Structure formation during the copolymerization of styrene and unsaturated polyester resin

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An integrated rheological, kinetic and morphological study was carried out to investigate microstructure formation in unsaturated polyester resins. Based on the experimental results, a mechanism for microstructure formation was proposed. The effects of reaction temperature and styrene molar fraction on the reaction kinetics, sample morphology and rheological changes were discussed.

(Keywords: unsaturated polyester resin; microstructure; inhomogeneous chain growth cross-linking copolymerizations; rheo-kinetics; sol/gel fraction)

INTRODUCTION

The reaction of styrene and unsaturated polyester (UPE) is a free radical chain-growth cross-linking copolymerization. Three different types of bonds can be formed during the polymerization, since the reaction can occur between styrene–polyester vinylene, styrene–styrene and polyester vinylene–polyester vinylene. A mixture of polyester and styrene may be described as many coiled polyester chains swollen in styrene monomer. Molecular weight, chain stiffness, thermodynamic compatibility and concentration of polyester chains determine the coil size. Chemical reactions may occur among C=C bonds inside, outside and at the surface of the coils. The styrene/UPE copolymerization progresses as the initiator decomposes and creates free radicals in the system. The free radicals link adjacent UPEs and styrene to form long chain molecules. These long chain molecules tend to form spherical-type structures due to the intramolecular cross-linking among the pendant C=C bonds of the polyester molecules. Dusek[1] described these spherical structures with locally high cyclization and cross-linking density as 'microgel particles'. Depending on the concentration of styrene and UPE, the morphology of reacted resins can be quite different[2].

It was the aim of this study to understand the mechanism of microstructure formation during the reaction of UPE resins. Partially reacted samples were prepared and the reaction kinetics, sample morphology, sol/gel fraction, sol composition and rheological changes were measured. A set of experiments was also carried out to study the effect of reaction temperature on microstructure formation.

EXPERIMENTAL

Materials

The UPE resin used in this study was provided by Ashland Chemical Company. The resin, a 1:1 mixture of maleic anhydride and propylene glycol, has an average of 10.13 vinylene groups per polyester molecule. The number average molecular weight of the UPE was 1580 g mol^{-1}, and the equivalent molecular weight/(mole C=C) was 156 g mol^{-1}.

Both UPE resin and styrene monomer were used as received without removing the inhibitor. Methyl ethyl ketone peroxide (MEKP, Lucidol) with 25 wt% cobalt naphthenate (COB) promoter was used as the initiator. Before the experiment, the UPE resin was weighed and mixed with styrene monomer in a flask at the specified molar ratio (*MR*). The MEKP was added and the solution was mixed with a magnetic stirrer for 60 min at room temperature and then stored below 5°C for further use. The COB was mixed into the solution at room temperature immediately before the kinetic and rheological measurements.

For most of the experiments in this study, the *MR* of styrene/UPE resin was chosen to be 4.0, which results in a styrene molar fraction of 0.8. The composition of this resin is given in *Table 1*. The reaction kinetics, rheological changes and microstructure formation of this resin were measured at 30, 40 and 50°C isothermally. Dichloromethane with 1% benzoquinone was used to stop the reaction of partially reacted resins.

Instrumentation and procedures

Reaction kinetics measured by differential scanning calorimetry (*d.s.c.*). The reaction kinetics were measured by a differential scanning calorimeter (Perkin-Elmer DSC-2C). All reactions were conducted in volatile aluminum sample pans capable of withstanding at least 2 atm internal pressure after sealing. Isothermal runs were ended when there was no further exotherm. Samples were then reheated from 320 to 520 K in the scanning mode with a heating rate of 10°C min^{-1} to determine the residual reactivity left in the isothermally cured samples. The reactions were also carried out in the scanning mode from 320 to 520 K at a heating rate of

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Table 1 Composition of the sample used in the study of temperature effect

Styrene[a]/UPE	UPE resin (wt%)	Styrene (wt%)	MEKP/COB (wt%)
$MR = 4$	26.95	71.8	1.0/0.25

[a] Styrene molar fraction = 0.8

10°C min^{-1} to determine the total heat of reaction from the area under the scanning curve.

The exotherm data measured during the reaction can be converted into reaction rate and conversion as a function of time[3–6].

Rheological measurements. For the rheological measurements, a Rheometrics Dynamic Analyzer-700 (RDA) in the oscillatory mode was used to measure the storage shear modulus (G') and loss shear modulus (G'') during reaction. Serrated disposable aluminum 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 and was changed to 1% after G' reached 10^6 dyn cm^{-2} in order to measure the moduli at high conversions.

Morphological study using scanning electron microscopy (SEM) and optical microscopy (OM). In the morphological study, the reaction of resins cured in the RDA sample chamber was stopped at a preset time and the partially reacted resin was sampled with a stainless steel spatula. The sample ($\sim$0.1 g) was put into an ice-cooled dichloromethane solution ($\sim$10 ml) to stop further reaction. (Dichloromethane is a good solvent for styrene and UPE.) The solution was stored in a refrigerator for at least 1 day in order to dissolve all soluble materials such as residual styrene monomers, polyester molecules and free polystyrene chains in the sample.

The undissolved sample, if any, was left on a filter paper and dried at room temperature for at least 6 h until the sample weight was constant. The remaining solution was kept in the refrigerator for the measurement of sol fraction, sol composition, and average molecular weights of unreacted polyester molecules and possibly ester–styrene copolymer in the sol. The dry sample was gold-coated and morphological measurements were made using a scanning electron microscope. A Hitachi S-510 scanning electron microscope with an accelerating voltage of 25 kV was used to observe the surface of each sample at a magnification of × 200–4000.

A drawback of SEM was that the partially reacted samples had to be dried before measurement, which may have changed the actual sample morphology. In order to visualize the structure formation during reaction under an unperturbed condition, an optical microscope with a hot stage was also used. This allowed for the measurement of morphological changes, when the size of the microstructure was > 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 mixed with initiator was bounded by two circular cover glasses. The set-up was mounted on a hot stage which was connected to a temperature controller, and microstructure formation was monitored as the reaction occurred.

The sol/gel fraction and average molecular weights of partially reacted samples. The measurement of the gel fraction in step growth cross-linking systems has been carried out by many researchers[7–9]. The experimental data for free radical cross-linking polymerizations however, have seldom been reported in the literature. For chemically cross-linked systems, there is no gel fraction before gelation. This, however, may not be true for other types of liquid–solid transition. For example, phase formation and inversion, or crystallization in a reacting system may also lead to 'gelation' (i.e. physical cross-linking). In such cases, the insoluble portion of the resin (i.e. equivalent to gel fraction) can be very large before 'gelation'[10]. For a heterogeneous cross-linking polymerization, such as the reaction of UPE resin, both chemical and physical cross-linking may occur. Knowing the sol/gel fraction of the sample during the reaction is valuable for determining the mechanism of microstructure formation.

In this study, the sol/gel fraction was determined by measuring the sample weight before and after solvent treatment. In order to check the accuracy of this approach, a second method used by several researchers[7–11] was also tried to determine the sol/gel fraction. Samples were finely ground and extracted in the solvent, and then dried under vacuum until no further weight loss was detected. The extraction procedure was repeated until the difference in sample weight between two extractions was $<1\%$. The results from the two methods showed very little difference for samples at low conversions (i.e. at or near the liquid–solid transition). Therefore, the sol/gel fraction reported in this work was measured based on the first method.

The molecular weight and molecular weight distribution (*MWD*) of polyester molecules in sol were measured by gel permeation chromatography (g.p.c., Waters) with two ultrastyragel columns (10^2 and 10^3 Å pore size).

Sol composition measured by Fourier transform infrared (FTi.r.) *spectrometry.* An *FT*i.r. spectrometer (Nicolet 20DX), equipped with a triglycine sulphate (TGS) detector, was used to measure the sol composition. One or two drops of the solution of the sol fraction was placed between two circular sodium chloride plates and the set-up was loaded in the *FT*i.r. spectrometer to determine the concentrations of styrene and UPE. The maximum resolution of the *FT*i.r. peaks was 4 cm^{-1} in the transmission mode. For the styrene/UPE system, two absorption peaks were used to determine the concentration of styrene and UPE. The styrene concentration is proportional to the absorption peak at 912 cm^{-1} (C=C bonds in styrene), while the UPE concentration is proportional to the absorption peak at 1730 cm^{-1} (C=O bonds).

A calibration curve was determined by preparing solutions with known styrene and UPE concentrations.

Sample opacity measured by a light detector. The change in sample during reaction was followed by detecting the light transmission through a thin sample bounded by two circular cover glasses. The set-up was mounted on a sample holder which was located in a temperature chamber controlling the reaction temperature. The amount of light transmitted through the sample was sensed by a photodial which transformed the light intensity into direct current voltage ranging from 0 to 4 V.

RESULTS AND DISCUSSION

Phase diagram of styrene/UPE system

The UPE resin used in this study was not totally compatible with styrene monomer. As the styrene molar fraction increased from 0 to 0.71 ($MR = 2.4$) at room temperature, the mixture became immiscible and separated into two layers. The lower layer was a mixture of styrene and UPE with styrene molar fraction = 0.71 ($MR = 2.4$), while the upper layer was a styrene-rich mixture with styrene molar fraction >0.98 ($MR = 50$). The styrene molar fractions in the upper and lower layers depended strongly on temperature. When the temperature was increased, the two-phase region became narrower. The phase diagram of the styrene/UPE system is shown in *Figure 1*, where the critical temperature for each composition was determined by the cloud point method. The critical temperature for the styrene/UPE solution with $MR > 50$ was not measured due to the experimental difficulty. Therefore, one side of the phase boundary is not drawn in *Figure 1*.

Resins cured at 30°C

An integrated result, combining reaction kinetics, rheological changes and light transmission, for the resin cured at 30°C is shown in *Figure 2*, where the change of transmitted light reflected the heterogeneous phase formation. To ensure the consistency of measurements, all experiments were carried out simultaneously using the same resin mixture. Several researchers[11–13] have suggested that the crossover of G' and G'' curves could be an indication of the liquid–solid transition (i.e. the gel point) for cross-linking polymers when the stress relaxation at the gel point follows a power law (i.e. $G'(\omega) = G''(\omega) = A\omega^{1/2}$) and the temperature is much higher than the glass transition temperature. However, for many cross-linking systems the relaxation exponent at the gel point[13,14] may have a value not equal to 1/2. Consequently, the gel point cannot be solely determined by the crossover of G' and G'' curves. In this study, both the method of increasing viscosity by extrapolating the viscosity to infinity (measured by a Haake viscometer) and the crossover of G' and G'' curves (measured by RDA) were used. The results showed that the gel time determined by the Haake viscometer was slightly larger than the time when $G' = G''$ was measured by RDA. At 40°C, the time when $G' = G''$ measured by RDA was 9.7 min, while the gel time determined by the Haake viscometer was 13.5 min. Similar differences were also found at other temperatures. In order to stop the reaction of partially reacted resins in different rheological states, RDA measurement was chosen in this study. The crossover of G' and G'' curves was easily detected and taken to be an indication of the liquid–solid transition for all samples. It should be noted that this may not be the actual gel point.

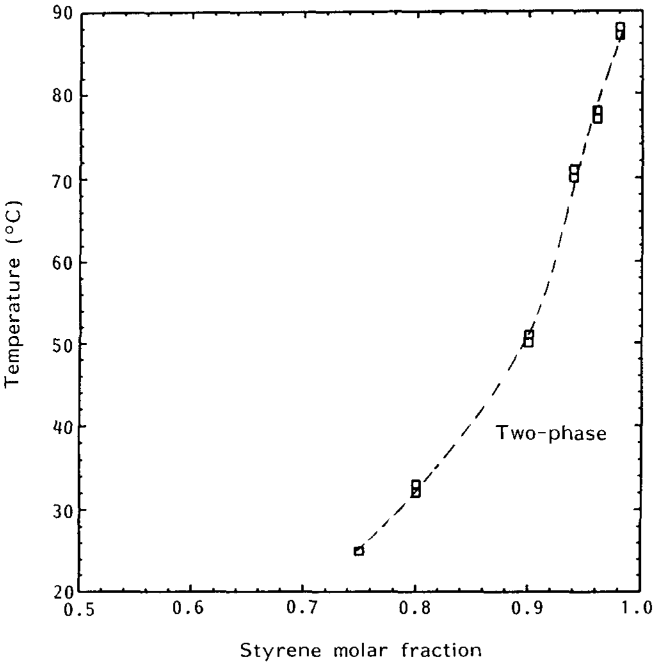

Figure 1 Phase diagram of the uncured styrene/UPE system at various temperatures

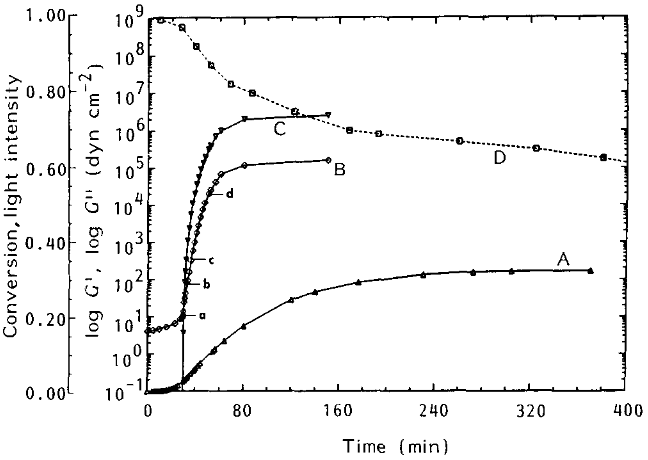

Figure 2 Comparison of conversion (A), G'' (B), G' (C) and opacity profiles (D) for the reaction of UPE resin with $MR = 4$ (styrene molar fraction = 0.8) at 30°C

Figure 2 shows that the major changes of G' and G'' occurred at the very beginning of the reaction where the total resin conversion increased from 2.5 to 5%. Both G' and G'' levelled off when the resin conversion reached 10%. The final conversion of this resin cured at 30°C was ~32%, so there were a large number of functional groups trapped in the polymer structure formed. In general, the transition of transmitted light intensity followed the change in reaction conversion.

In order to investigate the microstructure formation during reaction at 30°C, a set of partially reacted samples was prepared by stopping the reaction at different times. At the point when $G' = G''$, the partially reacted resin was a homogeneous, translucent soft gel, in which dichloromethane could dissolve nearly 95% of the sample. The partially reacted samples became harder as the reaction progressed, and the opacity also increased. Both sol fraction and sol composition were measured and the results are shown in *Figure 3* and *Table 2*. Points a, b, c and d shown in *Figures 2* and *3* are samples at the point when $G' = G''$, 2, 5 and 20 min after this point, respectively. At $G' = G''$, the measured sol fraction was nearly 100%. The sol fraction decreased rapidly after this point. It has been found by Yang and Lee[2] that the reactivities of styrene and polyester vinylene are not equal in the copolymerization. At low temperatures, the consumption rate of polyester vinylenes is higher than that of styrene vinyls in the early part of the reaction. Consequently, the styrene molar fraction in sol would

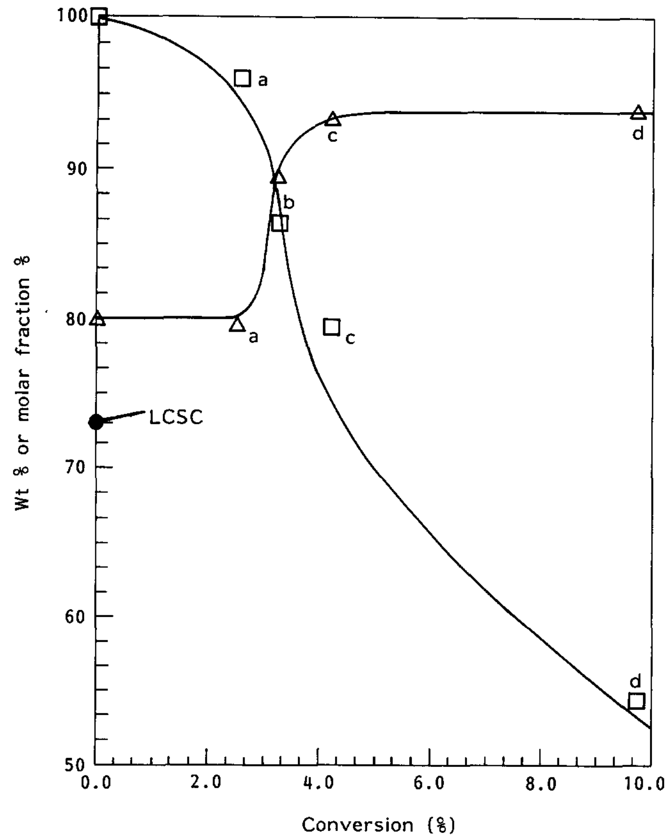

Figure 3 Change in sol fraction (□) and sol composition (Δ) of styrene/UPE resin with $MR = 4$ (styrene molar fraction = 0.8) during reaction at 30°C. Lower critical solution composition, LCSC

Table 2 Change in sol fraction and sol composition during cure (initial styrene molar fraction = 0.8, $MR = 4$ and $T = 30$°C)

Time (min)	30.1 ($t_{G'=G''}$)	32.1	35.1	50.1
Conversion (%)	2.54	3.23	4.23	9.73
Sol composition (styrene molar fraction)	0.80	0.90	0.94	0.94
Sol/gel fraction (%)				
Sol fraction	96.0	86.6	79.4	54.4
Gel fraction	4.0	13.4	20.6	45.6

increase during reaction when the initial styrene molar fraction is >0.5 ($MR > 1$) as shown in *Figure 3*.

The SEM micrographs of the gel fraction of these partially reacted samples are shown in *Figure 4*. Although the micrograph of the insoluble portion of the sample at $G' = G''$ shows only a loosely connected network, particulate structure could be observed under the optical microscope when the sample was unperturbed (i.e. *Figure 5a*). Because the conversion at $G' = G''$ was very low, particles had a very low cross-linking density. After the sample was submerged in dichloromethane, the soluble portion of the particles might have dissolved as only 'skins' remained in the gel fraction. Consequently, *Figure 4a* shows only the structure of the remaining skin of the particles. In the case of OM, the sample was not subjected to any external disturbances, thus an inhomogeneous phase could be identified at $G' = G''$. As the reaction progressed, more particles formed and the cross-linking density of the particles also increased. Consequently, particles were stronger and would not be deformed during solvent treatment. *Figures 4b–d* show the increase of the particle population during reaction. The particle size seems to remain constant (4–5 μm) during most of the reaction with a slight decrease (~1 μm) in the later stage of reaction. *Figure 5* shows the optical micrographs of sample morphology at $G' = G''$ and at final conversion. At $G' = G''$, particles could be clearly observed. The dark areas around each particle were microvoids resulting from polymerization shrinkage.

Mechanism of microstructure formation

Based on the above results, microstructure formation in the resin system is described schematically in *Figure 6*. For an UPE resin at a given temperature, there are two critical values of styrene molar fraction (SMF_c) between which styrene and UPE separate into two phases. If the initial styrene molar fraction (SMF_0) in the resin is in the two-phase region, the resin will separate into two layers as shown in *Figure 6a*. The upper layer is a styrene-rich mixture with the styrene molar fraction equal to the upper critical value, and the lower layer is a mixture with the styrene molar fraction equal to the lower critical value. In *Figure 6a*, the rate of global phase separation, R_s, is dependent on the chemical composition, molecular chain length and thermodynamic properties of UPE. For the system studied, it took ~30 min at room temperature to form the two stable phases.

When there is a chemical reaction in the resin and the reaction rate (R_x) is higher than R_s, phase separation may occur locally around the reacting sites as shown in *Figure 6b*. (The black dots in the figure represent the dispersed initiators.) When the initiators decompose to form free radicals, they link adjacent polyester chains together, which may result in locally UPE-rich areas where the styrene molar fraction is lower than the lower critical value. The UPE-rich area would be surrounded by a styrene-rich layer due to the mass balance. If this styrene-rich area is stable, it can prevent the migration of UPE resins in or out of the UPE-rich area. Once a particle with the above structure is formed, its size would remain constant or reduce slightly during reaction because of the intraparticle cross-linking. The macrogelation occurs through interparticle cross-linking between the pendant C=C bonds at or near the surface of the adjacent particles with styrene monomers serving as chain extenders. If the rate of formation of the particles is much higher than that of interparticle cross-linking, macro-gelation may also be reached by physical cross-linking, i.e. a phase inversion, during which particles merge from the dispersed phase to the continuous phase.

The schematic diagram shown in *Figure 6b* is more representative for highly dilute systems (i.e. low concentration of UPE) with low initiator concentration. In most commercial compounds, the local phase separation may be much more complicated. For instance, because of the high concentration of UPE resin, many local UPE-rich areas may be partially overlapped and cannot be totally separated by the styrene-rich layer. Furthermore, in a single UPE-rich area, there may be more than one polymeric radical (i.e. microgels) depending on the initiator concentration. A possible resin distribution in the cured sample is shown in *Figure 7*. The observed particle structure in the SEM micrographs represents the UPE-rich area (level 3), which may consist of many

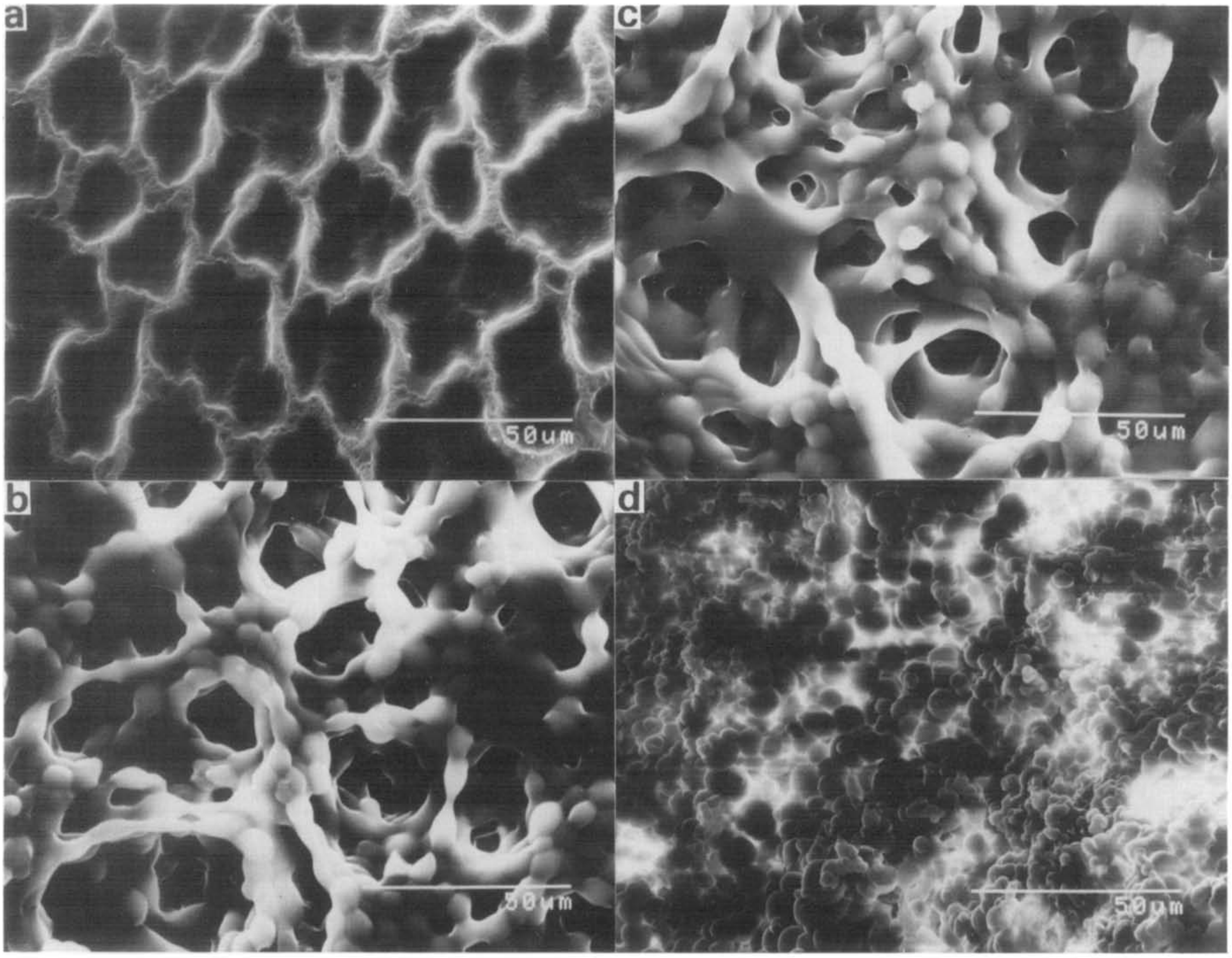

Figure 4 Scanning electron micrographs of styrene/UPE resins with $MR = 4$ (styrene molar fraction = 0.8) cured to various conversions at 30°C: (a) $G' = G''$ point; (b) 2 min; (c) 5 min; (d) 20 min after $G' = G''$

Table 3 Change in sol fraction and sol composition during cure (initial styrene molar fraction = 0.8, $MR = 4$)

	Temperature = 40°C				Temperature = 50°C		
Time (min)	9.7 ($t_{G'=G''}$)	11.7	13.7	19.7	2.9 ($t_{G'=G''}$)	3.9	4.9
Conversion (%)	1.02	1.89	2.84	6.07	0.18	0.49	1.03
Sol composition (styrene molar fraction)	0.80	0.85	0.89	0.92	0.80	0.80	0.82
Sol/gel fraction (%)							
Sol fraction	93.3	89.7	73.8	65.3	79.2	60.4	54.6
Gel fraction	6.7	10.3	26.2	34.7	20.8	39.6	45.4

polymeric radicals (i.e. microgels, level 2). This is probably why these particles are much larger than the 'expected' microgels described by other researchers[15,16].

Resins cured at other temperatures

The experimental results of reaction kinetics, rheological changes and morphological changes for the same resin cured at 40 and 50°C are shown in *Figure 8*. Like the results of the sample cured at 30°C, the major changes of G' and G'' occurred at the very beginning of the reaction, where the total resin conversion increased from 1 to 5% at 40°C and from 0.2 to 5% at 50°C. Both G' and G'' reached their plateau values when the resin conversion was ~6% at 40°C and 8% at 50°C. Unlike the resin cured at 30°C, the light intensity did not change until the reaction had reached the $G' = G''$ point. After that, the change in transmitted light intensity followed the change in reaction conversion, which is due to the formation of microparticles during the reaction.

A set of partially reacted samples was also prepared by stopping the reaction when samples were cured at 40 and 50°C (*Figure 8*). The sol fraction and sol composition of these samples are shown in *Figure 9* and *Table 3*. At 40°C, solvent treatment dissolved nearly 95% of the

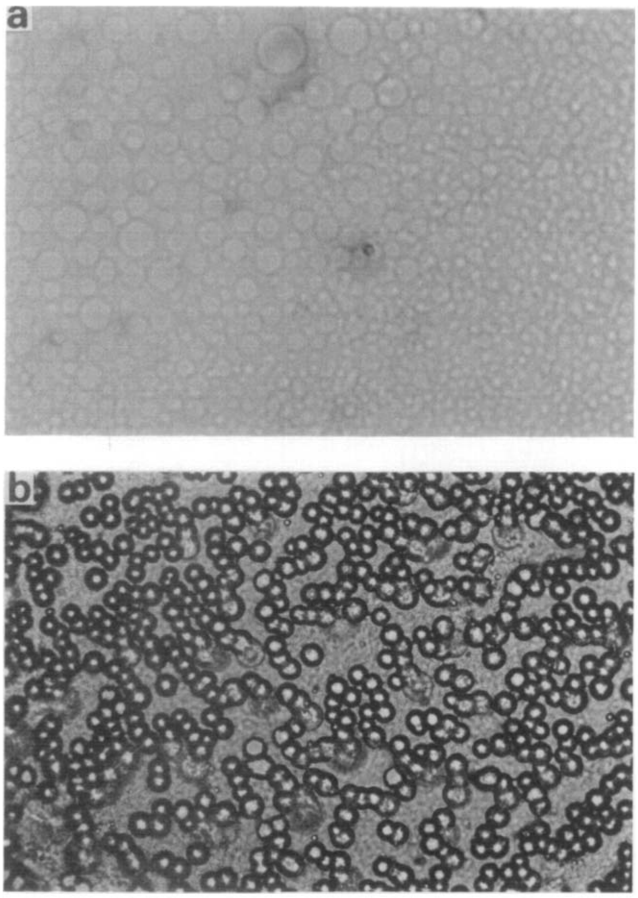

Figure 5 Optical micrographs of styrene/UPE resins with $MR=4$ (styrene molar fraction $=0.8$) cured at 30°C; (a) $G'=G''$; (b) final × ~400

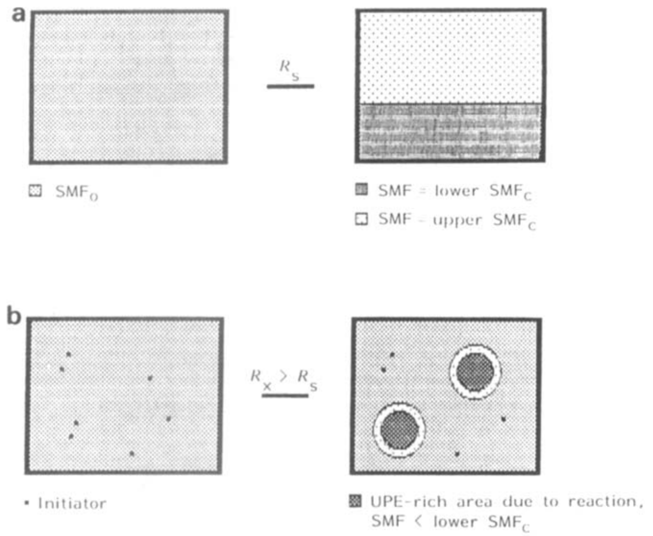

Figure 6 Schematic diagram of the microparticle formation: (a) styrene/UPE mixture without reaction (upper SMF$_c$ > SMF$_0$ > lower SMF$_c$); (b) styrene/UPE mixture with reaction (upper SMF$_c$ > SMF$_0$ > lower SMF$_c$)

sample at $G'=G''$. The sol fraction decreased rapidly after the sample reached this point as at 30°C. Again, the styrene molar fraction in sol increased during reaction because of the non-equal reactivity of styrene and polyester vinylenes. Compared to the change in transmitting light intensity, one may conclude that the styrene molar fraction of the sol fraction was in the single-phase region initially, but shifted into the two-phase region after the sample reached the $G'=G''$ point. Based on the concept of microstructure formation proposed in *Figure 6*, particles would not form until the styrene molar fraction in the sol was in the two-phase region. This is

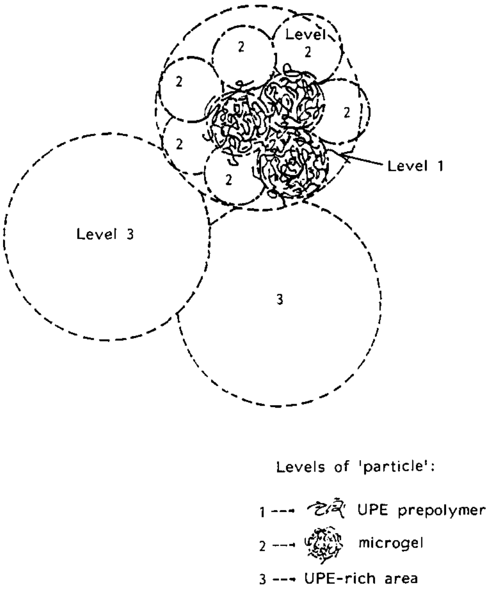

Figure 7 Schematic diagram of resin distribution in the cured sample

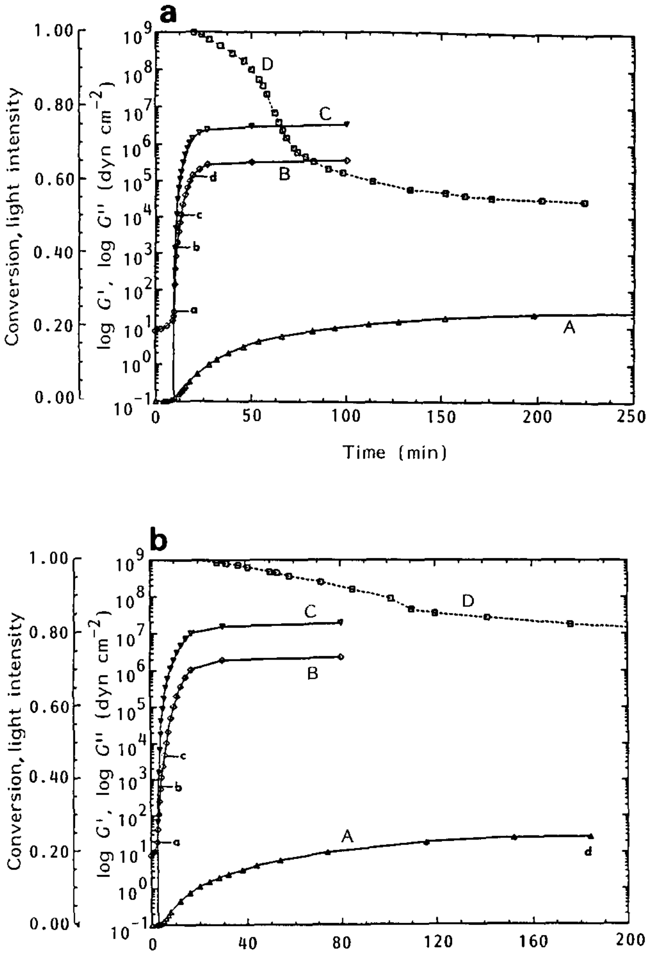

Figure 8 Comparison of conversion (A), G'' (B), G' (C) and opacity profiles (D) for the reaction of UPE resin with $MR=4$ (styrene molar fraction $=0.8$) at: (a) 40°C; (b) 50°C

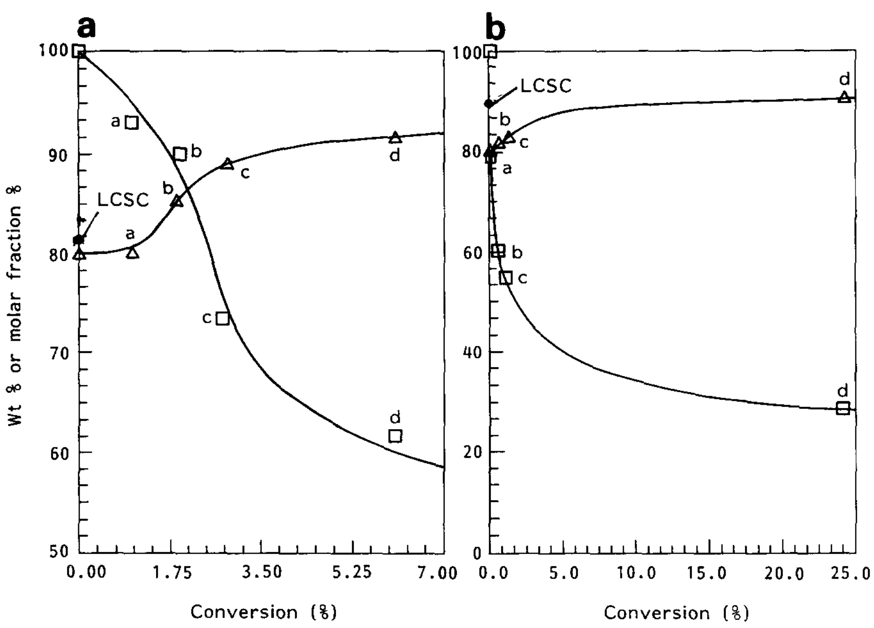

Figure 9 Change in sol fraction (□) and sol composition (Δ) of styrene/UPE resin with $MR = 4$ (styrene molar fraction = 0.8) during reaction at: (a) 40°C; (b) 50°C

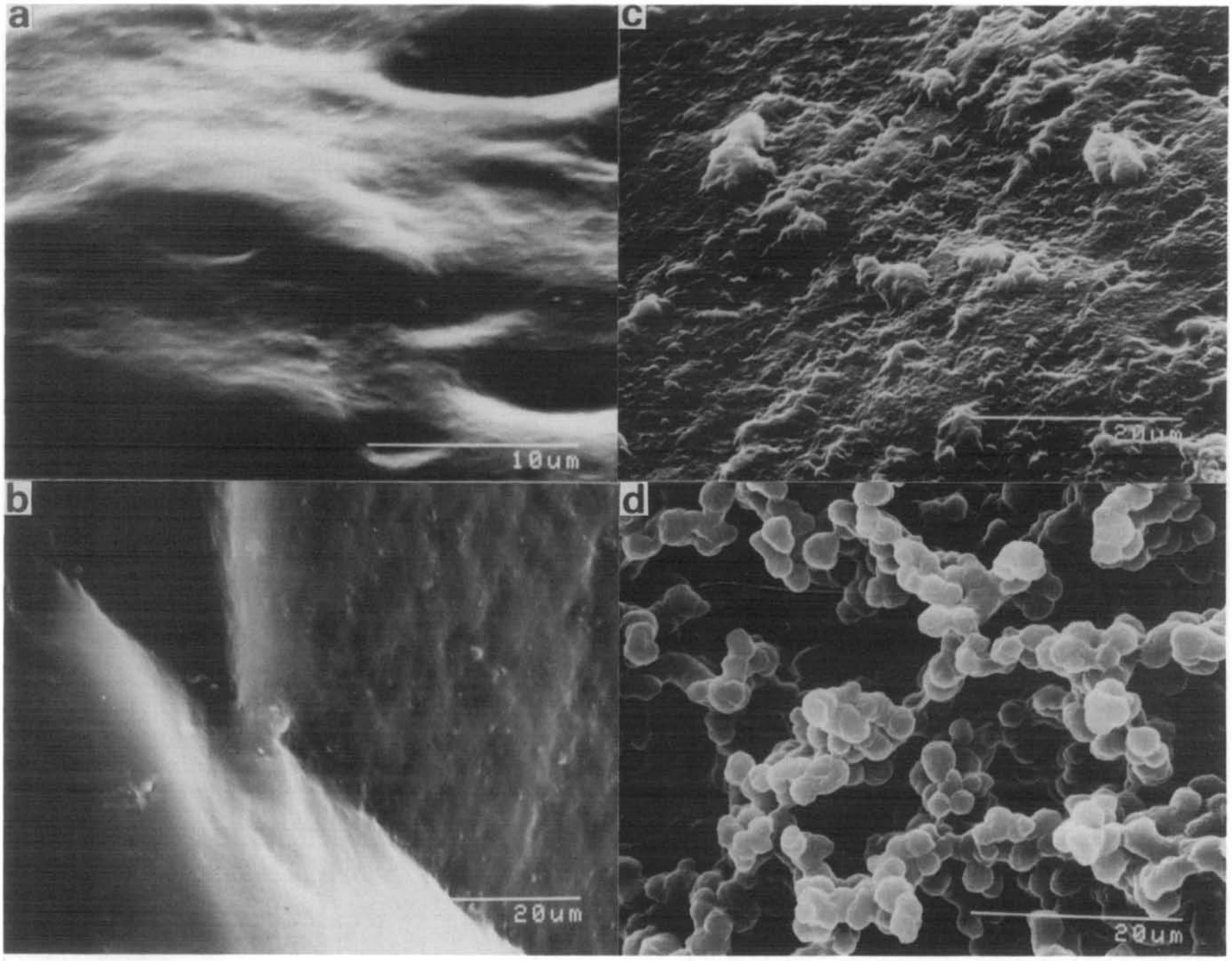

Figure 10 Scanning electron micrographs of styrene/UPE resins with $MR = 4$ (styrene molar fraction = 0.8) cured to various conversions at 40°C: (a) $G' = G''$; (b) 2 min; (c) 4 min; (d) 10 min after $G' = G''$

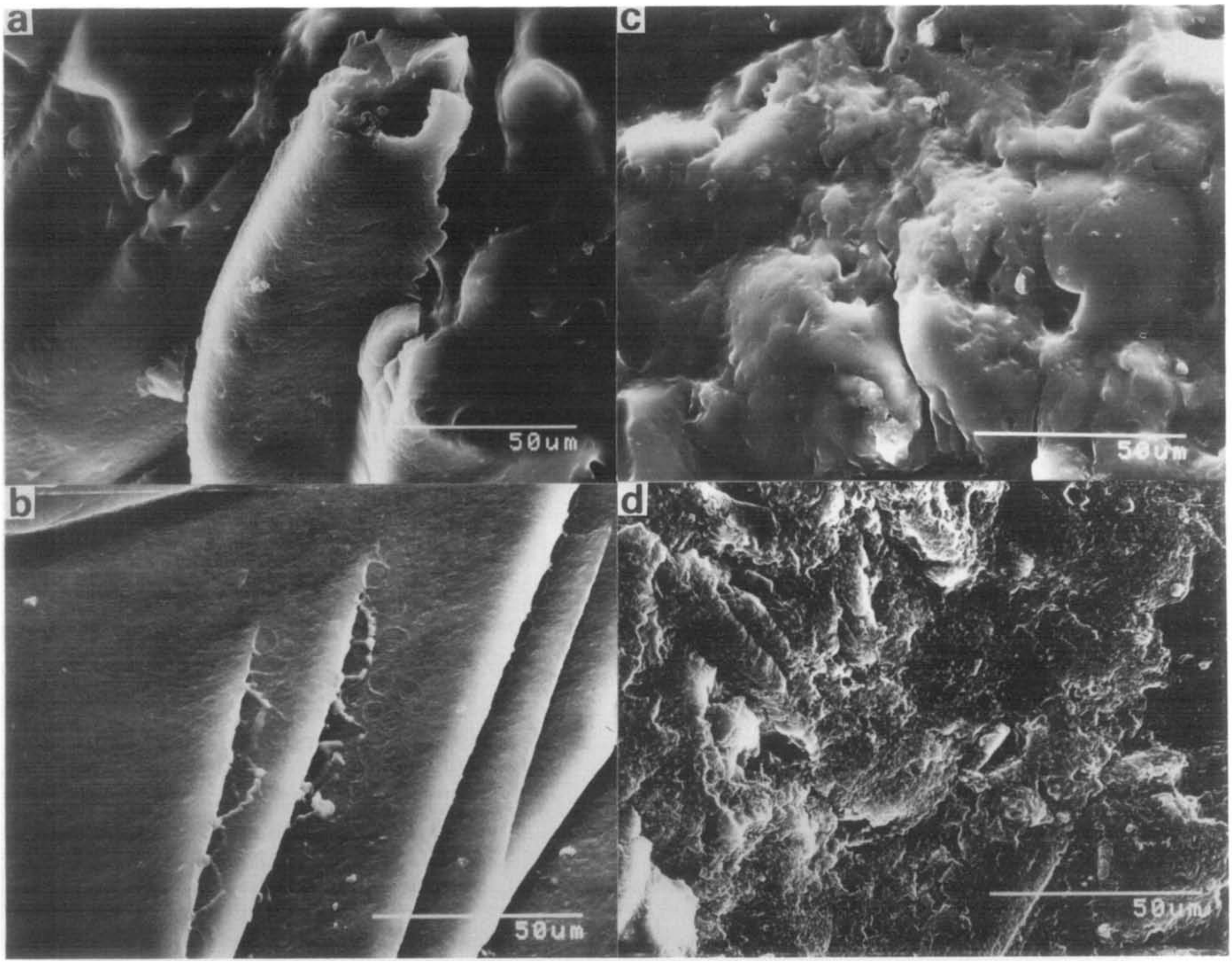

Figure 11 Scanning electron micrographs of styrene/UPE resins with $MR = 4$ (styrene molar fraction = 0.8) cured to various conversions at 50°C: (a) $G' = G''$; (b) 1 min; (c) 2 min after $G' = G''$; (d) final

the reason why the sample remained transparent after the reaction had progressed for a period of time, as shown in *Figure 8a*. At 50°C, because of the very high reaction rate, the measured sol fraction at the $G' = G''$ point was ~80%, which apparently reflected some experimental errors. The sol fraction of the sample cured at 50°C decreased sharply in the early reaction, but tended to level off at higher conversions. Transmitting light intensity showed that there was no phase separation until the conversion reached 10%.

The SEM micrographs of the gel fraction of this resin cured at 40°C at various conversion levels are shown in *Figure 10*. In *Figure 10a* the micrograph shows a flake-type morphology at the $G' = G''$ point. Small particles began to show on the sample surface as the styrene molar ratio in the sol fraction started to increase and the sample started to become opaque. More and more particles could be observed as the reaction progressed further. The micrograph of the sample cured 10 min after the $G' = G''$ point shows a 'dumb-bell'-type structure with particles covering the entire sample. The particle formation mechanism revealed in these micrographs supports the concept of microstructure formation proposed in *Figure 6*. The SEM micrographs of the gel fraction of this resin cured at 50°C at various conversion levels are shown in *Figure 11*. In *Figures 11a–c*, the micrographs show a flake-type morphology, while *Figure 11d* shows that the sample surface is not as smooth and individual particles can be found on the sample surface.

The microstructure formation during the cure of UPE resins seems to depend on the phase diagram of the sol fraction. During reaction, one would expect a continuous change of phase boundary because of the increase of polyester molecular weight through chemical reaction. For uncured resins, the phase boundary can be easily determined experimentally. Measuring the phase diagram of sol fraction however, is not a trivial task. For the resin used, g.p.c. results given in *Table 4* indicate that both number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) molecular weights of polyester molecules in the sol did

Table 4 Measured molecular weights and *MWD* of polyester molecules in sol (initial styrene molar fraction = 0.8, $MR = 4$ and $T = 40$°C)

Time (min)	0.0	9.7 ($t_{G'=G''}$)	11.7	13.7
$\bar{M}_n$ (g mol^{-1})	1580	1267	1013	1139
$\bar{M}_w$ (g mol^{-1})	5511	6955	5461	4882
MWD	3.49	5.49	5.39	4.29

not change much in the early reaction. In fact, $\bar{M}_n$ decreased slightly during the reaction. This implies that most polyester molecules which participated in the reaction were in the gel fraction and larger polyester molecules were more easily bound in the gel fraction.

Since the molecular weight of polyester molecules in the sol remained relatively unchanged during the reaction, the phase boundary of uncured resin may serve as a good indicator of microstructure formation. When the styrene molar fraction in the sol is in the single-phase region, the sample morphology is flake-like, while when the styrene molar fraction in the sol is the two-phase region, the newly formed sample structure shows particles. Experimental data in this study appear to support this argument.

CONCLUSIONS

For the styrene/UPE resin studied, microstructure formation and liquid–solid transition occurred at the very beginning of reaction, where the total conversion was $<5\%$. The transition of sample opacity followed the change in reaction conversion. Phase separation played an important role in microstructure formation. A mechanism describing the microstructure formation was proposed and was supported by the experimental results. The copolymerization of styrene and UPE resulted in spherical particles in the cured resin when the styrene molar fraction of the sol fraction was in the two-phase region, but a flake-like structure when the styrene molar fraction of the sol fraction was in the single-phase region.

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