

# Curing of Unsaturated Polyester Resins: Effects of Comonomer Composition. II. High-Temperature Reactions

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## SYNOPSIS

The effects of comonomer composition on the curing kinetics of unsaturated polyester (UP) resins at 100–120°C were investigated by differential scanning calorimetry (DSC) and infrared spectroscopy (IR) over the entire conversion range. One commercial UP resin, UP2821, with 6.82 unsaturated C=C bonds per polyester molecule, was used. For styrene/UP2821 reactions, experimental results of the initial and maximum reaction rates by DSC at 100–120°C revealed that the styrene content, as well as the reaction temperature, would affect the formation of microgel structures. As the initial molar ratio of styrene to polyester C=C bonds increased, the styrene swelling effect could enhance the intramicrogel cross-linking reactions, while the styrene dilution effect could diminish the intermicrogel cross-linking reactions. The competition between the two reactions would depend on the reaction temperatures. Finally, a microgel-based reaction mechanism was proposed for the high temperature reactions. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Unsaturated polyester (UP) resins result from the reaction of mixtures of saturated and unsaturated dicarboxylic acids with glycols, subsequently diluted with unsaturated monomers.<sup>1</sup> The unsaturated monomer, mostly styrene, both acts as a solvent for the polyester and provides a means for crosslinking the polyester chains to yield a thermoset product after the cure, where a free radical chain growth crosslinking copolymerization between the styrene and polyester C=C bonds is involved. High-temperature processing of UP resins includes compression molding of sheet molding compound (SMC), injection molding of bulk molding compound (BMC), pultrusion, etc. Although the above processing temperature ranges from 140–180°C, most of curing kinetic studies have been carried out below 130°C due to the limitation of instruments. For example, the commonly used differential scanning calorimeter (DSC) for the cure analysis of thermosets has a stabilization time of 1 min prior to the recording of data, which sets an upper bound for the

isothermal cure temperature in order to trace the entire DSC rate profile.

Horie et al.<sup>2</sup> used DSC to study the curing reaction of polyester fumarate with styrene at 60–100°C. They found that both the termination and propagation steps of the curing reaction were controlled by diffusion of polymeric segments and monomer molecules over almost the whole range of conversion. The final conversion of isothermal cure decreased with increasing crosslinking density and showed a maximum with increasing reaction temperature. Horie et al.<sup>2</sup> attributed the temperature dependence of the final conversion to the difference in the activation energies for two propagation rate constants, one for the propagation reaction of a fumarate unit in the polyester chain to a growing polymeric radical and the other for that of a styrene monomer to a growing polymeric radical.

Huang et al.<sup>3</sup> studied the effect of molar ratio of styrene to polyester C=C bonds on the curing kinetics of UP resins at 100°C by DSC. They found that as the molar ratio decreased from infinity (i.e., pure styrene) to 2/1, the shape of DSC rate profile was characterized by a large peak instead of two small peaks. The final overall C=C conversion also decreased from 100% to 85%. Lee and Han<sup>4</sup> investigated the effect of the structure of UP resin on its

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curing behavior at 110–130°C with DSC. They found that at the same styrene-to-fumarate molar ratio, the resin having isophthalates cured more slowly than the one having none. Also, everything else being equal, the resin having a high styrene-to-fumarate molar ratio cured faster than the resin having a low one. All of the phenomena could not be explained satisfactorily because these researchers treated the curing of UP resins as a simple free radical polymerization without differentiating between the conversions of styrene and polyester C=C bonds, and they disregarded the inhomogeneous styrene-crosslinked polyester network resulting from the cure of UP resins.

Yang et al.<sup>5</sup> used both DSC and Fourier transform infrared spectroscopy (FTIR) to study the cure kinetics of UP resins at 120°C with a molar ratio of styrene to polyester C=C bonds of 2/1. They found that at low conversions, the polyester C=C bond reaction was more favorable than the styrene reaction due to the intramolecular cyclization of polyester chains.<sup>6-7</sup> At high conversions, the styrene reaction became predominant because polyester molecules were more immobile than styrene monomers.

Yang and Lee<sup>6-7</sup> have studied the rheokinetics and microstructure formation in the cure of UP resins at 30°C. They pointed out that the formation of microgel particles is a key feature of the styrene-unsaturated polyester copolymerization. During the styrene and polyester copolymerization, the initiator decomposes and creates free radicals in the system. The free radicals grow and form long-chain molecules by both inter- and intramolecular reactions. These long-chain molecules tend to form a spherical type of structure, or "microgel particles," due to the intramolecular crosslinking among the pendant C=C bonds of polyester molecules. The microgel formation has a profound effect on the reaction kinetics of UP resins. It causes a fast consumption of polyester C=C bonds early in the reaction and it causes the delay of system gelation. Also, many pendant polyester C=C bonds may be trapped in the compact microgels and may become permanent residue.

In a previous article,<sup>8</sup> the effects of comonomer composition on the curing kinetics of UP resins at 40°C, have been investigated over the whole range of conversion by DSC and IR. A microgel-based reaction mechanism, which describes the formation of microgel particles and the competing processes of intramicrogel and intermicrogel crosslinking reactions at low temperatures, has also been proposed to explain the experimental results. The present article is a continuation of the study of the curing

kinetics of UP resins at high temperatures ranging from 100–120°C. Since the reaction temperature would affect the formation of microgel structures, the experimental results, different from those at low temperatures, were observed and are discussed by using a microgel-based reaction mechanism proposed for high temperatures.

## EXPERIMENTAL

### Materials

One unsaturated polyester resin, UP-2821, obtained from a local company, was employed in this study. The resin contained isophthalic acid, fumaric acid, and propylene glycol with a mole ratio of 1:1.46:2.79 by <sup>1</sup>H-NMR analysis. The number-average mol wt was measured to be 2092 g/mole by end-group titration. On the average, the calculated number of C=C bonds (i.e., degree of C=C unsaturation) in each polyester molecule was 6.82. The styrene content in UP resin was determined by evacuating styrene monomers in the vacuum oven at room temperature. All the detailed characterization procedures and the results were given elsewhere.<sup>8</sup>

Based on the characterization results, extra styrene was added to or evaporated from the resin so that the molar ratio of styrene to polyester C=C bonds was adjusted to be 1/1, 2/1, 3/1, and 6/1 in the preparation of sample solutions. Tert-butyl perbenzoate (TBPB, TX-C, Akzo Chemicals) was used to initiate the reaction, the concentration of which was 1% by weight of the total resin for all samples. All the materials were employed as received without further purification.

### Instrumentation and Procedures

A DuPont 9000 differential scanning calorimeter with a 910 pressurized DSC cell was used to follow the overall reaction rate profiles at atmospheric pressure. All the reactions were conducted in hermetic aluminum sample pans with sample weights of 7–12 mg. Isothermal reaction rate vs. time profiles were measured at 100–120°C. Isothermal DSC runs were ended when there was no further exotherm. Samples were then reheated from room temperature to 210°C in the scanning mode with a heating rate of 10°C/min to determine the residual reactivity left in the isothermally cured samples. Resins were also cured in the scanning mode at 10°C/min heating rate. The total heat of reaction was calculated

from the area under the scanning DSC curve. The rate of heat release measured by DSC can then be directly converted into the overall reaction rate and conversion as a function of time.<sup>8</sup>

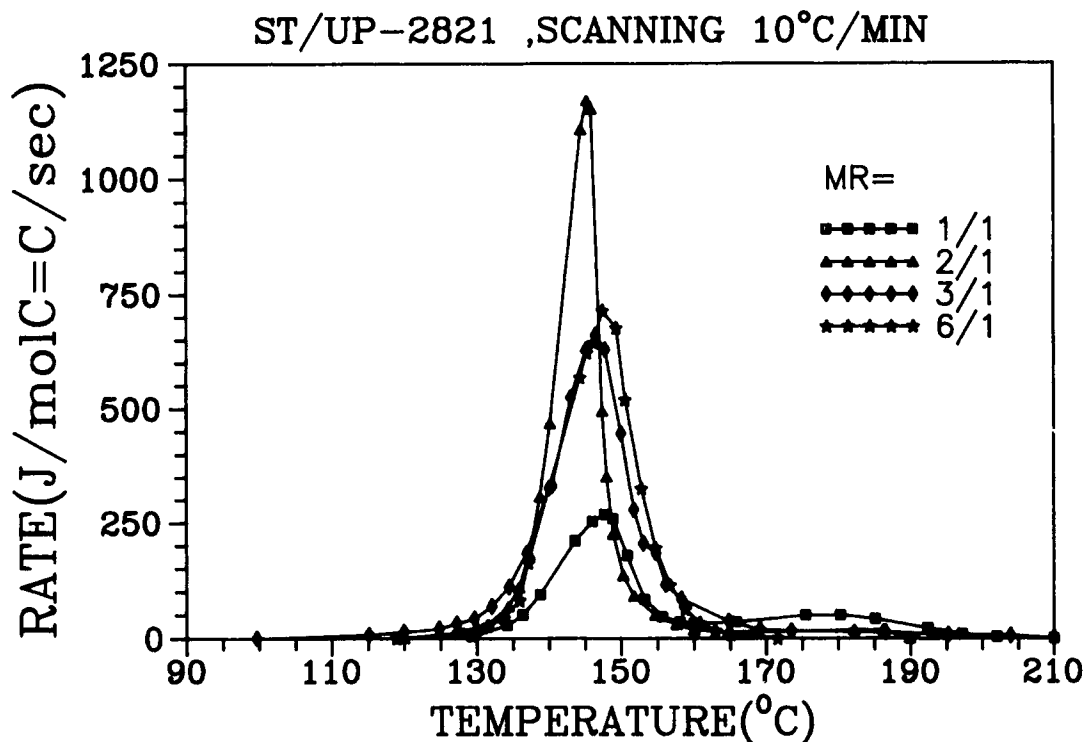
In this study, an IR spectrophotometer (Jasco, IR-700) with a resolution of  $4\text{ cm}^{-1}$  in the transmission mode was used for off-line conversion measurements of styrene and polyester C=C bonds during the reaction. The reaction of resin cured in the DSC cell at  $110^\circ\text{C}$  was stopped at a preset time by rapidly chilling the sample pan in liquid nitrogen. The sample was then milled, mixed with KBr, and pressed into a solid disk with 1 cm diameter prior to IR measurements. In the analysis of IR spectra, changes of absorbance at  $912\text{ cm}^{-1}$  and  $982\text{ cm}^{-1}$  were employed to calculate conversions of styrene and polyester vinylene groups, respectively. The absorbance at  $1730\text{ cm}^{-1}$  (C=O stretching) was picked as an internal standard. The absorbance at  $695\text{ cm}^{-1}$  (C—H out of plane bending in benzene ring of styrene) was also measured to correct for styrene loss due to its evaporation in grinding operations. Since the peaks at  $982\text{ cm}^{-1}$  and  $992\text{ cm}^{-1}$  overlapped, a simple subtraction method was used to separate the individual peaks.<sup>9-11</sup> Detailed calculation procedures were given elsewhere.<sup>11</sup>

## RESULTS

### Scanning Reaction by DSC

Figure 1 shows the scanning DSC rate profiles for styrene/UP2821 reactions with various molar ratios of styrene to polyester C=C bonds at  $10^\circ\text{C}/\text{min}$  from room temperature to  $210^\circ\text{C}$ . It can be seen that each reaction rate profile has one major peak. At a lower molar ratio  $\text{MR} = 1/1$ , a second small peak appeared, ranging from  $160^\circ\text{C}$ – $200^\circ\text{C}$ , which is less conspicuous at  $\text{MR} = 2/1$  having higher styrene content. At  $\text{MR} = 3/1$ , a shoulder emerged at about  $153^\circ\text{C}$ , whereas at  $\text{MR} = 6/1$ , it seems that two reaction peaks overlapped at  $145^\circ\text{C}$  and exhibited one major peak at  $147^\circ\text{C}$ . The rate profile for either  $\text{MR} = 3/1$  or  $\text{MR} = 6/1$  did not show a small peak at high temperature range when compared with that for  $\text{MR} = 1/1$ .

For comparison of reaction rates with different molar ratios, the reaction rate shown in Figure 1 is expressed as Joules per mole C=C bonds per sec instead of Joules per g of resin per sec, since the numbers of moles of total C=C bonds for every g of resin with differing molar ratio are different from one another, as shown in Table I. The rate profiles



**Figure 1** Scanning DSC rate profiles at  $10^\circ\text{C}/\text{min}$  for styrene/UP2821 reactions with various molar ratios of styrene to polyester C=C bonds.

**Table I Initiator Concentrations on the Molar Basis for the Prepared Samples of UP2821 Resin**

Molar Ratio of C=C Styrene/ Polyester (Molar Ratio in Parenthesis)	1/1	2/1	3/1	6/1
(1) total moles of C=C/g resin	$4.87 \times 10^{-3}$	$5.83 \times 10^{-3}$	$6.47 \times 10^{-3}$	$7.52 \times 10^{-3}$
(2) g TBPB/g resin	0.01	0.01	0.01	0.01
(3) mol TBPB/mol C=C ( $\propto$ [TBPB] <sub>0</sub> )	0.0106 (1)	$8.84 \times 10^{-3}$ (0.83)	$7.97 \times 10^{-3}$ (0.75)	$6.85 \times 10^{-3}$ (0.65)

shown in Figure 1, however, are not corrected for the variation of initial molar concentrations of the initiator, as shown in Row 3 of Table I.<sup>8</sup> Since the initial rate of polymerization is proportional to the square root of the initiator concentration, the maximum reaction rate will be corrected for the initiator concentration below by using that relationship.

The decreasing order of initial reaction rate, shown in Figure 1, is that MR = 3/1 > MR = 2/1 > MR = 6/1 > MR = 1/1. The increasing order of temperature to the maximum reaction rate,  $T_m$ , is that MR = 2/1 (145.4°C) < 3/1 (146.5°C) < 6/1 (147.5°C) < 1/1 (147.7°C), whereas the decreasing order of the maximum reaction rate,  $R_m$ , as shown in Table II, is that MR = 2/1 > 6/1 (at 147°C) > 3/1 > 6/1 (at 145°C) > 1/1. After correction for the variation of initiator concentration by using MR = 1/1 as the basis (Row 3 in Table I), the order of the corrected maximum reaction rate,  $R'_m$ , becomes MR = 2/1 > 6/1 (at 147°C) > 6/1 (at 145°C) > 3/1 > 1/1 (see Table II), with MR = 2/1 and MR = 1/1 being the highest and the lowest among all the molar ratios, respectively.

### Isothermal Reaction by DSC

Figure 2 shows the isothermal DSC rate profiles for samples with various molar ratios of styrene to polyester C=C bonds, MR = 1/1, 2/1, 3/1, and 6/1, at 120°C. It can be seen that as the molar ratio increases, the time to the maximum rate,  $t_m$ , decreases, and the initial reaction rate becomes faster. The decreasing order of the maximum reaction rate,  $R_m$ , is that MR = 3/1 > 2/1 > 6/1 > 1/1. After correction for the variation of initiator concentrations with differing molar ratios, as mentioned earlier, the order of reaction rate remains unchanged, but its magnitude varies somewhat (see Table II). Figure 3 shows the overall C=C conversion vs. time profiles. Since the total exotherm by direct DSC scanning,  $\Delta H_s$ , for MR = 1/1 is much lower than that for MR = 2/1 (see Table III), the conversion calculation at MR = 1/1 is based on  $\Delta H_s$  at MR = 2/1 as the corresponding total heat release for 100% conversion. Figure 3 reveals that the higher the molar ratio, the higher the overall conversion.

Figures 4 and 5 show the isothermal DSC rate

**Table II Maximum Reaction Rates at Various Molar Ratios for UP2821 Reactions Both at Isothermal and Scanning Modes**

Molar Ratio	Scanning Reaction		$T = 120^\circ\text{C}$		$T = 110^\circ\text{C}$		$T = 100^\circ\text{C}$	
	$R_m$	$R'_m$	$R_m$	$R'_m$	$R_m$	$R'_m$	$R_m$	$R'_m$
MR = 1/1	267.6	267.6	129.6	129.6	87.8	87.8	41.4	41.4
2/1	1167.9	1281.9	235.0	257.9	120.1	131.8	44.3	48.6
3/1	660.6	762.8	255.2	294.7	108.0	124.7	46.6	53.8
6/1	714.3	886.0	167.5	207.8	92.5	114.7	55.4	68.7
	(at 147°C)							
	643.3	797.9						
	(at 145°C)							

$R_m$  is the uncorrected maximum rate (J/mol C=C/sec), and  $R'_m$  is that after correction for the variation of initial initiator concentration by using MR = 1/1 as the basis (Row 3 in Table I).

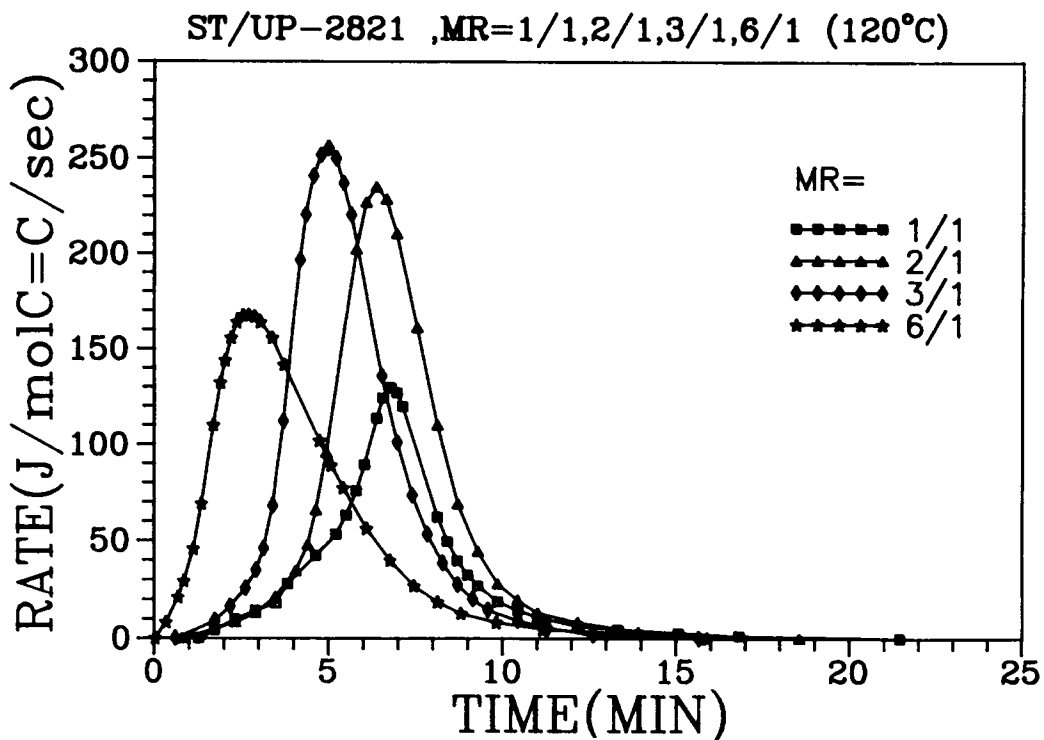


Figure 2 Isothermal DSC rate profiles for styrene/UP2821 reactions at 120°C with various molar ratios of styrene to polyester C=C bonds.

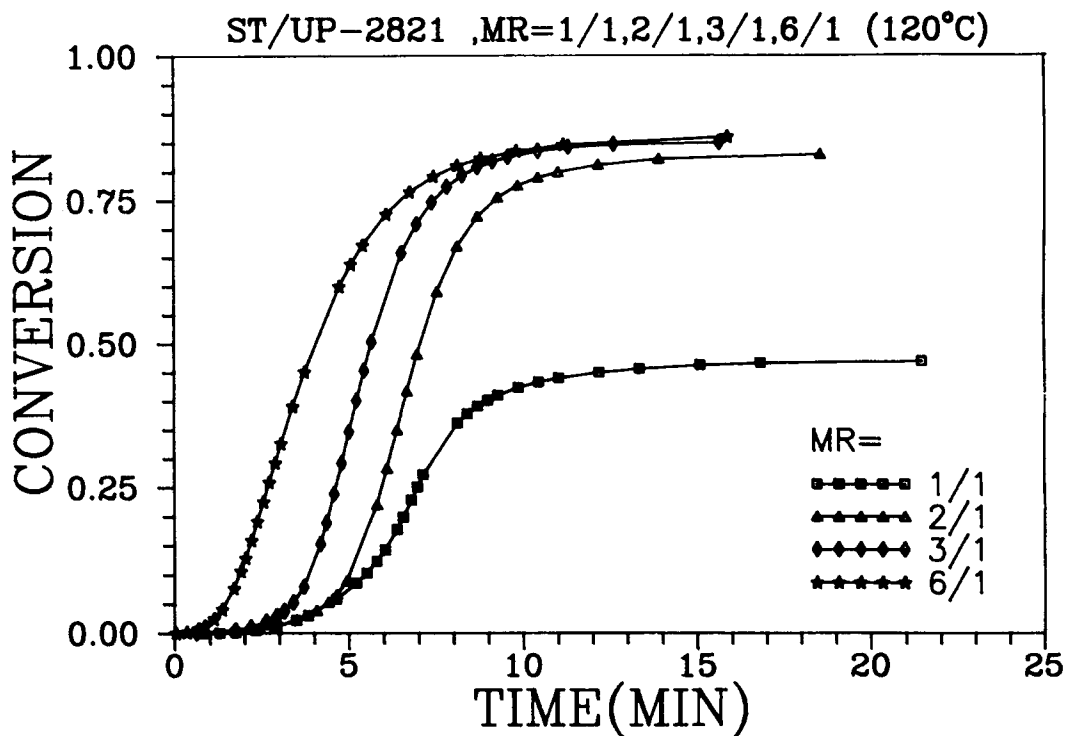


Figure 3 Isothermal DSC conversion profiles at 120°C corresponding to Figure 2.

**Table III Summary of Kinetic Information by DSC for Styrene/UP2821 Reactions Both at 100–120°C and in Scanning Modes**

	$\Delta H_{\text{iso}}^a$	$\Delta H_{\text{res}}$	$\Delta H_I$	$\Delta H_S$	$\alpha_I^b$	$\alpha_S$	$t_z^c$	$t_m$	$\alpha(t_m)$
<b>T = 100°C</b>									
MR <sup>d</sup> = 1/1	8.86	2.18	11.04	7.24	0.80	0.62 <sup>e</sup>	21.26	54.59	0.29
2/1	9.39	2.10	11.49	14.23	0.82	0.66	17.10	44.23	0.18
3/1	10.98	1.62	12.60	14.43	0.87	0.77	15.14	39.71	0.26
6/1	11.96	1.24	13.20	14.91	0.90	0.80	10.82	27.05	0.23
<b>T = 110°C</b>									
MR = 1/1	9.68	1.50	11.18	7.24	0.86	0.68 <sup>e</sup>	1.28	18.39	0.40
2/1	10.17	1.47	11.64	14.23	0.87	0.72	2.51	16.04	0.26
3/1	11.10	1.54	12.64	14.43	0.88	0.78	1.65	12.43	0.29
6/1	12.24	1.18	13.42	14.91	0.91	0.82	1.23	12.00	0.28
<b>T = 120°C</b>									
MR = 1/1	6.70	1.18	7.88	7.24	0.85	0.47 <sup>e</sup>	1.24	6.78	0.20
2/1	11.84	1.90	13.74	14.23	0.86	0.83	0.81	6.38	0.35
3/1	12.29	1.48	13.77	14.43	0.89	0.85	0.61	5.00	0.35
6/1	12.86	0.95	13.81	14.91	0.93	0.86	0.07	2.71	0.26

<sup>a</sup> The unit of  $\Delta H_{\text{iso}}$ ,  $\Delta H_{\text{res}}$ ,  $\Delta H_I$  ( $= \Delta H_{\text{iso}} + \Delta H_{\text{res}}$ ), and  $\Delta H_S$  is kcal/mol C=C, where  $\Delta H_{\text{iso}}$  is the heat release for isothermally cured sample,  $\Delta H_{\text{res}}$  is the heat release by rescanning the isothermally cured sample at 10°C/min from room temperature to 210°C, and  $\Delta H_S$  is the heat release at 10°C/min from room temperature to 210°C, and  $\Delta H_S$  is the heat release at 10°C/min scanning rate from room temperature to 210°C.

<sup>b</sup>  $\alpha_I$  is the overall conversion based on the  $\Delta H_I$  as 100% conversion, and  $\alpha_S$  is the overall conversion based on the  $\Delta H_S$  as 100% conversion.

<sup>c</sup>  $t_z$  is induction time (min),  $t_m$  is time to the maximum rate (min), and  $\alpha(t_m)$  is the overall conversion at maximum rate.

<sup>d</sup> MR is the mole ratio of styrene to polyester C=C bonds.

<sup>e</sup> The conversion  $\alpha_S$  for MR = 1/1 is based on the  $\Delta H_S$  at MR = 2/1 as the 100% conversion.

profiles with various molar ratios at 110°C and 100°C, respectively. It can be seen that  $t_m$  decreases with increasing molar ratio. At 110°C, a shoulder appears at the initial portion of the rate profile for MR = 1/1, which is more conspicuous than that in Figure 2 at 120°C. The order of initial reaction rate is that MR = 1/1 > 2/1 and MR = 3/1 > 6/1, while the decreasing order of the maximum rate is that MR = 2/1 > 3/1 > 6/1 > 1/1, which remains unchanged after correction for the variation of initiator concentrations (see Table II). At 100°C, as the molar ratio of styrene to polyester C=C bonds increases, the induction time,  $t_z$ , decreases and the initial reaction rate increases accordingly. The decreasing order of  $R_m$ , either uncorrected or corrected ones, is that MR = 6/1 > 3/1 > 2/1 > 1/1 (see Table II). Similar to Figure 3, the overall C=C conversion vs. time profiles (not shown) indicate that the higher the molar ratio, the higher the overall conversion for both reactions at 110°C and 100°C.

Table III summarizes the heat generated by the curing reaction, which includes the heat generated in isothermal cure,  $\Delta H_{\text{iso}}$ , the residual heat that was released when the sample was heated to 210°C from room temperature at 10°C/min upon completion of the isothermal cure,  $\Delta H_{\text{res}}$ , the total heat of cure,  $\Delta H_I$ , by adding  $\Delta H_{\text{iso}}$  and  $\Delta H_{\text{res}}$ , and the total heat release, by direct scanning from room temperature to 210°C at 10°C/min,  $\Delta H_S$ . Also displayed in Table III are the final conversion,  $\alpha_I$  and  $\alpha_S$ , based on  $\Delta H_I$  and  $\Delta H_S$ , respectively, induction time,  $t_z$ , time to the maximum rate,  $t_m$ , and conversion at the maximum rate,  $\alpha(t_m)$ . It can be seen that for ST/UP2821 reactions at MR = 1/1,  $\Delta H_S$  is the smallest among all the samples.  $\Delta H_I$  is greater than  $\Delta H_S$  for MR = 1/1, which is different from the trend for all the other molar ratios. In general, except for MR = 1/1, the overall conversion,  $\alpha_S$ , increases with increasing temperature. For MR = 1/1, the final conversion increases by elevating the reaction tem-

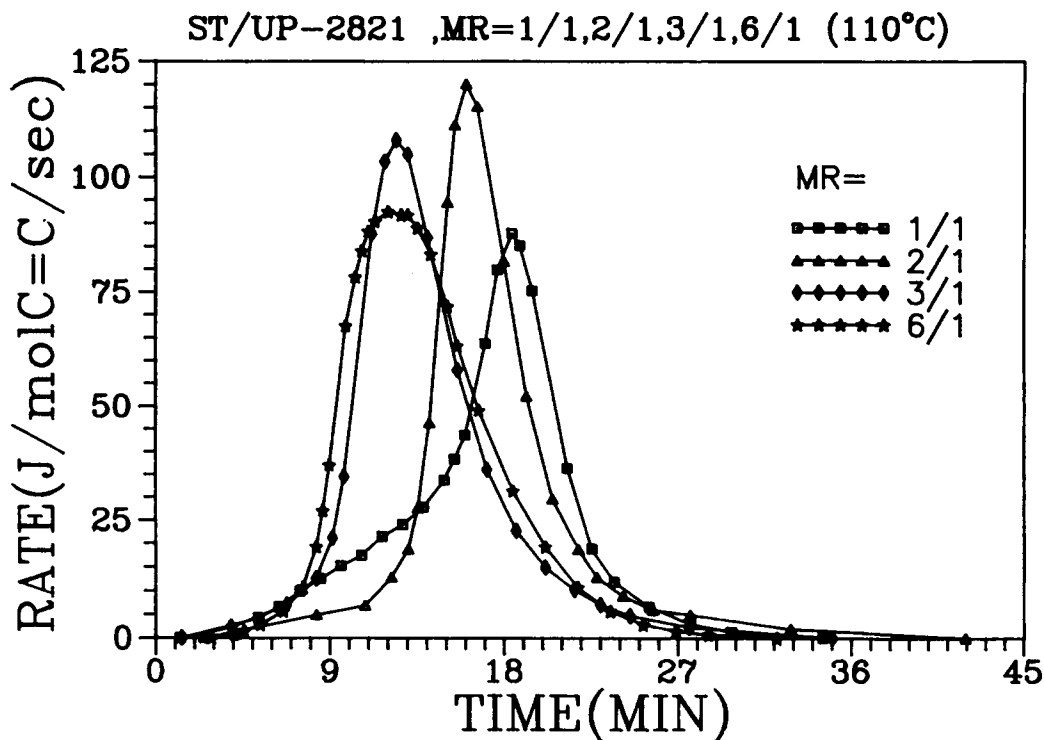


Figure 4 Isothermal DSC rate profiles for styrene/UP2821 reactions at 110°C with various molar ratios of styrene to polyester C=C bonds.

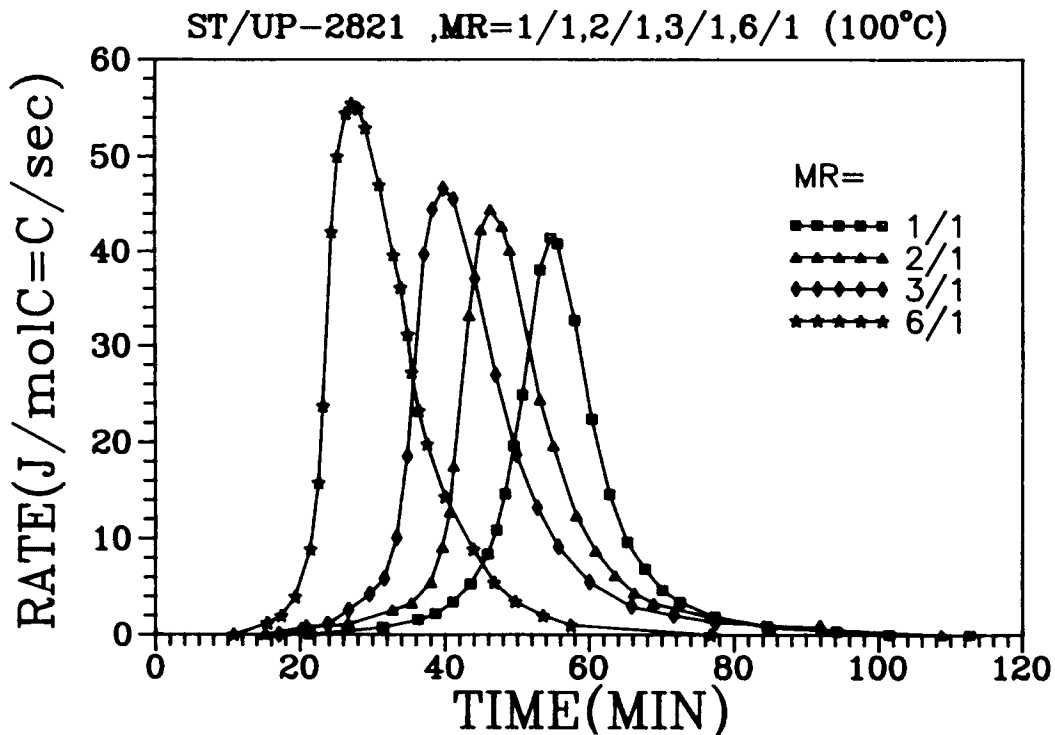


Figure 5 Isothermal DSC rate profiles for styrene/UP2821 reactions at 100°C with various molar ratios of styrene to polyester C=C bonds.

perature from 100°C to 110°C. However, it decreases by further increasing the reaction temperature to 120°C.

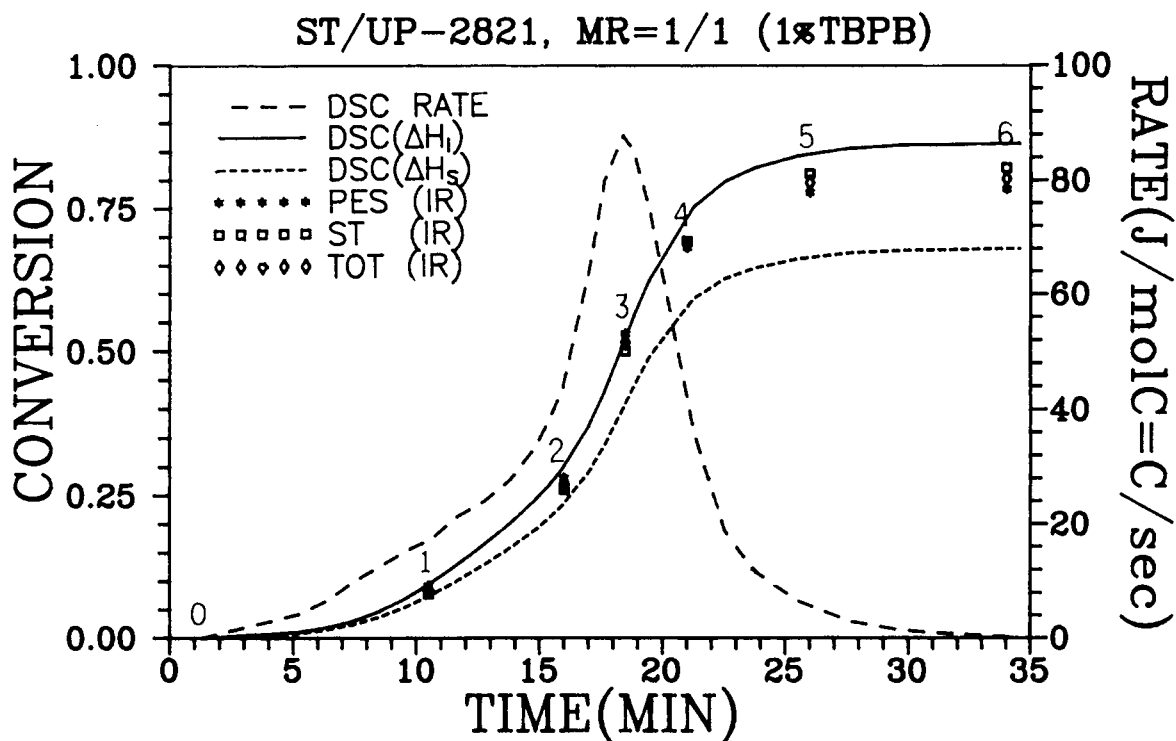
### Isothermal Reaction by IR

Figure 6 shows the conversion of styrene C=C bonds, polyester C=C bonds, and total C=C bonds vs. time profiles for UP2821 reaction with MR = 1/1 measured by IR. For comparison, the DSC rate profile, and DSC total conversion curves, based on both  $\Delta H_I$  (solid line) and  $\Delta H_S$  (dashed line), are also plotted. The overall conversion measured by IR lies between  $\alpha_I$  and  $\alpha_S$  measured by DSC, where  $\alpha_S$  is generally more close to the true overall conversion.<sup>8</sup> Therefore, the overall conversion measured by IR could be 10–15% higher than that of the true value, due to the experimental error. Although the discrepancy may be minimized by continuous monitoring of the conversions using FTIR, for the initial stage of reaction, the DSC and FTIR conversion profiles cannot be well matched,<sup>12</sup> as is the off-line measurement by IR shown here. Prior to the peak of DSC rate profile in Figure 6, the conversion of polyester C=C bonds is slightly higher

than that of styrene. After the peak (between points 3 and 4), the conversion of styrene gradually exceeds that of polyester C=C bonds. This is due to the fact that after the peak, propagation reactions become diffusion-controlled<sup>13</sup> and the mobility of small styrene molecules is less affected by the increase of crosslinking density than that of C=C units in large polyester molecules, leading to a higher conversion of styrene.

For the six reaction intervals in Figure 6, that is, 0 → 1, 1 → 2, 2 → 3, 3 → 4, 4 → 5, and 5 → 6, the average number of styrene C=C bonds consumed per polyester C=C bond reacted, known as the average crosslink length of styrene, for MR = 1/1 is 0.83, 0.95, 0.98, 1.32, 1.21, and 2.14, respectively, as listed in Table IV. This average crosslink length of styrene increases up to the 3 → 4 reaction interval, where the DSC rate profile declines from the peak, followed by a decrease in the subsequent interval, and increases again eventually. In the final copolymer, the average crosslink length of styrene is 1.05, which is close to the initial molar ratio of styrene to polyester C=C bonds.

Figures 7, 8, and 9 show the conversion profiles measured by IR for MR = 2/1, 3/1, and 6/1, re-



**Figure 6** Styrene, polyester vinylene and total C=C conversions vs. time profiles measured by IR for UP2821 reaction at 110°C with MR = 1/1. DSC rate profile (dashed curve) and total C=C conversion profiles based on both  $\Delta H_I$  (solid curve) and  $\Delta H_S$  (dashed curve) are also plotted for comparison.



**Table IV** Relative Consumptions of Styrene C=C Bonds Per Polyester C=C Bond Reacted for UP2821 Reactions with Various Molar Ratios at 110°C

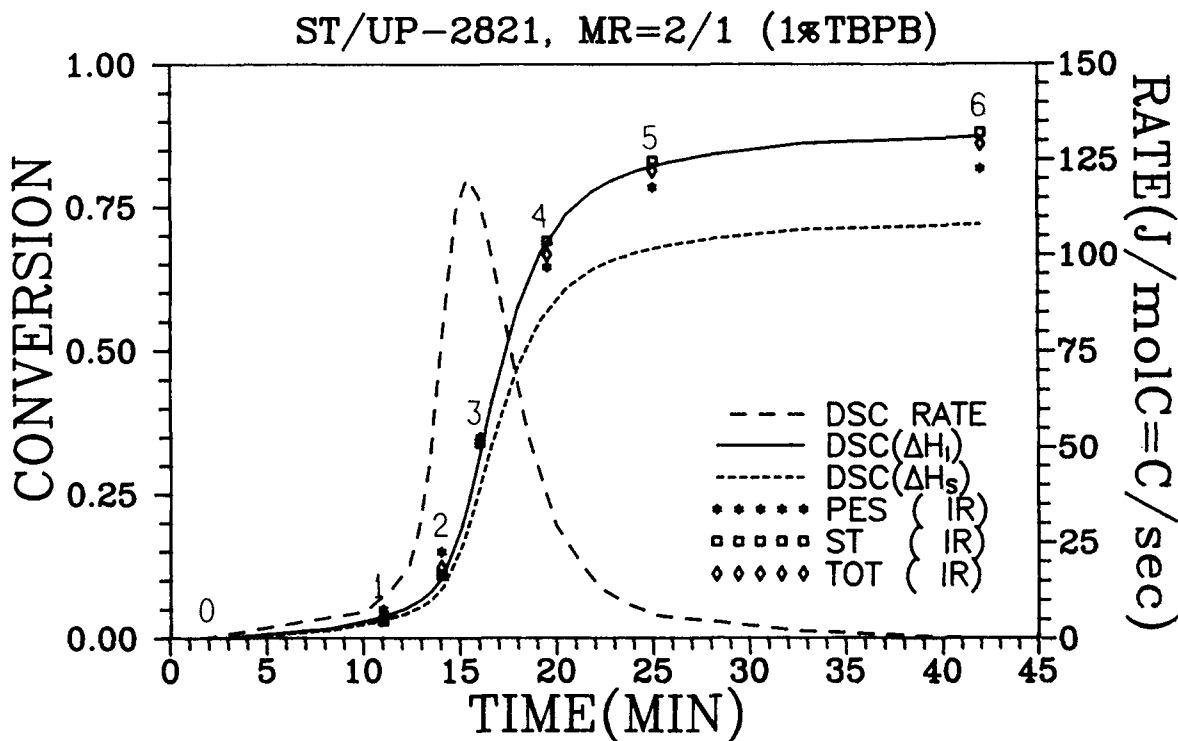
Reaction Intervals	0 → 1	1 → 2	2 → 3 <sup>a</sup>	3 → 4	4 → 5	5 → 6	0 → 6
Molar Ratio							
MR = 1/1	0.83	0.95	0.98	1.32	1.21	2.14	1.05
2/1	1.2	2.3	2.22	2.44	2.04	3.2	2.15
3/1	1.40	2.06	2.94	4.8	3.32	3.3	3.27
6/1	1.31	3.65	8.71	11.71	7.66	8.04	6.5

<sup>a</sup> Point 3 corresponds to the peak of the DSC rate profile for all the cases.

spectively. The overall conversion measured by IR is close to  $\alpha_T$  of the DSC curve, where the discrepancy of the conversion measurements by IR similar to Figure 6 appears again. The trend of conversion variations for styrene and polyester C=C bonds is similar to that for MR = 1/1, as shown in Figure 6. However, prior to the peak of the DSC rate profile, the difference of the two conversions is greater at a higher molar ratio. Although the change of crosslink length of styrene during the reaction, as shown in Table IV, exhibits a similar trend to that for MR = 1/1, the average crosslink length of styrene gen-

erally increases with increasing molar ratio at the corresponding intervals. In the final copolymer, it is again close to the initial molar ratio of styrene to polyester C=C bonds.

Figure 10 shows the relative conversion profiles of styrene vs. polyester C=C bonds for various molar ratios. It can be seen that before 50% conversion, all the curves show up-bending features. As the molar ratio increases, the curve generally moves to the right. This indicates that the conversion of polyester C=C bonds is more favorable than that of styrene in the beginning of reaction, and the higher styrene



**Figure 7** Conversion vs. time profiles measured by IR for UP2821 reaction at 110°C with MR = 2/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.

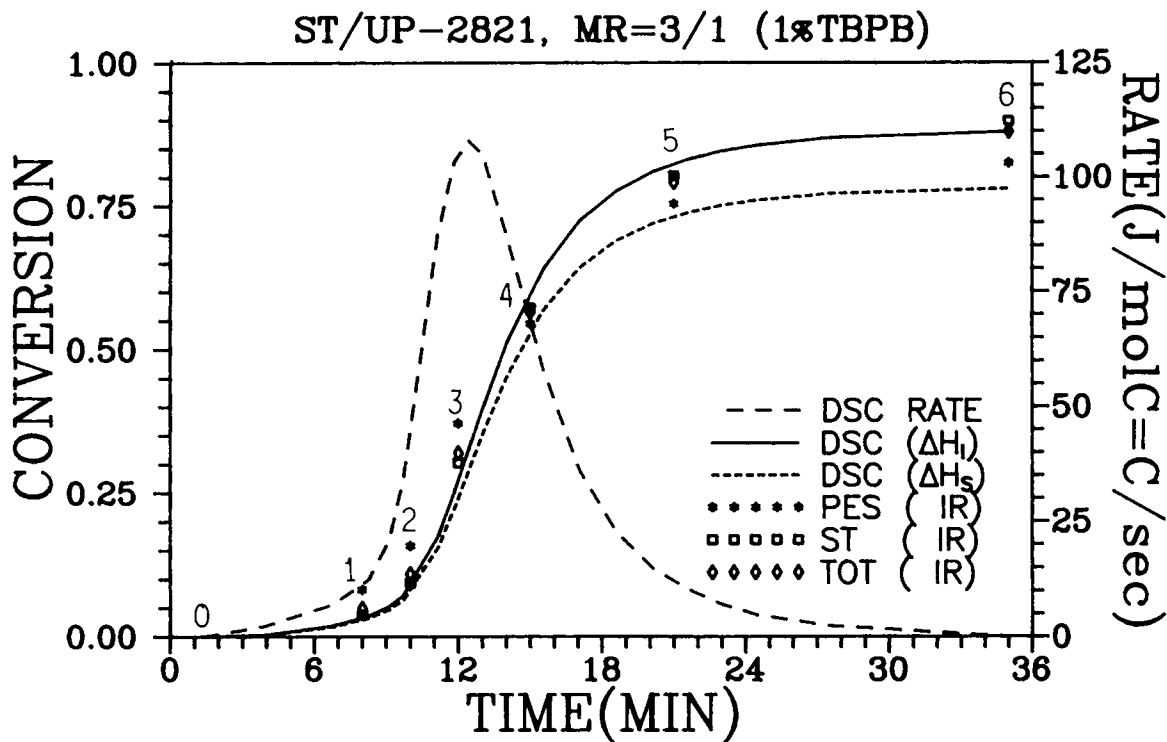


Figure 8 Conversion vs. time profiles measured by IR for UP2821 reaction at 110°C with MR = 3/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.

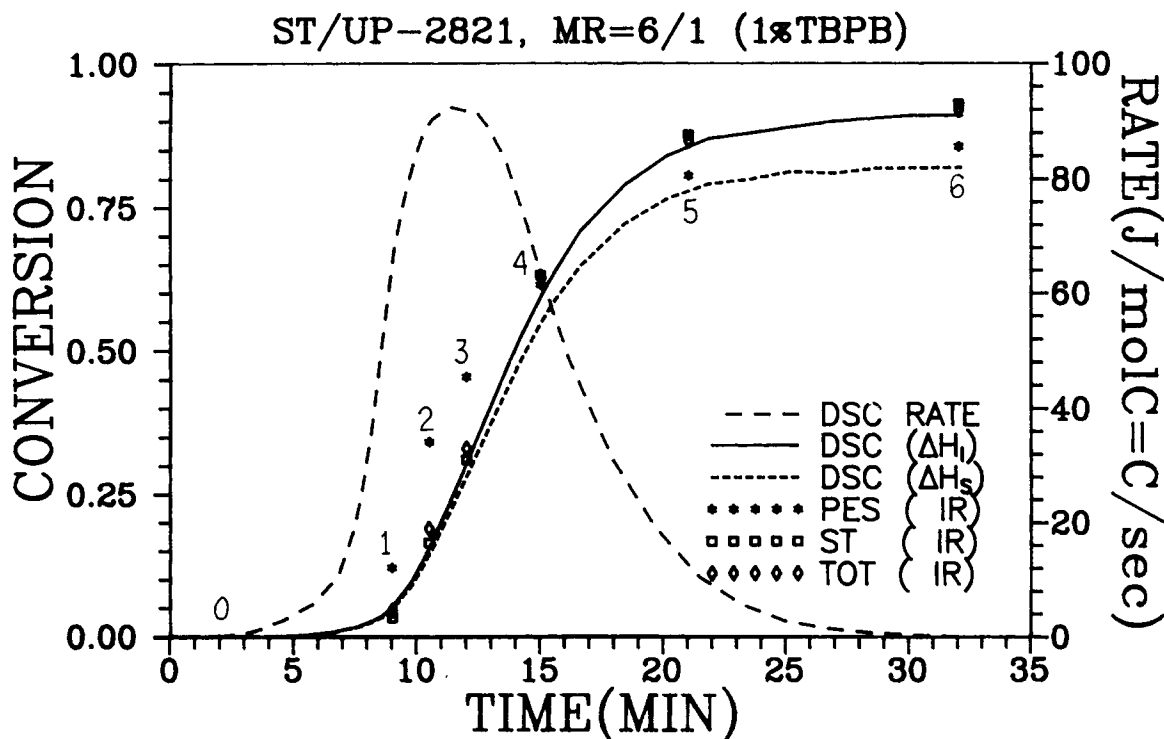
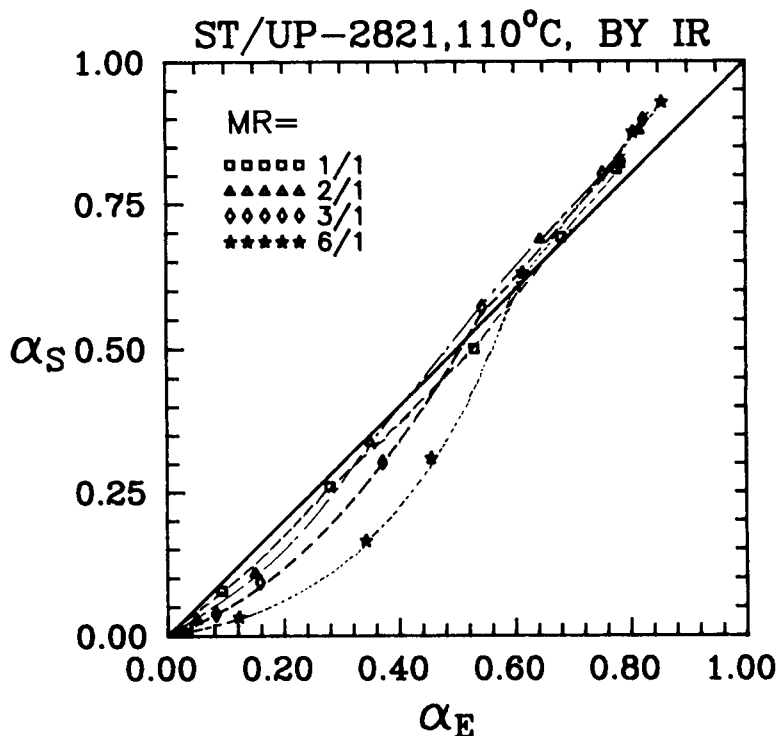


Figure 9 Conversion vs. time profiles measured by IR for UP2821 reaction at 110°C with MR = 6/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.



**Figure 10** Relative conversion of styrene to polyester C=C bonds at various molar ratios of styrene to polyester C=C bonds for UP2821 reaction at 110°C.

content is capable of facilitating the conversion of polyester C=C bonds. Below 40% conversion, all the curves fall below the 45° diagonal line, which denotes the azeotropic copolymerization, whereas they lie above the 45° line and are generally parallel to it above 65% conversion. These data reveal that at the later stage of reaction, the rates of change for both conversions of styrene and polyester C=C bonds are approximate. Although the relative conversion curves do not coincide with the 45° line for MR = 1/1 and 2/1, they are closer to the line than those of higher molar ratios, and the crosslink length of styrene before the reaction interval of 3 → 4, as shown in Table IV, also approximately takes on the value as the initial molar ratio for MR = 1/1 and 2/1. Therefore, these mixtures tend to exhibit near-azeotropic copolymerization, which occurs prior to 30–40% conversion around the peak of the DSC rate profile (see Table III for  $\alpha(t_m)$ ). Table V summarizes the final conversions measured by IR and the final average crosslink length of styrene at various molar ratios. The conversions of styrene ( $\alpha_S$ ) and polyester C=C bonds ( $\alpha_E$ ) increase with increasing molar ratios, as does the final average crosslink length of styrene.

## DISCUSSION

### Microgel-Based Reaction Mechanisms

#### *Isothermal Reaction*

The formation of microgel particles throughout the reaction would be the same as that proposed at a lower reaction temperature.<sup>8</sup> However, the microgel-based reaction mechanism for the isothermal curing of UP resins at high temperatures is somewhat different, based on the DSC rate profiles and conversion profiles by IR for both the UP2821 and UP536B<sup>14</sup> reactions.

Basically, the formation of microgel particles would continue from the beginning of the reaction until the microgels meet and closely overlap with one another throughout the system. After the peak of the DSC rate profile, the rate of microgel formation would then slow down considerably due to the diffusion-controlled propagation reactions for polyester C=C bonds. Sometime later, when the existing microgels were highly overlapped via crosslinking and a compact global network structure was formed, no new microgel particles would be generated.

**Table V** Summary of Kinetic Information by IR for Styrene/UP2821 Reactions at 110°C

Molar Ratio	$\alpha_S$	$\alpha_E$	$\alpha_{TOT}$	$\bar{\alpha}_S$	$\bar{\alpha}_E$	$n$
1/1	82.1%	78.4%	80.3%	41.1%	39.2%	1.05
2/1	88.0%	81.7%	85.9%	58.7%	27.2%	2.15
3/1	89.7%	82.4%	87.9%	67.3%	20.6%	3.27
6/1	92.9%	85.6%	91.9%	79.6%	12.2%	6.51

<sup>a</sup>  $\alpha_S$  is styrene conversion,  $\alpha_E$  is polyester vinylene conversion,  $\alpha_{TOT}$  is total conversion of C=C bonds,  $\bar{\alpha}_S$  and  $\bar{\alpha}_E$  are conversions based on the total initial C=C bonds, and  $n$  is the calculated final average crosslink length of styrene.

Prior to the peak of DSC rate profile, where the gel effect region predominates,<sup>13</sup> the intramicrogel crosslinking reaction would be highly competitive with the intermicrogel crosslinking reaction. This is different from that at a low reaction temperature, where the intermicrogel crosslinking reaction would predominate.<sup>8</sup> This is because, although the styrene monomers are apt to crosslink with the polyester C=C bonds near or at the surface of microgels (i.e., intermicrogel crosslinking reactions) during the process of diffusing into the microgels from outside, most local styrene, originally encompassed inside the microgels as well as part of the diffusing-in styrene, is allowed to crosslink with polyester C=C bonds inside the microgels (i.e., intramicrogel crosslinking reactions) at high reaction temperatures. In other words, once a microgel particle is formed, the intramicrogel crosslinking reaction would proceed more preferentially than would the intermicrogel crosslinking one. However, the extent to which the intramicrogel crosslinking reactions predominate over the intermicrogel crosslinking reactions should depend on the degrees of unsaturation of UP resins, the initial molar ratio of styrene to polyester C=C bonds, and the level of reaction temperatures. In general, the lower degree of unsaturation in UP resins, the higher molar ratio, and the lower reaction temperature, which could lead to either the looseness of microgel particles or the slow overlapping of them and thus the enhancement of diffusion rate of styrene into the microgels, would facilitate the intramicrogel crosslinking reactions, and vice versa.

After the peak in the DSC rate profile, the microgels would be gradually overlapped, and the high crosslinking density, either inside or outside the microgels, could lead to a diffusion-controlled propagation mechanism for the intramicrogel and intermicrogel crosslinking reactions. Meanwhile, competition between the intermicrogel and intramicrogel crosslinking reactions remains. In addition to the intermicrogel crosslinking reactions, styrene mono-

mers could still possibly diffuse into the microgels to crosslink with the pendant C=C bonds of polyester molecules inside, where the local network structure is allowed to be constructed further. Since the concentration of reactive pendant C=C bonds inside the microgels (i.e., those with less steric hindrance), and the degree to which styrene monomers could diffuse into the microgels from outside, may again depend on the degrees of unsaturation of UP resins, the initial molar ratio of styrene to polyester C=C bonds, and the level of reaction temperatures; the variation of the shape of rate profile at the later reaction would not be unexpected. Often, for lower crosslinking reaction systems, such as the UP536B resin with 4.16 C=C bonds per polyester molecule,<sup>8</sup> the rate profile can thus exhibit a reaction shoulder,<sup>14</sup> which is characteristic of the extensive intramicrogel reaction, at the later stage of reaction due to the loose microgel structure. In contrast, for a higher crosslinking reaction system such as the UP2821 one, the microgel structure is so compact that the reaction shoulder could not be readily observed, even at higher molar ratios. The intermicrogel crosslinking reaction would then prevail after the peak of the DSC rate profile, especially at lower molar ratios.

As the intramicrogel crosslinking reaction proceeds, after the peak of rate profiles, the crosslinking density inside the microgel would increase with time, and the aggravating diffusion-controlled propagation reactions for C=C units in large polyester molecules could result in a reduction of the normal styrene-polyester crosslinking. Hence, branching growth of styrene on polyester C=C bonds would then gradually predominate as the reaction goes on. This would be also true of the ongoing intermicrogel crosslinking reactions. When the small styrene molecule is also encountered with diffusion-controlled propagation reactions later on for both the intermicrogel and intramicrogel crosslinking reactions, the DSC rate profile decays gradually and eventually drops to zero where the local glass tran-

sition temperature of the system, either inside or outside the microgels, is equal to the reaction temperature.<sup>13</sup> The styrene-crosslinked polyester network thus formed would be inhomogeneous.

### Nonisothermal Reaction

As to the reaction mechanism for the nonisothermal curing of UP resins, such as the scanning reaction by DSC in this study, it would be essentially the same as that for isothermal reaction described above. However, since the reaction temperature keeps increasing as the scanning reaction goes on, it may lead to several features, as follows.

In general, prior to the first peak of DSC rate profile, intramicrogel crosslinking reactions would predominate over the intermicrogel crosslinking ones more than for isothermal reactions. This is because the gradual increase of temperature scan from low to high temperatures would lead to the build-up of crosslinking density in a moderate manner, which, in turn, could facilitate styrene monomers to keep on diffusing into the microgels for the intramicrogel reactions. Moreover, the evenly increasing temperature could help overcome the reaction resistance, due to the increase of crosslinking density, that would hamper the intramicrogel reactions. Hence, the reduction of pendant C=C bonds buried inside the microgels could be greatly facilitated during this stage. However, the extent to which the intramicrogel crosslinking reactions predominate should also depend on the scanning rate in reaction temperature other than the three factors mentioned earlier for isothermal reactions. Quite often, the slower scanning rate would facilitate the intramicrogel crosslinking reactions. This is because, under such circumstances, the chemical reaction, which is characterized by the slower overlapping of microgel particles by intermicrogel crosslinking reactions, as well as a moderate reaction rate for intramicrogel crosslinking ones, would adversely affect the transport process, which is due to the diffusion of styrene into the microgels, to a lesser extent.

After the first peak of the DSC rate profile, the evenly increasing temperature should enhance the intermicrogel crosslinking reactions more than the intramicrogel crosslinking ones, since the crosslinking density outside the microgels would be lower and the polyester C=C bonds would encounter less steric hindrance during the reaction. In general, branching growth of styrene on polyester C=C bonds outside the microgels would be the major reaction since the diffusion-controlled propagation reactions for polyester C=C bonds has set in after

the first peak of the rate profile. As the molar ratio increases, independent styrene homopolymerization, which does not pertain to the styrene/polyester network, could take place during the higher temperature range of scanning. Since competition between the intramicrogel and intermicrogel crosslinking reactions remains, either a reaction shoulder similar to that for isothermal reaction or a broad reaction rate profile would appear under higher molar ratios when the intramicrogel crosslinking reaction is enhanced. For the C=C bonds buried inside the compact microgels, such as in the case of lower initial molar ratio of styrene to polyester C=C bonds, they may await further temperature scanning to higher temperature range for the intramicrogel reaction and a second reaction peak could thus occur.

### Scanning Reaction by DSC

Figure 1 shows that the maximum reaction rate,  $R'_m$ , for MR = 1/1 is low, being 0.21 times the  $R'_m$  of MR = 2/1 (see Table II). Since the lower styrene content for MR = 1/1 would cause an insufficient styrene swelling effect to loosen microgel structures formed during the reaction in comparison to that for MR = 2/1 and higher molar ratios, many C=C bonds would be buried inside the local microgels. The considerable reduction of the intramicrogel crosslinking reactions would be greater than the enhancement in the intermicrogel crosslinking reactions, due to the high-temperature crosslinking system, leading to a much lower  $R'_m$  value at MR = 1/1 than that at MR = 2/1. Often, for UP resins with lower degrees of C=C unsaturation, such as the UP536B resins,<sup>14</sup> the  $R'_m$  value at MR = 1/1 is not as low as that for the UP2821 system here, being 0.88 times the  $R'_m$  of MR = 2/1. This is because it leads to a lower crosslinking density for the UP536B system in the crosslinking reaction. The intramicrogel crosslinking reactions would not be reduced much and could fairly equally contribute to the overall reaction rate along with the intermicrogel crosslinking reactions.

Except for MR = 1/1, the reaction rate of the first peak generally decreases with an increasing molar ratio of styrene to polyester C=C bonds. Horie et al.<sup>15</sup> pointed out that for the copolymerization of diethyl fumarate and styrene, the reactivity ratio is  $r_1 = 0.30-0.40$  and  $r_2 = 0.07-0.09$  at 60–130°C, where monomer 1 is styrene, and monomer 2 is diethyl fumarate. Therefore, the reaction rate for the copolymerization of styrene with polyester C=C bonds would be greater than that of self-

bonding of styrene, as also reported by Huang et al.<sup>3</sup> As the molar ratio increases, since the average number of styrene linking two neighboring C=C units among the polyester molecules in the crosslinking reactions increases, the reaction rate of the first peak would thus be reduced. As to the second reaction peak or shoulder, except for MR = 2/1 where the reaction is fast and almost complete during the lower temperature range of scanning, the reaction rate increases with an increasing molar ratio. This is because the higher styrene content would cause a looser microgel structure and a greater amount of excess styrene monomers could participate the self-bonding in the crosslinking reactions or homopolymerization inside the microgels during the second reaction peak.

### Styrene Swelling and Dilution Effects on Reaction Rates

In Figure 2, since the rate of crosslinking reactions for C=C units in polyester chains at 120°C is fast, the extent of compactness of the microgel structures formed in the reaction would be more closely related to initial styrene content than that in the 40°C reactions<sup>8</sup> with lower reaction rates. Generally, as the molar ratio increases, the styrene swelling effect would loosen the microgel structures. Hence, the intramicrogel crosslinking reaction is facilitated. On the other hand, the accompanying styrene dilution effect would increase the probability of crosslinking reactions through the linkage of more styrene. Due to the rate of copolymerization of styrene with polyester C=C bonds being higher than that of the self-bonding of styrene, as mentioned earlier, the styrene dilution effect could then depress the rate of the intermicrogel crosslinking reaction. Although it may also adversely affect the rate of the intramicrogel crosslinking reaction, the styrene dilution effect should be well compensated by the styrene swelling effect and the rate of the intramicrogel crosslinking reaction would be favored by raising the styrene content.

It is inferred from Figure 2 that at 120°C, the initial stage of reaction prior to the peak of rate profile would be attributed mainly to the intramicrogel reaction, which is associated with the formation of microgel particles and the local structure build-up inside the microgels. This is because the reaction rate is a summation of the intramicrogel and the intermicrogel crosslinking reactions. A higher initial reaction rate at a higher molar ratio reveals that the styrene swelling effect is dominant over the styrene dilution effect. In other words, the intramicrogel crosslinking reactions predominate.

Figure 2 also indicates that the sample with a higher initial reaction rate does not necessarily possess a higher maximum rate. Therefore, it appears that at the maximum reaction peak, the relative importance of both intramicrogel and intermicrogel crosslinking reactions may change.

At MR = 1/1, the maximum reaction rate, which again would be a summation of the reaction rates for both intramicrogel and intermicrogel crosslinking reactions, remains the lowest. This is because the least styrene dilution effect, which enhances the intermicrogel reactions, is less important than the insufficient styrene swelling effect, which reduces the intramicrogel reactions under such a low molar ratio. As the molar ratio increases up to MR = 3/1, the maximum reaction rate is elevated, indicating that the favorable styrene swelling effect would be still greater than the unfavorable styrene dilution effect on the intramicrogel and intermicrogel crosslinking reactions, respectively. However, further increasing the molar ratio to MR = 6/1 results in a decrease in maximum rate, revealing that the styrene dilution effect would excel the styrene swelling effect under such a high molar ratio. It is probably because the higher styrene content would cause a longer crosslink length of styrene, not only between the microgels, which could greatly reduce the rate of intermicrogel crosslinking reactions, but also inside the microgels, which could to some extent counterbalance the favorable styrene swelling effect, and thus lessen the overall reaction rate. As to the final conversion, since the better swelling effect with a higher molar ratio could considerably loosen the microgels, and fewer C=C bonds would thus be buried inside the microgels, the final C=C conversion increases with increasing molar ratio, as shown in Figure 3.

Assuming that one free radical could generate one primary microgel particle,<sup>16</sup> decreasing the reaction temperature from 120°C to 110°C should reduce the styrene swelling effect in facilitating the intramicrogel crosslinking reactions. Because the rate of formation of microgel particles would be curtailed at a lower reaction temperature, the microgels would overlap each other less. As a consequence, the rate of styrene diffusion into the microgels for the participation of intramicrogel crosslinking reactions would be less affected by the initial styrene content. On the other hand, the styrene dilution effect in reducing the intermicrogel crosslinking reactions would also tend to be decreased with decreasing temperature. This is because the concentration of the microgel particles formed during the reaction decreases with decreasing temperature, and the fre-

quency of the occurrence of the intermicrogel crosslinking reactions would then be reduced. Since the reaction temperature is not too low for the intermicrogel crosslinking reactions to compete with the intramicrogel crosslinking ones at 110°C, overall, as the molar ratio increases, the reduction of intermicrogel crosslinking reactions could be more than the enhancement of intramicrogel crosslinking reactions. Therefore, in Figure 4, higher styrene content in either low molar ratios (i.e.,  $MR = 1/1$  and  $2/1$ ) or high molar ratios (i.e.,  $MR = 3/1$  and  $6/1$ ) becomes unfavorable for the initial reaction rate, the order of which is  $MR = 1/1 > 2/1$  and  $MR = 3/1 > 6/1$ . Also, for the maximum reaction rate, the largest value turns out to be that at  $MR = 2/1$  for the 110°C reaction instead of that at  $MR = 3/1$  for the 120°C reaction. The lowest value for  $R_m$  still goes to  $MR = 1/1$  because at the maximum rate, the crosslinking density of the reaction system would be so high that a great reduction of intramicrogel crosslinking reactions, for lack of styrene swelling effect, may result.

From Figure 5, since both the initial reaction rate and the maximum reaction rate increase with increasing molar ratio, at 100°C the styrene swelling effect becomes predominant over the styrene dilution effect. In other words, prior to the peak of rate profile, although both intramicrogel and intermicrogel crosslinking reactions may occur, the intramicrogel crosslinking reactions would predominate. This could be due to the fact that further decreasing the reaction temperature from 110°C to 100°C would lower the rate of microgel formation to a great extent. Hence, the microgel particles formed are well separated at the initial stage of reaction and tend not to overlap with each other tightly at the peak of rate profile, leading to the dominance of intramicrogel crosslinking reactions over the intermicrogel crosslinking ones.

### Shielding and Activation Energy Effects on Final Conversions

From Table III, the final conversion of isothermal cure (i.e.,  $\alpha_S$ ) shows a maximum with increasing reaction temperature at  $MR = 1/1$ . This could be due to the fact that the number of  $C=C$  bonds per polyester molecule for UP2821 resin is 6.84, and at  $MR = 1/1$ , the  $C=C$  units in polyester chains with great steric hindrance would be encountered during the reaction due to a lack of styrene swelling effect to loosen the microgel structures. On one hand, increasing temperature would facilitate the final conversion of the  $C=C$  units due to their acquiring

more activation energy to overcome the steric hindrance during the reaction. On the other hand, increasing temperature could enhance the rate of formation of microgel particles. The fast intermicrogel crosslinking reactions could then bring about the highly overlapped microgels so that for the intramicrogel crosslinking reactions, the diffusing-in styrene monomers from outside the microgels would mostly react with the  $C=C$  units near the surface of microgel particles where the diffusion barrier is lower. Often, this leads to the formation of "shielding walls" that prevent styrene monomers from further diffusing into the interior of microgels and greatly curtails the final conversion of  $C=C$  units due to the incomplete intramicrogel crosslinking reactions. If the activation energy effect is more favorable than the accompanied shielding effect, the final conversion would increase with increasing temperature. This is the case at lower reaction temperatures, 100–110°C. At a higher temperature, such as 120°C, the shielding effect would be dominant over the activation energy effect, leading to a lower final conversion than that at lower temperatures. In contrast, the peculiar temperature dependence of final conversion with  $MR = 1/1$  for UP2821 reactions cannot be observed for UP536B reactions over the temperature range of 90–110°C.<sup>14</sup> This is because the crosslinking density for the UP536B system, with a degree of  $C=C$  unsaturation of 4.16, is lower than that for the UP2821 system, the steric hindrance of the  $C=C$  units during the reaction even at  $MR = 1/1$  for the UP536B system is not severe enough to alter the expected temperature dependence.

The abnormal temperature dependence of the final conversion has also been found<sup>2</sup> for UP reaction systems initiated by benzoyl peroxide (BPO) at 60–100°C. By taking into account the degree of  $C=C$  unsaturation of the resin and comonomer composition, abnormal temperature dependence occurred for one UP resin with a degree of  $C=C$  unsaturation of 9.61 and the mole ratio of styrene to polyester  $C=C$  bonds ( $MR$ ) of 1.6/1, as well as another UP resin with a degree of  $C=C$  unsaturation of 13.86 and  $MR = 1/1$ . In comparison to our system, both highly crosslinking reaction systems would thus lack of styrene swelling effect. In contrast, the normal temperature dependence of the final conversion occurred for the other UP resin with a degree of  $C=C$  unsaturation of 5.45 and  $MR = 3.3/1$ , where the styrene content would suffice to swell the microgels during the reaction. Therefore, the inhomogeneous styrene-crosslinked polyester network would be appropriate in explaining the dependency of final conversion on the curing temperature.

### Isothermal Reaction by IR

For  $MR = 1/1$ , as shown in Figure 6, since the number of styrene  $C=C$  bonds consumed is 83% that of polyester  $C=C$  bonds reacted during the interval of  $0 \rightarrow 1$  (also see Table IV), some intermolecular or intramolecular crosslinking reactions exist without the linkage of styrene monomers. In other words, homopolymerization of polyester  $C=C$  bonds may occur at the early stage of reaction. This is presumably because of the continuous formation of microgel particles and prevailing intramicrogel crosslinking reactions under the lower styrene content that enhance the consumption of polyester  $C=C$  bonds. As the reaction goes on via the intervals of  $1 \rightarrow 2$ ,  $2 \rightarrow 3$ , and  $3 \rightarrow 4$ , more and more styrene monomers are involved in the crosslinking reactions. The average crosslink length of styrene reaches the first maximum for the interval of  $3 \rightarrow 4$ , where the rate profile descends from the peak and the diffusion-controlled propagation reaction for  $C=C$  units in large polyester molecules sets in. The average crosslink length of styrene decreases somewhat for the interval of  $4 \rightarrow 5$ , where the diffusion-controlled propagation reaction for small styrene molecule begins. At the final interval of  $5 \rightarrow 6$ , the average crosslink length of styrene increases because the conversion of polyester  $C=C$  bonds is more depressed than that of styrene under the highly crosslinked network structure.

For  $MR = 2/1$ , as shown in Figure 7, since the average crosslink length of styrene is 1.2 for the interval of  $0 \rightarrow 1$ , where the intramicrogel crosslinking reactions would predominate as mentioned earlier, homopolymerization of polyester  $C=C$  bonds would seldom occur at  $MR = 2/1$ , and most intermolecular and intramolecular crosslinking reactions would proceed through the linkage of one or two styrene monomers in making crosslinks between two adjacent  $C=C$  units. For  $MR = 3/1$  as shown in Figure 8, with the higher styrene content than that at  $MR = 2/1$ , the accompanied better swelling effect of styrene would cause a less compact microgel structure formed during the reaction. A higher conversion of polyester  $C=C$  bonds in the early part of reaction would then result due to the  $C=C$  bonds being encountered with less steric obstruction to the reaction inside the well swollen microgels. For  $MR = 6/1$ , as shown in Figure 9, prior to the peak of DSC profile, the difference of the two conversions is larger for  $MR = 6/1$  than for  $MR = 3/1$  since the styrene swelling effect is greater for the former system to better loosen the microgel structures. Nevertheless, this could be also due to the fact that

for  $MR = 6/1$  the large initial styrene content would inevitably cause a smaller calculated conversion of styrene compared with that of polyester  $C=C$  bonds. From Table IV, it can be seen that as the molar ratio increases, the homopolymerization of polyester  $C=C$  bonds at the initial stage of reaction (i.e.,  $0 \rightarrow 1$ , and  $1 \rightarrow 2$  intervals) is more and more unlikely, and either intermolecular or intramolecular crosslinking reactions would mostly proceed through the linkage of more styrene at higher molar ratios.

In Figure 10, compared with the low-temperature reaction at  $40^\circ\text{C}$ ,<sup>8</sup> the effect of increasing styrene content on the conversion increase of polyester  $C=C$  bonds is less significant here. Since the relative conversion profiles for  $MR = 1/1$  and  $2/1$  at  $110^\circ\text{C}$  fall below the  $45^\circ$  line, whereas they lie above the line at  $40^\circ\text{C}$ , it is revealed that a higher reaction temperature would raise the conversion of polyester  $C=C$  bonds more than that of styrene in the initial stage of reaction (i.e., approximately prior to the peak of DSC rate profile). Therefore, the activation energy of polyester  $C=C$  bonds is higher than that of styrene. The same is also true of  $MR = 3/1$  because the relative conversion profile at  $110^\circ\text{C}$  deviates more from the  $45^\circ$  line than it does at the  $40^\circ\text{C}$ . However, the enhancement of the conversion of polyester  $C=C$  bonds with increasing reaction temperature is less evident as the molar ratio increases. In contrast, at  $MR = 6/1$ , the relative conversion profile at  $110^\circ\text{C}$  is closer to the  $45^\circ$  line than it is at  $40^\circ\text{C}$  in the initial stage of reaction. This is because the higher reaction temperature could greatly increase the conversion of styrene, which is inevitably lower due to the inability to acquire the activation energy for the excess styrene monomers at low reaction temperatures.

### CONCLUSIONS

The effects of comonomer compositions on the curing kinetics of unsaturated polyester resins at high temperatures have been studied by DSC and IR over the entire conversion range. Microgel-based reaction mechanisms for the curing of UP resins at high reaction temperatures have been proposed. In general, prior to the peak of the DSC rate profile, the intramicrogel crosslinking reactions would predominate, whereas after the peak, the intermicrogel crosslinking reactions would be more favorable, which is in opposition to the trend at low reaction temperatures. The competition between the intramicrogel and intermicrogel crosslinking reactions depends on the degrees of unsaturation of UP resins,



the initial molar ratio of styrene to polyester C=C bonds, and the level of reaction temperatures.

For UP resin with a higher degree of C=C unsaturation, such as the UP2821 one, at a lower molar ratio of styrene to polyester C=C bonds, the final overall conversion of C=C bonds would show a maximum with increasing reaction temperature. This is associated with the competition between the shielding and activation energy effects during the reaction for the inhomogeneous styrene-crosslinked polyester network.

As the molar ratio of styrene to polyester C=C bonds increases, the styrene swelling effect favors the intramicrogel reactions, whereas the styrene dilution effect adversely affects the intermicrogel reactions. Since the overall reaction rate is a summation of the intramicrogel and intermicrogel reaction rates, the magnitude of initial reaction rate, as well as maximum rate, depend on the relative importance of the two effects. Quite often, for a UP resin with a lower degree of C=C unsaturation, such as the UP536B one, the higher the molar ratio, the lower the maximum rate, which is relatively independent of reaction temperatures.<sup>14</sup> However, for a UP resin with a higher degree of C=C unsaturation, such as the UP2821 one, the order of maximum rate depends on the reaction temperature in a complicated manner. Generally speaking, at a higher reaction temperature, the styrene dilution effect is usually predominant over the styrene swelling effect, leading to a higher maximum rate as the molar ratio decreases. However, at a lower reaction temperature, the trend is reversed. At any rate, at too low a molar ratio, such as MR = 1/1, the maximum rate is always ranked last due to the lack of styrene swelling effect.

For the reaction systems studied, both the UP2821 and UP536B systems,<sup>14</sup> a higher temperature reaction at 110°C would facilitate the conversion of polyester C=C bonds relative to that of styrene at the early part of reaction when compared with a low temperature reaction at 40°C. This is due to the fact that the activation energy of polyester C=C bonds is greater than that of styrene. When the initial styrene content is low, such as at a lower

molar ratio of MR = 1/1, the homopolymerization of polyester C=C bonds occurs at the early stage of reaction for the high temperature reaction at 110°C, which could not be observed for the low temperature reaction at 40°C.

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