Effects of Resin Chemistry on Redox Polymerization of Unsaturated Polyester Resins

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ABSTRACT: Unsaturated polyester resins are the most widely used thermoset resins in the composite industry. In this study, three well-defined unsaturated polyester resins were used. These resins have similar number-average molecular weights, and they have different numbers of C=C bonds per molecule. The reaction kinetics of unsaturated polyester resins was studied using a differential scanning calorimeter (DSC) and a Fourier transform infrared (FTIR) spectrometer. The glass transition temperature of the isothermally cured resin was also measured. Trapped radicals were observed in the cured polyester resin from electron spin resonance (ESR) spectroscopy. Considering the diffusion-limitation effect, a simple kinetic model was developed to simulate the reaction rate and conversion profiles of polyester vinylene and styrene vinyl groups, as well as the total reaction rate and conversion. Experimental results from DSC and FTIR measurements compare favorably with the model prediction. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 211–227, 2002; DOI 10.1002/app.10317

Key words: thermosets; curing of polymers; crosslinking; networks; glass transition

INTRODUCTION

Among various thermoset resins, unsaturated polyesters (UPs) are the most widely used matrix materials in polymeric composites.[1,2] UP resins are step-growth products formed by unsaturated acids (or anhydrides), saturated aromatic acids, and difunctional alcohols. They are usually diluted by adding a low molecular weight comonomer (e.g., styrene) to adjust the viscosity of the mixture. The advantages of UP resins include their low cost, thermal and dimensional stability, good electrical insulation, excellent mechanical properties, good chemical resistance, and low density. UPs have many applications in automotive, aircraft, electrical, and appliance components. They are processed over a wide temperature range involving hand lay-up at low temperatures, resin-transfer molding at medium temperatures, and sheet-molding compound (SMC) compression molding, bulk-molding compound (BMC) injection molding, and pultrusion at high temperatures.[3] Their processibility and properties can be adjusted by changing either the nature of the UP chain or the ratio of the styrene/polyester content.

The reaction of a UP resin is a free-radical chain-growth crosslinking copolymerization between the styrene monomer and the UP molecules. The reaction involves a sequence of steps: initiation, inhibition and/or retardation, propagation, and termination. Polyester molecules are the crosslinkers while styrene serves as the agent to link adjacent polyester molecules.[4] The polymer chains grow and become crosslinked in three possible reactive processes: styrene–polyester co-

Table I   Properties of Three Well-Defined UP Resins

	Monomers	M_W/C=C (g/mol)	M_n (g/mol)	M_w (g/mol)	Molecular Weight Distribution (MWD)	N (Average No. of C=C/Molecule)
UP-3	PPG-425 MA	505	1682	3577	2.13	3.1
UP-6	TPG MA	272	1517	6615	2.85	5.6
UP-10	PG MA	156	1600	N/A	N/A	10

polymerization, styrene homopolymerization, and polyester homopolymerization.

The curing behavior is complex due to the interaction between the resin chemistry and the variation of the physical properties. Before the free-radical polymerization proceeds, the resin is a viscous liquid. During the curing reaction, the chain length of the resin molecules grows through the crosslinking reaction of functional groups and the resin becomes more viscous. As the curing advances further, the reacting system forms a highly crosslinked network, which results in a rapid increase in the resin viscosity. Gelation corresponds to the formation of the first insoluble fraction of the polymer with an infinite molecular weight. The gel conversion for UPs is usually less than 5%.[5,6] It was found that the actual crosslinking behavior of UPs deviates greatly from the classical Flory gelation theory, which assumes no intramolecular reaction. The explanations for this deviation include cyclization due to the intramolecular reaction, the reduced activity of pendant vinyl groups, and the shielding effect of microgel formation on the reaction of pendant vinylene groups.[7] The intramolecular reaction allows the long-chain molecules to form a spherical-type structure with high cyclization and crosslinking density, described as a "microgel."[8] Inside the microgel, some of pendant groups may remain unreacted because of the shielding effect of the network. This nonideal crosslinking strongly influences the reaction kinetics, rheological behaviors, and properties of the UP resins.

The glass transition temperature, T_g, is the most important material parameter of a glassy polymer. Processing of a reactive polymer must be performed at temperatures above the T_g of the uncured material, so that it is in a liquid state. To reach the maximum conversion, the reaction temperature needs to be higher than the T_g of the fully cured resin. Gillham and Enns[9] suggested that the glass transition temperature could be used to monitor the extent of a cure, since T_g is

much more sensitive to resin conversion in the later stage of a cure. The relationship between T_g and the fractional conversion determines when solidification (vitrification) occurs during a cure.[10–12] If T_g is much lower than the curing temperature, then the reaction of a thermoset polymer proceeds at a rate dictated by the reaction kinetics. When T_g is near or higher than the curing temperature, the reaction rate decreases by as much as several orders of magnitude due to the lack of mobility of reactive groups.[13]

The reaction kinetics and rheological behaviors of UP resins were studied extensively[10,14–21] based on commercial resins, which have different chemical structures. In this study, three well-defined polyester resins were used. These resins have similar number-average molecular weights and different numbers of C=C bonds per molecule. The effects of the degree of resin unsaturation on the curing behaviors of polyesters were investigated.
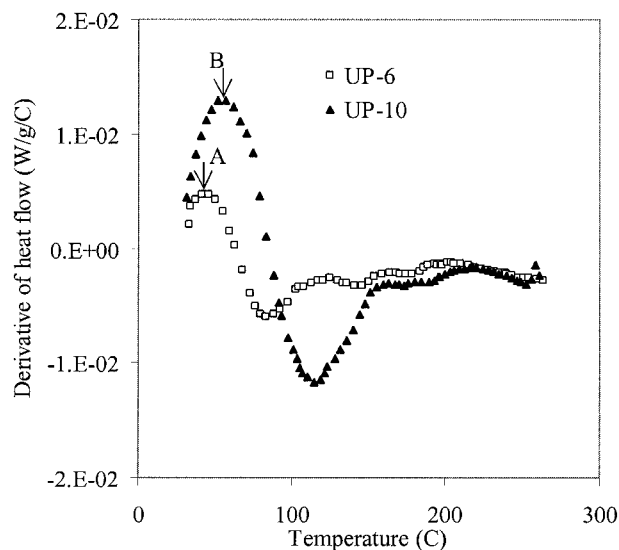

Figure 1 Identification of glass transition temperatures for unsaturated polyester resins partially cured at 35°C in DSC (0.8 wt % MEKP, 0.1 wt % Co).
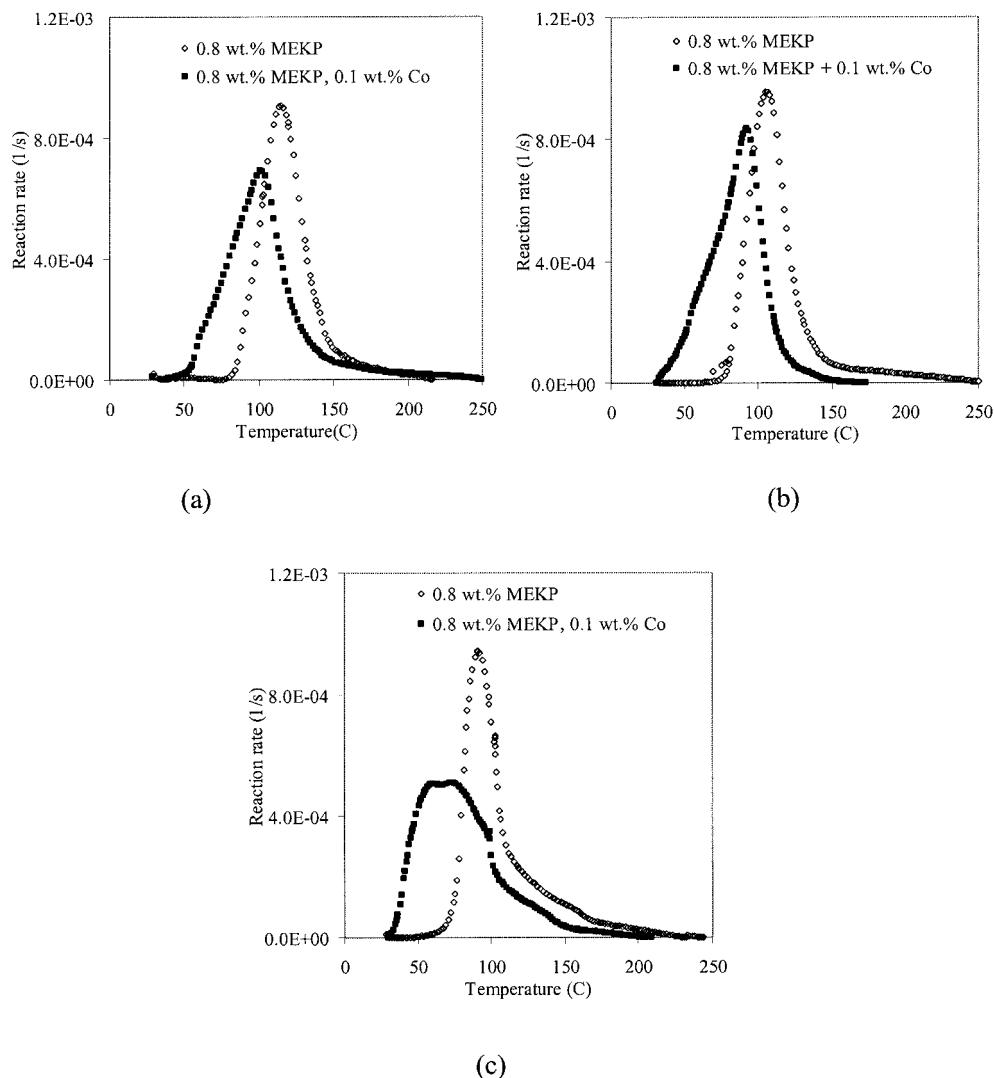
(a)

(b)

(c)

Figure 2   Scanning reaction rate profiles measured by DSC for (a) UP-3, (b) UP-6, and (c) UP-10.

EXPERIMENTAL

Materials

The three resins used are based on maleic anhydride and several different types of propylene glycols. Maleic anhydride is used to provide vinylene groups for the polyester resins. Different degrees of unsaturation of the resins are obtained by choosing various propylene glycols. Polypropylene glycol, tripropylene glycol, and propylene glycol were used as chain extenders for the three resins, respectively. The curing temperature was 199°C and the ratio of the hydroxy to carboxy group was maintained at 1.1. The reaction was stopped when the number-average molecular weight was around 1600 g/mol, as measured by gel permeation chromatography (GPC). Detailed properties of the materials and their corresponding resin codes are given in Table I. The number-average molecular weights for the three resins are similar, ranging from 1517 to 1682 g/mol, but the degree of unsaturation varies. The average number of vinylenes per molecule ranges from 3.1 to 10. The resin codes UP-3, UP-6, and UP-10 correspond to the average degree of unsaturation. UP-10 has the highest degree of unsaturation, while UP-3 has the lowest degree of unsaturation. For all three polyester resins, different amounts of styrene were added to achieve a molar ratio of 2 between styrene and UP vinylene C=C bonds.
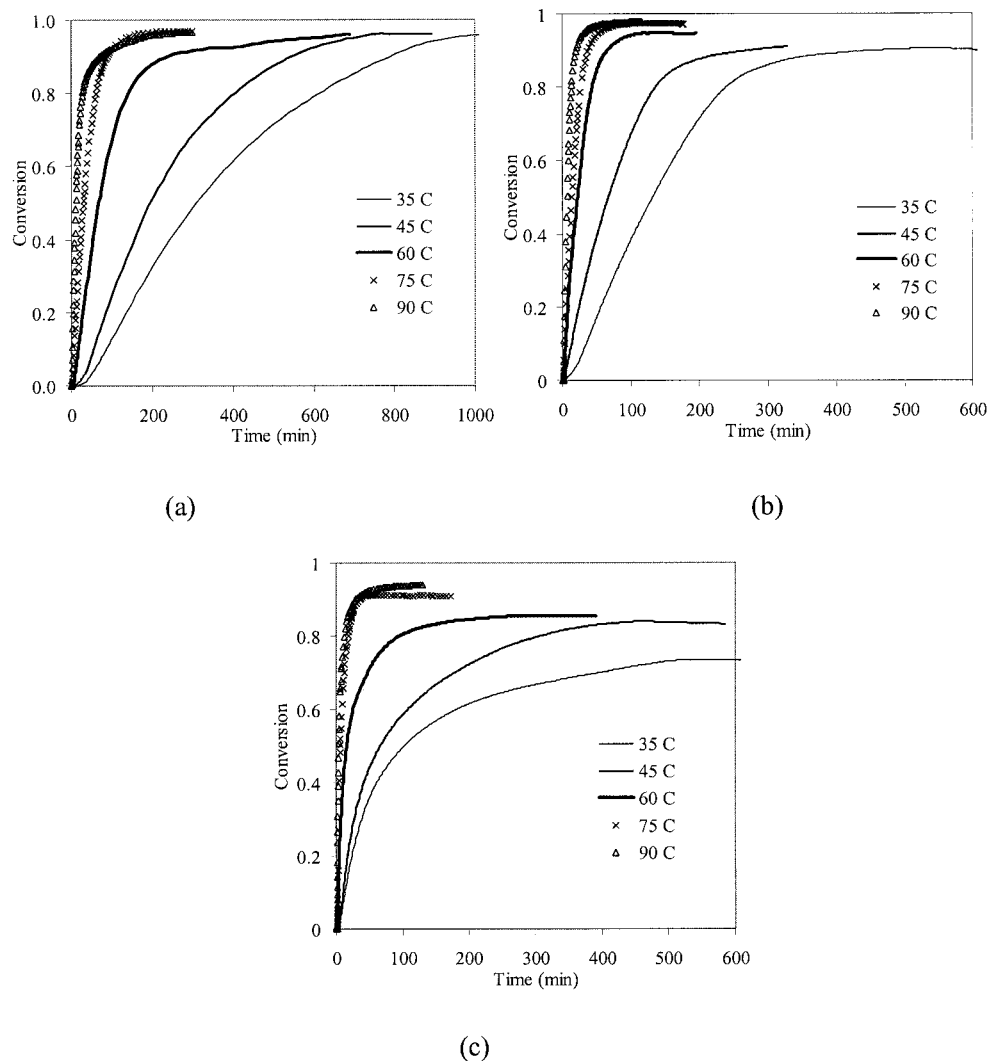
Figure 3 Conversion profiles of unsaturated polyester resins at different temperatures measured by DSC for (a) UP-3, (b) UP-6, and (c) UP-10 (0.8 wt % MEKP, 0.1 wt % Co).

An amount of 0.8 wt % methyl ethyl ketone peroxide (MEKP) from Fluka and 0.1 wt % cobalt octoate (Co) from Pfaltz & Bauer were used as the initiator and promoter, respectively. All materials were employed as received without further purification.

Instrumentation and Procedures

A differential scanning calorimeter (Model 2910, TA Instruments) was used to measure the overall reaction rate profiles. Differential scanning calorimetry (DSC), which measures the rate of heat generated (dQ/dt) during a chemical reaction, is used extensively in the determination of kinetic

parameters for curing thermoset resins. The principle of DSC kinetic measurements is based on the fact that the change in heat flow is proportional to the change in the extent of the reaction, α, that is,

$$\frac{d\alpha}{dt} = \frac{1}{Q_0}\frac{dQ}{dt} \tag{1}$$

where Q_0 is the overall heat of the reaction. The reaction conversion is then evaluated as a function of time by the integration of eq. (1).

The experimental procedures to measure the overall reaction rate using DSC were as follows:

The reactions were conducted in volatile aluminum sample pans, which are capable of withstanding at least 2 atm internal pressure after sealing. When using DSC, the sample size may affect the exotherm profile. To keep the consistency, the DSC samples of 10 mg were used in this study to measure the reaction exotherm. The isothermal reaction rate was measured from 35 to 90°C. Isothermal DSC runs were ended when there was no furthur exotherm, and scanning runs of isothermally cured samples were carried out from room temperature to 300°C with a heating rate of 5°C/min to determine the residual heat and the glass transition temperature of the partially cured sample. The total heat of reaction is the sum of the isothermal reaction heat and the residual heat. For the uncured samples, the reaction exotherm was also measured in the scanning mode, ranging from an ambient temperature to 300°C at a heating rate of 2°C/min.

Because the cured UP-3 resin is a rubberlike material, the glass transition temperature of the cured resin is below the temperature range studied. For UP-6 and UP-10, DSC was used to determine the glass transition temperature of the partially cured resins. All measurements were performed at a program ramp rate of 5°C/min from room temperature to 300°C. For the partially cured sample, a peak was observed in the derivative of the heat-flow curve right before the beginning of the reaction, as shown in Figure 1. The corresponding peak temperature represents the glass transition temperature of the partially cured resin sample.[22] For example, points A and B in Figure 1 correspond to the glass transition temperatures for UP-6 and UP-10, respectively.

In the polyester–styrene reaction, the initiator decomposes chemically, generating free radicals. These radicals react with either styrene vinyl or the polyester vinylene groups. The DSC can measure the overall heat release during the reaction, but cannot differentiate among multiple overlapping reactions. In this study, an FTIR spectrometer (Nicolet, Magna-IR 550) was used to differentiate the rates of isothermal reactions of polyester and styrene carbon–carbon double bonds based on the spectral changes of different functional groups. The FTIR spectrometer was operated at a resolution of 4 cm^{-1} in the transmission mode and equipped with a heating device. After the sample was prepared, a drop of the mixture was pasted between two sodium chloride plates without a spacer, then mounted onto a sample holder in the FTIR instrument. The
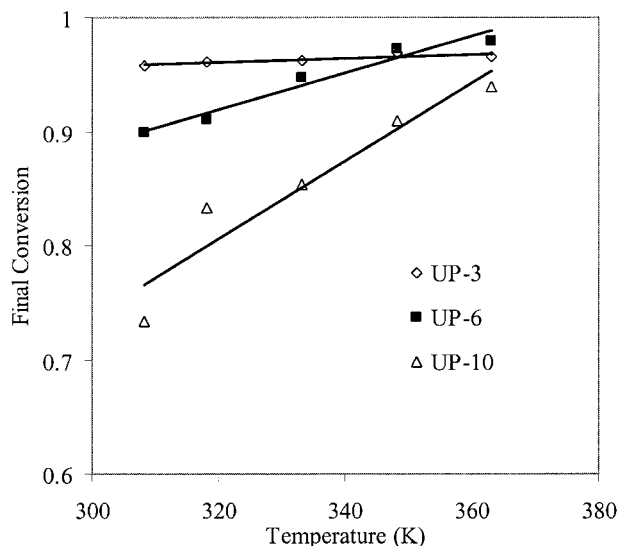

Figure 4 Final conversion as a function of curing temperature for various unsaturated polyester resins.

conversions of polyester and styrene carbon–carbon double bonds were calculated based on the changes of the corresponding absorbance spectra obtained by the FTIR. For the styrene–UP resins, the content of the styrene monomer can be determined from the peaks at 912 and 992 cm^{-1} (CH$_2$=CH deformation), while that of the C=C bonds of UP resins can be determined from a peak at 982 cm^{-1} (*trans*-CH=CH deformation).[19] To compensate for changes of the sample thickness and opacity during curing, the peak at 700 cm^{-1} was used as the internal standard to normalize the spectral area. All IR spectra in this study are shown in absorbance. The sampling interval was set at 1–2 min. The software *OMINIC Macros* was used to perform automatic sampling at specified time intervals, and the measurement was ended when no changes were observed in the absorbance peak area. Detailed measurement procedures for the FTIR were given elsewhere.[4,19]

The gel time of the polyester resins were measured in a temperature-controlled water bath. The resin mixture was poured into a glass vial with a screw cap. Then, the vial was placed in the water bath for the isothermal reaction. The vial was stirred gently during the reaction to maintain uniform temperature distribution. The gel time was recorded when the resin changed from a viscous liquid to a gel.

An electron spin resonance (ESR) spectroscope (Bruker ESP 300) was used to measure the concentration of free radicals in the cured polyester

Table II   Values of Parameters in the Linear Relation Between the Final Conversion and the Curing Temperature, $\alpha_f(T) = A + BT$ (T in K)
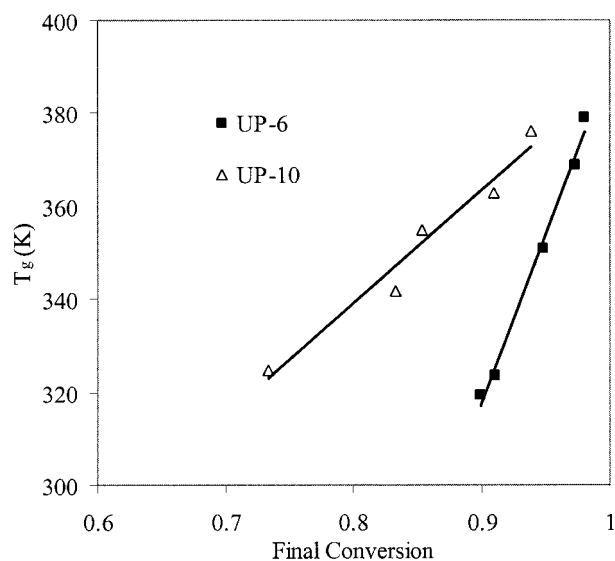
Resin Type	A	$B \times 10^4$
UP-3	0.91	2
UP-6	0.41	16
UP-10	−0.28	34

Table III   Values of Parameters in the Linear Relation Between the Glass Transition Temperature and the Final Conversion, $T_g = a + b\alpha_f$ (T_g in K)

Resin Type	a	b
UP-6	−342	733
UP-10	145	243

resin. The polyester resin was placed into the quartz ESR sample tube after the curing agents were added. Then, the sample tube was placed in a water bath and the reaction temperature was kept at 60°C. After the reaction was completed, the cured resin sample was measured by ESR within 24 h. ESR spectroscopy directly traces the behavior of unpaired electrons. The measured overall intensity of the absorption line reflects the number of paramagnetic species in the sample. The concentration of radicals is determined by the double integration of the observed ESR spectrum.[23]

RESULTS AND DISCUSSION

Reaction Kinetics Measured by DSC

Figure 2 shows the DSC scanning curves of polyester resins cured at a heating rate of 2°C/min under two different conditions: with MEKP and

Figure 5 Glass transition temperature (T_g) as a function of final conversion.

with both MEKP and Co. It was observed that with MEKP the reaction was caused mainly by the thermal decomposition of peroxides. Only one exotherm peak is observed and the maximum reaction rates are similar for all resins. The difference among them is the temperature to initiate the reaction. As shown in Figure 2, the temperatures that initiates the reaction for UP-3, UP-6, and UP-10 are 80, 75, and 60°C, respectively.

With the aid of a metallic promoter such as cobalt octoate, the formation of radicals may result from the redox decomposition of peroxides, allowing the reaction to occur at low temperatures. The mechanism of the redox decomposition of peroxides is shown in eqs. (2) and (3):

$$\text{ROOH} + \text{Co}^{2+} \xrightarrow{k_{d1}} \text{RO}^{\bullet}(\text{R}^{\bullet}) + \text{OH}^- + \text{Co}^{3+} \quad (2)$$

$$\text{ROOH} + \text{Co}^{3+} \xrightarrow{k_{d2}} \text{ROO}^{\bullet}(\text{R}^{\bullet}) + \text{H}^+ + \text{Co}^{2+} \quad (3)$$

where ROOH is the initiator, Co^{2+} (Co^{3+}) is the promoter, and $R^{\bullet}$ represents the primary free radicals that are decomposed from the initiator. k_{d1} and k_{d2} are rate constants of the redox decomposition. Either Co^{2+} or Co^{3+} is able to generate free radicals in a redox (reduction and oxidation) cycle. Therefore, a small amount of a promoter can induce a large amount of an initiator due to the regeneration of cobalt ions. For all three polyester resins, when the promoter (Co) is added, the maximum reaction rate decreases, particularly for UP-10. With both MEKP and Co, the scanning reaction of UP-3 occurs at about 50°C. In contrast, for UP-6 and UP-10, the scanning reaction occurs at an even lower temperature, at approximately 30°C. Thus, the polyester resin with a higher degree of unsaturation tends to be more reactive at low temperatures.
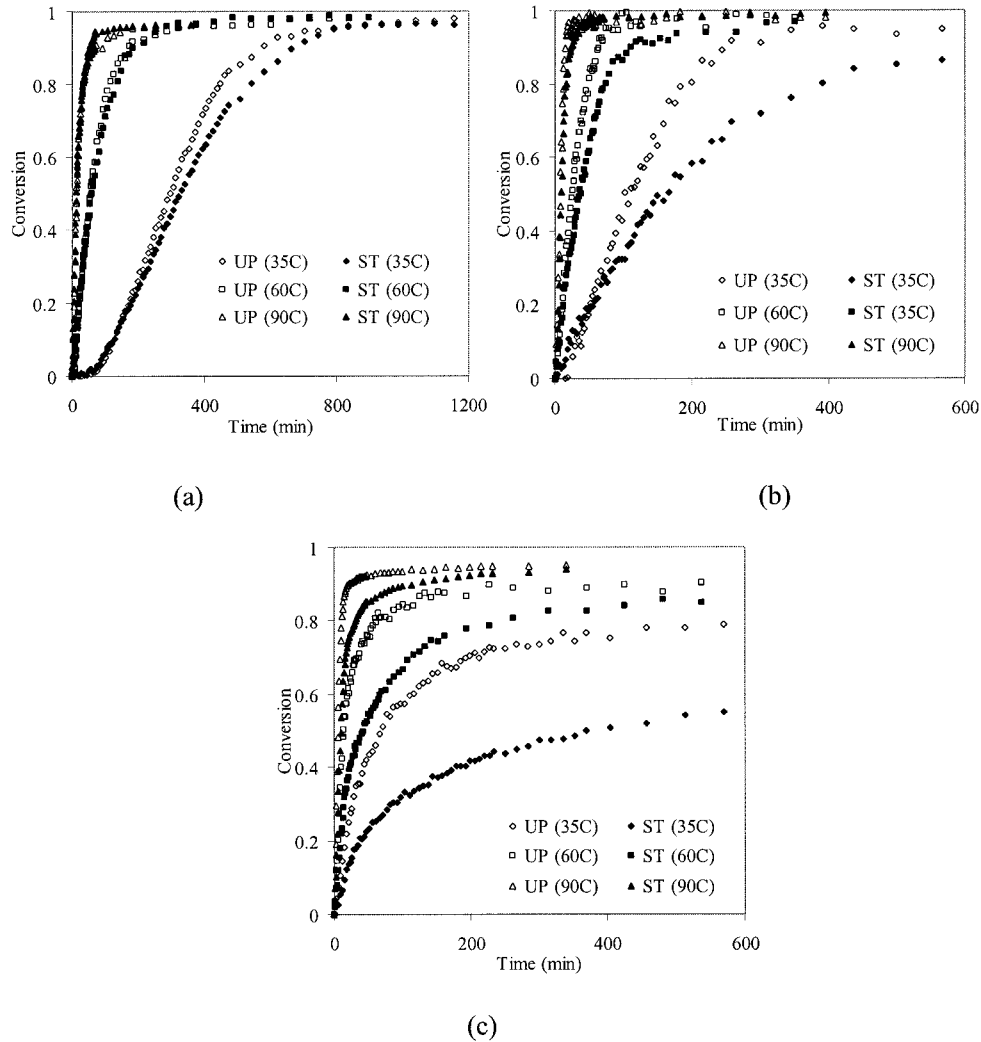
Figure 6 Conversion profiles of unsaturated polyester vinylene and styrene vinyl groups measured by FTIR at different temperatures for (a) UP-3, (b) UP-6, and (c) UP-10 (0.8 wt % MEKP, 0.1 wt % Co).

To examine the effect of the curing temperature on the reaction kinetics, isothermal polymerizations were conducted at 35, 45, 60, 75, and 90°C using DSC. Figure 3 shows the conversion profiles of the three resins at different temperatures, demonstrating that for all three resins the time required to reach the final conversion is reduced with increasing temperature. For UP-3, the final conversion did not change significantly for curing temperatures between 35 and 90°C, although at lower temperatures, UP-3 required a longer time to reach the final conversion. The final conversions at different curing temperatures for UP-3 were unchanged, because the curing temperature (between 35 and 90°C) is higher than is the glass transition temperature of the

cured resin. The maximum final conversion of UP-3 is approximately 97%. On the other hand, for UP-6 and UP-10, a higher temperature results in a higher final conversion. The final conversion of UP-6 at 35, 45, 60, 75, and 90°C is 90.0, 92.0, 95.2, 97.2, and 98.2%, respectively, while for UP-10, it is 69.5, 83.9, 88.8, 91.9, and 96.5%, respectively. It was shown that the polyester resin with a higher degree of unsaturation has a lower final conversion at the same temperature. A possible reason is that the crosslink density in UP-6 and UP-10 is relatively high. For the resin with a higher degree of unsaturation, more unreacted $C{=}C$ bonds are trapped inside the matrix when the resin vitrifies, resulting in a lower final conversion. The relationship between the final con-
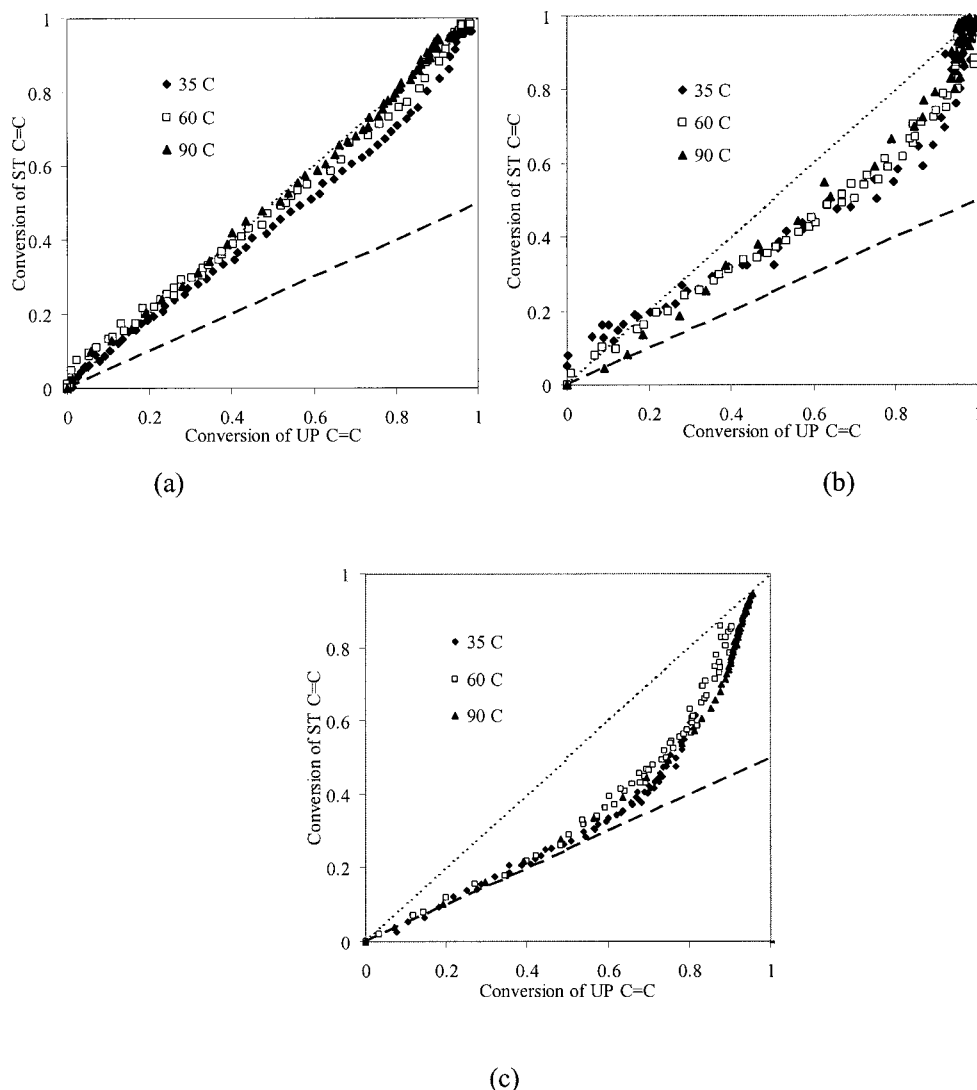
Figure 7 Relative conversions of styrene vinyl versus unsaturated polyester vinylene groups at different temperatures for (a) UP-3, (b) UP-6, and (c) UP-10 (0.8 wt % MEKP, 0.1 wt % Co).

version and the curing temperature for the three resins is clearly seen in Figure 4. For the temperature range studied, the final conversion can be described as a linear function of the curing temperature:

$$\alpha_f(T) = A + BT \qquad (4)$$

where parameters A and B are obtained by fitting the experimental results from the DSC. The values of the parameters are shown in Table II. Parameter B indicates the sensitivity of the final conversion to the temperature change. As can be seen in Table II, by increasing the temperature,

the final conversion of UP-10 is increased more significantly than in UP-6. For UP-3, the temperature has no significant effect on the final conversion.

Glass Transition Temperature

In Figure 5, the glass transition temperatures of the partially cured samples are plotted as a function of the final conversion, α_f, at different temperatures. For both UP-6 and UP-10, the glass transition temperature of the partially cured samples increases progressively with an increase in the final conversion. A linear function is used to correlate the relation between the glass transition

Table IV   Gel Time and Gel Conversion of Polyester Resins

Resin Type	Gel Time (min)	Total Gel Conversion (%)
UP-3	62.0 ± 1.0	5.27 ± 0.18
UP-6	10.0 ± 0.6	1.36 ± 0.20
UP-10	5.3 ± 0.5	2.47 ± 0.76

temperature and the final conversion within the conversion range studied:

$$T_g = a + b\alpha_f \tag{5}$$

where parameters a and b are obtained by fitting experimental results from the DSC measurements. The parameter b indicates the sensitivity of the glass transition temperature to the change in the final conversion. The values of a and b for the two polyester resins are shown in Table III. It can be seen that, by increasing the final conversion, the glass transition temperature increases more significantly for the resin with a lower degree of unsaturation. A possible explanation is that for the resin with a higher degree of unsaturation more C=C bonds are trapped inside the formed polymer. These trapped C=C bonds may engage in the intramolecular reaction, increasing the density of the polymer; however, the intramolecular reaction does not contribute significantly to the increase of the glass transition temperature. On the other hand, for the resin with a lower degree of unsaturation, more C=C bonds may engage in the intermolecular reaction, which would increase the glass transition temperature more efficiently.

Relative Conversion Profiles as Measured by FTIR

Figure 6 shows the conversion profiles of polyester and styrene C=C bonds as measured at different temperatures by FTIR. It was found that for UP-3 the polyester and styrene C=C bonds have similar reaction rates, and the final conversions of polyester and styrene C=C bonds do not vary much with temperature. By contrast, for
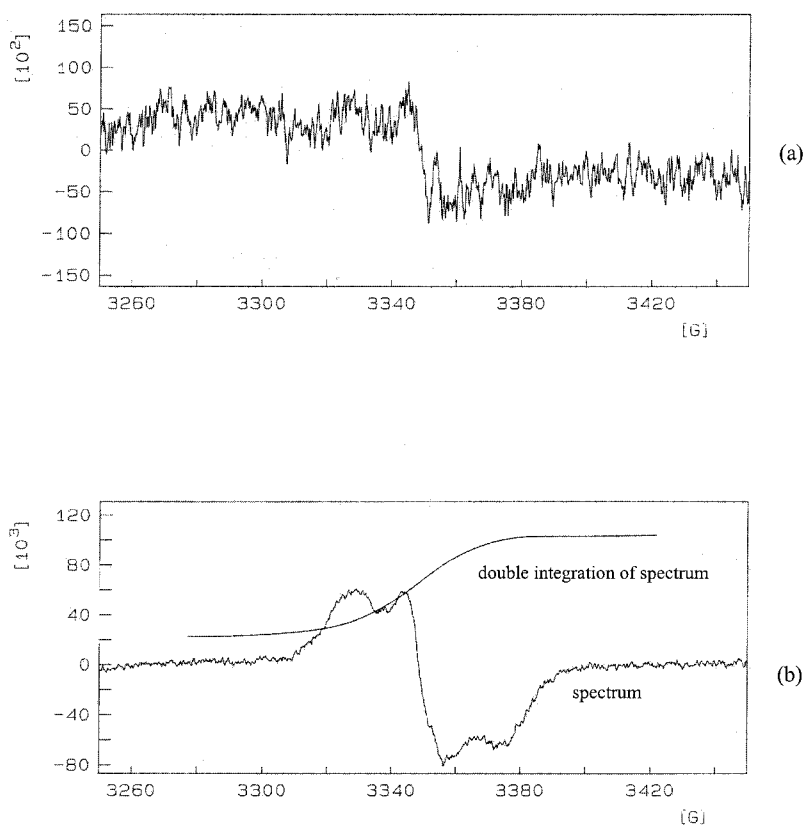
Figure 8   ESR spectra for (a) the cured UP-3 resin and (b) the cured UP-10 resin (0.8 wt % MEKP, 0.1 wt % Co, cured at 60°C).

Table V Values of Parameters in the Kinetic Model for Polyester Resins

Resin Type	Temperature (°C)	K_d ($\times 10^6$) (1/s)	K_{p10} (1/s)	K_{p20} (1/s)	m
UP-3	35	6	0.0027	0.0021	1.1
	60	8	0.0248	0.0218	
	90	10	0.287	0.29	
UP-6	35	6	0.013	0.0063	1.5
	60	8	0.182	0.086	
	90	10	1.66	1.056	
UP-10	35	6	0.106	0.015	3
	60	8	1.09	0.185	
	90	10	10.1	1.81	

UP-6 and UP-10, a higher temperature results in a higher final conversion of both polyester and styrene C=C bonds, and at all temperatures, the conversion of polyester C=C is higher than for styrene during the entire reaction. The difference between these two conversions, however, becomes smaller at higher temperatures. Also, the difference between the styrene and UP C=C conversions increases with an increase in the degree of resin unsaturation. This observation may be explained by the existence of highly crosslinked polymer molecules in the polyester resin. As discussed before, the polymer molecules in UP-10 may be more compacted than in UP-6, since more C=C bonds can undergo the intramolecular reaction in UP-10. Therefore, the mobilities of polyester C=C bonds are lower in UP-10 than in UP-6. Consequently, the conversion difference between the polyester and styrene C=C bonds is larger in UP-10 than in UP-6.

Figure 7 shows the relative conversion of styrene versus polyester C=C bonds at different temperatures. The two dashed lines shown in the figure represent two extreme cases: The lower one represents the alternating condition and the upper one represents the azeotropic copolymeriza-

tion. For UP-3, when the temperature varies between 35 and 90°C, the three curves all fall around the diagonal line, indicating that the consumption ratio of the styrene C=C versus the polyester C=C is 2 (i.e., azeotropic copolymerization). It was also found that the relative reaction rate is independent of temperature during the entire reaction for UP-3. This indicates that the temperature does not change the reaction mechanism. For UP-6, the relative conversion profiles are between these two extremes. At the early stage of the reaction, the average consumption rate is 1.6 styrene C=C bonds per polyester C=C bond. This indicates that, at the beginning of the reaction, the polyester C=C bonds in UP-6 are more reactive than are the styrene C=C bonds, which causes the consumption ratio of the styrene C=C versus the UP C=C to be less than the initial ratio (i.e., 2). The relative reaction rate for UP-6 also is independent of temperature as shown in Figure 7(b). At the late stage of the reaction, the three curves show a concave upward shape. For UP-10, when the conversion of the UP C=C bonds is less than 60%, the three relative conversion curves coincide with the alternating copolymerization curve. This indicates that the

Table VI Arrhenius Parameters for Rate Constants in the Kinetic Model

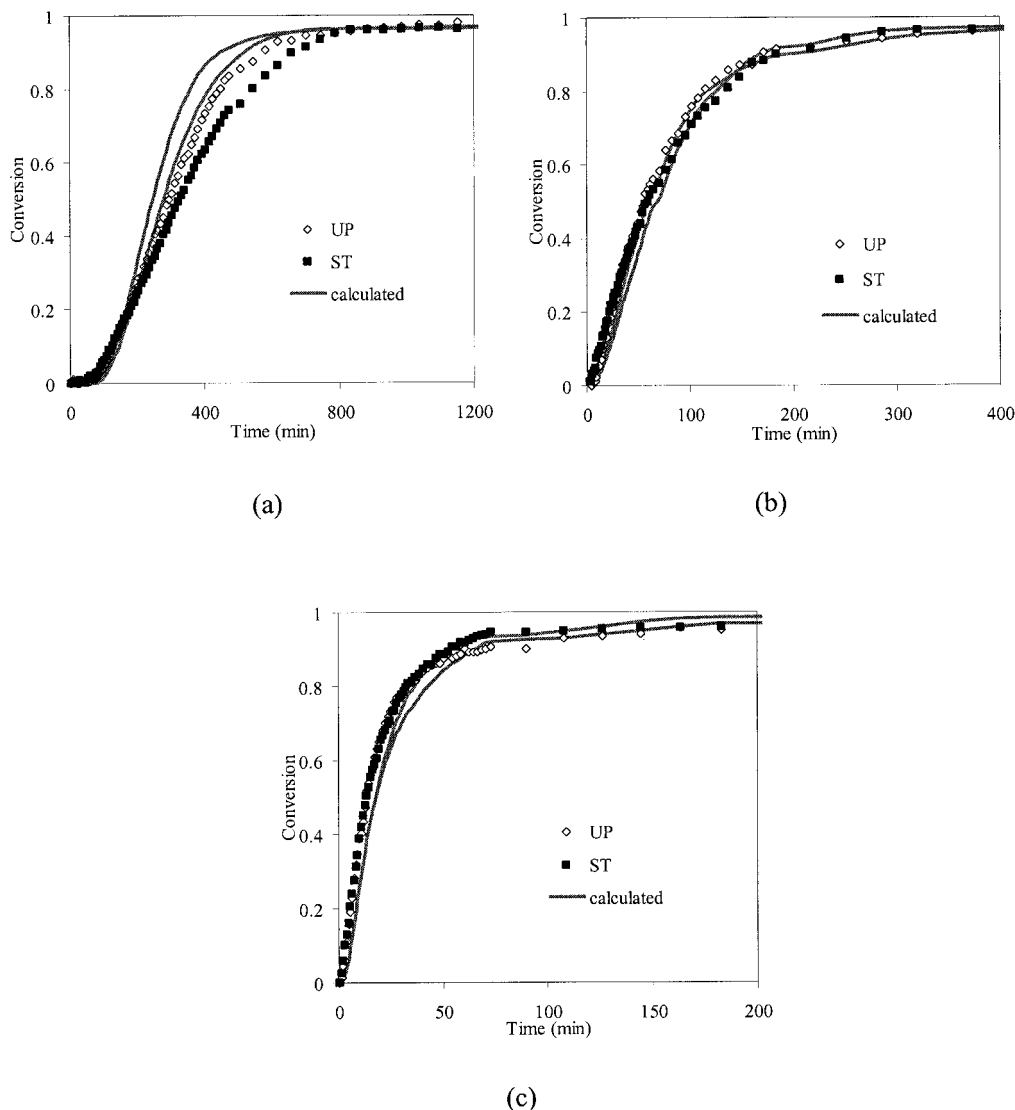| Resin Type	C=C	A_d (1/s)	E_d (kJ/mol)	$A_p \times 10^{-12}$ (1/s)	E_p (kJ/mol)
UP-3	UP	1.8×10^{-4}	8.4	0.067	79.13
	ST			0.308	83.70
UP-6	UP			1.12	82.01
	ST			3.13	86.63
UP-10	UP			1.26	77.08
	ST			0.87	81.07

(a)

(b)

(c)

Figure 9 Conversion profiles of polyester vinylene and styrene vinyl groups measured by FTIR and calculated by the kinetic model at (a) 35°C, (b) 60°C, and (c) 90°C (UP-3, 0.8 wt % MEKP, 0.1 wt % Co).

average consumption rate is one styrene C=C bond per one polyester C=C bond. For UP-10, as the reaction proceeds, the reactivity of polyester C=C changes significantly due to the diffusion-limitation effect, which has a more profound influence at the late stage of the reaction. When the conversion of the UP C=C bonds is higher than 60%, the three curves show a concave upward shape. For both UP-6 and UP-10, when the conversion of the polyester C=C bonds is larger than 80%, the reactivity of the poly(ester vinylene) groups levels off, while the styrene reactivity remains relatively high at all temperatures. This means that the styrene conversion increases

without involving a significant polyester C=C bond reaction. The reaction among styrene vinyl groups dominates due to the immobility of polyester vinylene groups in the highly crosslinked network.

Gel Time and Gel Conversion

The gel time measured at 35°C for the three polyester resins is shown in Table IV. The corresponding gel conversions measured by DSC are also listed in the table. It was found that the gel time decreases significantly when the degree of unsaturation of the polyester resins increases, which
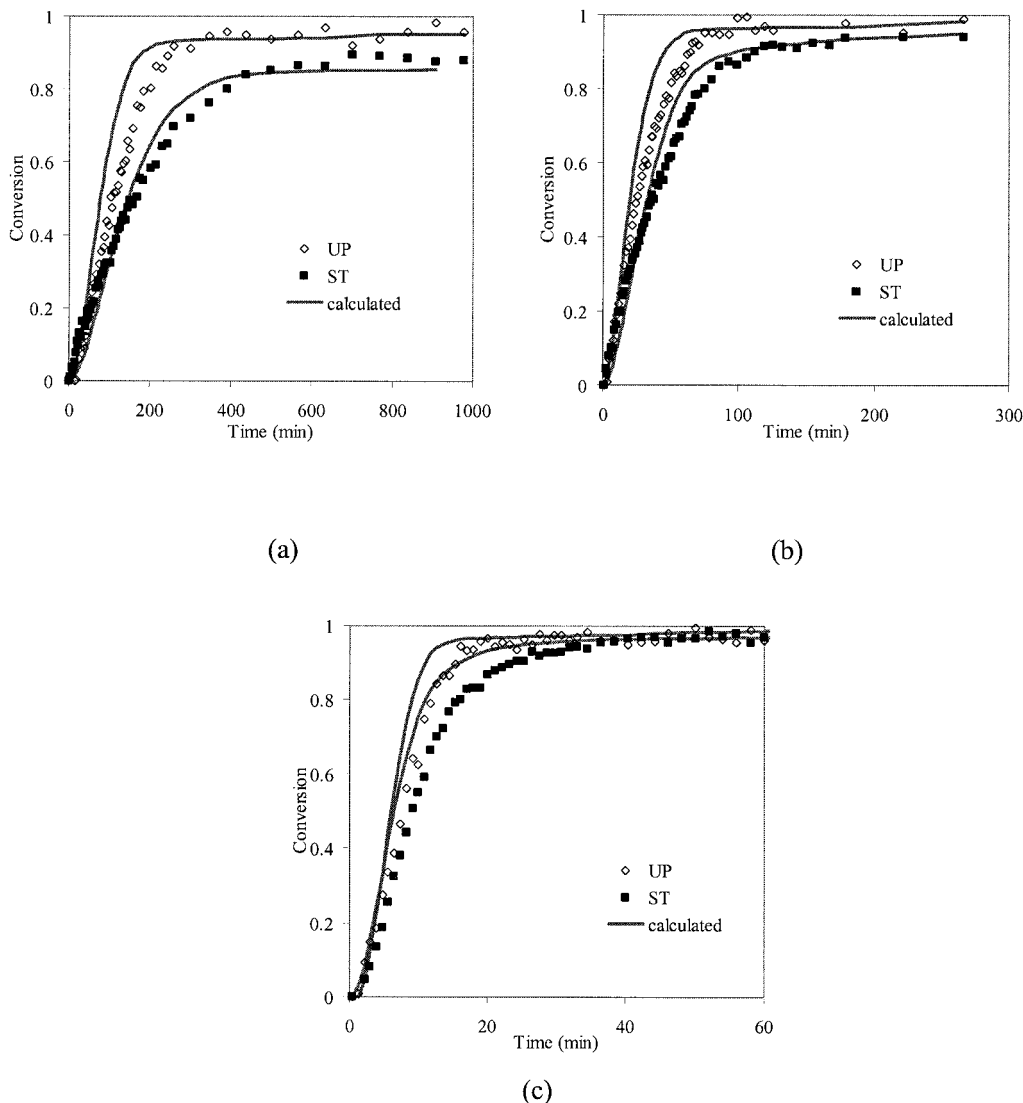
(a)

(b)

(c)

Figure 10 Conversion profiles of polyester vinylene and styrene vinyl groups measured by FTIR and calculated by the kinetic model at (a) 35°C, (b) 60°C, and (c) 90°C (UP-6, 0.8 wt % MEKP, 0.1 wt % Co).

agrees with the fact that the degree of unsaturation increases the reaction rate, resulting in faster gelation. The gel conversion for UP-3 is approximately 5%, and for UP-6 and UP-10, about 1–2%. A possible reason for the difference in the gel conversion is that for UP-3 more styrene molecules participate in the copolymerization (e.g., two styrene C=C bonds consumed per one reacted UP C=C bond). Since the styrene molecules are monofunctional, they contribute less to the network formation as compared to the polyester molecules. Therefore, the gel conversion of UP-3 is relatively high.

Radical Behavior Measured by ESR

Figure 8 shows ESR spectra for the cured UP-3 and UP-10 resins. For UP-3, very weak signals are obtained, as shown in Figure 8(a). A possible reason is that the formed polymer molecules are less compacted in UP-3, since the radicals are more mobile and thus most of them terminate soon after generation. Strong signals are obtained for UP-10, indicating that more radicals remain in the cured resin. This implies that the radicals are less mobile in the resin with a higher degree of unsaturation, since the polymer molecules are highly crosslinked, while the radicals are easily

trapped in the polymer matrix and remain unreacted.

Reaction Kinetic Model

Considering the diffusion-limitation effect, a simple mechanistic kinetic model was developed by Yang and Lee[24] to describe the reaction kinetics of the styrene/vinylester resin. The same approach can also be used for the styrene/polyester resin because the reaction in both polyester and vinylester resins is free-radical copolymerization.

To describe the propagation steps in the free-radical copolymerization of polyester resins, two propagation rate constants were used in this study: one for the propagation reaction of a polyester vinylene group in the polyester chain to a growing polymeric radical, and the other for the propagation reaction of a styrene vinyl group in the styrene monomer to a growing radical. The reaction rates of the polyester vinylene and styrene vinyl groups are expressed by the following equations[24]:

$$\frac{d\alpha_{UP}}{dt} = k_{p10}\left(1 - \frac{\alpha_{UP}}{\alpha_{UPf}}\right)^m (1 - \alpha_{UP})$$

$$\times \left\{ f\bar{I}_0 \left[1 - \exp\left(-\int_{t_z}^{t} k_d [I_p]^{1/2}\, dt\right)\right]\right\} \quad (6)$$

$$\frac{d\alpha_{ST}}{dt} = k_{p20}\left(1 - \frac{\alpha_{ST}}{\alpha_{STf}}\right)^m (1 - \alpha_{ST})$$

$$\times \left\{ f\bar{I}_0 \left[1 - \exp\left(-\int_{t_z}^{t} k_d [I_p]^{1/2}\, dt\right)\right]\right\} \quad (7)$$

where k_{p10} and k_{p20} are the rate constants for the propagation of polyester vinylene and styrene vinyl groups, respectively; α_{UP} and α_{ST}, the conversions of polyester vinylene and styrene vinyl groups, respectively; and α_{UPf} and α_{STf}, the final conversions of polyester vinylene and styrene vinyl groups, respectively. f is the efficiency of the initiator, $\bar{I}_0$ is the concentration of initiator after all the inhibitor has been consumed; t_z, the induction time before propagation; k_d, the decomposition rate constant of the initiator; and I_p, the concentration of the promoter.

Since the concentration of the promoter changes little because of the regeneration func-

tion shown in eqs. (2) and (3), k_d and $I_{p^{1/2}}$ are combined into the new parameter K_d. Because k_{p10}, k_{p20}, f, and $\bar{I}_0$ are constants at a given temperature, they are combined into two new parameters, $K_{p10} = k_{p10}f\bar{I}_0$ and $K_{p20} = k_{p20}f\bar{I}_0$. Then, the reaction rates of the polyester vinylene and styrene vinyl groups can be expressed as follows:

$$\frac{d\alpha_{UP}}{dt} = K_{p10}\left(1 - \frac{\alpha_{UP}}{\alpha_{UPf}}\right)^m (1 - \alpha_{UP})$$

$$\times \left[1 - \exp\left(-\int_{t_z}^{t} K_d\, dt\right)\right] \quad (8)$$

$$\frac{d\alpha_{ST}}{dt} = K_{p20}\left(1 - \frac{\alpha_{ST}}{\alpha_{STf}}\right)^m (1 - \alpha_{ST})$$

$$\times \left[1 - \exp\left(-\int_{t_z}^{t} K_d\, dt\right)\right] \quad (9)$$

K_d, K_{p10}, and K_{p20} are assumed to be Arrhenius-type temperature-dependent:

$$K_d = A_d \exp\left(\frac{-E_d}{RT}\right), \quad K_{p10} = A_{p10} \exp\left(\frac{-E_{p10}}{RT}\right),$$

$$K_{p20} = A_{p20} \exp\left(\frac{-E_{p20}}{RT}\right) \quad (10)$$

In this model, the final conversions, α_{UPf} and α_{STf}, are obtained from the FTIR results. The values of the model parameters are obtained from the isothermal FTIR results using a nonlinear fitting algorithm and are listed in Table V. The parameter m is 1.1, 1.5, and 3 for UP-3, UP-6, and UP-10, respectively, which indicates that the diffusion limitation is more pronounced for the resin with a higher degree of unsaturation. The significant diffusion limitation in UP-10 also accounts for the fact that the final conversion of UP-10 is the lowest among the three polyester resins at the same conditions. The propagation rate constants K_{p10} and K_{p20} increase as the degree of unsaturation increases, which may be a result of increased intramolecular reaction in UP-6 and UP-10. For UP-3, K_{p10} and K_{p20} at different temperatures are approximately the same because the reaction rates of UP C=C bonds and styrene C=C bonds in UP-3 are similar, as shown in Figure 6(a). For both UP-6 and UP-10, K_{p10} is larger than is K_{p20},
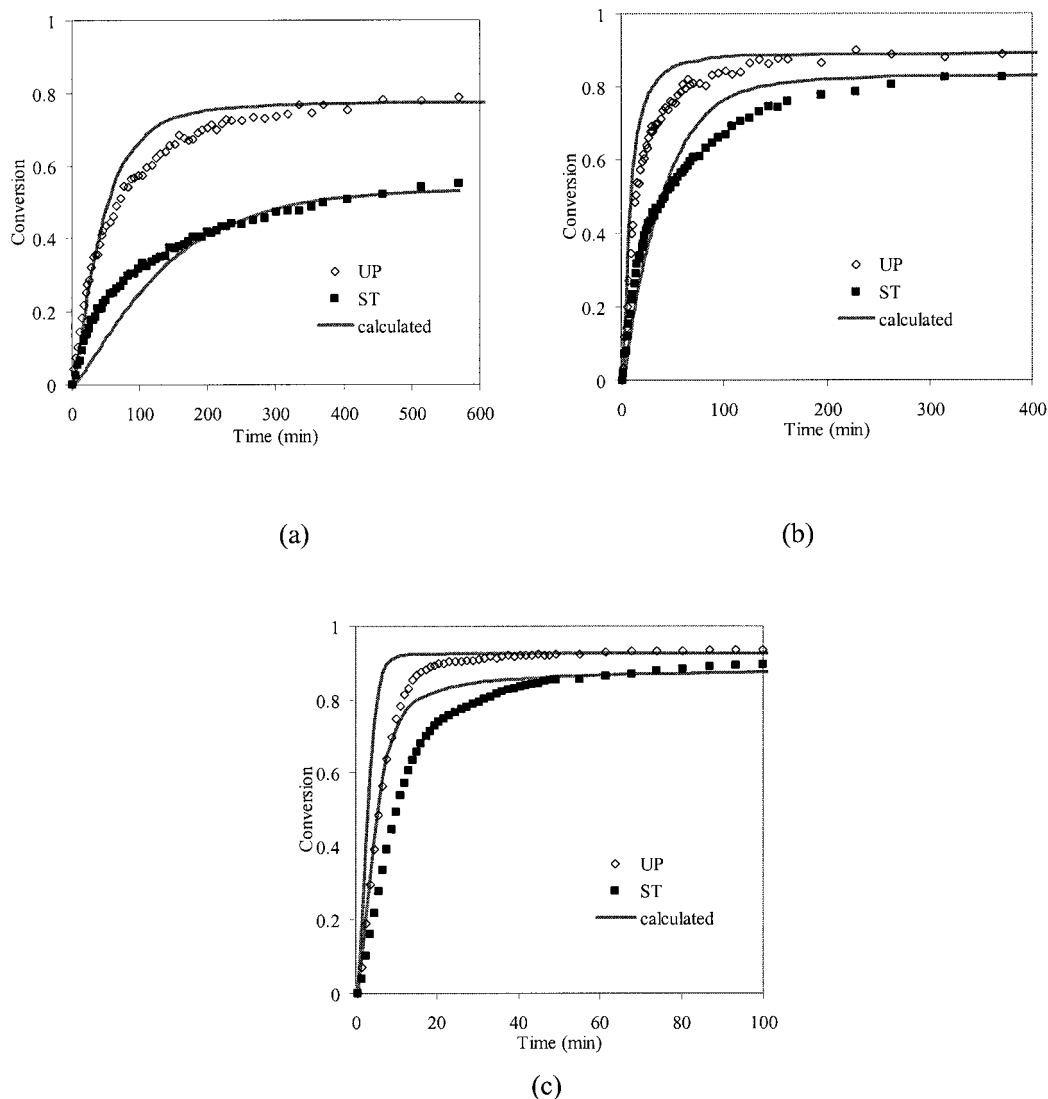
(a)

(b)

(c)

Figure 11   Conversion profiles of polyester vinylene and styrene vinyl groups measured by FTIR and calculated by the kinetic model at (a) 35°C, (b) 60°C, and (c) 90°C (UP-10, 0.8 wt % MEKP, 0.1 wt % Co).

particularly for UP-10. This is also in agreement with the fact that the conversion of UP C=C bonds is higher than that for styrene C=C bonds during the entire reaction of UP-6 and UP-10. The preexponential factors and the activation energies are determined based on the ln K versus $1/T$ curves and are given in Table VI.

Figures 9–11 compare the calculated conversion profiles of polyester vinylene and styrene vinyl groups with the experimental results obtained by FTIR at 35, 60, and 90°C for the three polyester resins. It can be seen that the model calculation agrees well with the experimental data.

By assuming that the polyester and styrene C=C bonds have the same contribution to the total C=C conversion, the total conversion profiles are calculated from the FTIR results, as shown in eq. (11):

$$\alpha_{\text{Total}} = \alpha_{\text{UP}} \times \frac{1}{3} + \alpha_{\text{ST}} \times \frac{2}{3} \qquad (11)$$

Figure 12 shows the total conversion profiles obtained from both FTIR and DSC measurements as well as the model prediction for the three polyester resins at different temperatures. It can be
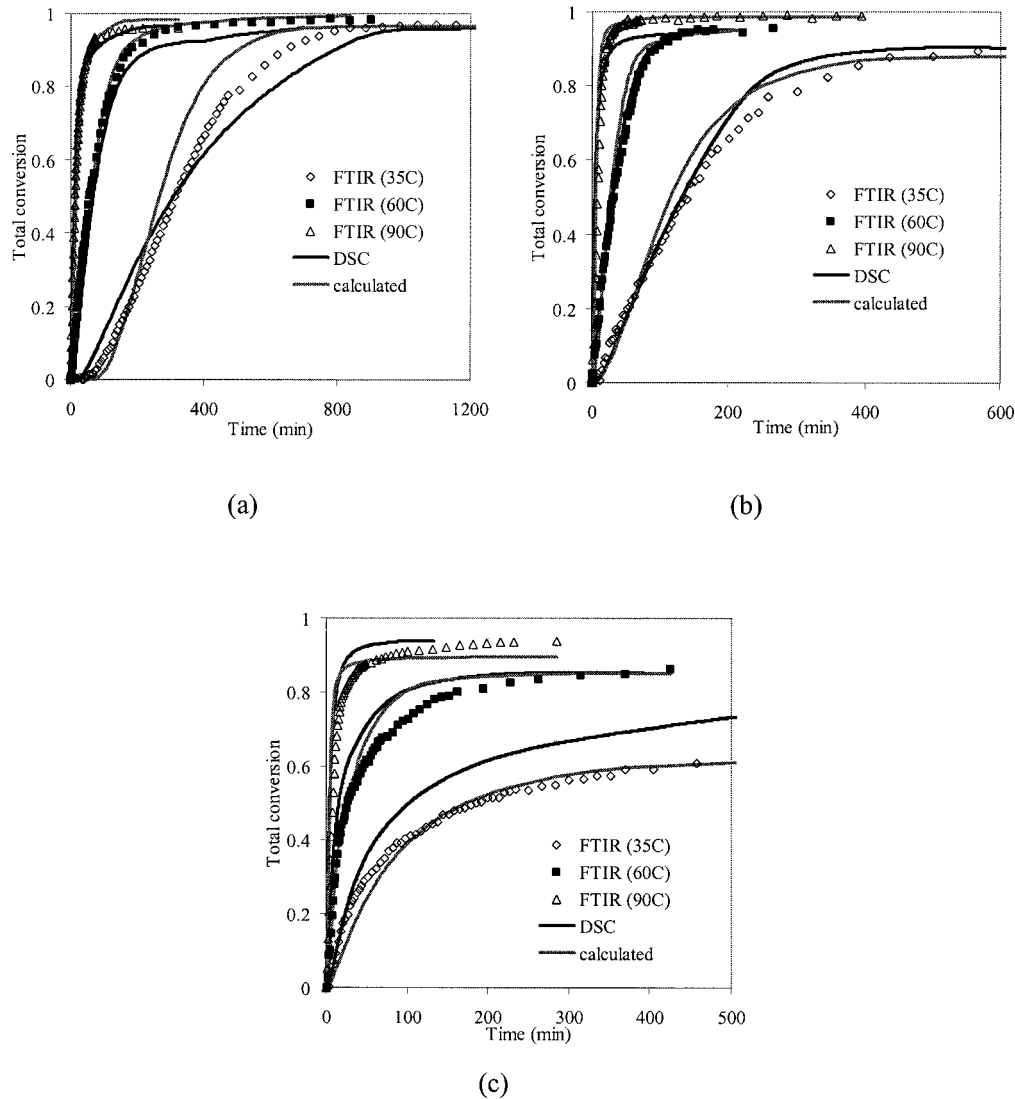
(a)

(b)

(c)

Figure 12 Comparison of total conversion profiles from FTIR and DSC measurements as well as the model calculations at different temperatures for (a) UP-3, (b) UP-6, and (c) UP-10 (0.8 wt % MEKP, 0.1 wt % Co).

seen that the results from FTIR and DSC agree fairly well, and the kinetic model provides a reasonable prediction of the overall conversion profiles at different temperatures.

Nonisothermal scanning was conducted using both FTIR and DSC to verify the kinetic model. The scanning rate was 2°C/min. The conversion profiles in the scanning reaction measured by DSC and FTIR are shown in Figure 13. The proposed kinetic model is used to predict the conversion profiles. It was found that the model can predict the conversion profiles at nonisothermal conditions reasonably well.

CONCLUSIONS

The reaction kinetics of a series of well-defined polyester resins at temperatures between 35 and 90°C was studied using DSC and FTIR. The effect of the degree of resin unsaturation on the curing behaviors was investigated. Experimental results from FTIR and DSC measurements agree with each other reasonably well. The higher the degree of C=C unsaturation per molecule, the higher is the reaction rate. The diffusion-limitation effect is more significant for the polyester resin with a higher degree of unsaturation, leaving more un-
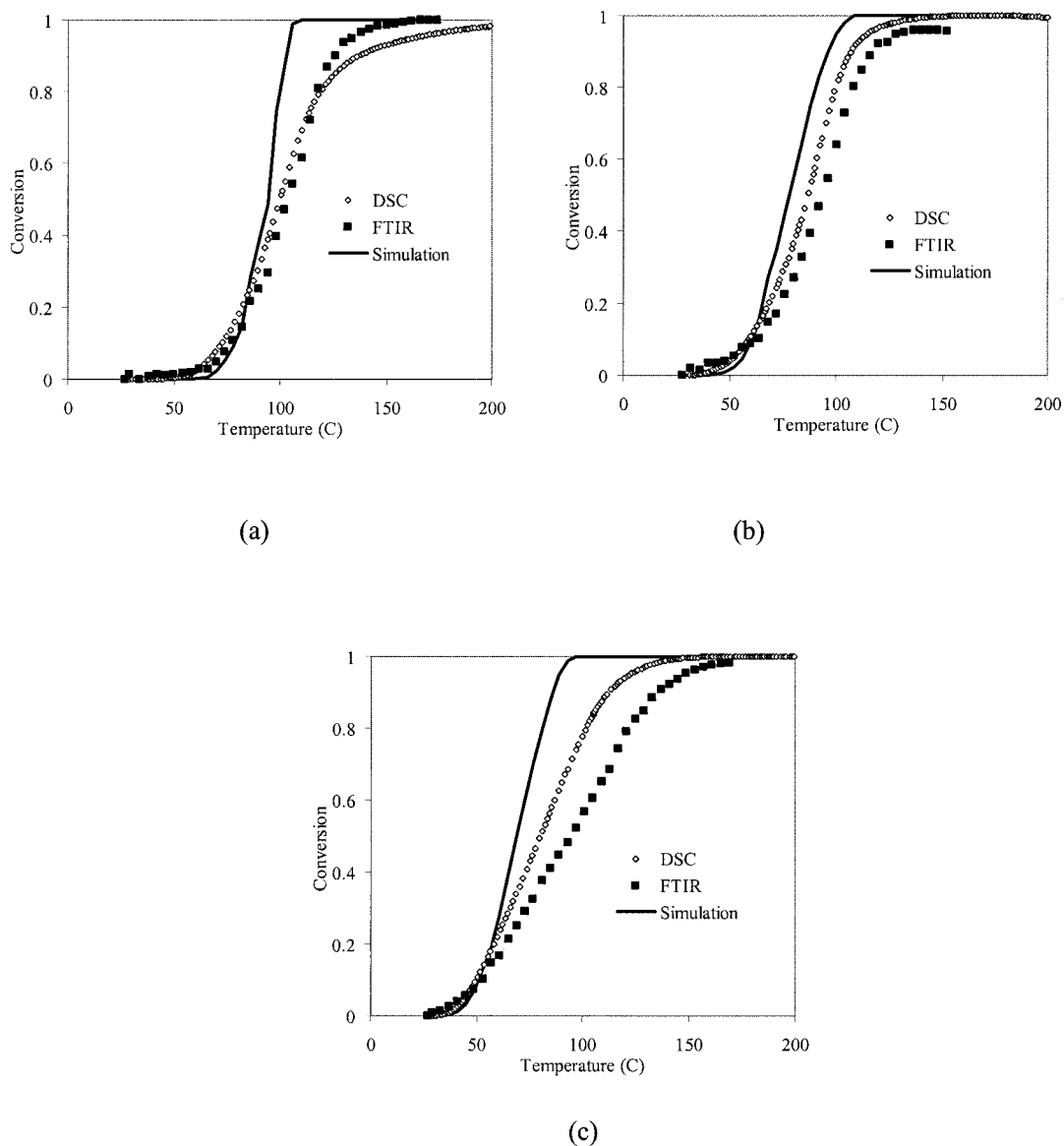
(a)

(b)

(c)

Figure 13   Comparison of conversion profiles of the scanning reaction of the polyester resins measured by FTIR and DSC and simulation results for (a) UP-3, (b) UP-6, and (c) UP-10 (0.8 wt % MEKP, 0.1 wt % Co).

reacted C=C bonds trapped inside the matrix after vitrification, resulting in lower final conversions of polyester and styrene C=C bonds. The glass transition temperature measured by the DSC is a linear function of the final conversion within the temperature range studied, and it is used to monitor the change of the final conversion. ESR measurements show that for the polyester resin with a higher degree of unsaturation the polymer formed is more compacted due to more intramolecular reaction, and more radicals are trapped in the cured resin without termina-

tion. Considering the diffusion-controlled propagation reaction, a simple mechanistic kinetic model was developed, capable of reasonably predicting the reaction rate and conversion profiles of polyester vinylene and styrene vinyl groups, as well as the total reaction rate and conversion at different temperatures and at nonisothermal conditions.

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