

Curing of Unsaturated Polyester Resins—Effects of Comonomer Composition. I. Low-Temperature Reactions

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SYNOPSIS

The effects of comonomer composition on the curing kinetics of unsaturated polyester (UP) resins at 40°C were studied by differential scanning calorimetry (DSC) and infrared spectroscopy (IR) over the entire conversion range. Two commercial UP resins, including UP2821 and UP536B, which on the average contained 6.82 and 4.16 unsaturated C=C bonds per polyester molecule, respectively, by ¹H-NMR analysis, were used. Experimental results showed that for UP536B reactions initiated by BPO (benzoyl peroxide)/DMA (*N,N*-dimethyl aniline) amine accelerated system, at higher molar ratio of styrene to polyester C=C bonds, the DSC rate profile at 40°C exhibited a shoulder after the peak, which could be caused by the grafting reaction of styrene on C=C bonds of the polyester chain inside the microgel particles. In contrast, for UP2821 resin, no shoulder was observed presumably because UP2821 reaction systems would lead to a higher crosslinking density during the cure, and styrene molecule could not readily diffuse into the microgel structure at the later stage of the reaction for the reaction shoulder to appear. A microgel-based reaction mechanism was thus proposed due to the experimental results. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

All polyester molding compounds consist essentially of unsaturated polyester, styrene, glass fiber, and filler. With the development of bulk molding compound (BMC) and sheet molding compound (SMC), substantial penetration into a variety of major areas, such as transportation, electrical, appliances, and building and construction, has taken place as a result of their design flexibility, dimensional stability, corrosion resistance and heat resistance, and electrical insulation and fire resistance.¹ The great emphasis on weight saving in the U.S. automobile industry has given impetus to the use of SMC in some auto bodies. To date, unsaturated polyester (UP) resins are the most widely used thermoset in polymeric composites.

Several researchers²⁻⁵ directed toward the analysis of ultimate individual conversion in the cure

studies of UP resins. Imai² used infrared spectroscopy to analyze the final styrene and polyester content in the crosslinking network structure for the isothermally cured film at 20°C. Sakaguchi³ investigated the final conversion of styrene and fumarate double bonds in the copolymerization of unsaturated polyesters and styrene at 20°C by the extraction of the soluble component in the cured resin. Sakaguchi and Takemoto⁴ studied the effect of chemical structure, molecular weight, and the initial mole fraction of styrene on the final conversion of fumarate double bond in the copolymerization of UP resins with styrene at room temperature for 24 h followed by a 2-h post-cure at 100°C. They provided support for the supposition that styrene homopolymer was produced as a byproduct in copolymerization of styrene with UP resins. Recently, Urban et al.⁶ have used Fourier transform infrared spectroscopy (FTIR) to study polyester/styrene crosslinking reactions at 26°C. Their study indicated that, during the crosslinking reaction, styrene monomers polymerized forming atactic polystyrene segments which were an integral part of the polyesters/styrene network. Cook and Delatycki⁵ investigated the final network structure

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of a range of styrene-UP cured at 60°C for 24 h and followed by post-curing at 150°C for 1.5–2.0 h. Their results indicated that, in addition to styrene-fumarate copolymerization, a fumarate-fumarate crosslinking reaction occurred when the styrene concentration was low.

Han and Lem⁷ used a differential scanning calorimeter (DSC) to continuously monitor the curing kinetics of UP resins at 40–60°C isothermally. However, individual conversion profile of styrene and polyester vinylene could not be measured by DSC. Yang and Lee^{8,9} used both DSC and FTIR to measure the curing kinetics of UP resins at 30°C. In addition to reaction rate and overall conversion profiles measured by DSC, detailed reaction conversion profiles of styrene and polyester vinylenes were provided by FTIR. They showed that overall conversion results from both DSC and FTIR could be used to calibrate with each other. They also found that⁹ the final conversion of polyester C=C bonds increased with increasing mole ratio of styrene to polyester C=C bonds ranging from 1 : 1 to 4 : 1, but the variation of final styrene conversion depended upon the type of resins.

Furthermore, Yang and Lee¹⁰ showed that the formation of microgel particles is a key feature of the styrene-unsaturated polyester copolymerization. The final network structure for the cured UP resins at 30°C for 8 h could be coral-like or flakelike depending on the concentration and type of polyester resins in the initial reacting system. Formation of microgels enhanced the intraparticle crosslinkings, which caused a fast consumption of polyester C=C bonds at early reaction. Many pendant polyester C=C bonds might be trapped in the compact microgels and became permanent residue.

Zheng et al.¹¹ studied the curing kinetics of unsaturated polyester with vinyl monomers at room temperature using IR and electron spin resonance spectroscopy (ESR). The reaction system contained long-lived polymer radicals, the ESR spectra of which revealed that the polymer radicals formed with cobalt accelerated initiator system were more long-lived than those with the dimethyl aniline accelerated system. Hence, the crosslinking reaction initiated by the former was more effective than that by the latter.

Despite the widespread studies in the curing kinetics of UP resins for the past three decades, in-depth cure kinetic studies over the whole conversion range have not been carried out extensively.^{8,9,11} This is because most of the research works have been either product-oriented or engineering-oriented. The former^{2–5} concentrated on the final conversion

analysis for styrene and polyester vinylene without paying attention to the whole conversion profiles for each species. On the other hand, the latter⁷ considered the curing reaction as a simple free radical homopolymerization without differentiating between the conversions of styrene and polyester C=C bonds.

Since the curing of UP resins is a free radical chain growth crosslinking copolymerization between styrene and unsaturated polyester resin, as one may expect, the number of C=C bonds per polyester molecule in the resin (i.e., degree of C=C unsaturation), initial molar ratio of styrene C=C to polyester C=C bonds, reaction temperatures and temperature histories of curing, and whether or not the initiator system is accelerated by promoter, would affect the curing behaviors of UP resins in different ways. The Part I of this series is concerned with the low-temperature curing kinetics of UP resins at 40°C initiated by BPO/DMA system, using DSC and IR. The experimental results are discussed by using a microgel-based reaction mechanism.

EXPERIMENTAL

Materials

Two unsaturated polyester resins, UP2821 and UP536B, obtained from two local companies were employed in this study. Nuclear magnetic resonance spectroscopy (JOEL JUM-FX100 100 MHz NMR) was used to characterize the resin structures and their compositions. To prepare samples for NMR analysis, one drop of UP resins was added in an ¹H-NMR sample tube (ID = 4 mm), and at least five times as much of acetone was used to dilute the viscous UP resins. The tube was placed in a vacuum oven for 5 h at room temperature, with the addition of acetone several times to facilitate removing styrene monomers contained in the resin. Deuteriochloroform (CDCl₃) was then added up to a height of above 3 cm, and the dissolved UP resins were ready for NMR analysis.

The amount of styrene monomers contained in the UP resins was determined by evacuating the styrene from the UP resin, again diluted with copious acetone, in the vacuum oven at room temperature for 8 h. With the repetition of above procedures several times till the weight of resins remained unchanged, styrene content could then be calculated from the weight loss. The acid value of the resins was determined by end-group titration, and the number-average molecular weight \bar{M}_n could then be

estimated as $\bar{M}_n = 56,000/\text{acid value}$ by assuming that each unsaturated polyester prepolymer on the average has one hydroxyl group and one carboxylic group at each end. Also, the initial viscosity of the resin was measured by a Brookfield viscometer.

Based on the characterization results, extra styrene was added to or evaporated from the resin so that the molar ratio of styrene to the C=C unsaturation on polyester molecules was adjusted to be 1/1, 2/1, 3/1, 4/1, or 6/1 in the preparation of sample solutions. To start the measurement, 3% by weight (based on resins) of benzoyl peroxide (BPO, an initiator, Lucidol W-75, Akzo Chemicals), and 0.2% by weight of inhibitor NLC (p-tert-butyl catechol, NLC-10, Akzo chemicals) were added in the resin and thoroughly mixed at room temperature first. Because the dissolution of the solid peroxide in the polyester resins required some time, the presence of an accelerator in the first step might cause premature curing during the mixing. Hence, only in the second step, 0.3% by weight of accelerator DMA (*N,N*-dimethyl aniline, Akzo Chemicals) was added and quickly mixed together. The mixture was then sampled and placed in related instruments for kinetic measurements. In this study, all the materials were employed as received without further purifications.

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 5–10 mg. Isothermal reaction rate vs. time profiles were measured at 40°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. If we make three assumptions that density and heat capacity of the resin change little with reaction from liquid to solid within the temperature range used, that heats of polymerization associated with styrene and polyester C=C bonds are approximate, and that the reaction can be complete as long as the temperature is high enough for a long period of time, the rate of overall reaction can be directly converted from the rate of heat release measured by DSC as follows:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T} \frac{d\Delta H_t}{dt} \quad (1)$$

and

$$\alpha = \frac{1}{\Delta H_T} \int_0^t \frac{d\Delta H_t}{dt} dt = \frac{\Delta H_t}{\Delta H_T} \quad (2)$$

where $d\alpha/dt$ and α are the overall reaction rate and total conversion at a given time, ΔH_t is the heat release before the time t , and ΔH_T is the total heat release, which may be the summation of isothermal and residual scanning heat releases (i.e., $\Delta H_T = \Delta H_{\text{iso}} + \Delta H_{\text{res}}$, and $\Delta H_T = \Delta H_I$), or the heat release from direct scanning DSC run (i.e., $\Delta H_T = \Delta H_S$).

In this study, an IR spectrophotometer (Jasco, IR-700) with a resolution of 4 cm^{-1} in the transmission mode was used for kinetic measurements of styrene reaction and the reaction of polyester vinylene groups. After the reactants were mixed, one drop of mixture (5–10 mg) was pasted between two potassium bromide plates, which were then mounted on a sample holder located in the IR chamber. A temperature control chamber was designed to maintain the reaction temperature isothermally. A scan of 2.5 min from 2000 to 600 cm^{-1} was taken at each sampling time. Measurement was ended when there were no changes in absorbance peak areas. All IR spectra were expressed in absorbance where individual reaction conversion of styrene and polyester vinylene could be determined as a function of time. For low-temperature 40°C reaction, styrene loss was negligible as evidenced by the invariant absorbance at 695 cm^{-1} (C—H out of plane bending in benzene ring of styrene) during the reaction. In the analysis of IR spectra, changes of absorbance at 912 and 982 cm^{-1} were employed to calculate conversions of styrene and polyester vinylene group, respectively. The absorbance at 1730 cm^{-1} (C=O stretching) was picked as an internal standard. Since the peaks at 982 and 992 cm^{-1} were overlapped, a simple subtraction method was used to separate the overlapping peaks.^{12,13} Detailed calculation procedures were given elsewhere.¹³

RESULTS

The Resin Structure and Composition

Figure 1 shows the $^1\text{H-NMR}$ spectrum of UP2821 resin at 100 MHz in CDCl_3 after removal of styrene. By referring to the qualitative analysis results of NMR spectra for UP resins,¹⁴ the resin structure

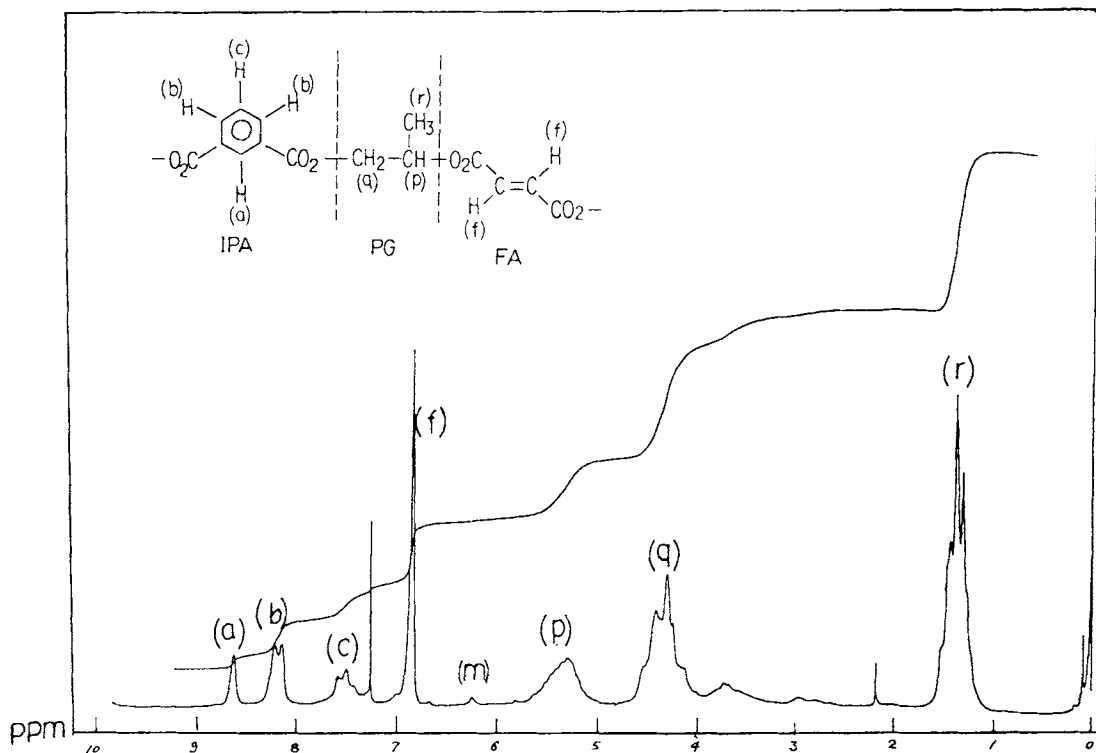


Figure 1 ¹H-NMR spectrum (at 100 MHz in CDCl₃ at room temperature) of UP2821 resin after removal of styrene monomers.

could readily be identified, and was included in the figure. The three peaks designated a, b, and c at chemical shift $\delta = 8.8\text{--}7.3$ ppm suggest an isophthalic acid (IPA) residue. The peak appearing at $\delta = 7.3$ is due to the solvent CDCl₃. The single peak designated f at $\delta = 7.0\text{--}6.7$ ppm suggests a fumaric acid (FA) residue. The small peak designated m at about $\delta = 6.3$ ppm is due to maleic anhydride (MA), the amount of which is less than $\frac{1}{40}$ that of FA presumably because the maleate isomerizes to the fumarate extensively during the synthesis of UP resins. The three peaks designated p, q, and r suggest a constituent of propylene glycol (PG) residue. The small peak at $\delta = 2.1$ ppm is due to acetone left behind in the sample preparation step.

Now that the resonance has been identified, the quantitative analysis is straightforward from peak area measurement in Figure 1 using the integral curve. For UP2821 resin, the relative compositions are calculated as

$$\begin{aligned} \text{IPA} : \text{FA} : \text{PG} &= \frac{\text{IPA (a, b, c)}}{4} : \frac{\text{FA (f)}}{2} : \frac{\text{PG (r)}}{3} \\ &= 1 : 1.46 : 2.79 \quad (3) \end{aligned}$$

where IPA (a, b, c) is the summation of peak areas due to H(a), H(b), and H(c), FA (f) is the peak area due to H(f), and PG (r) is the peak area due to H(r).

Figure 2 shows the ¹H-NMR spectrum of UP536B resin with the same conditions of analysis as in Figure 1. The two peaks appearing at $\delta = 8.0\text{--}7.3$ ppm are due to phthalic acid (PA) residue.¹⁴ As in Figure 1, fumaric acid (FA) and propylene glycol (PG) residues can also be identified. Since the peak area for H(q) in PG is so large that the ratios of relative peak areas for H(p), H(q), and H(r) are unequal to 1 : 2 : 3, it suggests that other constituents must exist. This composition appears to be diethylene glycol (DEG) with two proton groups, H(e) at $\delta = 4.6\text{--}4$ ppm and H(d) at $\delta = 3.9\text{--}3.3$ ppm. It can be seen from the figure that H(e) overlaps with H(q) in PG. Since the peak area H(d) was judged to be due to proprietary unknown ingredients other than diethylene glycol, in the calculation of DEG content, the area of H(e) was employed. A simple subtraction method should be used to separate the overlapping peaks due to H(e) and H(q) based on the calculated peak area for H(q) in PG. For UP536B resin, the relative compositions are calculated as

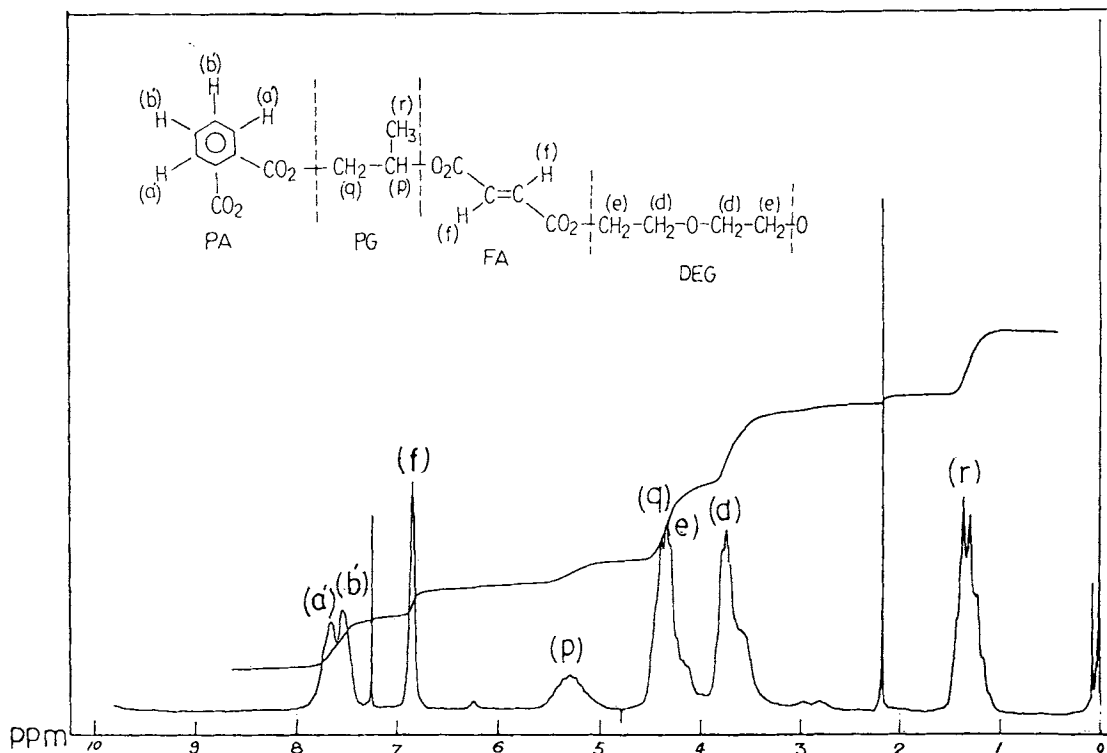


Figure 2 $^1\text{H-NMR}$ spectrum (at 100 MHz in CDCl_3 at room temperature) of UP536B resin after removal of styrene monomers.

PA : FA : PG : DEG

$$= \frac{\text{PA}(a', b')}{4} : \frac{\text{FA}(f)}{2} : \frac{\text{PG}(r)}{3} : \frac{\text{DEG}(e)}{4}$$

$$= 1 : 1.07 : 1.9 : 0.73 \quad (4)$$

The detailed characterization results for the two UP resins are displayed in Table I. The unit molecular weight per mole of $\text{C}=\text{C}$ bonds along the polyester chain, M_0 , calculated from row 1 is given in row 6. By dividing \bar{M}_n by M_0 , the average number of $\text{C}=\text{C}$ bonds per polyester molecule is obtained as shown in row 7. Although the chemical composition, average functionality, and molecular weight are varied for the two UP resins, the difference in average functionality would mostly account for the peculiarity in their curing behaviors. For UP2821, on the average, there are 6.82 $\text{C}=\text{C}$ bonds for each polyester molecule, which is greater than that for UP536B with 4.16 $\text{C}=\text{C}$ bonds. Therefore, UP2821 with more crosslinkable $\text{C}=\text{C}$ sites than UP536B would end up with higher crosslinking density than that of UP536B after the cure.

By convention, the addition of initiator, accel-

erator, and inhibitor was based on the weight percentage of the UP resins used. To facilitate later discussion, the conversion of the weight basis into the molar basis was performed, and the results are listed in Table II. It can be seen that the number of total $\text{C}=\text{C}$ bonds including styrene vinyls and polyester vinylene groups per gram of UP resins shown in row 1 increases with the molar ratio. If we neglect the density variation of the sample solutions with different molar ratio of styrene to polyester $\text{C}=\text{C}$ bonds, the values in rows 5, 6, and 7 would reflect the magnitudes of molar concentrations for BPO, DMA, and NLC. It can be seen that with the same weight percentage of BPO, DMA, and NLC relative to the resin, the molar concentration, however, would decrease with increasing molar ratio of $\text{C}=\text{C}$ bonds. On the other hand, at the same molar ratio of styrene to polyester $\text{C}=\text{C}$ bonds, the molar concentrations are about 10–20% higher for UP536B sample solutions than for UP2821 ones. Also, the higher the molar ratio, the smaller the difference. Row 10 gives the product of Rows 5 and 6, and is proportional to the initial rate of free radical formation for the amine-accelerated initiator system, i.e.,

Table I The Unsaturated Polyester Resins Used in This Study

	UP-2821	UP-536B
(1) Parts (mol %), ingredients of UP resin (molar ratio in parentheses)		
IPA (isophthalic acid)	19.05 (1)	—
PA (phthalic acid)	—	21.27 (1)
FA (fumaric acid)	27.81 (1.46)	22.76 (1.07)
MA (maleic acid)	0.057	0.022
PG (propylene glycol)	53.14 (2.79)	40.42 (1.9)
DEG (diethylene glycol)	—	15.53 (0.73)
(2) Molar ratio of glycols to dicarboxylic acids	1.13	1.27
(3) Styrene content in UP resins (wt %)	36.42	29.58
(4) Viscosity (CP)	1763.3	856.7
(5) Acid number (X)	26.77	34.43
\bar{M}_n (= 56,000/X)	2092	1627
(6) Unit MW/mol polyester C=C, M_0	306.6	391.0
(7) Avg. no. C=C/polyester (= \bar{M}_n/M_0)	6.82	4.16
(8) Molar ratio of C=C bonds for styrene/polyester	1.69	1.58

$$R_i \propto [\text{DMA}]_0 [\text{BPO}]_0 \quad (5)$$

where R_i is the rate of free radical formation, $[\text{DMA}]_0$ is the initial molar concentration of accelerator DMA, and $[\text{BPO}]_0$ is the initial molar concentration of initiator BPO. The number in parenthesis shown in rows 5, 6, 7, and 10 represents the relative value by taking the value at molar ratio of 1/1 as unity.

Scanning Reaction of UP2821 by DSC

Figure 3 shows the scanning DSC rate profiles of styrene/UP2821 reactions for various molar ratios of styrene to polyester C=C bonds at 10°C/min from 0 to 210°C. It can be seen that, as the molar ratio increases, the shape of rate profile changes from one peak to two peaks. The first peak results from the copolymerization by redox-type initiation between the peroxide BPO and the promoter DMA, whereas the second peak is due to the reaction solely initiated by thermal decomposition of peroxide upon the consumption of the promoter, as was explained by other researchers.^{8,15} For comparison of reaction rates with different molar ratios, the reaction rate shown in Figure 3 was expressed as J/mol C=C bonds/s instead of J/g resin/s, since the number of moles of total C=C bonds for every gram of resin with differing molar ratio is different from one another, as shown in Table II.

The rate profiles shown in Figure 3 were not corrected for the variation of molar concentrations of the initiator system shown in Table II. Since the initial rate of polymerization¹⁶ is proportional to the square root of the initial rate of free radical formation, R_i , i.e.,

$$\begin{aligned} R_p &= k_p [\text{M}\cdot] [\text{M}] \\ &= k_p [\text{M}] (R_i/2k_t)^{1/2} \end{aligned} \quad (6)$$

where R_p is the polymerization rate, k_p and k_t are the rate constants for propagation and termination, respectively, $[\text{M}\cdot]$ is the total concentration of all chain radicals, $[\text{M}]$ is the monomer concentration, and R_i is the rate of initiation, eq. (6) can then be used to correct the reaction rates later on. It should be pointed out that it appears inconvenient to correct the experimental reaction rates by using eq. (6) because much of the recent research^{17,18} suggests that there is not a pseudo-steady state for free radicals in these systems, and most probably there is a continuous increase in the concentration of radicals along the polymerization. However, Chiu et al.¹⁹ and Huang et al.²⁰ have shown that, for the diffusion-controlled free radical homopolymerization, the apparent termination rate constant k_t decreases as the reaction goes on, and the use of eq. (6) based on the pseudo-steady-state assumption on the growing radical population can still give a continuous increase in the concentration of radicals, especially in

Table II Initiator, Promoter, and Inhibitor Concentrations on the Molar Basis for the Prepared Samples of UP2821 and UP536B Resins Used in This Study

Molar Ratio of C=C Styrene/ Polyester (Molar Ratio in Parentheses)	1/1	2/1	3/1	4/1	6/1
(a) The UP2821 Resin					
(1) Total moles of C=C/g resin	4.87×10^{-3}	5.83×10^{-3}	6.47×10^{-3}	6.92×10^{-3}	7.52×10^{-3}
(2) g BPO/g resin	0.03	0.03	0.03	0.03	0.03
(3) g DMA/g resin	0.003	0.003	0.003	0.003	0.003
(4) g NLC/g resin	0.002	0.002	0.002	0.002	0.002
(5) mol BPO/mol C=C	0.0255	0.0213	0.0192	0.0179	0.0165
	(1)	(0.84)	(0.75)	(0.70)	(0.65)
(6) mol DMA/mol C=C	5.09×10^{-3}	4.25×10^{-3}	3.83×10^{-3}	3.58×10^{-3}	3.30×10^{-3}
	(1)	(0.83)	(0.75)	(0.70)	(0.65)
(7) mol NLC/mol C=C	2.47×10^{-3}	2.07×10^{-3}	1.86×10^{-3}	1.74×10^{-3}	1.60×10^{-3}
	(1)	(0.84)	(0.75)	(0.70)	(0.65)
(8) mol DMA/mol BPO	0.2	0.2	0.2	0.2	0.2
(9) mol NLC/mol BPO	0.097	0.097	0.097	0.097	0.097
(10) $(5) \times (6) (\propto [\text{DMA}]_0 [\text{BPO}]_0)$	1.30×10^{-4}	9.05×10^{-5}	7.35×10^{-5}	6.41×10^{-5}	5.45×10^{-5}
	(1)	(0.70)	(0.57)	(0.49)	(0.42)
(b) The UP536B Resin					
(1) Total moles of C=C/g resin	4.04×10^{-3}	5.01×10^{-3}	5.69×10^{-3}	6.20×10^{-3}	6.90×10^{-3}
(2) g BPO/g resin	0.03	0.03	0.03	0.03	0.03
(3) g DMA/g resin	0.003	0.003	0.003	0.003	0.003
(4) g NLC/g resin	0.002	0.002	0.002	0.002	0.002
(5) mol BPO/mol C=C	0.0307	0.0247	0.0218	0.0200	0.0180
	(1)	(0.80)	(0.71)	(0.65)	(0.59)
(6) mol DMA/mol C=C	6.14×10^{-3}	4.95×10^{-3}	4.36×10^{-3}	4.00×10^{-3}	3.59×10^{-3}
	(1)	(0.81)	(0.71)	(0.65)	(0.58)
(7) mol NLC/mol C=C	2.98×10^{-3}	2.40×10^{-3}	2.12×10^{-3}	1.94×10^{-3}	1.75×10^{-3}
	(1)	(0.81)	(0.71)	(0.65)	(0.59)
(8) mol DMA/mol BPO	0.2	0.2	0.2	0.2	0.2
(9) mol NLC/mol BPO	0.097	0.097	0.097	0.097	0.097
(10) $(5) \times (6) (\propto [\text{DMA}]_0 [\text{BPO}]_0)$	1.88×10^{-4}	1.22×10^{-4}	9.50×10^{-5}	8.00×10^{-5}	6.46×10^{-5}
	(1)	(0.65)	(0.51)	(0.43)	(0.34)

the gel effect region. Moreover, recent kinetic models^{21,22} derived from the basic eq. (6) for the cure of polyester resins over the entire conversion range have also shown reasonable agreement on the theoretical and experimental rate and conversion profiles.

The first peak of the reaction rate profile shown in Figure 3 occurs at 50–100°C, and the increasing order of temperature to the maximum reaction rate, T_m , is that molar ratio MR = 2/1 (75°C) < 3/1 (80°C) < 1/1 (84°C) < 4/1 (87°C) < 6/1 (97°C). The decreasing order of the maximum reaction rate R_m is that MR = 2/1 (306.3 J/mol C=C/s) > 3/1 (211.3 J/mol C=C/s) > 1/1 (209.1 J/mol C=C/s) > 4/1 (162.1 J/mol C=C/s) > 6/1

(123.4 J/mol C=C/s). After correction for the variation of R_i by using MR = 1/1 as the basis (row 10 in Table II), the order of R_m turns out to be that MR = 2/1 (366.1 J/mol C=C/s) > 3/1 (279.9 J/mol C=C/s) > 4/1 (231.6 J/mol C=C/s) > 1/1 (209.1 J/mol C=C/s) > 6/1 (190.4 J/mol C=C/s). Hence, the order remains the same except that R_m for MR = 1/1 lies between MR = 4/1 and MR = 6/1. The effect of R_i variation on the order of reaction rate for the samples with different molar ratios is essentially insignificant. Except for MR = 1/1, R_m decreases with increasing molar ratio, and R_m for MR = 2/1 exhibits the highest value. It is similar to that observed by Huang et al.²³ under isothermal DSC reactions at 100°C.

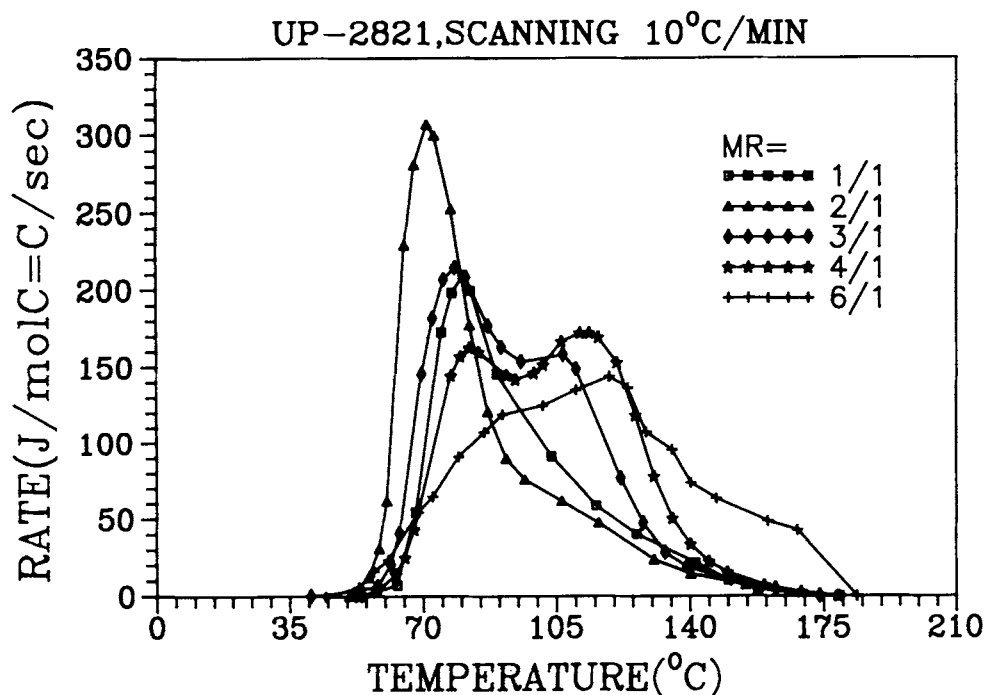


Figure 3 Scanning DSC rate profiles at 10°C/min for styrene/UP-2821 reactions with various molar ratios of styrene to polyester C=C bonds.

The second peak shown in Figure 3 occurs at 100–180°C. For MR = 1/1 and 2/1, the peak cannot be observed except for a shoulder. The increasing order of T_m for the second peak is that MR = 3/1 (110°C) < 4/1 (117°C) < 6/1 (123°C). The order of the second peak value, R_m , is that MR = 6/1 (145.6 J/mol C=C/s) < 3/1 (158.1 J/mol C=C/s) < 4/1 (173.8 J/mol C=C/s). Due to the variation of BPO concentration at various molar ratio, this factor should be corrected for in the calculation of R_m of the second peak, where the promoter DMA has been consumed. By use of the molar ratio in parenthesis in row 5 of Table II, the corrected value is that $R'_m = R_m/[BPO]^{1/2}$. The increasing order of R'_m is still that MR = 6/1 (180.6 J/mol C=C/s) < 3/1 (182.6 J/mol C=C/s) < 4/1 (207.7 J/mol C=C/s).

Isothermal Reaction of UP2821 by DSC

Figure 4 shows the isothermal DSC rate profiles at 40°C for samples with various molar ratios of styrene to polyester C=C bonds, MR = 1/1, 2/1, 3/1, 4/1, and 6/1. It can be seen that the rate profile has a bell-like shape, and one maximum point. The higher the molar ratio, the longer the tail of the rate profile would be. The time to the maximum reaction rate, t_m , is that MR = 1/1 (6.8 min) < 2/1 (8.2 min) < 4/1 (10.6 min) < 3/1 (15.2 min) < 6/1

(16.7 min). The decreasing order of the maximum rate, R_m , is that MR = 1/1 (54.36 J/mol C=C/s) > 2/1 (48.73 J/mol C=C/s) > 4/1 (35.05 J/mol C=C/s) > 3/1 (26.61 J/mol C=C/s) > 6/1 (18.76 J/mol C=C/s). After correction for the differences in the rate of free radical formations shown in row 10 of Table II, the order of corrected maximum rate $R'_m (= R_m/R_i^{1/2})$ is that MR = 2/1 (58.24 J/mol C=C/s) > 1/1 (54.36 J/mol C=C/s) > 4/1 (50.07 J/mol C=C/s) > 3/1 (35.25 J/mol C=C/s) > 6/1 (28.95 J/mol C=C/s). Again, except that the order for MR = 1/1 and MR = 2/1 is reversed, the order for other samples remains the same.

Figure 5 shows the isothermal conversion profiles corresponding to Figure 4. The conversion profiles of the five samples in Figure 5 were calculated on the basis of ΔH_S for each sample shown in Table III, which is the total heat release from DSC scanning run at 10°C/min. It can be seen that the higher the molar ratio, the higher the overall conversion would result except for MR = 6/1. For MR = 6/1, the overall conversion turns out to be the lowest among the samples. As will be shown later on, however, the conversion of the partially cured sample can be raised by post-cure at higher temperatures.

Table III summarizes the heat generated by the curing reaction, which includes the heat generated

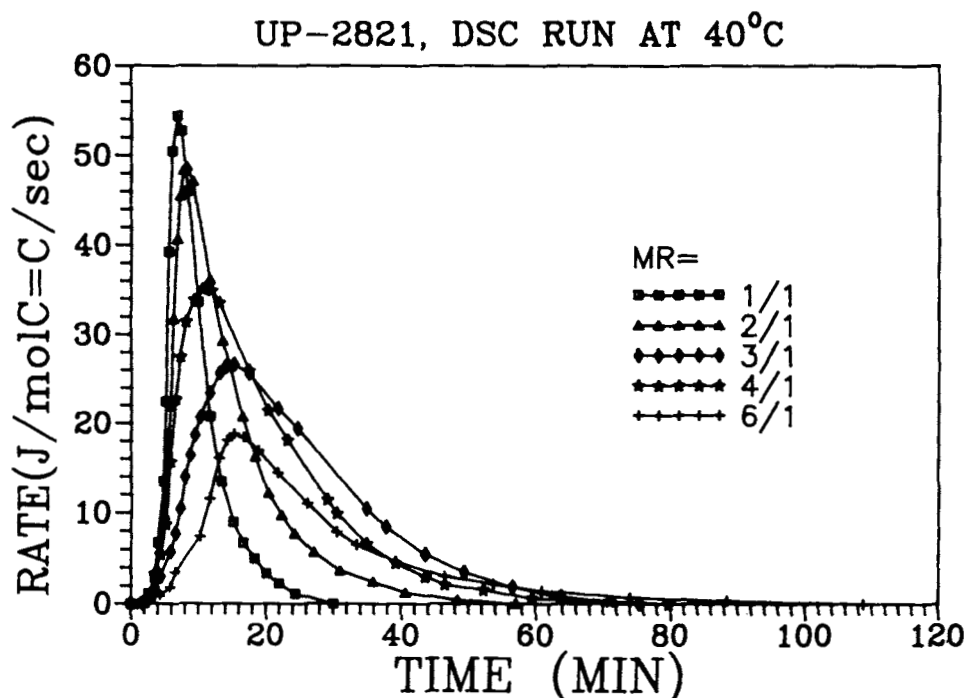


Figure 4 Isothermal DSC rate profiles for styrene/UP2821 reactions at 40°C with various molar ratios of styrene to polyester C=C bonds.

in isothermal cure, ΔH_{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, ΔH_{res} , the total heat of cure,

ΔH_I , by adding ΔH_{iso} and ΔH_{res} , and the total heat release by direct scanning from 0 to 210°C at 10°C/min, ΔH_S . Also listed in Table III are the final conversion, α_I and α_S , based on ΔH_I and ΔH_S , respec-

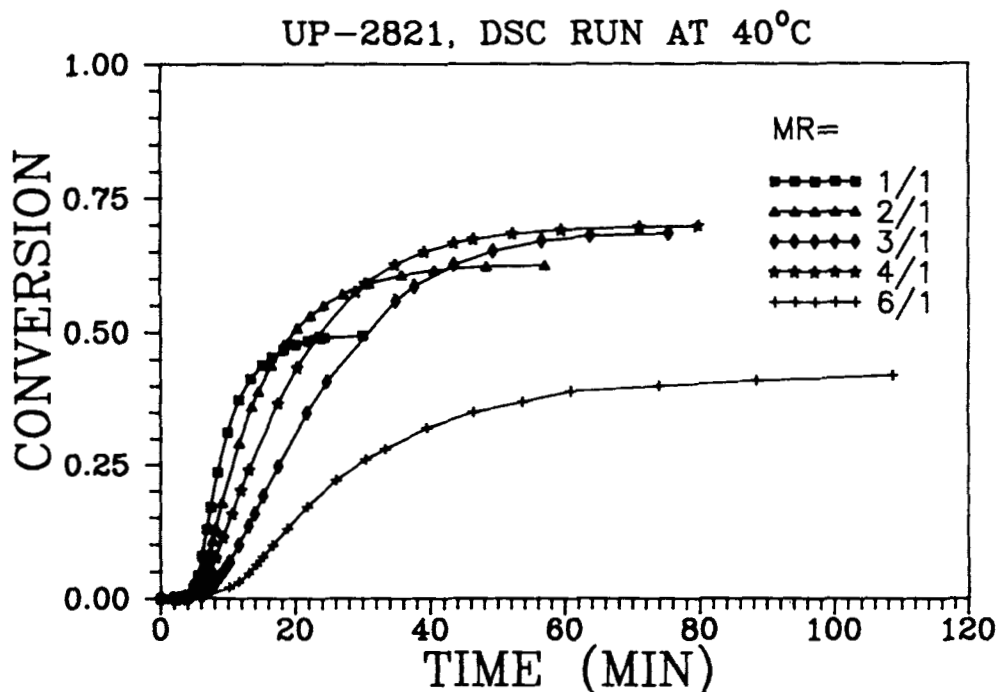


Figure 5 Isothermal DSC conversion profiles corresponding to Figure 4.

Table III Summary of Kinetic Information by DSC for Styrene/UP2821 Reactions Both at 40°C and in Scanning Modes

Molar Ratio of Styrene/Polyester C=C	1/1	2/1	3/1	4/1	6/1
Isothermal, rescanning and total heats of reaction (kcal/mol C=C)					
ΔH_{iso}	5.25	8.22	9.85	10.11	6.43
ΔH_{res}	4.67	3.45	2.86	2.56	5.39
$\Delta H_I = \Delta H_{iso} + \Delta H_{res}$	9.92	11.67	12.71	12.67	11.82
Total heat of reaction by direct scanning (kcal/mol C=C), ΔH_S	10.64	13.16	14.41	14.50	15.15
Total conversion based on ΔH_I and ΔH_S					
α_I	0.53	0.70	0.78	0.80	0.54
α_S	0.49	0.62	0.68	0.70	0.42
Induction time t_z (min)	2.61	1.93	1.74	1.45	2.03
Time to max rate t_m (min)	6.81	8.16	15.22	10.58	16.67
Conversion at max rate, $\alpha(t_m)$	0.14	0.16	0.20	0.19	0.09

tively, 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 ΔH_S increases with increasing molar ratio. Table III also shows that ΔH_I is always lower than ΔH_S . Thus, the way of direct scanning is more effective than the isothermal cure with a subsequent rescanning procedure for the C=C bonds to be fully reacted. However, the overall conversion of the sample with MR = 6/1 was measured to be 96.5% by IR at the end of direct DSC scanning run at 10°C/min. Therefore, for the highly crosslinked resin system like ST/UP2821, there are still some residual C=C bonds buried inside the network structure despite the sample experiencing direct scanning by DSC. In general, the lower the scanning rate, the slightly higher the heat of reaction would be.²⁴

Isothermal Reaction of UP2821 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 bell-shaped DSC rate profile, and DSC total conversion curves based on both ΔH_I (solid line) and ΔH_S (dashed line) are plotted together as well. It can be seen that the overall conversion measured by IR lies between α_I and α_S measured by DSC, and the difference of conversions by IR and DSC is within 2%. During the entire reaction course, the conversion of styrene, α_S , is always higher than that of polyester C=C bonds, α_E . The difference between α_S and α_E generally increases as the reaction goes on. The conversion of styrene steadily increases with time, while the increase of polyester C=C

conversion slows down after point A, where the overall conversion is about 30%. This is because after point A the DSC rate profile has passed the maximum point, and the diffusion-controlled propagation reaction sets in.²¹ Due to the highly crosslinked network formation after point A, the C=C units of large polyester molecules are relatively immobile compared to the C=C units of small styrene molecules. Hence, the conversion of polyester C=C bonds is considerably hampered, while the conversion of styrene keeps on increasing.

As far as the reacted C=C bonds are concerned, the average number of styrene C=C bonds consumed for each polyester C=C bond reacted is 1.3 from the beginning of the reaction to point A shown in Figure 6. The average number increases to 3.7 and 7 from point A to B and from point B to C, respectively. Since the final conversions of styrene and polyester C=C bonds are 69.2 and 35.1%, respectively, on the average, 1.97 styrene C=C bonds would be consumed for each polyester C=C bond reacted. Provided that all the styrene monomers contribute to the crosslinking reactions with polyester, for the final copolymer formed with MR = 1/1, the average crosslink length of styrene,¹³ n , is 1.97. In other words, about two styrene C=C bonds are required to link two adjacent C=C units on polyester molecules, either by intramolecular reactions or by intermolecular reactions.

Figure 7 shows the conversion profiles measured by IR for MR = 2/1. The overall conversion by IR is close to α_S of the DSC curve. From the beginning of the reaction to the maximum point of the DSC rate profile, the conversions of polyester C=C bonds and styrene C=C bonds are approximately

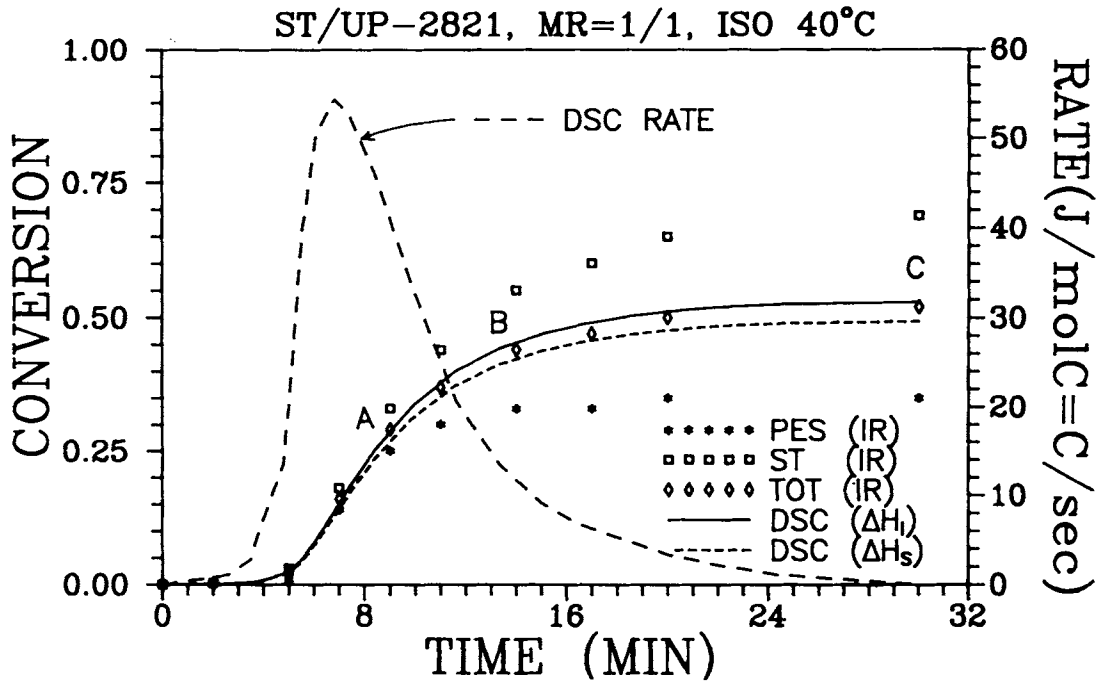


Figure 6 Styrene, polyester vinylene, and total C=C conversions vs. time profiles measured by IR for UP2821 reaction with MR = 1/1. DSC rate profile (dashed curve) and total C=C conversion profiles based on both ΔH_s (solid curve) and ΔH_i (dashed curve) are also plotted for comparison.

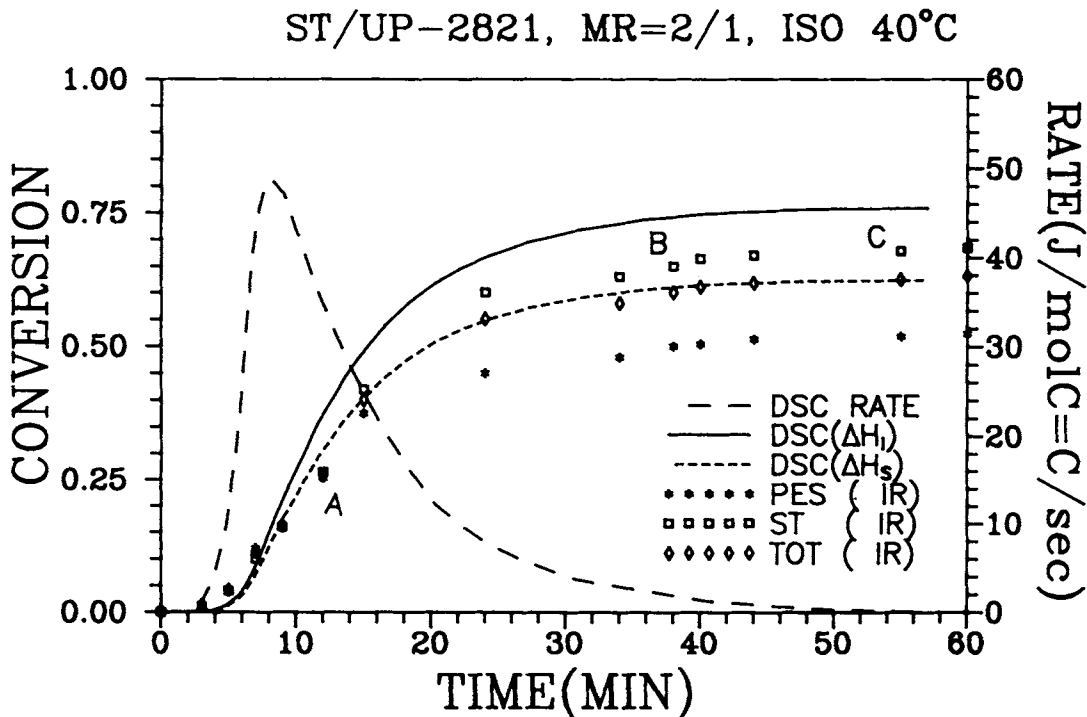


Figure 7 Conversion vs. time profiles measured by IR for UP2821 reaction with MR = 2/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.

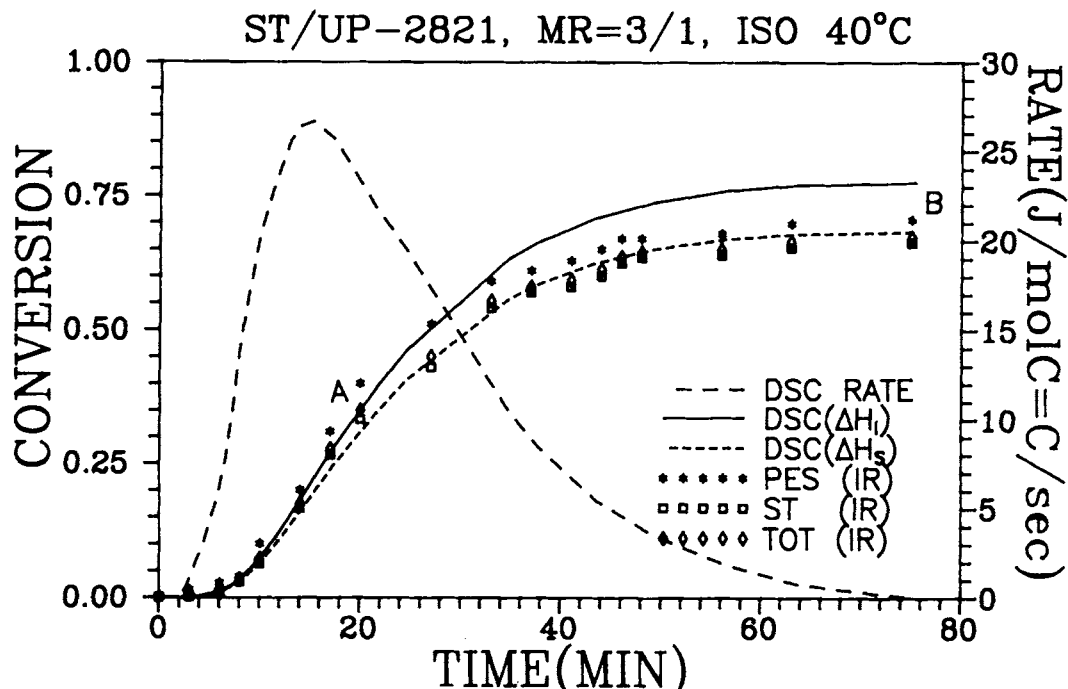


Figure 8 Conversion vs. time profiles measured by IR for UP2821 reaction with MR = 3/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.

the same, and exhibit the near-azeotropic copolymerization. After point A with an overall conversion of 25%, the conversion of styrene gradually exceeds that of polyester C=C bonds due to the diffusion limitation of propagation reactions for styrene being less than that for polyester C=C units. For the reaction periods from the beginning to point A, from A to B, and from B to C shown in Figure 7, the calculated average crosslink length of styrene is 2, 3, and 5, respectively. For the final copolymer formed, the conversions of styrene and polyester C=C bonds are 68.5 and 52.3%, and the average crosslink length of styrene is 2.62 accordingly.

Figure 8 shows the conversion profiles by IR for MR = 3/1. The overall conversion by IR is close to α_S . During the entire reaction course, the conversion of polyester C=C bonds is always greater than that of styrene. However, their difference is mostly within 5%. The final conversions of polyester C=C bonds and styrene are 70.6 and 66.3%, respectively, with a difference of 4.3%, which is not the largest difference for the two conversions during the reaction. Rather, it occurs at the time between 20 min (point A after the peak of DSC rate profile) and 28 min, where a small shoulder appears to emerge. The difference of conversions is about 6.7–8%. It can be seen from Figure 8 that the conversion of C=C units for either small styrene molecules or large

polyester molecules increases steadily with time, but the rate of conversion increase declines somewhat after point A. The conversion curve gradually levels off after 40 min. This is different from the case of MR = 1/1 or MR = 2/1, where the conversion of polyester C=C bonds increases slightly at the latter part of reaction (see Figs. 6 and 7) and the final conversion of polyester vinylene groups is much less than that of MR = 3/1 here (35.1 and 52.3% vs. 70.6%). The calculated average crosslink lengths of styrene are 2.5 and 3.2 for the reaction intervals from the beginning to point A and from A to B, respectively. For the final copolymer formed, the average crosslink length of styrene is 2.82 provided that all the styrenes reacted contribute to the network structure formations.

Figure 9 shows the conversion vs. time profiles measured by IR for MR = 4/1. It can be seen that the total conversion of C=C bonds by IR is also close to α_S measured by DSC. The conversion of polyester C=C bonds is always higher than that of styrene during reaction with an average difference of 15%. The final conversions of polyester C=C bonds and styrene are 79.8 and 65.4%, respectively, with a difference of 14.4%. It can be seen that in the beginning of the reaction, the conversion of polyester C=C bonds is much higher than that of styrene with a difference of 10%. Again, the con-

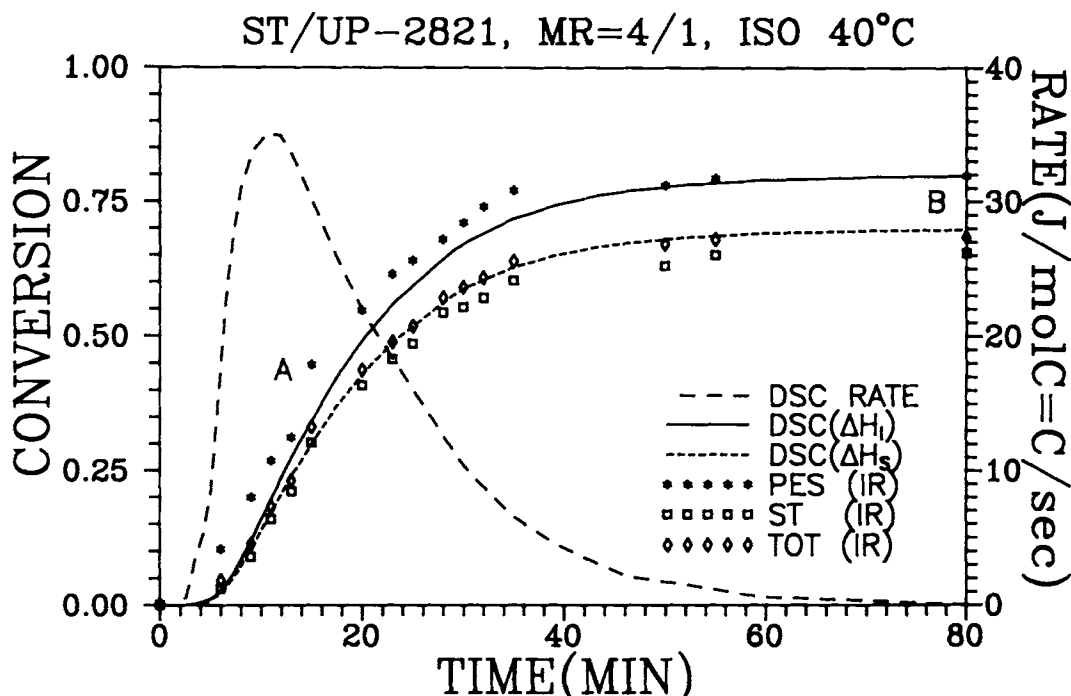


Figure 9 Conversion vs. time profiles measured by IR for UP2821 reaction with MR = 4/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.

versions of styrene and polyester C=C bonds generally increase steadily with time. Although the rate of conversion increase after point A, where the DSC rate profile has passed the peak, is slightly depressed, it is higher than that for MR = 3/1 with either styrene or polyester C=C conversion during the same period (see Figs. 8 and 9). The calculated average crosslink lengths of styrene are 2.71, 4.07, and 3.28 for the reaction intervals from the beginning to point A, from A to B, and from the beginning to B (i.e., the entire reaction interval), respectively.

Figure 10 shows the conversion profiles measured by IR for MR = 6/1. It can be seen that the total conversion measured by IR is again close to α_S by DSC, and the former is lower than the latter after 15% conversion with a largest difference of 5%. Similar to Figures 8 and 9, the conversion of polyester C=C bonds is always higher than that of styrene during reaction. The final conversions of styrene and polyester C=C bonds are 35.0 and 69.5%, respectively, the former being much lower than those in Figures 8 and 9 (35.0% vs. 66.3 and 65.4%).

Table IV summarizes the final conversions measured by IR, and the final average crosslink length of styrene at various molar ratios. Figure 11 shows the relative conversion of styrene (α_S) to that of polyester C=C bonds (α_E). All the curves show up-bending characteristics, and move to the right

as molar ratio increases. The curves for MR = 1/1 and 2/1 lie above 45° diagonal line, which represents the azeotropic copolymerization. Due to the high crosslinking density for the reaction system under such low molar ratios, at the latter part of reaction, the styrene conversion becomes more favorable than polyester C=C conversion (also see Table IV). It should be noted that, at MR = 2/1, it leads to an azeotropic copolymerization prior to $\alpha_E = 0.25$ since the curve falls on the 45° line. For molar ratios higher than MR = 2/1, the curves lie below 45° line, and the conversion of polyester C=C bonds is always higher than that of styrene. Since these curves only show a slightly up-bending feature, the styrene conversion appears to be less favorable compared to that for low molar ratio. After 35, 45, and 55% of α_E for MR = 3/1, 4/1, and 6/1, respectively, the relative conversion profiles shown in Figure 11 are approximately parallel to the 45° line. It reveals that, at the later reaction interval, the number of styrene vinyls consumed per polyester vinylene reacted is close to the initial molar ratio of styrene to polyester C=C bonds, i.e., 3, 4, and 6 for MR = 3/1, 4/1, and 6/1, respectively. This is because at higher molar ratios the crosslinking density of the system is lower, the conversions of styrene and polyester C=C bonds can then be promoted at the same pace for the later reaction due to the comparable mobil-

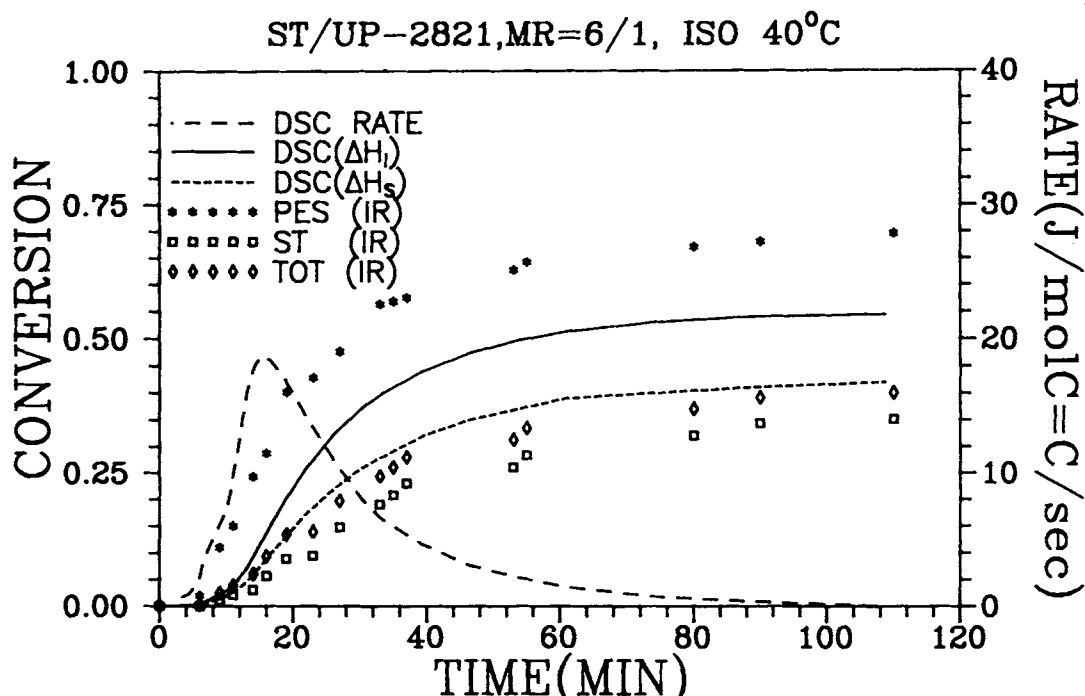


Figure 10 Conversion vs. time profiles measured by IR for UP2821 reaction with MR = 6/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.

ities of the C=C units in either small styrene or large polyester molecule. Except for MR = 6/1, it can also be seen from Figure 11 that, as the molar ratio increases, at the end of reaction α_E increases, while α_S slightly decreases (also see Table IV).

The final conversions of styrene and polyester C=C bonds for MR = 6/1 are 35.0 and 69.5% as shown at point A. After a post-cure from 25 to 210°C at 10°C/min by DSC, the final conversions α_S and α_E increase to 97.1 and 90.2%, respectively as shown at point B. Similarly, for MR = 2/1, α_S and α_E are 68.5 and 52.3%, respectively, as shown at point C, and they can be elevated to 95.4 and 85.2%, as shown at point D after the same post-cure by DSC scan. Therefore, post-curing enhances the styrene conversion to over 95%, and the polyester C=C con-

version to 85–90%. There are still 14.8 and 9.8% of unsaturated polyester C=C bonds being buried permanently inside the network structure for the samples of MR = 2/1 and 6/1, respectively, even after the post-curing treatment. Also, the lower the molar ratio, the more permanent residue of polyester C=C bonds.

Scanning Reaction of UP536B by DSC

Figure 12 shows DSC scanning rate profiles for ST/UP536B reactions at various molar ratios of styrene to polyester C=C bonds. It can be seen that as the molar ratio increases to MR = 4/1, the rate profile changes from one peak to two peaks, the reason of which is the same as that in Figure 3. The increasing

Table IV Summary of Kinetic Information by IR for Styrene/UP2821 Reactions at 40°C^a

Molar Ratio	α_S	α_E	α_{TOT}	$\bar{\alpha}_S$	$\bar{\alpha}_E$	n
1/1	69.2%	35.1%	52.1%	34.6%	17.6%	2
2/1	68.5%	52.3%	63.1%	45.7%	17.4%	2.62
3/1	66.3%	70.6%	67.4%	49.7%	17.7%	2.82
4/1	65.4%	79.8%	68.3%	52.3%	16.0%	3.28
6/1	35.0%	69.5%	39.9%	30.0%	9.9%	3.02

^a α_S is styrene conversion, α_E is polyester vinylene conversion, α_{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.

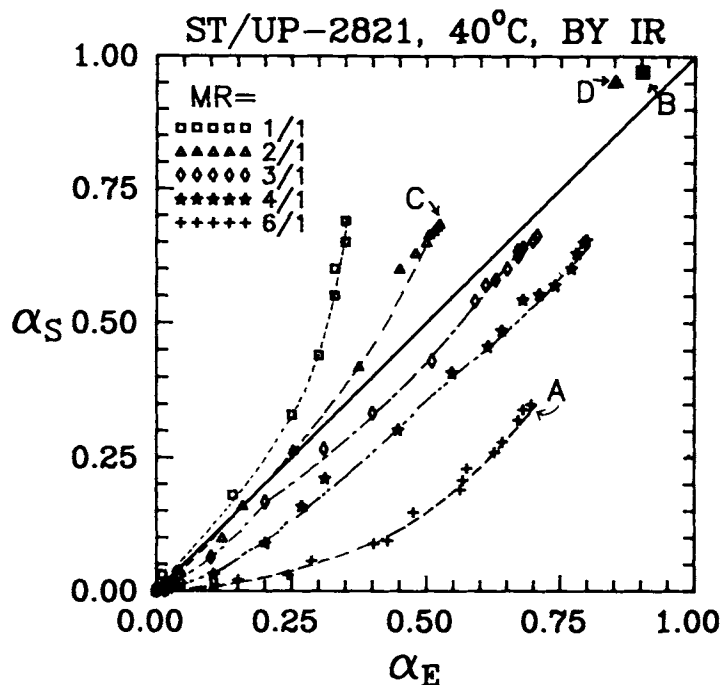


Figure 11 Relative conversion of styrene to polyester C=C bonds at various molar ratio of styrene to polyester C=C bonds for UP2821 reaction at 40°C.

order of peak temperature T_m is that MR = 1/1 (61°C) < 2/1 (66°C) < 3/1 (69°C) < 4/1 (71°C) < 6/1 (81°C), which is different from UP2821 re-

actions shown in Figure 3 with MR = 2/1 (75°C) < 3/1 (80°C) < 1/1 (84°C) < 4/1 (87°C) < 6/1 (97°C), and showing higher peak temperatures. The

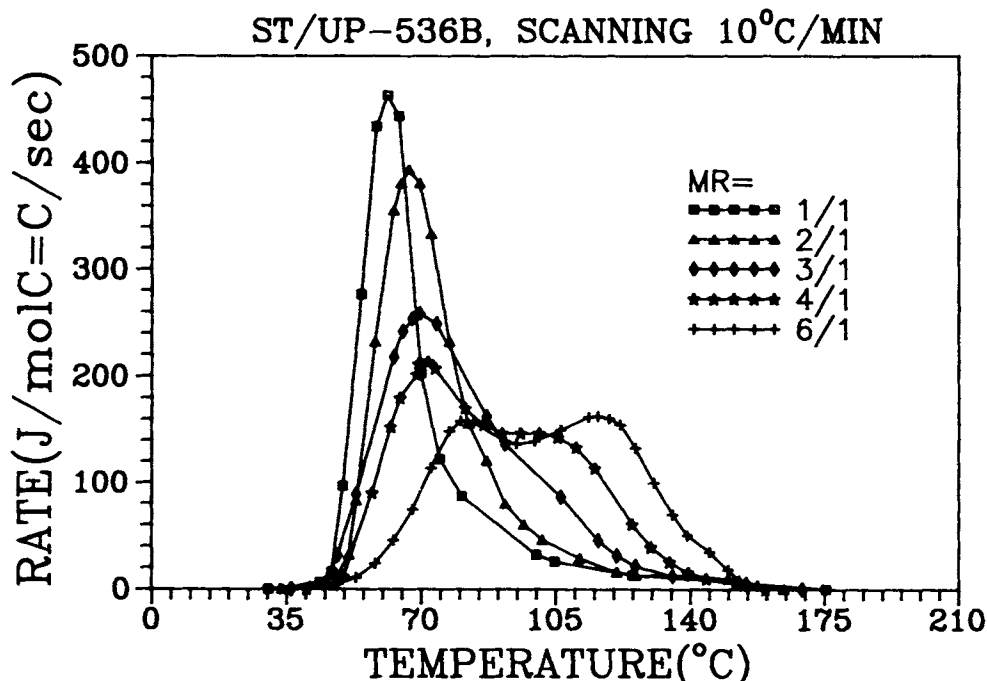


Figure 12 Scanning DSC rate profiles at 10°C/min for styrene/UP536B reactions with various molar ratios of styrene to polyester C=C bonds.

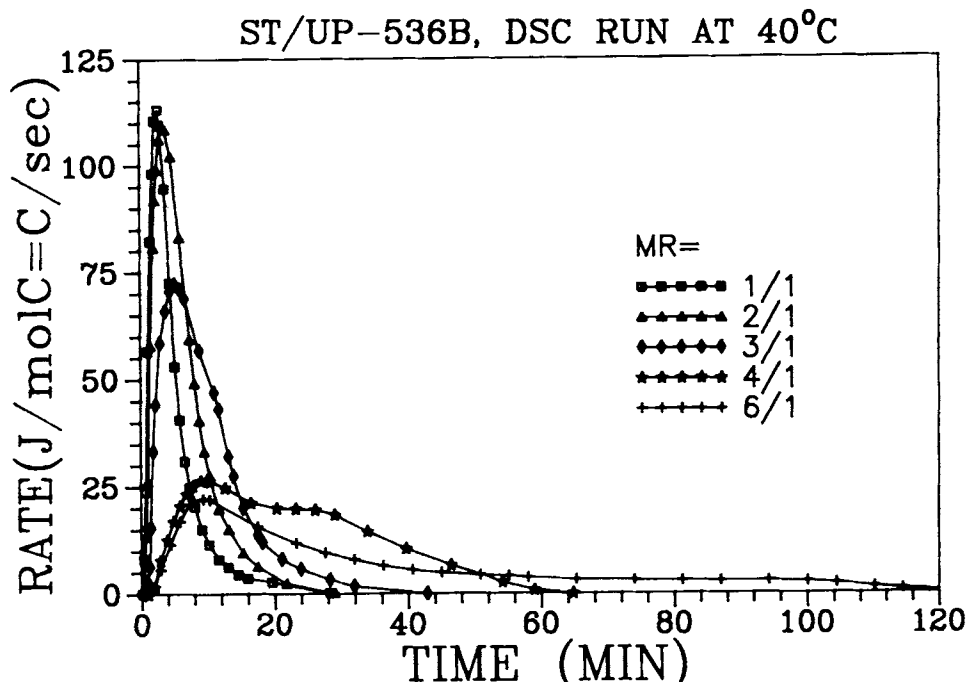


Figure 13 Isothermal DSC rate profiles for styrene/UP536B reactions at 40°C with various molar ratios of styrene to polyester C=C bonds.

first peak rate of the DSC rate profile, R_m , is that MR = 1/1 (462.80 J/mol C=C/s) > 2/1 (393.59 J/mol C=C/s) > 3/1 (258.19 J/mol C=C/s) > 4/1 (213.16 J/mol C=C/s) > 6/1 (158.08 J/mol C=C/s). After correction for the difference in rate of free radical formations as mentioned earlier, the corrected peak value R'_m is that MR = 2/1 (488.19 J/mol C=C/s) > 1/1 (462.80 J/mol C=C/s) > 3/1 (361.54 J/mol C=C/s) > 4/1 (325.07 J/mol C=C/s) > 6/1 (271.10 J/mol C=C/s). The first peak rate becomes the largest for MR = 2/1, and the order for the other molar ratios remains the same. The increasing order of the second peak temperature is that MR = 4/1 (105°C) < MR = 6/1 (116.5°C). The second peak value of the reaction rate, R_m , is that MR = 4/1 (147.06 J/mol C=C/s) < MR = 6/1 (165.47 J/mol C=C/s), and the order remains unchanged after correction for the variation of initiator concentrations (row 5 of Table II), i.e., MR = 4/1 (182.41 J/mol C=C/s) < MR = 6/1 (215.42 J/mol C=C/s).

Isothermal Reactions of UP536B by DSC

Figure 13 shows the isothermal rate profiles at 40°C for UP536B reactions at various molar ratios of styrene to polyester C=C bonds. It can be seen that the increasing order of time to the maximum rate,

t_m , is that MR = 1/1 (2.61 min) < 2/1 (3.26 min) < 3/1 (5.07 min) < 4/1 (8.89 min) < 6/1 (9.28 min), and the decreasing order of the maximum rate, R_m , without correction for the variations of free radical formation rates is that MR = 1/1 (113.13 J/mol C=C/s) > 2/1 (109.22 J/mol C=C/s) > 3/1 (72.22 J/mol C=C/s) > 4/1 (26.44 J/mol C=C/s) > 6/1 (22.16 J/mol C=C/s). After the correction by using MR = 1/1 as the basis [row 10 of Table II(b)], the maximum rate R'_m is that MR = 2/1 (135.47 J/mol C=C/s) > 1/1 (113.13 J/mol C=C/s) > 3/1 (101.13 J/mol C=C/s) > 4/1 (40.32 J/mol C=C/s) > 6/1 (28.85 J/mol C=C/s). Except that the order for MR = 2/1 changes from the second to the first, the order for the others remains the same; i.e., the lower the molar ratio, the higher the peak rate. It can also be seen that as the molar ratio increases, the reaction time is prolonged. For MR = 1/1 and 2/1 (i.e., low styrene content), the rate profile has only one peak, whereas for MR = 3/1 it has one additional shoulder to the right of the peak. For MR = 4/1, the shoulder turns out to be more distinct and develops to become another peak. As the molar ratio further increases to MR = 6/1, the second peak becomes a relatively constant plateau extending over the later stage of reaction. In order to further study this phenomenon, the conversions of styrene and polyester C=C

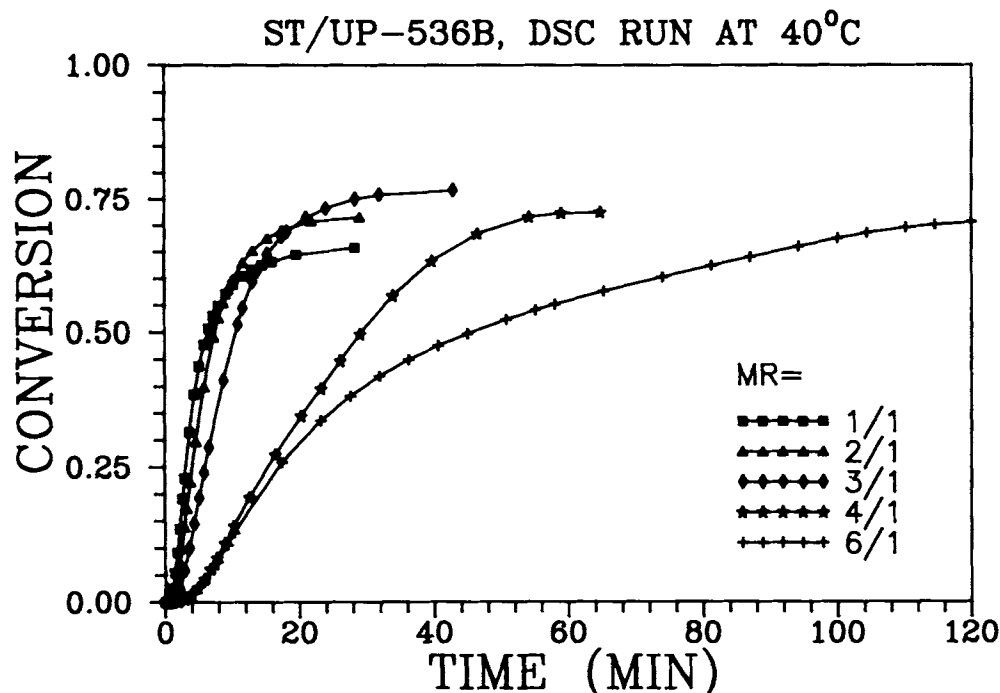


Figure 14 Isothermal DSC conversion profiles corresponding to Figure 13.

bonds have been measured during the entire reaction, which will be shown later on.

Figure 14 shows the DSC overall conversion vs. time profiles. The overall conversion increases as the molar ratio increases up to MR = 3/1. Further increasing the molar ratio to MR = 4/1 and 6/1, however, somewhat reduces the conversion. Table V summarizes kinetic information for ST/UP536B reaction measured by DSC. Compared with Table III for the UP2821 reaction system having a higher degree of C=C unsaturation, the isothermal heat of reaction, ΔH_{iso} , is higher for the UP536B system, leading to a higher conversion α_S based on ΔH_S . Also, the heat of reaction for the direct scanning, ΔH_S , is generally higher for the UP536B system, and the difference between ΔH_S and ΔH_I is smaller. Thus, the effect of temperature history on heat of reaction is relatively unaffected for the UP536B system.

Isothermal Reactions of UP536B by IR

Figure 15 shows the conversion vs. time profiles measured by IR for ST/UP536B reactions with MR = 1/1. The overall conversion measured by IR is close to α_I rather than α_S by DSC. The IR conversion profiles could then be subjected to some experimental errors. Prior to the peak of DSC profile, the conversions of styrene and polyester C=C bonds are

approximate, which reveals an azeotropic copolymerization and is different from that in Figure 6 for UP2821 system with MR = 1/1, where a higher styrene conversion than the conversion of polyester C=C bonds is shown. Compared with Figures 6 and 15, for the UP536B system, in the initial stage of reaction, the conversion of polyester C=C bonds is more favorable than for the UP2821 one. For the rest of the reaction course, the conversion of styrene is higher than that of polyester C=C bonds, and the difference between α_S and α_E increases with time. The conversion of styrene increases steadily with time, while the conversion of polyester C=C bonds gradually levels off after 50% overall conversion, shown as point A at the latter part of the rate profile. Again, this is due to the diffusion-controlled propagation for the C=C units of large polyester molecules. From the beginning of reaction to point A ($\alpha_S = 0.59$ and $\alpha_E = 0.47$) in Figure 15, the average crosslink length of styrene, n , is 1.27. For the reaction intervals between points A and B and between points B and C, n increases to 2.4 and 5.5, respectively. The final conversions of styrene and polyester C=C bonds are 83.1 and 54.1%, respectively, and the average crosslink length of styrene is 1.54.

Figure 16 shows the conversion profiles measured by IR for MR = 2/1. It can be seen that the overall conversion of C=C bonds measured by IR mostly lies between α_S and α_I measured by DSC. The con-

Table V Summary of Kinetic Information by DSC for Styrene/UP536B Reactions Both at 40°C and in Scanning Modes

Molar Ratio of Styrene/Polyester C=C	1/1	2/1	3/1	4/1	6/1
Isothermal, rescanning and total heats of reaction (kcal/mol C=C)					
ΔH_{iso}	8.18	11.42	12.04	11.56	10.65
ΔH_{res}	4.26	3.14	3.21	2.93	3.07
$\Delta H_I = \Delta H_{iso} + \Delta H_{res}$	12.45	14.56	15.25	14.49	13.72
Total heat of reaction by direct scanning (kcal/mol C=C), ΔH_S					
	14.90	15.53	15.71	15.94	15.07
Total conversion based on ΔH_I and ΔH_S					
α_I	0.66	0.78	0.79	0.80	0.78
α_S	0.55	0.72	0.76	0.73	0.71
Induction time t_z (min)	0.29	0.37	0.51	0.77	0.97
Time to max. rate t_m (min)	3.26	4.06	5.07	8.89	9.28
Conversion at max. rate, $\alpha(t_m)$	0.16	0.21	0.22	0.14	0.13

versions of styrene and polyester C=C bonds are approximately the same from the beginning of the reaction to the maximum point of the DSC rate profile, which is again characteristic of the near-azeotropic copolymerization. After an overall conversion of 30%, the conversion of styrene gradually exceeds that of polyester C=C bonds due to the diffusion-controlled propagation of polyester C=C bonds.

The average crosslink lengths of styrene for the reaction intervals from the beginning to point A, from A to B, from B to C, and from the beginning to C (i.e., the whole reaction), are 2, 2.69, 3.13, and 2.45, respectively.

Figure 17 shows the conversion profiles measured by IR for MR = 3/1. It can be seen that the overall conversion measured by IR lies between α_S and α_I ,

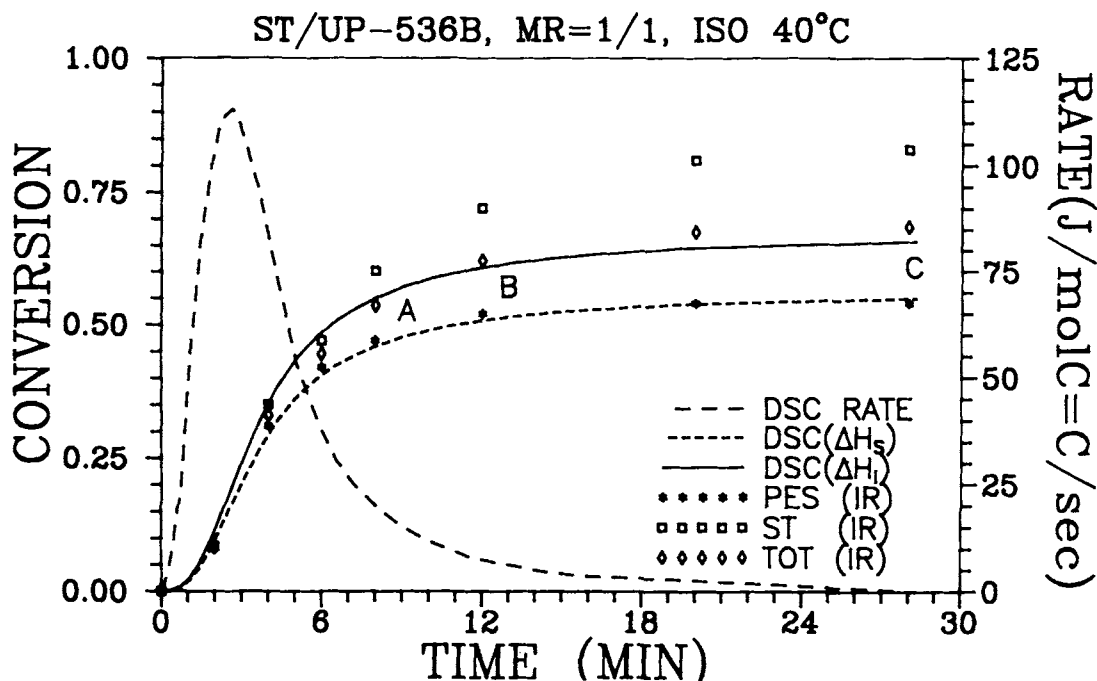


Figure 15 Styrene, polyester vinylene, and total C=C conversions vs. time profiles measured by IR for UP536B reaction with MR = 1/1. DSC rate profile (dashed curve) and total C=C conversion profiles based on both ΔH_S (solid curve) and ΔH_I (dashed curve) are also plotted for comparison.

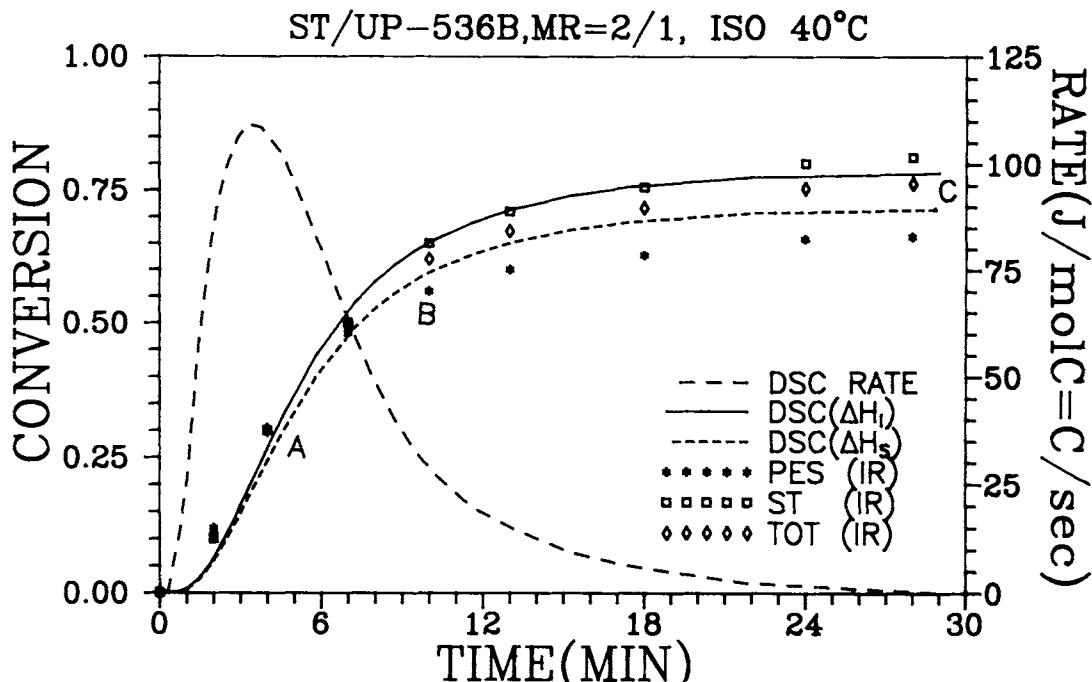


Figure 16 Conversion vs. time profiles measured by IR for UP536B reaction with MR = 2/1. Similar to Figure 15, DSC rate and conversion profiles are also plotted for comparison.

but close to α_s . For the most part of the reaction up to point B" shown in Figure 17, the conversion of polyester C=C bonds exceeds that of styrene. After

a conversion of 65% (point B"), the trend is reversed. At the end of reaction, the final conversions of styrene and polyester C=C bonds are 78.4 and

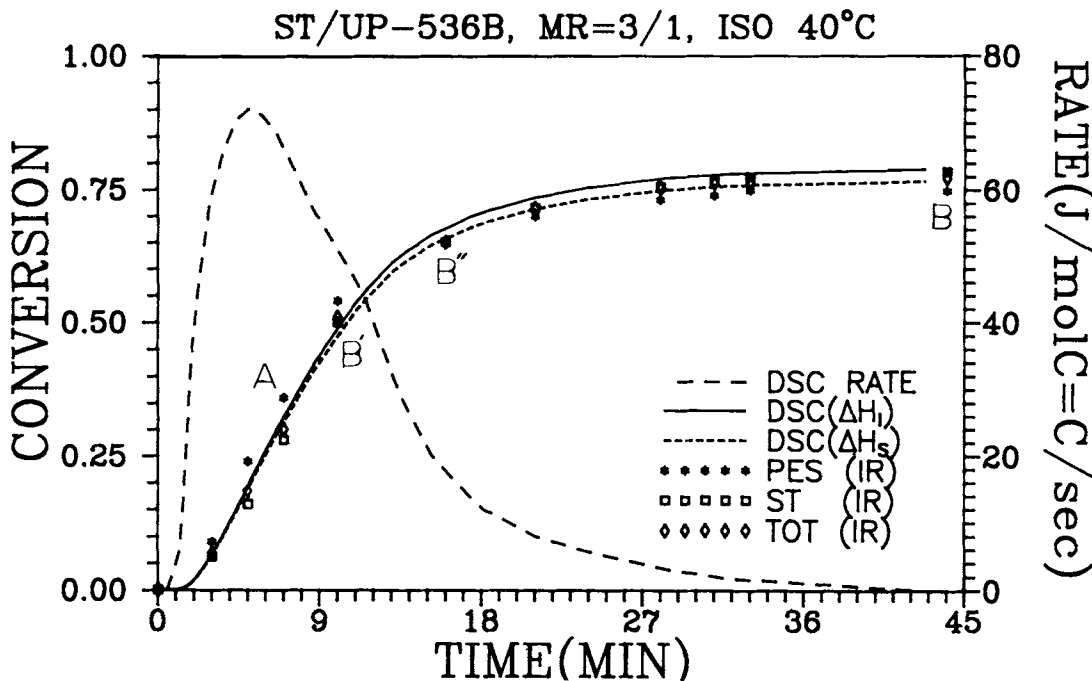


Figure 17 Conversion vs. time profiles measured by IR for UP536B reaction with MR = 3/1. Similar to Figure 15, DSC rate and conversion profiles are also plotted for comparison.

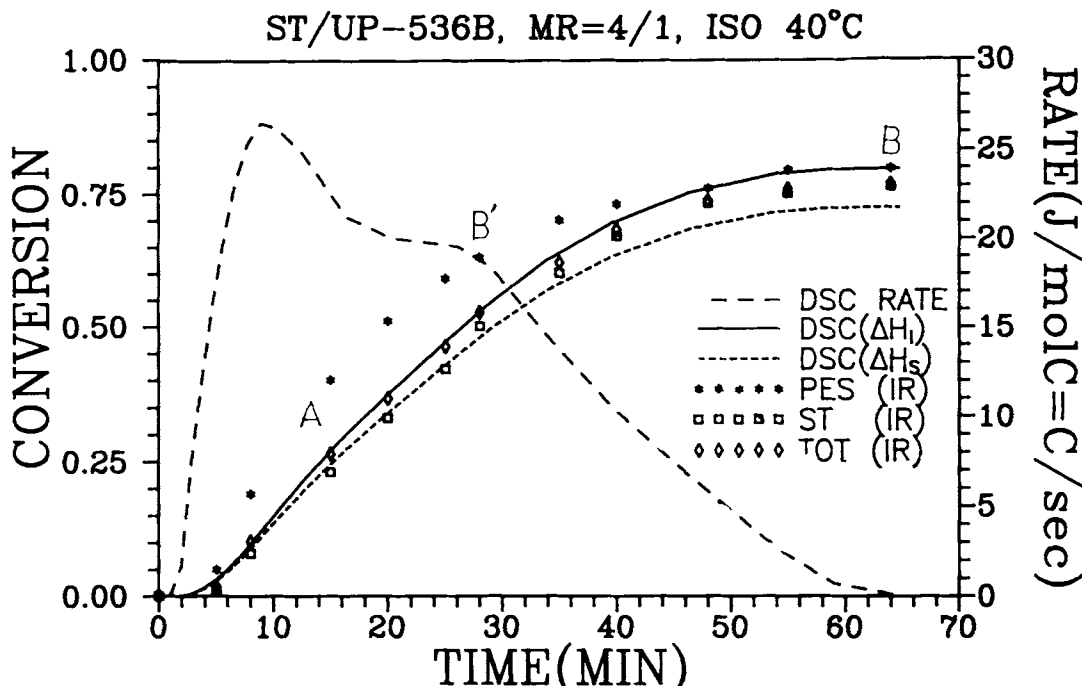


Figure 18 Conversion vs. time profiles measured by IR for UP536B reaction with MR = 4/1. Similar to Figure 15, DSC rate and conversion profiles are also plotted for comparison.

74.8%, respectively. It can be seen that a shoulder after the peak of DSC rate profile, between points A and B', emerges where the ratio of conversion increase in styrene to that in polyester C=C bonds is 1.30. This reveals that, on the average, 3.9 styrene C=C bonds have been consumed for each polyester C=C bond reacted. In contrast, for the UP2821 system with MR = 3/1 shown in Figure 8, the shoulder after the peak of DSC rate profile is less conspicuous. For the relative consumption of both C=C bonds, the average crosslink lengths of styrene, n , for the reaction intervals from the beginning to point A, from A to B', from B' to B'', from B'' to B, and from the beginning to B (i.e., the whole reaction), are 2.33, 3.60, 4.26, 4.05, and 3.14, respectively.

Figure 18 shows the conversion profiles measured by IR for MR = 4/1. It can be seen that the overall conversion measured by IR mostly lies between α_S and α_I measured by DSC. The conversion of polyester C=C bonds always exceeds styrene conversion during the reaction. The reaction interval of the shoulder from point A ($\alpha_S = 0.23$, $\alpha_E = 0.41$) to point B' ($\alpha_S = 0.50$, $\alpha_E = 0.63$) reveals that the average crosslink length of styrene is 3.68. Overall, the crosslink lengths of styrene for the reaction intervals from point B' to B ($\alpha_S = 0.775$, $\alpha_E = 0.81$) and from A to B are 4.58 and 4.08, respectively.

Figure 19 shows the conversion profiles measured

by IR for MR = 6/1. It can be seen that the overall conversion of C=C bonds measured by IR mostly lies between α_I and α_S measured by DSC. The conversion of polyester C=C bonds always far exceeds styrene conversion. It is probably due to the large amount of initial styrene content at MR = 6/1 inevitably causing a low calculated conversion of styrene, as similar to Figure 10. Although there is no shoulder in the rate profile as at MR = 4/1 shown in Figure 18, a plateau of rate profile appears at the latter part of the reaction. For the plateau region from point A to point B, the average number of styrene C=C bonds consumed is 8.52 for each polyester C=C bond reacted, which is much more than those for MR = 3/1 and MR = 4/1.

Figure 20 shows the relative conversion profiles of styrene to polyester C=C bonds at various molar ratios of styrene to polyester vinylene groups for UP536B reactions. It can be seen that all the curves show up-bending features, and as the molar ratio increases, the curve moves to the right, which is essentially similar to those for UP2821 reactions as shown in Figure 11. For MR = 2/1, before 30–50% conversion, the reaction is approximately characterized by the azeotropic copolymerization because the curve shown in Figure 20 coincides with the 45° line. Unlike the UP2821 system, for MR = 1/1, it shows an azeotropic copolymerization before 25% as well. As the molar ratio is greater than MR = 2/

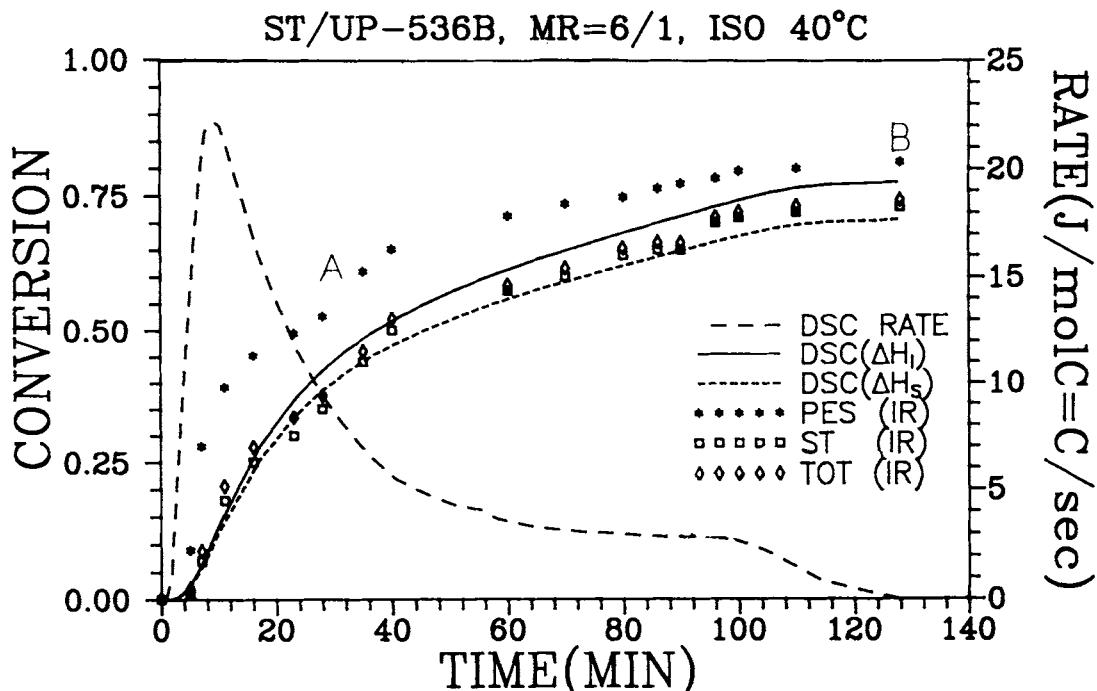


Figure 19 Conversion vs. time profiles measured by IR for UP536B reaction with MR = 6/1. Similar to Figure 15, DSC rate and conversion profiles are also plotted for comparison.

1, however, the curves tend to deviate from the 45° line, and the conversion of polyester C=C bonds is more favorable.

Table VI lists the conversions of styrene and polyester vinylene by IR at various molar ratios. It can be seen that the total conversion increases with

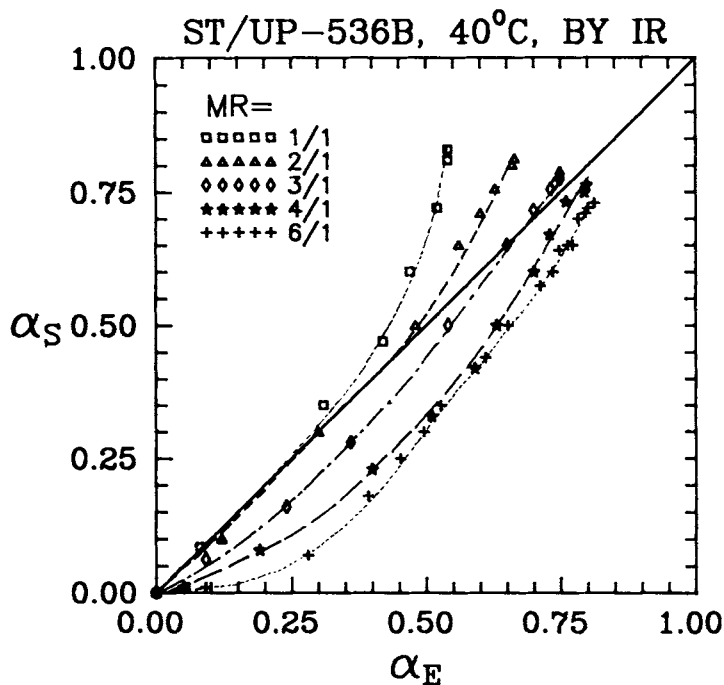


Figure 20 Relative conversion of styrene to polyester C=C bonds at various molar ratio of styrene to polyester C=C bonds for UP536B reaction at 40°C.

Table VI Summary of Kinetic Information by IR for Styrene/UP536B Reactions at 40°C^a

Molar Ratio	α_S	α_E	α_{TOT}	$\bar{\alpha}_S$	$\bar{\alpha}_E$	n
1/1	83.1%	54.1%	68.5%	41.5%	27.0%	1.54
2/1	81.3%	66.4%	76.3%	54.2%	22.1%	2.45
3/1	78.4%	74.8%	77.3%	58.8%	18.7%	3.14
4/1	76.4%	79.8%	77.1%	61.1%	16.0%	3.82
6/1	73.0%	81.2%	74.3%	62.6%	11.6%	5.40

^a Symbols are the same as those in Table IV.

increasing molar ratio up to MR = 3/1, followed by a decrease with further increasing molar ratio. It results from the fact that, although the polyester vinylene conversion is enhanced by increasing molar ratio, the conversion of styrene is lowered. It is seen that the average crosslink length of styrene in final copolymer increases with increasing molar ratio. The value is not far away from the initial molar ratio of styrene to polyester vinylenes. For instance, for MR = 1/1, $n = 1.54$, and for MR = 2/1, $n = 2.45$, and so on. This trend can not be observed for UP2821 reactions as shown in Table IV.

DISCUSSION

Microgel-Based Reaction Mechanisms

For the highly crosslinking reaction system of styrene/UP, the initial reaction mechanism was proposed by Yang and Lee¹⁰ as shown in Figures 21 (a) and (b). After the reaction starts, the initiator decomposes to generate free radicals, which link the C=C bonds of the system through either inter- or intramolecular crosslinking reaction to form long-chain polyester molecules [see Fig. 21 (a)]. These long-chain polyester molecules tend to form spherical type of structure due to the intramolecular crosslinking of pendant C=C bonds, and the microgel particles are thus formed [see Fig. 21 (b)]. Inside the microgel particles, it can be seen that many C=C bonds are still buried and remain unreacted.

Isothermal Reaction

Based on the DSC rate profiles and conversion profiles by IR for both UP2821 and UP536B reactions, a microgel-based reaction mechanism for the isothermal curing of UP resins at low temperatures can be stated as follows.

For the curing of unsaturated polyester resins under lower temperatures, where the rate of cross-

linking reaction is quite moderate, intramicrogel and intermicrogel crosslinking reactions are involved in the following manner. The formation of microgel particles would be continued from the beginning of the reaction until the microgels meet and closely overlap with one another throughout the system. After the peak of 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 are highly overlapped via crosslinking and a compact global network structure is formed, no new microgel particles would be generated.

In general, prior to the peak of DSC rate profile, where the gel effect region predominates,²¹ the intermicrogel crosslinking reaction proceeds more preferentially than does the intramicrogel crosslinking reaction. It is because the styrene monomers are apt to crosslink with the polyester C=C bonds near or at the surface of microgels during the process of diffusing into the microgels from outside, while only part of the diffusing-in styrene as well as some local styrene encompassed inside the microgels is allowed to crosslink with polyester C=C bonds inside the microgels, especially at low reaction temperatures. However, the extent to which the intermicrogel crosslinking reactions predominate should depend on the degrees of unsaturation of UP resins and the initial molar ratio of styrene to polyester C=C bonds. Either the higher degree of unsaturation in UP resins or the lower molar ratio would facilitate the inter-microgel crosslinking reactions.

After the peak of DSC rate profile, the microgels are so closely overlapped that the crosslinking density outside the microgels is higher than that inside the microgels. Therefore, most styrene monomers tend to 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 further constructed. As the crosslinking density inside the microgel increases with time, diffusion-

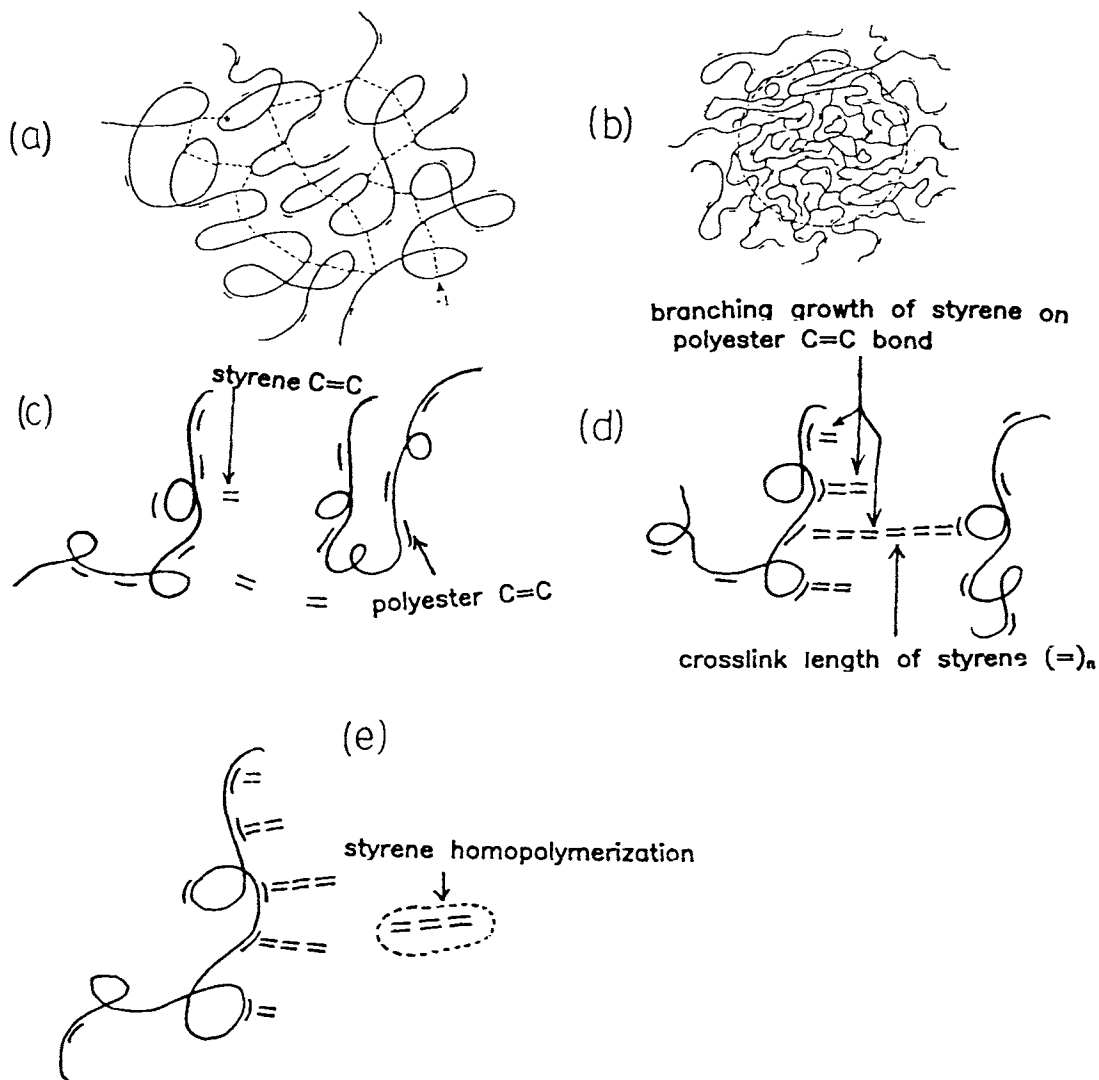


Figure 21 Schematic diagram showing microgel formation and some possible ways of bonding in the styrene-polyester reaction: (a) growth of free radicals¹⁰; (b) formation of microgel particles¹⁰; (c) reaction system before reaction; (d) branching growth of styrene on polyester C=C bonds and the formation of crosslink length of styrene; (e) styrene homopolymerization.

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 [see Fig. 21(d)] would then gradually predominate as the reaction goes on after the peak of rate profile. When the small styrene molecule is also encountered with diffusion-controlled propagation reactions later on, the DSC rate profile decays gradually and eventually drops to zero where the glass transition temperature of the system (i.e., inside the microgels) equals the reaction temperature.²¹ Since the styrene-crosslinked polyester network thus

formed would be inhomogeneous, for different spots in the system, the glass transition temperature, which is connected with free volume fraction and crosslinking density and hence generally increases with reaction time, would reach the reaction temperature at different pace. Based on the reaction mechanism described above, the pace of approach of the two temperatures would be faster outside the microgels than inside the microgels under the low-temperature reaction condition.

Although the intramicrogel reactions are much more favorable than the intermicrogel reactions at the latter part of the reaction, since the concentra-

tion 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 and the initial molar ratio of styrene to polyester C=C bonds, the variation of the shape of rate profile at the later reaction would not be unexpected. Quite often, for lower crosslinking reaction system such as UP536B one at higher molar ratio, the rate profile can thus exhibit a reaction shoulder or a plateau region, which is characteristic of the extensive intramicrogel reaction, at the later stage of reaction due to the loose microgel structure. In contrast, for higher crosslinking reaction system such as UP2821 one, the microgel structure is so compact that the reaction shoulder would not be conspicuous even at higher molar ratio.

Nonisothermal Reaction

As to the reaction mechanism for the nonisothermal curing of UP resins such as the scanning reaction by DSC in this study, for the first peak of DSC rate profile, both intermicrogel and intramicrogel crosslinking reactions could occur, with intramicrogel reactions predominating. It is because the gradual increase of temperature scan from low to high temperatures would lead to the buildup 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. Although the diffusion rate of styrene would be decreasing as a result of the increase of crosslinking density in the microgels during the reaction, the diffusing-in styrene could, to some extent, sustain the intramicrogel reactions for a relatively long period of time. Thus, the reduction of pendant C=C bonds buried inside the microgels is facilitated. It should be noted that local styrene monomers originally encompassed inside the microgel could also directly crosslink with polyester C=C bonds during the intramicrogel reactions. In addition, the evenly increasing temperature could help mitigate the reaction resistance due to the increase of crosslinking density that would hamper the intramicrogel reactions. Hence, the conversion inside the microgels may be remarkably enhanced during this stage.

For the second peak of rate profile, since the crosslinking density inside the microgel has increased to the extent that the styrene monomers could not readily diffuse into it, the intermicrogel crosslinking reactions would become more significant. 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 [see Fig. 21(e)] would be dominant during the higher temperature range of scanning.

Scanning Reaction of UP2821 by DSC

For UP2821 system, each polyester molecule has 6.82 C=C bonds, and each styrene molecule has only one. Therefore, as the molar ratio of styrene to polyester C=C bonds increases, the crosslinking density of the system network structure would be lowered under the same conversion of C=C bonds.

Since the reaction with a molar ratio of 2/1 is characterized by the near-azeotropic copolymerization, the composition of MR = 1/1 would probably exhibit the deficiency of styrene monomer. The crosslinking density of the system network could then be so high that the reaction rate would be severely curtailed due to the steric hindrance encountered by the C=C units during the reaction. Hence, for MR = 1/1 in Figure 3 the corrected R_m is the second lowest. For scanning DSC rate profiles, the decline of the first maximum rate would be due to the onset of diffusion-controlled propagation reaction associated with the C=C units of polyester molecules during the copolymerization of styrene and unsaturated polyester, where the rate constant for propagation, k_p , in eq. (6) is greatly reduced.^{21,22} As the molar ratio decreases, the polyester C=C units would be generally affected by the diffusion-controlled propagation reaction at an earlier time or temperature due to a higher crosslinking density of the network structure. Therefore, except for MR = 1/1, the smaller the molar ratio, the lower the onset temperature to the maximum rate. On the other hand, for MR = 1/1, the initial reaction rate is lowered due to the steric hindrance during the reaction. Compared with MR = 2/1 and 3/1, the crosslinking density increases more slowly to the extent that the mechanism of propagation reaction is affected by diffusion, leading to a higher T_m for MR = 1/1.

For MR = 1/1 and 2/1, after the rate profile has passed the first maximum peak, the network structure would be more compact than that of higher molar ratios having higher styrene contents. Despite the temperature sweep to high temperature facilitating the increase of both k_p and $[M\cdot]$ shown in

eq. (6) and thus enhancing R_p greatly, the severe steric hindrance which is encountered by $C=C$ bonds in the network structure results in a considerable reduction in k_p . Consequently, the evenly increasing temperature could preferentially sustain the reaction, as evidenced by a shoulder right after the peak of rate profile, but no conspicuous second reaction peak would result due to too low a k_p value depressing R_p . However, as the molar ratio increases, the swelling effect of styrene monomers causes a loose network structure so that k_p would not be too adversely affected over the high temperature range where BPO initiator is solely decomposed. Accordingly, right after the first peak, the increase of $[M \cdot]$ due to BPO decomposition makes possible the remarkable enhancement of R_p , and a second reaction peak arises. Except for $MR = 6/1$, since the higher molar ratio results in a looser network structure, the reaction rate of the second peak increases with increasing molar ratio. With $MR = 6/1$, the network structure would be so sparsely crosslinked that the range of second reaction peak is much broader than that of $MR = 3/1$ and $4/1$, causing a lowest reaction rate of the second peak. Although the decline of the second maximum peak can be regarded as the onset of diffusion-controlled propagation reactions within the high temperature range, it would be associated with $C=C$ units in styrene monomers rather than in polyester molecules. As the molar ratio increases, the global network structure becomes looser, and the onset temperature of the second peak would delay to a higher temperature.

Isothermal Reaction of UP2821 by DSC and IR

The initial molar ratio of styrene to unsaturated polyester $C=C$ bonds (i.e., styrene content) in the reactant compositions has two competing effects on the curing behavior. The styrene monomer could swell the microgel structure, which is formed as microgel particles in the initial stage of the reaction and is composed of overlapped microgel particles as the reaction goes on. A reduction in diffusion barriers encountered by the $C=C$ units during the intramicrogel crosslinking reaction would then result. On the other hand, the increase in styrene content would be accompanied by a concentration decrease in unsaturated polyester $C=C$ bonds, especially outside the microgel particles. Hence, the styrene swelling effect enhances the intramicrogel crosslinking reactions, whereas the styrene dilution effect diminishes the intermicrogel crosslinking reactions. Since the crosslinking reactions could occur either inside or outside the microgels, the overall reaction

rate would be a summation of both the intramicrogel and the intermicrogel crosslinking reaction rates. Therefore, when the styrene swelling effect becomes predominant over dilution effect, the cure rate, either in the initial stage of the reaction or at the time to the maximum rate, is favorable. The overall effect is dependent upon such factors as the degree of $C=C$ unsaturation of the resins, styrene content, curing temperature, and the initiator system.

Although the degree of $C=C$ unsaturation of UP2821 resin is high, since the reaction was carried out at a lower temperature 40°C , the microgel structure formed generally would not be compact enough to entail more styrene to swell the microgels with a view to reaching a higher reaction rate. Generally speaking, the styrene dilution effect exerts more influence over the styrene swelling effect since $MR = 2/1$ and $1/1$, which have lower styrene content and thus higher concentration of unsaturated polyester $C=C$ bonds, possess higher R'_m values than those of $MR = 4/1$, $3/1$, and $6/1$, as shown in Figure 4. However, the styrene swelling effect to loosen the microgels is still in effect for UP2821 resin cured at 40°C since either for low styrene content ($MR = 1/1$ and $2/1$) or for medium styrene content ($MR = 3/1$ and $4/1$), the sample with a higher styrene content (i.e., $MR = 2/1$ and $4/1$, respectively) would exhibit a higher R'_m value than that with a lower styrene content (i.e., $MR = 1/1$ and $3/1$, respectively).

For $MR = 6/1$, due to the excess styrene content being well over that needed to swell the microgel structure and crosslink the polyester $C=C$ bonds, the surplus styrene monomers would rely on homopolymerization for the reaction to be completed. Huang et al.²³ found that even at 100°C the rate of styrene homopolymerization at the peak of DSC rate profile would be 10 times lower than that of copolymerization between styrene and polyester $C=C$ bonds. Since the reaction temperature (40°C) is too low to provide higher activation energy than that of styrene/polyester copolymerization for sufficient styrene homopolymerization, the overall conversion turns out to be the lowest for $MR = 6/1$ among the samples as shown in Figure 5. The lower conversion of styrene has also been confirmed by Figure 10.

It can be seen from Table III that ΔH_S increases with increasing molar ratio because the looser network structure would facilitate reducing the $C=C$ bonds buried inside the microgel structure at the end of the reaction. Table III also shows that ΔH_I is always lower than ΔH_S , which indicates that the temperature history during the reaction would influence the competition between the intramicrogel

and intermicrogel crosslinking reactions, and, in turn, the buildup of network structure and the amounts of C=C bonds buried inside the microgels. After the isothermal cure, since the crosslinking density inside the microgels would be very high, it is more difficult to reduce the unreacted C=C bonds through the intramicrogel crosslinking reactions in the subsequent rescanning step than that by direct scanning with evenly increasing temperature scheme as explained before.

The good agreement between IR and DSC techniques has been illustrated in Figure 6–10. Since the total heat of reaction by direct scanning, ΔH_S , would more genuinely represent the 100% conversion than ΔH_I would, the overall conversion by IR should be more close to α_S , as evidenced by the UP2821 reactions (see Figs. 6–10). It is seen that the difference of the final overall conversion between α_S and α_I by DSC can be as high as 15%.

By referring to Figure 4 and 11, it is seen that the approximate molar ratio leading to an azeotropic copolymerization is 2/1, and the azeotropic reaction also shows the highest polymerization rate (after correction for the variation of the initiation rate) at the peak of DSC rate profile, which is a result of the competition between the styrene swelling and the styrene dilution effects as explained before. In addition, the azeotropic copolymerization behavior occurs only approximately prior to the peak of DSC rate profile. Although the transition point is at about 25% conversion in this case, it would be varied with initiator and promoter concentrations.¹³ Further discussion on azeotropic reaction will be given for UP536B system later.

Scanning Reaction of UP536B by DSC

Since the number of crosslinkable C=C sites on unsaturated polyester chains is fewer for UP536B than for UP2821, under the same conversion the network structure formed is less compact for UP536B, and the steric hindrance encountered by C=C units during reaction is remarkably mitigated. Therefore, it causes an earlier onset of peak temperature than that of UP2821 resin with the same molar ratio (see Figs. 3 and 12). For UP536B resin, the lower the molar ratio, the lower the peak temperature. It reveals that the lower molar ratio, even at MR = 1/1, could facilitate both intramicrogel and intermicrogel crosslinking reactions at the early stage of reaction, and would lead to an earlier onset of peak temperature.

Compared with UP2821 and UP536B systems, the one with the lower degree of unsaturation (i.e.,

UP536B) shows higher initial reaction rate and first peak reaction rate at the same molar ratio. As the molar ratio increases, the conspicuous second peak appears at MR = 4/1 for UP536B reactions, while it appears at MR = 3/1 (lower styrene content) for UP2821 reactions. All of these suggest that the first peak is due to both intermicrogel and intramicrogel crosslinking reactions, whereas the second peak is essentially attributed to the intermicrogel reactions or independent styrene homopolymerization outside the microgels. Also, under the scanning reactions, the intramicrogel crosslinking reactions would predominate over the intermicrogel crosslinking reactions for the first peak in the rate profile. Based on the proposed reaction mechanism, since the microgel structure is less compact for UP536B than for UP2821 system, the intramicrogel crosslinking reaction is much more favorable for UP536B, leading to higher initial reaction rate and first peak rate. On the other hand, that the intramicrogel crosslinking reactions are more favorable for UP536B than for UP2821 means that the former entails more styrene monomers to participate the intramicrogel crosslinking reactions than the latter does. Therefore, it would be at higher styrene content for UP536B system than for UP2821 one (i.e., MR = 4/1 vs. 3/1) when excess styrene monomers could not readily diffuse into the microgels and would mainly turn to the intermicrogel crosslinking reaction over the high temperature, as implied by the appearance of a conspicuous second reaction peak.

Compared with Figures 3 and 12, the shapes of rate profiles for MR = 3/1 and 4/1 of UP2821 resin are similar to those for MR = 4/1 and 6/1 of UP536B resin, respectively. Also, the onset temperatures and the reaction rates are comparable in values for the second peak of the rate profiles. The trend of magnitudes of the second peak rates is the same, i.e., the higher the molar ratio, the higher the second peak rate. The tendency of magnitudes of the first peak rates, however, is reversed.

The magnitude of the first peak rate would be a summation of both intermicrogel and intramicrogel crosslinking reaction rates. As the molar ratio increases, styrene swelling effect favors the intramicrogel reactions, while styrene dilution effect adversely affects the intermicrogel reactions as mentioned earlier. Therefore, except for MR = 1/1, as the molar ratio increases, the styrene swelling effect could be less than the styrene dilution effect, leading to a lower first peak rate with increasing molar ratio (i.e., MR = 2/1 > 3/1 > 4/1 > 6/1). For MR = 1/1, the styrene swelling effect is much more insufficient for UP2821 system with a higher cross-

linking density than the UP536B one. Hence, the R'_m is ranked the second lowest (i.e., $MR = 4/1 > 1/1 > 6/1$) for the former, while it is ranked the second largest (i.e., $MR = 2/1 > 1/1 > 3/1$) for the latter. On the other hand, the magnitude of the second peak rate would reflect the intermicrogel reaction rate over the high temperature range. As the molar ratio increases, the intermicrogel crosslinking reaction would be much less favorable over the low temperature range where the first peak appears in the rate profile, which may well await further high temperature scanning for the reaction to be completed. Hence, the second peak rate generally increases with increasing molar ratio.

For UP2821 reaction with $MR = 6/1$, the reaction rate shown in Figure 3 is slower due to the styrene dilution effect. Prior to the consumption of the promoter DMA, the rate profile is on the way toward the first maximum peak, and the C=C units of the large polyester molecules have not yet been affected by the mechanism of diffusion-controlled propagation reactions. Meanwhile, the BPO-initiated polymerization sets in and generates the second reaction peak. These two reaction peaks in the rate profile are thus slightly overlapped with each other. Also, the second peak tends to decay to zero in a longer time period, which is in contrast to a rapid decay to zero for UP536B system shown in Figure 12. As mentioned earlier, the shape of rate profile for $MR = 4/1$ of UP2821 system is similar to that for $MR = 6/1$ of UP536 one, and the onset temperature and the reaction rate are comparable in values for the second peak of the rate profile. Therefore, for $MR = 6/1$ of UP2821 system independent styrene homopolymerization outside the microgels would proceed more preferentially than that for $MR = 6/1$ of UP536B one over the high temperature range of scanning. The lower rate of styrene homopolymerization relative to that of styrene/polyester copolymerization results in a longer tail in the rate profile for UP2821 reaction system. Since the crosslinking density of UP536B system is lower than that of UP2821 one, the intramicrogel crosslinking reactions over the lower temperature range of scanning would be more complete for the former system so that fewer pendant C=C bonds are buried inside the microgels. These unreacted C=C bonds would mostly remain permanent residues even at the later higher temperature range of scanning since styrene monomers could not readily diffuse into the compact microgel structures at the later stage of reaction, where intermicrogel crosslinking reactions or independent styrene homopolymerization predominate. Consequently, the heats of reactions for the

scanning runs are higher than those of UP2821 system (see Tables III and V). For the UP536B system, the final conversions are over 93% if the largest heat generated with $MR = 4/1$ is employed as a basis for 100% conversion. In general, the higher the molar ratio, the higher the final conversion (or the heat of reaction).

Isothermal Reactions of UP536B by DSC and IR

In Figure 14, the maximum of overall conversion of C=C bonds occurs at $MR = 3/1$. It is probably due to the fact that for the ST/UP536B system with molar ratio ranging from 3/1 to 4/1, the styrene content would be sufficient to swell the microgel structures for the reduction of steric hindrance encountered by C=C units during the reaction. As the molar ratio increases above $MR = 4/1$, the excess styrene over that required for generating maximum swelling effect would entail its homopolymerization to reach full conversion. Therefore, at 40°C, excess styrene content, such as in the cases of $MR = 4/1$ and 6/1, would lead to a lower overall conversion due to its inability to obtain sufficient activation energy for styrene homopolymerization, as mentioned earlier.

Compared with Tables III and V, the difference between ΔH_s and ΔH_f is smaller for the UP536B system than that for the UP2821 one. This indicates that, due to the network structure being less compact for UP536B system, the C=C bonds buried inside the microgel structures upon the completion of isothermal curing are still mobile enough for the reaction by temperature rescanning. The lower induction time as well as the lower time to maximum rate for the UP536B system also reveals that it has a higher reaction rate than that for the UP2821 one having a higher degree of unsaturation. Again, the conversion at maximum rate, $\alpha(t_m)$, is roughly an index where the diffusion-controlled propagation reaction sets in. In general, $\alpha(t_m)$ is higher for the UP536B system than for the UP2821 one (within 5% difference) since the former system has a lower crosslinking density, and monomer conversion can reach a higher level before experiencing the reduction of its mobility.

Compared with the case of $MR = 1/1$ for ST/UP536B system shown in Figure 15 and for ST/UP2821 system shown in Figure 6, due to the lower crosslinking density of the former system, the overall conversion at which the polyester C=C bond conversion begins to level off is lower for UP2821 than for UP536B (30% vs. 50%). The network structure is more compact for UP2821 system due to its higher

crosslinking density, leading to an earlier onset of diffusion-controlled propagation for C=C units of large polyester molecules. During the reaction interval from point B to point C at the latter part of reaction, the average crosslink length of styrene is higher for UP2821 than for UP536B (7 vs. 5.5). It results from the fact that, for UP536B, the microgel structure is less compact and more polyester C=C bonds have access to the diffusing-in styrene monomers, and the number of styrene consumed for each polyester C=C bond reacted is thus reduced. At the end of reaction, the average crosslink length of styrene to link two adjacent C=C units of polyester molecules is lower for UP536B than for UP2821 (1.54 vs. 1.97).

By referring to Figures 15, 16, and 20, both MR = 2/1 and MR = 1/1 exhibit the azeotropic copolymerization behavior prior to the peak of DSC rate profile for UP536B system. In contrast, it shows the same feature only for MR = 2/1 for the UP2821 system, as shown in Figure 11. Again, the azeotropic reaction also causes the higher polymerization rate at the peak of DSC rate profile than that of other molar ratios, as shown in Figure 13. In this case, MR = 2/1 still gives the highest maximum reaction rate (after correction for the variation of the initiation rate) and MR = 1/1 is the second highest. It is inferred that the azeotropic copolymerization would occur at a molar ratio of styrene to polyester C=C bonds where the styrene swelling and styrene dilution effects are commensurate so that the intramicrogel and intermicrogel crosslinking reaction rates are approximately the same. Under such circumstances, the average crosslink length of styrene throughout the whole reaction system could possibly equal the initial molar ratio of styrene to polyester C=C bonds, leading to an azeotropic reaction. Since the intramicrogel and intermicrogel reactions would be comparable to each other only prior to the peak of DSC rate profile, where the onset of diffusion-controlled propagation reaction has not occurred yet, the azeotropic copolymerization could persist up to the peak of rate profile. For the UP536B system, the crosslinking density is lower than that of the UP2821 one, and the styrene swelling effect is less significant for the former. Consequently, the molar ratio leading to an azeotropic reaction for the UP536B system can thus range from MR = 2/1 down to MR = 1/1, rather than at MR = 2/1 with higher styrene content for UP2821 system.

For MR = 3/1, as shown in Figure 17, considering that the average crosslink length of styrene from point A to B' is 3.9, the shoulder in the DSC rate profile could thus be attributed to the branching

growth of styrene monomers on polyester C=C bonds inside the microgel structure, which would be swollen by styrene and become looser at MR = 3/1 with higher styrene content. In contrast, for UP2821 system with MR = 3/1 shown in Figure 8, the shoulder is less evident. It is due to the compact microgel structure exerting more resistance to diffusing-in styrene monomers and the branching growth rate of styrene on polyester C=C bonds being reduced. For MR = 4/1 as shown in Figure 18, starting from the reaction, the polyester C=C bonds probably proceeds quickly via both intramolecular and intermolecular reactions through the linkage of styrene monomers, forming a microgel structure that would be looser than that for MR = 3/1. The appearance of a remarkable shoulder after the peak of DSC rate profile would be due to the fast branching growth of styrene monomers on polyester C=C bonds inside the well swollen microgel structures. For MR = 6/1 as shown in Figure 19, basically, the plateau region would be mainly due to the branching growth of styrene on polyester C=C bonds inside the well-swollen and loose microgel structures. Independent styrene homopolymerization outside the microgel structure would be scarce; otherwise the styrene conversion for UP2821 reaction with MR = 6/1 as shown in Figure 10 would not be at a pretty low level. Also, the inability of styrene monomer to diffuse into the compact microgels formed by UP2821 systems at the later reaction leads to a lower final conversion of styrene and no plateau region in the latter part of the DSC rate profile.

CONCLUSIONS

The effects of comonomer compositions on the curing kinetics of unsaturated polyester resins have been studied by DSC and IR over the entire conversion range for two UP resins. Although the chemical composition, average functionality, and molecular weight are varied for the two UP resins, the difference in average functionality would mostly account for the peculiarity in their curing behaviors. The UP resin with a lower degree of C=C unsaturation (i.e., average functionality) shows an earlier onset of the reaction and higher initial and maximum rates. The reaction rate is a summation of both reaction rates for intramicrogel and intermicrogel crosslinking reactions. As the molar ratio increases, the styrene swelling effect favors the intramicrogel reactions, whereas the styrene dilution effect adversely affects the intermicrogel reactions. The

overall effect on the reaction rate depends on the degrees of C=C unsaturations of UP resins and the initial molar ratio of styrene to polyester C=C bonds. For a given UP resin, except MR = 2/1, the higher the molar ratio, the lower the maximum rate.

At MR = 2/1, it not only exhibits the near-azeotropic copolymerization behavior prior to the peak of DSC rate profile but also possesses the highest maximum reaction rate among all the molar ratios. However, for UP resin with a lower degree of C=C unsaturation, the similar near-azeotropic copolymerization behavior arises ranging from MR = 2/1 down to MR = 1/1. Nevertheless, MR = 2/1 still gives the highest maximum reaction rate. It is inferred that the azeotropic copolymerization would occur at a molar ratio of styrene to polyester C=C bonds where the styrene swelling and styrene dilution effects are commensurate so that the intramicrogel and intermicrogel crosslinking reaction rates are approximately the same. Under such circumstances, the average crosslink length of styrene throughout the whole reaction system could possibly equal to the initial molar ratio of styrene to polyester C=C bonds, leading to an azeotropic reaction.

Microgel-based reaction mechanisms for the curing of UP resins have been proposed. For isothermal low-temperature reactions, prior to the maximum peak of DSC rate profile, intermicrogel crosslinking reactions would be more favorable than intramicrogel crosslinking reactions. After the peak, the trend would be reversed. At higher molar ratios of styrene to polyester C=C bonds, the DSC rate profile exhibits a shoulder or a plateau region which could be characterized by the intramicrogel reactions associated with extensive branching growth of styrene on polyester C=C bonds at the later reaction. The phenomena are more distinct for the UP resin with a lower degree of C=C unsaturation. In contrast, for nonisothermal reaction by DSC scanning, for the first peak of rate profile, the intramicrogel crosslinking reactions would proceed more preferentially than would the intermicrogel crosslinking reactions. For the second peak of rate profile, the intermicrogel reactions, including branching growth of styrene on polyester C=C bonds and independent styrene homopolymerization, would predominate.

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