

Free-radical crosslinking copolymerization of styrene/unsaturated polyester resins: 2. Electron spin resonance study

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Electron spin resonance (e.s.r.) spectroscopy provided useful information regarding the nature of propagating radicals and the radical concentration during the free-radical copolymerization of styrene (ST)/unsaturated polyester (UPE) resins. The hyperfine structure of the spectrum showed that there were three types of radicals in the ST/UPE copolymerization at low temperatures. Changes of these radical species were determined by the e.s.r. spectrum simulation method. The behaviour of trapped radicals formed during polymerization was also examined by temperature scanning.

(Keywords: copolymerization; free radicals; electron spin resonance)

INTRODUCTION

The copolymerization between styrene (ST) and unsaturated polyester (UPE) is a heterogeneous free-radical chain-growth crosslinking reaction. Yang and Lee¹ measured the relative reaction rate of ST vinyl and polyester vinylene groups by FTi.r. At low conversions, they found that the reaction of polyester vinylene C=C bonds was favoured over the ST vinyl reaction, especially for samples showing a particulate structure. This result indicated that intramolecular reaction played a major role in the polymerization.

Because free radicals are generated during polymerization, electron spin resonance (e.s.r.) spectroscopy can be applied². E.s.r. spectroscopy can trace the behaviour of unpaired electrons. The measured total intensity of the absorption line reflects directly the number of paramagnetic species in the sample. The hyperfine splitting constant and the *g*-value of the spectrum make it possible to analyse the detailed structure of the paramagnetic species^{3,4}. The line-shape of the spectrum is sensitive to the electron distribution, molecular orientation, molecular motion of the paramagnetic species and the nature of their environment⁵⁻⁷. In principle, e.s.r. spectroscopy can measure directly the structure, the electron state and the concentration of propagating radicals. In the study of the radical polymerization of vinyl compounds, e.s.r. spectroscopy is capable of determining the propagation rate constant and the nature of propagating radicals.

The traditional method used in e.s.r. studies is to freeze samples with liquid nitrogen and then to measure the radical concentration and spectra in the frozen condition. With improvements in hardware and software, on-line measurements of radical concentration and the spectrum have become possible. The transition from liquid-state

to solid-state can also be detected from the change of radical spectra⁸⁻¹¹.

Most studies of free-radical polymerizations by e.s.r. have focused on determination of the kinetic parameters of linear systems where quasi-steady-state hypothesis is valid¹²⁻¹⁷. The propagation rate constant K_p and the termination rate constant K_t were determined from the polymerization rate measured from kinetic experiments and the radical concentration measured by e.s.r. For non-linear reaction systems, the bulk free-radical copolymerization of methyl methacrylate and ethylene glycol dimethacrylate was investigated by Zhu *et al.* using on-line e.s.r. spectroscopy^{10,18,19}. They found that radicals were trapped during the polymerization, and the propagation rate constant K_p decreased as the radical concentration increased. Therefore, the quasi-steady-state hypothesis was no longer valid for systems at high levels of crosslinking.

Kloosterboer *et al.*²⁰⁻²² also studied the trapped radicals in photo-initiated polymerization using e.s.r. spectroscopy. They stated that the trapped radicals had a mid-chain instead of a chain-end structure, which prevented the termination of radicals. A similar structure of trapped radicals was reported by Liang *et al.*²³, where poly(*n*-butyl acrylate) was exposed under a mercury lamp to produce radicals. Polymerization of UPE resins was performed by Zheng *et al.*²⁴ using e.s.r. They compared the polymerization with two redox initiator systems: cobalt naphthalate (CoN)/1-hydroxycyclohexyl hydroperoxide (HCH) and dimethylaniline (DMA)/benzoyl peroxide (BPO). The polymer radicals formed with CoN/HCH lived longer than those formed with DMA/BPO, and the crosslinking efficiency of CoN/HCH was better than that of DMA/BPO. These results suggested that the stability of the trapped radicals was related to the degree of crosslinking.

In this study, e.s.r. spectroscopy was used to monitor the changes of radical concentration and radical species

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Table 1 Composition of the samples

| ST/UPE molar ratio | Ingredients (parts by weight) | | |
|-----------------------|-------------------------------|------|-----------|
| | UPE | ST | MEKP/COB |
| 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 |
| 8 | 24.3 | 75.7 | 1.0/0.25 |

during the cure of ST/UPE resins. The radical species formed during the reaction and their ratio were determined by the e.s.r. spectrum simulation method. The behaviour of trapped radicals inside cured ST/UPE resins was also investigated by e.s.r. spectroscopy under temperature scanning mode.

EXPERIMENTAL

Materials

The UPE used in this study was Q6585 provided by Ashland Chemical Company. The properties of Q6585 and the material preparation procedures have been described in part 1²⁵. The compositions of resins used in this study are given in Table 1.

Instrumentation and procedures

A differential scanning calorimeter (d.s.c.) and a Rheometrics Dynamic Analyzer (RDA) were used to determine the reaction conversion and changes of storage shear modulus (G') during reaction. Details of instrumentation and procedures are given in part 1²⁵.

Radical concentration. An e.s.r. spectroscope (Bruker ESP 300, 9.5 GHz X band) was used to measure the free-radical concentration profile during the cure of the UPE resins. The reaction proceeded in quartz e.s.r. sample tubes with o.d. of 4 mm and i.d. of 3 mm. The sample tube was positioned at the same location in the cavity for all runs to ensure measurement consistency. When a molecule containing magnetic dipoles (which arise from net spin of net orbital angular moments or from combinations of these) interacts with the magnetic component of microwave radiation in a static magnetic field, adsorption attributed to magnetic dipole transitions may occur at one or more characteristic frequencies. The concentration of radicals was determined by double integration of the observed e.s.r. spectrum, which is the first derivative of the absorption spectrum. The liquid-solid transition of samples can also be observed through the signal changes during the reaction^{2,8,9,24}.

A calibration curve was generated by preparing stable free radicals based on solutions of 2,2-diphenyl-1-picrylhydrazyl hydrate (Aldrich) in benzene, and measuring the signal strength of each solution. Solutions of this standard were prepared in the range of 10^{-2} to 10^{-7} mol l⁻¹. The free-radical concentration profile during the reaction was established by converting the signal strength at each measuring time to a concentration value based on the calibration curve⁸.

RESULTS AND DISCUSSION

Measurement and simulation of e.s.r. radical spectra

Typical e.s.r. spectra observed during the copolymerization of ST and UPE resins at 40°C with ST/UPE

molar ratio (MR) of methyl ethyl ketone peroxide (MEKP)/cobalt naphthenate (COB) are given in Figure 1. At the beginning of the reaction, the radical spectrum showed a five-line shape (curve A). As the reaction started, the five-line shape spectrum rapidly changed to three-line (curve C) and finally became a single-line shape (curve D) at the gel point. After the resin system reached its gel point, the radical spectrum gradually changed from the single-line shape to a three-line shape (curve E). The five-line spectrum was actually a combination of four-line and single-line spectra. From the changes of e.s.r. spectra line-shape, three types of radicals, which relate to the four-, single- and three-line spectra, can be identified.

It is well known from the literature^{3,24,26-28} that the polystyryl radical has a triplet (i.e. three-line) shape e.s.r. spectrum. The chemical formula and structure of the radical are given in Figure 2. The hyperfine splitting of triplet is about 17G, which corresponds to radicals I and II shown in Figure 2. In radical I, the unpaired electron interacts with one α -proton and one β -proton. The second β -proton has the same hyperfine splitting constant as another β -proton, and only causes the broadening of lines. Radical II also has a triplet shape and similar splitting. Because of the symmetric structure of polymer chain around the unpaired electron site, only two β -protons interact with the radical. The other two β -protons contribute only to the broadening of lines.

The quartet line-shape in the e.s.r. spectrum can be assigned to the UPE radical, as shown in Figure 3. There is one α -proton and one β -proton in the site of the unpaired electron. The α -proton causes a doublet hyperfine splitting with a constant of 11G. The hyperfine splitting effect caused by one β -proton should have a doublet line-shape. However, because of the stereo structure of the radical, the β -proton may locate in two different positions, as shown in Figure 3. The splitting constants of β -proton at different positions are not equal. Therefore, the measured hyperfine splitting shape is triplet with a constant of 11G^{2,7}. Combining the hyperfine splitting of α -proton and β -proton, the e.s.r. spectrum shows a quartet line-shape with a splitting constant of

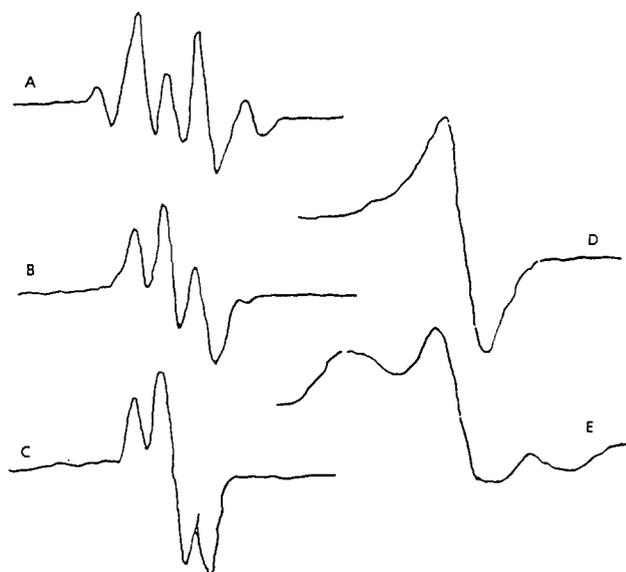


Figure 1 Typical e.s.r. spectra observed during the reaction of ST/UPE resins: A, induction period; B, reaction start; C, transition; D, macrogelation; E, cured

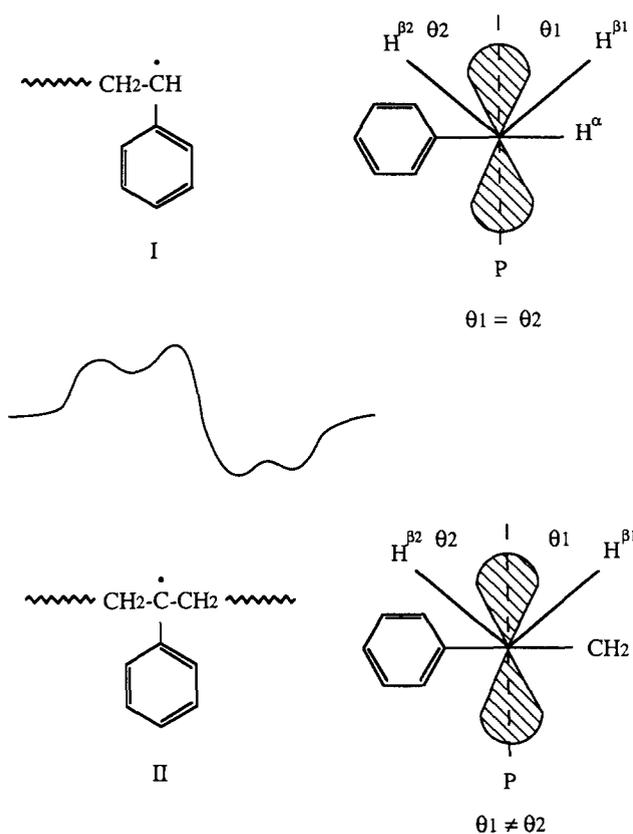


Figure 2 Chemical formula, radical structure and e.s.r. spectrum of ST-end stable radicals (P is polymer chain)

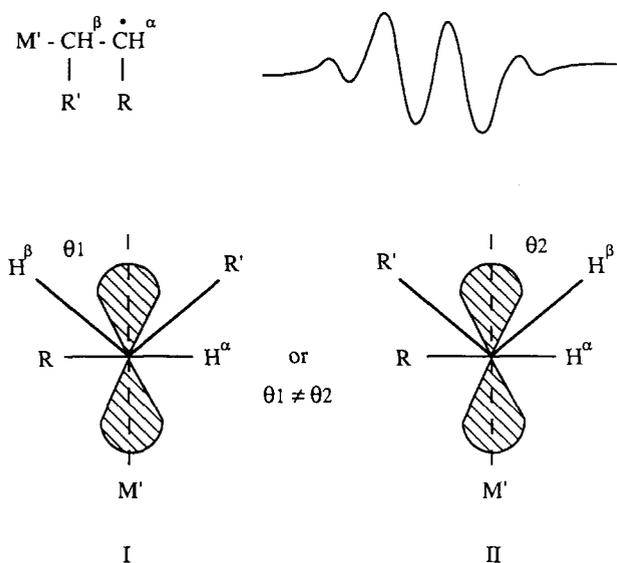


Figure 3 Chemical formula, radical structure and e.s.r. spectrum of UPE-end growing radicals (R and R' are repeating unit of UPE chain and M' is oligomer formed through chain reaction)

11G. These radicals can link UPE vinylenes or ST vinyls through chain-growth copolymerization. Therefore, we name this type of radical the UPE-end growing radical. These radicals can be either terminated with other radicals or transformed into a more stable structure through internal hydrogen migration².

The chemical formula and radical structure of UPE radical with a more stable structure are shown in Figure 4. When the UPE-end growing radicals react with

other UPE molecules through ST monomers, their mobility may be greatly reduced because of the increase of chain size. Consequently, both the propagation and the termination rates are likely to decrease. When the polymer chain size reaches a certain level, the possibility of further propagation or termination becomes so low that the β -proton on the UPE-end growing radical may exchange with the unpaired radical through internal hydrogen migration to form a more stable radical, as shown in Figure 4. This radical has no α -proton but has two β -protons, thus a singlet spectrum is observed in the e.s.r. measurement. The propagation rate constant of this type of radical should be much smaller than that of the UPE-end growing radical due to the molecular structure of the radical. Therefore, we name this type of radical the UPE-end stable radical. The UPE-end stable radical can be observed easily by dissolving the pure UPE monomer in toluene with 1.0% MEKP/COB at room temperature. Because the homopolymerization rate of UPE monomer is very small, most of the radicals formed would be transformed into the UPE-end stable radicals. Figure 5a shows the measured e.s.r. spectrum which is indeed the singlet shape.

The transformation of UPE-end growing radicals to UPE-end stable radicals can also be observed by cooling the reacting ST/UPE resin from room temperature to below its freezing point. Because the environment around the radicals is changed from liquid to solid upon freezing, the UPE-end growing radicals transform into stable radicals. A quartet line-shape (Figure 5b) was observed before cooling when the resin system was in the liquid state. As the temperature decreased, the quartet line-shape gradually transformed into a singlet line-shape (Figure 5c). The slight difference between the spectra in Figure 5a and c was due to the radical concentration. The radical concentration of UPE in toluene was 10 times larger than the radical concentration of the reacting ST/UPE resin at -50°C .

The above-mentioned e.s.r. spectra of radicals can also be simulated with mathematical equations. Table 2 summarizes the parameters such as line-widths and proton hyperfine coupling constants, which best fit the spectra of radicals generated during the ST/UPE copolymerization. The Lorentzian line-shape approach was selected for the calculation of UPE-end growing and

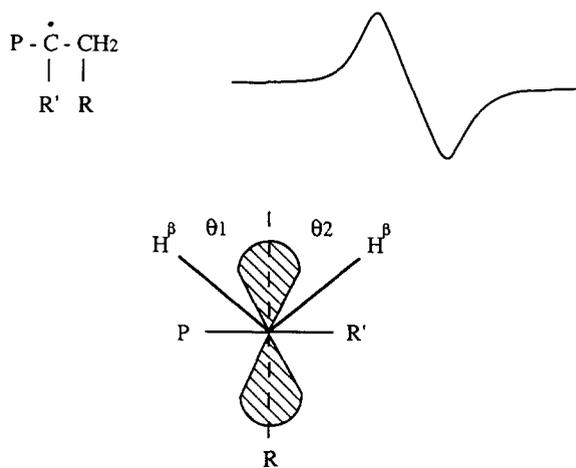


Figure 4 Chemical formula, radical structure and e.s.r. spectrum of UPE-end stable radicals (R and R' are repeating unit of UPE chain and P is polymer chain)

Table 2 E.s.r. parameters of radicals generated during ST/UPE copolymerization

| Radical ^a | Spectral feature | Line width, ΔH | g value | Proton hyperfine coupling constant, G |
|--|------------------|------------------------|-------------------|---|
| ST-end stable $C_6H_5\dot{C}H(P)CH_2$ | Triplet | 20G | 2.002 ± 0.001 | 17 ± 1 |
| UPE-end growing $M'\dot{C}H(R')\dot{C}H(R)$ | Quartet | 5G | 2.002 ± 0.001 | 11 ± 0.5 |
| UPE-end stable $(P)\dot{C}(R)CH_2(R)$ | Singlet | 4~10G | 2.002 ± 0.001 | — |

^a R and R' are the repeating unit of UPE resin, P is polymer chain and M' is oligomer formed through chain reaction

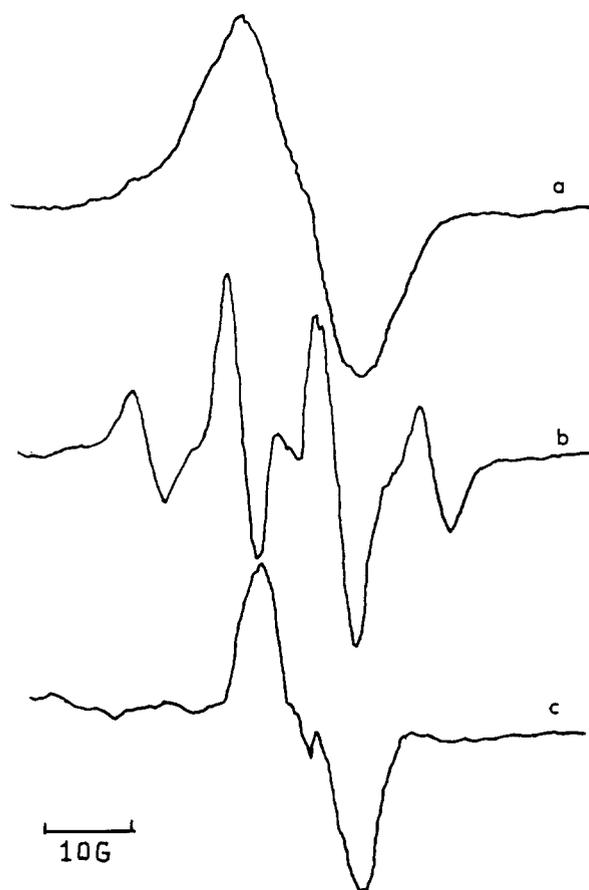


Figure 5 E.s.r. spectra of UPE in toluene with 1.0% MEKP/COB after 1 week (a); ST/UPE resin with MR=2 and 1.0% MEKP/COB at room temperature (b) and at $-50^\circ C$ (c)

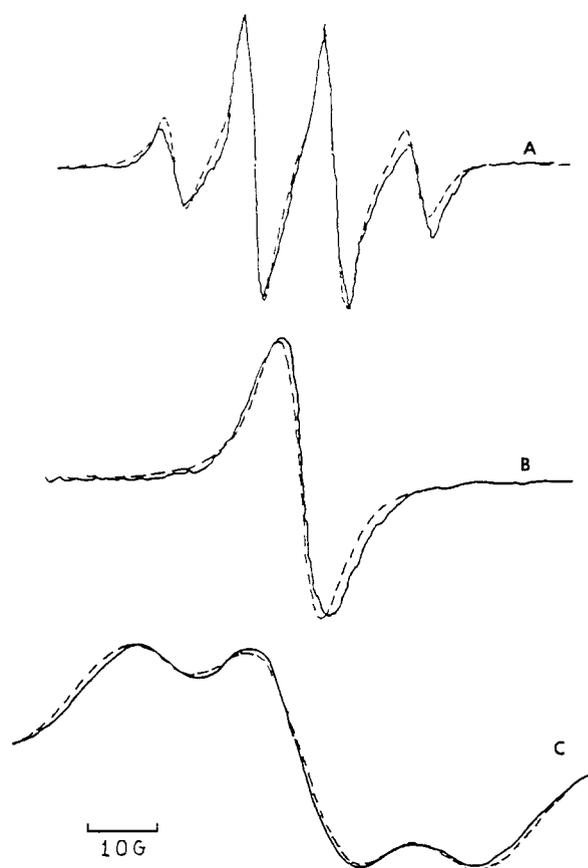


Figure 6 Comparison of simulated (---) and measured (—) e.s.r. spectra of various radicals: A, UPE-end growing radical; B, UPE-end stable radical; C, ST-end stable radical

UPE-end stable radicals because the measured e.s.r. line-shape before macrogelation of the resin system was more like the liquid state, which fulfilled the characteristics of Lorentzian line-shape². The Gaussian line-shape approach was chosen for the calculation of ST-end stable radicals because the measured e.s.r. line-shape of ST-end radical was more like the solid state, which fulfilled the characteristics of Gaussian line-shape². The calculated and measured e.s.r. spectra of these three radicals are shown in *Figure 6*. The line-width of UPE-end stable radicals changed from 4 to 10G during the reaction, as shown in *Table 2*, because the line-width is a function of radical concentration. The actual relationship between the line-width and the radical concentration is not clear at this point. If we assume a linear relationship between the line-width and the concentration of UPE-end stable radicals in the spectrum calculation, the line-width, ΔH ,

can be expressed as $\Delta H = 4 + 6X$, where X is the percentage of stable radicals.

The radical concentration profiles measured by e.s.r. for the reactions of ST/UPE resins with various amounts of MEKP/COB cured at $40^\circ C$ are shown in *Figure 7*. For the resin with 1.0% MEKP/COB, a constant radical concentration region existed for the first 250 s, which was due to the equilibrium between the initiator and the inhibitor. This period is the so-called induction time. As the induction period ended, radical concentration started to increase. The radical concentration increased sharply after around 300 s, which was due to phase separation caused by formation of polymers. This result again agreed well with results from time-resolved light scattering and optical microscope measurements presented in part 1²⁵. The radical concentration kept increasing, but at a slower rate, after the resin reached its gel point ($G' = G''$, time

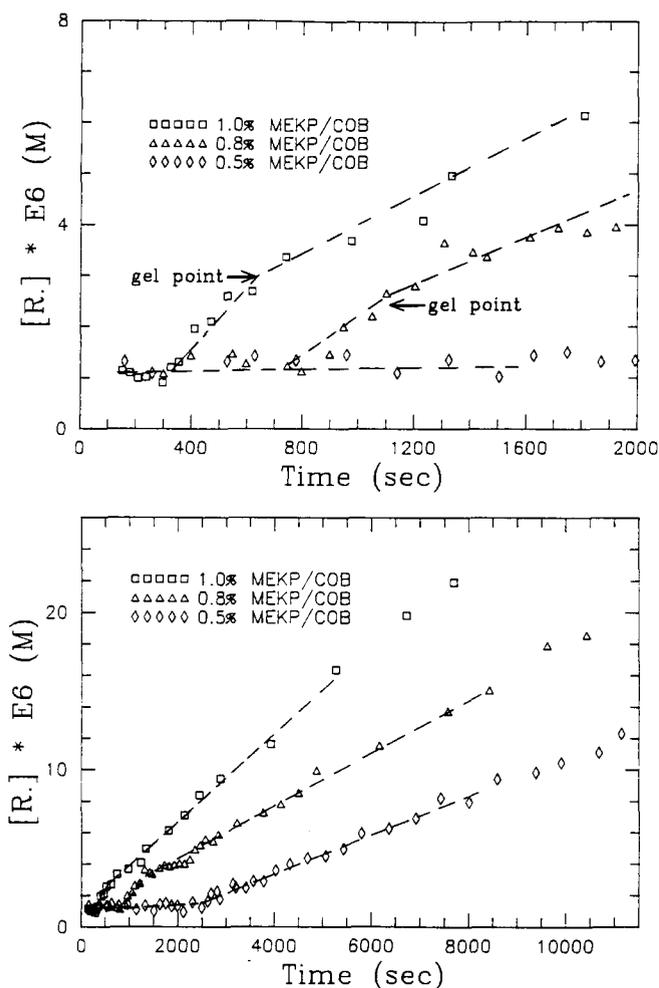


Figure 7 Radical concentration versus time for ST/UPE resins with MR=4 and various amounts of initiator cured at 40°C

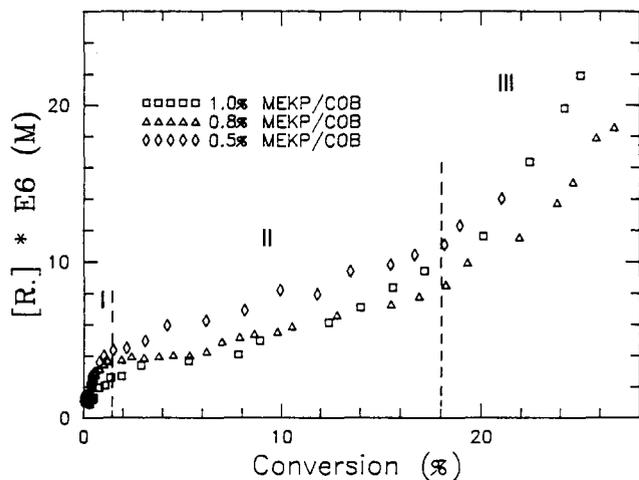


Figure 8 Radical concentration versus conversion for ST/UPE resins with MR=4 and various amounts of initiator cured at 40°C

≈ 580 s). Similar results were also observed for resins with 0.8 and 0.5% MEKP/COB, but at a slower pace.

Combining the radical concentrations (Figure 7) and kinetic data given in part 1²⁵, data for the reactions of UPE resins with MR=4 and various amounts of MEKP/COB cured at 40°C are shown in Figure 8. All three curves tended to merge together to form a master curve. However, slight differences still existed, possibly

due to the effect of time on the phase separation process. These curves can be divided into three stages. In the first stage, radical concentration increased while the change of conversion was insignificant. The starting point of the second stage was near the $G' = G''$ point, where the conversion increased faster than the radical concentration. The d.s.c. measurement showed that the reaction had entered the major reaction exotherm. In the third stage, the conversion reached a high value and started to level off, but the radical concentration kept increasing. Therefore, the radical concentration increased faster than the conversion. In this stage the d.s.c. measurement showed that the reaction exotherm gradually decayed to zero.

The shear storage modulus versus free-radical concentration for the reactions of ST/UPE resins with MR=4 and various amounts of initiator concentration cured at 40°C is shown in Figure 9. These curves merged together and formed a master curve for all three resin systems. Therefore, the storage moduli can be expressed as a function of radical concentration for a given resin system.

The shear storage modulus versus free-radical concentration for the reactions at 30, 40 and 50°C is shown in Figure 10. The major change of storage modulus occurred

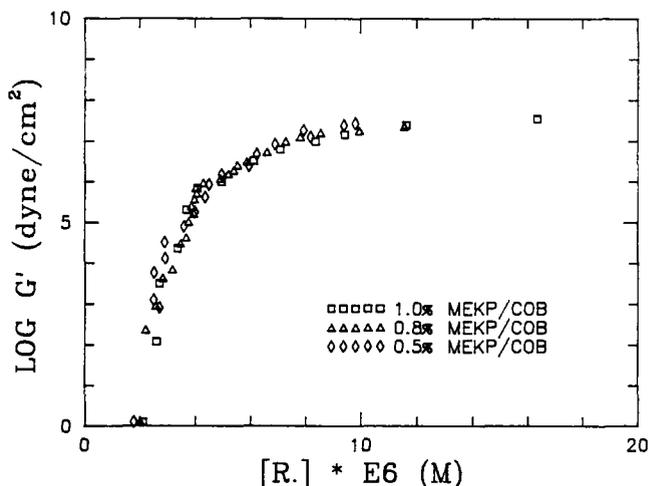


Figure 9 Shear storage modulus versus radical concentration for ST/UPE resin with MR=4 cured at 40°C

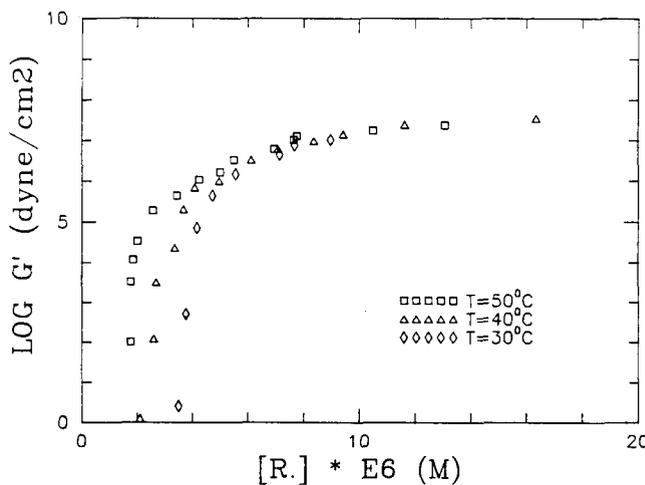


Figure 10 Shear storage modulus versus radical concentration for ST/UPE resin with MR=4 and 1.0% MEKP/COB cured at various temperatures

near the gel point, where the value of G' increased quickly to more than 10^6 dyn cm^{-2} . The radical concentration increased by only a few per cent of the final value during this period. There was a transition in the curve for the reaction of ST/UPE resin with MR=4. At the beginning, the curve of $T=40^\circ\text{C}$ was close to the curve of $T=50^\circ\text{C}$, but the curve of $T=40^\circ\text{C}$ shifted towards the curve of $T=30^\circ\text{C}$ during the first stage. After the storage modulus reached the high value, all three curves tended to merge together during the final stage. The shear storage modulus versus free-radical concentration for the reactions of ST/UPE resins with MR=2, 4 and 8 cured at 40°C is shown in Figure 11. At the beginning, all three curves followed the same pattern as the storage modulus increased. However, these curves ended at different values of storage modulus due to the change of UPE content in the resin system. The UPE resin with MR=2 had the highest storage modulus, while the resin with MR=8 had the lowest storage modulus after being cured.

Table 3 summarizes the time taken to reach the $G' = G''$ point and radical concentration at the $G' = G''$ point for ST/UPE resins cured under various conditions. Although the reaction times required to reach the $G' = G''$ point were different, radical concentrations at the $G' = G''$ point, except that of the resin with phase separation, were nearly the same for resins cured under various conditions. These results again suggest that radical concentration is a good

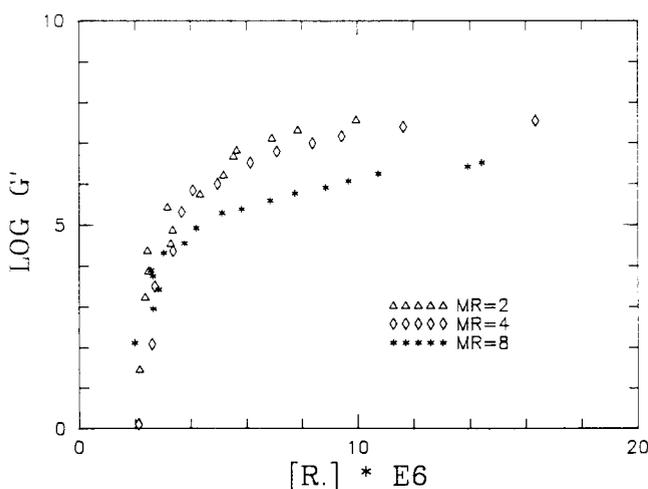


Figure 11 Shear storage modulus versus radical concentration for ST/UPE resin with 1.0% MEKP/COB cured at 40°C with various values of MR

Table 3 Time taken to reach the $G' = G''$ point and radical concentration at the $G' = G''$ point for ST/UPE resins cured under various conditions

| Sample designation | Time $_{G'=G''}$ (min) | Radical concentration ($\times 10^6$ M) |
|----------------------------------|------------------------|--|
| MR=4, 1.0% MEKP | | |
| 30°C | 30.1 ± 1.0 | 3.5 ± 0.1 |
| 40°C | 9.7 ± 1.0 | 2.3 ± 0.4 |
| 50°C | 2.9 ± 1.0 | 2.0 ± 0.3 |
| $T=40^\circ\text{C}$, 1.0% MEKP | | |
| MR=2 | 23.2 ± 1.0 | 2.2 ± 0.3 |
| MR=8 | 4.6 ± 1.0 | 2.2 ± 0.5 |
| MR=4, $T=40^\circ\text{C}$ | | |
| 0.8% MEKP | 16.7 ± 1.0 | 2.2 ± 0.3 |
| 0.5% MEKP | 49.6 ± 1.0 | 2.3 ± 0.3 |

parameter for the analysis of free-radical polymerizations. For the reaction of ST/UPE resin with MR=4 cured at 30°C , the radical concentration at the gel point, $t \approx 30.1$ min, was higher than that at 40°C , as shown in Table 3. However, the solid-like spectrum showed up at $t \approx 18.3$ min where the free-radical concentration was 2.1×10^{-6} M. The appearance of a solid-like spectrum before the gel point indicated that the reaction rates of the ST-rich phase and the UPE-rich phase were different. The delay of macrogelation might be due to the slower reaction in the ST-rich phase, where the interparticle reaction occurred and led to the network formation. For the reaction of ST/UPE resin with MR=4 cured at 50°C , the first measurable radical spectrum was already in the transition region at a reaction time of 2.1 min. The solid-like spectrum was observed at a reaction time near 3.9 min, which was longer than the time to reach the $G' = G''$ point measured by RDA, as shown in Table 3. Because the reaction time to reach the $G' = G''$ point was very short, the deviation between e.s.r. and RDA measurements might be due to experimental error.

Transition of growing radicals to stable radicals in the pregelation stage

The transition of growing radicals to stable radicals in the cure of ST/UPE resins can be investigated using the e.s.r. spectra simulation technique. From early studies, it is known that the homopolymerization rate of ST with 1% MEKP/COB cured at 30 – 50°C is very small, and the consumption rate of UPE vinylenes is higher than that of ST vinyls at the early stage of ST/UPE reaction¹. Therefore, the ST-end stable radicals are rarely found before macrogelation. The transition of growing radicals to stable radicals before macrogelation could be considered as primarily the transition of UPE-end growing radicals to UPE-end stable radicals. This argument is supported by the e.s.r. results presented in the previous section (i.e. Figures 1 and 6). The e.s.r. absorption spectra show a quartet or a quintet line-shape when the radical system is dominated by the growing radicals. The quintet line-shape is a combination of a quartet line-shape (UPE-end growing radicals) and a singlet line-shape (UPE-end stable radicals). As the amount of stable radicals increased, the central peak of the quintet line-shape became larger. Finally, the central peak, which is related to the UPE-end stable radicals, dominated the entire spectrum and a singlet line-shape spectrum was observed.

Based on this simulation technique, the transition of growing radicals to stable radicals during reaction can be quantified as shown in Figure 12. By comparing the simulated and the experimental e.s.r. absorption spectra, the amount of stable radicals at a given reaction time can be estimated. This estimation can be double-checked by further comparing the first derivative of the absorption spectrum between the simulation and the e.s.r. experiments.

The estimated transition of UPE-end growing radicals to UPE-end stable radicals as a function of reaction time for ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C is shown in Figure 13. In the first 600 s, 80% of the radicals were UPE-end growing type. After that, the percentage of UPE-end stable radicals increased rapidly from 20% to $>90\%$. In the same time period, the radical concentration increased from 1.0×10^{-6} to 2.0×10^{-6} M. These results suggest that the growing

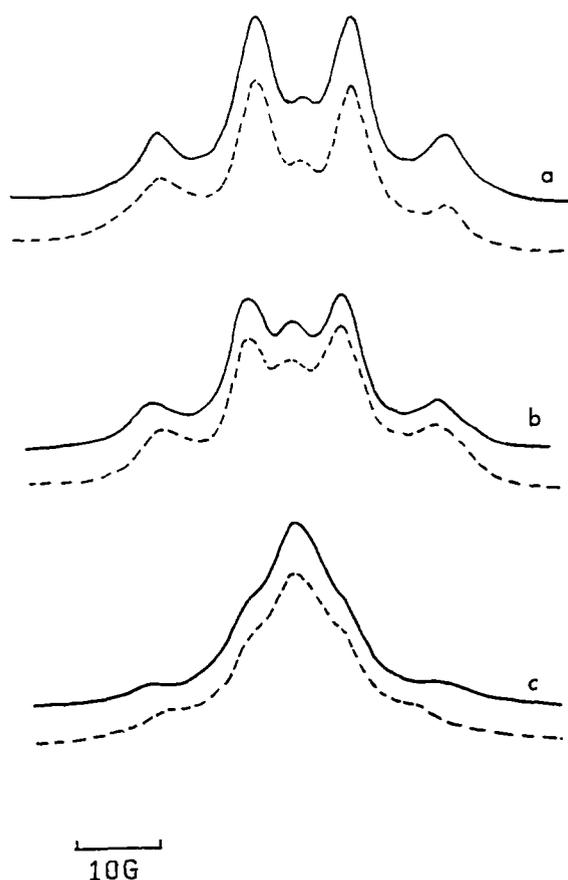


Figure 12 Comparison of simulated and experimental e.s.r. absorption spectra of ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C: —, simulated spectra assuming (a) 20%, (b) 40%, (c) 80% UPE-end stable radical; ---, measured spectra at reaction times of (a) 100, (b) 760, (c) 1090s

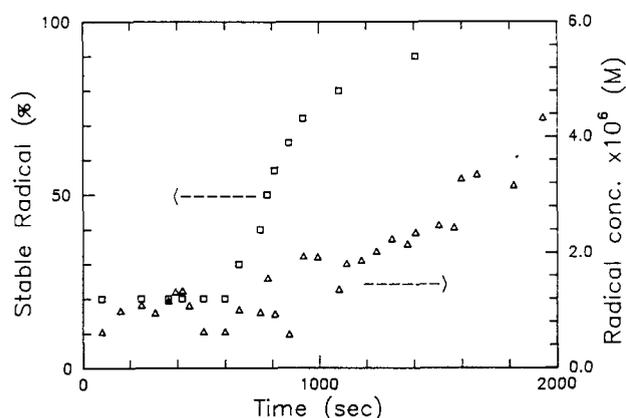


Figure 13 Stable radical percentage and radical concentration versus reaction time for ST/UPE resin with MR=2 and 1.0% MEKP/COB cured at 40°C

radicals quickly converted into stable radicals as the copolymerization started. Since the stable radical has a longer lifetime than the growing radical, the measured radical concentration also increased as the reaction progressed.

A similar transformation of growing radicals to stable radicals was observed for ST/UPE resin with MR=4 and 0.8% MEKP/COB cured at 40°C. The stable radical percentage versus reaction time is shown in Figure 14. The percentage of stable radicals remained the same in the first 300 s. It started to increase when the reaction

began. As mentioned in part 1²⁵, phase separation of this reaction occurred at a reaction time near 500 s. The amount of stable radicals increased with a higher rate when phase separation began. The radical concentration also started to increase during this period.

E.s.r. study of trapped radicals in ST/UPE resins

As mentioned in the previous discussion, the ST-end and UPE-end radicals formed during the cure of ST/UPE resins had a stable structure. At the end of reaction, these radicals would be trapped in the cured samples. Cured samples were kept in the same glass tubes as used in the e.s.r. experiment and were sealed with a plastic cap during room temperature storage. The radical concentration of cured samples was measured at room temperature 30 days after the reaction. Comparison with the radical concentrations measured shortly after the samples were cured shows that the radical concentrations did not change much after 1 month of storage, as shown in Table 4. For most cases, the radical concentration decreased by less than 10%. For resin systems where phase separation occurred, i.e. MR=4 cured at 30°C and MR=8 cured at 40°C, a larger decrease in radical concentration was observed (~20%).

During storage, the e.s.r. spectrum of cured ST/UPE resin samples with phase separation (e.g. MR=4 cured

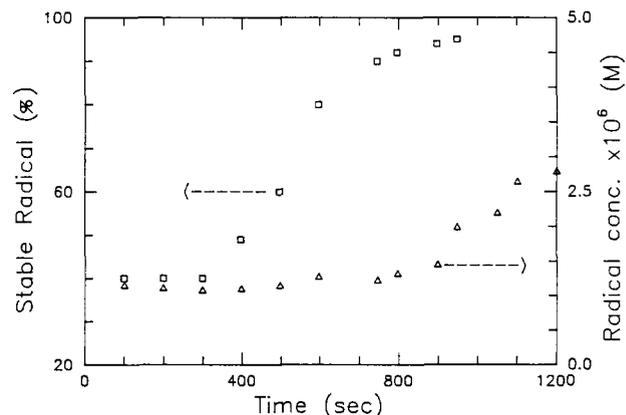


Figure 14 Stable radical percentage and radical concentration versus reaction time for ST/UPE resin with MR=4 and 0.8% MEKP/COB cured at 40°C

Table 4 Radical concentration of ST/UPE resins cured under various conditions

| Sample designation | Radical concentration ($\times 10^4$ M) | | |
|----------------------------------|--|--------------------|------------|
| | End of reaction | 1 month after cure | Change (%) |
| MR=4, $T=40^\circ\text{C}$ | | | |
| 1.0% MEKP | 1.91 ± 0.05 | 1.73 ± 0.2 | -9.4 |
| 0.8% MEKP | 1.59 ± 0.1 | 1.52 ± 0.1 | -4.4 |
| 0.5% MEKP | 1.30 ± 0.1 | 1.25 ± 0.1 | -4.8 |
| MR=4, 1.0% MEKP | | | |
| 30°C | 0.21 ± 0.02 | 0.17 ± 0.02 | -19.0 |
| (with phase separation) | | | |
| 50°C | 1.65 ± 0.2 | 1.62 ± 0.1 | -1.9 |
| $T=40^\circ\text{C}$, 1.0% MEKP | | | |
| MR=8 | 1.55 ± 0.1 | 1.15 ± 0.1 | -25.8 |
| (with phase separation) | | | |
| MR=2 | 1.72 ± 0.2 | 1.52 ± 0.1 | -11.6 |

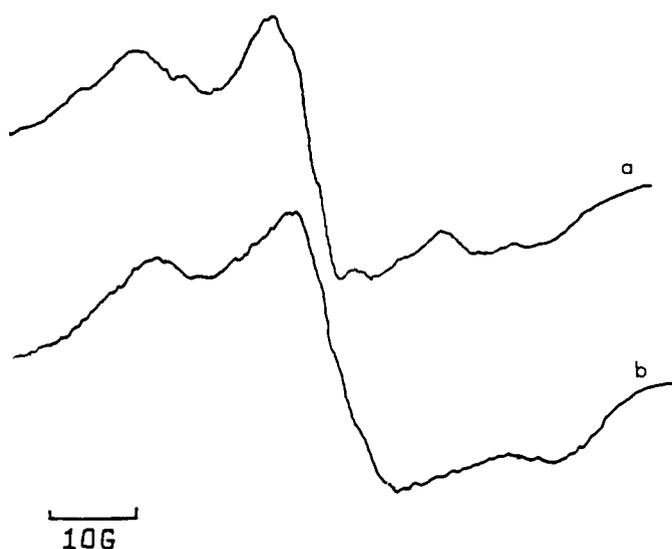


Figure 15 E.s.r. spectra of the 30°C isothermally cured ST/UPE resin with MR=4: (a) end of curing; (b) after storage for 1 month

at 30°C) also experienced a change of radical ratio. The e.s.r. spectrum showed a triplet line-shape at the end of isothermal polymerization, as shown in Figure 15a, but after 1 month of storage the measured e.s.r. spectrum showed a substantial increase of the central peak, which indicated a mix of triplet and singlet line-shapes, as shown in Figure 15b. The change of line-shape was apparently due to the decrease of ST-end stable radicals. Both UPE-end and ST-end stable radicals existed at the end of copolymerization, with ST-end stable radicals dominating. During the storage period, some of the ST-end radicals were terminated, while the UPE-end radicals remained at the same level. Consequently, the relative amount of UPE-end radicals increased during the storage period. Similar spectral changes were also found in the ST/UPE resin with MR=8 cured at 40°C. For ST/UPE samples cured under other conditions where phase separation did not occur, storage for 1 month did not change the shape of e.s.r. spectra except that the radical concentration decreased slightly, as shown in Table 4.

It has been found²⁹ that phase separation in the ST/UPE resin system resulted in a ST-rich phase with MR greater than 40 and a UPE-rich phase with MR near 2.5. The composition of the UPE-rich phase was close to the sample with MR=2 and this sample showed only a small decrease of radical concentration after storage, therefore, we can conclude that the larger decrease of radical concentration shown in Table 4 must have occurred in the ST-rich phase. Because the crosslinking was not strong in this phase, chain movement and termination were possible. Oxygen in the air might also be able to diffuse into the loosely crosslinked network and terminate the radicals. The termination of polystyrene radicals in ST/UPE resin copolymerization at room temperature was also observed by Zheng *et al.*²⁴.

The thermal effect on the trapped radicals was investigated by heating the cured samples in the e.s.r. spectroscopy from 37°C to about 107°C at a rate of 2°C min⁻¹. Temperature scanning was stopped at 107°C because of the limitation of the e.s.r. instrument. The relative radical concentration *versus* temperature for ST/UPE resins with various values of MR and 1.0%

MEKP/COB cured at 40°C is shown in Figure 16. For all samples, the radical concentration remained at the same level from room temperature to 47°C, then started to increase. The increase in radical concentration during temperature scanning can be explained by the fact that when the temperature became higher than the glass transition temperature of the isothermally cured sample, the remaining MEKP and COB could react with residual functional groups, which might form more trapped radicals in a highly crosslinked system.

Radical concentration continued to increase until the temperature reached around 97°C. The increase of relative radical concentration for the sample with MR=2 was higher than that with MR=4. For the sample with MR=8 cured at 40°C, phase separation occurred. A very sharp increase of relative radical concentration was found during temperature scanning. The large increase of radical concentration seemed to be related to the phase separation during reaction. In order to understand the effect of phase separation on the increase of relative radical concentration, another set of experiments was conducted. ST-rich and UPE-rich samples were prepared by settling the ST/UPE resin with MR=4 and either 1.6% MEKP or 0.4% COB at room temperature until phase separation was completed. The upper layer was a ST-rich phase, while the lower layer was a UPE-rich phase. The top and bottom layers of the resin were separated into different glass vials with a pipette. The UPE-rich sample was prepared by mixing equal amounts of UPE-rich phase with MEKP and with COB at room temperature immediately before the measurement. The ST-rich sample was prepared in a similar way. These samples were then poured into e.s.r. sample tubes and cured isothermally at 40°C for 5 h before temperature scanning was carried out in e.s.r. The relative radical concentration *versus* temperature scanning curves for the isothermally cured ST-rich and UPE-rich samples are shown in Figure 17. The curve of the cured UPE-rich phase had a similar profile to the ST/UPE resin with MR=2 cured at 40°C, while the curve of the cured ST-rich phase had a similar profile to the ST/UPE resin with MR=8 cured at 40°C. The e.s.r. spectra of the UPE-rich sample had a triplet line-shape before and after temperature scanning, as shown in Figures 18a and b,

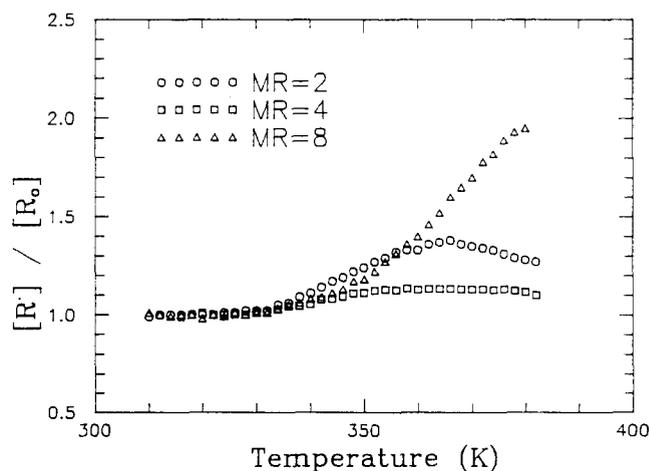


Figure 16 Relative radical concentration of temperature scanning reaction for 40°C isothermally cured ST/UPE resin with 1.0% MEKP/COB and various values of MR

while the e.s.r. spectra of the ST-rich sample showed a dramatic change from a singlet to a triplet line-shape during temperature scanning, as shown in Figures 19a and b. From the change of radical concentration and e.s.r. spectra of the ST-rich and UPE-rich samples, it is clear that the increase of relative radical concentration of resin systems with phase separation occurred in the ST-rich phase.

As shown in Figure 16, the radicals tended to be terminated at higher temperatures. To study this further, both 40°C isothermally cured and temperature-scanned

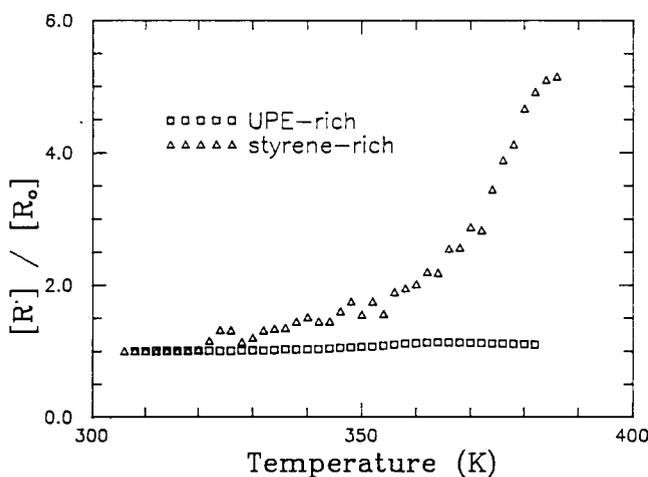


Figure 17 Relative radical concentration of temperature scanning reaction of 40°C isothermally cured ST-rich and UPE-rich samples

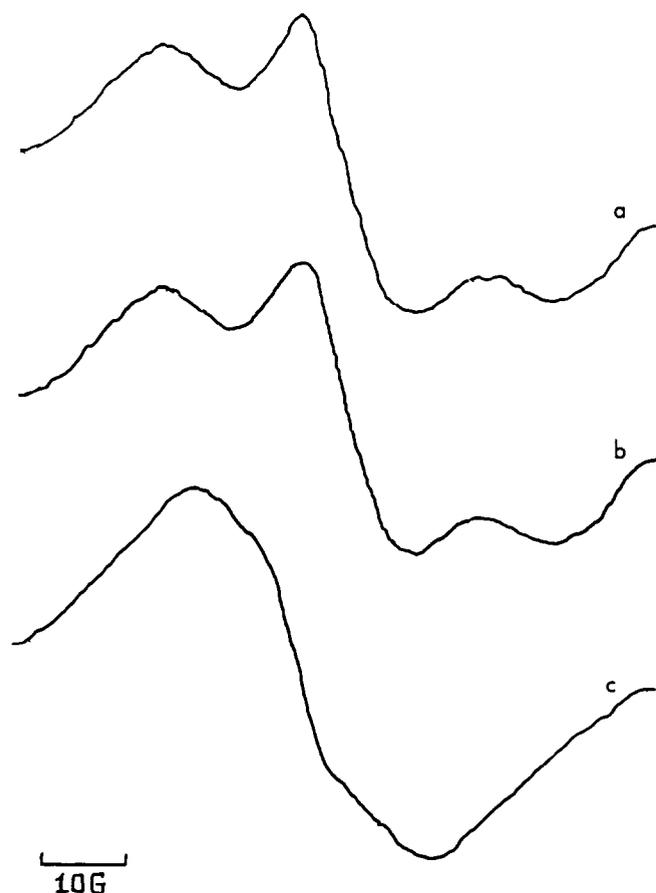


Figure 18 E.s.r. spectra of UPE-rich phase: (a) end of isothermal reaction at 40°C; (b) end of temperature scanning run at 113°C; (c) after 3 h of post-cure at 140°C

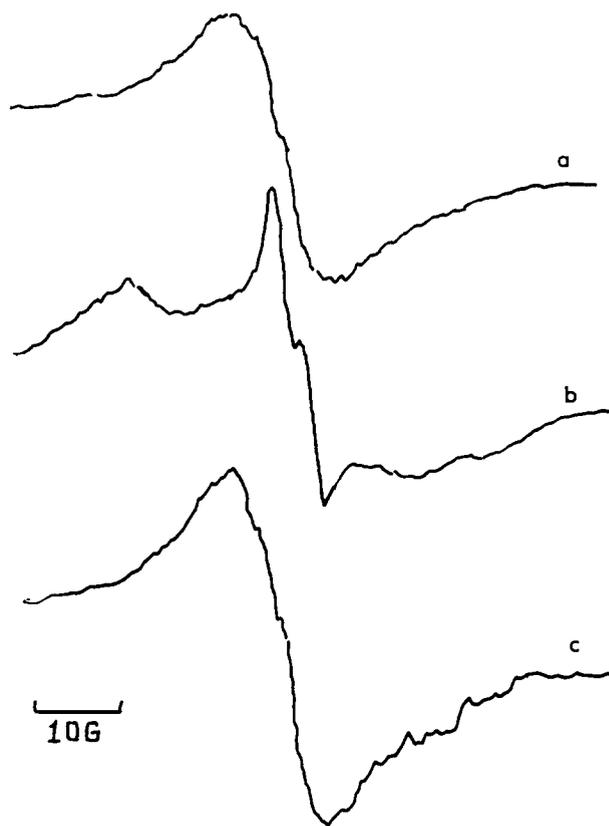


Figure 19 E.s.r. spectra of ST-rich phase: (a) end of isothermal reaction at 40°C; (b) end of temperature scanning run at 113°C; (c) after 3 h of post-cure at 140°C

Table 5 Radical concentration of ST-rich and UPE-rich samples after isothermal, temperature scanning and post-cure reactions

| Measuring condition | Radical concentration ($\times 10^4$ M) | |
|----------------------|---|-----------------|
| | ST-rich | UPE-rich |
| At the end of | | |
| Isothermal | 0.044 ± 0.002 | 2.79 ± 0.05 |
| Temperature scanning | 0.246 ± 0.005 | 2.99 ± 0.05 |
| Post-cure | 0.067 ± 0.01 | 0.70 ± 0.01 |

UPE-rich and ST-rich samples were post-cured at 140°C in nitrogen for 3 h. The measured e.s.r. spectra of post-cured samples are shown in Figures 18c and 19c. The e.s.r. spectra show that most of the ST-end radicals disappeared at the end of the post-cure, and the measured radical concentration also showed a decrease at the end of post-cure. The measured radical concentrations of ST-rich and UPE-rich samples after isothermal temperature scanning and post-cure reactions are given in Table 5. The decrease of radical concentration after post-cure was not caused by oxygen diffusion since the post-cure was conducted in nitrogen.

CONCLUSIONS

E.s.r. spectroscopy provided useful information for a better understanding of the nature of propagating radicals and the radical concentration in free-radical copolymerizations of ST/UPE resins. The hyperfine structure of the e.s.r. spectrum showed that three types of radicals were involved in the copolymerization. The

absorption spectra and the first derivative of absorption spectra can be simulated with mathematical equations to determine the nature and the quantity of radicals. At the beginning of the reaction, most of the radicals were of the UPE-end growing type with a small amount of UPE-end stable radicals. As the reaction progressed, the UPE-end growing radicals transformed into UPE-end stable radicals due to the polymerization. When the resin system reached the gel point, most of the growing radicals had transformed into stable radicals. Changes of the ratio of various radical species were determined by the e.s.r. spectrum simulation method. The ST-end stable radicals appeared after macrogelation. Both ST-end and UPE-end stable radicals existed in the post-gelation reaction, but ST-end stable radicals dominated near the end of the reaction.

The trapped radicals were studied after 1 month of storage by the temperature scanning method. The results indicated that radicals of cured resin without phase separation were very stable and only a small increase of radical concentration was observed at elevated temperatures. The decay of radical concentration at temperatures higher than 100°C occurred mainly in the ST-rich region, where crosslinking was not strong. The relative radical concentration of resins with phase separation increased greatly at elevated temperatures due to the changes inside the ST-rich area.

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