

Analysis of the Curing Behavior of Unsaturated Polyester Resins Using the Approach of Free Radical Polymerization

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Synopsis

The approach of free radical polymerization is adapted to develop a kinetic model for predicting the curing behavior of unsaturated polyester resins. The approach taken here is essentially similar to that advanced by Stevenson with some modifications, namely (1) the efficiency of the initiator is assumed to decrease with conversion, (2) no assumption was made a priori on the magnitude of the rate constants for the termination and inhibition reactions, and (3) the propagation rate constant was assumed to be represented by $k_p = A_o \exp(-E_p/RT) \cdot [1 - (\alpha/\alpha_f)]^m$, and the termination rate constant by $k_t = B_o \exp(-E_t/RT) [1 - (\alpha/\alpha_f)]^n$, in which A_o and B_o are preexponential constants, E_p and E_t are the activation energies for the propagation and termination reactions, respectively, R is the universal gas constant, T is the absolute temperature, α is the degree of conversion, α_f is the final degree of conversion, and m and n are constants to be determined by numerical simulation. A computer program was developed to search for the optimal values of all the parameters involved, to minimize the difference between the predicted and experimentally determined rate of conversion and the degree of conversion simultaneously. An experimental study was also conducted on the cure of unsaturated polyester resin, using differential scanning calorimetry (DSC) under isothermal conditions and infrared (IR) spectroscopy. The degree of cure was determined from the total heat generated during cure, with the aid of the IR spectra of the residual double bonds in the cured resin. The predictability of the mechanistic model developed is presented and the usefulness of the model for simulating various processing operations is discussed.

INTRODUCTION

Unsaturated polyester resins are very versatile in their applications. They are used in the fabrication of a broad range of products, including structural parts of automobiles, building materials, coating materials, electrical parts, appliances, boat hulls, and so on. Consequently, there are a variety of resin formulations, depending on specific applications as well as fabrication processes. Unsaturated polyester resins and their composites may be processed using, for instance, spray-up, decorative coating, compression molding, transfer molding, injection molding, pultrusion, reaction injection molding, among other methods. More recently, the industry has developed ultraviolet-curable resins, and interpenetrating network-type resins.

In general, unsaturated polyester resins are prepared by condensation reactions of saturated and unsaturated dicarboxylic acids with glycols and dilution with unsaturated monomers. Variation in the type and amount of individual components allow an enormous flexibility in the design of resin formulations. For example, it is generally known that isophthalic acid gives

resins having improved water and chemical resistance and higher heat distortion temperatures.

Since unsaturated polyester resins, and thermoset resins in general, contain reactive groups, their processing requires an understanding of the reaction kinetics of polymerization during cure, in addition to an understanding of their flow properties. Reactions of thermoset resins are exothermic, in general, and therefore the control of temperature during cure is of great importance in controlling the quality of the products.

An investigation dealing with complex systems, such as the curing reactions and processing of thermoset resins, requires a greater attention to fundamentals. Above all, a better understanding and control of curing reactions of thermoset resins is essential for controlling the industrial operations of thermoset processes, such as compression molding, pultrusion, and reaction injection molding.

It has been known for some time that the curing reaction of an unsaturated polyester resin requires chemical initiators that generate free radicals. Thus the kinetics of its curing reaction can be investigated, using the approach of free radical polymerization. Horie et al.¹ have investigated the curing reactions of polyester fumarate with styrene in the presence of benzoyl peroxide as initiator, using differential scanning calorimetry (DSC). They made a series of isothermal DSC runs and investigated the rate of cure as a function of the degree of cure (or conversion) at various temperatures. They pointed out that, in a manner similar to the free radical polymerizations of methyl methacrylate and styrene, the termination reaction between polymeric radicals and the propagation reaction of a fumarate unit in a polyester chain to a growing polymeric radical are controlled by the diffusion of polymeric segments. They also observed the somewhat unexpected result that, when the ratio of fumaric acid to diethylene glycol in a polyester prepolymer was increased, the final degree of conversion went through a maximum as the isothermal cure temperature was increased from 60 to 100°C. They attributed this to an increase in the crosslinking density of the cured resins having high fumaric acid/diethylene glycol ratios, at equal conversion, as the isothermal curing temperature is increased.

In recent years, several research groups²⁻⁷ have suggested methods of incorporating the effect of diffusion control into the expressions for the rate constants of termination and propagation in free radical polymerization. Reasonable success has been obtained with the aid of the free volume theory, in predicting experimentally observed results of conversion versus reaction time curves, in the free radical polymerizations of methyl methacrylate and styrene. The approach basically is to modify the rate expressions of termination and propagation, by introducing molecular parameters of the monomer and of the growing macromolecules, for example, free volume and glass transition temperature. In such an approach, however, some parameters in the rate expressions must be determined by fitting predicted conversion versus reaction time curves to experimentally obtained values, with the aid of an optimization scheme. The ultimate objective of such an approach is to obtain reasonably accurate and yet realistic kinetic expressions, which can be used to predict the performance of polymerization reactor operations, without having to determine rate constants. This would be desirable, for instance, when one

wishes to change the type, concentration or number of initiators for a particular free radical polymerization process under consideration.

It should be pointed out that the curing reaction of unsaturated polyester resin involves the formation of three-dimensional networks, whereas the polymerization of methyl methacrylate or styrene, for instance, gives rise to linear (uncrosslinked) macromolecules. This perhaps had prevented researchers, until very recently, from attempting to model the curing reaction of unsaturated polyester resin from the viewpoint of free radical polymerization. For instance, Kamal and co-workers^{8,9} have taken a semiempirical approach to express the curing kinetics of unsaturated polyester resin and have suggested an expression of the following form:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

where α is the degree of cure, k_1 and k_2 are rate constants, which depend on temperature following the Arrhenius relationship, and m and n are constants (the sum of m and n is the reaction order and $m + n = 2$ is assumed). Other investigators^{10,11} have found that Eq. (1) was in agreement with their experimental results.

However, very recently, Stevenson^{12,13} and Chern and Sundberg^{14,15} have attempted to model the curing behavior of unsaturated polyester resin, using the concept of free radical polymerization. Having realized the complexity of the curing reactions of unsaturated polyester resin, which, as a matter of fact, involves copolymerization, Stevenson considered several special cases, each based on different assumptions in order to simplify the rate expressions. He then compared theoretical predictions with experimental results.

There are a number of significant advantages to mechanistic kinetic models over empirical ones, in simulating various processing operations of an unsaturated polyester resin or its fiber-reinforced composites. For instance, mechanistic models will enable one to treat separately the effect of the type, concentration or number of initiators on the overall curing rate, once the values of various rate constants (e.g., propagation and termination steps) are determined. In other words, one does not need to conduct curing experiments each time the type, concentration, or number of initiators is changed. On the other hand, in the use of empirical models, for instance Eq. (1), one must determine the values of the rate constants k_1 and k_2 each time the type, concentration, or number of initiators is varied.

The purpose of this paper is to present our recent development of a mechanistic kinetic model for curing reactions of unsaturated polyester resin, using the concept of free radical polymerization coupled with the mechanism of diffusion-controlled reactions. We also present the results of an experimental study on the cure of a general-purpose unsaturated polyester resin.

THEORETICAL DEVELOPMENT

The curing reaction of unsaturated polyester resin involves the copolymerization of unsaturated polyester and styrene in the presence of an organic initiator. Like any other free radical polymerization (e.g., bulk polymerization of methyl methacrylate), the organic initiator first decomposes to form a free

radical initiator $[I.]$, which will then react with unsaturated polyester to form a polyester radical $[E.]$ and with styrene monomer to form a styrene radical $[S.]$. These radicals then react with unsaturated polyester and styrene monomer, respectively, to form radicals of larger size via the so-called propagation step. During the curing reaction, some radicals may be terminated via the so-called coupling termination step to form a covalent bond with loss of radical activity.

A rigorous treatment of all the propagation and termination reactions involved with different reactive species is a very difficult task. On the basis of some experimental evidence reported by Horie et al.¹ and the earlier study by Stevenson^{12,13}, we will make the following assumptions for the development of system equations: (1) any carbon double bond in the polyester resin or styrene monomer has the same rate constant for reaction with an initiator radical $[I.]$; (2) the rate of initiation can be lumped with the rate of conversion to give a rate expression of the total radical concentration $[R.]$; (3) the propagation reactions can be expressed by a single average rate constant; (4) all termination reactions can be combined in a single effective termination constant. Under these assumptions the following rate expressions may be written: For inhibitor;

$$d[Z]/dt = -k_z[Z][R.] \quad (2)$$

For initiator;

$$d[I_j]/dt = -k_{dj}[I_j]; \quad j = 1, 2, \dots, N \quad (3)$$

For monomer;

$$d[M]/dt = -k_p[M][R.] \quad (4)$$

For radicals;

$$d[R.]/dt = 2 \sum_{j=1}^N f_j k_{dj} [I_j] + k_z [Z][R.] - k_t [R.]^2 \quad (5)$$

in which $[Z]$ is the inhibitor concentration, $[I_j]$ is the concentration of the j -th initiator, $[M]$ refers to the total monomer concentration that is assumed to be the sum of the concentrations of the polyester resin $[E]$ and styrene $[M]$, $[R.]$ refers to the radical concentration that is assumed to be the sum of the concentrations of polyester radical $[E.]$, styrene radical $[S.]$, and the initiator radical $[I.]$ (i.e., $[R.] = [E.] + [S.] + [I.]$), k_z is the rate constant of the inhibition reaction, k_{dj} is the rate constant of the decomposition reaction of the j -th initiator, k_p is the rate constant of the propagation reaction, k_t is the rate constant of the termination reaction, and f_j is the efficiency of the j -th initiator.

In reference to Eqs. (2)–(5), the following observations can be made: (1) a number of initiators may participate in the free radical polymerization, and they are represented by $[I_j]$, $j = 1, 2, \dots, N$, and (2) no steady-state assumption is made for the rate of generation of free radicals. Equations (2)–(5) may

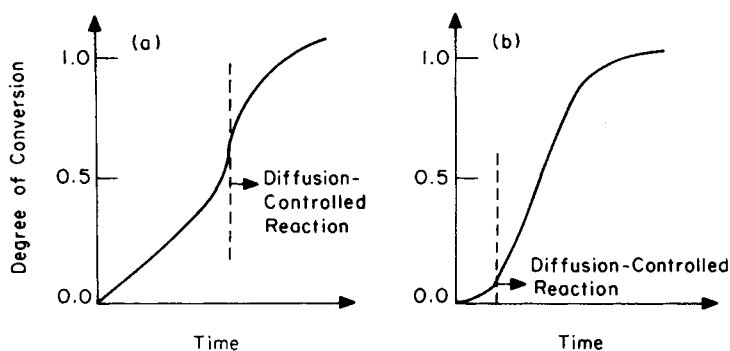


Fig. 1. Schematic of typical conversion profiles of polymerization: (a) bulk polymerization of methyl methacrylate; (b) curing reaction of unsaturated polyester resin.

be solved numerically for $[Z]$, $[I_j]$, $[M]$, and $[R.]$, with the given initial conditions, i.e., $[Z(0)] = [Z]_o$, $[I_j(0)] = [I_j]_o$, $[M(0)] = [M]_o$, and $[R.(0)] = 0$. However, before Eqs. (2)–(5) are solved, one must specify values of the three rate constants k_z , k_p , k_t , and the initiator efficiency f_j ($j = 1, 2, \dots, N$).

According to Horie et al.,¹ the crosslinking reaction of unsaturated polyester resin with styrene causes gelling to begin at a very early stage (i.e., at very low levels of conversion), say 3–5%. This implies that this reaction is diffusion controlled over almost the entire range of conversion. This is not the case, for instance, with the bulk polymerization of methyl methacrylate. This difference is demonstrated by the conversion versus time curves (shown in Figure 1) for the curing reaction of unsaturated polyester resin and the bulk polymerization reaction of methyl methacrylate. This suggests to us that the rate constants, k_p and k_t , must be represented in such a way that the reaction is identified as diffusion controlled. It would be most desirable for the free volume parameters to be introduced into the representation of the rate constants k_p and k_t , as suggested by Chern and Sundberg.^{14,15} However, there are practical difficulties with estimating free volume parameters for the curing reaction of unsaturated polyester resin.

We therefore have used the following empirical expressions

$$k_p = k_{p_o} \left(\frac{[M] - [M]_\infty}{[M]_o - [M]_\infty} \right)^m \quad (6)$$

and

$$k_t = k_{t_o} \left(\frac{[M] - [M]_\infty}{[M]_o - [M]_\infty} \right)^n \quad (7)$$

in which $[M]_o$ is the initial concentration of monomer, $[M]_\infty$ is the monomer concentration after the cure, and k_{p_o} and k_{t_o} are assumed to follow the Arrhenius relationship

$$k_{p_o} = A_o \exp(-E_p/RT) \quad (8)$$

$$k_{t_o} = B_o \exp(-E_t/RT) \quad (9)$$

where A_o and B_o are preexponential factors, E_p is the activation energy of the propagation reaction, E_t is the activation energy of the termination reaction, R is the universal gas constant, and T is the absolute temperature.

It should be mentioned that, in his study, Stevenson¹³ assumed that the termination rate constant k_t is independent of conversion, that is, $k_t = k_{t0}$, and used Eq. (6), reporting that a constant value of $m = 0.25$ appeared to fit his experimentally determined conversion curves reasonably well.

In solving Eqs. (2)–(5) with the aid of Eqs. (6) and (7), one must also specify the value of the initiator efficiency f_j ($j = 1, 2, \dots, N$). This is a very elusive quantity and very little is mentioned in the literature about it. Other investigators^{12–15} have assumed a constant value for f_j . However, we believe that the value of f_j decreases with the degree of conversion, because it would depend on the following two factors: (1) the reactivity of the initiator radicals generated, namely, the *initial* value of the initiator efficiency that is characteristic of the chemical structure of an initiator, and (2) the location of the initiator radicals generated, the so-called *caging effect* that depends on the amount of the initiator radicals that are entrapped in the system during the curing reaction. Note that the entrapped initiator radicals are not likely to be available for participation in the curing reaction and that the *caging effect* may be significant in the curing reaction of unsaturated polyester resin, because it forms a three-dimensional network structure.

In the present investigation, we have used the following expression:¹⁶

$$f_j = \frac{f_{jo}^2 \left(\frac{[M] - [M]_\infty}{[M]_o - [M]_\infty} \right)^2}{2(1 - f_{jo}) \left(\frac{[I_j] - [I_j]_\infty}{[I_j]_o - [I_j]_\infty} \right)} \left\{ \left[1 + \frac{4(1 - f_{jo}) \left(\frac{[I_j] - [I_j]_\infty}{[I_j]_o - [I_j]_\infty} \right)^{1/2}}{f_{jo}^2 \left(\frac{[M] - [M]_\infty}{[M]_o - [M]_\infty} \right)^2} \right] - 1 \right\} \quad (10)$$

where f_{jo} ($j = 1, 2, \dots, N$) is the initial value of the j -th initiator efficiency and $[I_j]_o$ is the initial concentration of the j -th initiator. Note that Eq. (10) indicates that the initiator efficiency *decreases* with the degree of conversion, which seems reasonable.

We solved Eqs. (2)–(5) with the aid of Eqs. (6), (7), and (10) to simulate the isothermal cure of unsaturated polyester resin. As part of the solution of the system equations, we first determined the parameters involved for a single initiator, namely, $j = 1$. These parameters, namely k_z , k_{p0} , k_{t0} , m , n , and f_{1o} , were determined by numerically solving Eqs. (2)–(5) together with Eqs. (6), (7), and (10), until the predicted values of the conversion (α) versus time (t) curve and the rate of conversion ($d\alpha/dt$) versus time (t) curve agreed with the experimentally determined values, within a prescribed tolerance.

EXPERIMENTAL

Materials

A commercially available general-purpose unsaturated polyester resin was used for the study. The resin contained a proprietary inhibitor. This resin was supplied to us by Owens-Corning Fiberglas Corporation. We have investigated the chemical structure of the resin using nuclear magnetic resonance (NMR)

spectroscopy and chemical methods. We have found that the resin consists of propylene glycol and fumarates, and contains 35 wt% of styrene as diluent. It is our understanding that this resin is for use in compression molding. In curing the resin we used *tert*-butyl perbenzoate (TBPB) (Pennwalt Chemical Corp.) as initiator. The formulation used for curing was resin/initiator = 100/1 (parts by weight).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to monitor the amount of heat generated during the curing reaction. For this, we used a DuPont 1090 Thermal Analyzer equipped with a 910 DSC Module, available in our laboratory. In all our experiments, we used 1 part of initiator to 100 parts of resin. In conducting DSC runs, the amount of heat evolved by the curing reaction was measured by first completing the reaction isothermally, at various temperatures. After completion of the isothermal curing reaction at a predetermined temperature, the sample was heated to 200°C at the rate of 10°C/min and the amount of heat released, termed "residual heat," was recorded. Thus, the total amount of heat (Q_{TOT}) generated by the curing reaction was determined from the sum of the heat generated during the isothermal cure (Q_T) and the residual heat (Q_R), i.e.,

$$Q_{TOT} = Q_T + Q_R \quad (11)$$

Infrared Spectroscopy

Infrared (IR) spectroscopy was used to determine the amount of ethylenic double bonds in the resin system (i.e., in both fumarate and styrene) before cure begins, and the amount of residual ethylenic double bonds after the sample is postcured (i.e., after the completion of isothermal cure followed by the heating of the sample to 200°C). This information, together with the information on the heat generated [see Eq. (11)], was used to determine the rate of cure and the degree of cure during the entire period of the isothermal cure, using the procedure described below.

RESULTS

Figure 2 gives typical plots of the rate of heat generated (dQ/dt) versus cure time under isothermal DSC conditions for the resin. By integrating the dQ/dt -cure time curve in Figure 2, we obtain the heat generated (Q_T) during the isothermal cure. Figure 3 gives plots describing the variation of Q_T and of the residual heat (Q_R) with the temperature that was used in the isothermal DSC runs. It is seen in Figure 3 that the sum of Q_T and Q_R may be considered to be constant, as reported earlier by Han and Lem.¹¹ In their investigation, Han and Lem used the average of several values of Q_{TOT} , defined by Eq. (11), to calculate the degree of cure (α), using the following expression

$$\alpha = Q_i(T)/Q_{TOT} \quad (12)$$

where $Q_i(T)$ is the heat generated at a particular time t at an isothermal curing temperature T . Note that Eq. (12) is based on the assumption that the

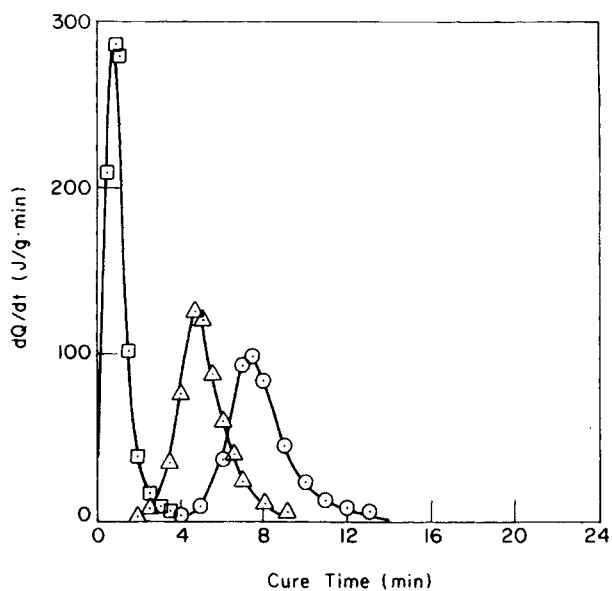


Fig. 2. dQ/dt versus cure time for the resin investigated at different isothermal cure temperatures ($^{\circ}\text{C}$): (○) 110; (△) 120; (□) 130.

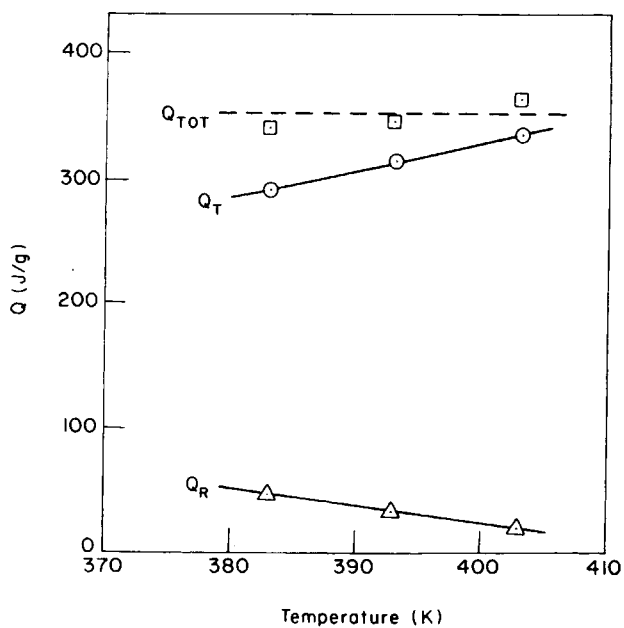


Fig. 3. Heat generated by cure reaction at various isothermal temperatures: (○) Q_T ; (△) Q_R ; (□) Q_{TOT} .

amount of heat generated by the cure reaction is directly proportional to the degree of cure, and that the cure is complete (i.e., $\alpha = 1$) after the resin sample has undergone an isothermal cure followed by the heating to 200°C. If this assumption is correct, then there should be *no* ethylenic double bonds remaining in the cured samples.

In order to check the validity of this assumption, with the aid of the IR spectra measured independently, we determined the degree of cure (α_{TOT}) by

$$\alpha_{TOT} = (A - B)/A \quad (13)$$

where A denotes the double bonds present in the resin system before the cure, and B denotes the residual (i.e., unreacted) double bonds in the postcured resin.

Figure 4 gives IR spectra of the resin employed, which was cured with TBPB. The identifications of the IR spectra of the unsaturated polyester resin are as follows: (a) the wave number 1730 cm^{-1} represents the absorbance due to the stretching modes of carbonyl groups; (b) the wave number 1650 cm^{-1} represents the absorbance due to the stretching modes of the double bonds in fumarates; (c) the wave number 1630 cm^{-1} represents the absorbance due to the stretching modes of the vinyl group in styrene; (d) the wave number 770 cm^{-1} represents the absorbance due to the out-of-plane C—H bending modes in styrene; (e) the wave number 730 cm^{-1} represents the absorbance due to the out-of-plane bending modes of a disubstituted phenyl

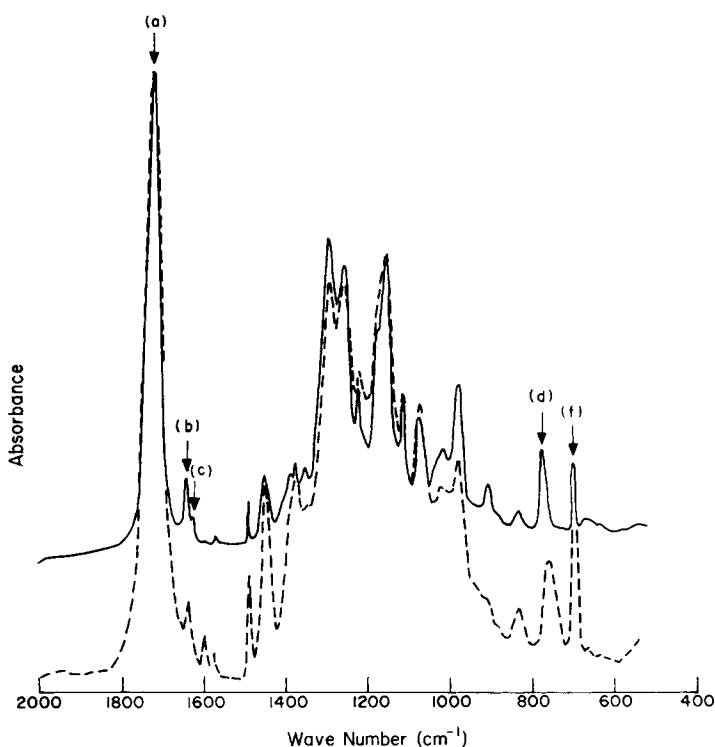


Fig. 4. IR spectra of the resin investigated.

ring; (f) the wave number 690 cm^{-1} represents the absorbance due to the out-of-plane bending modes of a monosubstituted phenyl ring.

In the past, several research groups used IR spectra to determine the degree of cure of unsaturated polyester resin. Imai¹⁷ used the ratio of the optical density at 695 cm^{-1} to that at 740 cm^{-1} as an index for determining the chemical composition of polyester resins, using standard samples as a calibration. Horie et al.¹ used the ratio of the optical density at 1650 cm^{-1} to that at 1730 cm^{-1} as an index of the amount of fumarates in an unsaturated polyester resin. Neag et al.¹⁸ used the ratio of the optical density at 770 cm^{-1} to that at 740 cm^{-1} as an index for determining the degree of cure.

In the present investigation, we have used the ratio of the optical densities at 1650 cm^{-1} and 1630 cm^{-1} to that at 1730 cm^{-1} in determining the degree of cure (α). In other words, we have used, as the internal reference, the absorbance at 1730 cm^{-1} due to the carbonyl groups in the unsaturated polyester resin.

Note that α_{TOT} defined by Eq. (13) represents the degree of cure corresponding to the total heat released, Q_{TOT} , defined by Eq. (11). Therefore it is clear that when α_{TOT} is less than 1, Q_{TOT} should not be used to calculate the degree of cure α during the isothermal cure. Indeed our IR data show that the value of α_{TOT} is 0.634. Thus, in the present investigation, we have used the following expression

$$\alpha = Q_i(T)/Q_{UT} \quad (14)$$

instead of Eq. (12), in determining the degree of cure. Note that Q_{UT} in Eq. (14) is defined by

$$Q_{UT} = Q_{TOT}/\alpha_{TOT} \quad (15)$$

It should be pointed out that Q_{UT} represents the ultimate heat that would have been generated if the complete cure (i.e., $\alpha = 1$) had been achieved. In the present investigation, our DSC data give 335 J/g for Q_{TOT} and therefore, according to Eq. (15), the value of Q_{UT} becomes 528 J/g . This value seems very reasonable, in view of the fact that the heat of reaction for copolymerization of diethyl fumarate and styrene is 506 J/g as reported by Horie.¹⁹

It should be pointed out that the rate of cure, $d\alpha/dt$, may be obtained from the expression

$$\frac{d\alpha}{dt} = \frac{1}{Q_{UT}} \left(\frac{dQ}{dt} \right)_T \quad (16)$$

with the aid of $(dQ/dt)_T$ obtained from DSC thermograms. Integrating Eq. (16) yields

$$\alpha = \frac{1}{Q_{UT}} \int_{t_i}^t \left(\frac{dQ}{dt} \right)_T dt \quad (17)$$

Figure 5 gives plots of $d\alpha/dt$ versus cure time and Figure 6 plots of α versus cure time for the resin investigated. It is seen that, as the cure

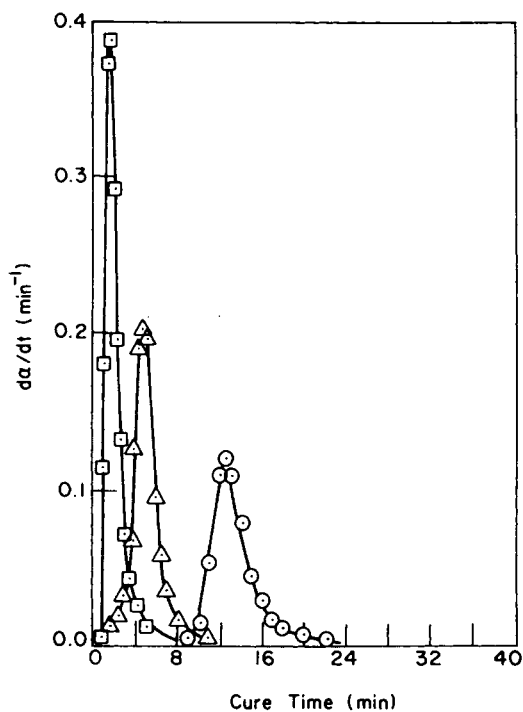


Fig. 5. da/dt versus cure time for the resin investigated. Symbols are the same as in Figure 2.

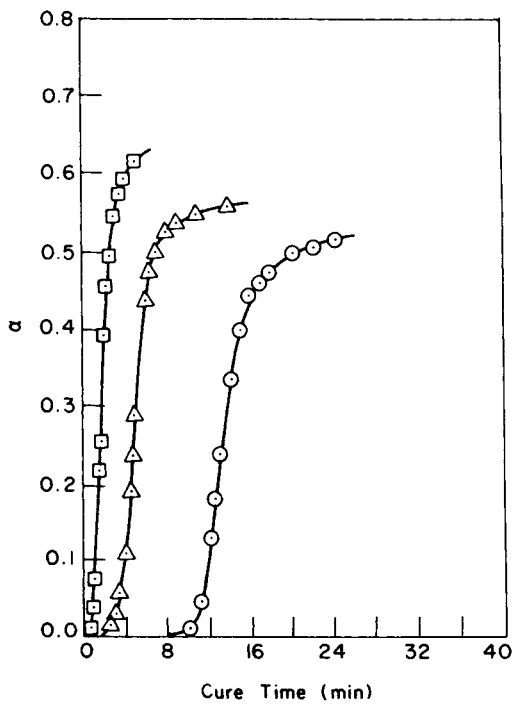


Fig. 6. α versus cure time for the resin investigated. Symbols are the same as in Figure 2.

temperature increases, both the rate of cure ($d\alpha/dt$) and the ultimate degree of cure (α) increase.

THEORETICAL PREDICTIONS

We now present the theoretical predictions obtained by numerically solving the system equations presented above. Briefly stated, for given initial conditions, and with numerical values assumed as initial guesses for the parameters k_z , k_{p0} , k_{t0} , m , n , f_0 , we integrated Eqs. (2)–(5) with the aid of Eqs. (6), (7), and (10), using a Runge-Kutta fourth-order method. Since in our experimental study we used a single initiator (*tert*-butyl perbenzoate), the concentration of initiator $[I_j]$ ($j = 1, 2, \dots, N$) becomes simply $[I]$.

In carrying out computations, we used the experimental conditions described above to specify the initial conditions, namely $[Z]_0 = 5.09 \times 10^{-4} M/L$, $[I]_0 = 5.716 \times 10^{-2} M/L$, and $[R.]_0 = 0$. In order to facilitate our computation, Eq. (4) was rewritten in the following form:

$$-\frac{1}{[M]_0} \frac{d[M]}{dt} = \frac{d\alpha}{dt} = k_p(1 - \alpha)[R.] \quad (18)$$

in which $[M]_0$ is the initial concentration of the total monomer (i.e., the sum of the initial concentrations of polyester resin and styrene), and α is defined by

$$\alpha = ([M]_0 - [M])/[M]_0 \quad (19)$$

Note that the definition of α given by Eq. (19) is consistent with that used in analyzing our experimental data [see Eq. (13)]. Therefore, in our computations, we used Eq. (18) in place of Eq. (4) and thus the initial condition for Eq. (18) is $\alpha = 0$ at $t = 0$. Also, we used the following expression for calculating the decomposition rate constant of the initiator

$$k_d = 8.524 \times 10^{15} \exp(-1.632 \times 10^4/T) \quad (20)$$

in which T is the absolute temperature.

In our computations, we determined the following parameters, namely k_z , k_{p0} , k_{t0} , m , and n until the sum of the squares of the differences between the computed values of both $d\alpha/dt$ and α and the experimentally measured ones become minimum throughout the entire period of cure, by using the Half-Interval and Fibonacci searching methods.

After a considerable amount of computation, we have learned that the value of k_{t0} has very little effect on the outcome of the simulation, indicating that the termination reaction plays only a small role in determining the system parameters. This then eliminated the necessity for including the parameters k_{t0} and n [see Eq. (7)] in further computations. Also, we have found that non-zero values of the parameter m in Eq. (6) give rise to much more reasonable predictions of $d\alpha/dt$ than $m = 0$. This is demonstrated in Figure 7. This observation is interpreted as an indication that the propagation reaction, hence the curing reaction, is diffusion controlled. This conclusion is

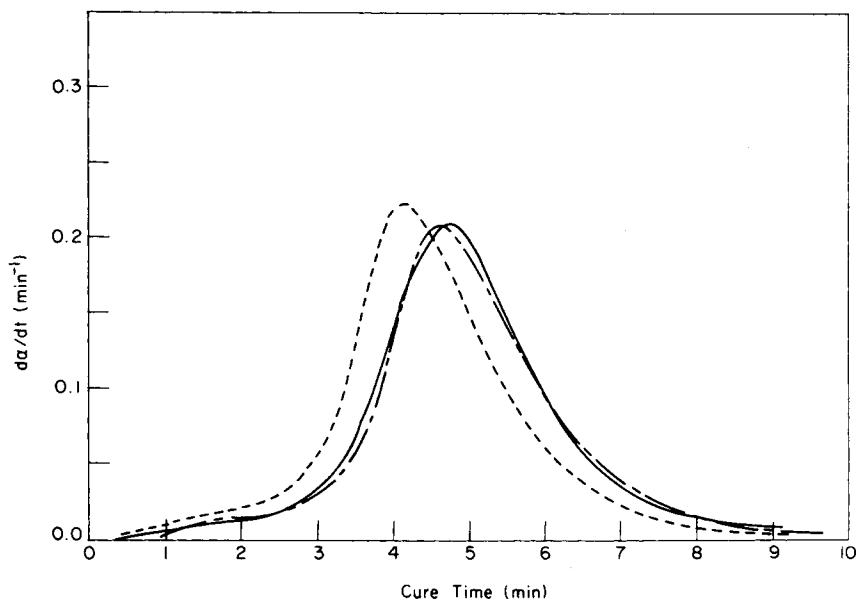


Fig. 7. The effect of the parameter m on the prediction of $d\alpha/dt$. (—) Experimental results; (-----) Theoretical prediction with $m = 0$; (-·-) Theoretical prediction with $m = 0.85$.

rather obvious when we carefully examine the experimentally observed α versus cure time curves, given in Figure 6 (see also Fig. 1).

Figure 8 gives a comparison of the computed $d\alpha/dt$ versus cure time curves with experimental results, and Figure 9 a comparison of the computed α versus cure time curves with experimental results, at five different values of

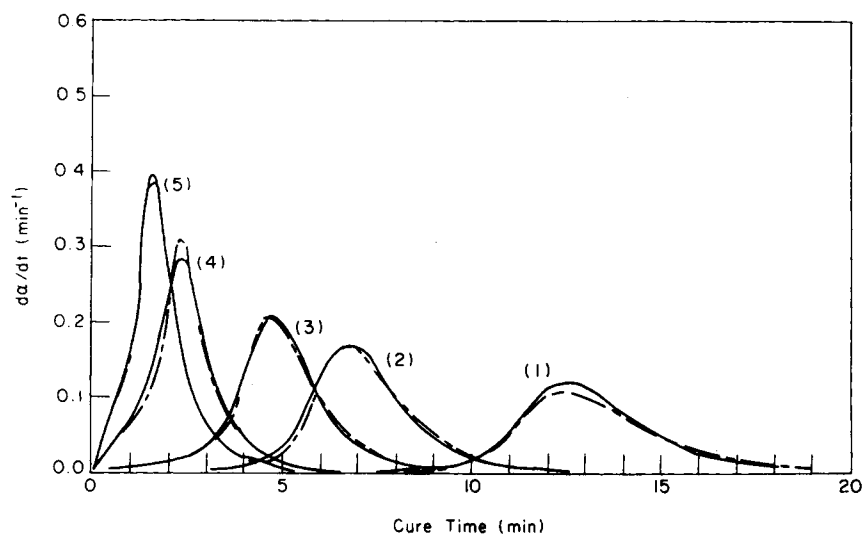


Fig. 8. Comparison of the experimental results (solid line) with the computed $d\alpha/dt$ (broken lines) at various isothermal cure temperatures. Curve 1 at 110°C; curve 2 at 115°C; Curve 3 at 120°C; Curve 4 at 125°C; Curve 5 at 130°C.

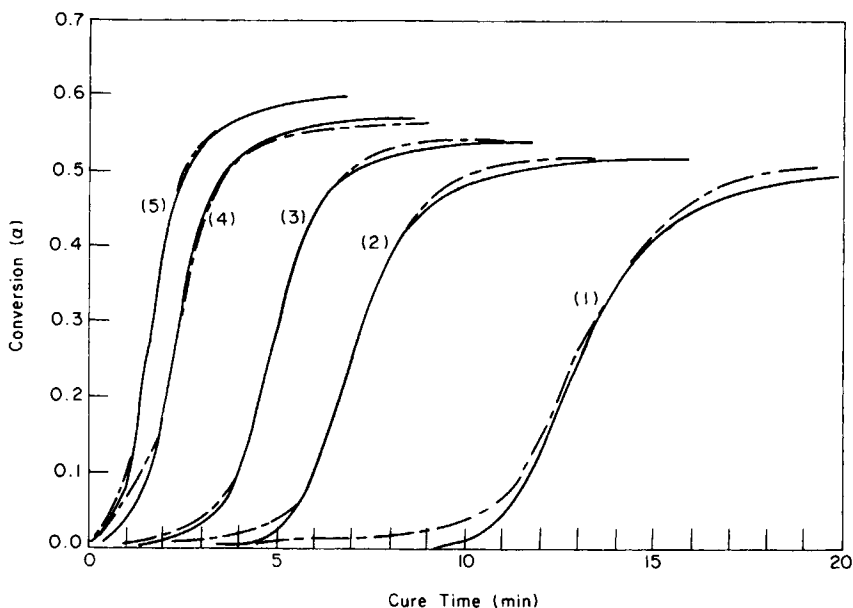


Fig. 9. Comparison of the experimental results (solid line) with the computed α (broken lines) at various isothermal cure temperatures. Symbols are the same as in Figure 8.

isothermal cure temperature. It is seen that agreement between the two is very good. It should be remembered that, during the computations, we have varied the parameters k_z , k_{p0} , and m , and fixed the value of f_0 equal to 0.2. The numerical values of k_z , k_{p0} , and m obtained in generating the results presented in Figures 8 and 9 are given in Table I.

Figure 10 gives profiles of the inhibitor concentration $[Z]$ and the degree of cure α during the entire period of the cure reaction. It can be said from Figure 10 that the cure reaction begins only after the inhibitor virtually disappears completely from the reacting system. This conclusion then supports the validity of the assumption made by Stevenson,^{12,13} that the inhibition reaction is followed by the curing reaction.

Figure 11 gives profiles of the initiator concentration $[I]$, and Figure 12 profiles of the radical concentration $[R]$ during the entire period of the cure reaction. Note that, as expected from Eq. (3), $[I]$ decreases with cure time,

TABLE I
Summary of the Kinetic Parameters Determined from Computations

Temperature (°C)	k_z (L/g · mol · min)	k_{p0} (L/g · mol · min)	m (dimensionless)
100	6.682×10^5	1.886×10^3	0.76
105	3.416×10^5	2.836×10^3	0.79
110	2.199×10^5	3.233×10^3	0.75
115	2.698×10^5	3.711×10^3	0.80
120	1.547×10^5	4.068×10^3	0.85
125	2.365×10^5	1.864×10^4	1.51
130	1.068×10^4	1.210×10^4	1.41

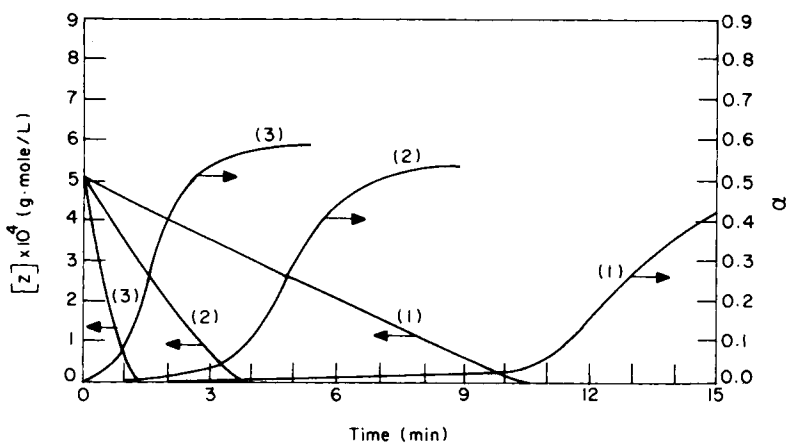


Fig. 10. Predicted profiles of inhibitor concentration $[Z]$ and degree of cure α at three isothermal cure temperatures ($^{\circ}\text{C}$): (1) 110; (2) 120; (3) 130.

and that $[I]$ decreases with increasing cure temperature. This is very reasonable because the rate of decomposition of initiator increases with cure temperature.

Figure 13 gives plots of k_{po} versus the reciprocal of absolute cure temperature. Using least-squares regression analysis, we obtain the following expression

$$k_{po} = 1.541 \times 10^{15} \exp(-20,413/RT) \tag{21}$$

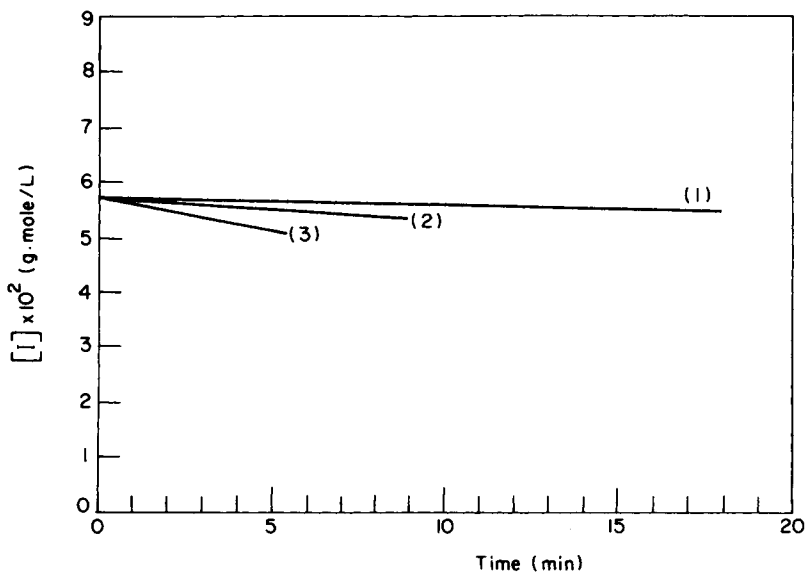


Fig. 11. Predicted profiles of initiator concentration $[I]$ at three isothermal cure temperatures ($^{\circ}\text{C}$): (1) 110; (2) 120; (3) 130.

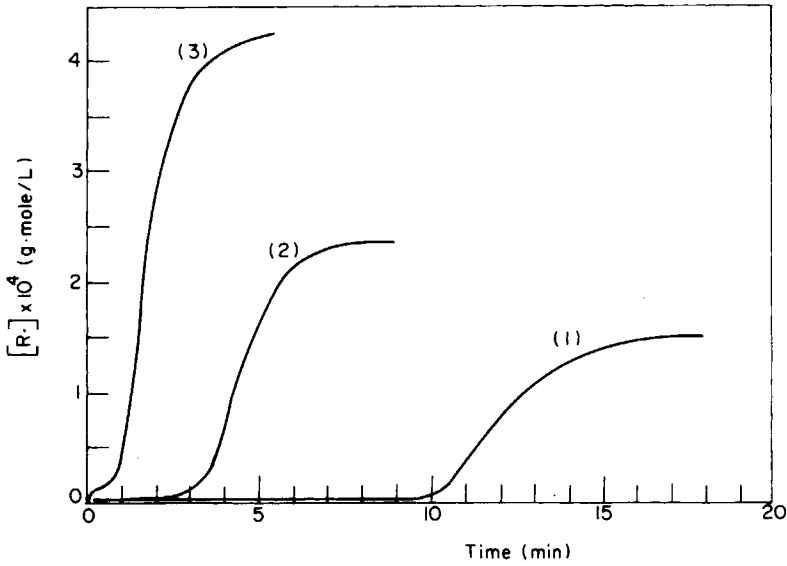


Fig. 12. Predicted profiles of radical concentration $[R.]$ at three isothermal cure temperatures ($^{\circ}\text{C}$): (1) 110; (2) 120; (3) 130.

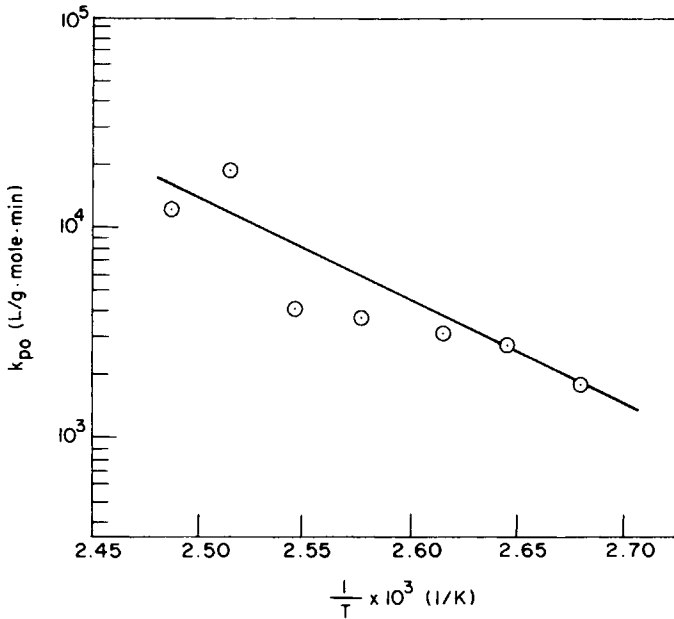


Fig. 13. Arrhenius plot of the propagation rate constant k_{po} .

DISCUSSION

Based on the idea postulated by Gordon²⁰ that the termination reaction between radicals should not be zero, Chern and Sundberg^{14,15} considered two types of termination reaction, in their development of a kinetic model for curing reaction of unsaturated polyester resin. One type is the residual

termination process that involves two radicals, both of which are attached to the crosslinked networks, and the other type is the termination process which involves two radicals, one a stationary radical that is attached to the crosslinked networks and the other a mobile radical that is not attached to the crosslinked networks. However, as mentioned above, in the present investigation we have found that numerical values of the rate constant of termination k_t (more specifically, numerical values of the parameters k_{to} and n in Eq. (7)) have little effect on the outcome of the simulation. Therefore, to all intents and purposes, one can assume that $k_t = 0$, supporting the earlier findings of Stevenson.^{12,13} This seems to indicate that, although a termination reaction does occur during the cure of unsaturated polyester resin, its role may be negligibly small compared to that of the propagation reaction, insofar as controlling overall curing reactions is concerned.

We have found also that numerical values of the rate constant of inhibition k_z have little effect on the prediction of the curing behavior of unsaturated polyester resin. It should be pointed out that inhibitors are known to have side reactions during polymerization.²¹ As may be seen in Table I, the magnitude of k_z is very large compared to that of k_{po} , in the range of temperatures 100–120°C. Earlier, Stevenson¹² assumed a very large value of k_z to k_{po} ratio (i.e., $k_z/k_{po} = 200$). Our study seems to indicate that such an assumption is reasonable.

It is seen in Table I that the value of m increases with increasing cure temperature. This implies, according to Eq. (6), that the cure reaction of unsaturated polyester resin becomes more diffusion controlled as the cure temperatures increases. In his study, Stevenson¹³ assumed a constant value of m (i.e., $m = 0.5$), which was chosen somewhat arbitrarily. In the present investigation, however, the value of m was determined as part of the solution of the system equations, to minimize the sum of the squares of the differences between the computed values of both $d\alpha/dt$ and α and the experimentally measured ones. In reference to Table I, at present we cannot explain why the value of m increases very rapidly at temperatures above 125°C.

It seems appropriate to mention at this juncture that Horie et al.¹ reported that the crosslinking density of cured resins increased with cure temperature. They attributed this experimental observation to the mobility of the reactants (i.e., radicals and monomers) becoming more restricted as cure temperature increases, due to the increased crosslink density. Thus the cure reactions become more diffusion controlled.

CONCLUDING REMARKS

A mechanistic kinetic model for the curing reaction of unsaturated polyester resin is developed using the concept of free-radical polymerization. In the model, we have included an admittedly empirical, conversion-dependent (i.e., diffusion-controlled) propagation rate constant and, also, a conversion-dependent initiator efficiency. We are well aware of the fact that some investigators²⁻⁷ have suggested that the free volume theory be used for incorporating the effect of diffusion control into the expressions for the rate constants of propagation and termination in free-radical polymerization. However, in practice, one encounters great difficulties with even estimating some of the free

volume parameters involved. This is especially difficult when dealing with the curing reactions of thermosetting resins, such as the unsaturated polyester resin considered in the present investigation.

Due to the complexity of the real situation involved with the curing of unsaturated polyester resin, we have made several simplifying assumptions to develop a mechanistic kinetic model presented above. Considering the simplifications made, it is very encouraging to see that the model predictions are very reasonable. One of the advantages of this kind of mechanistic model over an empirical model [e.g., Eq. (1)] lies in that, without having to conduct experiments to determine the parameters involved in an empirical model [see, e.g., Eq. (1)], one can easily investigate the effect of process variables (e.g., the type of initiator, the concentration of initiator and/or inhibitor, and the concentration of monomer) on the performance of various processing operations of unsaturated polyester resin. In future publications, we shall report applications of this mechanistic model to simulate processing operations such as pultrusion and compression molding of unsaturated polyester resin.

This study was supported in part by the National Science Foundation under Grant MSM-8517707 and Owens-Corning Fiberglas Corporation, for which we are very grateful. We wish to acknowledge that Dr. James Stevenson at GenCorp kindly provided us with his manuscripts before their publication.

References

1. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci., A-1*, **8**, 2839 (1970).
2. J. N. Cardenas and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 883 (1976).
3. J. N. Cardenas and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1883 (1977).
4. F. L. Marten and A. E. Harmilec, in *Polymerization Reactors and Processes*, ACS Symp. Ser. 104, J. N. Henderson and T. C. Bouton, Eds., Am. Chem. Soc., Washington, D.C., 1973, p. 43.
5. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489 (1982).
6. W. Y. Chiu, G. M. Garratt, and D. S. Soong, *Macromolecules*, **16**, 348 (1983).
7. S. K. Soh and D. C. Sundberg, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1299 (1984).
8. M. R. Kamal, S. Sourour, and M. E. Ryan, *SPE Tech. Pap.*, **19**, 187 (1973).
9. M. R. Kamal and S. Sourour, *Polym. Eng. Sci.*, **13**, 59 (1973).
10. S. Y. Pusatcioglu, A. L. Fricke, and J. C. Hassler, *J. Appl. Polym. Sci.*, **24**, 937 (1979).
11. C. D. Han and K. W. Lem, *J. Appl. Polym. Sci.*, **28**, 3155 (1983).
12. J. F. Stevenson, SPE Annu. Tech. Conf., 38th Prep. p 452 (1982).
13. J. F. Stevenson, Paper Presented at the Annu. AIChE Meeting, Washington, D.C., November 1983; *Polym. Eng. Sci.*, **26**, 746 (1986).
14. C. S. Chern and D. C. Sundberg, paper presented at the Winter AIChE Meeting, Atlanta, Georgia, March 1984.
15. C. S. Chern and D. C. Sundberg, *ACS Polymer Preprints*, **26**(1), 296 (1985).
16. J. S. Biesenberger and D. H. Sebastian, *Principles of Polymerization Engineering*, Wiley, New York, 1983, p. 193.
17. T. Imai, *J. Appl. Polym. Sci.*, **11**, 1055 (1967).
18. C. M. Neag, G. M. Carlson, and T. Provder, *Proc. Annu. Tech. Conf., Reinf. Plast./Compos. Inst., Soc. Plast. Ind.*, **39**, 16-F (1984).
19. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci.*, **7**, 2561 (1969).
20. J. S. Gordon, *J. Polym. Sci., Part A-1*, **6**, 2851 (1968).
21. F. W. Billmeyer, *Textbook of Polymer Science*, 2nd Edit., Wiley, New York, 1971, p. 285.

Received June 24, 1986

Accepted September 23, 1986