

Cure analysis of unsaturated polyester resins using electron spin resonance spectroscopy, differential scanning calorimetry and rheometry

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The polymerization of unsaturated polyester resins was studied using electron spin resonance (e.s.r.) spectroscopy, differential scanning calorimetry (d.s.c.), and Rheometrics dynamic analyser (RDA). The effects of crosslinking and thermoplastic additive on radical concentration and reaction kinetics were investigated. Variables studied included initiator concentration, resin composition and curing temperature. It was found that the radicals formed were very stable and their concentration was much higher than that for the linear polymerizations. From the e.s.r. spectrum, the liquid–solid transition could be identified, which agreed well with the gel time measured by RDA.

(Keywords: electron spin resonance spectroscopy; unsaturated polyester resin; free radical concentration; reaction kinetics; gelation)

INTRODUCTION

Unsaturated polyester resins (UPEs) are among the most widely used thermosets in polymeric composites because they offer a good balance of properties, are relatively inexpensive and are amenable to most fabrication processes¹. With the aid of fillers, reinforcement and additives they are usually available in the form of compounds for compression moulding (sheet moulding compounds), injection moulding (bulk moulding compounds), resin transfer moulding and pultrusion².

The curing reaction of UPE is a free-radical chain growth polymerization. Before the reaction, the system contains styrene monomers, unsaturated polyester molecules and curing agents. When the reaction starts, the initiators decompose to form free radicals which trigger polymerization. Free radicals link adjacent unsaturated polyesters and form primary polymer chains through connecting styrene monomers by both inter- and intramolecular reactions. These long chain molecules tend to form spherical structures due to the intramolecular crosslinking among the pendant C=C bonds of the polyester molecule³. Dusek⁴ described such sub-micrometre structures with high cyclization and crosslinking density as 'microgels'. Because of the high crosslinking of the microgel, the free radicals on the polymer ends are likely to be buried in the microgels. This means that termination among the polymer radicals may not be an important factor. As the polymerization proceeds, the concentration of the microgels increases continuously. This leads to macrogelation in the system. If thermoplastic additives (i.e. low profile additives) are

added to the resin system, local phase separation between the reacting resin and the thermoplastic additives may also occur. This tends to form large particles (0.5–2 μm diameter) in the reacting mixture⁵.

Studies of resin kinetics, rheological changes, structure formation and resin shrinkage have been conducted in our laboratory^{3,5–11}. It was found that gelation often took place at a conversion less than 0.1%. Structure formation and resin shrinkage also occurred at very low conversions. *Figure 1* shows a typical result of resin conversion, storage modulus and volume change *versus* reaction time for a UPE resin. It is clear that most of the physical changes occurred before any measurable conversion, which makes it difficult to relate these changes to the resin conversion as in the cases of step growth crosslinking polymerizations^{12,13}.

In free-radical chain crosslinking polymerizations, it is important to know the radical histories during reaction. The first attempts to measure radical concentrations *versus* time during reaction were made by Bamford *et al.*¹⁴ and Atherton *et al.*¹⁵. The measurements were made in an electron spin resonance (e.s.r.) spectrometer with frozen samples to study radical trapping due to crosslinking. Using the same method, Bresler *et al.*¹⁶ and Kamachi and Kuwae¹⁷ measured the radical concentrations at initial stages of several homopolymerizations, and Ballard *et al.*¹⁸ measured reaction rate constants of the emulsion polymerization of methyl methacrylate (MMA). There are, however, several limitations of measuring radical concentrations in frozen samples. First, changes may still be occurring in the quenched sample, and consequently the actual reaction time is hard to determine. Another problem is that in the quenching process the sample may absorb water which tends to

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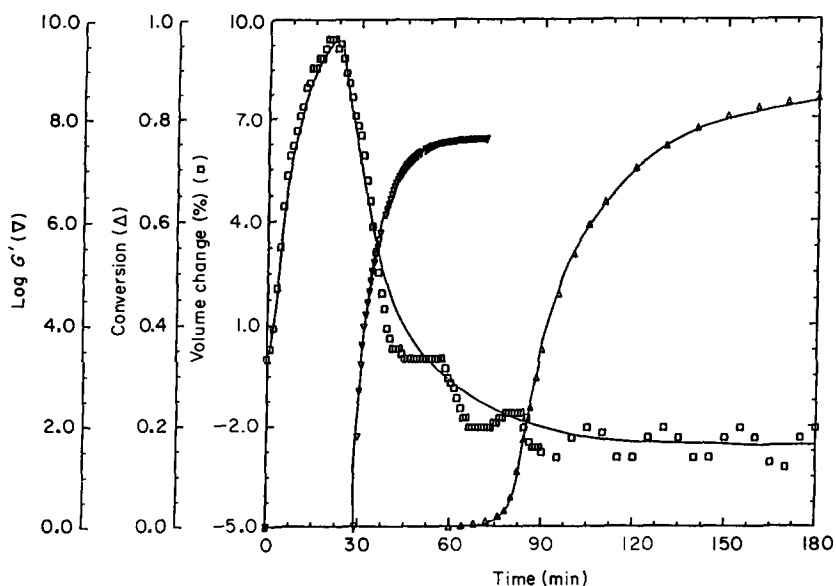


Figure 1 Interactions of rheological changes, volume change and conversion for UPE/styrene resin with 15% PVAc cured at 80°C

diminish the resolution of the instrument. Therefore, e.s.r. results from quenched polymer samples are questionable.

Improvements in instrument resolution and automation have allowed the on-line measurement of radical concentrations. For example, when it was discovered that flat magnetic field profiles improved the sensitivity of samples with high dielectric constants, new cavity designs and flat sample cells were made¹⁹. With the use of these cavities, radical concentrations as low as $10^{-7} \text{ mol l}^{-1}$ could be detected. Another improvement in the sensitivity of e.s.r. measurements was made by Shen *et al.*²⁰ They designed a sample cell made of glass capillaries glued side by side, which allowed measurements of radical concentrations in the region of $10^{-8} \text{ mol l}^{-1}$.

The overall improvement in the e.s.r. method allowed the study of free-radical polymerizations in more detail²¹⁻²⁵. Zhu *et al.*^{26,27} studied the radical concentration histories for the bulk free-radical copolymerization of MMA and ethylene glycol dimethacrylate (EGDMA). They found that at low EGDMA levels there existed four stages of radical concentration changes during reaction. In the first stage, the radical concentration remained relatively constant. This is in agreement with the quasi-steady-state hypothesis. In the second stage there was a dramatic increase in radical concentration, which agreed with the hypothesis that the autoacceleration in the free-radical polymerization is due to an increase in the radical concentration. After the radical concentration reached a peak value there was a small decrease and then in stage four the concentration increased gradually and levelled off.

Another study of the network structure of free-radical crosslinked polymers was done by Zheng and Zhou²⁸. They investigated the polymerization of an unsaturated polyester, prepared by polycondensation of bisphenol A-di-(2-hydroxypropyl)ether and maleic anhydride with vinyl monomers, by i.r. spectrometry and e.s.r. The two vinyl monomers used were styrene and MMA. The reactions were initiated by two redox initiator systems (cobalt naphthalate (CoN)/1-hydroxycyclohexyl hydroperoxide (HCH), and dimethylaniline (DMA)/benzoyl peroxide (BPO)) in order to identify any initiator effects. They found that the reaction mixtures contained

long-lasting polymer radicals, and the radical concentration was independent of the initiator system used. However, the life-span of the trapped radicals was highly dependent on the initiator system. By comparing the e.s.r. spectra it was found that the polymer radicals formed with the CoN/HCH system lived longer than those formed with the DMA/BPO system. From sol/gel extraction experiments it was found that CoN/HCH was more efficient for crosslinking than DMA/BPO. These results suggested that the stability of the trapped radicals was related to the degree of crosslinking.

In this work, the polymerization of unsaturated polyester resins was studied using differential scanning calorimetry (d.s.c.), rheometry and e.s.r. spectroscopy. The effects of crosslinking and thermoplastic additives on resin conversion and trapping of free radicals were investigated. Variables studied included initiator concentration, resin composition and curing temperature. The interaction between radical behaviour, reaction kinetics and rheological changes is discussed.

EXPERIMENTAL

Materials

The unsaturated polyester resin used in this study was made from a 1:1 molar mixture of maleic anhydride and propylene glycol containing 35 wt% styrene (Ashland Chemicals, Q6585). The average number of vinylene groups per polyester molecule was 10.13.

The initiators used were 2,5-dimethyl-2,5-bis(2-ethylhexanoyl-peroxy)hexane (DMB) and t-butyl-peroxy-2-ethyl hexanoate (PDO), obtained from Lucidol. A poly(vinyl acetate) (PVAc) (Union Carbide, LP-40A) was used as a low profile additive. Both unsaturated polyester and styrene monomer (Aldrich) were used as received without removing the inhibitor. The molar ratio of styrene/C=C bonds in unsaturated polyester resin was chosen to be 2.0. Before the experiment the UPE and styrene were weighed and mixed in a flask with the appropriate weight ratio. The PVAc was added to this mixture in such a way that its weight amounted to 15% of the total weight of the sample. The composition of the

Table 1 Composition of the sample

Ingredient	Weight %
UPE resin (Q6585, UPE 65% in styrene)	56.0
Styrene	6.5
PVAc (LP-40A, PVAc 40% in styrene)	37.5

sample is shown in Table 1. MMA (Plaskolite Chemical Company) was used without any additional treatment.

Instrumentation and procedures

Reaction kinetics measured by d.s.c. The reaction kinetics were measured using a differential scanning calorimeter (Thermal Analysis DSC-10). The reactions were conducted in volatile aluminium sample pans that were capable of withstanding at least 0.2 MPa of internal pressure. The weight of the samples ranged between 5 and 15 mg with an empty pan as a reference. Isothermal runs were complete when the exotherm ended. The residual and scanning runs started at room temperature and increased to 240°C at a rate of 10°C min⁻¹.

The isothermal runs showed the onset time of reaction. The exotherm signal was integrated to determine the isothermal heat of reaction. Any leftover reaction was computed from the residual scan. The scanning method was used to find the onset temperature of reaction. The exotherm signal was integrated with respect to time to determine the total heat of reaction³. The exotherm data can be converted into the reaction rate and conversion as a function of time based on the assumptions that thermophysical properties of the reacting resin remain unchanged during reaction and the total heat of reaction measured from the scanning experiment represents 100% conversion.

Rheological changes measured by Rheometrics dynamic analyser. The rheological measurements were made with a Rheometrics dynamic analyser (RDA, model 700). The storage shear modulus (G') and loss shear modulus (G'') were measured during the isothermal reaction. The liquid–solid transition (i.e. gelation) was assumed to occur at the point at which G' and G'' intersected.

The reaction occurred on serrated aluminium plates, 25 mm in diameter. A 1.1 mm gap was set between the two plates. The bottom plate oscillated at 10 rad s⁻¹. The strain was set at 10% for low G' and changed to 1% when the torque reached 0.01 N m⁻¹ so that the moduli could be measured at high conversions.

Radical concentration measured by e.s.r. A Bruker Instruments (ESP 300 9.5 GHz X band) e.p.r. system was used to measure radical concentration. The reaction proceeded in quartz e.p.r. sample tubes (o.d. 4 mm, i.d. 3 mm). The sample tube was positioned at the same spot in the cavity for all runs to ensure measurement consistency. Before measurement, cavity calibration was carried out using a sample without initiator in order to achieve the maximum modulation amplitude. The sampling time interval was 38 s. Both isothermal and scanning experiments were carried out following the same temperature profiles described in d.s.c. analysis. Owing to the differences in instrument and sample size, the actual sample temperature profiles and/or heat transfer may vary between the d.s.c. experiments and the e.s.r.

experiments. The discrepancy was kept low by choosing low temperatures (347–368 K) and a low scanning rate (10°C min⁻¹) for the given reaction systems.

Radical concentration data were obtained after calibrating the e.s.r. system with a standard compound, i.e. a compound whose solution produces stable free radicals. The standard used in this study was 2,2-diphenyl-1-picryl hydrazyl hydrate (DPPH) from Aldrich. Solutions of DPPH were prepared in the range of 10⁻²–10⁻⁷ mol l⁻¹. Benzene in spectroscopic grade was the solvent used for dilution. The starting solution was prepared by dissolving a known amount of DPPH (0.3669 g) in a 10 ml volumetric flask. The remaining solutions were made by step-wise dilutions. The radical concentration of these solutions could be determined with the known molecular weight (394.34 g mol⁻¹) and free radical purity (0.95) of DPPH. The calibration curve is shown in Figure 2.

Experimental design

Table 2 lists the experimental runs for the polymerization of UPE and styrene. The radical concentration was also measured in the free-radical polymerization of MMA at 348 K. This, in conjunction with runs 1 and 3, allowed us to study the effect of physical changes on reaction kinetics. The polymerization of MMA represents a linear system and the polymerizations of UPE and styrene with and without PVAc represent crosslinking systems. The effect of initiator concentration was studied in runs 1 to 4. Runs 5 to 7 studied the effect of reaction temperature.

RESULTS AND DISCUSSION

Figure 3 shows the radical concentration profile and radical spectra measured by e.s.r. at 348 K for the UPE resin with 1% DMB. The radical spectra showed a transition from narrow line-shape (spectrum A) to broader line-shape (spectrum E). The line-shape of the spectrum was dependent on the excitation and relaxation mechanisms of the radical. In an e.s.r. experiment, radicals are excited under the influence of an external magnetic field. The excitation and relaxation of these radicals produce the observed line-shape. For radicals in a liquid environment, the excitation and relaxation processes are very fast, which results in a narrow line-shape of a millitesla width. The excitation and relaxation processes for radicals in the solid state are slower, which results in a much broader line-shape²⁹.

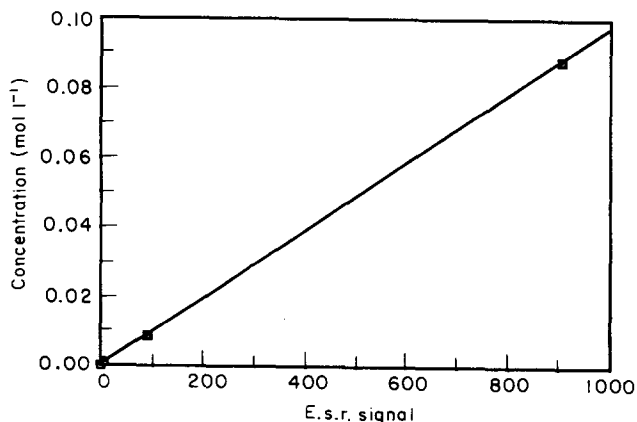
**Figure 2** DPPH calibration curve

Table 2 Experimental runs

Run number	Initiator		Thermoplastic additive	Temperature (K)	Analysis
	Type	(wt%)			
1	DMB	1.0	—	348 ^a	e.s.r., RDA, d.s.c.
2	DMB	3.0	—	348 ^a	e.s.r., RDA, d.s.c.
3	DMB	1.0	PVAc	348 ^a	e.s.r., RDA, d.s.c.
4	DMB	3.0	PVAc	348 ^a	e.s.r., RDA, d.s.c.
5	PDO	1.0	PVAc	347	e.s.r., d.s.c.
6	PDO	1.0	PVAc	358	e.s.r., d.s.c.
7	PDO	1.0	PVAc	368	e.s.r., d.s.c.

^aScanning and residual experiments were also performed

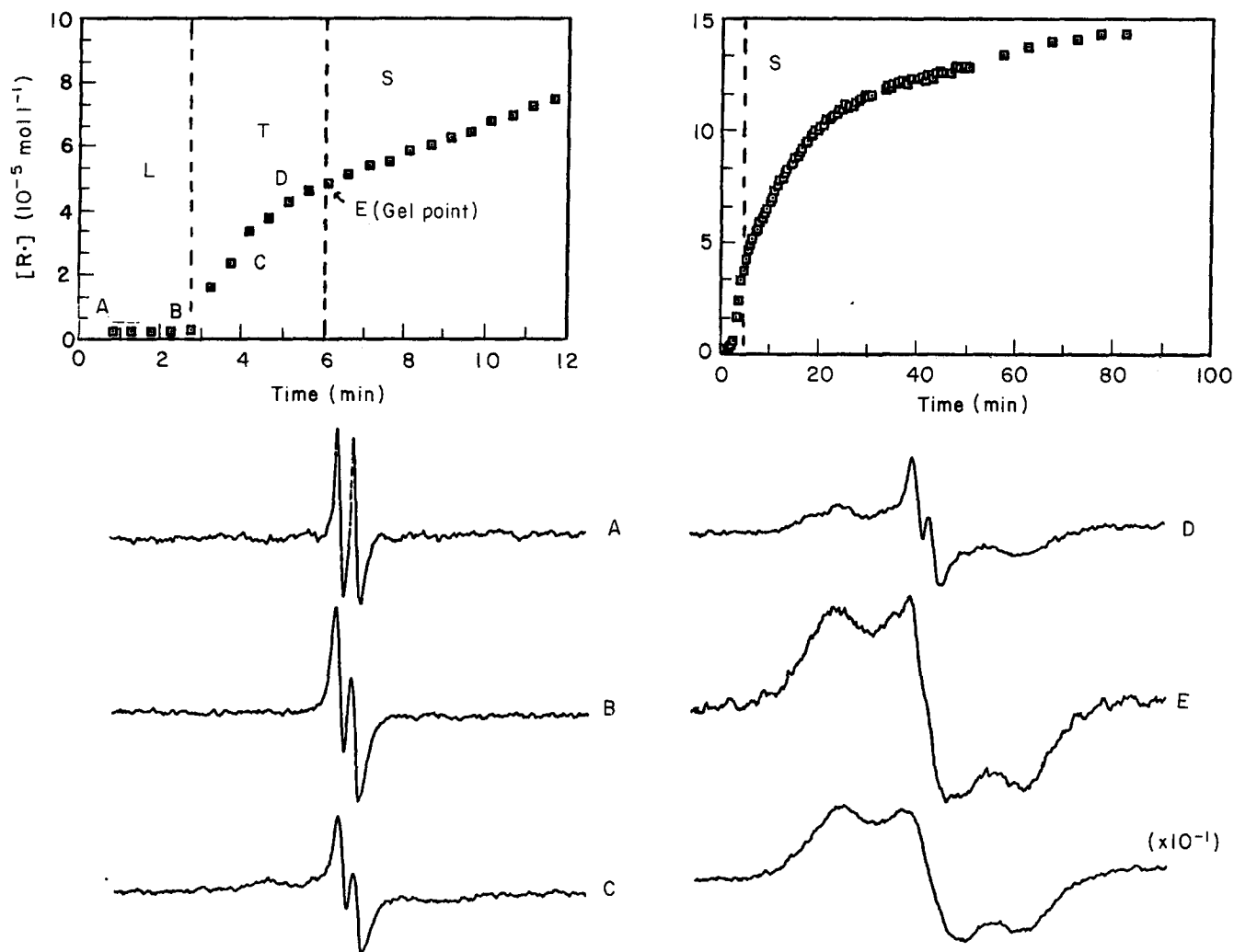


Figure 3 Run 1: radical concentration profile and radical spectra (see text for discussion)

Spectra B to D are results of a combination of solid-like and liquid-like radicals, at different ratios. These spectra represent the liquid–solid transition of the reacting medium. Overall, the radical concentration profile shows three distinct regions according to the line-shape of the e.s.r. spectrum. The profile shows an initial steady-state region (region L) in which liquid-like spectra were observed. In this region radical concentrations of

$10^{-6} \text{ mol l}^{-1}$ were found. This steady-state region lasted about 2 min. After that, a sharp increase in radical concentration occurred and the line-shape of the radical spectra showed contributions from both the liquid-like and solid-like radicals (spectra B to D). This is a transition region (region T) where the reacting mass was heterogeneous in terms of radical environment. The transition region lasted 3 min. After point E all radicals

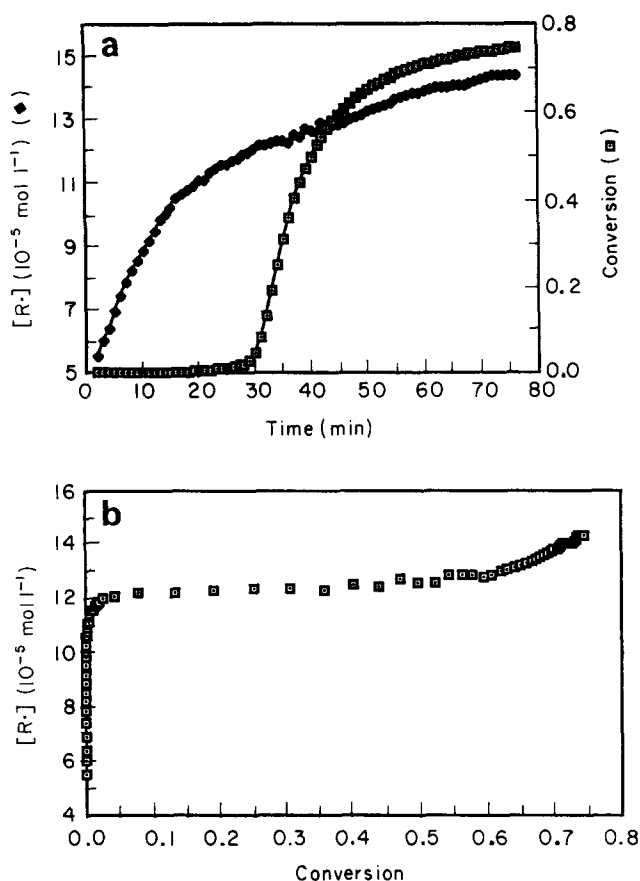


Figure 4 Run 1: (a) radical concentration and conversion *versus* time; (b) radical concentration *versus* conversion

became solid-like (region S) and the radical concentration continued to increase and finally levelled off. The final radical concentration was $1.44 \times 10^{-4} \text{ mol l}^{-1}$.

From the e.s.r. and RDA data, it was found that the liquid–solid transition point (i.e. $G' = G''$) occurred when the spectra became nearly solid-like (point E). The gel times, t_{gel} , measured by e.s.r. were only slightly different from the average of three RDA experiments: $7.5 \pm 0.5 \text{ min}$ for RDA and $7.8 \pm 0.6 \text{ min}$ for e.s.r.

Figure 4a shows radical concentration and conversion *versus* time for the sample with 1% DMB. The radical concentration attained more than 75% of its maximum value before any measurable increase in conversion could be detected. Figure 4b shows radical concentration *versus* conversion. This curve can be divided into three stages. In the first stage radical concentration increased, while no change in conversion could be detected. The onset of reaction occurred in the second stage, where the conversion increased faster than the radical concentration. In the third stage the conversion reached a high value and started to level off. In this stage the radical concentration increased faster than the conversion.

The addition of a thermoplastic additive to an unsaturated polyester resin causes phase separation. The thermoplastic additive used was PVAc. (PVAc formed a single phase solution with uncured resins but caused phase separation during reaction.) The addition of PVAc resulted in a decrease of the heat of reaction measured by d.s.c. The onset of reaction was also delayed by the addition of PVAc, while a longer gel time was measured by RDA.

The radical concentration profiles of UPE with PVAc are shown in Figure 5. They also reveal the three-region

shape as found in pure UPE. The most prominent effect of the addition of PVAc on the radical concentration profile was the reduction in the radical generation rate. Another difference in these profiles was the duration of the transition region, which lasted about 50% longer for the sample with PVAc. The liquid region, which preceded the transition region, lasted 6 min. Again, this region ended with the appearance of the first totally solid-like spectrum. The gel time measured by RDA also agreed very well with the end of the transition region. Figure 6a shows the radical concentration and conversion *versus* time, and Figure 6b shows the radical concentration *versus* conversion.

The free-radical polymerization of MMA with 1% DMB was studied as an example of a homogeneous linear polymerization system. The isothermal e.s.r. experiment was run for 50 min before any signal could be detected. After that, the radical concentration remained relatively constant at $10^{-6} \text{ mol l}^{-1}$ for more than 2 h.

Figure 7 compares the radical concentration profiles for the three systems (i.e. MMA polymerization, run 1 and run 3). The UPE/styrene polymerizations showed much larger radical concentration than the MMA polymerization. This was caused by the ability of crosslinked systems to trap radicals. Among the two UPE/styrene systems, the one without PVAc showed the largest radical concentration of all. Perhaps PVAc acted as a radical scavenger, possibly by proton abstraction. The presence of PVAc might also partition the initiator between the phases in such a way as to change the radical concentration. Further experiments are needed to explain this difference. The very low radical concentration during MMA polymerization was due to the lack of the molecular shielding effect in linear systems. It was discussed by Bamford *et al.*¹⁴ that the amount of radicals remaining after the reaction, the so-called trapped radicals, is proportional to the degree of occlusion. The degree of occlusion of the radicals is the magnitude of the polymer barrier protecting a radical from reagent molecules. In a homogeneous linear polymerization system, the degree of occlusion, more recently named the shielding effect, is very small. Hence the trapped radical concentration should be relatively small. This weak shielding makes residual radicals unstable. After the isothermal experiments, the residual radical concentration decayed within a few seconds at room temperature. On the other hand, the residual radicals in the two UPE/styrene systems were very stable at room temperature. The radical concentration did not decay for 2 weeks at ambient temperature and lasted much longer when the samples were stored in nitrogen gas. Similar results for other radical crosslinking polymerizations have been reported elsewhere²⁵.

Figure 8 shows the changes in radical concentration as a result of addition of PVAc and the change in initiator concentration for the UPE/styrene system. Increasing the initiator concentration from 1 to 3 wt% resulted in an increase of the radical concentration by a factor of approximately 2.5. The transition region decreased by a factor of 3.0. The gel time also decreased by a factor of 3.0. Table 3 summarizes the data from d.s.c., RDA and e.s.r. for the UPE/styrene systems with DMB as initiator.

As mentioned before, Atherton *et al.*¹⁵ found that radicals in crosslinked system are thermally stable, and

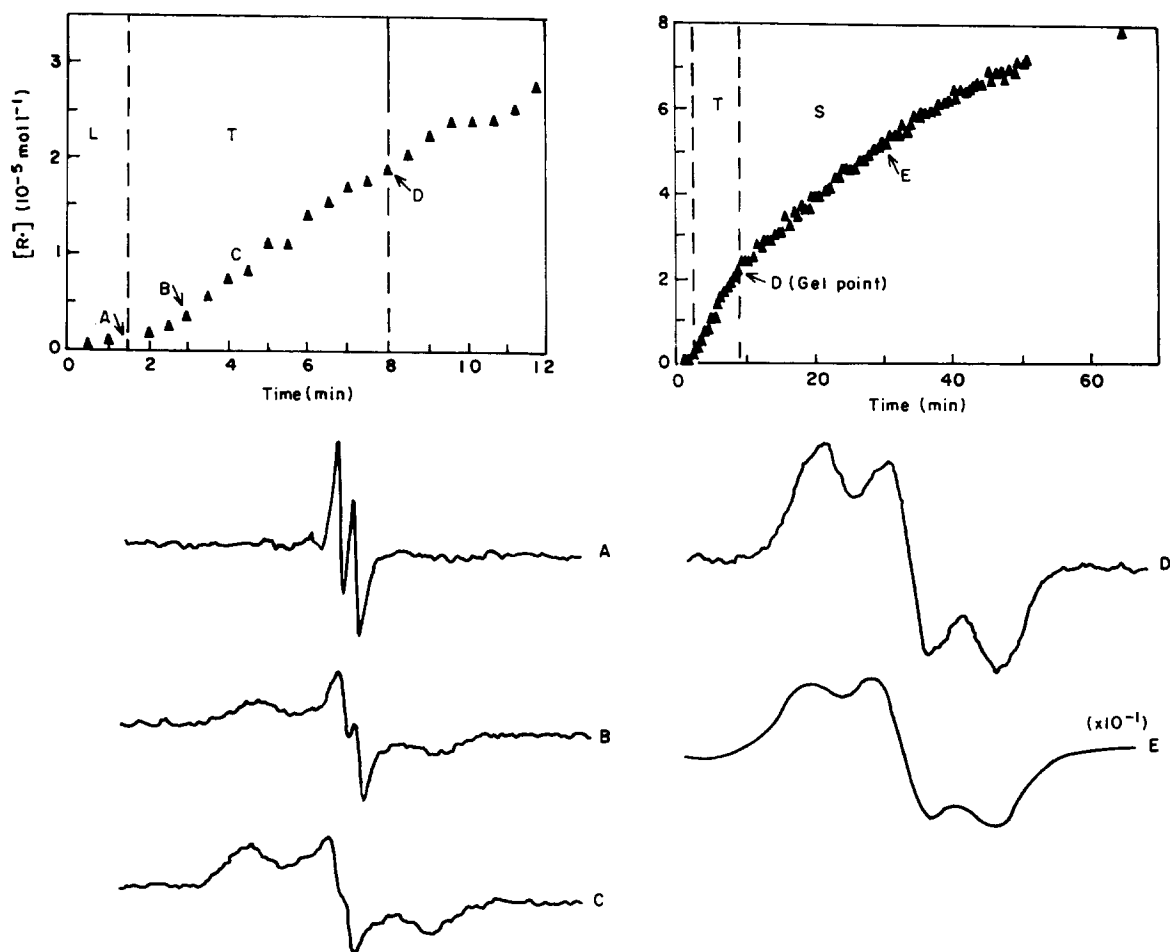


Figure 5 Run 3: radical concentration profile and radical spectra

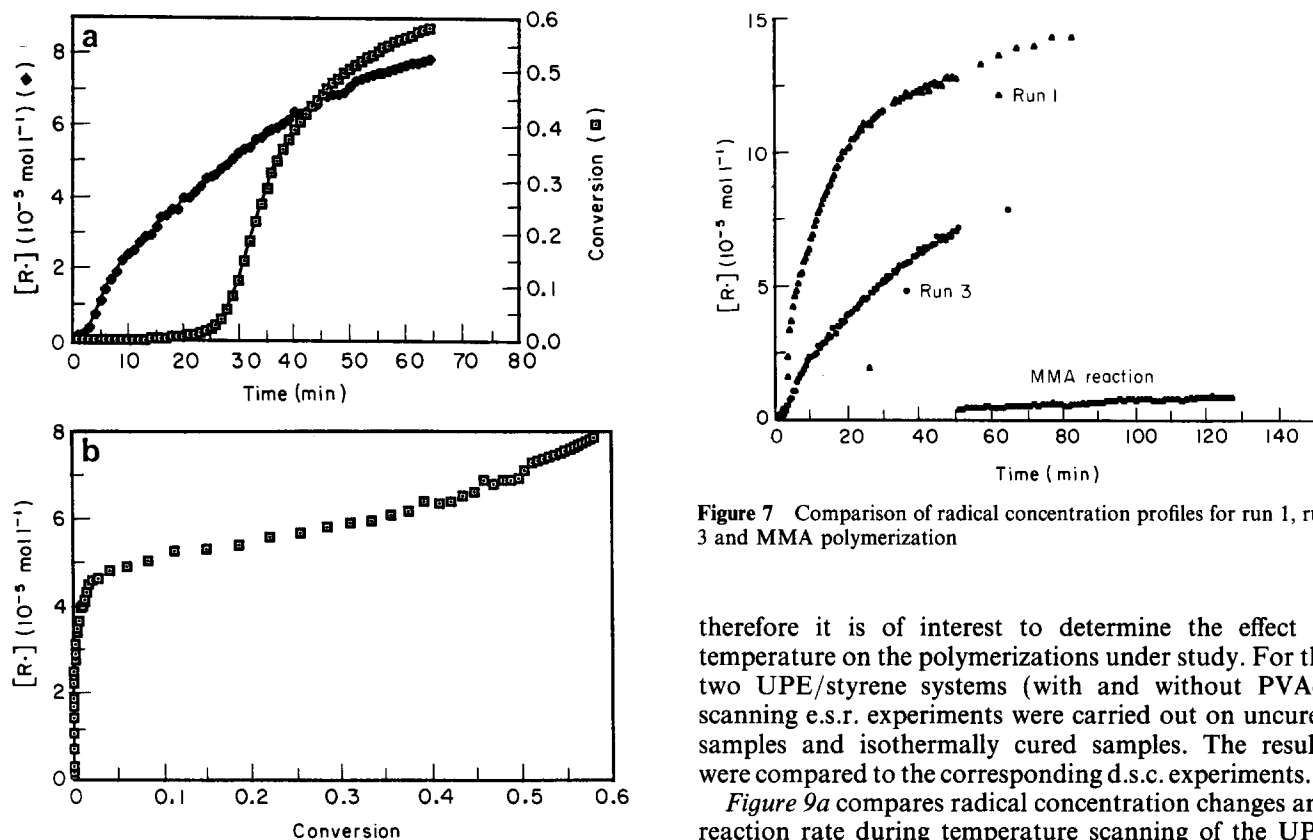


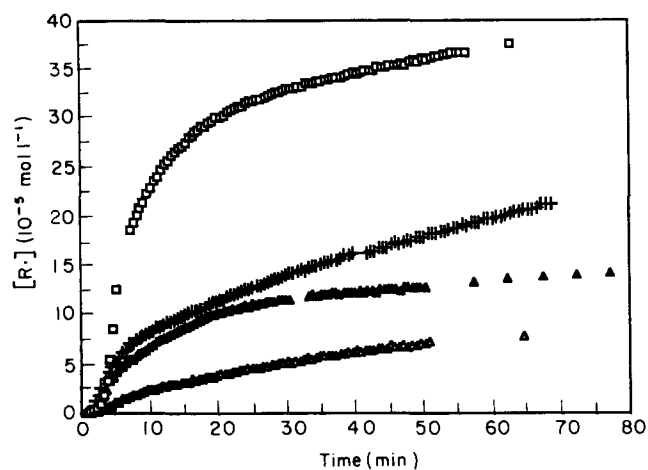
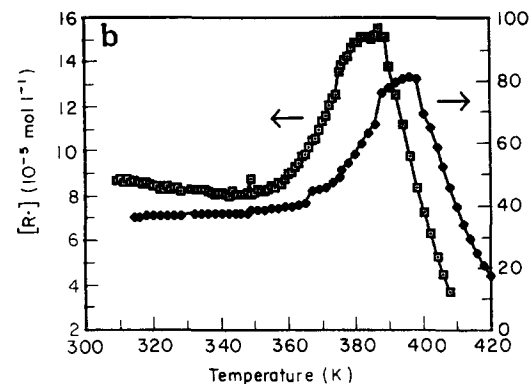
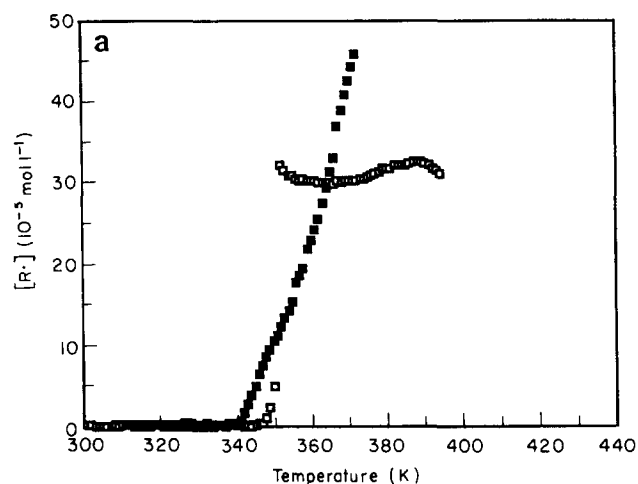
Figure 7 Comparison of radical concentration profiles for run 1, run 3 and MMA polymerization

therefore it is of interest to determine the effect of temperature on the polymerizations under study. For the two UPE/styrene systems (with and without PVAc) scanning e.s.r. experiments were carried out on uncured samples and isothermally cured samples. The results were compared to the corresponding d.s.c. experiments.

Figure 9a compares radical concentration changes and reaction rate during temperature scanning of the UPE resin with 3 wt% DMB initiator without PVAc. The scanning curve showed a step increase of radical

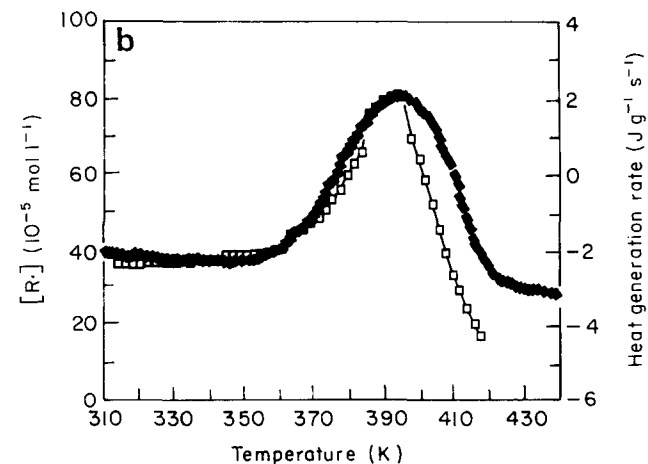
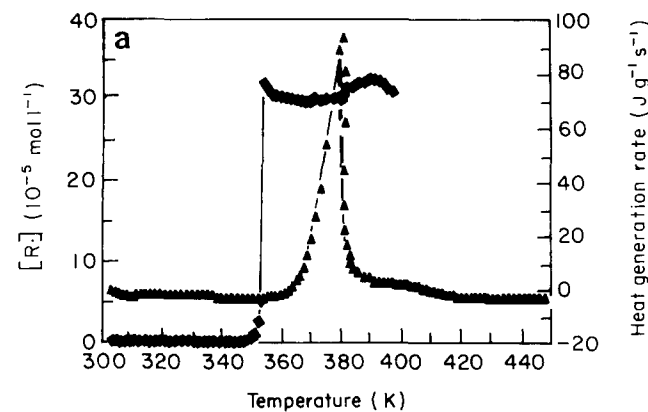
Table 3 Summary of results from d.s.c., RDA and e.s.r.

	1% initiator (DMB)		3% initiator (DMB)	
	without PVAc	with PVAc	without PVAc	with PVAc
Scanning heat (J g^{-1})	514.5	468.3	507.4	435.0
Isothermal heat (J g^{-1})	399.5	342.1	388.9	316.9
Conversion (%)	77.66	73.07	76.63	72.86
Residual heat (J g^{-1})	95.8	108.0	111.3	103.5
t_{gel} (RDA) (min)	7.5	8.0	2.6	3.5
t_{gel} (e.s.r.) (min)	7.8	8.3	2.2	3.6
$[\text{R}\cdot]_{\text{max}}$ (mol l^{-1})	1.5×10^{-4}	7.88×10^{-5}	3.68×10^{-4}	2.14×10^{-4}


Figure 8 Effect of initiator concentration and addition of PVAc on radical concentration: \blacktriangle , run 1; \square , run 2; \triangle , run 3; $+$, run 4

Figure 10 (a) Radical concentration during scanning experiment for run 2 (\square) and run 4 (\blacksquare). (b) Radical concentration during scanning experiment for the isothermally cured UPE/styrene samples for run 2 (\blacklozenge) and run 4 (\square)

concentration around 350 K which was about 20°C lower than the onset temperature of reaction measured by d.s.c. This could be attributed to the experimental error caused by temperature control in two techniques. The change of the line-shape of the radical spectrum (i.e. from liquid-like to solid-like) also occurred around 350 K.

Results of the scanning of the 348 K isothermally cured resin are given in *Figure 9b*, which shows that the radical concentration started to increase around 350 K. The radical concentration profile showed a peak around 393 K, and then decayed quickly. The residual reaction profile measured by d.s.c. followed almost the same trend as the radical concentration profile. The increase in radical concentration during the residual scanning run can be explained by the fact that when temperature


Figure 9 Run 2: (a) radical concentration and heat generation rate during scanning experiment (\blacklozenge , e.s.r.; \blacktriangle , d.s.c.); (b) radical concentration and heat generation rate during scanning experiment for the isothermally cured sample (\square , e.s.r.; \blacklozenge , d.s.c.)

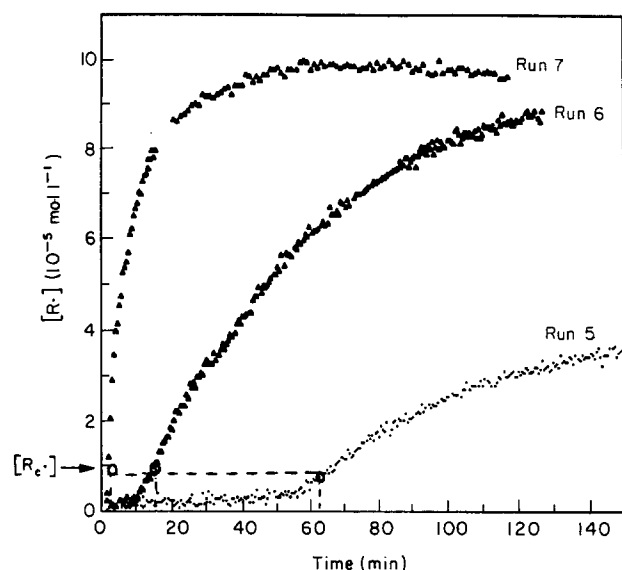


Figure 11 Effect of temperature on radical concentration

becomes higher than the glass transition temperature of the isothermally cured resin, reaction of residual functional groups may occur, which tends to form more trapped radicals in highly crosslinked systems. These radicals tend to be terminated at higher temperatures.

Figure 10a compares the results of the scanning experiments for the uncured UPE/styrene samples with and without PVAc. The fact that two very different profiles were obtained during the scanning experiments implied that the reaction kinetics were affected by the addition of PVAc. For isothermally cured samples under temperature scanning, the radical profiles were similar for samples with and without PVAc (Figure 10b), but the radical concentration for the latter was five times larger than that for the former.

The effect of temperature on the radical concentration was also studied. The initiator used was PDO which allowed for higher reaction temperatures. Figure 11 shows the radical concentration for the reaction of UPE with styrene at temperatures of 347, 358 and 368 K (i.e. runs 5 to 7). The concentration of trapped radicals increased with temperature. When compared with the rheological changes, it was found that the liquid–solid transition (i.e. $G' = G''$) occurred when the radical concentration reached the same critical value, $[R_c \cdot]$, about $3 \times 10^{-6} \text{ mol l}^{-1}$ in this case, at various temperatures. This result can be very useful for modelling the gelation of chain crosslinking polymerizations^{11,30}.

CONCLUSIONS

(1) For the curing of UPE with styrene, the radical concentration profiles showed an initial quasi-steady-stage region in which the radicals were in a liquid environment. After this initial region, the radical concentration began to increase and showed contributions from liquid-like and solid-like radicals. At the end of this transition region the radicals became solid-like and the radical concentration continued to increase and finally levelled off. The end of the transition region correlated reasonably well with the gel time measured by RDA.

- (2) For the resin system studied, the radical concentration was about 75% of its final value before any change in the conversion was observed.
- (3) The radicals in crosslinked systems were much more stable than those from linear systems. The radical concentrations for the linear systems were much smaller than for the crosslinked systems.
- (4) When the initiator concentration was increased from 1 to 3 wt%, the radical concentration increased by a factor of 2.5 and the transition regions were three times shorter.
- (5) The results of the scanning experiments for isothermally cured samples showed that more trapped radicals were generated at higher temperatures. This agreed well with the onset of residual reaction measured by d.s.c.
- (6) The radical concentration profiles obtained from isothermal and scanning e.s.r. experiments for uncured samples with and without PVAc were very different. This indicated that the reaction mechanism may be different due to the addition of PVAc.

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