

Free-radical crosslinking copolymerization of styrene/unsaturated polyester resins: 1. Phase separation and microgel formation

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(Received 22 October 1992; revised 29 January 1993)*

An important feature of free-radical crosslinking copolymerization of styrene (ST)/unsaturated polyester (UPE) resins is the formation of a heterogeneous structure through strong intramolecular reactions and phase separation. Such structure formation affects not only the cure behaviour and rheological changes of the resin but also the physical properties of final products. In this study, the phase separation process was investigated by optical microscopy and time-resolved light scattering goniometry. Partially reacted samples of ST/UPE resin before macrogelation were also prepared by stopping the polymerization at preset times. The size and composition of primary polymers were determined using dynamic light scattering goniometry and Fourier transform infra-red spectroscopy.

(Keywords: copolymerization; microgel; phase separation)

INTRODUCTION

The reaction between styrene (ST) and unsaturated polyester (UPE) is a heterogeneous free-radical chain-growth crosslinking copolymerization. An important feature of this copolymerization is the formation of a heterogeneous structure through strong intramolecular reactions¹⁻³ and phase separation. Such structure formation affects not only the cure behaviour and rheological changes of the resin but also the physical properties of final products. Phase separation is a common phenomenon in multicomponent polymeric systems due to incompatibility among polymeric materials. For thermoplastic polymer blends, phase separation is often caused by heating or cooling the materials from the one-phase region to the two-phase region. For reactive resin systems, phase separation may be induced by changes of phase boundary or resin composition during reaction. Many researchers⁴⁻⁷ have studied both experimentally and theoretically the phase separation phenomenon in thermoplastic polymer blends. However, the dynamics of phase separation in reactive systems have not been analysed in detail.

The network formation process in free-radical chain-growth crosslinking polymerizations is quite different from that in step-growth crosslinking polymerizations^{8,9}. Many researchers¹⁰⁻¹³ have found that the measured gel conversions of multifunctional monomers in chain-growth polymerizations were much higher than those predicted based on the tree-like models, assuming no intramolecular reactions. This discrepancy increased as the content of multifunctional monomers increased. Three possible mechanisms have been proposed to explain the deviations of the experimental gel conversions from the theoretical calculations: (i) ring formation or

cyclization due to intramolecular reaction; (ii) reduced reactivity of pendent vinyl groups; and (iii) molecular shielding effect on the reaction of the pendent vinyl groups due to microgel formation¹.

The ring formation or cyclization due to intramolecular reaction is the most frequent explanation for the deviation of free-radical crosslinking polymerizations from the classical Flory gelation theory. The ring formation consumes vinyl groups but does not contribute to the network formation. Holt and Simpson¹⁰ and Wiley¹⁴ investigated the effect of distance between vinyl groups in the ring formation process. They concluded that the tendency towards cyclization decreased with increasing distance between the vinyl groups on the divinyl monomer. Several other researchers reached the same conclusion for various free-radical crosslinking copolymerizations^{11,15-18}. The intramolecular cyclization has also been classified into either a primary cyclization or a secondary cyclization¹⁹. The former occurs during the formation of the primary polymer chains, while the latter takes place on the formed primary polymer chains. For methyl methacrylate-ethylene glycol dimethacrylate copolymerization, Landin and Macosko^{3,19} found that both primary and secondary cyclizations were strongly affected by the concentration of divinyl component, amount of inert solvent and chain transfer agent.

The reduced reactivity of pendent vinyl groups is another factor causing the elevated gel conversions in free-radical crosslinking polymerizations. Hild and Okasha²⁰⁻²² investigated the kinetics of copolymerization systems, such as ST/n-divinyl benzene (DVB), ST/p-DVB, and styrene diisopropenyl benzene, using light scattering goniometry, viscometry, size exclusion chromatography and titration methods. They concluded that the reactivity of the pendent vinyls was lower than that of the vinyls on the unreacted divinyl components in the early stage of the copolymerization process. Therefore, the

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crosslinking reaction was limited until the portion of the unreacted divinyl components was decreased to a certain level. After that, the relative amount of pendent vinyls over the unreacted divinyls was high, which resulted in an increase of the reaction of pendent vinyls and the formation of polymer network.

The molecular shielding effect due to microgel formation also plays an important role in free-radical crosslinking polymerizations. Although the delay of gelation had been largely attributed to the strong cyclization and the low reactivity of pendent vinyls, these two effects cannot explain the fact that the extent of cyclization decreases, rather than increases, with an increase of the content of divinyl component in the reactants¹³. Experimental evidence suggested that compact microgel-like particles were formed both in bulk polymerizations^{12,23-25} and emulsion polymerizations²⁶⁻³⁰. The microgels can be described as polymer particles with sizes in the submicrometre range, and have characteristics such as permanent shape, surface area and solubility of both particles and common macromolecules. Although the proposed 'microgel' mechanism has not been verified directly in any experiment, the concept has been widely accepted and has also been used in some applications^{2,31,32}. Recently, Boots and Pandey³³ simulated free-radical crosslinking polymerizations with microgel formation using percolation theory. Their simulation agreed qualitatively with measured reaction conversions.

EXPERIMENTAL

Materials

The UPE resin used in this study was a 1:1 mixture of maleic anhydride and propylene glycol, which has an average of 10.13 vinylene groups per polyester molecule. The number-average molecular weight of the unsaturated polyester was 1580 g mol⁻¹, and the equivalent molecular weight/(mol C=C) was 156 g mol⁻¹. The UPE resin contained 35 wt% ST and was provided by Ashland Chemical Company (Q6585). Poly(vinyl acetate) (PVAc), with a number-average molecular weight of 56 000 and a weight-average molecular weight of 174 000, was purchased from Aldrich Chemical Co.

Both UPE resin and ST monomer were used as received without removing the inhibitor. Methyl ethyl ketone peroxide (MEKP, Lucidol) with 25 wt% cobalt naphthenate (COB) promotor was used as the initiator for the cure carried out at 40°C. t-Butyl peroxy-2-ethyl hexanoate (PDO, Lucidol) was used as the initiator for reaction conducted at 80°C. Before the experiment, the unsaturated polyester resin was weighed and mixed with ST monomer in a flask at the specified molar ratio. MEKP or PDO was added and the solution was mixed with a magnetic stirrer for 10 min at room temperature and then stored below 5°C for further use. COB was mixed into the solution at room temperature immediately before the measurement. The compositions of resin used in this study are given in Table 1. For most cases, no phase separation occurred during polymerization, except for samples with high ST/UPE molar ratio (MR=4) reacted at 40°C (ref. 34) and samples with PVAc.

Instrumentation and procedures

Reaction kinetics. The reaction kinetics were measured by a differential scanning calorimeter (TA Instrument

Table 1 Composition of the samples

ST/UPE molar ratio	Ingredients (parts by weight)				
	UPE	ST	MEKP/COB	PVAc	PDO
4	42.0	58.0	1.0/0.25		
4	42.0	58.0	0.8/0.20		
4	42.0	58.0	0.5/0.125		
2	65.9	34.1	1.0/0.25		
2	56.0	29.0		15.0	1.1

DSC 10). All reactions were conducted in volatile aluminium sample pans which are capable of withstanding at least 0.2 MPa internal pressure after sealing. Isothermal runs were ended when no further exotherm was measured. The reactions were also carried out in the scanning mode from 37 to 247°C at a heating rate of 10°C min⁻¹ to determine the total heat of reaction.

The exothermal data measured during reaction were converted into reaction rate and conversion as a function of time³⁴⁻³⁶.

Rheological measurement. A Rheometrics Dynamic Analyzer (RDA) 700 in the oscillatory mode was used to measure the storage shear modulus (G') and loss shear modulus (G'') during reaction. Serrated disposable aluminium parallel plates with 25 mm diameter were used to hold the sample. The gap between the plates was set at 1.1 mm and the frequency used was 10 rad s⁻¹ for all experiments. The strain ratio was set at 10% at low moduli. The crossover of G' and G'' curves was used as an indication of the liquid–solid transition (i.e. the gel point) for crosslinking polymers³⁷.

Morphological study. An optical microscope with a phase contrast attachment and a hot stage was used to observe the phase separation process. This allowed the measurement of morphological changes when the size of the microstructure was greater than 3 μm. The optical microscope used was an Olympus polarizing microscope (model BH-2) equipped with an Olympus 35 mm camera (model PM-6). A drop of resin was bounded by two circular cover glasses. The set-up was mounted on a hot stage which was connected to a temperature controller, and the microstructure formation was monitored as the reaction occurred.

Dynamics of microstructure formation. A time-resolved light scattering (t.r.l.s.) goniometer was used to monitor the on-line phase separation and microstructure formation processes. A 5 mW He/Ne laser with wavelength (λ) of 632.8 nm was used as a light source. The laser beam passed through a neutral density filter to attenuate the laser beam to a proper power. A sample stage made of copper with four 34 W/120 V cartridge heaters was used as a thermal chamber. The thermal chamber was maintained at the desired curing temperature by a temperature controller. The sample was filtered with a 0.1 μm filter, then loaded into a sample cell. The sample cell was placed in the thermal chamber, which was located at the centre of the goniometer with a tilting angle of 45°. The sample cell consisted of two quartz discs, a metal spacer and a metal holder component.

Two photomultipliers (PM) (Hamamatsu R928) were used as the detectors. One PM, located at the rotating arm, was used to collect the data at various angles during the experiment, and another PM tube was located at zero angle to monitor the light intensity as a reference. A microcomputer was used to control the stepping motor driver which moved the goniometer with the PM detector on its rotating arm. The data acquisition process was also controlled by the microcomputer. Current signals from PM tube were converted into voltage signals (0–10 V) through a 470 k Ω resistance, and the signals were stabilized with a capacitor. More details about t.r.l.s. are available elsewhere³⁸.

The average diameter of the dispersed domain (R_s) is estimated from Bragg's equation^{39–41}:

$$R_s = \lambda / [2n \sin(\theta_m/2)] = 2\pi/nq_m \quad (1)$$

where θ_m is the maximum scattering angle, n is the refractive index of the solution, q_m is the maximum scattering vector, where the scattering vector q is defined by $q = (4\pi/\lambda)\sin(\theta/2)$, and λ is the wavelength of the incident light.

Polymer composition. An FTi.r. spectrometer (Nicolet 20DX), equipped with a triglycine sulfate detector, was used to measure the composition of partially reacted samples. The measuring procedure is described elsewhere⁴². For the ST/UPE system, two absorption peaks were used to determine the concentration of ST and UPE. The ST concentration is proportional to the absorption peak at 1495 cm^{-1} (benzene ring in ST and polystyrene), while the unsaturated polyester concentration is proportional to the absorption peak at 1730 cm^{-1} (C=O bonds). The vinylene conversion of UPE monomer can also be determined by following the peak change at 982 cm^{-1} .

Particle size. A dynamic light scattering (d.l.s.) goniometer (Brookhaven BI-2030AT) with a digital correlator was used to measure the particle size of partially reacted samples. An Excel 3000 ion laser system, with a maximum output power of 8 W and a wavelength of 488 nm, served as the light source. This device has the capability of measuring particle size down to 1 nm, which covers the size range of microgels. The laser power used in most measurements was 0.3 ± 0.1 W, and the sample time was 0.1 ns. The operation setting was dependent on the particle size and concentration of solution.

The partially reacted sample was diluted with dichloromethane (DCM) and the solution was filtered with a 0.2 μm filter before measurement. The measuring angle was fixed at 90° for all measurements. The particle size was measured at 25, 35 and 45°C.

RESULTS AND DISCUSSION

Table 2 summarizes the reaction kinetics of UPE resins with MR=4 and various amounts of MEKP/COB, and with MR=2 and 1.0% MEKP/COB cured at 40°C. Because of the compatibility between ST and UPE resin³⁴, reaction-induced phase separation occurred for resin with MR=4 cured at 40°C, while there was no phase separation for resin with MR=2 cured at 40°C. The induction time and the time to reach the maximum reaction exotherm were different for resin with MR=4 and various amounts of MEKP/COB, but the final

Table 2 Reaction kinetics^a for ST/UPE resins with various curing conditions

Sample designation	t_{start} (min)	t_{max} (min)	Conversion (%)
MR=4, $T=40^\circ\text{C}$			
1.0% MEKP	2.08	15.35	27.6
0.8% MEKP	11.64	29.41	26.1
0.5% MEKP	65.67	108.94	29.4
MR=2, $T=40^\circ\text{C}$			
1.0% MEKP	28.14	44.93	39.4

^a t_{start} , induction time; t_{max} , time to reach the maximum reaction exotherm

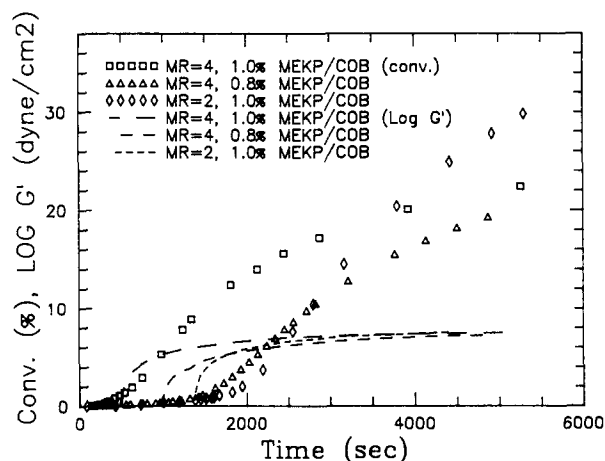


Figure 1 Resin conversion and storage shear modulus versus time for ST/UPE resins with MR=4 and MR=2 cured at 40°C

conversions were similar. The final conversion of resin with MR=2 was higher than that of resin with MR=4 cured at 40°C. D.s.c. and RDA results are shown in Figure 1. It is clear that most rheological changes occurred at the very beginning of the reaction.

Schematic diagrams comparing the thermally induced and reaction-induced phase separation are shown in Figures 2a and b. For thermoplastic polymeric blends, phase separation occurs when system temperature changes from the one-phase region to the two-phase region. Phase separation follows two possible dynamic processes: spinodal decomposition and nucleation. For reactive processes, phase separation occurs due to the changes of phase boundary and reactant composition during polymerization. These changes force the polymeric system to move from the one-phase region into the two-phase region. Although the causes of phase separation in thermoplastic polymeric blends and reactive processes are different, similar microstructure can be found for samples prepared by these two methods, as shown in Figures 2c and d. The microstructure in Figure 2c is a result of freeze-drying of a 10% poly(methyl methacrylate) solution in sulfolane quenched from 50 to 0°C, while Figure 2d is a partially cured UPE resin.

The reaction-induced phase separation of the UPE resin cured with 1.0% MEKP/COB at 40°C was observed under an optical microscope with a phase contrast attachment. The polymerization was conducted on a hot stage with a temperature controlling device. Before any reaction, the ST/UPE resin system with MR=4 at 40°C was a homogeneous mixture. Phase separation started

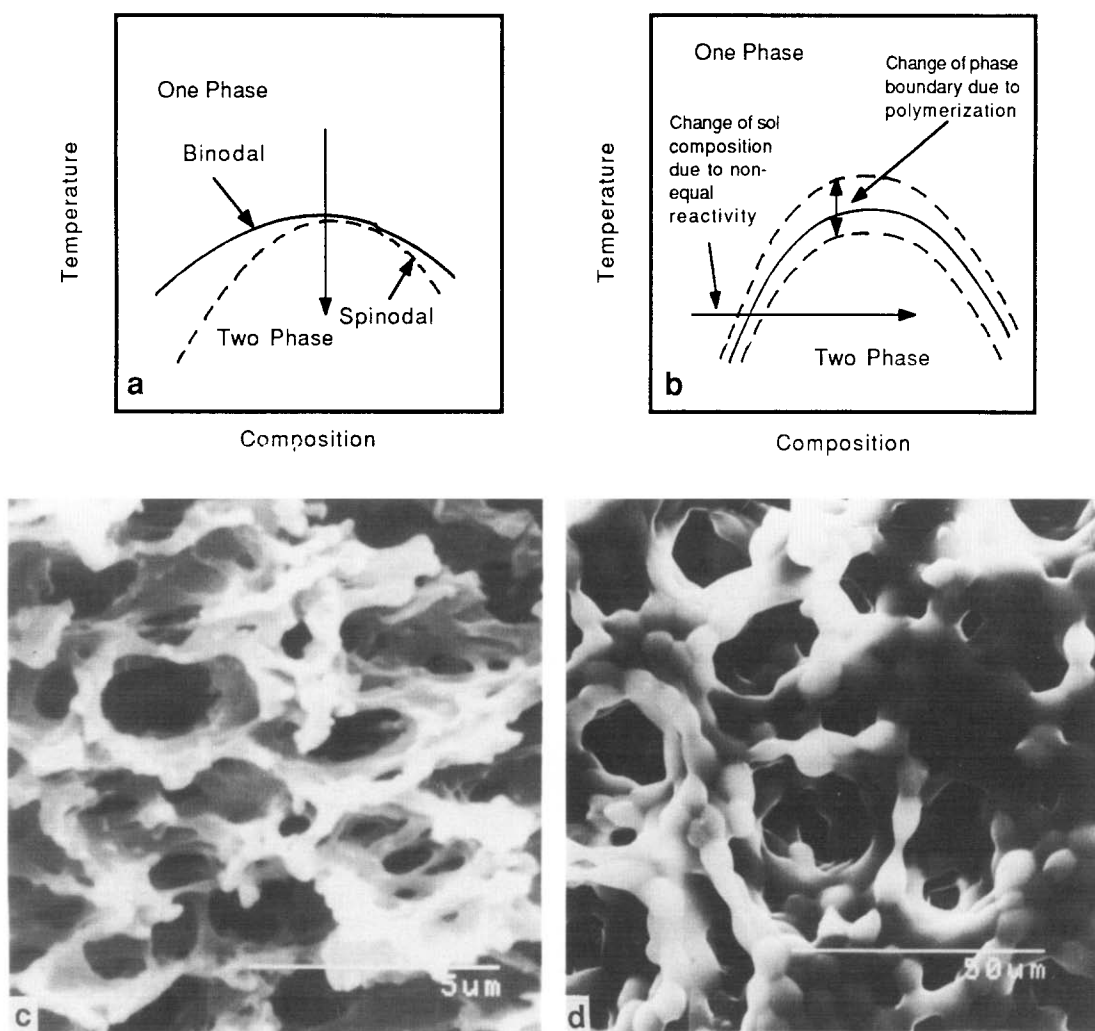


Figure 2 Phase separation due to (a) temperature jump; (b) ST/UPE copolymerization. SEM micrographs of the solid fraction structure prepared by various methods: (c) 10% PMMA in sulfolane quenching from 50 to 0°C; (d) ST/UPE resin with 1.0% MEKP/COB and MR=4 cured at 30°C for 2 min after $G' = G''$

at a reaction time of approximately 300 s, as shown in *Figure 3a*, where the resin was still in the liquid state. As the reaction progressed, more dispersed droplets formed (*Figure 3b*). The phase boundary became vague (*Figure 3c*). Finally, the phase boundary disappeared after around 1320 s (*Figure 3d*). There were still two phases in the sample, but the phase boundary was indistinguishable because of matched refractive index between the two phases. The change of relative refractive indices was due to the polymerization in each phase. Phase boundary showed up again (*Figure 3e*) after 1680 s. Comparing *Figures 3b* and *f*, a refractive index inversion between the two phases could be observed.

The $G' = G''$ point occurred at a reaction time of 592 s. It is clear that phase separation occurred much earlier, before the $G' = G''$ point. The phase separation process stopped when the whole system reached the gel point as seen in the micrographs in *Figures 3b* to *f*. The average particle size and the number of particles remained the same from *Figures 3c* to *f*. The dispersed phase shown in *Figure 3* was UPE-rich, while the continuous phase was ST-rich. A similar phase separation process was observed for ST/UPE resins with MR=4 and 0.8% or 0.5% MEKP/COB cured at 40°C.

Because the optical microscopy is limited to size resolution of several micrometres, a t.r.l.s. goniometer

was built to investigate the microstructure formation process in the submicrometre range. The same UPE reaction was first analysed using the t.r.l.s. goniometer. The results are shown in *Figure 4*. The resin system started as a single phase then entered into the two-phase region during reaction. The sample started to scatter light at a reaction time of around 300 s, which indicated the formation of heterogeneous structure inside the resin. This result agreed with the optical microscopy observation shown in *Figure 3*, where the heterogeneous structure was observed at the same time. The maximum scattering vector occurred near $q=1.5$ after the phase separation began, and moved slightly until gelation. After gelation, the maximum scattering vector stayed at the same angle. This indicated that the domain size of the heterogeneous structure remained constant throughout the rest of the reaction. The domain size estimated from Bragg's equation was 3.6 μm , which again agreed with the optical microscopy observation. The maximum scattering intensity went through an increasing-decreasing-increasing cycle due to the change of resin refractive index during reaction.

The t.r.l.s. measurement of the same UPE resin with MR=2, 15% PVAc and 1.1% PDO cured at 80°C is shown in *Figure 5*. Due to the presence of PVAc, smaller domains in the submicrometre range were formed.

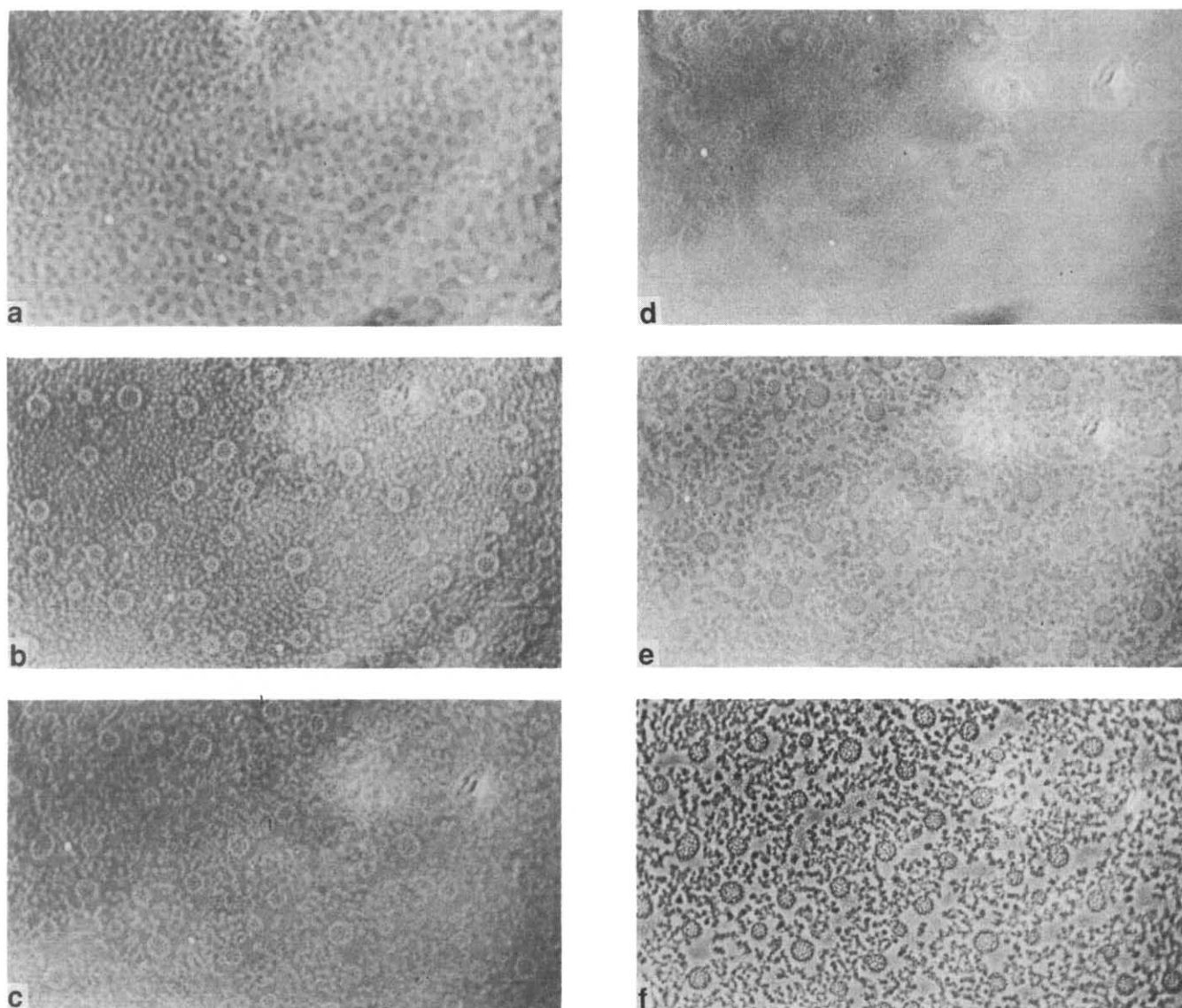


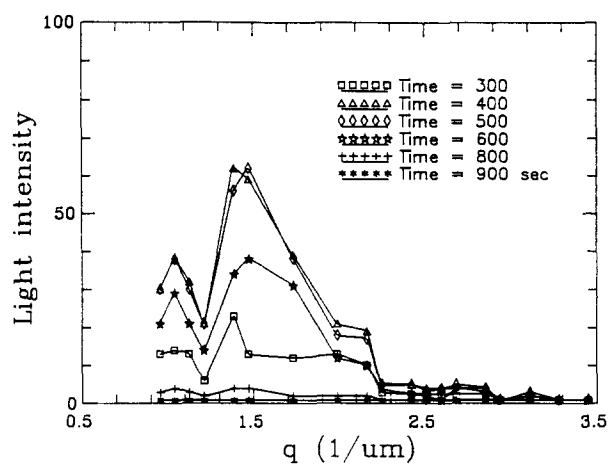
Figure 3 OM micrographs of the ST/UPE resin with MR=4 and 1.0% MEKP/COB cured at 40°C for: (a) 300 s; (b) 420 s; (c) 1020 s; (d) 1320 s; (e) 1680 s; (f) 2640 s

Domains started to form at a reaction time near 300 s where the overall conversion was less than 1%. At this point the resin was in the liquid state. The maximum scattering vector occurred near $q = 3.8$ and remained at the same position through the entire reaction. The domain size estimated from Bragg's equation was near $1.0 \mu\text{m}$, which agreed with the SEM micrograph of resin microstructure at the end of reaction⁴³. The t.r.l.s. measurement provided information of microstructure formation in the early stage of reaction, which cannot be determined from SEM observation due to the sample preparation procedures involved in the SEM technique.

Partially reacted samples of ST/UPE resins before macrogelation were prepared by stopping the polymerization at preset times. The reaction was conducted in a temperature-controlled water bath. The mixed resin was poured into a glass vial with a screw cap, then the vial was placed in the water bath for isothermal reaction. The vial was stirred gently during the reaction to keep the reactant temperature uniform. The reaction was stopped by pouring DCM with 1 wt% inhibitor into the vial during the polymerization. The solvent/reactant weight ratio was 5 for every run. Methanol was then

poured into the solution. Because methanol is a non-solvent for both UPE prepolymer and partially reacted polymer, the amount of methanol was chosen such that mainly the partially reacted polymers would precipitate out of the solution. The amount of methanol was the same as that of DCM in this study. The solution was then centrifuged for at least 30 min. Most of the precipitated polymers formed a thin layer on the bottom surface of the container after the solution was centrifuged. The top portion of the solution was removed with a pipette. The precipitated polymers were washed several times with methanol to remove the residual UPE and ST monomers. Around 3–5 ml DCM was then added to the precipitated polymers. The solution was stored in a refrigerator for further analysis.

The particle size of the primary polymer was estimated from the d.l.s. experiment. The measured results of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C are given in Table 3. No phase separation occurred during this reaction. The induction time was about 10 min, and the gel time was about 23.2 min for this reaction. The particle size measured by d.l.s. (Figure 6) showed a broad distribution from 7 to 13 nm at a reaction



more primary polymers formed but the average particle size of primary polymers only increased slightly, as shown in Figures 7 to 9 and Table 3. The small increase of particle size may be due to the addition of more monomers to the primary polymers during polymerization. A second particle group with a size around 30 nm showed up when the resin system reacted closer to its gel point (i.e. 20.7 min). These larger particles were apparently a

Table 3 Particle size distribution during the cure of UPE resin with MR=2 and 1.0% MEKP/COB at 40°C

Reaction time (min)	Particle size (nm) at measuring temperature		
	25°C	35°C	45°C
10.3	9.9	10.5 (6.1%) ^a	10.6 (7.1%)
13.8	12.2	12.6 (3.3%)	13.2 (8.2%)
17.2	12.5	13.1 (4.8%)	13.5 (8.0%)
20.7	12.4	30.5 (2.4%, 11.5%)	13.1 38.2 (5.6%, 25.2%)
gel ^b (23.2)	27.8	101.8 (4.3%, 3.6%)	30.5 106.5 (9.7%, 4.6%)

^a Numbers in parentheses are percentage size change compared to the size at 25°C

^b Measured particle size was the soluble portion of the partially cured resin at gel point

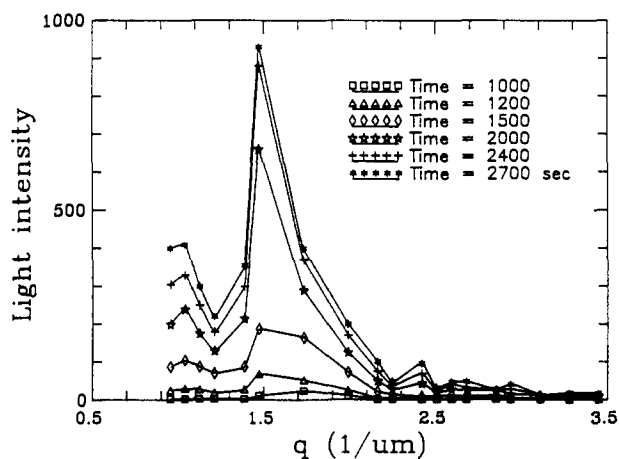


Figure 4 Time-resolved light scattering data of ST/UPE resin with MR=4 and 1.0% MEKP/COB cured at 40°C

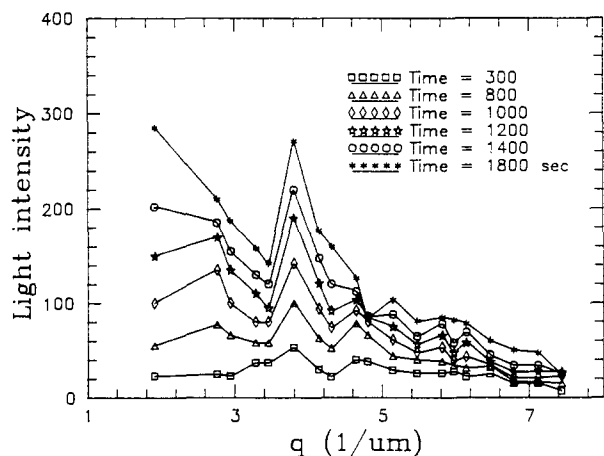


Figure 5 Time-resolved light scattering data of ST/UPE resin with MR=2 and 15% PVAc cured at 80°C

time of 10.3 min and measuring temperature of 25°C. The number-average particle size was 9.9 nm. The d.l.s. measurement also indicated the existence of small particles 1 nm in size. These small particles were UPE monomers which were precipitated in the sample preparation. The particle size of primary polymers in DCM was also measured at 35 and 45°C. The average particle size increased slightly and the distribution of particle size shifted to a larger value at higher measuring temperatures.

As the reaction progressed from 10.3 to 20.7 min,

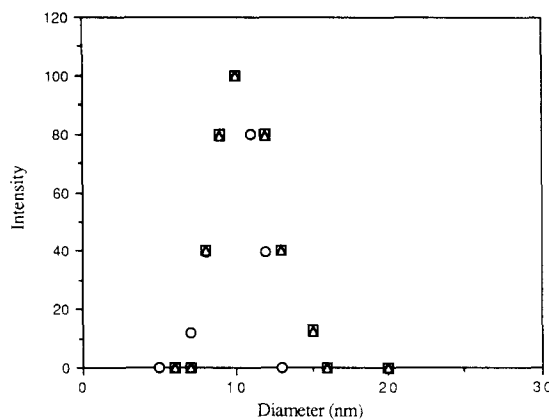


Figure 6 Particle size distribution of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C; reaction time = 10.3 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

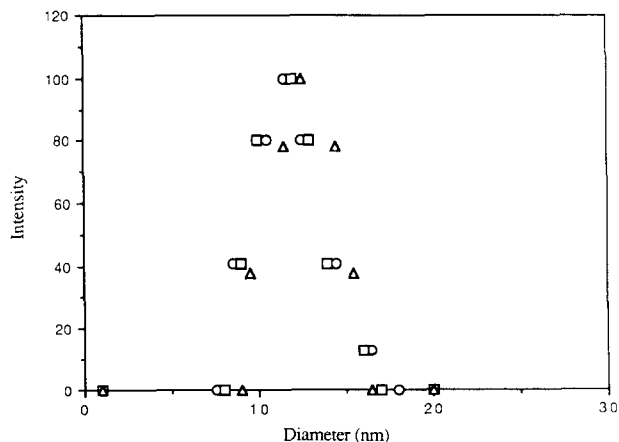


Figure 7 Particle size distribution of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C; reaction time = 13.8 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

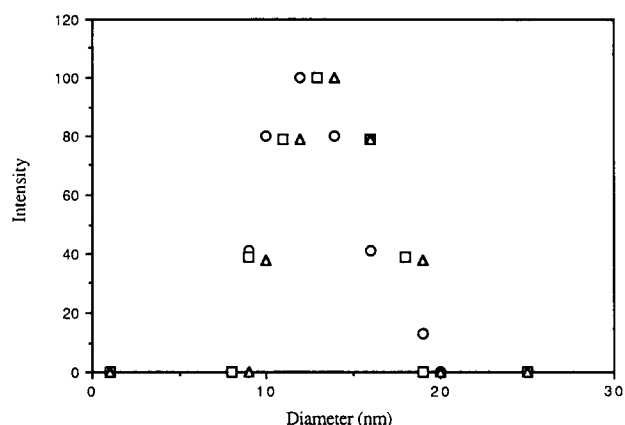


Figure 8 Particle size distribution of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C; reaction time=17.2 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

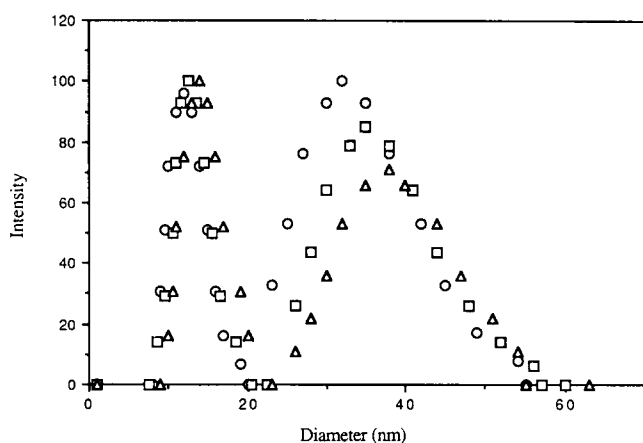


Figure 9 Particle size distribution of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C; reaction time=20.7 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

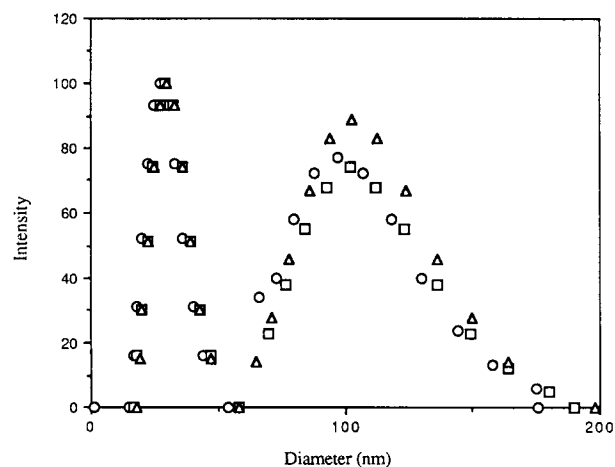


Figure 10 Particle size distribution of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C at $G' = G''$ point. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

combination of a group of primary polymers. As the resin system reached the gel point, the primary polymers disappeared, merging into two larger particle groups. The largest particles had a very broad particle distribution, as shown in Figure 10, and its lower tail overlapped with the upper tail of the other particle group.

To compare the size expansion of ST/UPE primary polymers with the size change of linear polymers at elevated temperatures, the particle size of a linear polymer, polystyrene with $M_w = 180\,000$, was also measured under the same conditions. The results are shown in Table 4. The polystyrene showed an average of 11% size expansion for every 10°C temperature increase. On the other hand, the size change of ST/UPE primary polymers formed from 10.3 to 20.7 min was about 4% for every 10°C temperature increase, as shown in Table 3. This is because the molecular structure of UPE primary polymers is not linear, since some primary intramolecular crosslinking has already occurred. The relatively constant size expansion coefficient of UPE primary polymers formed from 10.3 to 20.7 min seems to imply that the secondary intramolecular crosslinking was small after the primary polymers were formed during this stage of reaction. The larger particles formed at 20.7 min had a larger size expansion coefficient. This larger size expansion coefficient indicates that the connection between primary polymers was loose at this stage. At gel point, both large particle groups had a relatively low size expansion coefficient. This indicates that a tighter connection between primary polymers had formed and the crosslinking density of primary polymers at gel point might be higher than that of the original primary polymers. It seems that the secondary intramolecular reaction has started at this point.

The composition and vinylene conversion of partially reacted primary polymers were measured by FTi.r. spectroscopy, and the results are given in Table 5. The composition of primary polymers showed a very low amount of ST on the polymer chain with $MR \approx 0.1$. Because there are 10 vinylene groups for each UPE monomer, on average, the composition of primary polymers indicates that each UPE monomer was connected through one ST monomer to the primary polymer. On average, one vinylene group per UPE monomer has reacted during the primary polymer formation. Both the composition and the vinylene

Table 4 Particle size distribution of polystyrene

Particle size (nm) at measuring temperature		
25°C	35°C	45°C
21–23	24–25 (11.4%) ^a	26–27 (20.5%) ^a

^a Percentage size change compared to the size at 25°C

Table 5 ST/UPE molar ratio (MR) and UPE vinylene conversion in primary polymer formed during the reaction of UPE resin with MR=2 and 1.0% MEKP/COB at 40°C

Reaction time (min)	Molar ratio	UPE vinylene conversion (%)
10.3	0.12 ± 0.02	8.6 ± 2.0
13.8	0.12 ± 0.02	8.1 ± 2.0
17.2	0.13 ± 0.02	9.1 ± 2.0
20.7	0.13 ± 0.02	12.3 ± 2.0
gel ^a (23.2)	0.14 ± 0.02	12.2 ± 2.0

^a The measured molar ratio and conversion were for the soluble portion only. The gel portion at gel point: $MR = 0.27 \pm 0.04$ and UPE vinylene conversion = $8.7 \pm 1.0\%$

conversion of primary polymers remained at the same level for the reaction time from 10.3 to 17.2 min. As the resin system approached the gel point, both the ST molar ratio and the vinylene conversion of UPE in primary polymers increased, indicating the start of secondary intramolecular crosslinking. These results agree well with the measured size expansion coefficient of particles.

The sizes of polymers formed during the reaction of ST/UPE resin with MR = 4 and 0.8% MEKP/COB cured at 40°C are given in Table 6. The experimental results showed that phase separation of this reaction occurred after around 9 min. The induction time was about 6.5 min and the gel time was about 16.7 min. No primary polymer was found at the reaction time of 5 min, where the resin system was still in the induction stage. The measured particle with size of 1 nm was UPE monomer which precipitated during the sample preparation. At the reaction time of 6.9 min, the particle size measured at 25°C by d.l.s. showed a broad distribution from 10 to 21 nm (Figure 11). The average particle size was 15.0 nm. The d.l.s. measurement also indicated the presence of some UPE monomers with a size of 1 nm. The particle size of primary polymers in DCM was also measured at 35 and 45°C to check the size expansion coefficient. The size change of primary polymers shown in Table 6 is about 3.3% for every 10°C temperature increase, which is again smaller than the size expansion coefficient of linear polymers. This result again supports the microgel-like structure argument for the reaction of multifunctional

Table 6 Particle size distribution during the cure of UPE resin with MR = 4 and 0.8% MEKP/COB at 40°C

Reaction time (min)	Particle size (nm) at measuring temperature					
	25°C		35°C		45°C	
6.9	15.0		15.5		16.0	
			(3.3%) ^a		(6.7%)	
10.4	25.2	96.8	27.0	106.4	32.2	113.5
			(7.1%, 9.9%)		(27.8%, 17.3%)	
13.9	28.2	108.1	31.6	114.6	35.1	120.6
			(12.1%, 6.0%)		(24.5%, 11.6%)	
gel ^b (16.7)	31.1	110.0	31.3	111.8	31.5	115.2
			(0.6%, 1.6%)		(1.3%, 4.7%)	

^a Numbers in parentheses are percentage size change compared to the size at 25°C

^b Measured particle size was the soluble portion of the partially cured resin at gel point

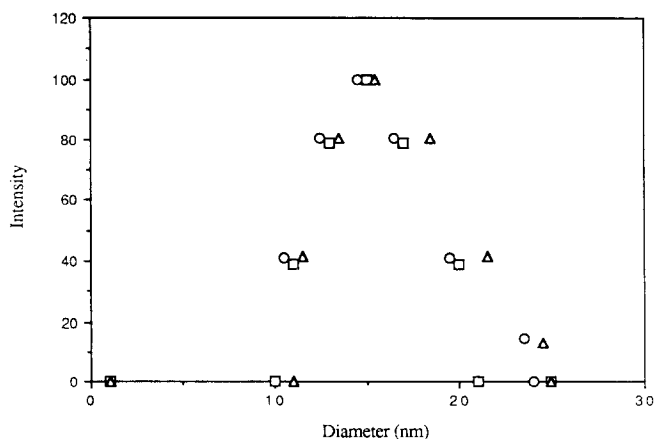


Figure 11 Particle size distribution of ST/UPE resin with MR = 4 and 0.8% MEKP/COB cured at 40°C; reaction time = 6.9 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

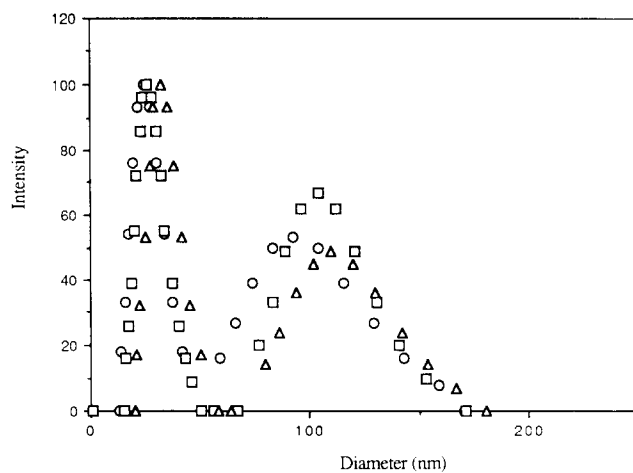


Figure 12 Particle size distribution of ST/UPE resin with MR = 4 and 0.8% MEKP/COB cured at 40°C; reaction time = 10.4 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

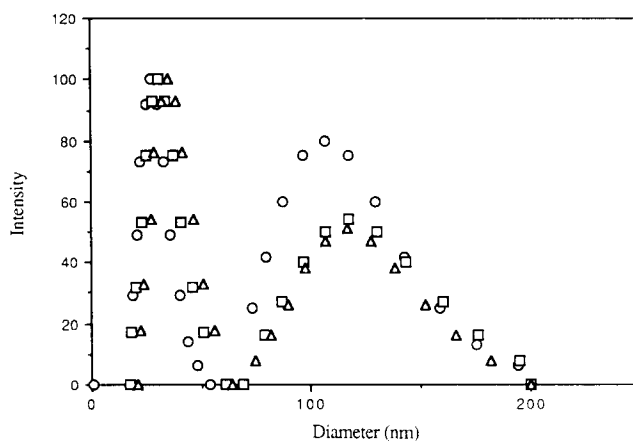


Figure 13 Particle size distribution of ST/UPE resin with MR = 4 and 0.8% MEKP/COB cured at 40°C; reaction time = 13.9 min. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

chain growth polymerizations. Compared with the reaction of MR = 2, this reaction seems to form primary polymers with a larger size and a broader size distribution, but a slightly lower size expansion coefficient.

As the resin system passed the phase separation point, primary polymers tended to react with each other and formed two larger particle groups with the average sizes of 25.2 and 96.8 nm, respectively. Both particle groups had higher size expansion coefficients than the primary polymers when they were formed at the reaction time of 10.4 min. The higher size expansion coefficient of larger particles again indicates that the connection between primary polymers was loose at this point. The size distribution of both particle groups was very large, 16–44 and 68–168 nm, respectively, as shown in Figure 12. As the reaction progressed, the average particle size of both groups increased and the size expansion coefficient decreased (Figure 13). Unlike the UPE resin systems without phase separation, where the intra- and interparticle reaction did not occur until the resin system approached the gel point, results here indicate that both inter- and intraparticle reactions had already started after the phase separation occurred. When the resin system reached the gel point, the size expansion coefficient of both particle groups decreased to a very small number,

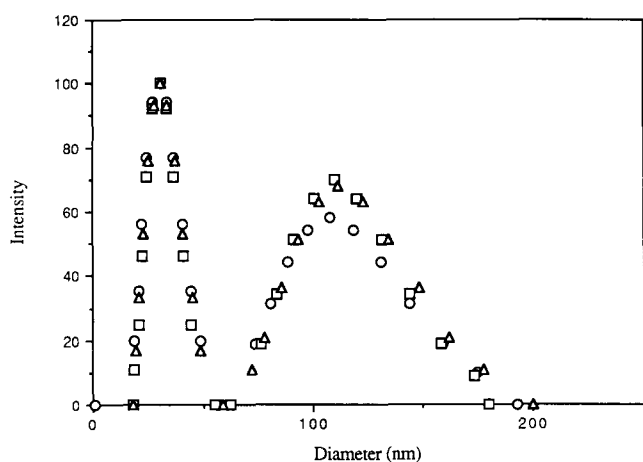


Figure 14 Particle size distribution of ST/UPE resin with MR=4 and 0.8% MEKP/COB cured at 40°C at $G'=G''$ point. Measuring temperature: ○, 25°C; □, 35°C; △, 45°C

Table 7 ST/UPE molar ratio (MR) and UPE vinylene conversion in primary polymer formed during the reaction of UPE resin with MR=4 and 0.8% MEKP/COB at 40°C^a

Reaction time (min)	Molar ratio	UPE vinylene conversion (%)
6.9	0.16 ± 0.02	14.1 ± 2.0
10.4	0.16 ± 0.02	14.7 ± 2.0
13.9	0.25 ± 0.02	19.5 ± 2.0
gel ^b (16.7)	0.26 ± 0.02	19.2 ± 2.0

^a Phase separation occurred at the reaction time of 9.1 min

^b The measured molar ratio and conversion were for the soluble portion only. The gel portion at gel point: MR = 0.33 ± 0.04 and UPE vinylene conversion = 9.5 ± 1.0%

indicating a tight connection between primary polymers and a high crosslinking density in primary polymers, as shown in *Figure 14*.

The composition and vinylene conversion of partially reacted primary polymers of ST/UPE resin with MR=4 and 0.8% MEKP/COB cured at 40°C were also measured by FTi.r. spectroscopy, and the results are given in *Table 7*. The composition of primary polymers showed a slightly higher amount of ST on the polymer chain compared to that in *Table 5*. Since there are 10 vinylene groups for each UPE monomer, the composition of primary polymers indicates that UPE monomers were connected through 1.6 ST monomers, on average, to form the primary polymer. This indicates that each UPE monomer was again connected through one ST monomer to the primary polymer, but there was a substantial amount of primary intramolecular reaction during microgel formation. The amount of ST in the polymer chain and the vinylene conversion increased as the secondary intramolecular reaction and the interparticle reaction occurred when the resin system approached the gel point.

CONCLUSIONS

For the reaction of ST/UPE resins, phase separation would occur right after the primary polymers formed if the resin system had moved into the two-phase region. The phase separation process stopped after the resin

reached its gel point, and the domain size of the separated phase remained the same throughout the rest of the reaction period.

The formation of microgels at the beginning of the reaction is an important feature in multifunctional free-radical chain-growth polymerization. In this study, the size, composition and UPE vinylene conversion of primary polymers at different stages before macrogelation were investigated by d.l.s. and FTi.r. measurements. The experimental data showed that the characteristics of primary polymers formed agreed well with the description of microgels. These microgels remained unchanged before phase separation and gelation. Secondary intramolecular reaction and interparticle reaction of microgels occurred when there was phase separation or when the reaction approached gelation. These reactions increased the ST content in the polymer chain and the vinylene conversion.

ACKNOWLEDGEMENTS

This research was partially supported by grants from the National Science Foundation (Grant No. CBT-8820674) and the Engineering Research Center at The Ohio State University. The authors thank Ashland Chemical Company and Union Carbide for material donation.

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