

# Free-radical crosslinking copolymerization of styrene/unsaturated polyester resins:

## 3. Kinetics–gelation mechanism

C. P. Hsu and L. James Lee\*

Department of Chemical Engineering, The Ohio State University, Columbus, OH 43210, USA  
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Based on the results of integrated analysis given in parts 1 and 2, a kinetics–gelation mechanism of styrene (ST)/unsaturated polyester (UPE) resins is proposed. The curing process can be divided into five stages: induction, microgel formation, transition with or without phase separation, macrogelation and post-gelation. A summary of the experimental results at different stages of ST/UPE resins with ST/UPE molar ratios of 2 and 4 at 40°C is given. The kinetics–gelation mechanism based on the concept of microstructure formation is then discussed.

(Keywords: copolymerization; kinetics; gelation)

### INTRODUCTION

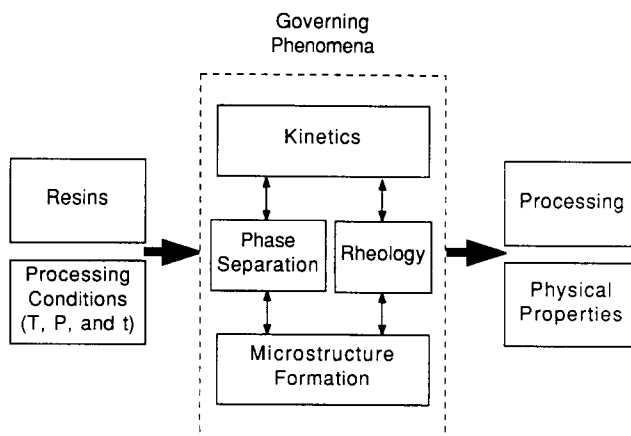
In the reactive processing of inhomogeneous thermosetting polymers such as styrene (ST)/unsaturated polyester (UPE) resins, several governing phenomena, such as reaction kinetics, phase separation, rheological changes and microstructure formation, control the polymer processibility and final product properties. A schematic diagram describing the relation between these governing phenomena is shown in *Figure 1*. Strong interactions may exist between reaction kinetics, microstructure formation and material rheology. In order to improve the design and control of the structure and, consequently, the properties of polymers formed, it is very important to have a comprehensive understanding of the interactions among these governing phenomena.

Although some reaction modelling has been carried out for free-radical chain-growth crosslinking copolymerizations, very few studies have considered the formation of inhomogeneity during reaction. Most of the modelling has been conducted for monovinyl/divinyl systems<sup>1</sup>. In general, these works can be classified into three groups: (i) copolymerization models; (ii) gelation models; and (iii) kinetics–gelation models<sup>2</sup>. The most simplified kinetic model<sup>3</sup> assumed that the divinyl monomer has equally reactive vinyl groups and the reactivity of the vinyl groups is unchanged during reaction (i.e. no substitution and molecular shielding effects).

This model has been extended to include chemically controlled termination<sup>4</sup> and diffusion-controlled termination<sup>5</sup>. Since this model did not consider the intramolecular reaction, its application in chain-growth crosslinking copolymerization is very limited. Dusek *et al.* modified this kinetic model by considering the substitution effect<sup>6</sup> and the cyclization effect<sup>7</sup>. Fink<sup>8</sup> also developed a kinetic model which included a cyclization reaction by pendent vinyls and a multiple crosslinking reaction. None of these

models, however, considered the effect of inhomogeneity on the reaction kinetics.

Most models developed so far describe either the reaction kinetics or the gel formation. The interactions of reaction kinetics and gelation have seldom been considered in these models. Mikos *et al.*<sup>2</sup> proposed a kinetics–gelation model for the ST/divinyl benzene (DVB) chain growth crosslinking copolymerization. This model was based on the method of moment. The gel point was defined as the point when the average number of effective crosslinks per chain was equal to two. There was, however, no experimental verification in their work. Recently, the percolation method<sup>9–12</sup> has also been applied for the simulation of network formation in an *n*-dimensional space to show the high extent of cyclization and inhomogeneity in the reaction system. This method is, however, inappropriate for handling time-dependent reaction paths (e.g. reaction rates)<sup>13</sup>.



**Figure 1** Schematic diagram of the relationship between governing phenomena in reactive processing of inhomogeneous thermoset polymers

\* To whom correspondence should be addressed

To model a complex reaction system such as ST/UPE crosslinking polymerization is not a trivial task. A detailed knowledge base needs to be established through in-depth experimental analysis. For the structure build-up, this includes an understanding of the formation and growth of primary microgels, the formation of multivinyl-monomer-rich phases and macrocrosslinking. For the reaction kinetics, this includes the understanding of detailed copolymerization mechanisms such as the reaction rate, composition and size of primary polymer chains (i.e. microgels), and the reaction kinetics of both intra- and interparticle reactions. In this work, we propose a physical kinetics-gelation model for ST/UPE reactions based on the results from parts 1 and 2<sup>14,15</sup>. Although the model is qualitative in nature, it should serve as a good basis for mathematic modelling in the future.

## INTEGRATED ANALYSIS

Based on the changes of electron spin resonance (e.s.r.) spectra and microstructure formation discussed in parts 1 and 2<sup>14,15</sup>, the curing process of UPE resin can be divided into five stages: induction, microgel formation, transition with or without phase separation, macrogelation and post-gelation. A list of key features occurring during the polymerization of ST/UPE resin with ST/UPE molar ratio (MR)=2 and 4 at 40°C is given in Table 1. The first reaction was without phase

separation, while the second showed a reaction-induced phase separation. A summary of the experimental data at different stages of these two representative reactions follows.

### ST/UPE resin with MR = 2 and 1.0% MEKP/COB cured at 40°C

For the reaction of ST/UPE resin with MR=2 and 1.0% methyl ethyl ketone peroxide (MEKP)/cobalt naphthenate (COB) cured at 40°C, the induction stage was the first 9.5 min, in which no polymer was formed. The e.s.r. spectrum remained unchanged with 20% UPE-end stable radicals and 80% UPE-end growing radicals. The radical concentration also remained unchanged with a value of about  $1.0 \times 10^{-6}$  M. The storage shear modulus ( $G'$ ) and loss shear modulus ( $G''$ ) remained constant. A very small reaction exotherm was observed, which was due to the initiator decomposition and inhibition reaction during this time.

As the reaction entered the microgel formation stage at a reaction time of 9.5 min, polymers with a size of 10 nm were observed. The MR value and UPE vinylene conversion of these polymers were about 0.12 and about 9%, respectively, and both values remained unchanged during this stage (9.5–20 min). The measured radical concentration started to increase at a rate of  $0-1.2 \times 10^{-7}$  M min<sup>-1</sup> from  $1.0 \times 10^{-6}$  to  $1.8 \times 10^{-6}$  M. The e.s.r. spectrum showed that the UPE-end stable radicals increased from 20% during the induction stage to

Table 1 Key features of ST/UPE polymerizations

Stage	MR = 2, at 40°C	MR = 4, at 40°C
Induction	0–9.5 min No polymer formation No e.s.r. spectrum change: 20% UPE-end stable radicals and 80% UPE-end growing radicals No radical conc. change: [R*] = $1.0 \times 10^{-6}$ M No rheological change No reaction exotherm	0–6.5 min No polymer formation No e.s.r. spectrum change: 40% UPE-end stable radical and 60% UPE-end growing radicals No radical conc. change: [R*] = $1.0 \times 10^{-6}$ M No rheological change No reaction exotherm
Microgel formation	9.5–20 min Presence of microgels with size = 10 nm Change of e.s.r. spectrum to 82% UPE-end stable radicals Increase of radical conc. to $1.8 \times 10^{-6}$ M No measurable rheological change Very small reaction exotherm, 0.5% of total exotherm	6.5–9.2 min Presence of microgels with size = 14 nm Change of e.s.r. spectrum to 70% UPE-end stable radicals Increase of radical conc. to $1.2 \times 10^{-6}$ M No measurable rheological change Very small reaction exotherm, 0.6% of total exotherm
Transition	20–23.2 min Formation of clusters with size = 30 nm Change of e.s.r. spectrum to 90% UPE-end stable radicals Increase of radical conc. to $2.2 \times 10^{-6}$ M No phase separation Increase of $G'$ Small reaction exotherm, 1.0% of total exotherm	9.2–17 min Formation of clusters with size = 93 nm Change of e.s.r. spectrum to 95% UPE-end stable radicals Increase of radical conc. to $2.2 \times 10^{-6}$ M $G'$ unchanged at the beginning of phase separation, but increased at a reaction time of around 15 min Small reaction exotherm, 1.5% of total exotherm
Macrogelation	23.2 min Clusters with size = 30 and 106 nm in sol fraction 7.0% gel fraction $G' = G''$ Start of major reaction exotherm	17 min Clusters with size = 31 and 110 nm in sol fraction 6.7% gel fraction $G' = G''$ Start of major reaction exotherm
Post-gelation	Presence of ST-end radicals Increase of radical conc. at a rate of $1.4 \times 10^{-7}$ M min <sup>-1</sup> Presence of major reaction exotherm	Presence of ST-end radicals Increase of radical conc. at a rate of $1.27 \times 10^{-7}$ M min <sup>-1</sup> Presence of major reaction exotherm

82% at the reaction time of 20 min. Both  $G'$  and  $G''$  changed little during this stage. A very small reaction exotherm was observed ( $\sim 0.5\%$  of the total isothermal reaction exotherm) during this stage.

The reacting resin system entered the transition stage at a reaction time of around 20 min; slightly larger polymers with an average size of 12 nm and polymer clusters with an average size of 30 nm were found at a reaction time of 20.7 min. The MR and UPE vinylene conversion of these polymers were 0.13 and 12.3%, respectively. Compared with the MR and vinylene conversion of polymers in the microgel formation stage, some intramolecular reaction had occurred. The radical concentration increased at a rate of  $1.2 \times 10^{-7}$ – $1.4 \times 10^{-7} \text{ M min}^{-1}$  from  $1.8 \times 10^{-6}$  to  $2.2 \times 10^{-6} \text{ M}$ . The e.s.r. spectrum showed a change from 82 to 90% UPE-end stable radicals during the transition stage (i.e.  $\sim 20$ – $23$  min).  $G'$  and  $G''$  started to increase at a reaction time of about 21 min. The reaction exotherm showed that about 1.0% of the isothermal reaction exotherm was observed at the end of this stage.

When the  $G''$  value became the same as the  $G'$  value, it was assumed that the resin system reached its gel point (reaction time  $\sim 23.3$  min). About 7.0% gel fraction was found at this point. In the sol fraction, no isolated primary polymers could be observed. Instead, primary polymers coagulated into two groups of clusters with average sizes of 30 and 106 nm, respectively. The MR and UPE vinylene conversion of polymers were 0.14 and 12.2%, respectively. The radical concentration increased at a constant rate of  $1.4 \times 10^{-7} \text{ M min}^{-1}$ , which was the same as that in the transition stage, to a value of  $2.2 \times 10^{-6} \text{ M}$ . The e.s.r. spectrum showed 90% UPE-end stable radicals at the gel point. The overall monomer conversion was about 2% at the gel point.

As the resin system entered the post-gelation stage, the radical concentration increased at a rate of  $1.4 \times 10^{-7} \text{ M min}^{-1}$ , then gradually levelled off at the end of reaction. The ST-end stable radicals appeared in this

stage and dominated the radical population at the end of reaction. The major reaction exotherm also appeared in this stage. Figure 2 compares the changes of conversion, radical concentration, and  $G'$  during the cure of ST/UPE resin with MR=2 and 1.0% MEKP/COB at 40°C.

#### ST/UPE resin with MR=4 and 0.8% MEKP/COB cured at 40°C

For the reaction of ST/UPE resin with MR=4 and 0.8% MEKP/COB cured at 40°C, the reaction-induced phase separation occurred at a reaction time of about 9 min because of limited compatibility of ST, UPE resin and formed polymer<sup>16</sup>. From the change in e.s.r. spectrum and dynamic light scattering (d.l.s.) measurements, the induction stage was during the first 6.5 min of the reaction. The e.s.r. spectrum showed a mixture of 40% UPE-end stable radicals and 60% UPE-end growing radicals in this stage. The radical concentration was again about  $1.0 \times 10^{-6} \text{ M}$  throughout the induction stage. Values of  $G'$  and  $G''$  remained constant during this stage. A very small reaction exotherm was observed, which was due to the initiator decomposition and inhibition reaction during this time period.

As the reaction entered the microgel formation stage at a reaction time of 6.9 min, polymers with a size of 14 nm were observed. The MR and UPE vinylene conversion of these polymers were 0.16 and 14.1%, respectively, and both values remained unchanged until the transition stage. The e.s.r. spectrum started to change at a reaction time of 6.6 min. The e.s.r. spectrum showed that the UPE-end stable radicals increased from 40% during the induction stage to 70% at a reaction time of 9.2 min. Near the end of this stage, the measured radical concentration increased slightly at a rate of  $0$ – $5.6 \times 10^{-8} \text{ M min}^{-1}$  from  $1.0 \times 10^{-6}$  to  $1.2 \times 10^{-6} \text{ M}$ . Values of  $G'$  and  $G''$  changed little during this stage. A small reaction exotherm, about 0.6% of the total isothermal reaction exotherm, was observed at the end of this stage.

Phase separation occurred at a reaction time of around 9.2 min, with a UPE-rich domain size of  $2 \mu\text{m}$ . As the reaction progressed, more dispersed domains were formed but the size remained nearly the same. The phase separation process ended at the gel point. No isolated polymers could be found during this stage. Instead, formed polymers coagulated into two groups of clusters with average sizes of 24 and 93 nm, respectively. The radical concentration increased at a rate of  $5.6 \times 10^{-8}$ – $1.92 \times 10^{-7} \text{ M min}^{-1}$  from  $1.2 \times 10^{-6} \text{ M}$  to  $2.2 \times 10^{-6} \text{ M}$ . The e.s.r. spectrum showed a quick change from 70 to 80% UPE-end stable radicals during the reaction time from 10 to 10.4 min. At the end of the transition stage, the e.s.r. spectrum showed nearly 95% UPE-end stable radicals. The MR and UPE vinylene conversion of these clusters were 0.16 and 14.7%, respectively, at a reaction time of 10.4 min. As the reaction progressed, both MR (0.248) and UPE vinylene conversion (19.5%) increased, as measured at the reaction time of 13.9 min. This implied that a substantial amount of intramolecular reaction had occurred. The  $G''$  value started to increase sharply at a reaction time of 15 min. The reaction exotherm showed nearly 1.5% of the total isothermal reaction exotherm at a reaction time of 13.9 min.

As the resin system reached its gel point (reaction time  $\approx 17$  min), the MR and UPE vinylene conversion of

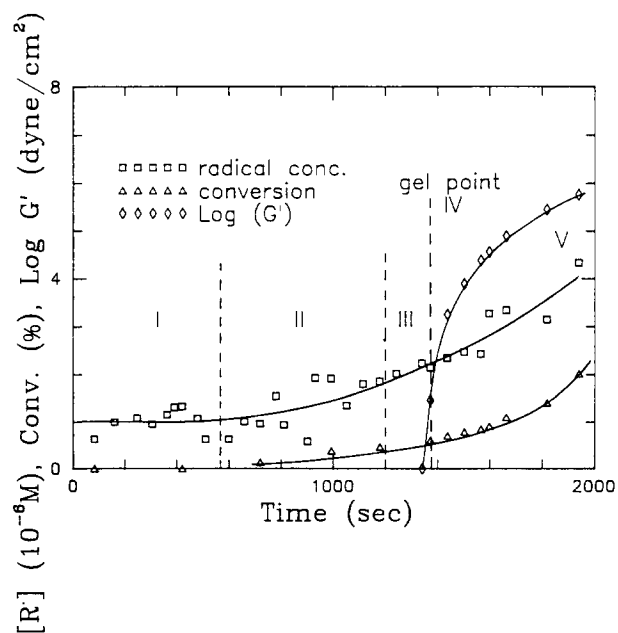
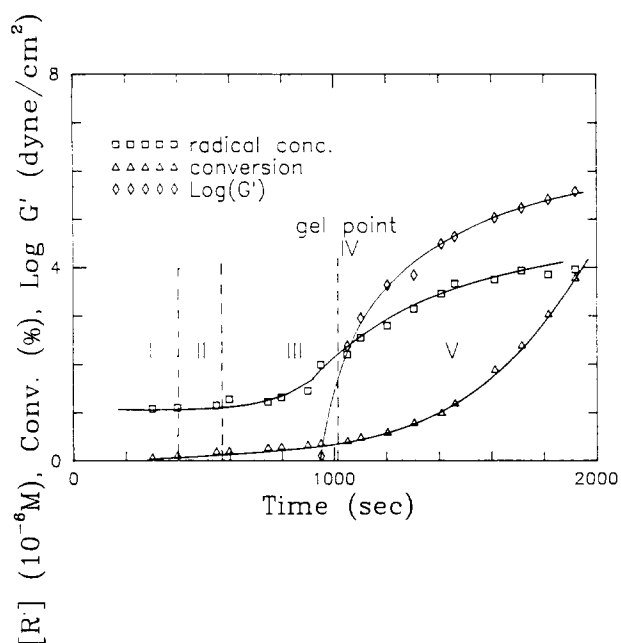


Figure 2 Radical concentration, conversion, and  $\log(G')$  versus reaction time for ST/UPE resins with MR=2 and 1.0% MEKP/COB cured at 40°C



**Figure 3** Radical concentration, conversion, and  $\log(G')$  versus reaction time for ST/UPE resins with MR=4 and 0.8% MEKP/COB cured at 40°C

polymers were 0.255 and 19.2%, respectively. The d.l.s. measurement showed that two particle groups, with sizes of 31 and 110 nm, were present. The radical concentration increased at a constant rate of  $1.27 \times 10^{-7} \text{ M min}^{-1}$ , which was less than that in the phase separation stage. The radical concentration was  $2.2 \times 10^{-6} \text{ M}$  at this moment. The e.s.r. spectrum showed 95% UPE-end stable radicals at a reaction time of 16 min. The reaction exotherm showed that it had entered the early stage of the major reaction exotherm. The reaction exotherm showed nearly 2.3% of the total isothermal reaction exotherm at a reaction time of 16.7 min.

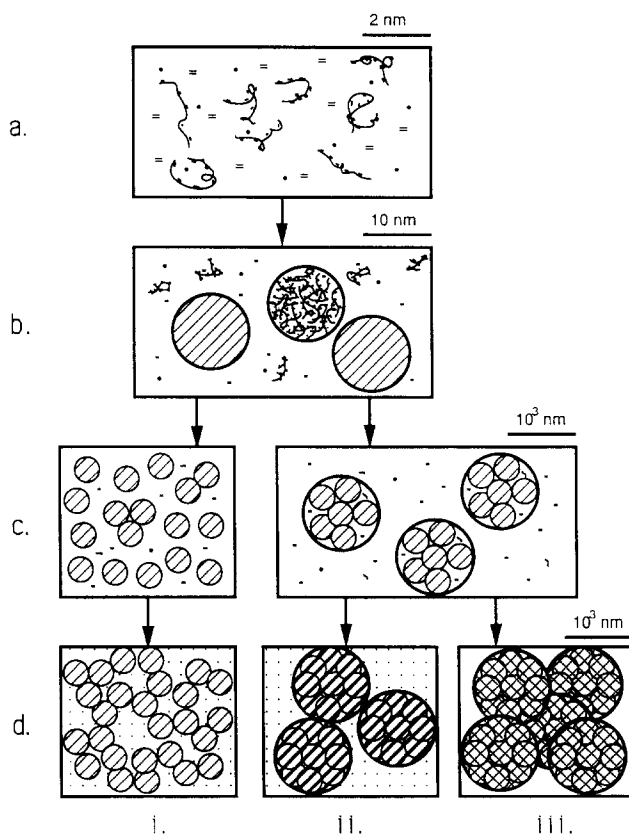
As the resin system entered the post-gelation stage, the radical concentration increased at a rate of  $1.27 \times 10^{-7} \text{ M min}^{-1}$ , then gradually levelled off at the end of reaction. The ST-end stable radicals appeared during this stage and dominated the radical population at the end of reaction. The major reaction exotherm also appeared during this stage. *Figure 3* compares the changes of conversion, radical concentration and  $G'$  during the cure of ST/UPE resin with MR=4 and 0.8% MEKP/COB at 40°C.

#### KINETIC-GELATION MECHANISM

According to the experimental results summarized in the previous section, we can conclude that the curing process of ST/UPE resins can be divided into five stages: induction, microgel formation, transition with or without phase separation, macrogelation and post-gelation. A schematic diagram describing the first four stages is given in *Figure 4*. In the induction stage, initiators decomposed and reacted with monomer to form monomeric radical. Since no primary polymers were found in this stage, the propagation reaction did not occur among monomeric radicals and monomers, probably due to the inhibition effect. In the microgel formation stage, radicals linked adjacent UPEs and STs to form primary polymers (microgels). The composition and conversion of these

microgels stayed nearly the same throughout the entire stage. In the transition stage, intermolecular reaction occurred among microgels to form larger clusters. Phase separation could occur in this stage due to the changes of resin composition and phase boundary. If there were no phase separation, both microgels and clusters could be found in this stage. For resin systems with phase separation, phase separation started at this stage and ended at the gel point. Dispersed UPE-rich domains with size around  $2 \mu\text{m}$  were formed. When the reaction progressed, more domains were formed and were connected with each other to form a co-continuous structure. The domain size, however, remained largely unchanged. The size and structure of microgels changed after the onset of phase separation. Only large microgel clusters could be found at this stage and a substantial extent of intramolecular crosslinking occurred in the clusters. At the gel point, a crosslinking network was formed through either the intermolecular reaction among microgels, microgel clusters or dispersed UPE-rich domains as shown in *Figures 4di* and *ii*. For systems with very strong phase separation and low interphase reaction rate, such as in the presence of low profile additives<sup>16</sup>, macrogelation could occur through the phase inversion (i.e. physical crosslinking) process as shown in *Figure 4diii*.

A schematic diagram combining important characteristics such as radical concentration, radical species, structure formation, reaction conversion and rheological changes is shown in *Figure 5*. Generally speaking, radical concentration and rheological properties of the resin system remained unchanged during the induction stage.



**Figure 4** Schematic diagram of kinetics-gelation mechanism for ST/UPE resins: (a) induction stage; (b) microgel formation stage; (c) transition stage (with/without phase separation); (d) macro-gelation stage (i and ii, chemical cross-linking; iii, physical cross-linking, i.e. phase inversion)

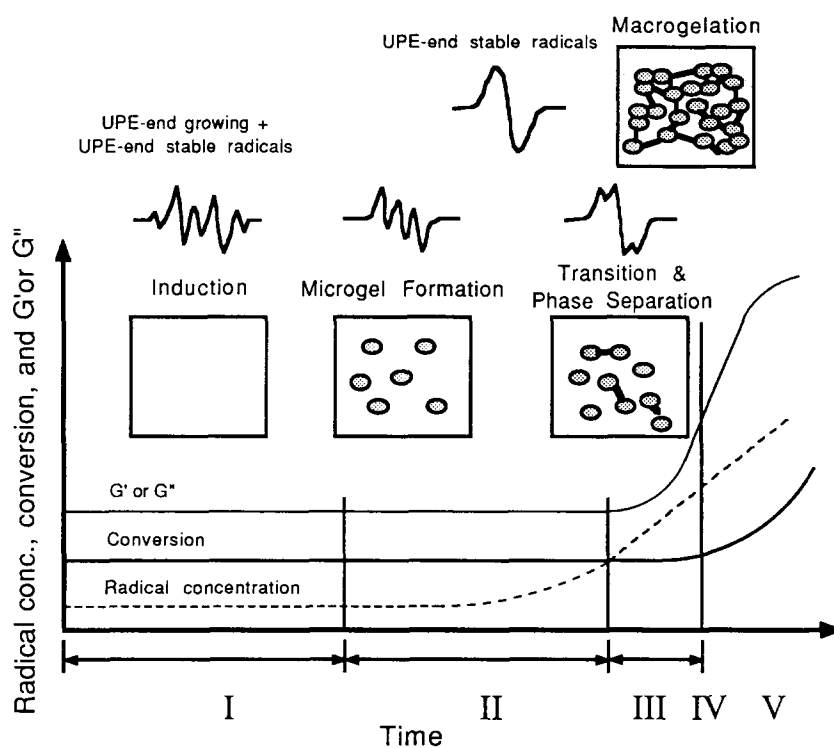


Figure 5 Changes of radicals, conversion,  $G'$  and  $G''$  during reaction: I, induction; II, microgel formation; III, transition; IV, macrogelation; V, post-gelation

As the resin system entered the microgel formation stage, the radical concentration started to increase, but the rheological properties remained nearly the same.  $G''$  started to increase as the resin system reached the transition stage. The major reaction exotherm did not occur until the resin system reached or passed its gel point. A detailed description of the reaction mechanism for ST/UPE resins follows.

#### Induction stage

The induction stage is caused by the presence of inhibitor which consumes the radicals generated by initiators. Because of the high reaction rate constant between the radical and the inhibitor, propagation of radicals is suppressed by the inhibition effect. Several key characteristics in the induction stage can be summarized from the experimental measurements or known polymerization theories.

1. Radical concentration remained at a constant value because of the balance between radical generation and inhibition effect. The e.s.r. spectrum remained the same where most radicals were UPE-end growing radicals with a small amount of UPE-end stable radicals<sup>15</sup>. A possible mechanism is that free radicals formed from initiator decomposition might react with both ST and UPE monomers to form monomeric radicals. Among them, the ST-type monomeric radicals could be quickly terminated by the inhibitor, while the UPE-type monomeric radicals have a longer lifetime because of the molecular shielding effect. Some of the UPE-type monomeric radicals might transform to a more stable radical structure through internal hydrogen transfer.
2. The reaction exotherm was negligible<sup>14</sup> except for initiator decomposition.

#### Primary polymer (microgel) formation stage

As the amount of inhibitor was reduced to a very low level at the end of the induction period, monomeric radicals gained the chance to link with adjacent monomers and form primary polymers. The radical concentration started to increase gradually and reached a constant rate because of the formation of stable radicals during the microgel formation stage. The key characteristics in the microgel formation stage include the following.

1. The e.s.r. spectrum started to change from more UPE-end growing radicals towards more UPE-end stable radicals, and the radical concentration also started to increase. In other words, once the growing radicals had linked to other monomers through chain reaction and formed primary polymers, these radicals were either terminated or transformed into more stable radicals. The increase of radical concentration was due to the formation of stable radicals because the stable radicals had a longer lifetime than the growing radicals<sup>15</sup>.
2. Primary polymers (microgels) with a size of around 10 nm could be observed. Since each UPE monomer has a size of around 1 nm, a primary polymer should have a degree of polymerization of around 1000. Compared with the measured radical concentration and radical structure, we can conclude that the reactivity of the propagating radical decreased when more UPE molecules were added to the polymer chain and some intramolecular crosslinking occurred. Eventually, the growing molecular shielding effect reduced the reactivity of the radical to a point at which it could transfer to a more stable UPE-end stable radical through internal hydrogen transfer, rather than connect to more monomers. This 'radical trapping'

process determined the size of the formed polymer. The microgels can be described as weakly crosslinked networks<sup>14</sup>.

- (a) The UPE vinylene conversion of microgels was near 10% for resin with MR=2 and 14% for resin with MR=4. Because there were an average of 10 vinylene groups on each UPE monomer chain, the experimental data implied that each UPE monomer was connected through one ST monomer to form the microgel. The UPE vinylene conversion of microgels indicated that a small amount of primary intramolecular crosslinking occurred when polymers were formed, but most pendent vinylenes were unreacted. The ST/UPE molar ratio of microgels remained the same until the resin system entered the next stage (transition and phase separation)<sup>14</sup>.
- (b) The polymer size and size expansion coefficient did not change too much during this stage. In other words, the crosslinking density of primary polymers remained about the same and few secondary intramolecular and interparticle reactions occurred during this period. The major reaction during this stage was the formation of more primary polymers with the same size and structure. This phenomenon can be explained by the fact that the newly formed radicals were more likely to react with free ST and UPE monomers to form microgels than to react with the pendent vinylenes on the polymer chain, because of the lower reactivity of the pendent vinylenes.
3. No significant rheological changes could be measured by the rheometer used.
4. A reaction exotherm could be observed, but it was very small compared to the major reaction exotherm.

#### Transition and phase separation stage

During the transition stage, microgels started to coagulate through the interparticle reaction. In this stage, the number of microgels reached a high level and the amount of unreacted UPE monomers decreased to such a level that the ratio between pendent vinylenes and unreacted UPE monomers was very high. Consequently, pendent vinylene groups of microgels started to react with other microgels. For resin systems with and without phase separation during polymerization, the mechanism of the transition stage was different. If the resin system had phase separation during reaction, the transition period was longer (see *Figure 3*). If the resin system had no phase separation during reaction, the transition period was much shorter (see *Figure 2*). The key characteristics of the transition stage for resin systems with and without phase separation are as follows.

#### A. Systems without phase separation

1. Radical concentration increased at a constant rate until the resin system passed its gel point. E.s.r. spectra changed from more solid-like (UPE-end stable radicals) to totally UPE-end stable radicals as the resin system reached the gel point.
2. Large microgel clusters started to form due to the interparticle reaction between microgels, and the relative amount of cluster increased. The microgel cluster had a smaller size expansion coefficient near the gel point compared to the original microgels, due to the secondary intramolecular reaction. The UPE

vinylene conversion and MR of formed particles increased to a higher value, which also indicated the secondary intramolecular reaction during this stage.

3. Both  $G'$  and  $G''$  started to increase at the beginning of the transition stage. The transition stage was very short and started very close to the  $G'=G''$  point. A possible explanation is that the increase in shear moduli was due to the connection of microgels through intermolecular reaction. This reaction could not occur until the number of microgels reached a high level. Therefore, the microgel formation stage was long and the transition stage was short and occurred very close to the gel point, as shown in *Figure 2*.
4. The reaction rate started to increase and the system entered the early stage of major reaction exotherm.

#### B. Systems with phase separation

1. Phase separation occurred after the microgel formation stage because the formation of microgels shifted the resin system from the one-phase region to the two-phase region. The phase separation in the ST/UPE resin system resulted<sup>17</sup> in a ST-rich phase with MR greater than 40 and a UPE-rich phase with MR near 2.5. The phase separation process stopped when the whole system reached the gel point. The relative refractive index between the UPE-rich phase and the ST-rich phase changed due to the polymerization in each phase.
  - (a) Radical concentration increased at a constant rate until the resin system passed its gel point. After that the radical concentration increased at a lower rate.
  - (b) After phase separation occurred, e.s.r. spectra showed that the rate of transition of UPE-end growing radicals to UPE-end stable radicals became higher than that during the microgel formation stage. The changes of the e.s.r. spectrum mainly reflected changes inside the UPE-rich phase. This result indicates that the reaction rates of the UPE-rich and ST-rich phases were different. The UPE-rich phase had a higher reaction rate than the ST-rich phase, which resulted in a higher transition rate of UPE-end stable radicals.
2. Both microgels and larger microgel clusters existed, and the relative amount of clusters increased. The microgel clusters had a larger size expansion coefficient when they first formed, which indicates that the connection between microgels was loose at this time. The average MR increased and the size expansion coefficient of the microgel clusters decreased as the reaction progressed. Apparently both inter- and intraparticle reactions occurred in the microgel clusters.
3. Values of  $G'$  and  $G''$  did not change at the beginning of phase separation since the UPE-rich phase was the dispersed phase after phase separation. The measured  $G'$  and  $G''$  values reflected mainly the properties of the continuous phase, i.e. ST-rich phase. Values of both  $G'$  and  $G''$  increased near the gel point.
4. The reaction exotherm increased gradually and the system entered the early stage of major reaction exotherm.

#### Macrogelation stage

As the polymerization progressed, more and more microgels formed and the resin system reached the gel

point when a polymer network was formed through either chemical or physical crosslinking. The key characteristics of polymerization in this stage are as follows.

- (a) Radical concentration increased at a constant rate as in the transition stage for resin systems without phase separation, but at a lower constant rate than in the transition stage for resin systems with phase separation. The radical concentration at the  $G' = G''$  point for resins cured at the same temperature had a similar value ( $\sim 2.2 \times 10^{-6}$  M). However, for resins with strong phase separation (i.e. MR=4, 30°C), the radical concentration at the  $G' = G''$  point was higher. This was due to the unequal initiator distribution and monomer reactivity among various phases.
- (b) For systems without phase separation, the e.s.r. spectra turned into UPE-end stable radicals at about the same time as the system reached the  $G' = G''$  point. For systems with phase separation, the e.s.r. spectra became totally UPE-end stable radicals before the  $G' = G''$  point. This is because the UPE-rich phase gelled before the entire system gelled. The gel fraction of resin systems used in this study was less than 10%, therefore we can conclude that chemical crosslinking dominated the transition process. However, for resin systems with low profile additives, it has been found<sup>17</sup> that the gel fraction around the gel point is greater than 50%. For these systems, it appears that physical crosslinking plays a major role.
2. Very few individual microgels existed in the resin system. Most microgels had been coagulated to larger clusters. The MR and vinylene conversion of polymers increased due to the intraparticle reaction.
3. Both  $G'$  and  $G''$  increased dramatically.
4. A major reaction exotherm started to show up. For resins with strong phase separation, conversion at the  $G' = G''$  point was larger than that for resins without phase separation, which is again due to the unequal initiator distribution and monomer reactivity among various phases.

#### Post-gelation stage

The radical concentration increased at a constant rate at the beginning of the post-gelation stage then gradually levelled off at the end of reaction. The final radical concentration depended on the crosslinking density of the resin system. The ST-end stable radicals appeared during this stage and dominated the radical population at the end of reaction. The radical concentration of cured sample decreased by around 5% after 1 month of storage for UPE resins without phase separation. For UPE resins with phase separation, the decrease of radical concentration was about 20%. The major reaction exotherm also appeared in this stage. The final conversion of resin systems cured at room temperature range was around 30%, and the conversion after post-cure could increase to over 70%. Both  $G'$  and  $G''$  increased dramatically at the beginning of the post-gelation stage then gradually levelled off at the end of reaction.

#### CONCLUSIONS

Most of the structure formation and rheological changes occurred at the very beginning of reaction for free-radical

crosslinking polymerizations, which made a correlation between property changes and resin conversion impractical. Radical concentration served as an important parameter, which correlated structure formation and reaction kinetics very well.

The reaction mechanism described in this paper was based on many experimental results. The curing process of ST/UPE resin before macrogelation can be described in four stages: induction, microgel formation, transition with or without phase separation and macrogelation. An important observation is that microgels form first, then a network is formed through the intermolecular reaction of these microgels. A similar reaction mechanism was proposed by Hild and Okasha<sup>18,19</sup> for the copolymerization of ST/DVB system. 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 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 results in an increase of the reaction of pendent vinyls and the formation of a polymer network.

The primary polymers formed at the beginning of the ST/UPE polymerization had sizes in the submicrometre range and had characteristics similar to a loosely linked network. Dusek *et al.*<sup>20</sup> proposed that, at the early stage of the reaction of multifunctional polymeric systems, the occurrence of cyclization resulted in primary polymers with internal crosslinking and rigid structures such as permanent shape, surface area and solubility. Many pendent vinyls were buried in the core of the microgels and showed a reduced or completely suppressed reactivity. The experimental data described in parts 1 and 2<sup>14,15</sup> support such a concept.

A possible mechanism for the copolymerization of methyl methacrylate/*p*-DVB was proposed by Ishizu *et al.*<sup>21</sup> from experimental results. They stated that at the beginning of copolymerization, primary polymers were formed through intermolecular and intramolecular crosslinking reactions. The intramolecular crosslinking reaction became the major reaction until the compactness of microgel particles stopped any further intraparticle cyclization. Macrogelation was observed when crosslinking occurred between adjacent microgel particles<sup>22</sup>. In the ST/UPE system, the reaction mechanism agreed with that proposed by Ishizu *et al.* in general. However, the primary intramolecular reaction stopped after the microgels formed. The secondary intramolecular reaction did not occur until the resin system entered the transition stage.

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