Curing of Unsaturated Polyester Resins— Effects of Comonomer Composition. III. Medium-Temperature Reactions

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SYNOPSIS

The effects of comonomer composition on the curing kinetics of unsaturated polyester (UP) resins at 70–90°C were studied by differential scanning calorimetry (DSC) and infrared (IR) spectroscopy over the whole conversion range. One commercial UP resin, UP2660PF2, with cobalt promoter added and with 8.85 unsaturated $C=C$ bonds per polyester molecule, was used. It was found that a marked shoulder in the initial DSC rate profile, rather than that reported after the peak of rate profile for low-temperature and high-temperature reactions, appeared when the molar ratio of styrene to polyester $C=C$ bonds was greater than 1. With the initiator system accelerated by cobalt promoter, the formation rate of microgel particles would be enhanced at the early stage of reaction, as supported by the much higher conversion of polyester $C=C$ bonds than that of styrene by IR spectroscopy. Those relatively greater number of microgel particles tended to facilitate the intramicrogel crosslinking reactions, which would be independently identified from the initial DSC rate profile as a shoulder. Consequently, the reaction mechanism was elucidated by decomposing the reaction rate profile into two individual profiles accounting for the intramicrogel dominated and the intermicrogel dominated crosslinking reactions, respectively. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Unsaturated polyester (UP) resins have been processed at various temperature range. One example of medium-temperature processing of UP resins over 60–100°C is resin transfer molding (RTM), for which more than 10 min cure time is typical. It has now been recognized that the formation of microgel particles is a key feature in the curing of UP resins,[1-4] where a free radical chain growth crosslinking copolymerization between styrene and unsaturated polyester occurs. In general, during the styrene and polyester copolymerization, the initiator decomposes and creates free radical in the system. The free radicals grow and form long-chain molecules by both inter- and intramolecular reactions. These long-chain molecules tend to form a spherical type of structure or "microgel particles" due to the intramolecular crosslinking among the pendant $C=C$ bonds of polyester molecules. The microgel formation has a profound effect on the reaction kinetics of UP resins.[4-8]

The investigation of the effect of pressure on the curing of UP resins,[4] by an approach of integrated reaction kinetics–rheology–morphology measurements, has supported the intramicrogel and intermicrogel crosslinking reactions that are characteristic of the curing of UP resins. This has led to an in-depth understanding of the kinetic nature of the copolymerization process over the entire conversion range being achieved for low-temperature[6,7] (30–50°C) and high-temperature[8] (100–120°C) reactions. For isothermal curing of UP resins at low temperatures, it has been proposed that the intermicrogel crosslinking reaction predominates over the intramicrogel crosslinking one in the early part of the reaction, whereas the intramicrogel crosslinking reaction becomes more favorable in the later

part of the reaction. In contrast, for isothermal curing of UP resins at high temperatures, the trend of the competing processes of intramicrogel and intermicrogel crosslinking reactions is reversed.

The present work is to continue to deal with the effect of comonomer composition on the curing kinetics of UP resins at medium temperatures ranging from 70 to 90°C with promoter-accelerated initiator system using differential scanning calorimetry (DSC) and infrared (IR) spectroscopy. Peculiar curing behavior different from those at low and high temperatures was observed. Based on the experimental results, a microgel-based reaction mechanism for medium-temperature reactions is proposed.

EXPERIMENTAL

Materials

One unsaturated polyester resin, UP2660PF2, obtained from one local company was employed in this study. UP2660PF2 resin contains isophthalic acid, fumaric acid, and propylene glycol with a mole ratio of 1:1.76:3.09 by ^{1}H-NMR analysis. The number-average molecular weight of the resin, $\bar{M}_n$, was measured to be 2485 g/mol by end-group titration. On the average, the calculated number of C=C bonds (i.e., degree of C=C unsaturation) in each polyester molecule is 8.85. The styrene content in UP resins was determined by evacuating styrene monomers in the vacuum oven at room temperature. In order to identify the metal composition of the promoter added in the UP resins, 10 mg of UP resin after removal of styrene was dissolved in 10 mL of xylene at 45°C for 24 h with continuous stirring. The sample solution was then ready for AAS (atomic absorption spectrometry) analysis. The transition metal in the promoter was found to be cobalt, the amount of which was 260.6 ppm. The elemental composition for the organic portion of the promoter could not be identified by AAS, but the local company would mostly employ cobalt octoate rather than cobalt naphthenate. All the other detailed characterization procedures are similar to those reported in a previous study,[7] and the results are listed in Table I.

Based on the characterization results, extra styrene was added to or evaporated from the resin so that the molar ratio of styrene to polyester C=C bonds was adjusted to be 1/1, 2/1, 3/1, and 6/1 in the preparation of sample solutions. Along with the cobalt promoter, *tert*-butyl perbenzoate (TBPB, TX-C, Akzo Chemicals) was used as an initiator,

Table I Unsaturated Polyester Resin Used in This Study[a]

	UP2660PF2
Ingredients of UP resin[b]	
IPA (isophthalic acid)	17.09 (1)
PA (phthalic acid)	—
FA (fumaric acid)	30.09 (1.76)
MA (maleic acid)	0.029
PG (propylene glycol)	52.82 (3.09)
Molar ratio of glycols to dicarboxylic acids	1.12
Styrene content in UP resins (wt %)	43.93
Viscosity (CP)	505.3
Acid number (X)	22.54
$\bar{M}_n$ (=56000/X)	2485
Unit molecular weight/mol polyester C=C, M_0	280.9
Average no. of C=C/polyester (=$\bar{M}_n/M_0$)	8.85
Molar ratio of C=C bonds for styrene–polyester	2.12
Cobalt content in UP resins after removal of styrene (ppm)	260.6

[a] Parts by mol %.
[b] Molar ratio in parentheses..

the concentration of which was 1% by weight of the total resin for all samples. All the materials were employed as received without further purification.

Instrumentation and Procedures

A DuPont 9000 differential scanning calorimeter with a 910 pressurized DSC cell was used to follow the overall reaction rate profiles at atmospheric pressure. Isothermal reaction rate vs. time profiles were measured at 70–90°C. Resins were also cured from room temperature to 210°C in the scanning mode at 10°C/min heating rate. In addition, an IR spectrophotometer (Jasco, IR-700) with a resolution of 4 cm^{-1} in the transmission mode was used for off-line conversion measurements of styrene and polyester C=C bonds during the isothermal reaction at 80°C. Detailed experimental and calculation procedures regarding DSC and IR analysis in this study are the same as those described elsewhere.[8]

RESULTS

Scanning Reaction by DSC

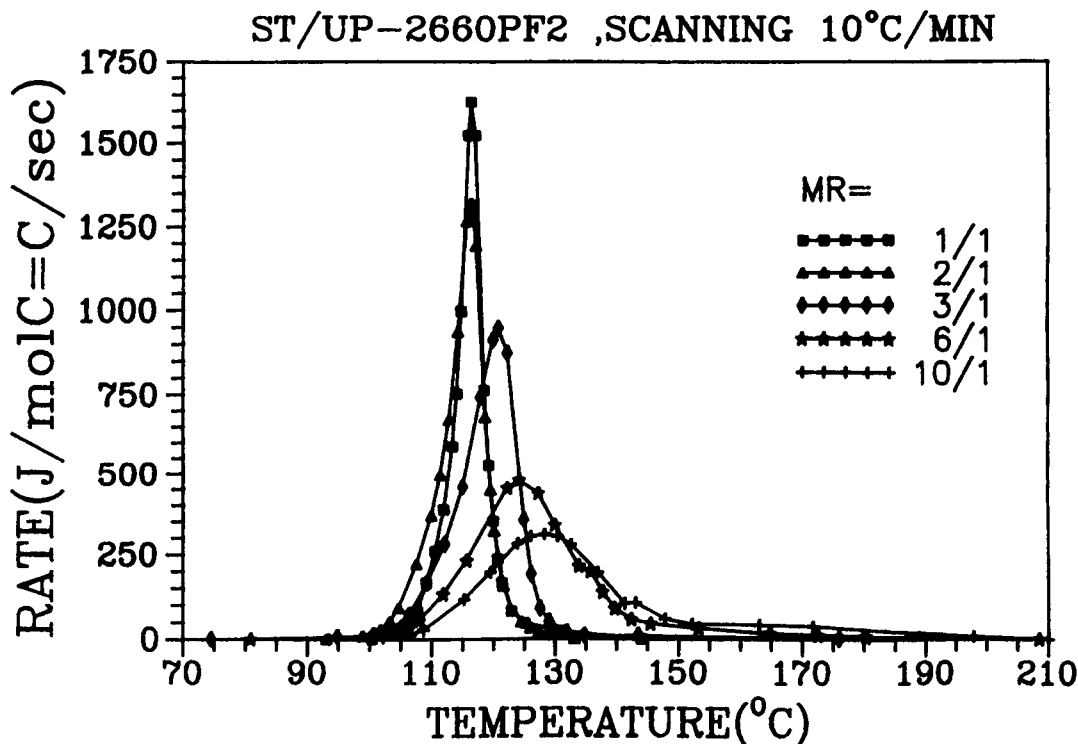Figure 1 shows the scanning DSC rate profiles for styrene/UP2660PF2 reactions with various molar

Figure 1 Scanning DSC rate profiles at 10°C/min for styrene–UP2660PF2 reactions with various molar ratios of styrene to polyester $C=C$ bonds.

ratios of styrene to polyester $C=C$ bonds at 10°C/ min from room temperature to 210°C. It can be seen that each reaction rate profile has one major peak. As the molar ratio (MR) increases to 6/1, a small shoulder to the right of the major peak appears at 134°C. At MR = 10/1, a shoulder emerges at about 142°C followed by a plateau region extending from 154 to 200°C.

For comparison of reaction rates with different molar ratios, the reaction rate shown in Figure 1 is expressed as joules per mole $C=C$ bonds per second instead of joules per gram of resin per second since

Table II Initiator and Promoter Concentrations on Molar Basis for Prepared Samples of UP2660PF2 Resin Used in This Study

	Molar Ratio of $C=C$, Styrene–Polyester[a]				
	1/1	2/1	3/1	6/1	10/1
Total moles of $C=C$/g resin	5.20×10^{-3}	6.14×10^{-3}	6.75×10^{-3}	7.74×10^{-3}	8.33×10^{-3}
g TBPB/g resin	0.01	0.01	0.01	0.01	0.01
g Co/g resin	1.90×10^{-4}	1.50×10^{-4}	1.23×10^{-4}	8.09×10^{-5}	5.54×10^{-5}
mol TBPB/mol $C=C$ ($\propto$-[TBPB]$_0$)	0.00990 (1)	0.00839 (0.85)	0.00763 (0.77)	0.00665 (0.67)	0.00618 (0.62)
mol Co/mol $C=C$ ($\propto$-[Co]$_0$)	6.20×10^{-4} (1)	4.15×10^{-4} (0.67)	3.09×10^{-4} (0.50)	1.77×10^{-4} (0.29)	1.13×10^{-4} (0.18)
mol Co/mol TBPB	0.0626	0.0495	0.0405	0.0266	0.0183
($\propto$-[Co]$_0$ [TBPB]$_0$)[b]	6.14×10^{-6} (1)	3.48×10^{-6} (0.57)	2.36×10^{-6} (0.38)	1.18×10^{-6} (0.19)	6.98×10^{-7} (0.11)

[a] Molar ratio in parentheses.
[b] Row 4 × row 5.

Table III   Maximum Reaction Rates R_m at Various Molar Ratios for UP2660PF2 Reactions at Both Scanning and Isothermal Modes[a]

Molar Ratio	Scanning Mode	$T = 90°C$	$T = 80°C$	$T = 70°C$
1/1	1626.4	260.0	105.6	41.1
2/1	1318.2	209.5	110.5	39.6
3/1	944.9	160.2	76.4	32.9
6/1	481.5	148.4	83.3	41.6
10/1	312.4	92.9		

[a] R_m is the uncorrected maximum rate (J/mol C $=$ C/s).

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 row 1 of Table II. It should be noted that as the molar ratio increases, the molar concentrations of initiator and promoter, which can be expressed as those shown in rows 4 and 5 of Table II, respectively, decrease. However, the rate profiles shown in Figure 1 are not corrected for the variation of initial initiation rate, which is proportional to the product of initial initiator and promoter concentrations, as shown in row 7 of Table II,[7] and decreases with increasing molar ratio. Since the initial rate of polymerization is proportional to the square root of the initiation rate under the as-

sumption of pseudo–steady state for free radicals, the maximum reaction rate could be corrected for the initiation rate by using this relationship unless the monomer conversion at the maximum rate is so high that the assumption no more represents a reasonably accurate approximation.

The decreasing order of initial reaction rate shown in Figure 1 is that MR = 2/1 > MR = 3/1 > MR = 1/1 > MR = 6/1 > MR = 10/1. The increasing order of temperature to the maximum reaction rate, T_m, is that MR = 1/1 $\approx$ MR = 2/1 (116.5°C) < 3/1 (120.9°C) < 6/1 (124.2°C) < 10/1 (128.3°C), whereas the decreasing order of the maximum reaction rate, R_m, as shown in Table III,
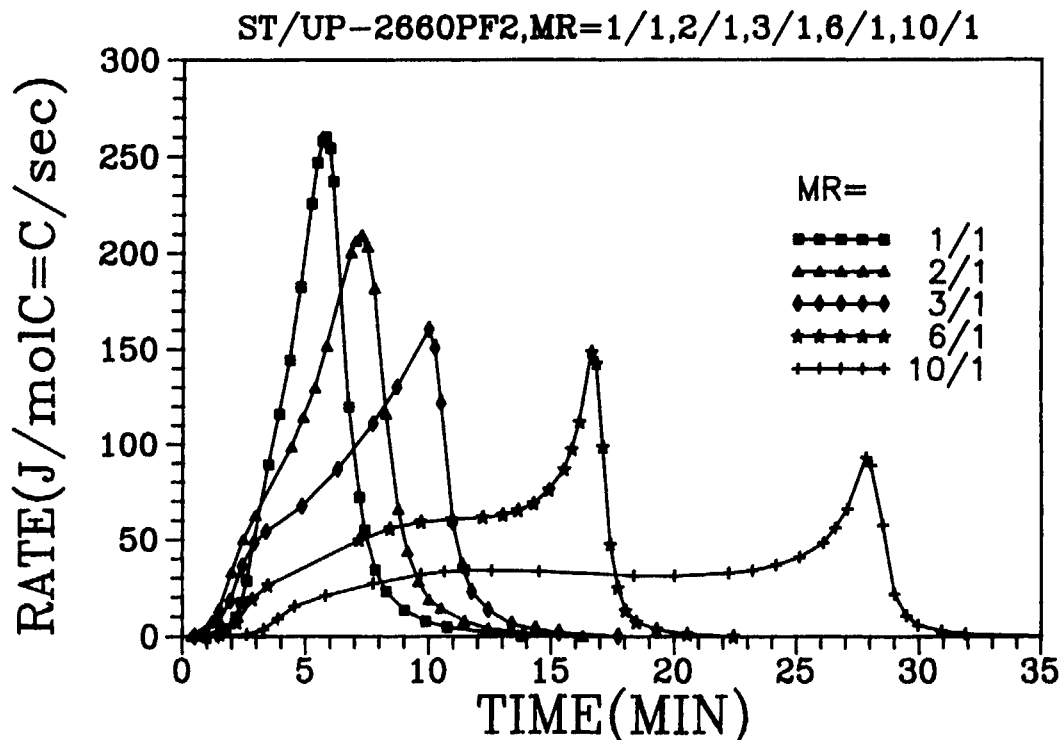

Figure 2 Isothermal DSC rate profiles for styrene–UP2660PF2 reactions at 90°C with various molar ratios of styrene to polyester C $=$ C bonds.

is that MR = $1/1 > 2/1 > 3/1 > 6/1 > 10/1$. Unlike scanning reactions for UP2821 resin initiated by BPO (benzoyl peroxide)/DMA (N,N-dimethyl aniline) amine accelerated system,[7] it is calculated from Figure 1 that the monomer conversion at the maximum rate is over 50% rather than at a lower level of 25–35% for the UP2821 system. Hence, no correction for the variation of initiation rate has been made here due to the inaccurate approximation of the pseudo-steady-state assumption for free radicals.

Isothermal Reaction by DSC

Figure 2 shows the isothermal DSC rate profiles for styrene/UP2660PF2 reactions with various molar ratios of styrene to polyester C=C bonds, MR = $1/1, 2/1, 3/1, 6/1$, and $10/1$ at 90°C. A remarkable change in the shape of rate profiles can be observed as the molar ratio varies. At MR = $1/1$, the shape of the rate profile is bell-like. As the molar ratio increases to MR = $2/1$, a shoulder prior to the peak of the rate profile appears at 2–3 min. Further increasing the molar ratio gives rise to a more pronounced shoulder extending over a longer period of time. However, it results in a lower height of the shoulder, which denotes a lower reaction rate. At the higher molar ratios of MR = $6/1$ and $10/1$, the shoulder is actually followed by a longer plateau region before reaching the maximum rate. Although the above shoulder or plateau region in the DSC

rate profile was also observed[7,8] for UP536B resin system with 4.16 of C=C unsaturation at 40°C and at 90–110°C, it occurred after the peak of the rate profile rather than before the peak, as shown here. It can be seen from Figure 2 that the order of initial reaction rate is that MR = $2/1 > 3/1 > 1/1 > 6/1 > 10/1$. As the molar ratio increases, the time to the maximum rate, t_m, increases. As to the maximum reaction rate, R_m, the decreasing order is that MR = $1/1 > 2/1 > 3/1 > 6/1 > 10/1$ (also see Table III). The conversion at the maximum reaction rate, $\alpha(t_m)$, increases as the molar ratio increases (see Table IV). Figure 3 shows the overall C=C conversion versus time profiles. It can be seen that the higher the molar ratio, the higher the overall conversion.

For low-temperature[7] and high-temperature[8] isothermal reactions, where the monomer conversion at the maximum reaction rate is generally below 30%, the maximum reaction rate could still be corrected for the initiation rate by assuming the pseudo–steady state for free radicals. However, since the conversion at the maximum reaction rate ranges from 40 to 80% for medium-temperature isothermal reactions here (see Table IV), correction for the variation of initiation rate with differing molar ratios is not convenient and no correction has been made.

Figures 4 and 5 show the isothermal DSC rate profiles with various molar ratios at 80 and 70°C, respectively, where the shape of rate profiles is similar to that at 90°C, shown in Figure 2. The order

Table IV   Summary of Kinetic Information by DSC for Styrene–UP2660PF2 Reactions at Both 70–90°C and Scanning Modes[a]

T (°C)	MR	ΔH_{iso}	ΔH_{res}	ΔH_I	ΔH_S	α_1	α_S	t_z	t_m	$\alpha(t_m)$
70	1/1	10.30	1.34	11.64	13.62	0.89	0.76	11.59	50.72	0.34
	2/1	12.22	1.21	13.43	15.01	0.91	0.81	10.14	52.75	0.55
	3/1	11.98	0.88	12.86	14.55	0.93	0.82	10.15	58.84	0.48
	6/1	12.44	0.63	13.07	14.56	0.95	0.85	27.05	99.32	0.82
80	1/1	10.61	1.22	11.83	13.62	0.90	0.78	5.02	16.04	0.43
	2/1	12.57	0.76	13.33	15.01	0.94	0.84	2.20	15.89	0.50
	3/1	12.26	0.50	12.76	14.55	0.96	0.84	3.86	24.40	0.65
	6/1	12.86	0.41	13.27	14.56	0.97	0.88	5.92	39.73	0.78
90	1/1	11.21	0.77	11.98	13.62	0.94	0.82	0.87	5.78	0.49
	2/1	13.15	0.52	13.67	15.01	0.96	0.87	0.39	7.25	0.59
	3/1	12.82	0.25	13.07	14.55	0.98	0.88	0.48	10.00	0.71
	6/1	13.31	0.17	13.48	14.56	0.99	0.91	1.00	16.64	0.80

[a] The unit of ΔH_{iso}, ΔH_{res}, ΔH_I (=ΔH_{iso} + ΔH_{res}), and ΔH_S is kcal/mol C=C, where ΔH_{iso} is the heat released for isothermally cured sample, ΔH_{res} is the heat released by rescanning the isothermally cured sample at 10°C/min from room temperature to 210°C, and ΔH_S is the heat released at 10°C/min scanning rate from room temperature to 210°C. α_I is the overall conversion based on the ΔH_I as 100% conversion, and α_S is the overall conversion based on ΔH_S as 100% conversion. t_z is induction time and t_m is time to the maximum rate (minutes), and $\alpha(t_m)$ is the overall conversion at maximum rate. MR is the mole ratio of sytrene to polyester C=C bonds.
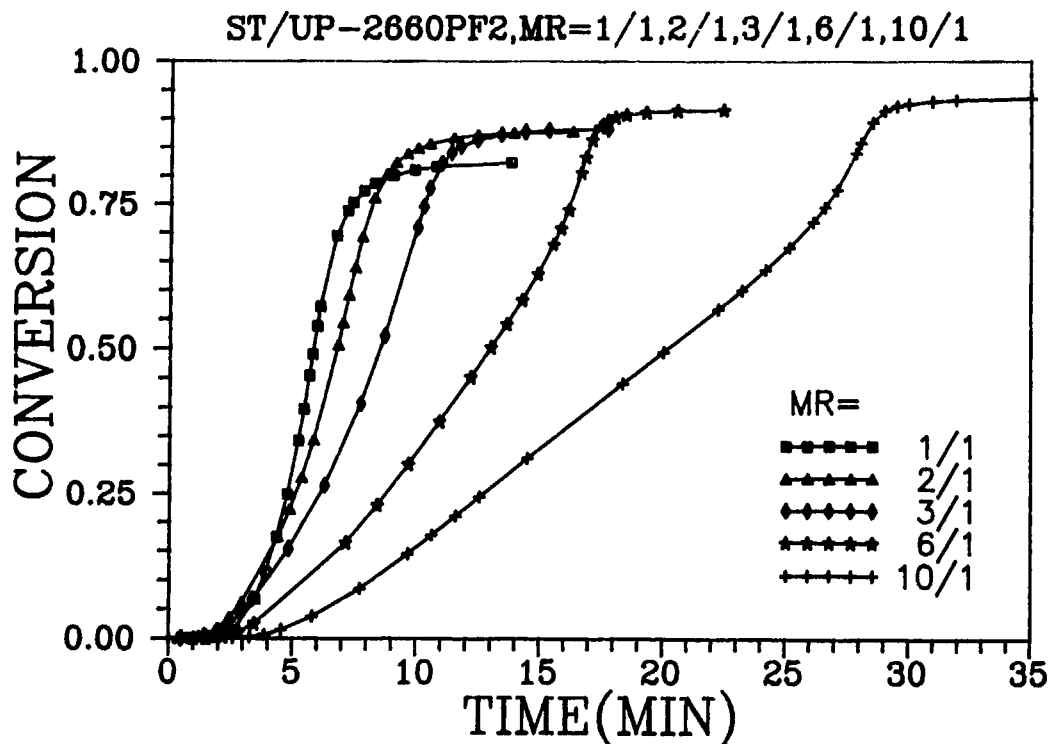
Figure 3   Isothermal DSC conversion profiles at 90°C corresponding to Figure 2.
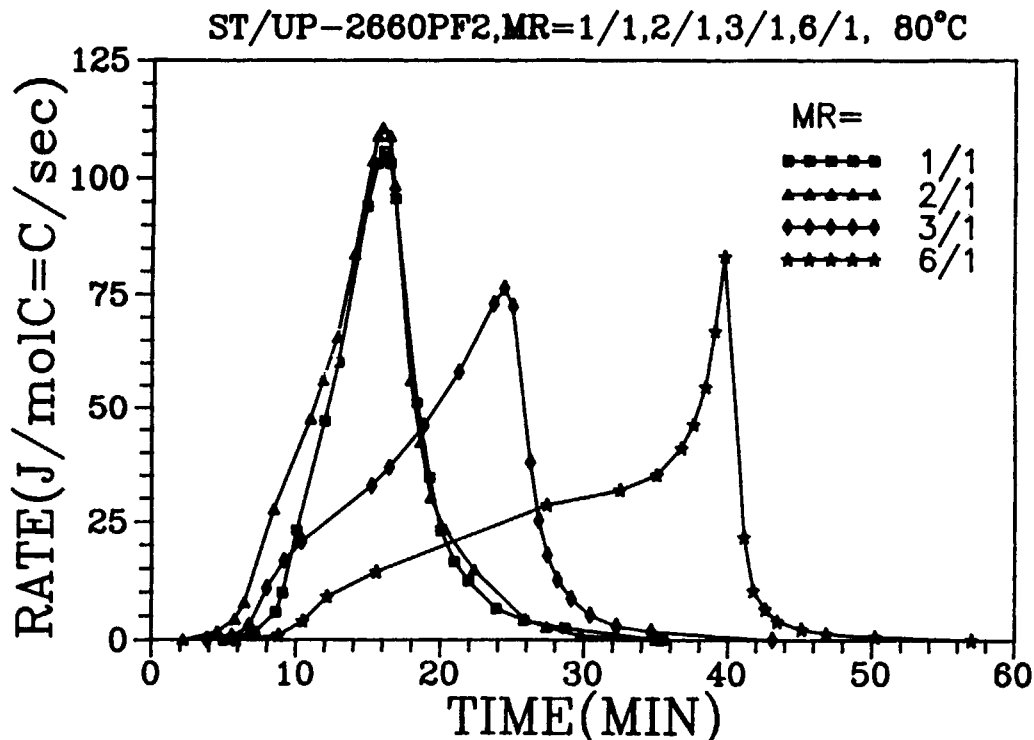

Figure 4   Isothermal DSC rate profiles for styrene-UP2660PF2 reactions at 80°C with various molar ratios of styrene to polyester C=C bonds.
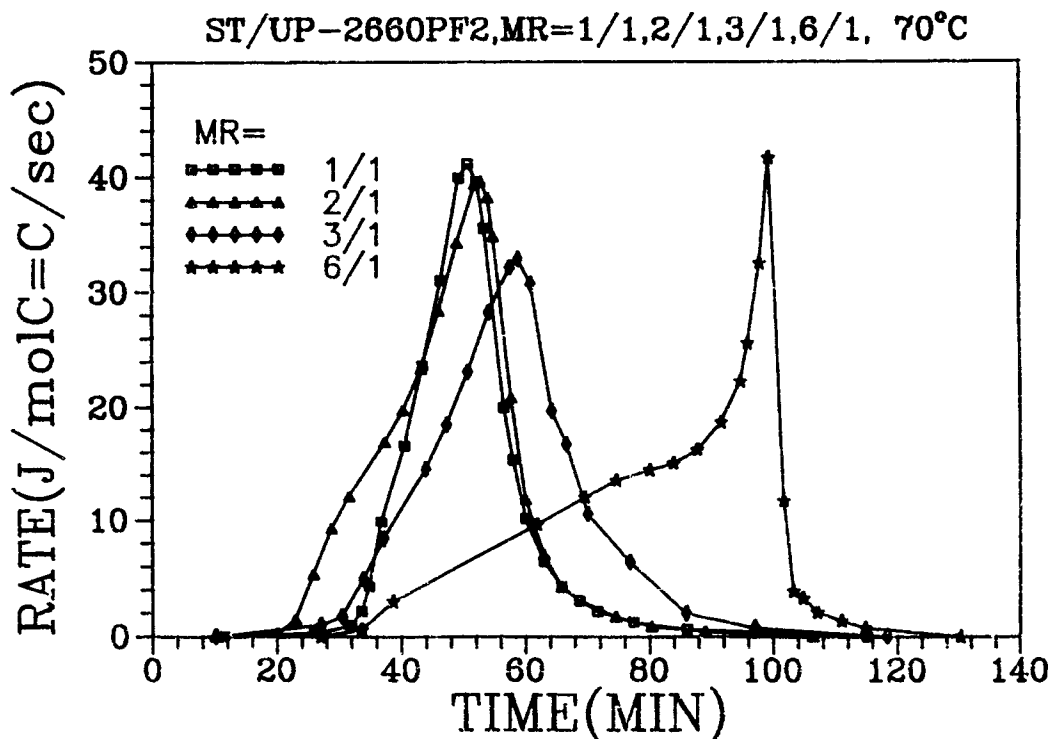
Figure 5   Isothermal DSC rate profiles for styrene-UP2660PF2 reactions at 70°C with various molar ratios of styrene to polyester C=C bonds.

of the initial reaction rate is MR = $2/1 > 3/1 > 1/1 > 6/1$, which is again the same as that at 90°C. It can be seen that the time to the maximum rate as well as the conversion at the maximum reaction rate generally increases with increasing molar ratio (see Table IV). For the overall C=C conversion versus time profiles (not shown), again, the higher the styrene content, the higher the final conversion.

Table IV summarizes the heat generated by the curing reaction for the UP2660PF2 system, which includes the heat generated in isothermal cure, ΔH_{iso}; the residual heat that was released when the sample was heated from room temperature to 210°C 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 room temperature to 210°C at 10°C/min, ΔH_S. Also displayed in Table IV are the final conversions, α_I and α_S, based on ΔH_I and ΔH_S, respectively; induction time, t_z; time to the maximum rate, t_m; and conversion at the maximum rate, $\alpha(t_m)$. The total heat release ΔH_S is greater than ΔH_I for all the molar ratios. In general, under the same molar ratio, the overall conversion, α_S, increases with increasing temperature. Also, under the same reaction temperature, α_S increases with increasing molar ratio.

Isothermal Reaction by IR

Figure 6 shows the conversion of styrene C=C bonds, polyester C=C bonds, and total C=C bonds versus time profiles for UP2660PF2 reaction with MR = 1/1 measured by IR spectroscopy. For comparison, the DSC rate profile, and DSC total conversion curves based on both ΔH_I (solid line) and ΔH_S (dashed line) are also plotted. It can be seen that the overall conversion measured by IR spectroscopy lies between α_I and α_S measured by DSC but much closes to α_S, where α_S is generally considered an index of the true overall conversion.[7] Therefore, the overall conversion measured by IR spectroscopy and DSC (using ΔH_S) shows a very good agreement. Prior to the peak of the DSC rate profile in Figure 6, the conversion of polyester C=C bonds is higher than that of styrene. After the peak (between points 3 and 4), the conversion of styrene gradually exceeds that of polyester C=C bonds. It is due to the fact that after the peak, propagation reactions become diffusion controlled[9] and the mobility of the small styrene molecule is less affected by the increase of crosslinking density than that of C=C units in large polyester molecules, leading to a higher conversion of styrene.
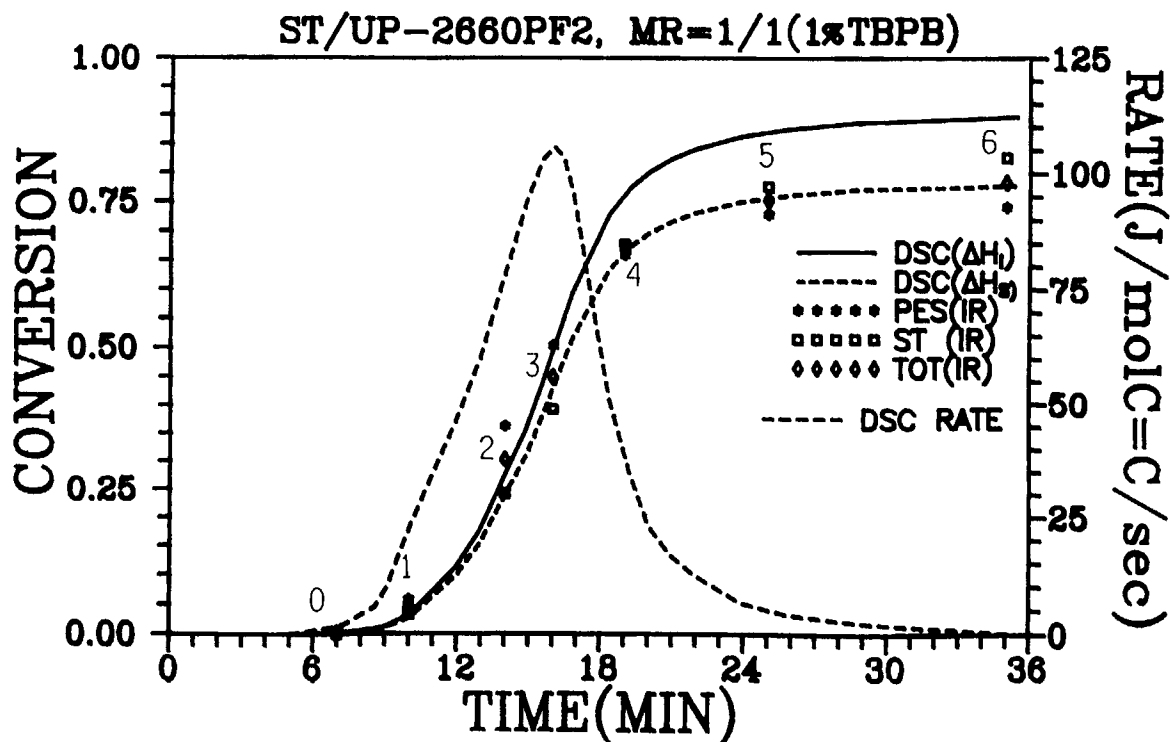
For the six reaction intervals in Figure 6, i.e.,

Figure 6 Styrene, polyester vinylene, and total $C = C$ conversions versus time profiles measured by IR spectroscopy for UP2660PF2 reaction at 80°C with MR = 1/1. The DSC rate profile (dashed curve) and total $C = C$ conversion profiles based on both ΔH_I (solid curve) and ΔH_S (dashed curve) are also plotted for comparison.

0 → 1, 1 → 2, 2 → 3, 3 → 4, 4 → 5, and 5 → 6, the average numbers of styrene $C = C$ bonds consumed per polyester $C = C$ bond reacted, known as the average crosslink length of styrene, for MR = 1/1 are 0.59, 0.68, 1.07, 1.89, 1.62, and 1.90, respectively, as listed in Table V. It increases up to the reaction interval of 3 → 4, where the DSC rate profile declines from the peak, followed by a decrease in the subsequent interval, and increases again eventually. In the final copolymer, the average crosslink length of styrene is 1.11, which is close to the initial molar ratio of styrene to polyester $C = C$ bonds.

Figures 7 and 8 show the conversion profiles measured by IR spectroscopy for MR = 2/1 and

MR = 6/1, respectively. It can be seen that the overall conversion by IR spectroscopy is generally close to α_S of the DSC curve, indicating the agreement of the conversion measurements by IR spectroscopy and DSC at both molar ratios. The trend of conversion variations for styrene and polyester $C = C$ bonds is similar to that for MR = 1/1, as shown in Figure 6. Also, the change of crosslink length of styrene during the reaction, as shown in Table V, exhibits the similar trend to that for MR = 1/1. Among all the molar ratios, the average crosslink length of styrene is the largest for MR = 6/1 at the corresponding intervals.

Figure 9 shows the relative conversion profiles of

Table V Relative Consumption of Styrene $C = C$ Bonds Per Polyester $C = C$ Bond Reacted for UP2660PF2 Reactions With Various Molar Ratios at 80°C

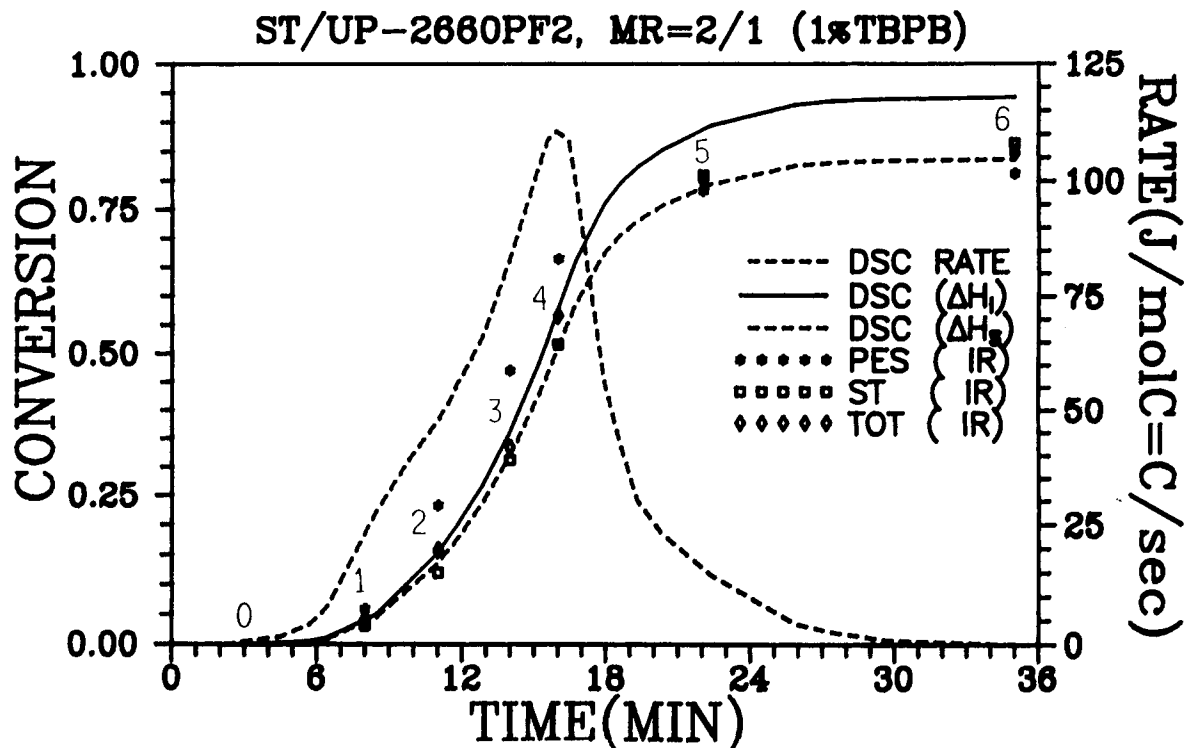| Molar Ratio | By Reaction Intervals | | | | | | |
	0 → 1	1 → 2	2 → 3	3 → 4	4 → 5	5 → 6	0 → 6
1/1	0.59	0.68	1.07	1.89	1.62	1.90	1.11
2/1	1.07	0.99	1.62	2.17	4.74	3.61	2.13
6/1	3.0	2.52	4.62	8.04	12.40	82.50	6.43

Figure 7 Conversion versus time profiles measured by IR spectroscopy for UP2660PF2 reaction at 80°C with MR = 2/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.
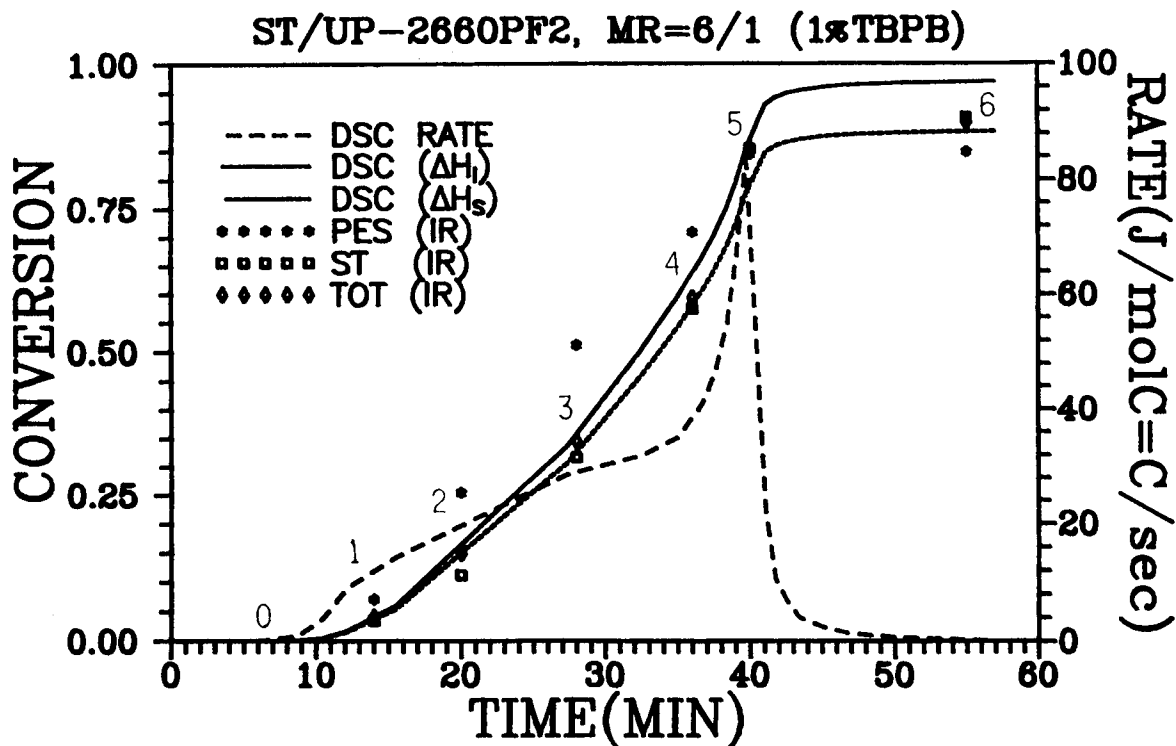

Figure 8 Conversion versus time profiles measured by IR spectroscopy for UP2660PF2 reaction at 80°C with MR = 6/1. Similar to Figure 6, DSC rate and conversion profiles are also plotted for comparison.
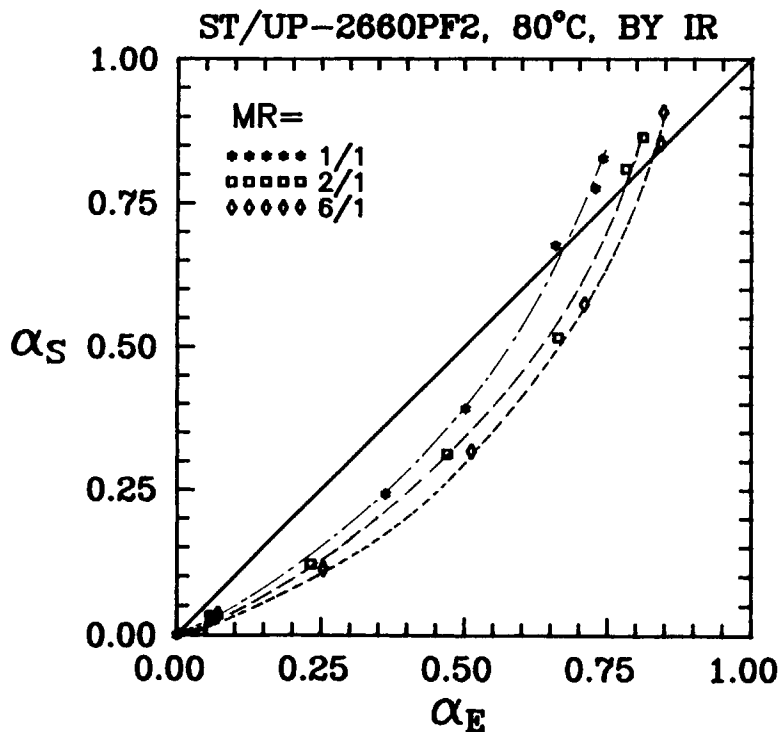
Figure 9   Relative conversion of styrene to polyester C$=$C bonds at various molar ratios of styrene to polyester C$=$C bonds for UP2660PF2 reaction at 80°C.

styrene versus polyester C$=$C bonds for styrene/ UP2660PF2 reactions with various molar ratios. It can be seen that all the curves show up-bending features. It indicates that the conversion of polyester C$=$C bonds is more favorable than that of styrene in the beginning of the reaction, and the styrene conversion catches up at the later reaction. As the molar ratio increases, they generally move to the right. Hence, the higher styrene content is capable of facilitating the conversion of polyester C$=$C bonds. Below 65, 77, and 83% conversions for MR $= 1/1, 2/1$ and $6/1$ respectively, the curves fall below the 45° diagonal line that denotes the azeotropic copolymerization. Unlike low-temperature reaction at 40°C,[7] the azeotropic copolymerization at MR

$= 2/1$ cannot be observed, which is similar to that for the high-temperature reaction at 110°C.[8] Table VI summarizes the final conversions measured by IR spectroscopy and the final average crosslink length of styrene at various molar ratios. The conversions of styrene (α_S) and polyester C$=$C bonds (α_E) increase with increasing molar ratios, so does the final average crosslink length of styrene.

Another commercial UP resin, UP2597PF6, with cobalt promoter added (232.1 ppm) and with 2.16 unsaturated C$=$C bonds per polyester molecule has also been studied. This resin consists of phthalic acid, fumaric acid, and propylene glycol with a mole ratio of 1.0:0.35:1.56 and with $\bar{M}_n = 1663$ g/mol. Because of space limitation, the results for styrene/

Table VI   Summary of Kinetic Information by IR Spectroscopy for Styrene–UP2660PF2 Reactions at 80°C

Molar Ratio	α_S, %	α_E, %	α_{TOT}, %	$\bar{\alpha}_S$, %	$\bar{\alpha}_E$, %	n
1/1	83.2	74.2	78.7	41.6	37.1	1.12
2/1	86.4	81.3	84.7	57.6	27.1	2.13
6/1	90.7	84.6	89.8	77.7	12.1	6.43

[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.

UP2597PF6 reactions have not been shown here. For the two resin systems studied, UP2660PF2 and UP2597PF6, unlike low-temperature and high-temperature reactions,[7,8] the degrees of C=C unsaturations have less significant effects on the curing time for the entire reaction as well as the cure characteristics under the moderate temperature range of reaction with the promoter-accelerated initiator system. However, there are several salient differences in the isothermal curing behavior between the two resin systems. First, at MR = 1/1, the initial reaction rate is the fastest among all the molar ratios for the UP2597PF6 system, rather than at MR = 2/1 for the UP2660PF2 system. Second, the shoulder prior to the peak of the rate profile appears broader for the UP2597PF6 system than for UP2660PF2 at the same molar ratio. Third, the resin with a lower degree of C=C unsaturations (i.e., UP2597PF6) leads to higher ultimate conversions of styrene and polyester C=C bonds.

DISCUSSION

Scanning Reaction by DSC

For the scanning reactions with the TBPB/cobalt promoter initiator system shown in Figure 1, the starting cure temperature is about 20°C lower than that for the UP2821 system using TBPB as an initiator without adding promoter in our previous work[8] (70 vs. 90°C). Since the degrees of C=C unsaturation for the UP2660PF2 and UP2821 resins are 8.85 and 6.82, respectively, they can be regarded as similar in average functionality. Therefore, that the cure starts at a lower temperature in Figure 1 is due to the fact that the cobalt promoter results in a reduction in the activation energy of initiation reaction for TBPB.

Basically, the reaction mechanism for the scanning reactions with the TBPB/cobalt promoter initiator system here would be similar to that for UP2821 scanning reactions with TBPB as an initiator alone.[8] This is because the starting reaction temperature is only 20°C lower than that for UP2821 systems. Prior to the peak of the rate profile, intramicrogel crosslinking reactions would predominate over the intermicrogel crosslinking ones, whereas after the peak, the intermicrogel crosslinking reactions would become more favorable. However, the lowering of the cure temperature range caused by the promoter could have a profound effect on the reaction kinetics. Under the moderate cross-

linking rate at a lower temperature, the microgel particles continuously formed prior to the peak of rate profile during the reaction would experience a slower buildup of the local crosslinking density. Also, these microgel particles tend not to overlap with each other very rapidly and styrene monomers could readily diffuse into the very interior of the individual microgel. Therefore, either the styrene monomer originally encompassed inside the microgel particles or that diffusing into the microgels extensively with less diffusion resistance could easily crosslink with the C=C bonds of polyester molecules inside the microgel, leading to an enhancement in the intramicrogel crosslinking reactions. The C=C conversion could thus be greatly facilitated early prior to the peak of the rate profile by the intramicrogel reactions. This is supported by the somewhat unsymmetrical rate profile shown in Figure 1 with a slightly broader profile before the peak than after it. In contrast, for the reaction solely initiated by TBPB,[8] an essentially symmetrical rate profile with respect to the peak results. It should be noted that for a resin system with a lower degree of C=C unsaturation, the broader curve at the initial portion of the scanning rate profile would be more prominent than that for the UP2660PF2 system in Figure 1. This is because the intramicrogel crosslinking reactions would proceed more preferentially for the resin system with a lower degree of C=C unsaturation.[8]

At high molar ratios such as MR = 6/1 and 10/1, although the microgel structure could be much more swollen by the high styrene content when compared with that by the low one, the styrene swelling effect would diminish the crosslinking reaction rate due to the extensive self-bonding of styrene monomers in the copolymerization of styrene and polyester C=C bonds.[6–8] The shoulder appearing at the later stage of reaction would be due to the further intramicrogel crosslinking reactions under the higher reaction temperature range where the buried C=C bonds inside the microgel could obtain sufficient activation energy of reaction at this stage. The plateau region from 150 to 200°C at MR = 10/1 for the UP2660PF2 system would result from thermal homopolymerization of the styrene monomer, which is in excess of that needed to copolymerize with polyester C=C bonds. Since the UP2660PF2 system possesses a relatively high crosslinking density, it would entail more styrene to swell its compact microgel structure in the crosslinking process of styrene–polyester copolymerization than a resin system with a lower degree of C=C unsaturation would, leading to a plateau region at a higher molar ratio.

Isothermal Reaction by DSC

Before any conclusion is drawn on how the reaction shoulder appears as shown in Figures 2, 4, and 5, isothermal DSC reactions for UP2821 resins at MR = 6/1 with and without cobalt octoate have been carried out, where the promoter (cobalt octoate, 8% solution) and initiator (TBPB) added are 0.3 and 1% by weight of the total resin, respectively. The UP2821 resins have the same chemical compositions as UP2660PF2 resins[7] and similar average functionality to UP2660PF2 ones as mentioned earlier. Figure 10 shows that with the addition of cobalt promoter, the isothermal rate profile at 90°C exhibits a shoulder prior to the peak, whereas there is no shoulder in the isothermal rate profile at 110°C when the TBPB is employed alone. Therefore, the reaction shoulder obviously results from the copolymerization initiated by the TBPB–cobalt promoter system.

The reaction mechanism for isothermal reactions at medium temperatures with the TBPB–cobalt promoter initiator system here would resemble that for UP2821 isothermal reactions solely initiated by TBPB at high temperatures.[8] Again, this results from the fact that the reaction temperature range is only 20–30°C lower than that for UP2821 reac-

tions at high temperatures. In general, at the early part of the reaction, intramicrogel crosslinking reactions would predominate over the intermicrogel crosslinking ones, whereas at the later part of the reaction, the intermicrogel crosslinking reactions would become more favorable. In particular, with the initiator system accelerated by cobalt promoter, the rate of free radical formation is greatly elevated. Assuming one free radical would generate one primary microgel particle,[4,10] the formation rate of microgel particles could thus be enhanced, especially prior to the peak of the reaction rate profile, where the microgel particles generated would not be closely overlapped. Due to the moderate crosslinking rate at the medium temperature range of 70–90°C, those relatively fast increasing numbers of microgel particles tend not to overlap rapidly with each other at the early stage of reaction. Hence, the intramicrogel crosslinking reactions can be facilitated considerably once a microgel particle is formed, which would be independently identified from the initial DSC rate profile as a shoulder.

In Figures 2, 4, and 5, the molar ratio of styrene to polyester C=C bonds leading to a marked shoulder or plateau region is greater than 1/1. On the one hand, it would be due to the fact that the
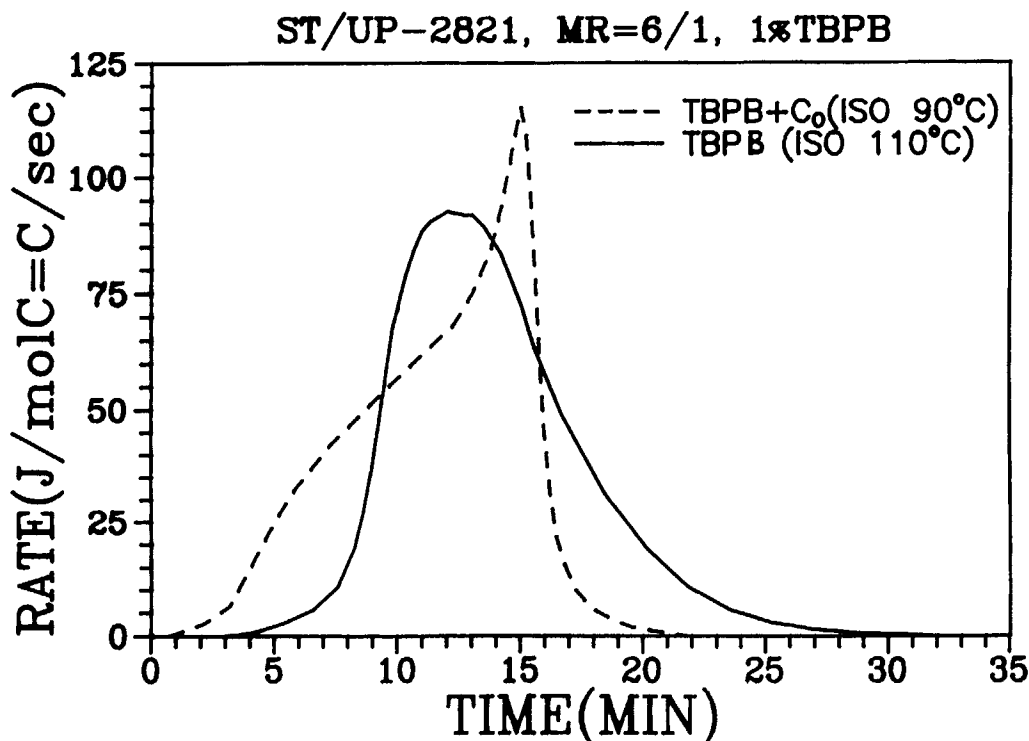

Figure 10   Differential scanning calorimetry rate profiles for reactions of styrene–UP2821 with MR = 6/1 at 110°C with 1% TBPB (solid curve) and at 90°C with 1 wt % TBPB + 0.3 wt % cobalt octoate (dashed curve).

styrene swelling effect under the higher styrene content could cause a loose structure for the microgel particle that is continuously formed starting from the reaction. Since the higher the molar ratio, the more favorable the intramicrogel crosslinking reactions as a result of the much more swollen microgel structure, a noticeable shoulder or plateau region arises accordingly. On the other hand, the overlapping of the increasing number of microgel particles would be delayed to a later time as the molar ratio increases, and hence the shoulder or plateau region characteristic of the intramicrogel crosslinking reactions could extend over a longer period of time. Quite often, when the microgel particles formed are gradually overlapped with each other, the intermicrogel crosslinking reactions become predominant over the intramicrogel crosslinking one, and the rate profile rapidly increases to the maximum point due to the fast crosslinking rate of the intermicrogel reactions.

The isothermal DSC rate profile could then be viewed as a summation of two individual reaction rate profiles, as illustrated in Figure 11 for UP2660PF2 reactions at 90°C with MR = 2/1, 3/1, 6/1, and 10/1, respectively. The first reaction rate profile (curve 1) would account for the intramicrogel-dominated crosslinking reactions at the early part of reaction, whereas the second reaction rate profile (curve 2) accounts for the intermicrogel-dominated crosslinking reactions at the later part of reaction. It is proposed that the intermicrogel-dominated reaction would not proceed appreciably until the rate of intramicrogel-dominated reaction declines from the peak. At lower molar ratios, such as MR = 2/1 and 3/1, the shape of the intramicrogel-dominated reaction rate profile is bell-like. This indicates that along with the continuous formation of microgel particles, the intramicrogel reaction would experience the gel effect region[9] at the early stage of reaction, where the rate profile rises sharply to the maximum point, due to the lower styrene swelling effect on the relatively compact microgel structure. It is followed by a glass effect region[9] after the peak of the rate profile, where the intramicrogel-dominated reaction rate decays to zero due to the fast increasing crosslinking density inside the microgels.

In contrast, at higher molar ratios, such as MR = 6/1 and 10/1, the intramicrogel-dominated reaction would first encounter a prolonged plateau
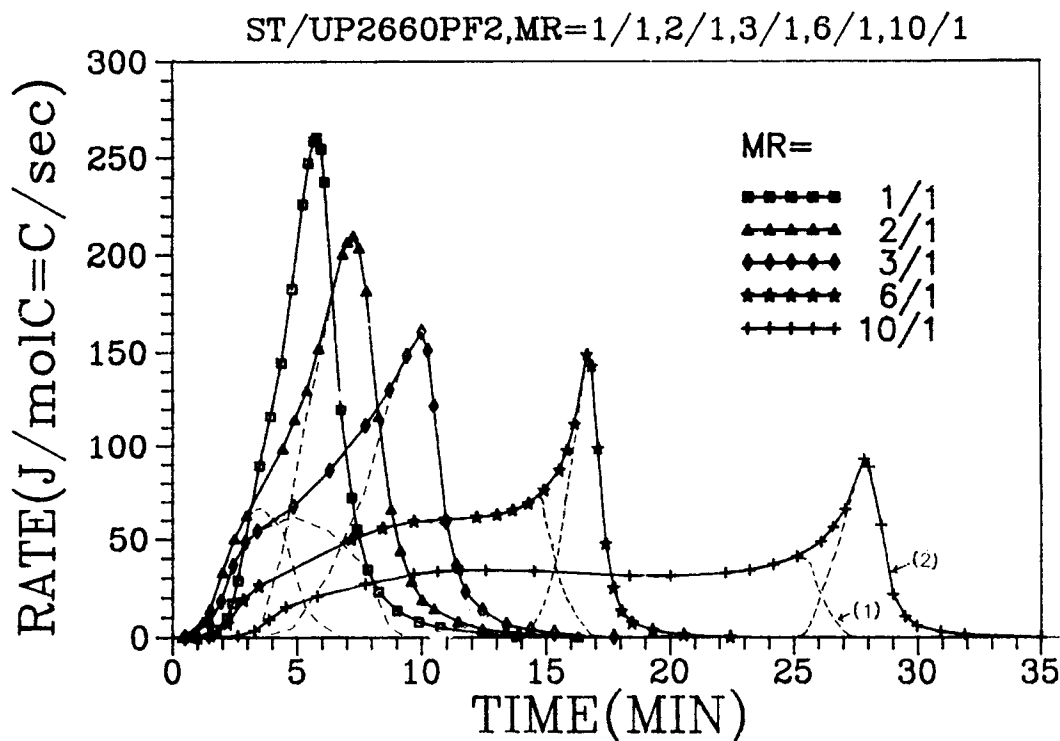

Figure 11   Reaction rate profiles of styrene–UP2660PF2 at 90°C showing the decomposition into two individual rate profiles due to the intramicrogel-dominated reaction (curve 1) and the intermicrogel-dominated reaction (curve 2) for MR = 2/1, 3/1, 6/1, and 10/1.

characterized by the kinetic-controlled region[9] prior to the peak, where the propagation and termination reactions are relatively unaffected by the diffusion limitation, due to the loose microgel structure caused by the better styrene swelling effect. Subsequently, a less noticeable gel effect region, which starts from 10 to 14.5 min for MR = 6/1 and from 20 to 25 min for MR = 10/1, arises, followed by a glass effect region similar to that for MR = 2/1 and MR = 3/1. At the later stage of reaction, the intermicrogel-dominated reaction rate profile would exhibit a bell-like shape at all the molar ratios. This is because the microgel particles generated would be gradually overlapped with each other, and the intermicrogel reaction could only undergo the gel effect and the glass effect regions without experiencing the kinetic-controlled region. As a result of the microgel-based reaction mechanism, the ultimate styrene-cross-linked polyester network structure would be inhomogeneous, with varied crosslinking network structure inside and outside the microgels.

As mentioned earlier, the highest initial reaction rate for UP2660PF2 reactions goes to MR = 2/1. Except for MR = 1/1, the initial reaction rate decreases with increasing molar ratio, the order of which is MR = 2/1 > 3/1 > 1/1 > 6/1 > 10/1. Our explanation is that the initial reaction is mainly due to the intramicrogel crosslinking reaction, the rate of which would be affected by the styrene dilution effect and the styrene swelling effect. In general, as the molar ratio increases, the styrene dilution effect enhances the self-bonding of the styrene monomers in the copolymerization of styrene with polyester $C=C$ bonds inside the microgels and thus decreases the rate of intramicrogel crosslinking reaction.[8] On the other hand, the styrene swelling effect loosens the microgel structure and thus enhances the intramicrogel crosslinking reaction rate by reducing the steric hindrance of reaction encountered by polyester $C=C$ bonds. Therefore, the resulting order of initial reaction rates reveals that except for MR = 1/1, the styrene dilution effect would be more important than the styrene swelling effect. This is because the moderate crosslinking reaction rate at the medium-temperature range of 70–90°C could reduce the advantage of the styrene swelling effect in facilitating the rate of intramicrogel crosslinking reactions due to a slower buildup of the crosslinking density inside the microgel. For MR = 1/1, the styrene content could cause an insufficient styrene swelling effect for the UP2660PF2 resin with a relatively high degree of $C=C$ unsaturation. Accordingly, the initial reaction rate would not be ranked the first. In contrast, for a resin with

a lower degree of $C=C$ unsaturation, such as the UP2597PF6 system, relatively loose microgel structures would result for the reacting system. The highest initial reaction rate goes to MR = 1/1 since the styrene swelling effect would be sufficient at such a low styrene content.

Isothermal Reaction by IR Spectroscopy

For styrene–UP2660PF2 reactions with MR = 1/1 as shown in Figure 6, the conversion of polyester $C=C$ bonds is much higher than that of styrene prior to the peak of the DSC rate profile, as compared with that for UP2821 reactions with MR = 1/1 at 110°C without cobalt promoter.[8] The average crosslink lengths of styrene in the intervals of $0 \rightarrow 1$ and $1 \rightarrow 2$ are 0.59 and 0.68, respectively. This reveals that homopolymerization of polyester $C=C$ bonds could proceed in the copolymerization of polyester with styrene monomer at the early stage of reaction. The percentage of the reacted polyester $C=C$ bonds as a result of polyester homopolymerization, through either the intermolecular or the intramolecular reaction of polyester $C=C$ bonds, would amount to at least 41 and 32% for the $0 \rightarrow 1$ and $1 \rightarrow 2$ intervals, respectively. In contrast, for UP2821 reactions at 110°C initiated by TBPB alone with MR = 1/1, the percentage of the reacted polyester $C=C$ bonds due to polyester homopolymerization is much lower and at a level of 17 and 5% for the first two reaction intervals, respectively. Therefore, with the initiator system accelerated by cobalt promoter, a much enhanced intramicrogel crosslinking reaction would involve at the early stage of reaction, since the fast consumption of polyester $C=C$ bonds and extensive polyester homopolymerization are ordinarily characteristic of the intramicrogel crosslinking reactions at the early reaction.

For styrene–UP2660PF2 reactions with MR = 2/1 as shown in Figure 7, the conversion of polyester $C=C$ bonds also greatly exceeds that of styrene prior to the peak of the rate profile due to the effect of cobalt promoter when compared with the UP2821 reaction with MR = 2/1 at 110°C solely initiated by TBPB.[8] However, since the average crosslink lengths of styrene for the first two reaction intervals $0 \rightarrow 1$ and $1 \rightarrow 2$ are 1.07 and 0.99, respectively, alternating copolymerization of styrene and polyester $C=C$ bonds would be the major reaction and little homopolymerization of polyester $C=C$ bonds would occur. This is due to the fact that as the molar ratio increases from MR = 1/1 to MR = 2/1, the styrene swelling effect would cause

a less compact microgel structure so that styrene monomers could diffuse to the polyester $C=C$ bonds with less difficulty and participate in the styrene–polyester crosslinking reaction.

For the styrene–UP2660PF2 reaction with MR = 6/1 as shown in Figure 8, the conversion of polyester $C=C$ bonds is again much higher than that of styrene prior to the peak of the rate profile. However, it generally makes no distinction to that for UP2821 reactions solely initiated by TBPB at 110°C with MR = 6/1.[8] This is because whether the cobalt promoter is added to the reaction system or not, the better styrene swelling effect at MR = 6/1 would further loosen the microgel structure to enhance the intramicrogel crosslinking reactions, leading to an elevated conversion of polyester $C=C$ bonds relative to that of styrene. On the other hand, this could also be attributable to the higher initial styrene content at MR = 6/1 that would inevitably cause a lower calculated styrene conversion. Nevertheless, the noticeable shoulder or plateau region at MR = 6/1 could not be observed for UP2821 reactions solely initiated by TBPB at 110°C with MR = 6/1.

In Figure 9, the relative conversion curves for the UP2660PF2 system, especially at MR = 1/1 and 2/1, show considerable deviation from the 45° line when compared with the UP2821 reactions at 110°C initiated by TBPB alone.[8] This illustrates that the effect of cobalt promoter could facilitate the conversion of polyester $C=C$ bonds to a great extent.

CONCLUSIONS

For the isothermal curing of unsaturated polyester resins at 70–90°C initiated by the TBPB–cobalt promoter system, the formation rate of microgel particles would be much more enhanced at the early stage of reaction than that without cobalt promoter. Under the medium reaction temperatures, where the crosslinking reaction rate is moderate, the microgel particles continuously generated during the reaction tend not to rapidly overlap with each other. The great number of microgel particles could result in an extensive intramicrogel crosslinking reaction, which has been supported by the much higher conversion of polyester $C=C$ bonds than that of styrene by IR spectroscopy prior to the peak of the DSC rate profile as well as by the appearance of a shoulder in the initial DSC rate profile. As the molar ratio of styrene to polyester $C=C$ bonds increases, the favorable styrene swelling effect could further

enhance the intramicrogel reactions, and a more noticeable shoulder or even a plateau region in the DSC rate profile could arise.

A microgel-based reaction mechanism for isothermal medium-temperature reactions with a promoter-accelerated initiator system has been elucidated, where the reaction rate can be regarded as a summation of intramicrogel- and intermicrogel-dominated crosslinking reaction rates. At the early stage of reaction, the intramicrogel crosslinking reactions would predominate, whereas at the later stage of reaction, the intermicrogel crosslinking reactions would be more favorable. Unlike low-temperature and high-temperature reactions, the degree of $C=C$ unsaturations of UP resins has less significant effects on the curing time for the entire reaction as well as the cure characteristics under the moderate-temperature range of reaction (i.e., 70–90°C) with the promoter-accelerated initiator system.

In order to further support the microgel-based reaction mechanisms proposed in this work, scanning electron micrographs showing the formation of microgel structure throughout the reaction should be provided and will be the subject of a forthcoming publication.

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