Kinetics of Free Radical Polymerizations in Reactive Polymer Processing

A kinetic model has been developed for radical chain growth type of reactive polymer processing operations. This model incorporates considerations of the molecular diffusion that is described by a free volume theory and the basic reaction mechanism of the free-radical chain polymerization. Experimental results from the bulk styrene polymerization and a reaction of sheet molding compound (SMC) showed good agreement with the model.

Y. J. HUANG and L. J. LEE

Department of Chemical Engineering
Ohio State University
Columbus, OH 43210

SCOPE

Reactive polymer processing is one of the fastest growing areas in the polymer industry. A large number of polymer products involve polymerization in fabricating the final shape. Examples are rubber compression, transfer, and injection molding; thermoset polyester compression and injection molding; polyurethane, nylon, and epoxy reaction injection molding; and polymer encapsulation of electronic parts. These polymers have outstanding mechanical properties, and most of the processes are able to handle fiber-reinforced materials with high reinforcement loadings and long fiber lengths. Due to the desirability of lightweight composite materials for structural applications in the aerospace, automotive, and housing industries, these processes offer great potential for growth in the future.

Reaction in the reactive polymer processing operation is much more complicated than that in the conventional polymerization methods. For example, in order to combine with the processing step, the reaction usually occurs in the bulk state. For the purpose of competing with traditional injection and compression molding processes, the reaction rate has to be very high to reduce the reaction time (i.e., the cycle time is in minutes or seconds instead of the hours common in a typical polymerization reactor). Quite often, the reactions are also highly exothermic (Lee and Macosko, 1980; Lee, 1981). Another complexity of the reaction arises from the ingredients of compounds used. Resins, such as styrene, unsaturated polyester, and polyurethane, are primary components. Initiators, inhibitors, or catalysts are added to control the reaction course. Fillers and reinforcement materials like calcium carbonate, glass fibers, and carbon black are usually added to reduce the cost and to increase the mechanical properties of the final product. Other ingredients, such as low-profile materials, lubricants, and foaming agents, are sometimes employed for different purposes (Epel et al., 1978; Lee, 1980).

In the kinetic aspect, the reactions usually involve either a radical chain growth polymerization, such as styrene or polyester, or a step growth polymerization, for instance, polyurethane or epoxy in the bulk state. Most reactions are further complicated by the occurrence of multiple physical changes during polymerization. These changes include domain formation, in which materials change from a single phase to multiple phases because of the thermodynamic incompatibility of polymer segments or blocks; gelation, in which materials change from a viscous fluid to a network gel with chemical or physical crosslinking; and glass transition or crystallization, in which the reacting mixture changes from a rubbery material to a glassy polymer or from an amorphous material to a semicrystalline polymer with increasing degree of polymerization and packing of polymer segments.

These changes occur during the course of reaction and may certainly interact with the ongoing chemical reaction. Basically, the chemical reaction is controlled by the kinetic effect. On the other hand, the physical changes will cause diffusion effects, which in turn may result in a number of undesirable phenomena during reaction. For example, the Trommsdorff, or gel, effect, which is well known for free radical polymerizations, may result in a rapid conversion with an excessive temperature rise, that, when coupled with the low thermal diffusivity of the polymer, may lead to the thermal runaway problem. The glass transition effect, where the material changes from the rubbery state to the glassy state and cessation of the reaction subsequently follows, may cause an incomplete reaction (Lee, 1981).

To date, the kinetics of these reactions is still poorly understood. How the physical changes develop during polymerization and how the reactant composition influences the reaction kinetics are seldom considered. This work provides a fundamental study of kinetics in reactive polymer processing operations that involve free radical chain growth polymerizations.

CONCLUSIONS AND SIGNIFICANCE

The rate of bulk polymerization of styrene and a sheet molding compound (SMC) over the whole range of conversion was determined using a differential scanning calorimeter operated in both isothermal and scanning modes. It was found that

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Correspondence concerning this paper should be addressed to L. J. Lee.

the effect of molecular diffusion may drastically change the rate of reaction, the reaction profile, and the degree of conversion.

A realistic kinetic model has been developed for the radical chain growth type of reactive polymer processing operations. This model, which is expressed by a single equation, incorporates considerations of the molecular diffusion described by a free volume theory and the basic reaction mechanism of the free radical chain polymerization. The model can predict not only the reaction rate and conversion profiles but also the onset of the gel effect and the glass transition effect.

All the parameters were estimated step by step from three isothermal DSC experiments by either graphical or analytical procedures. The temperature dependence of model parameters was determined by relating the isothermal parameters in the Arrhenius relationship or a polynomial form.

Model predictions have been compared with experimental data for polymerization of both styrene and SMC. The agreement was reasonably good on conversion and rate profiles under both isothermal and nonisothermal conditions. This model has provided a simple and useful means for analyzing and modeling the reaction kinetics of reactive polymer processing operations that exhibit free radical chain growth polymerizations.

BACKGROUND

In most studies of reactive polymer processing, researchers (Kamal et al., 1973; Pusatcioglu et al., 1979; Lee and Macosko, 1980; Barone and Caulk, 1979) used empirical models to fit the reaction profiles. A typical model is

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (1)$$

These models fit the experimental results well but had little physical meaning. Stevenson (1980) and Lee (1981) developed a series of kinetic models for free radical copolymerizations based on the usually accepted reaction mechanism. Their models fit the reaction data fairly well. Unlike the empirical models, these mechanistic models provided the necessary kinetic information for heat transfer modeling and also elucidated the functions of initiators, inhibitors, and monomers in the reaction up to the medium conversion region. However, several important phenomena, such as the incomplete reaction at lower molding temperatures and apparent diffusion control in the later stages of the curing reaction, were not treated.

For vinyl polymerizations, a number of kinetic experiments have been carried out in an attempt to elucidate the effects of various ingredients on the rate of polymerization and the reactor performance (Balke and Hamielec, 1973; High et al., 1979). Mechanistic modeling of free radical vinyl polymerizations in the bulk state has also been developed in great detail. Horie et al. (1968) investigated the bulk polymerization of methyl methacrylate and styrene using a differential scanning calorimeter (DSC). The variation of rate profiles was interpreted on the basis of the diffusion behavior of monomer molecules and polymeric radicals. They explained the diffusion effect using the kinetic theory developed by Rabinowitch, as well as free volume theories developed by Fujita et al. (1960), Fujita and Kishimoto (1961), and Bueche (1962). However, no kinetic model was proposed in their study. Cardenas and O'Driscoll (1976, 1977a,b, 1979) developed a kinetic model that accounted for the coupling between the molecular weight development and the gel effect by assuming that the termination constant for entangled radicals varied as the reaction went on. This model, however, did not account for the glassy state transition and hence could not predict the observed limiting conversion. Marten and Hamielec (1979, 1982) proposed a model for free radical homopolymerizations based on the free volume theory of Bueche (1962). Their model accounted for diffusion-controlled termination and propagation and also the limiting conversion due to the glass transition. This model seemed to agree well with the measured kinetic data for bulk and solution polymerizations of methyl methacrylate, styrene, and vinyl chloride. However, the prediction of the weight average molecular weight was less than satisfactory. In a series of papers, Soh and Sundberg (1982a,b,c,d) elucidated the importance of the diffusion effect in the bulk state vinyl polymerization. They claimed that the vinyl polymerization of monomer soluble in its own polymer consisted of four phases of distinctive polymerization behavior: conventional kinetics, gel effect, limited gel effect, and limiting conversion. Depending on the monomer used or reaction conditions, one or more of the four phases might be absent. Their model predicted the conversion profile and molecular weight distributions very well, except that the limiting conversion phase was not in good agreement. They attributed this to the disregard of the restricted diffusion on the initiator dissociation rate and chain transfer reactions to monomer and polymer at the final stage of reaction. Recently, Chiu et al. (1983) have developed a mathematical model to describe free radical polymerization reactions exhibiting a strong gel effect. Unlike other kinetic models, diffusion effect was evaluated from the very beginning of the polymerization. Fujita's free volume theory as well as the random walk statistics on polymer radicals (Bird et al., 1977) had been applied in their study. This model predicted the conversion profile very well, yet the prediction of the weight average molecular weights was less than satisfactory.

Although all the above models achieved differing degrees of success in fitting experimental data, they are too complex to be used in the reactive polymer processing operations where the reaction is under nonisothermal conditions and the heat transfer through the mold surface has to be considered.

THE MODEL

The major assumptions regarding the reaction kinetics are as follows:

1. No monomer reacts until the number of initiator radicals created is equal to the effective number of inhibitor molecules initially presented.
2. Termination is predominated by combination.
3. Chain transfer reactions are neglected for convenience.
4. Single initiator and inhibitor are used in the reaction.

For the reaction of sheet molding compounds (SMC) where reactants include styrene monomer and unsaturated polyester molecules (Gaylord, 1974), the following assumptions are also adopted.

5. Homopolymerization of unsaturated polyester is negligible.
6. Copolymerization of styrene and polyester can be expressed by a single average rate constant.
7. Termination is totally diffusion controlled.

Assumptions 1, 4, and 6 have been discussed in detail by Stevenson (1980) and Lee (1981). A typical SMC often uses only one major initiator. No inhibitor is added in most cases, but some inhibitor is contained in the styrene monomer and resins as received.

Assumption 1 is used to uncouple the inhibition from the polymerization. Since the inhibitors commonly used are highly effective, e.g., the inhibition constant $k_z/k_p > 500$ for benzoquinone in styrene monomer, this assumption should introduce little error.

As cited by Lee (1981), literature data on copolymerization of styrene and diethyl fumarate suggest fumarate groups in unsaturated polyesters tend not to homopolymerize when styrene is present. This inherently low reactivity is further reduced by the relative immobility of the polyester-styrene network formed early in the reaction. On the other hand, homopolymerization of styrene monomer is significant relative to the copolymerization between styrene and fumarate groups. However, since SMC reaction is very close to an azeotropic copolymerization, a single average rate constant for all the reactions occurring during curing can be assumed. Because the heat of reaction of styrene homopolymerization (~16.4 kcal/mol) is close to that of styrene-polyester copolymerization (~14 kcal/mol), the total heat of reaction should not be affected much by this assumption. Diffusion dominated termination is justified in SMC reaction because only 3 to 5% conversion gels the typical styrene-polyester system (Stevenson, 1980), and most of the reaction occurs after the gelation. The large increase in viscosity with gelation leads to a sharp reduction in termination rates but only a moderate reduction in propagation rates.

With these assumptions, the kinetic mechanism can be expressed as

$$\text{Initiation: } I \xrightarrow{k_d} 2R$$

$$R + M \xrightarrow{k_i} M\cdot \quad k_i \gg k_d$$

$$\text{Inhibition: } M_n^{\cdot} + Z \xrightarrow{k_z} P_n + Z\cdot \tag{2}$$

$$\text{Propagation: } M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot}$$

$$\text{Termination: } M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_t} P_{n+m}$$

The governing equations can then be written as

$$\text{Inhibition: } qz_O = 2fI_O\left(1 - e^{-\int_0^t zk_d dt}\right) = 2f(I_O - \bar{I}_O) \tag{3}$$

$$\text{Propagation: } \frac{dM}{dt} = -k_p MM\cdot \text{ or } \frac{d\alpha}{dt} = k_p(1-\alpha)M\cdot \tag{4}$$

$$\text{Termination: } \frac{dM\cdot}{dt} = 2fk_d I - k_t M_{\cdot}^2 \tag{5}$$

The fractional conversion α is defined as $(M_O v_O - Mv)/M_O v_O$. Here M_O and v_O are the monomer concentration and the system volume, respectively, at $\alpha = 0$. The volume contraction with conversion is considered by assuming that

$$v = v_O(1 - \epsilon\alpha) \tag{6}$$

The determination of self-diffusion coefficients of polymer chains and monomer molecules has been generally based on either the reptation concept, introduced by de Gennes (1971), or varied versions of free volume theory (Fujita et al., 1960; Bueche, 1962; Vrentas et al., 1980). We apply here an approach similar to that of Chiu et al. (1983) to explain the diffusion-affected propagation, as shown in Figure 1a. The radius l_c can be viewed as a length scale characterizing the effective sphere swept by the free radical end and is assumed to be a constant. Monomer concentration within the sphere, M', remains constant. (l here is the length scale of diffusion.) The molecular diffusion described in Figure 1a can be simplified to a one-dimensional mass transfer process at a phase boundary, as shown in Figure 1b, where M is the bulk monomer concentration and δ_e is the equivalent diffusion distance. At pseudosteady state, the diffusion rate of monomers to the surface of radical centers bounded by l_c should be equal to the reaction rate of propagation there.

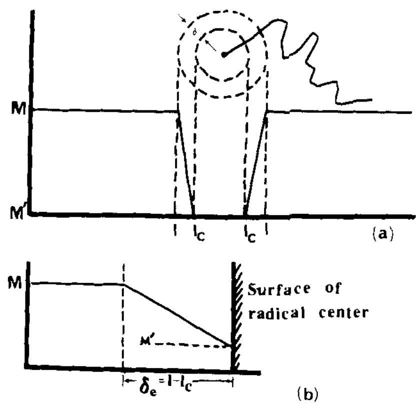

Figure 1. Diagrams of monomer diffusion: (a) in the propagation process; (b) to the surface of radical center.

$$r'_p = D_M \frac{A_e}{\delta_e}(M - M') = k_{pO} M'M\cdot v_s \tag{7}$$

The overall reaction rate is ordinarily expressed as $k_p MM\cdot$, as given by Eq. 4. This rate is the same as $k_{pO}M'M\cdot$, so that we have

$$k_p MM\cdot = k_{pO} M'M\cdot \tag{8}$$

Equations 7 and 8 give the following result:

$$\frac{1}{k_p} = \frac{1}{k_{pO}} + \frac{A'M\cdot}{D_M} \tag{9}$$

An analog derivation yields the following equation for the termination process:

$$\frac{1}{k_t} = \frac{1}{k_{tO}} + \frac{A''M\cdot}{D_P} \tag{10}$$

To describe D_P and D_M semiempirically, we employ Bueche's (1962) free volume theory to give

$$D_M = A'_M \exp\left(\frac{-B_M}{V_f}\right) \tag{11}$$

$$D_P = A'_P \exp\left(\frac{-B_P}{V_f}\right) \tag{12}$$

where A'_M is a function of temperature only, A'_P is a function of both temperature and molecular weight, and $B_M = B_P = 1.0$, as derived by Bueche. Equations 11 and 12 can be substituted into Eqs. 9 and 10, respectively, to give

$$\frac{1}{k_p} = \frac{1}{k_{pO}} + M\cdot A_M \exp\left(\frac{B_M}{V_f}\right) \tag{13}$$

$$\frac{1}{k_t} = \frac{1}{k_{tO}} + M\cdot A_P \exp\left(\frac{B_P}{V_f}\right) \tag{14}$$

If we neglect the volume contraction effect of the system, V_f is given as (Bueche, 1962; Soh and Sundberg, 1982c)

$$V_f = [V_{fgP} + \lambda\beta_P(T - T_{gP})]\alpha + [V_{fgM} + \beta_M(T - T_{gM})](1 - \alpha) \tag{15}$$

$$\lambda = 1.0 \text{ for } T \geq T_{gP},\ \lambda = 0.3 \text{ for } T < T_{gP} \tag{16}$$

For polystyrene, $V_{fgM} = V_{fgP} = 0.025$ (Bueche, 1962).

For free radical polymerizations, the quasisteady state assumption of free radicals represents a reasonably accurate approximation. Equation 5 yields

$$M\cdot = \left(\frac{2fk_dI}{k_t}\right)^{1/2} \tag{17}$$

Combining Eqs. 3, 4, 13, 14, and 17 gives

$$\frac{d\alpha}{dt} = \frac{1-\alpha}{\dfrac{1}{\sqrt{\pi_1 + (\pi_2\pi_3)^2} + \pi_2\pi_3} + \pi_4} \tag{18}$$

where

$$\pi_1 = \frac{2f\bar{I}_O k_d k_{pO}^2}{(1-\epsilon\alpha)k_{tO}} \exp\left(-\int_{t_z}^{t} k_d dt\right) \tag{18a}$$

(kinetic effect on propagation and termination)

$$\pi_2 = \frac{A_P}{F} \exp\left(\frac{B_P}{V_f}\right) \tag{18b}$$

(diffusion effect on termination)

$$\pi_3 = \frac{f\bar{I}_O k_{pO} F k_d}{1-\epsilon\alpha} \exp\left(-\int_{t_z}^{t} k_d dt\right) \tag{18c}$$

(kinetic effect on propagation)

$$\pi_4 = A_M \exp\left(\frac{B_M}{V_f}\right) \tag{18d}$$

(diffusion effect on propagation)

and F is a parameter defined as (Huang, 1983)

$$F = \frac{\text{free radical concentration assuming that the termination is totally diffusion controlled}}{\text{free radical concentration assuming no termination}}$$

(Lee, 1981)

$$= \frac{k_d A_P \exp(B_P/V_f)}{[(1-\epsilon\alpha)\exp(k_d(t-t_z)) - 1]} \tag{19}$$

For reactions such as the SMC reaction where the termination process is diffusion-controlled, $\pi_1 \ll (\pi_2\pi_3)^2$. Equation 18 can be simplified to

$$\frac{d\alpha}{dt} = \frac{1-\alpha}{\dfrac{1}{2\pi_2\pi_3} + \pi_4} \tag{20}$$

For reactions such as vinyl radical polymerization in the dilute solution, the diffusion effects are negligible, i.e., $\pi_2 = \pi_4 = 0$. Equation 18 can be simplified to

$$\frac{d\alpha}{dt} = \sqrt{\pi_1}(1-\alpha) \tag{21}$$

which is the well-known kinetic expression for the steady state radical polymerization (Odian, 1970).

EXPERIMENTAL

The SMC compound and styrene used are listed in Table 1. A Perkin-Elmer differential scanning calorimeter (DSC-2C) was used to follow the reaction rate profiles for all the studies. All the reactions were conducted in volatile sample pans, which were capable of withstanding at least 30 psia (207 kPa) internal pressure after sealing. The weight loss of the sample due to vaporization of styrene monomer was found to be negligible.

The kinetic parameters in Eq. 18 were determined using data from DSC runs. For the styrene polymerization, isothermal reaction rate vs. time profiles were measured at three temperatures, 80, 90, and 100°C. For temperatures lower than 80°C, the cure time was greater than 6 h. For temperatures higher than 100°C, the reaction rate was too fast to follow.

TABLE 1. SMC AND STYRENE USED IN THIS STUDY

Ingredient	Sample Designation, Parts by Weight SMC Paste A	Styrene B
Styrene	—	100
65% Unsaturated polyester in styrene (P-340 from OCF)	57.0	—
35% PMMA in styrene (P-701 from OCF)	43.0	—
Filler $CaCO_3$ (Camel White)	138.0	—
Thickening agent $Mg(OH)_2$ (MARICO H)	4.8	—
Lubricant zinc stearate	5.0	—
Initiator TBP*	1.1	—
Initiator BPO†	—	3.0
Inhibitor BQ‡	—	0.26

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* TBP is *t*-butyl perbenzoate, a high temperature initiator.
† BPO is benzoyl peroxide, a low temperature initiator.
‡ BQ is benzoquinone, an inhibitor.

Isothermal DSC runs were ended when there was no further exotherm. Samples were then reheated from 45 to 200°C in the scanning mode with a heating rate of 10°C/min to determine the residual reactivity left in the isothermally cured samples. Styrene reaction was also carried out in the scanning mode from 45 to 200°C at a heating rate of 5°C/min. Higher heating rate would cause the styrene evaporation problem before the reaction was completed.

For the SMC reaction, isothermal reaction rate vs. time profiles were measured at 107, 117, and 127°C. Isothermal runs were treated the same way as in the styrene polymerization. SMC cure was also carried out in the scanning mode from room temperature to 200°C at heating rates of 10 and 20°C/min. The total heat of reaction was calculated from the area under the DSC curves in each case. Since nearly all thermosetting materials are amorphous, density and heat capacity change little with reaction from liquid to solid or within the temperature range of a typical cure (Van Krevelan, 1972). The rate of reaction can be directly converted from the rate of exotherm measured by DSC.

RESULTS AND DISCUSSION

DSC curves of reaction rate vs. time for SMC reactions in the isothermal mode are shown in Figure 2. In general, the reaction started after an induction time and passed through a maximum. Scanning of the cured samples indicated that the conversion was

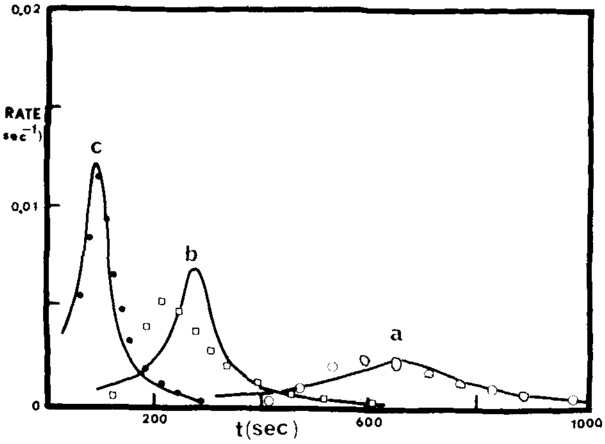

Figure 2. Isothermal DSC curves for SMC reaction; *a*, 107°C; *b*, 117°C; *c*, 127°C. —— model prediction; symbols: experimental data.

TABLE 2. SUMMARY OF ISOTHERMAL DSC RUNS FOR SMC AND STYRENE REACTIONS

Temp. °C	t_z min	Residual Reactivity %	Limiting Conversion %	ΔH cal/g*
		a. SMC Reaction		
107	5.25	19.5	80.5	22.0
117	1.50	6.6	93.4	23.6
127	0.45	1.7	98.3	25.3
		b. Styrene Reaction		
30**	—	17.6	82.4	—
40**	—	15.4	84.6	—
60**	—	8.1	91.9	—
80	64.8	0	100	158.5
90	21.6	0	100	151.2
100	7.4	0	100	158.0

* S.I. conversion: J/g = cal/g × 4.19.
** From Marten and Hamielec (1982).

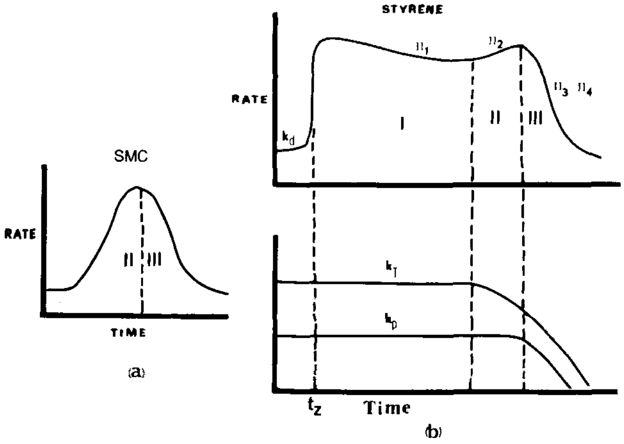

Figure 4. Difference between (a) SMC and (b) styrene reaction, and procedures for parameter estimation.

incomplete for isothermal runs. If one assumed that thermal scanning had brought the reaction to the ultimate cure, the amount of residual reactivity could be calculated. The result together with the induction time, t_z, and heat of reaction for three isothermal experiments is listed in Table 2a.

For the styrene reaction the isothermal rate profiles obtained from DSC shown in Figure 3 are quite different from those for the SMC reaction. The profiles exhibit two peaks, while for the SMC reaction there is only one peak. Again the reaction started after an induction time and reached the first maximum point soon. Subsequently, the reaction rate decreased to a certain point, then climbed up to the second maximum point, and finally decayed rapidly to zero. The higher the temperature was, the faster the reaction rate would get. Unlike the SMC material, no exothermic peak was observed during the scanning runs of the isothermally reacted styrene samples. This suggested that styrene polymerized completely under the given isothermal conditions (i.e., 80–100°C). The limiting conversion of the styrene reaction, however, was found at lower temperatures by Marten and Hamielec (1982), as shown in Table 2b. For styrene reactions, the heat of polymerization calculated from DSC curves shows very good agreement with values reported in the literature (Horie et al., 1968).

The difference between the SMC reaction and the styrene reaction is schematically illustrated in Figure 4. For the styrene polymerization, the earlier part of the reaction, region I, is mainly kinetic controlled since the diffusion effects on both polymer chains and monomers are very insignificant. Both the propagation rate constant, k_p, and the termination rate constant, k_t, remain essentially unchanged. The reaction rate decays primarily due to the consumption of the monomers until a point where the influence of diffusion on the polymer radicals becomes significant. This point is usually called the onset of the gel effect. From then on, as the polymerization proceeds, the termination rate constant decreases appreciably while the propagation rate constant changes very little, as shown in region II. The combined effect is a sharp rise of the reaction rate. This phenomenon is not unexpected in light of the fact that termination is getting more difficult as the radical chains keep growing and appreciable chain entanglements may occur. Meanwhile, the monomer molecules, since they are relatively small, remain less limited to diffusion. Finally, at the later stage of the reaction as shown in region III, because of the high viscosity of the system, even the diffusion of small monomer molecules can fall appreciably. As a consequence, both the termination and propagation rate constants drop, and the reaction rate decreases until the glass transition point where the material changes from the rubbery state to the glass state. This transition essentially freezes the whole reacting system and thus terminates the entire reaction.

For the SMC material, each unsaturated polyester molecule, on the average, has ten or more double bonds (Stevenson, 1980). This would cause the network structure to be formed at the very be-

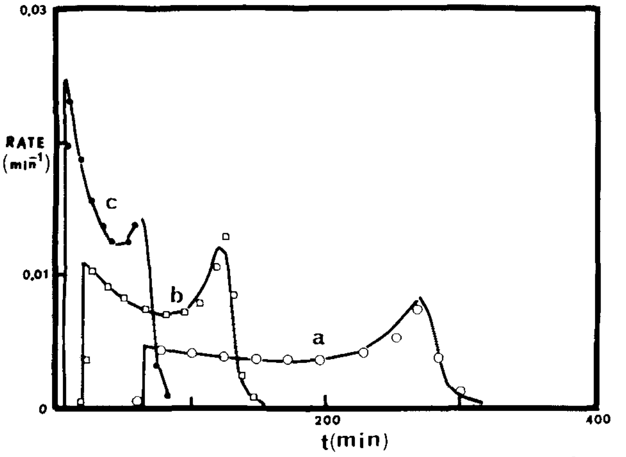

Figure 3. Isothermal DSC curves for styrene reaction; *a*, 80°C; *b*, 90°C; *c*, 100°C. —— model prediction; symbols: experimental data.

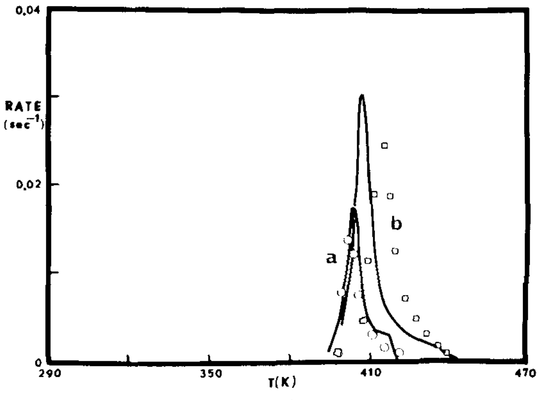

Figure 5. Rate vs. temperature for SMC reaction at scanning rates of: *a*, 10°C/min, *b*, 20°C/min. —— model prediction; symbols: experimental data.

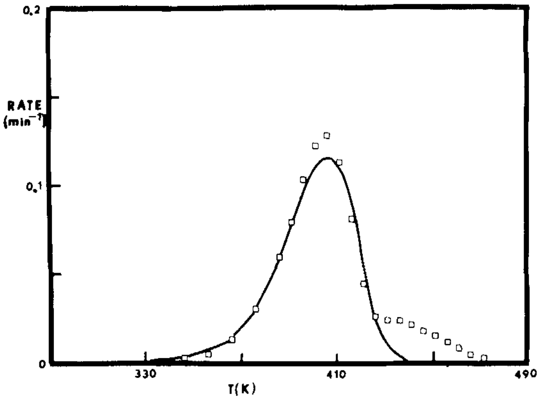

Figure 6. Rate vs. temperature for styrene reaction at scanning rate of 5°C/min. —— model predictions; symbols: experimental data.

ginning of the copolymerization and most of the reaction proceeds after the gelation. Consequently, the reaction is affected by the diffusion effect through almost the entire reaction course, and thereby no region I is observed.

Figures 5 and 6 show the scanning DSC curves of SMC and styrene reactions.

Model Prediction

The kinetic parameters k_d, $2f\bar{I}_O k_{pO}F$, A_M, B_M, $2f\bar{I}_O k_d k_{pO}{}^2/k_{tO}$, A_P/F, B_P and the expression of the free volume fraction V_f are estimated from three isothermal DSC experiments. The expression of the free volume fraction V_f may be established from limiting conversion data (Huang, 1983). From the induction time, k_d can be estimated (Lee, 1981). From the later stage of reaction (i.e., region III—the totally diffusion-controlled region for both free radical chains and monomers), π_3 and π_4 are allowed to be evaluated. From the earlier state of reaction (i.e., region I—the conventional kinetic reaction), π_1 can be determined. Finally, using the above calculated three lumped-sum parameters, π_2 is able to be estimated by fitting the whole reaction curve. A detailed calculation and correlation of these parameters can be found elsewhere (Huang, 1983). A list of numerical values used in the model prediction is given in Tables 3 (styrene) and 4 (SMC) where all parameters assume an Arrhenius temperature dependence except A_P/F because it is a complex function of temperature and molecular weight (Bueche, 1962) that changes continuously as the reaction goes on. For the time being, a second-order polynomial is employed to correlate A_P/F.

TABLE 3. NUMERICAL VALUES OF PARAMETERS FOR MODEL PREDICTION (STYRENE)

$2f\bar{I}_O k_{pO}F$ (min^{-1}) = 0.01 exp(2,681/RT)
$2f\bar{I}_O k_d k_{pO}{}^2/k_{tO}$ (min^{-2}) = 1.8 × 10^{23} exp(−45,214/RT)
A_M (min) = 2.73 × 10^{11} exp(−27,454/RT)
B_M = 0.42
B_P = 0.01837

$$\frac{A_P}{F}\,(\text{min}) = \exp\left[a' + b'\left(\ln\frac{1}{V_f} - \ln\frac{1}{\bar{V}_{fO}}\right) + c'\left(\ln\frac{1}{V_f} - \ln\frac{1}{\bar{V}_{fO}}\right)^2\right]$$

where
$a' = -14.83 + 6{,}845/T$
$b' = -14.17 + 5{,}213/T$
$c' = -8.56 + 2{,}473/T$
$\ln 1/\bar{V}_{fO} = 3.2824$

TABLE 4. NUMERICAL VALUES OF PARAMETERS FOR MODEL PREDICTION (SMC)

$2f\bar{I}_O k_{pO}F$ (s^{-1}) = 0.023 exp(2,297/RT)
$2f\bar{I}_O k_d k_{pO}{}^2/k_{tO}$ (s^{-2}) = 0
A_M (s) = 2.42 × 10^{-27} exp(48,406/RT)
B_M = 0.09
B_P = 4.48 × 10^{-5} exp(7,901/RT)

$$\frac{A_P}{F}\,(\text{s}) = \exp\left[a' + b'\left(\ln\frac{1}{V_f} - \ln\frac{1}{\bar{V}_{fO}}\right) + c'\left(\ln\frac{1}{V_f} - \ln\frac{1}{\bar{V}_{fO}}\right)^2\right]$$

where
$a' = \exp(-9.22 + 4{,}866/T)$
$b' = 282.1 - 12{,}263/T$
$c' = 1{,}366.85 - 7.36/T + 0.0098T$
$\ln 1/\bar{V}_{fO} = 2.28 + 384/T$

The predicted rate of reaction vs. time curves and conversion profiles of isothermal DSC experiments for the SMC reaction are shown in Figures 2 and 7. For comparison, predictions from a kinetic model with no-diffusion and no-termination assumptions developed in a previous work (Lee, 1981) are also shown in Figure 7. The new model apparently predicts the experimental data much better, especially at higher conversions where the limiting conversion exists.

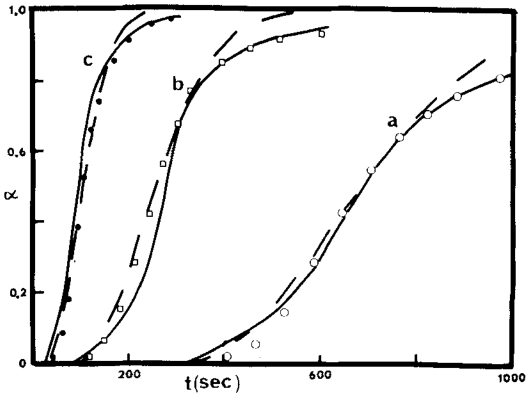

Figure 7. Conversion vs. time for isothermal SMC reactions; *a*, 107°C; *b*, 117°C; *c*, 127°C. —— model prediction; ---- no diffusion, no termination model (Lee, 1981); symbols: experimental data.

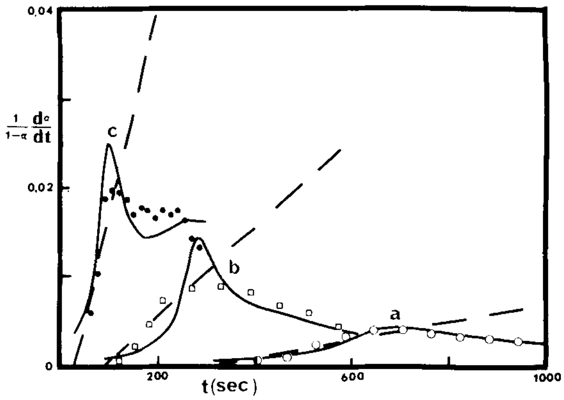

Figure 8. Accuracy of various kinetic models for SMC reactions; *a*, 107°C; *b*, 117°C; *c*, 127°C. —— model prediction; ---- no diffusion, no termination model (Lee, 1981); symbols: experimental data.

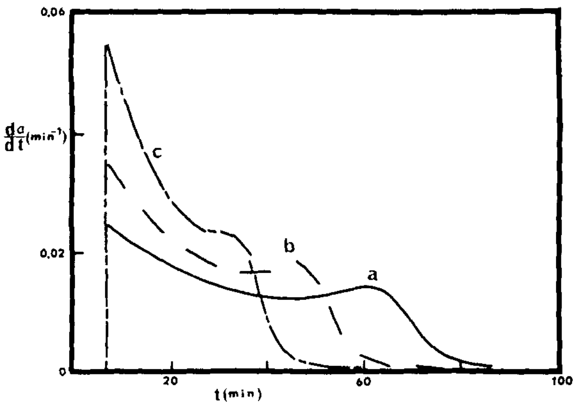

Figure 9. Effect of changing π_1 on isothermal rate profiles of styrene reaction at 100°C; *a*, $\pi_1 = \pi_{10}$; *b*, $\pi_1 = 2\pi_{10}$; *c*, $\pi_1 = 5\pi_{10}$.

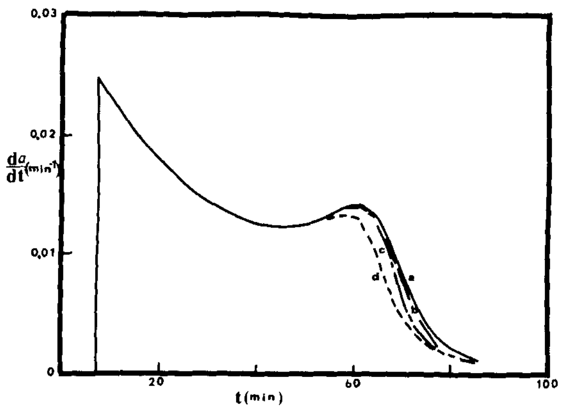

Figure 11. Effect of changing π_4 on isothermal rate profiles of styrene reaction at 100°C; *a*, $\pi_4 = 0$; *b*, $\pi_4 = \pi_{40}$; *c*, $\pi_4 = 10\pi_{40}$; *d*, $\pi_4 = 100\pi_{40}$.

Under isothermal conditions, the accuracy of various kinetic models for SMC reaction can also be judged by plotting $1/(1 - \alpha)d\alpha/dt$ vs. time. For the no-diffusion and no-termination model (Lee, 1981)

$$\frac{1}{1-\alpha}\frac{d\alpha}{dt} \approx 2f\bar{I}_O k_{pO} k_d (t - t_z) \qquad (22)$$

If the model governed by Eq. 22 is correct, a nearly straight line should result. Experimental data in Figure 8, however, show an appreciable deviation in the later part of the reaction. The new model developed in this work, which considers both diffusion and termination effects, gives a much better prediction.

For styrene reactions, Figure 3 gives the comparison of calculated curves vs. experimental data. For the isothermal reactions at 100, 90, and 80°C, this model successfully predicts the rate profiles.

In order to test the validity of the model, Eq. 18 has also been applied to predict the rate of reaction curves of scanning DSC experiments, as shown in Figure 5 for the SMC reaction and Figure 6 for the styrene reaction. The Runge-Kutta-Gill fourth-order method has been used in the numerical calculation of the model prediction (Carnahan et al., 1969). For the SMC reaction, predictions of the model are fairly good considering that the kinetic mechanism for the complicated SMC compound is much simplified. For the styrene reaction, the proposed model is not able to predict the second peak of the scanning rate profile (Figure 6). This discrepancy is partially due to the existence of the thermal initiation of styrene monomers at higher temperature, which the model has not accounted for. Literature data (Cuadrado et al., 1983; Marten and Hamielec, 1982) have shown that significant thermal initiation occurs at temperatures higher than 160°C for the styrene reaction. Invalidity of diffusion parameters extrapolated to the higher temperature range may also cause some errors in the model prediction. Such assumptions as neglecting of chain transfer reaction and the pseudosteady state assumption of the growing radical chain may also be improper (Soh and Sundberg, 1982d) when applied to the styrene reaction.

Calculated Effects of Parameters on Reaction Kinetics

The effects of the four lumped-sum parameters on the reaction kinetics have been simulated using the model prediction curve of the styrene reaction at 100°C as a reference.

Figure 9 shows the effect of changing π_1 on the reaction rate. π_1 can be increased by increasing the initiator concentration or by choosing a low temperature initiator (increasing k_d). As expected, increasing π_1 speeds up the reaction rate at the earlier stage of the reaction. Figure 10 shows the effect of changing π_2 or π_3 on the reaction rate profiles. According to Eq. 18, π_2 and π_3 are multiplied by each other to give a joint effect on the reaction kinetics. This is because the larger the termination resistance, the faster the prop-

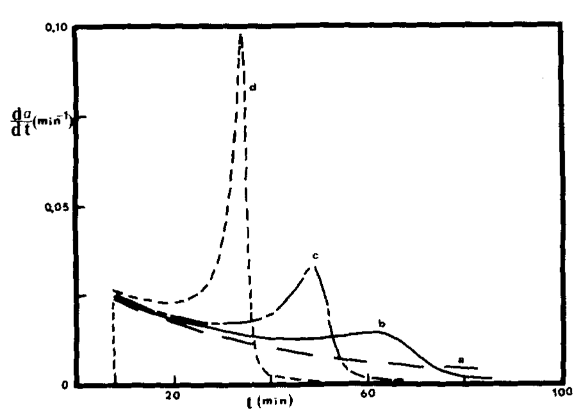

Figure 10. Effect of changing π_2 or π_3 on isothermal rate profiles of styrene reaction at 100°C; *a*, $\pi_2\pi_3 = 0$; *b*, $\pi_2\pi_3 = \pi_{20}\pi_{30}$; *c*, $\pi_2\pi_3 = 2\pi_{20}\pi_{30}$; *d*, $\pi_2\pi_3 = 5\pi_{20}\pi_{30}$.

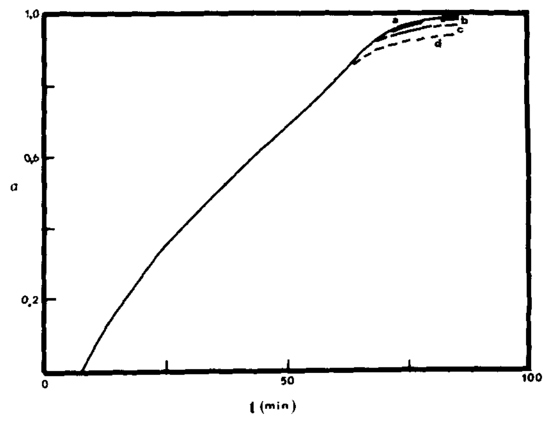

Figure 12. Effect of changing π_4 on isothermal conversion profiles of styrene reaction at 100°C; *a*, $\pi_4 = 0$; *b*, $\pi_4 = \pi_{40}$; *c*, $\pi_4 = 10\pi_{40}$; *d*, $\pi_4 = 100\pi_{40}$.

agation rate, and a mathematical multiplication effect thus results. π_2 can be increased by decreasing the reaction temperature, increasing the reaction pressure, or adding a crosslinking agent to the system. Employing pressure may lower the free volume of the system while decreasing temperature or adding a crosslinking agent may reduce the molecular diffusivity. π_3 can be increased in the same way as π_1. Figure 10 shows that increasing π_2 or π_3 raises the reaction rate over the gel effect region and causes an earlier onset of the gel effect. π_4 can be increased essentially in the same way as π_2. Figure 11 shows the effect of changing π_4 on the reaction rate. As expected, increasing π_4 lowers the reaction rate at the later part of the reaction. Figure 12 shows that varying π_4 also changes the limiting conversion.

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NOTATION

A_e = equivalent mass transfer area for propagation
A_M = A'/A'_M
Ap = A''/A'_p
A' = $v_s \delta e/Ae$
A'_e = same as Ae except for termination
A'_M, B_M = parameters for monomer diffusion
A'_p, B_p = parameters for polymer diffusion
A'' = $v'_s \delta e'/Ae'$
D_M = self-diffusivity of monomer
D_p = self-diffusivity of polymer radical
f = initiator efficiency
F = parameter defined in Eq. 19
ΔH = heat of reaction
I = initiator (concentration)
I_o = initial initiator concentration
$\bar{I}_o$ = initiator concentration after all inhibitors have been consumed
K_1, K_2 = constants
k_d = initiator decomposition rate constant
k_i = initiation rate constant
k_p = propagation rate constant
k_{po} = true propagation rate constant
k_t = termination rate constant
k_{to} = true termination rate constant
k_z = inhibition rate constant
l = length scale of diffusion
l_c = radius of diffusion sphere
m,n = order of reaction
M = monomer (concentration)
M' = monomer concentration within the diffusion sphere
M'_j = growing polymer radical with degree of polymerization j (concentration)
P_j = dead polymer with degree of polymerization j
q = inhibitor efficiency
R = primary initiator radical
r'_p = global polymerization rate
t_z = induction time
T = reaction temperature
Tg = glass transition temperature
v = volume
v_s = volume of diffusion sphere for propagation
v'_s = same as v_s except for termination
V_f = free volume fraction
V_{fgm}, V_{fgp} = free volume fraction of monomer and polymer at glass state
Z = inhibitor (concentration)
Z_O = initial inhibitor concentration

Greek Letters

α = fractional conversion
β = difference of thermal expansion coefficients above and below Tg
δ_e = equivalent diffusion distance for propagation
δ'_e = equivalent diffusion distance for termination
ϵ = volume expansion coefficient
λ = numerical factor of ϵ due to the glass transition
$\pi_1, \pi_2, \pi_3, \pi_4$ = lumped-sum parameters defined in Eq. 18

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