Curing of unsaturated polyester resins. Effects of temperature and initiator: 1. Low temperature reactions

Yan-Jyi Huang* **and Jiing-Shing Leu**
Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 107, Republic of China

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The effects of temperature and initiator on the curing kinetics of unsaturated polyester resins at 30–50°C were studied by d.s.c. and i.r. spectroscopy over the whole conversion range. It was found that at the beginning of reaction, the kinetic mechanism was dominated by near-azeotropic copolymerization, while styrene conversion became much more favourable than that of polyester C=C bonds later in the reaction. The transition point of the near-azeotropic copolymerization and the crosslink length of styrene varied with the concentrations of initiator and promoter used. The experimental results have been explained by a kinetic model relating to microgels.

(Keywords: curing kinetics; unsaturated polyester resins: d.s.c.; i.r. spectroscopy; microgel)

INTRODUCTION

Unsaturated polyester (UP) resins are the most widely used thermosets in polymeric composites[1]. They are processed over a wide temperature range involving hand lay-up at low temperature, transfer moulding at medium temperature, and sheet moulding compound (SMC) compression moulding, bulk moulding compound (BMC) injection moulding and pultrusion at high temperature[2].

Extensive research has been devoted to the curing of UP resins in the literature[3–14]. Although the reaction of styrene and UP resin is a free radical chain growth crosslinking copolymerization, most of the above-mentioned research, however, either treated the reaction as a simple free radical polymerization by using d.s.c. without differentiating between styrene and polyester vinylene conversions[4,10–14] or concentrated on the analysis of ultimate individual conversion by chemical analysis and spectroscopic methods without considering the whole conversion profile for each species[3–7]. Very few studies[8,9] carried out an investigation of the curing kinetics of UP for each species over the complete reaction course by i.r. spectroscopy.

It has now been recognized that[15,16] the reaction of UP resin is a free radical chain growth crosslinking copolymerization between the styrene monomer and UP molecule. Polyester molecules are the crosslinkers while styrene serves as an agent to link the adjacent polyester molecules. A mixture of polyester and styrene may be pictured as many coiled polyester chains swollen in the styrene monomer. Chemical reactions may occur among C=C bonds inside, outside and at the surface of the coils. The styrene–UP copolymerization progresses as the initiator decomposes and creates free radicals in the system. The free radicals link adjacent UPs and form long chain molecules through connecting styrene monomers by both inter- and intramolecular reactions (*Figure 1a*). These long chain molecules tend to form spherical type structures due to the intramolecular crosslinking among the pendant C=C bonds of the polyester molecules (*Figure 1b*). Some researchers described these spherical structures with locally high cyclization and crosslinking density as 'microgel particles'[17,18]. For UP resins, the reaction mechanism throughout the entire reaction after the formation of microgel particles in the early reaction has scarcely been discussed in the literature. This is because only a few researchers[18] have recognized that the crosslinked structure of cured polyester resins is inhomogeneous. Unless detailed kinetic measurements have been carried out over the whole conversion range, the reaction mechanism can hardly be elucidated from the viewpoint of microgel formation.

The purpose of this paper is to deal with the effects of temperature, initiator concentration and promoter concentration on the curing kinetics of UP resins over the whole conversion range. The resulting kinetic characteristics and variations of the reaction mechanism, as revealed by macroscopic observations from both d.s.c. and i.r. measurements, are discussed from a microscopic point of view based on microgels.

EXPERIMENTAL

Materials

The UP resin used (UP-2821) contained isophthalic acid, fumaric acid and propylene glycol in a molar ratio of 1:1.46:2.79 (by ^1H n.m.r.). The number-average molecular weight of the resin was found to be 2090 g mol^{-1} by end-group titration. On average, the calculated number of C=C double bonds in each polyester molecule was 6.67. Styrene (39.9 wt%) was added to the resin to give a molar ratio of styrene to UP C=C double bonds of 2:1, which is a typical composition for an SMC. At 30–50°C, the

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* To whom correspondence should be addressed

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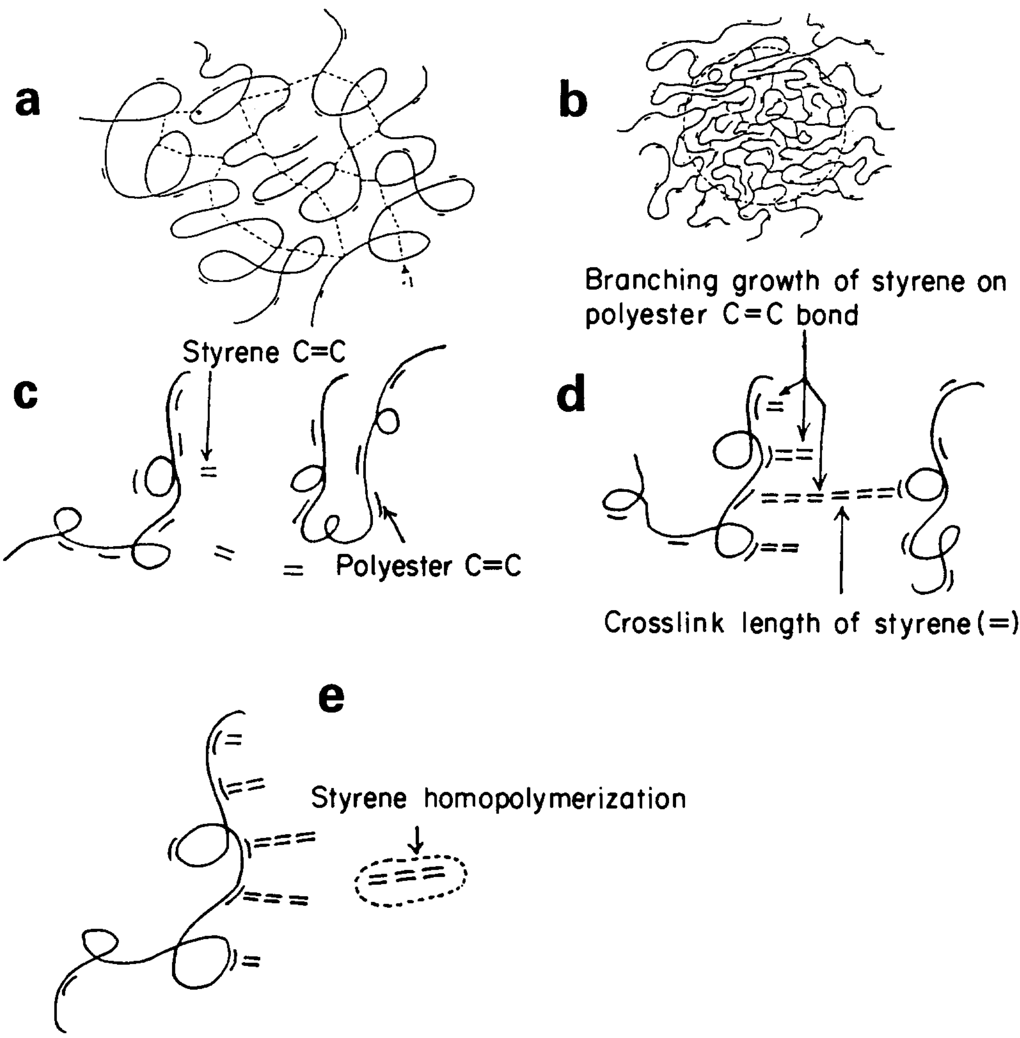

Figure 1 Schematic diagram showing microgel formation and some possible ways of bonding in the styrene–polyester reactions: (a) growth of free radicals[15]; (b) formation of microgel particles[15]; (c) reaction system before reaction; (d) branching growth of styrene on polyester C=C bonds and the formation of crosslink length of styrene; (e) styrene homopolymerization

reaction was initiated by an amine-accelerated system with 3% benzoyl peroxide (BPO; an initiator, Lucidol W-75, Akzo), 0.3% *N*,*N*-dimethyl aniline (DMA, a promoter, Akzo) and 0.3% p-tert-butyl catechol (NLC-10, an inhibitor, Akzo). All the materials were used as received.

Instrumentation and procedure

A Dupont 9000 differential scanning calorimeter with a 910 pressurized d.s.c. cell was used to follow the overall reaction rate profiles at atmospheric pressure. All the reactions were conducted in hermetic aluminium sample pans with sample weights of 5–10 mg. Isothermal reaction rate *versus* time profiles were measured at 30–50°C. Isothermal d.s.c. 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 5°C min^{-1} to determine the residual reactivity left in the isothermally cured samples. Resins were also cured in the scanning mode at a heating rate of 5°C min^{-1}. The total heat of reaction was calculated from the area under the scanning d.s.c. curve. If we assume that the density and heat capacity of the resin changed little with reaction from the liquid to the solid state within the temperature range used, the rate of overall reaction can be directly converted from the rate of heat release measured by d.s.c.

In this study, an i.r. spectrophotometer 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 KBr plates which were then mounted on a sample holder located in the i.r. chamber. A temperature control chamber was designed to maintain the reaction temperature isothermally. A 2.5 min scan from 1900 to 600 cm^{-1} was taken at each sampling time. Measurement was ended when there were no changes in absorbance peak areas. All i.r. spectra were expressed in absorbance where the individual conversion of styrene and polyester vinylene could be determined as a function of time.

CONVERSION CALCULATION

Figure 2 shows an i.r. spectrum from 600 to 3500 cm^{-1} for the UP-2821 resin before reaction. The absorption peaks at 695 and 1730 cm^{-1} are characteristic of styrene (C–H out-of-plane bending in benzene ring) and polyester (C=O stretching in ester linkage), respectively. Reaction conversion can be determined from the consumption of styrene C=C bonds at 912 and 992 cm^{-1} (C–H out-of-plane bending in CH_2=CHR) and the consumption of polyester C=C bonds at 982 cm^{-1} (C–H out-of-plane bending in *trans* CHR=CHR). During the reaction, the styrene

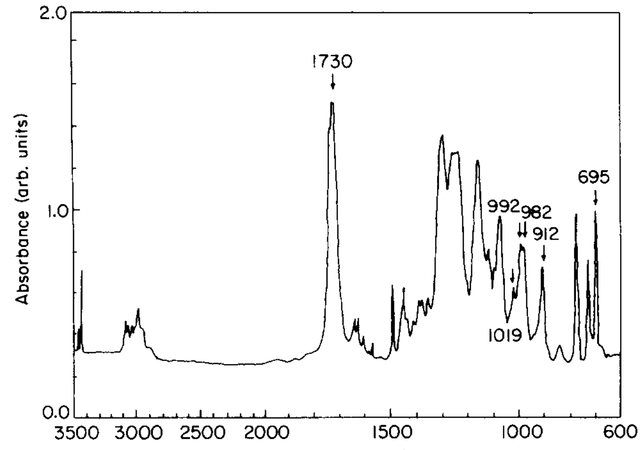

Figure 2 I.r. spectrum for UP-2821 resin before reaction

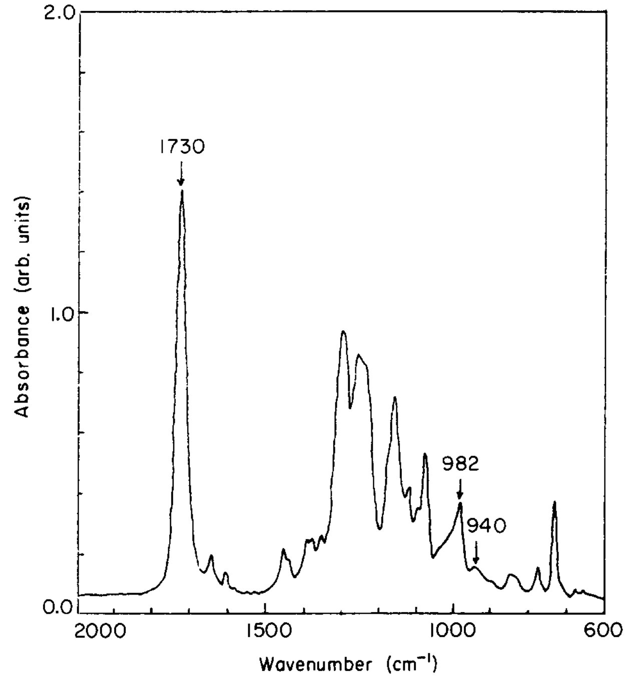

Figure 3 I.r. spectrum for UP-2821 resin before reaction after the removal of styrene monomers

consumption can be determined easily from the peak area change at 912 cm^{-1}, but the consumption of polyester C=C bonds and the total consumption of C=C bonds cannot be followed directly from the peaks at 982 and 992 cm^{-1} because they overlap with each other. A subtraction method was used to separate the overlapping peaks[19,20].

Figure 3 shows the i.r. spectrum of UP-2821 resin after the styrene monomer was removed. It can be seen that the absorption peaks at 992, 912 and 695 cm^{-1} disappear, but an absorption peak at 940 cm^{-1} (O–H out-of-plane bending in polyester terminal groups) emerges. *Figure 4* shows the i.r. spectrum for pure styrene. The absorption peak at 1019 cm^{-1} is an inert functional group. Since it overlaps somewhat with the absorption peak at 992 cm^{-1}, correction should be made to obtain the true absorption at 992 cm^{-1}. The absorption peak at 695 cm^{-1} is an inert peak during the reaction, and can be used to calculate the amount of styrene that had evaporated.

According to Beer's law:

$$A_i = a_i b C_i \tag{1}$$

where A_i is the absorbance of species i which can be determined from the peak area, a_i is the absorptivity which is characteristic of absorbing species, i, b is the path length and C_i is the concentration of the absorbing species i. In this study, the C=O peak at 1730 cm^{-1} was chosen as the internal standard to correct for thickness change in the sample during reaction. The percentage of styrene consumption, which includes reaction conversion and evaporation loss, can be determined from the peak area change at 912 cm^{-1}, i.e.

$$\alpha'_{\mathrm{S}} = 1 - \left(\frac{\bar{A}^t_{912}}{\bar{A}^0_{912}}\right) \tag{2}$$

where $\bar{A}^0$ and $\bar{A}^t$ are the normalized absorbance of the functional group before the reaction and after a reaction time t, i.e. $\bar{A}^t_{912} = A^t_{912}/A^t_{1730}$ and $\bar{A}^0_{912} = A^0_{912}/A^0_{1730}$. Since the absorption peaks at 912 and 940 cm^{-1} overlap each other, α'_{S} should be calculated as:

$$\alpha'_{\mathrm{S}} = 1 - \left(\frac{\bar{A}^t_{912+940} - \bar{A}^t_{940}}{\bar{A}^0_{912+940} - \bar{A}^0_{940}}\right) \tag{3}$$

where $A_{912+940}$ is the peak area at 912 and 940 cm^{-1} together, and the absorption peak at 940 cm^{-1} is assumed to be unchanged during reaction (i.e. $\bar{A}^t_{940} = \bar{A}^0_{940}$), which can be calculated from *Figure 3*. From the i.r. spectrum shown in *Figure 3*, the C–H out-of-plane bending at 695 cm^{-1} due to isophthalic acid in UP-2821 resin can be neglected. The percentage of styrene due to evaporation can thus be calculated as:

$$\alpha''_{\mathrm{S}} = 1 - \left(\frac{\bar{A}^t_{695}}{\bar{A}^0_{695}}\right) \tag{4}$$

The styrene conversion can then be expressed as:

$$\alpha_{\mathrm{S}} = \alpha'_{\mathrm{S}} - \alpha''_{\mathrm{S}} \tag{5}$$

In this study, styrene loss was negligible, as evidenced by the invariant absorbance at 695 cm^{-1} for styrene by a separate test in the low temperature range of 30–50°C and $\alpha''_{\mathrm{S}} = 0$.

Another conversion, α_{p}, can be defined as the peak area change at 982 and 992 cm^{-1}:

$$\alpha_{\mathrm{p}} = 1 - \left(\frac{\bar{A}^t_{982+992+1019} - \bar{A}^t_{1019}}{\bar{A}^0_{982+992+1019} - \bar{A}^0_{1019}}\right) \tag{6}$$

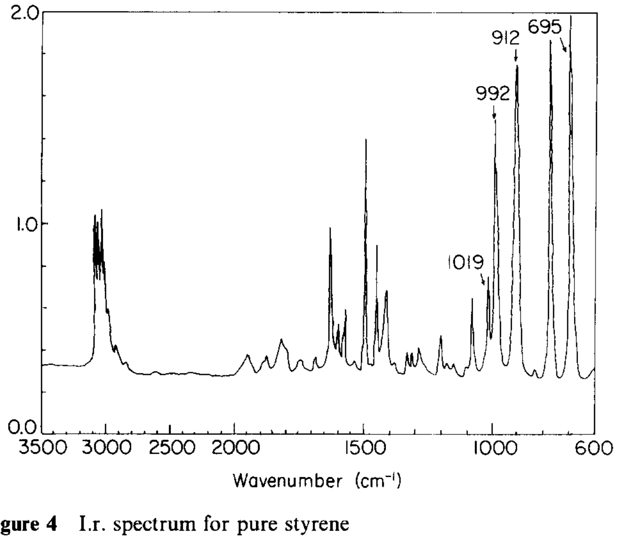

Figure 4 I.r. spectrum for pure styrene

Since the absorption peaks at 982, 992 and 1019 cm^{-1} were overlapped, they had to be considered together. The absorption peak at 1019 cm^{-1} was assumed to be solely contributed by styrene monomer[20] since isophthalic acid showed no absorption peak due to the C–H in-plane bending[21] at 1019 cm^{-1} and the C–O stretching of polyester at 1019 cm^{-1} was assumed to be negligible. Hence, $\bar{A}^{t}_{1019}=\bar{A}^{0}_{1019}(1-\alpha''_{S})$.

To determine α_P using equation (6), $\bar{A}^{0}_{1019}$ should be known. First, the absorptivity ratio, $B(=a_{982}/a_{992})$, is calculated by the following equation[20]:

$$\frac{BI}{1+BI}=\frac{1}{\dfrac{\bar{A}^{0}_{982}+\bar{A}^{0}_{992}+\bar{A}^{0}_{1019}}{\bar{A}^{0}_{982}}-\dfrac{B_1}{BI}} \tag{7}$$

where $B_1=a_{1019}/a_{992}=A^{0}_{1019}/A^{0}_{992}$, which can be calculated from the i.r. spectrum of pure styrene shown in *Figure 4*, $I=(C_E/C_S)_0$, the units for C_{E0} and C_{S0} being g polyester cm^{-3} and g styrene cm^{-3}, respectively, before the reaction, $\bar{A}^{0}_{982}+\bar{A}^{0}_{992}+\bar{A}^{0}_{1019}$ is the absorbance of the three overlapped peaks at 982, 992 and 1019 cm^{-1} before the reaction and $\bar{A}^{0}_{982}$ can be calculated from *Figure 3*. The B value from equation (7) was calculated to be 1.15. Calibration curves by preparing monomer–dichloromethane solutions of known concentration for polyester and styrene, respectively, could also be established to calculate the B value[8].

$\bar{A}^{0}_{1019}$ can now be calculated as:

$$\bar{A}^{0}_{1019}=\bar{A}^{0}_{982}\frac{B_1}{BI} \tag{8}$$

The conversion of C═C bonds in polyester can be derived and calculated as[19]:

$$\alpha_E=1-\frac{1}{BI}[(1-\alpha_p)(1+BI)-(1-\alpha'_S)] \tag{9}$$

Finally, the overall conversion of C═C bonds can be expressed as:

$$\alpha_T=\frac{\alpha_S+I'\alpha_E}{1+I'} \tag{10}$$

where $I'=(C'_E/C'_S)_0$, and the units of C'_{E0} and C'_{S0} are moles of C═C bonds for polyester cm^{-3} and moles of C═C bonds for styrene cm^{-3}, respectively, before the reaction.

RESULTS AND DISCUSSION

Effect of temperature

Figure 5 shows the reaction rate profiles obtained by d.s.c. at 30, 40 and 50°C. The higher the temperature, the faster the reaction rate. The induction time, t_z, and the time to maximum rate, t_m, are shorter with increasing temperature. *Figure 6* shows the corresponding overall conversion profiles, and as expected the ultimate overall conversion increases with temperature.

Table 1 displays t_z, t_m, ultimate overall conversions, α_{iso}, by d.s.c., and the individual conversions of styrene and polyester vinylene groups, α_S and α_E, measured by i.r. The d.s.c. overall conversion at 50°C reaches 71%, and those at 40 and 30°C are ~66%. The sum of heat release for the isothermally cured sample, ΔH_{iso}, and the rescanned

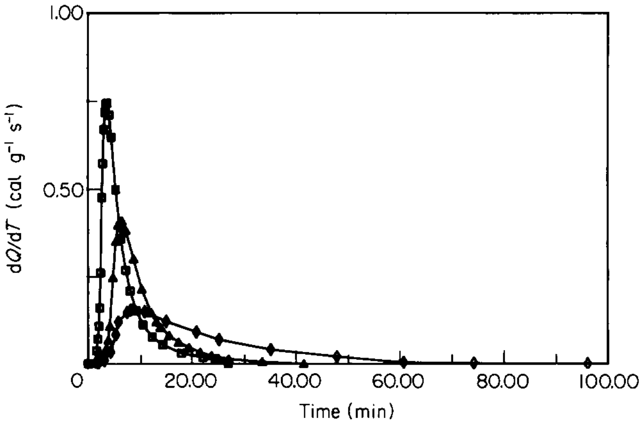

Figure 5 D.s.c. rate profiles at (◇) 30, (△) 40, and (□) 50°C initiated by 3% BPO+ 0.3% DMA+0.3% NLC

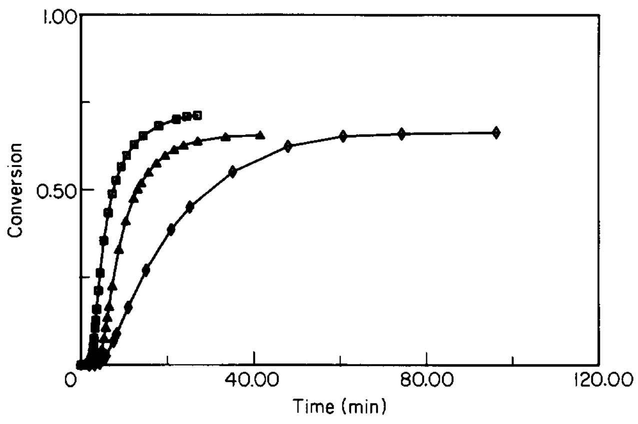

Figure 6 D.s.c. conversion profiles at 30, 40 and 50°C corresponding to *Figure 5*. Symbols as in *Figure 5*

Table 1 Kinetic information from d.s.c. and i.r. spectroscopy for UP-2821 reactions initiated by 3% BPO+0.3% DMA+0.3% NLC at 30–50°C

	D.s.c.							I.r.		
Temperature (°C)	t_z[a] (min)	t_m[a] (min)	ΔH_s[b]	ΔH_{iso}[b]	ΔH_r[b]	ΔH_{iso}[b] $+\Delta H_r$	α_{iso}[c] (%)	α_S[c] (%)	α_E[c] (%)	α_T (i.r.)[c] (%)
50	1.3	3.6	55.3	39.3	8.8	48.2	71.3	74.4	58.5	68.1
40	1.7	6.2	55.3	36.8	8.8	45.7	66.2	70.5	52.8	64.2
30	1.9	8.2	55.3	36.8	9.6	46.5	66.0	69.6	51.0	63.3

[a] t_z is the induction time and t_m is the time to maximum rate

[b] The units of ΔH_s, ΔH_{iso}, ΔH_r and $\Delta H_{iso}+\Delta H_r$ are kJ mol^{-1} C═C, where ΔH_s is the heat release at 5°C min^{-1} scanning rate from room temperature to 210°C, ΔH_{iso} is the heat release for isothermally cured sample, ΔH_r is the heat release by rescanning the isothermally cured sample at 5°C min^{-1} from room temperature to 210°C

[c] α_{iso} is the overall conversion by d.s.c. based on the ΔH_s at 100% conversion, α_s is styrene conversion by i.r., α_E is conversion of polyester vinylene by i.r. and α_T is the overall conversion by i.r.

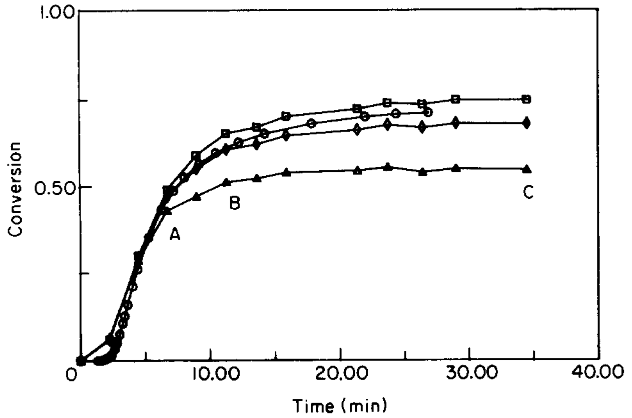

Figure 7 Conversion profiles from d.s.c. and i.r. at 50°C initiated by 3% BPO+0.3% DMA+0.3% NLC: (○) total conversion (d.s.c.); (□) styrene C=C conversion (i.r.); (△) polyester C=C conversion (i.r.); (◇) total conversion (i.r.)

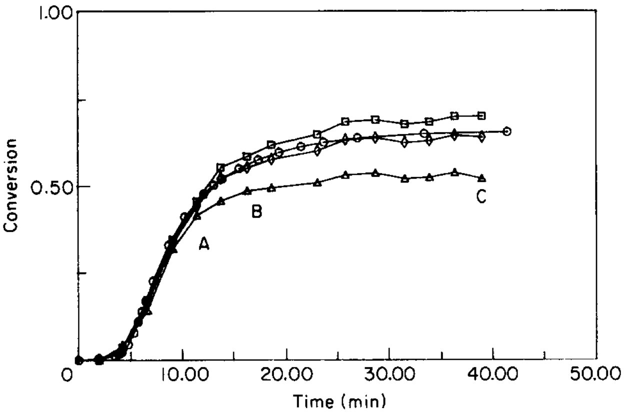

Figure 8 Conversion profiles from d.s.c. and i.r. at 40°C initiated by 3% BPO+0.3% DMA+0.3% NLC. Symbols as in *Figure 7*

one, ΔH_r, is $46\,\text{kJ}\,\text{mol}^{-1}$ C=C, which is 15% lower than the heat release at the scanning mode of $5°\text{C}\,\text{min}^{-1}$ ($\Delta H_s = \sim 55\,\text{kJ}\,\text{mol}^{-1}$ C=C). Yang and Lee[15] claimed that microgel formation is the main feature in the curing of UP resins, and substantial amounts of residual C=C bonds would be buried in the microgel structure after the reaction. The difference between $\Delta H_{\text{iso}} + \Delta H_r$ and ΔH_S implies that temperature history during the reaction could greatly affect the structure of the microgel formed and, in turn, the extent of unreacted C=C bonds. As shown in *Table 1*, for the isothermally cured samples the unreacted C=C bonds of styrene and polyester vinylene groups are ~25–30 and 40–50%, respectively. The higher the temperature, the higher the conversions of C=C bonds for individual species. The overall conversion measured by i.r. is slightly lower than that by d.s.c. This may suggest that $\Delta H_s = \sim 55\,\text{kJ}\,\text{mol}^{-1}$ C=C does not correspond to a heat release equivalent to 100% conversion of C=C bonds. A projected heat release of $\sim 58\,\text{kJ}\,\text{mol}^{-1}$ C=C was calculated, and ~96% of overall C=C bonds was reacted rather than 100%.

Figures 7–9 show the conversion *versus* time profiles by i.r. and d.s.c. at 50, 40 and 30°C, respectively. It can be seen that at 50°C the conversions of styrene and polyester vinylene measured by i.r. are similar (within 3% conversion) at the beginning of the reaction. After 40% conversion, the change of polyester conversion slows down, while the styrene conversion increases steadily. The final conversion of styrene is higher than that of polyester vinylene, and the overall conversions measured by both i.r. and d.s.c. are approximate. The conversion profiles at 40 and 30°C, shown in *Figures 8* and *9*, exhibit the same trend as that at 50°C except that the reaction rate is slower with a lower temperature. *Figure 10* shows the relative conversion profiles of styrene to polyester vinylene for the three temperatures. The relative relationship appears to be independent of temperature during the range studied. At low conversions up to 35%, both conversions are approximately the same, which is characteristic of the near-azeotropic copolymerization represented by the 45° line. After 35% conversion, the data points fall above the 45° line, indicating a higher conversion of styrene than that of polyester vinylene.

It should be pointed out that the real onset point where the styrene conversion, α_S, exceeds polyester vinylene conversion, α_E, is 30, 16 and 12% for 50, 40 and 30°C reactions, respectively, as shown in *Figures 7–9*. The difference between styrene and polyester vinylene conversion does not increase until point A as shown in the figures, where the transition point of near-azeotropic copolymerization is defined. The real onset point for $\alpha_S > \alpha_E$ corresponds to a time that is very close to the time to

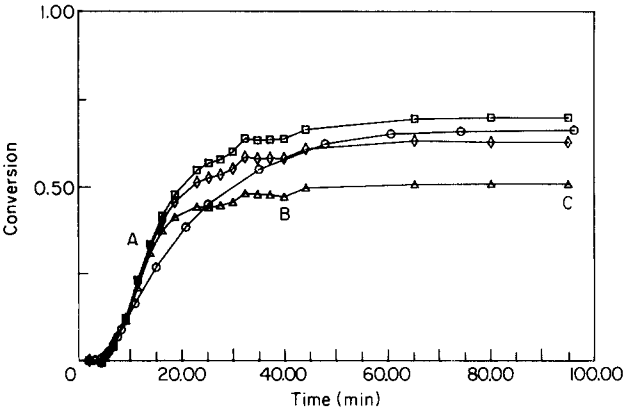

Figure 9 Conversion profiles from d.s.c. and i.r. at 30°C initiated by 3% BPO+0.3% DMA+0.3% NLC. Symbols as in *Figure 7*

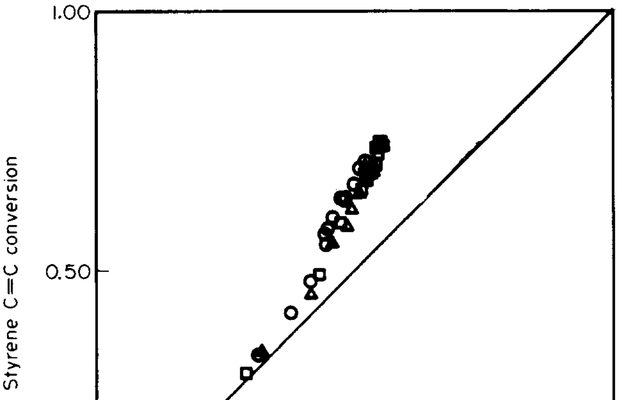

Figure 10 Relative conversions of styrene *versus* polyester vinylene at (○) 30, (△) 40 and (□) 50°C

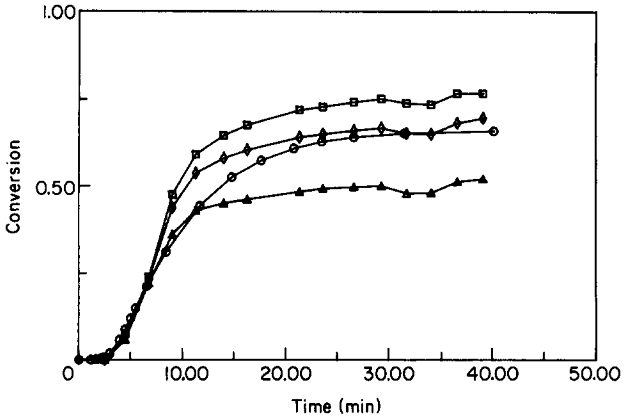

Figure 11 Conversion profiles from d.s.c. and i.r. at 40°C initiated by 4% BPO+0.3% DMA+0.3% NLC. Symbols as in *Figure 7*

the maximum rate, t_m, in the d.s.c. rate profiles shown in *Figure 5* (i.e. 3.6, 6.2 and 8.2 min as shown in *Table 1* for 50, 40 and 30°C, respectively). This reveals that the decline of the reaction rate from the peak would be due to the variation in composition in the styrene–polyester copolymer. Also, the lower the reaction temperature, the lower the onset conversion for $\alpha_S > \alpha_E$. This is probably due to the fact that a lower temperature reduces the mobility of C=C units in large polyester molecules more than in small styrene molecules, and the conversion of styrene is easier to catch up that of polyester at lower conversions.

At the beginning of the UP-2821 reaction where the near-azeotropic copolymerization mechanism dominates, the crosslinking density of the reacting system would not be sufficiently high to appreciably influence the propagation mechanisms of the styrene and polyester vinylene groups. In the later stage of the reaction, the crosslinking density would increase to some extent so that the mobility of vinylene units in the large polyester molecules declines remarkably, while that of small styrene monomers is less affected. Consequently, the relative probability of the styrene propagation reaction is elevated, causing a higher conversion of styrene than of polyester vinylene.

Literature data on the copolymerization of styrene and diethyl fumarate[22] indicate that the extent of the bonding of styrene monomer to itself in the chain sequence is significant during the copolymerization. This is why the initial molar ratio of styrene to polyester vinylene is usually maintained at 2:1 in UP resins (as in this study). At the start of the reaction, the number of styrene vinyl groups consumed for every polyester vinylene reacted in the copolymer structure equals 2 as a result of azeotropic copolymerization. This is called the average crosslink length of styrene, *n*, through which the vinylene groups either in two adjacent polyester molecules (i.e. intermolecular crosslinking, see *Figure 1d*) or in the same polyester molecule (i.e. intramolecular crosslinking) are connected. For the final cured sample, it can be calculated from *Table 1* that $n=2.55$, 2.67 and 2.73 at 50, 40 and 30°C, respectively. Higher temperature seems to enhance the conversion of polyester vinylene (51.0% *versus* 52.8% *versus* 58.5%) more than that of styrene (69.6% *versus* 70.5% *versus* 74.4%), and hence *n* decreases with increasing temperature. On average, for each polyester vinylene reacted with per styrene vinyl in the final copolymer structure, 1.55, 1.67 and 1.73 additional styrenes were bonded to themselves prior to crosslinking with another polyester vinylene at 50, 40 and 30°C, respectively. Since the vinylene in the large polyester molecules would have to orient itself to react with styrene vinyls, which would take some time due to the lower mobility of C=C units in polyester molecules, a higher temperature could facilitate the rate of orientation and, in turn, enhance the relative rate of copolymerization with styrene in reference to styrene self-bonding. Therefore, a reduction in the self-bonding length of styrene in the crosslinked copolymer chain would then be expected at higher temperature.

For the 50°C reaction, point A in *Figure 7* represents the end of the near-azeotropic copolymerization stage at 35% conversion, and $n=2$ prior to point A. This transition is located at ~4.5 min and corresponds to a point just traversing the peak of the d.s.c. rate profile with $t_m = 3.6$ min (see *Figure 5*). For the reaction interval from points A to B, after which the conversion of polyester vinylene remains essentially unchanged, $n=3.1$. For the interval from points B to C, the increases in styrene and polyester vinylene conversions are 9.4 and 4.3%, respectively, $n=4.4$ (see *Figure 1d*). Therefore, in the later reaction stage the consecutive self-bonding of styrene would be more significant, and this could proceed via side chain growth as shown in *Figure 1d*. The polystyrene segment would then become part of the styrene–polyester copolymer. On the other hand, styrene homopolymerization, leading to independent polystyrene chains as shown in *Figure 1e*, would not occur easily. This is because the molar ratio of styrene to polyester C=C bonds is not sufficiently high[6] and styrene monomers would be likely to encounter polyester C=C bonds during propagation, leading to little formation of free polystyrene which does not pertain to the network. The characteristics of the average crosslink length of styrene during the reaction course at 30 and 40°C bear resemblance to that at 50°C.

Effect of initiator

Figures 11, *7* and *12* show conversion *versus* time profiles using i.r. and d.s.c. with 4, 3 and 2% BPO at 40°C, respectively. For the reaction initiated by 4% BPO shown in *Figure 11*, the near-azeotropic copolymerization persists up to 25% conversion (6.7 min), followed by a period with a higher conversion of styrene than that of polyester vinylene. The final conversion of styrene is 22% higher than that of polyester. The conversion profiles with 3% and 2% BPO are similar to that with 4% BPO. However, a decrease in initiator concentration would result in a higher conversion and a longer time at the transition point of near-azeotropic copolymerization (25% *versus* 35% *versus* 40% and 6.7 min *versus* 9.1 min *versus* 12.5 min) and a

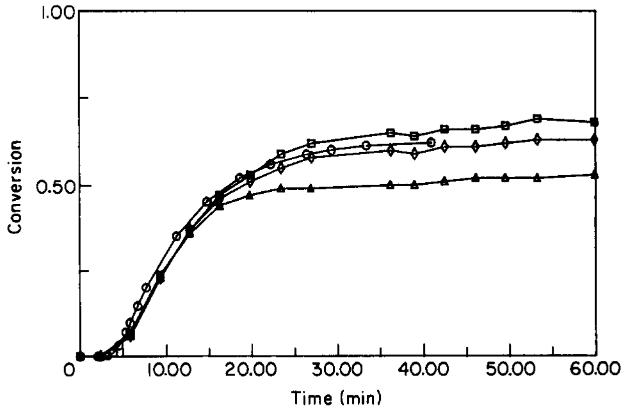

Figure 12 Conversion profiles from d.s.c. and i.r. at 40°C initiated by 2% BPO+0.3% DMA+0.3% NLC. Symbols as in *Figure 7*

smaller difference between the final conversions of styrene and polyester vinylene (22% *versus* 18% *versus* 15%) as shown in *Table 2.*

The variation in the transition of near-azeotropic copolymerization can be explained as follows. Provided that one primary free radical would generate one microgel, then the lower the initiator concentration, the lower the rate of formation of microgel particles during the early stage of reaction. For the subsequent reaction region prior to approximately the peak of the rate profile, intermicrogel crosslinking reactions would predominate. Although the system with a lower initiator concentration would have a lower rate of intermicrogel reaction, the intramicrogel reactions should be more favourable than that with a higher initiator concentration. This is because in the former case styrene monomers could diffuse more successfully into the less overlapped microgel particles and react with pendant C=C bonds inside the microgels. Therefore, under essentially the same conversion of C=C bonds, the system with a lower initiator concentration could then lead to a looser crosslinked network structure outside the microgels. As a result, the onset of diffusion limitation for the propagation reaction of polyester vinylene units at a lower initiator concentration was delayed further and a higher conversion at the transition was observed. Since the extent of deviation from the near-azeotropic copolymerization would be less for a looser network structure in the later stages of the reaction, it was not surprising that the difference in final conversions of individual species was observed to be smaller as the initiator concentration decreased.

Figure 13 shows the d.s.c. rate profiles with the three initiator concentrations used. It appears that the initiator concentration does not have an appreciable effect on the cure time for the low temperature reaction systems. However, as initiator concentration decreases, the t_m increases slightly. The conversion at maximum rate, $\alpha(t_m)$, is higher for a higher initiator concentration as shown in *Table 2* (12% *versus* 15% *versus* 16%), but the difference in measured $\alpha(t_m)$, especially for 4% and 3% BPO, is small. The maximum rate in the d.s.c. profile would reflect the summation of both rates for inter- and intramicrogel crosslinking reactions. At a higher initiator concentration, such as 4% BPO, although the rate of intermicrogel reaction is higher, as revealed by the higher initial reaction rate, the rate of intramicrogel reaction is lower due to closely overlapped microgels restricting styrene monomers from diffusing into the microgels. As the initiator concentration is reduced to 3% BPO, the decrease in the rate of intermicrogel reactions is well compensated by the increase in the rate of intramicrogel reactions. This leads to a higher maximum rate with 3% BPO than with 4% BPO. Further decreasing initiator concentration to 2% BPO reduces the rate of intermicrogel reaction to such an extent that even the more favourable intramicrogel reaction could no longer appreciably facilitate the maximum rate. Accordingly, a lowest maximum rate results with 2% BPO.

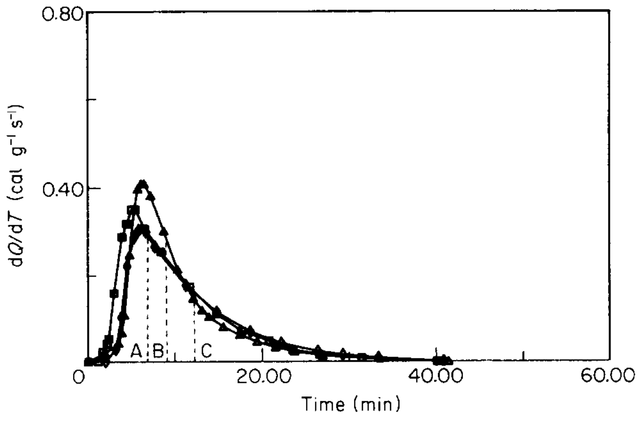

Figure 13 D.s.c. rate profiles at 40°C initiated by (□) 4% BPO, (△) 3% BPO and (◇) 2% BPO mixed with 0.3% DMA+0.3%NLC. A, B and C are the transition points of near-azeotropic copolymerization for 4, 3 and 2% BPO, respectively. The transition times are 6.7, 9.1 and 12.5 min, respectively

The transition point and time for the near-azeotropic copolymerization are also specified in *Figure 13* (denoted by A, B and C for 4, 3 and 2% BPO, respectively). Since the transition occurs after the time when the maximum reaction rate is reached, which is followed by a reaction stage where the monomer propagation reaction may encounter diffusion-controlled limitation[23], the mechanism of near-azeotropic copolymerization would change once the diffusion-controlled propagation reaction sets in. Again, the mobility of styrene molecules is greater than that of the vinylene units in polyester molecules, and hence the impact by diffusion limitation is alleviated for styrene, causing a higher conversion of styrene than that of polyester vinylene from the transition point to the end of the reaction.

Figure 14 shows the d.s.c. conversion *versus* time profiles. It is seen that the overall conversion is lower for a lower initiator concentration. *Table 2* lists the kinetic information obtained from d.s.c. and i.r. *Figure 15* shows the relative conversions of styrene *versus* polyester vinylene. It appears that as initiator concentration is raised, the styrene conversion is more favourable than polyester vinylene conversion in the later stage of the reaction, and the final relative conversion of styrene to polyester vinylene is also higher (see *Table 2*). For the final cured samples, as initiator concentration increases, the calculated average crosslink length of styrene increases (2.56 *versus* 2.68 *versus* 2.82).

The sum up, it is our speculation that for the curing of UP resins at lower temperatures, where the rate of crosslinking reaction is quite moderate, intra- and inter-

Table 2 Kinetic information from d.s.c. and i.r. spectroscopy for UP-2821 reactions initiated by 4% BPO, 3% BPO and 2% BPO mixed with 0.3% DMA+0.3% NLC at 40°C[a]

	D.s.c.							I.r.		
BPO	t_z (min)	t_m (min)	ΔH_s	ΔH_{iso}	ΔH_r	$\alpha(t_m)$ (%)	α_{iso} (%)	α_S (%)	α_E (%)	α_T (i.r.) (%)
4%	1.2	5.2	55.3	36.8	23.9	16	66.0	76.0	54.0	69.5
3%	1.7	6.2	55.3	36.8	8.8	15	66.2	70.5	52.8	64.2
2%	2.0	6.3	55.3	34.3	12.6	12	66.0	68.0	53.0	63.0

[a] Symbols and units are the same as in *Table 1*, and $\alpha(t_m)$ is the conversion at the time to maximum rate

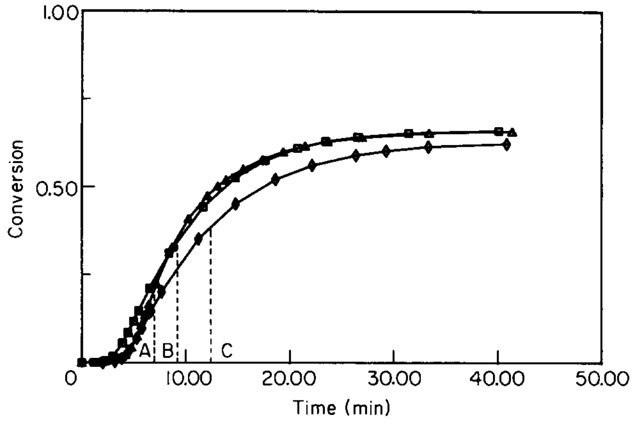

Figure 14 D.s.c. conversion profiles at 40°C corresponding to *Figure 13*. Symbols as in *Figure 13*

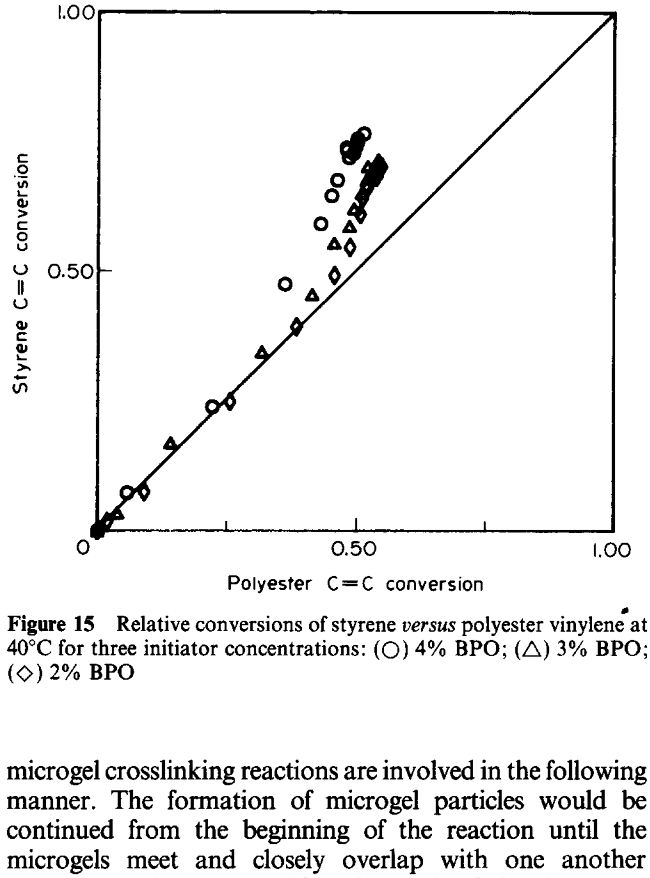

Figure 15 Relative conversions of styrene *versus* polyester vinylene at 40°C for three initiator concentrations: (○) 4% BPO; (△) 3% BPO; (◇) 2% BPO

microgel 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 the d.s.c. rate profile, the rate of microgel formation would then slow down considerably. Sometime later, when the existing microgels are highly overlapped via crosslinking and a compact network structure is formed, no new microgel particles would be formed. Prior to the peak of the d.s.c. rate profile, where the gel effect region predominates, the intermicrogel crosslinking reaction proceeds more preferentially than does the intramicrogel crosslinking reaction. This is because the styrene monomers are apt to crosslink with the polyester C=C bonds near to or at the surface of microgels during the process of diffusing into the microgels, while only part of the styrene diffusing in and some local styrene in the microgels is allowed to crosslink with polyester C=C bonds in the microgels. After the peak of the d.s.c. 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. With the crosslink length of styrene $n=4.4$ for the reaction interval from points B to C shown in *Figure 7*, it is inferred that the branching growth of styrene on polyester C=C bonds (see *Figure 1d*) would predominate during the reaction course after the peak of the rate profile. Although the intramicrogel reactions are much more favourable than intermicrogel reactions in the latter part of the reaction, since the concentration of reactive pendant C=C bonds (i.e. with less steric hindrance) is greatly reduced and the monomers are also encountered with the diffusion-controlled propagation mechanism, the d.s.c. rate profile decays gradually and eventually drops to zero. For the reaction system with a higher initiator concentration, the rate of formation of microgel particles is so high that the microgels are closely overlapped only to lower the probability of intramicrogel reactions in the early part of reaction. As a result, more intramicrogel reactions are only allowed to proceed in the later stage of the reaction, resulting in a higher relative styrene conversion to polyester vinylene conversion for a higher initiator concentration as shown in *Figure 15*.

Effect of promoter

Figure 16 shows the d.s.c. rate profiles at 30°C for two DMA promoter concentrations (0.6 and 0.3%). As the promoter concentration decreases, the reaction rate profile moderately climbs to a lower maximum point and decays less sharply to zero. The corresponding overall conversion *versus* time profiles shown in *Figure 17* indicate that doubling the promoter concentration slightly raises the final conversion (68% *versus* 66%). *Figure 18* shows the conversion *versus* time profile by d.s.c. and i.r. with 0.6% DMA. It can be seen from the i.r. curve that the reaction exhibits no conspicuous near-azeotropic copolymerization behaviour in the early stage of the reaction, which is different from the case of 0.3% DMA before 35% conversion shown in *Figure 9*. *Figure 18* also indicates that from the start of reaction up to 48% conversion the polyester vinylene conversion increases considerably, and its conversion is apparently higher than styrene conversion. After 48% conversion, conversion of styrene exceeds that of polyester vinylene. From the same figure the first period persists up

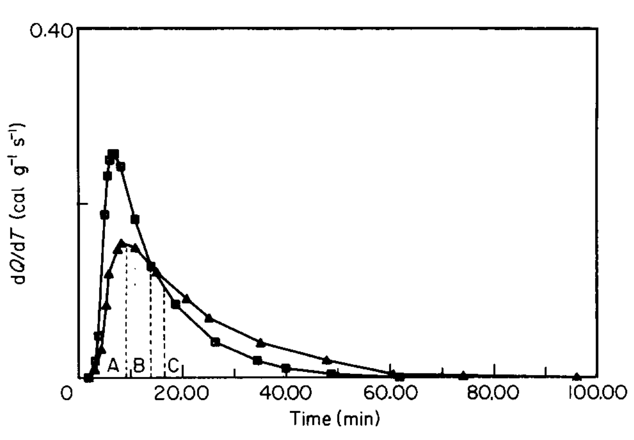

Figure 16 D.s.c. rate profiles at 30°C initiated by (□) 0.6% DMA and (△) 0.3% DMA mixed with 3% BPO+0.3% NLC. A is the onset point of $\alpha_S > \alpha_E$ for 0.3% DMA. The interval between B and C is where the onset point of $\alpha_S > \alpha_E$ is located for 0.6% DMA. The transition of near-azeotropic copolymerization for 0.3% DMA occurs after the onset point A

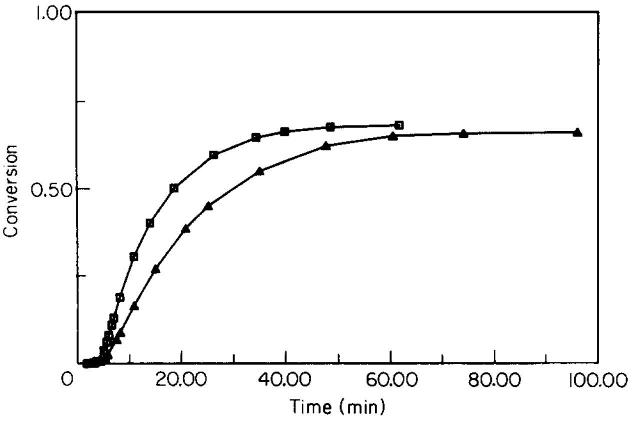

Figure 17 D.s.c. conversion profiles at 30°C corresponding to *Figure 16*. Symbols as in *Figure 16*

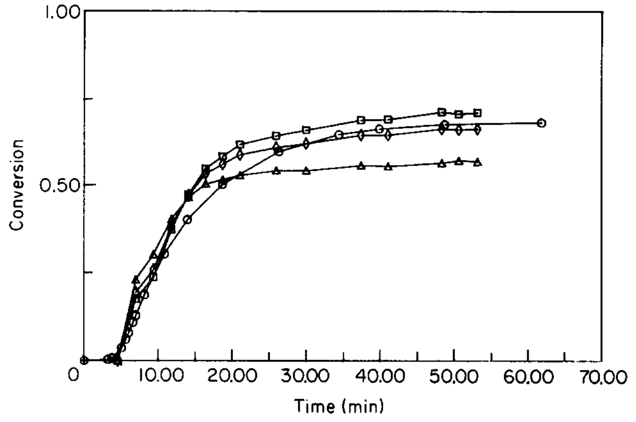

Figure 18 Conversion profiles from d.s.c. and i.r. at 30°C initiated by 0.6% DMA + 3% BPO + 0.3% NLC. Symbols as in *Figure 7*

to a time of 18 min which is based on the d.s.c. conversion curve under the same overall conversion for both d.s.c. and i.r., or up to a time of 13 min, by directly reading the time from the figure. The termination of the first period thus falls after the peak of the d.s.c. rate profile and is denoted by points C and B, respectively, as shown in *Figure 16*. Similarly, point A at ~9 min as shown in *Figure 16* for 0.3% DMA is obtained from *Figure 9*, where either approach to obtaining points B or C for 0.6% DMA ends up with the same point since the d.s.c. and i.r. overall conversion curves match in *Figure 9* for the low conversion range. The designated points represent the onset of $\alpha_S > \alpha_E$. For 0.3% DMA, it corresponds to a 12% conversion. However, the transition for the near-azeotropic copolymerization at 35% conversion occurs later and is ~18 min.

Due to a higher promoter concentration prompting a much higher free radical concentration[24], the rate of microgel formation would be much higher for 0.6% DMA than for 0.3% DMA. Therefore, the intermicrogel crosslinking reactions prior to the peak of the d.s.c. rate profile should be much more dominant over the intramicrogel reactions for 0.6% DMA. For intermicrogel reactions at this reaction stage, it is inferred that styrene monomer tends to copolymerize with C=C units of polyester molecules and the crosslink length of styrene would be <2. It is because the concentrations of reactive vinylene groups of polyester near or outside the microgels are very high and polyester vinylene groups are also easy to orient themselves for crosslinking with styrene during the low conversion range. On the other hand, for intramicrogel reactions at this stage, due to a lower concentration of pendant C=C bonds that are accessible to styrene monomers, the crosslink length of styrene would be >2 because the branching growth of styrene would be the major reaction once the styrene monomer diffuses into the microgel particles. In other words, the intermicrogel reaction favours the conversion of polyester vinylenes more than the styrene conversion, while the trend is reversed for the intramicrogel reaction. Consequently, in the early stage of the reaction for the case of 0.6% DMA, extensive intermicrogel reactions cause an exceedingly higher conversion of polyester vinylene groups relative to styrene conversion. Also, styrene conversion does not catch up until between points B and C as shown in *Figure 16*, where the diffusion-controlled propagation reaction could have already begun since these points are distant from the peak of the rate profile.

Figure 19 shows the relative conversion profile of styrene to polyester vinylene with six sets of data for both promoter concentrations plotted together. The trend indicates that increasing promoter concentration facilitates the conversion of polyester vinylene because the data points shift to the right for higher promoter concentration. The final conversions of styrene and polyester vinylene with 0.3% DMA are 69.6 and 51.0%, and those with 0.6% DMA are 71.3 and 57.0%, respectively (see *Table 3*). The calculated average crosslink length of styrene decreases with increasing promoter concentration (2.73 *versus* 2.48). It shows a similar trend with temperature but exhibits a reverse trend with initiator concentration.

The relative conversion of styrene to polyester vinylene is higher with a lower promoter concentration as shown in *Figure 19* since the corresponding data points shift to the left. This tendency appears to be different from that with the initiator concentrations shown in *Figure 15*. For the case of 0.3% DMA, the characteristics of the d.s.c. rate profile in *Figure 16* described earlier indicate that the intermicrogel reactions prior to the peak of the rate profile are less pronounced than for 0.6% DMA. The intramicrogel reactions following the peak of the rate profile should be

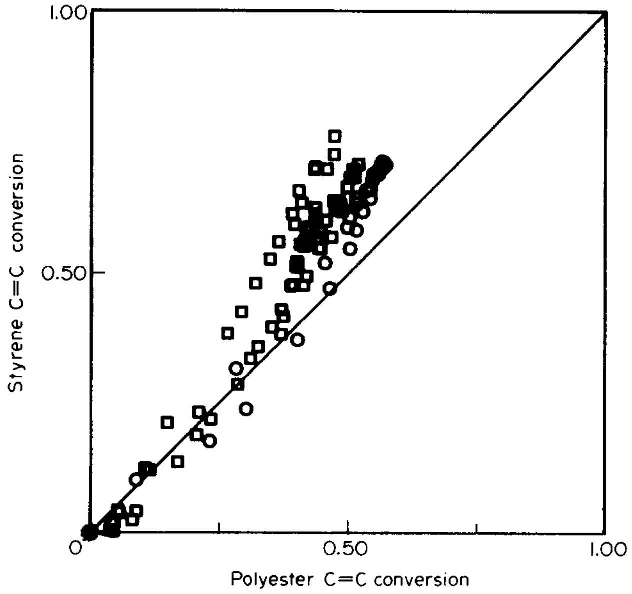

Figure 19 Relative conversions of styrene *versus* polyester vinylene at 30°C for two promotor concentrations: (○) 0.6% DMA; (□) 0.3% DMA

Table 3 Kinetic information from d.s.c. and i.r. spectroscopy for UP-2821 reactions initiated by 0.6% DMA, and 0.3% DMA mixed with 3% BPO+0.3% NLC at 30°C[a]

	D.s.c.							I.r.		
DMA	t_z (min)	t_m (min)	ΔH_s	ΔH_{iso}	ΔH_r	$\Delta H_{iso} + \Delta H_r$	α_{iso} (%)	α_S (%)	α_E (%)	α_T (i.r.) (%)
0.6%	1.8	8.1	55.3	37.7	16.3	54.1	68.4	71.3	57.0	66.5
0.3%	1.9	8.2	55.3	36.8	9.6	46.5	66.0	69.6	51.0	63.3

[a] Symbols and units are the same as in *Table 1*

more favourable for 0.3% DMA than for 0.6% DMA. This is because the microgel particles are less closely overlapped for the former and diffusion limitation of styrene monomer into the microgels is greatly reduced. More branching growth of styrene monomers inside the microgels elevates the relative conversion of styrene for a lower promoter concentration in the later stage of the reaction.

CONCLUSIONS

The curing of UP resins at low temperatures (30–50°C) has been studied by d.s.c. and i.r. For an initial molar ratio of styrene to polyester vinylene of 2:1, the reaction kinetics is characterized by the near-azeotropic copolymerization for the early stage of the reaction. When the mechanism of the diffusion-controlled propagation reaction of C=C units in the large polyester molecules predominates, which occurs somewhere after the peak of the d.s.c. rate profile, the conversion of styrene appreciably exceeds that of polyester vinylene groups. In the final copolymer formed, the crosslink lengths of styrene decreases with increasing temperature due to the easier orientation of C=C units in polyester molecules in copolymerization with styrene.

Decreasing initiator concentration leads to a higher conversion and a longer time at the transition point of the near-azeotropic copolymerization. The relative conversion of styrene to polyester vinylene is more favourable at a higher initiator concentration for the later reaction. On the other hand, increasing promoter concentration causes a disappearance of the near-azeotropic copolymerization region at the beginning of the reaction. Also, the conversion of polyester vinylene is considerably higher than styrene conversion from the start of the reaction up to a point well beyond the onset of the diffusion-controlled propagation reactions. The relative conversion of styrene to polyester vinylene becomes more favourable at a lower promoter concentration for the later reaction.

Microgel formation is the main feature in the curing of UP resins. It is proposed that at low temperatures, where the crosslinking reactions are quite moderate, prior to the peak of the d.s.c. rate profile, the intermicrogel crosslinking reaction is dominant over the intramicrogel crosslinking reaction. In the later stage of the reaction following the peak of the d.s.c. rate profile, intramicrogel reactions are more favourable than intermicrogel ones. The intermicrogel reaction enhances polyester vinylene conversion more than styrene conversion since styrene monomers tend to copolymerize with polyester vinylene with a smaller crosslink length of styrene. In contrast, the intramicrogel reaction is more favourable with styrene conversion due to the extensive branching growth of styrene on polyester C=C bonds inside the microgels with a larger crosslink length of styrene.

The macroscopic observations by d.s.c. and i.r. measurements alone probably do not lend themselves to the proposition of the microgel kinetic model described in this work. The investigation of the effect of pressure on the curing of UP resins[25], by an approach of integrated reaction kinetics–rheology–morphology measurements, has supported the intra- and intermicrogel crosslinking reactions which are characteristic of the curing of UP resins, but in a different manner to that discussed here. In subsequent publications, we will continue to discuss the effects of resin structures and compositions, and pressure on the curing kinetics of UP resins. More support will be provided for the microgel kinetic model.

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