. The value of C is, of course, dependent on the concentrations and rate

constants used in the kinetics model and varies with time.

Equation A1 can be rewritten as

$$P_n = \beta P_{n-1} + \delta P_{n+1} \tag{A3}$$

where $P_n = [R(X_n)\dot{X}]$, $\beta = A/(A + k_d + k_c)$, and $\delta = B/(A + k_d + k_c)$. The starting point for our analysis is to use eq A3 to develop an expression for P_1. From eq A3 we have

$$P_1 = \beta P_0 + \delta P_2 \tag{A4}$$

A further application of A3 gives

$$P_1 = \beta P_0 + \beta\delta P_1 + \delta^2 P_3 \tag{A5}$$

and an additional application gives

$$P_1 = (\beta + \delta\beta^2)P_0 + 2\delta^2\beta P_2 + \delta^3 P_4 \tag{A6}$$

The results of further applications of eq A3 are shown in Figures 8 and 9. In applying eq A3 repeatedly, we collect terms in P_0 and expand terms in P_n ($n \neq 0$) to generate additional terms in P_0. If eq A3 is applied an infinite number of times, we can express the result as

$$P_1 = KP_0 + \text{other terms} \tag{A7}$$

Our task is complete if we can show that K is finite and the "other terms" are zero.

From Figures 8 and 9 it can be seen that K is given by

$$K = \beta[1 + \beta\delta + 2(\beta\delta)^2 + 5(\beta\delta)^3 + 14(\beta\delta)^4 + \ldots K_n(\beta\delta)^n + \ldots] \tag{A8}$$

Figures 8 and 9 also illustrate that K_n is equal to the number of ways of reaching an absorbing wall at position $X = -1$ in $2n + 2$ steps of $X = \pm 1$ starting at position 0. The solution to this problem is known[8] and the result is

$$K_n = \frac{(2n)!}{n!n!} - \frac{(2n)!}{(n+1)!(n-1)!} \tag{A9}$$

$$= \frac{1}{n+1}\frac{(2n)!}{n!n!} \tag{A10}$$

Using this result, we find

$$\frac{K_{n+1}}{K_n} = \frac{(n+1)n!n![2(n+1)]!}{(n+2)(n+1)!(n+1)!(2n)!} = \frac{(n+1)(2n+1)(2n+2)}{(n+2)(n+1)(n+2)} = \frac{2(2n+1)}{(n+2)} \tag{A11}$$

In the limit $n \to \infty$

$$K_{n+1}/K_n = 4 \tag{A12}$$

Consequently, the series expansion for K (eq A8) is absolutely convergent (K is finite) if

$$4\beta\delta < 1 \tag{A13}$$

or

$$4Ak_d < (A + k_d + k_c)^2 \tag{A13a}$$

It should be noted, at this stage, that this is precisely the condition that must be satisfied for C ($C = [R(X_{n+1})\dot{X}]/[R(X_n)\dot{X}]$) to have a real value if C is *assumed* to be a constant independent of n (see earlier section of this paper). It should also be noted that if we *assume* that $[R(X_{n+1})\dot{X}]/[R(X_n)\dot{X}]$ is equal to a constant (C) for all n, then from eq A1 we find (vide supra)

$$C = \frac{1 - (1 - 4\beta\delta)^{1/2}}{2\delta} \tag{A14}$$

Expanding $(1 - 4\beta\delta)^{1/2}$, we find

$$C = [1 - (1 - 2(\beta\delta)^2 - (4\beta\delta)^3 - 10(\beta\delta)^4 - 28(\beta\delta)^5 - 84(\beta\delta)^6 \ldots)]/2\delta \tag{A15}$$

or

$$C = \beta[1 + \beta\delta + 2(\beta\delta)^2 + 5(\beta\delta)^3 + 14(\beta\delta)^4 + 42(\beta\delta)^5 + \ldots C_n(\beta\delta)^n + \ldots] \tag{A16}$$

A comparison of eq A8 and A16 shows that C and K have exactly the same values.

We must now show that the "other terms" in eq A7 are zero.

These "other terms" can be written down in terms of the quantity Q_n given by

$$Q_n = \sum_{m=1}^{n} l_{mn}(\delta)^{n-1+m}(\beta)^{n-m}P_{2m} \tag{A17}$$

In eq A17 the coefficients l_{mn} are the number of ways of reaching position $2m - 1$ starting at position 0 in $2n - 1$ moves of ± 1 with an absorbing wall at -1. The "other terms" in eq A7 are given by $\lim_{n\to\infty} Q_n$. We can again use the results given by Chandrasekhar[8] to evaluate these coefficients. The results given by Chandrasekhar[8] are

$$l_{mn} = \frac{(2n-1)!}{(m+n-1)!(n-m)!} - \frac{(2n-1)!}{(m+n)!(n-m+1)!} \tag{A18}$$

$$= \frac{(2n-1)!}{(m+n-1)!(n-m)!}\left(\frac{2m}{m+n}\right) \tag{A18a}$$

$$= \frac{2m}{m+n}\binom{2n-1}{n-m} \tag{A18b}$$

Equation A17 can be written as

$$Q_n = \sum_{m=1}^{n} l_{mn}(\beta\delta)^n(\delta/\beta)^m\delta^{-1}P_{2m} \tag{A19}$$

and since $(\beta\delta) < {}^1/_4$

$$Q_n < \sum_{m=1}^{n} l_{mn}(2)^{-2n}(\delta/\beta)^m\delta^{-1}P_{2m} \tag{A20}$$

Equation A3 can be written as

$$\beta P_{n-1} = P_n - \delta P_{n+1} \tag{A21}$$

and since $P_{n+1} \geq 0$

$$\beta P_{n-1} \leq P_n \tag{A22}$$

or

$$P_{n-1} \leq P_n/\beta \tag{A22a}$$

substituting eq A22a in (A20) gives

$$Q_n < \sum_{m=1}^{n} l_{mn}(2)^{-2n}(\beta\delta)^m\delta^{-1}P_0 \tag{A23}$$

Since $\sum_{m=1}^{\infty}(\beta\delta)^m\delta^{-1}P_0$ is finite ($\sum_{m=1}^{\infty}(\beta\delta)^m\delta^{-1}P_0 = \beta P_0\sum_{m=0}^{\infty}(\beta\delta)^m = \beta P_0/(1 - \beta\delta) < 4\beta P_0/3$), Q_n is zero in the limit $n \to \infty$ if $\lim_{n\to\infty}((2)^{-2n}l_{mn})$ is zero.[9] Since $l_{mn}(2)^{-2n+1}$ is the probability of a particle reaching position m after $2n - 1$ steps of ± 1 with an absorbing wall at position -1,

$(2)^{-2n}l_{mn} \to 0$ as $n \to \infty$ for all m. Consequently, Q_n is zero and we have, finally

$$P_1 = KP_0 = \frac{1 - (1 - 4\beta\delta)^{1/2}}{2\delta}P_0 \qquad \text{(A24)}$$

We can now use eq A3 to express P_2 in terms of P_1

$$P_2 = \beta P_1 + \delta P_3 \qquad \text{(A4')}$$

$$= \beta P_1 + \beta\delta P_2 + \delta^2 P_4 \qquad \text{(A5')}$$

$$= (\beta + \delta\beta^2)P_1 + 2\delta^2\beta P_3 + \delta^3 P_5 \qquad \text{(A6')}$$

etc.

Following the procedure outlined above, we find

$$P_2 = KP_1 = \frac{1 - (1 - 4\beta\delta)^{1/2}}{2\delta}P_1$$

Repeating the whole process for P_3, we find $P_3 = KP_2 = K^2P_1 = K^3P_0$, and, in general, $P_n = K^nP_0$, which is the desired result.

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$$l_{mn} = \frac{(2n-1)!}{(m+n-1)!(n-m)!}\left(\frac{2m}{m+n}\right) = \frac{2n!}{(m+n)!(n-m)!}\left(\frac{m}{n}\right)$$

or

$$l_{mn} = \frac{m}{n}\binom{2n}{n-m}$$

From this result we find that

$$\frac{l_{(m+1)n}}{l_{mn}} = \frac{(n-m)(m+1)}{m(m+n+1)}$$

and the maximum value for l_{mn} occurs at $m \approx (n/2)^{1/2}$ for large n. Since the maximum value of $\binom{2n}{n-m}$ is found at $m = 0$ and the maximum value of $(m/n)\binom{2n}{n-m}$ is found at $m \approx (n/2)^{1/2}$

$$l_{mn} \lesssim \binom{2n}{n}\left(\frac{1}{2n}\right)^{1/2}$$

and

$$(2)^{-2n}l_{mn} \lesssim (2)^{-2n}\binom{2n}{n}\left(\frac{1}{2n}\right)^{1/2}$$

using this result together with the fact that $\binom{2n}{n} < (2)^{2n}$, we find that $(2)^{-2n}l_{mn} \lesssim (1/2n)^{1/2}$ or $\lim_{n\to\infty}((2)^{-2n}l_{mn}) = 0$.

^{13}C NMR Studies of Solid Phenolic Resins Using Cross Polarization and Magic-Angle Spinning

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Received February 2, 1983

ABSTRACT: ^{13}C NMR data are presented for the cross polarization/magic-angle spinning experiment applied to phenol/formaldehyde resins of the Novolak type. Spectra were obtained at three magnetic field strengths, 1.41, 2.35, and 4.70 T. Although sensitivity is better at higher fields, there is no real gain in resolution at higher field. Spectral deconvolutions were carried out and tentative peak assignments made. The results confirm the view that the curing process involves cross-linking in each of the resins studied.

Introduction

The chemical shift in a ^{13}C NMR experiment is a powerful tool for structural elucidation in macromolecules such as polymers and resins. Due to the limited solubility of many of these materials, especially cured resins, the use of solid-state ^{13}C NMR with cross polarization (CP) and magic-angle spinning (MAS) is very valuable.[1-3] This approach renders the question of solubility irrelevant and eliminates structural uncertainties associated with dissolution. The ^{13}C CP/MAS approach has been applied to several synthetic polymer systems but only sparingly to resins.[4-7] It is the application of this technique to two phenol/formaldehyde resins of the Novolak type on which this paper is based.

Phenol/formaldehyde resins have important commerical applications.[8] Details of the curing process are responsible for many of the important physical and mechanical characteristics of these materials. Thus, the development of tools that can provide structural information relevant to the curing process is important for understanding and improving the synthetic process.

Extensive ^{13}C NMR studies on phenol/formaldehyde resins have been carried out in the liquid state,[9-12] but

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0024-9297/83/2216-1669$01.50/0