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An ESR Study of the Curing Reaction of Unsaturated Polyester with Vinyl Monomers and the Thermal Behavior of the Cured Polymers

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AN ESR STUDY OF THE CURING REACTION OF UNSATURATED POLYESTER WITH VINYL MONOMERS AND THE THERMAL BEHAVIOR OF THE CURED POLYMERS

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ABSTRACT

The curing reaction of an unsaturated polyester (BAPM), prepared by polycondensation of Bisphenol A-di-(2-hydroxypropyl)ether and maleic anhydride, with vinyl monomers was investigated by IR and ESR. Thermal properties of the resulting polymer were studied by DSC and TMA. For the curing reaction of BAPM with styrene initiated with the cobalt naphthalate/1-hydroxycyclohexyl hydroperoxide system, the copoly-

erization process could be satisfactorily analyzed by the Mayo-Lewis integral equation for the usual homogeneous copolymerization. The reaction mixtures contained long-lived polymer radicals, the ESR spectra of which gave important information on the curing reaction. The DSC and TMA results showed that a microphase separation occurred in the cured polymer from BAPM and styrene. The phase separation was accelerated by treatment at -3°C . However, heat treatment above 150°C eliminated the phase separation. These phenomena were also confirmed by TEM examination.

INTRODUCTION

Many workers have extensively investigated the properties and structures of networks in cured polymers [1-12], epoxy resins having received most attention [4-8]. Cured epoxy resins were reported to contain nonuniform structures involving globules [4], nodules [5], and domains embedded in and bound to regions of lower crosslinked structures [6], depending on chemical constitution of the materials, curing conditions, and thermal history.

On the other hand, less attention has been paid to free-radical crosslinked polymers because of their broad distribution of network chain length and of sol polymers trapped within the network. No detailed studies have been carried out on unsaturated polyesters in spite of their industrial importance, although Goto [13] and Saunders [14] examined their structures by chemical analysis.

In the present paper, we study the curing reaction of an unsaturated polyester (BAPM) which was prepared by polycondensation of maleic anhydride (MAN) and Bisphenol A-di-(2-hydroxypropyl) ether (BADHPE) with vinyl monomers. BADHPE has structural units similar to those of epoxy resins.

EXPERIMENTAL

Materials

BAPM was prepared by polycondensation of MAN and BADHPE (Kyoeisha Oil & Fats Co., average 2.3 hydroxyls per molecule) by heating up to 210°C for 8-9 h [15]. The resulting BAPM had a molecular weight of 2200 (as measured by acid number analysis and vapor pressure osmometry) and was purified by reprecipitation from toluene/hexane. Two redox sys-

tems were used as initiators in the present work, namely dimethylaniline (DMA)/benzoyl peroxide (BPO) and cobalt naphthalate (CoN)/1-hydroxycyclohexyl hydroperoxide (HCH). HCH, prepared by oxidation of cyclohexanone with hydrogen peroxide using nitric acid as catalyst, is known to have more than 6% of active oxygen and to contain three other peroxides as by-products [16]. HCH was used as a 50% paste with di-*n*-butyl phthalate.

Curing and Sample Preparation

BAPM was dissolved in styrene (St) or methyl methacrylate (MMA). The initiator system was added to the solution, mixed thoroughly by stirring, degassed with an aspirator, poured into a mold, and cured under the conditions specified.

Measurements

The conversions of both double bonds of BAPM and St were determined by IR spectroscopy: 1660 (C=C, BAPM), 1642 (C=C, St), and 1740 cm^{-1} (C=O, ester of BAPM). The absorption of ester carbonyl was used as a reference for sample thickness.

Samples for ESR measurement were prepared in a tube of Pyrex glass or polyethylene. They were transferred into an ESR tube and then degassed. ESR spectra were recorded with a JEOL FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity.

Thermal behavior of the cured polymers was examined by DSC (DuPont 1090) and TMA (Chenguan WX-1). In the former, the cured polymer powder was placed in a Perkin-Elmer aluminum sample pan and heated at 5 or 10°C/min. In the latter, a cylindrical sample (10 mm height, 10 mm diameter) was heated at 2°C/min. The area of the probe tip was 1 mm^2 , and the load was 4 kg.

Transmission electron microscopic (TEM) examination was performed with a Hitachi electron microscopy (H-800) (accelerating voltage, 100 kV). The cured polymer was cut into a sheet of 700 Å thickness by a microtome (Sorva MT-6000).

RESULTS AND DISCUSSION

Polymerization of Styrene and Methyl Methacrylate

In order to clarify the initiation behavior of the two redox initiator systems (CoN/HCH, DMA/BPO), the polymerizations of St and MMA with them in

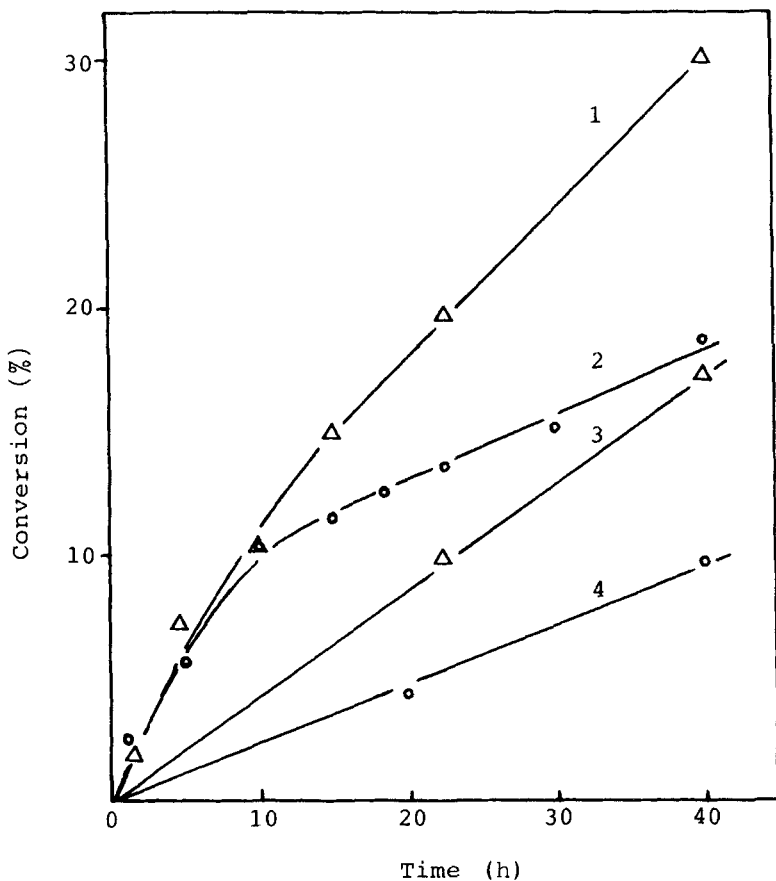


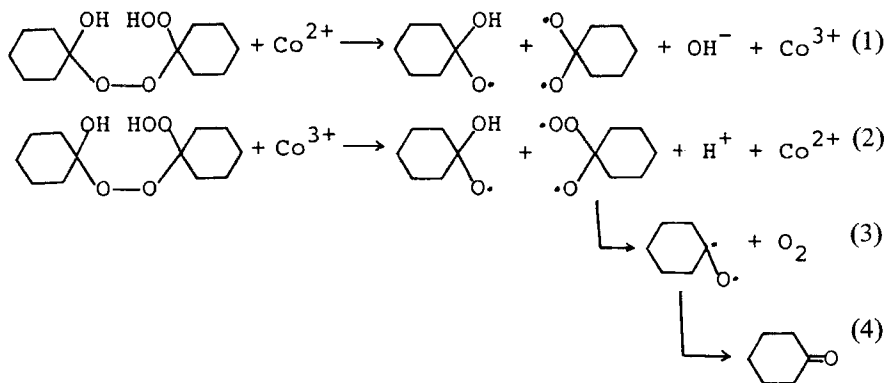
FIG. 1. Time-conversion curves for the bulk polymerization of St at 30°C with the initiator systems (1) CoN (0.12 wt%)/HCH (2 wt%), (2) DMA (0.1 wt%)/BPO (2 wt%), (3) HCH (2 wt%), and (4) BPO (2 wt%).

bulk at 30°C were investigated. These monomers were used as curing reagents in the present study. The concentrations of the initiator components were the same as those used below in the curing reactions with a gelation time of 20-30 min.

Figure 1 shows the time-conversion curves for the St polymerization. The rate of polymerization with the DMA/BPO system (Curve 2), which showed a high initial value, decreased rapidly with time. After about 10 h it became

nearly identical with that for initiation with BPO alone (Curve 4). This indicates that DMA of much lower concentration ($[DMA]/[BPO] \approx 0.1$) was exhausted in the initial 10 h, and after that, BPO alone acted as initiator.

On the other hand, comparison of Curves 1 and 3 reveals that the CoN/HCH redox system was effective for a long time although the initiating activity was gradually reduced. This is probably because cobalt ions can react to and fro between Co^{2+} and Co^{3+} as follows [16] :



In the early stage (the initial 6 h), the two redox initiator systems (Curves 1 and 2) were found to induce St polymerization at similar rates. The molecular weights of polystyrenes formed in 1 h with both initiator systems were determined by GPC as follows:

$$\begin{array}{l}
 \bar{M}_n = 16\,000, \bar{M}_w = 38\,000 \quad (\text{CoN/HCH system}) \\
 \bar{M}_n = 26\,000, \bar{M}_w = 61\,000 \quad (\text{DMA/BPO system}).
 \end{array}$$

These results suggests that the chain-transfer constant for the DMA/BPO initiator system is smaller than that for the CoN/HCH one.

Curves 1 and 2 in Fig. 2 show the relationship between the conversion and time in MMA polymerization initiated with the CoN/HCH and DMA/BPO systems, respectively. In both runs an autoacceleration was observed at about 10% conversion. DMA/BPO was found to be more effective for MMA than was CoN/HCH.

Curing Reaction of BAPM with Vinyl Monomers

BAPM was cured by copolymerization with St, MMA, and their mixture, with DMA/BPO or CoN/HCH as initiator. The resulting polymer mixtures

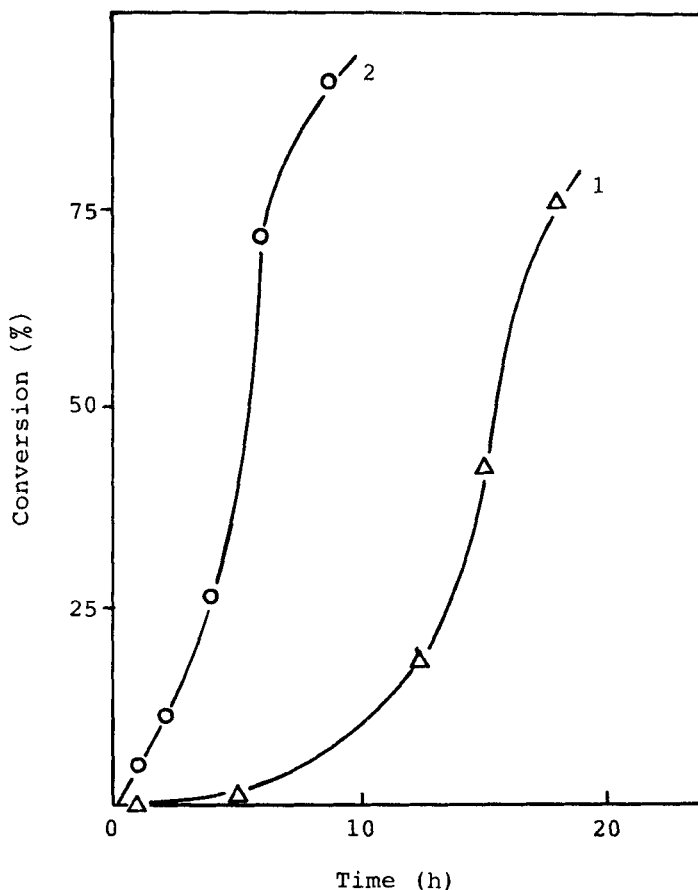


FIG. 2. Time-conversion curves for the bulk polymerization of MMA at 30°C with the initiator systems (1) CoN (0.12 wt%)/HCH (2 wt%) and (2) DMA (0.1 wt%)/BPO (2 wt%).

were made into powder (particle size $\sim 200 \mu\text{m}$) and extracted with acetone for 48 h in a Soxhlet apparatus. The results are shown in Table 1.

The percent extract decreased in the following order, depending on the monomer used: MMA > St/MMA mixture > St. Further, the MMA-crosslinked product was found to be well swollen in acetone. Thus, BAPM was more effectively crosslinked by St than by MMA.

TABLE 1. Curing Reaction of BAPM with Vinyl Monomers

Curing time	Percent extract ^a			
	MMA ^b (DMA/BPO) ^c	MMA:St ^b 1:1 (DMA/BPO) ^c	St ^b (DMA/BPO) ^c	St ^b (CoN/HCH) ^d
4.5 h	—	—	—	25.5
8.5 h	—	—	39.0	—
30.2 h	—	—	—	25.4
35.3 h	—	—	29.2	—
3.3 d	—	—	24.9	—
18 d	41.0	—	24.4	23.1
At 150°C for 4 h after 18 d	37.5	30.0	16.3	17.2

$$^a \text{Percent extract} = \frac{\text{weight of sol fraction}}{\text{weight of total cured polymer}} \times 100.$$

^bBAPM: monomers = 65:35 (w/w).

^cDMA, 0.1 wt%; BPO, 2 wt%.

^dCoN, 0.12 wt%; HCH, 2 wt%.

The percent extract observed in St-curing with the DMA/BPO system decreased gradually with time up to 80 h, whereas that with the CoN/HCH system reached a limiting value of 24.5% in 4.5 h. These findings indicate that CoN/HCH is more efficient for crosslinking than DMA/BPO. However, similar gelation times (20-30 min) were observed for both initiator systems, which agrees with the above result that the two systems showed similar initiating activity for St (Fig. 1). Radicals from the DMA/BPO system may have low reactivities toward the double bonds of BAPM.

Heating at 150°C for 3 h caused further crosslinking in both reaction systems.

IR Study on the Curing Reaction of BAPM

Copolymerization of BAPM with St initiated with the CoN/HCH system was investigated by IR spectroscopy.

Figure 3 shows the relationship between the reaction time and the conversion of the double bonds of St and BAPM as followed by IR. Gelation of the reaction system occurred at about 12% conversion of the BAPM double bonds. After the gel point, the conversion of the BAPM double bonds became higher than that of the St ones, although the former was lower than the latter in the early stages. At about 70% conversion of BAPM, St conversion again exceeded that of BAPM.

Heating at 40 and 150°C was found to accelerate the reaction. Cooling at -3°C for 3 d in the course of the reaction exerted little effect on the conversion of the components.

It is of interest to analyze the above results according to the Mayo-Lewis integral equation for radical copolymerization:

$$\log \frac{[m_2]}{[m_2]_0} = \frac{r_2}{1-r_2} \log \frac{[m_2]_0 [m_1]}{[m_1]_0 [m_2]} - \left(\frac{1-r_1 r_2}{(1-r_1)(1-r_2)} \right) \left(\log \frac{(r_1-1)[m_1]/[m_2] - r_2 + 1}{(r_1-1)[m_1]_0/[m_2]_0 - r_2 + 1} \right), \quad (5)$$

where $[m_i]_0$ and $[m_i]$ stand for the initial concentration of monomer M_i and that at the given time, respectively, and r_i is the monomer reactivity ratio.

Curve 1 in Fig. 4 was calculated by using $r_1 = 0.21$ and $r_2 = 0.025$ reported for the copolymerization of St (M_1) and dimethyl fumarate (DMF)

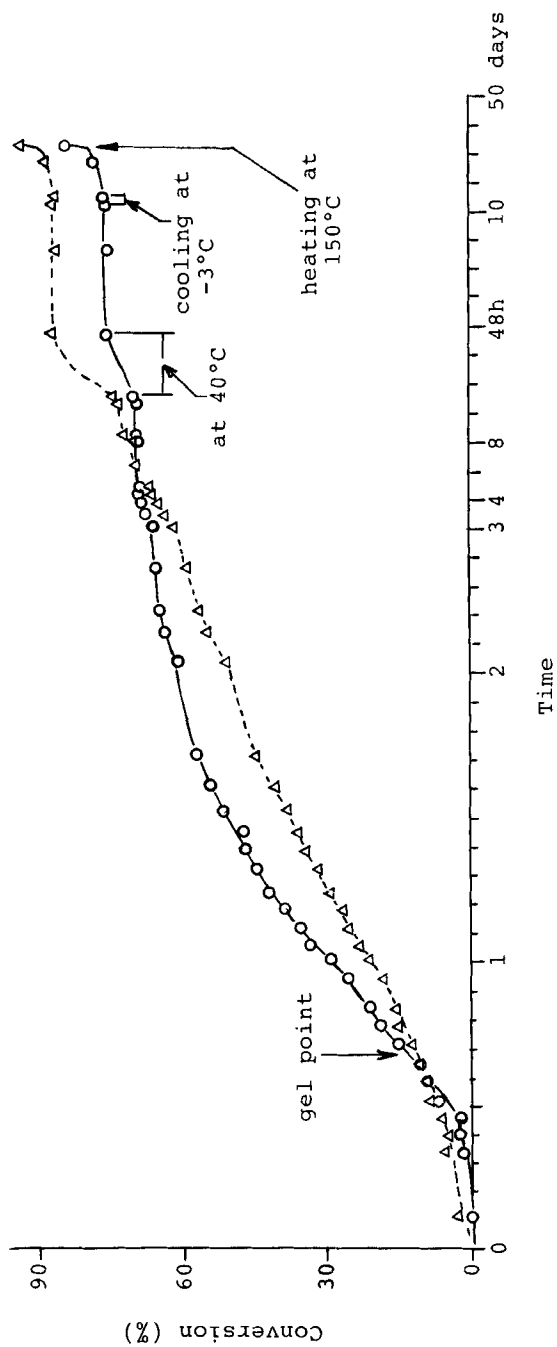


FIG. 3. Time-conversion curves for the curing reaction of St (Δ) and BAPM (\circ) (molar ratio of double bonds of the two = 1.9:1) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system at room temperature.

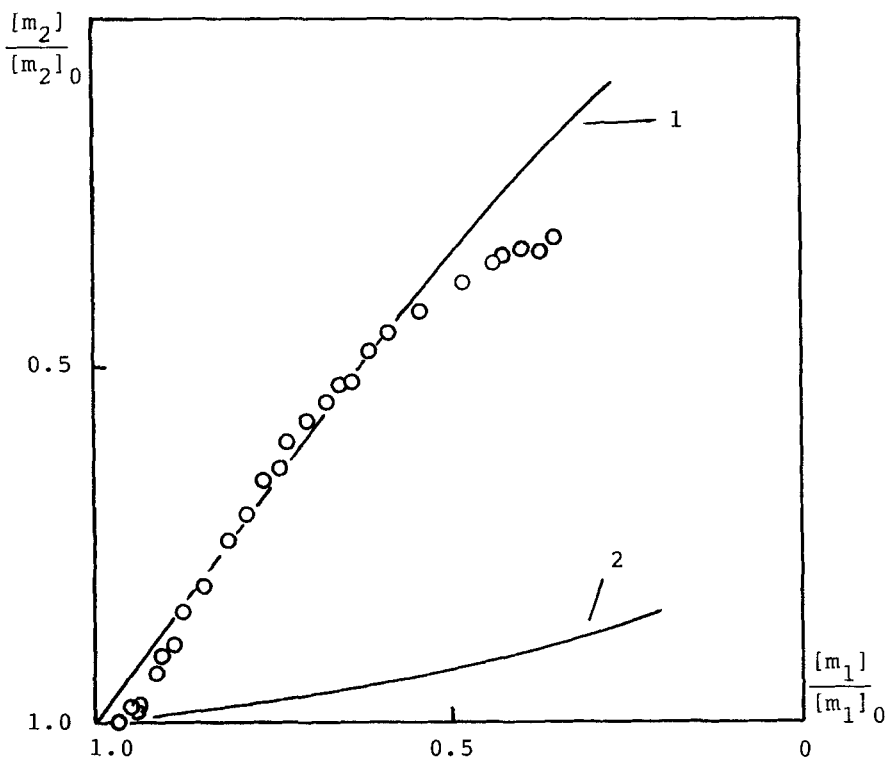


FIG. 4. Relative conversion curves calculated according to the Mayo-Lewis integral equation in the copolymerization of (1) St-dimethyl fumarate (molar ratio = 1.9:1) and (2) St-dimethyl maleate (molar ratio = 1.9:1). Circles: Observed data of the St-BAPM system in Fig. 3.

(M_2) [17], while Curve 2 was calculated by using $r_1 = 8.5$ and $r_2 = 0.03$ for the copolymerization of St (M_1) and dimethyl maleate (M_2) [17], where $[m_1]/[m_2] = 1.9$. It can be seen that the results of the present curing system fit Curve 1 well up to 60% conversion of the BAPM double bonds in spite of the fact that MAN was used for the preparation of BAPM. This indicates that BAPM contained fumarate ester units, formed by isomerization of the maleate units during the preparation of BAPM [18]. Further, it is noteworthy that the BAPM double bonds showed a reactivity similar to that of DMF even after gelation, suggesting that the double bonds are mobile enough to react well with St in the curing system.

ESR Study of the Curing Reaction of BAPM with Vinyl Monomer

In the curing reaction the resulting polymer radicals are expected to be long-lived because their diffusion is so restricted that bimolecular termination between them is suppressed.

Figure 5 shows the ESR spectral change with time observed in the BAPM/

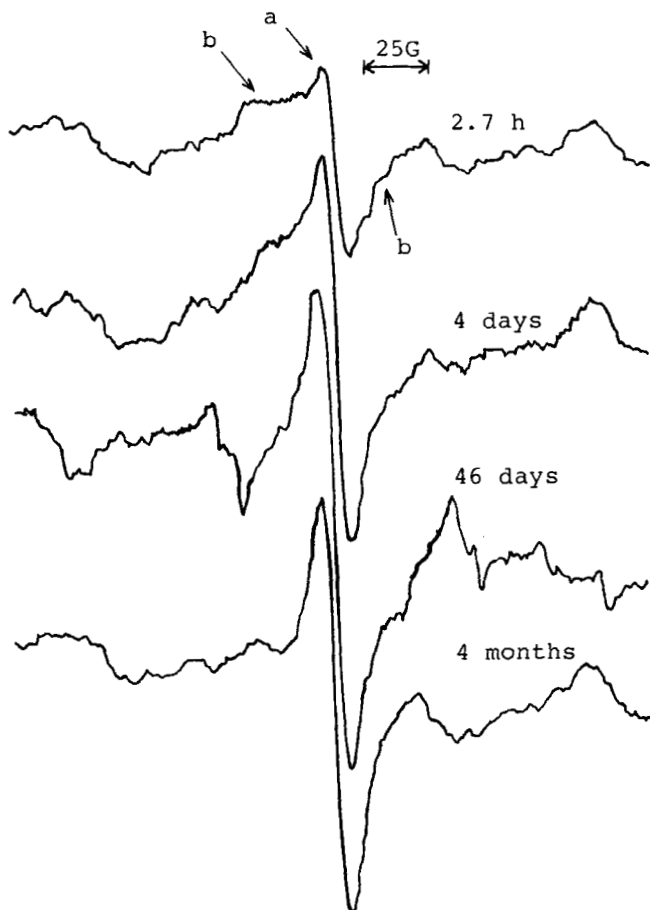


FIG. 5. ESR spectral change with time observed for the curing reaction of BAPM and St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system at room temperature.

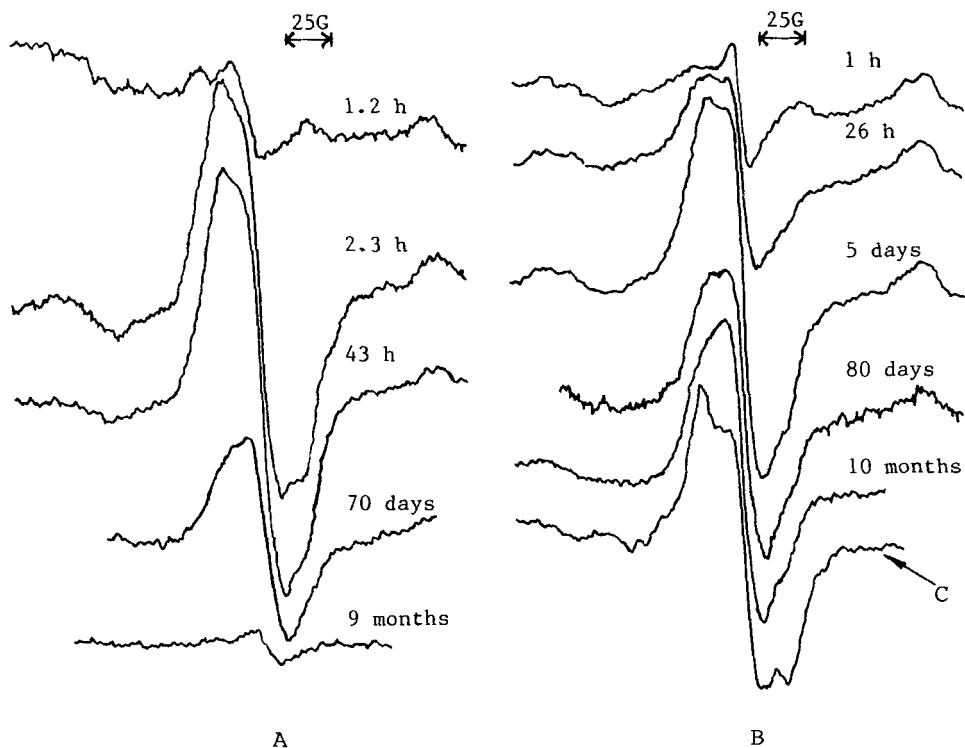


FIG. 6. ESR spectral change with time observed for the curing reaction of BAPM and St (30:70 w/w) with the initiator systems (A) DMA (0.1 wt%)/BPO (2 wt%) and (B) CoN (0.12 wt%)/HCH (2 wt%) at room temperature; (C) poly-(St) radical prepared according to the microsphere method.

St (65:35 w/w) system. The spectrum increases in intensity in the early stage and then decreases with time. The central peak, a, intensifies with time compared to the shoulder peaks, b.

Figure 6 shows the ESR spectra of the curing system of higher St content initiated by the two systems. Spectrum C is due to the polystyrene radical which was prepared according to the microsphere method [19]. Spectra A and B are nearly identical, indicating that the kinds and relative concentrations of the resulting radicals were almost independent of the initiator system used. The spectra in Fig. 6 show larger shoulder peaks than those in Fig. 5. Further, the former are similar to that of the polystyrene radical C in Fig. 6. Thus, the

shoulder peaks in Figs. 5 and 6 are assignable to the polystyrene radical. The sharp central peak seems to be due to radicals derived from BAPM.

As can be seen from Figs. 5 and 6, poly(BAPM) radicals are more stable than polystyrene radicals in the present system. This is probably because the former are located in the polymer backbone, while the latter are at the ends of polymer branches. Comparison of Spectra A and B in Fig. 6 reveals that the polymer radicals formed with the CoN/HCH system are more long-lived than those with the DMA/BPO system. This agrees to the above result that the former is more effective for crosslinking than the latter (Table 1).

Figure 7 shows the ESR spectral change observed in the BAPM/MMA (60:40 w/w) system initiated with DMA/BPO. At first, only poly(MMA) radicals were observed, and then the signal due to poly(BAPM) radicals increased in intensity with decreasing concentration of poly(MMA) radicals. As expected from the copolymerization data of DMF and MMA [20], MMA might be much more rapidly consumed than the BAPM double bonds in the early stage of curing. Subsequently, poly(BAPM) radicals were mainly formed by the reaction of BAPM with the poly(MMA) radical.

Thermal Behavior of Cured Polymers

The thermal properties of the cured polymers were investigated by DSC and TMA.

A BAPM/St (65:35 w/w) mixture containing the CoN/HCH initiator system was divided into two parts (Samples A and B). Sample A was cured at room temperature for 11 d. Sample B was allowed to react at room temperature for 10 d, at -3°C for 1 d, and further at room temperature for 7 d. After the reactions, both samples were powdered, extracted with acetone for 3 h, and dried at room temperature in vacuum.

Figure 8 shows DSC curves of the two samples. As can be seen from Curve a, Sample A had only one glass transition temperature (T_g) of 84°C . On the other hand, Curve b reveals that Sample B had two T_g 's, i.e., ~ 85 and 147°C . Curve c, observed in the second run with Sample B, showed one T_g around 130°C . These findings indicate that Sample B contained two different phases. This phase separation seems to be accelerated by treatment at -3°C . Further, heat treatment above 150°C eliminated phase separation.

The sample prepared by copolymerization of BAPM with St ([BAPM]/[St] = 65/35 w/w) at room temperature initiated with the CoN/HCH system also showed two T_g 's by TMA (Fig. 9). Each glass transition gradually became clearer with time from 10 h to 26 d (Curves a, b, and c) although the copolymerization scarcely proceeded further during this period as shown in Fig. 3.

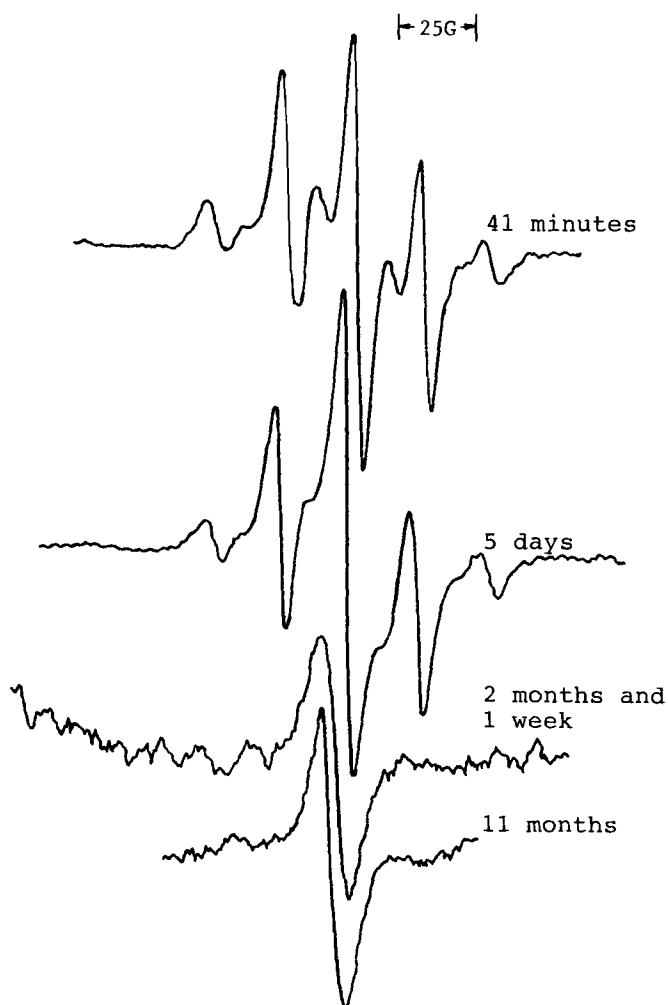


FIG. 7. ESR spectral change with time observed for the curing reaction of BAPM and MMA (60:40 w/w) with the DMA (0.1 wt%)/BPO (2 wt%) initiator system at room temperature.

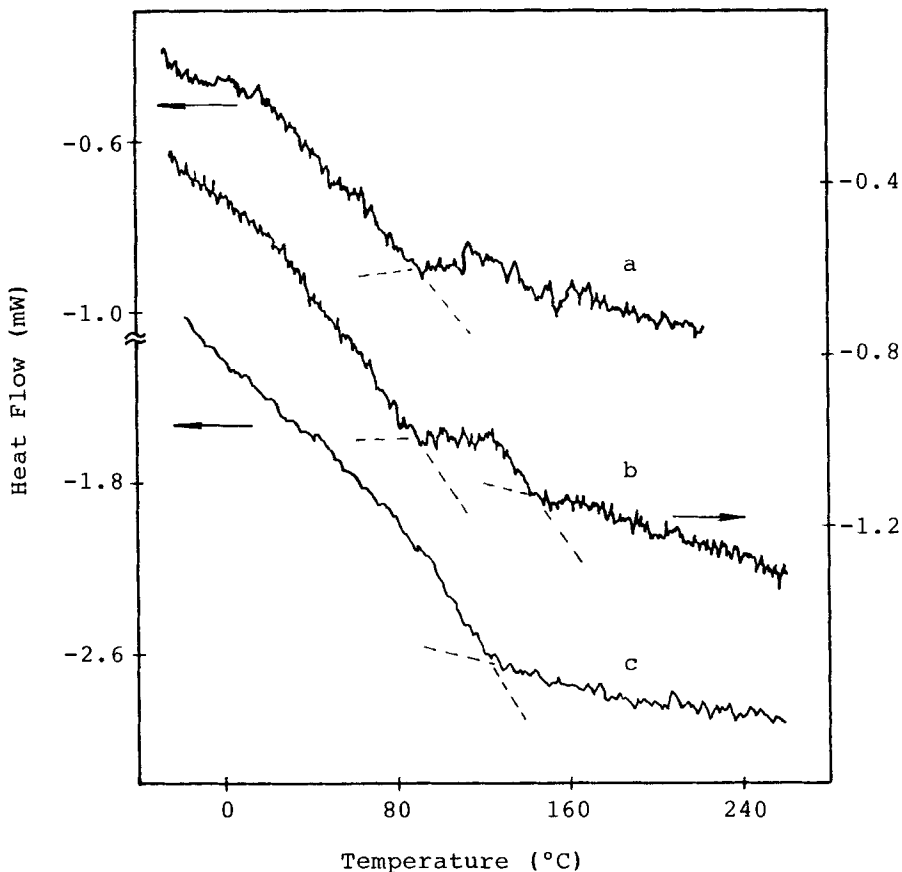


FIG. 8. DSC curves of the cured polymers obtained by the copolymerization of BAPM and St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system under the following conditions: (a) at room temperature for 11 days; (b) at room temperature for 10 days, at -3°C for 1 day, and then at room temperature for 1 week; and (c) the second run of the sample (b). The samples were extracted with acetone before DSC measurement; heating rate $5^{\circ}\text{C}/\text{min}$.

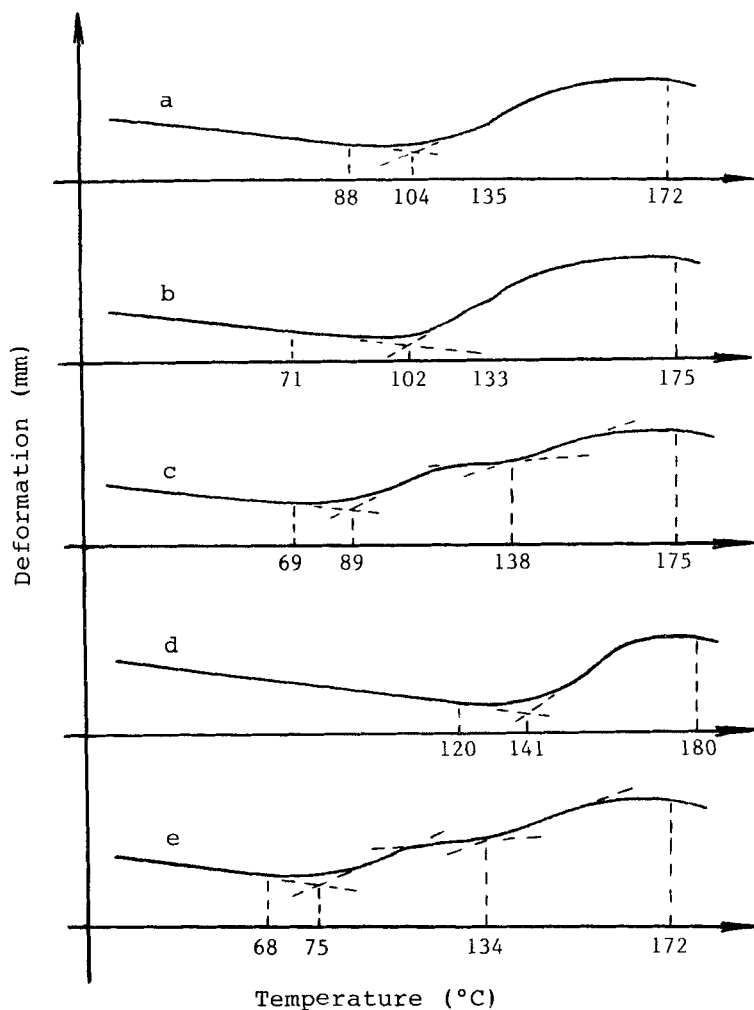


FIG. 9. TMA curves of the cured polymers obtained by the copolymerization of BAPM and St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system under the following conditions: (a) at room temperature for 10 h, (b) at room temperature for 11 days, (c) at room temperature for 26 days, (d) at room temperature for 26 days and at 150°C for 3 h, and (e) at room temperature for 11 days and at -3°C for 1.5 days.

As can be seen from Curve d, heat treatment at 150°C was again confirmed to remove one glass transition. On the other hand, treatment at -3°C for 1.5 d (Curve e) caused an earlier and clearer appearance of two glass transitions.

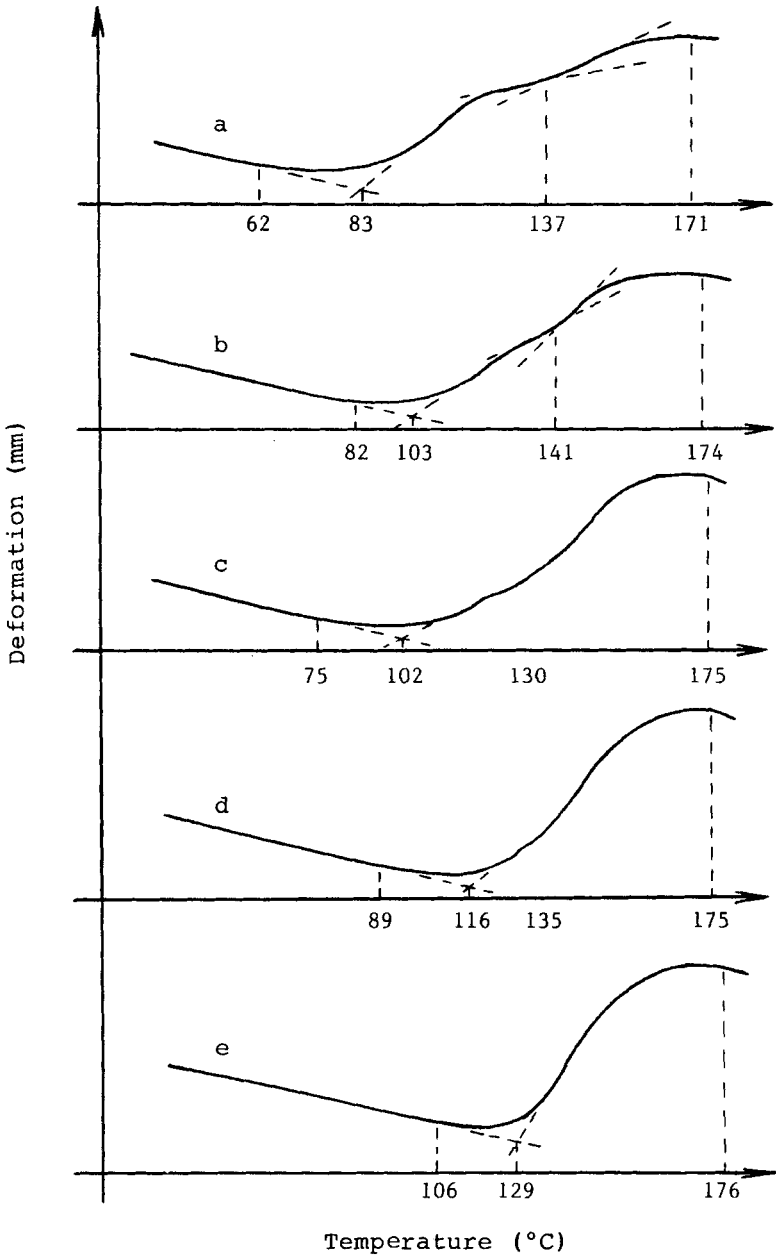
Thus, the present cured polymer contained two separate phases which coalesced by heating above 150°C. One phase might correspond to poly-(BAPM) and the other to poly(St) in the network. In the early stage of the curing reaction, the two glass transitions did not appear clearly; the heat of polymerization might prevent such a phase separation [21].

Figure 10 shows the TMA curves of the phase-separated polymer subjected to various subsequent thermal treatments. These results also support the above conclusion that the cured polymer has two separate phases which gradually mix with increasing temperature. The phase separation disappears completely above 150°C, a temperature near the higher of the T_g 's.

Figure 11 shows the temperature effect on the ESR spectrum of the cured polymer with phase separation which was obtained by curing a BAPM/St 65/35 w/w) mixture with the CoN/HCH system for a month at room temperature. The spectrum of the long-lived polymer radicals gradually increased in intensity with temperature. Then a large increase in intensity occurs around 80°C, which coincides with the lower T_g determined by DSC and TMA. Above 85°C, the polymer radical concentration decreased with temperature.

The increase in the polymer radicals with temperature indicates that some of initiators remained unreacted in the cured polymer. The unreacted initiator components were confined in the solidlike cured system, where the initiation reactions were suppressed. On heating above the lower T_g , the components were mobile enough to decompose, producing the long-lived polymer radicals of monomers. At still higher temperatures, an increase in mobility of the polymer radicals accelerated termination between them.

As mentioned in the above DSC and TMA studies, cooling at -3°C accelerates phase separation. Figure 12 shows the effect of thermal treatment at -3°C on the ESR spectrum of the cured polymer. Spectra B were observed for the sample cured at room temperature for 7 d (a) and then cooled at -3°C for 1 d (b), while Spectra A are for a similar sample kept at room temperature for 7 d (a) and a further day without cooling (b). In Spectra A, shoulder peaks due to polystyrene radicals disappeared on cooling at -3°C. On the other hand, no change was observed in Spectra B. The cooling is considered to cause a decrease in compatibility of poly(BAPM) and polystyrene parts to accelerate phase separation in the cured system containing sol polystyrene and unreacted monomer. This results in a concentration of polystyrene radicals in a separate polystyrene phase, which promotes termination.



The DSC curves in Fig. 13 were observed for the cured polymer formed by the reaction of BAPM, MMA, and St for 1.5 months at room temperature with DMA/BPO. The sample was subjected to the DSC measurement without extraction with acetone, which distinguishes it from the case in Fig. 8. The second run was found to show two T_g 's in spite of the fact that the sample was heated up to 240°C in the first run. Since MMA has poor copolymerizability with BAPM, the sample contained a significant amount of uncross-linked random copolymer of St and MMA. This might cause easy phase separation even after heating above 150°C, which is different from the phase separation mentioned above (Fig. 8).

Figure 14 shows curves of the sample prepared by copolymerization of BAPM and St for 1.5 months at room temperature with DMA/BPO. The sample was also not extracted with acetone before the DSC measurement. The second run also showed two T_g 's. As mentioned above (Table 1), the DMA/BPO system is not effective for crosslinking. As a result, an appreciable amount of polystyrene was not crosslinked, which is responsible for ready phase separation.

Exothermic peaks around 145°C in the first runs in Figs. 13 and 14 are due to the polymerization of residual monomers. It is of interest that polymerization in the cured polymers occurred at higher temperatures than did the rapid decomposition of BPO or the two T_g 's. An exothermic peak at a higher temperature (about 160°C) was observed in the more densely crosslinked network prepared by copolymerization of BAPM with St with CoN/HCH.

These findings indicate that the polymerization of monomers in the cured polymer is limited by the mobility of the molecular chains around them.

FIG. 10. Effect of the thermal treatment on TMA curves of the phase-separated polymers obtained by the curing reaction of BAPM and St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system. Conditions of the thermal treatments: (a) at 25°C for 2 weeks, (b) at 40°C for a week, (c) at 60°C for 4 days, (d) at 80°C for 2 days, and (e) at 100°C for 1 day.

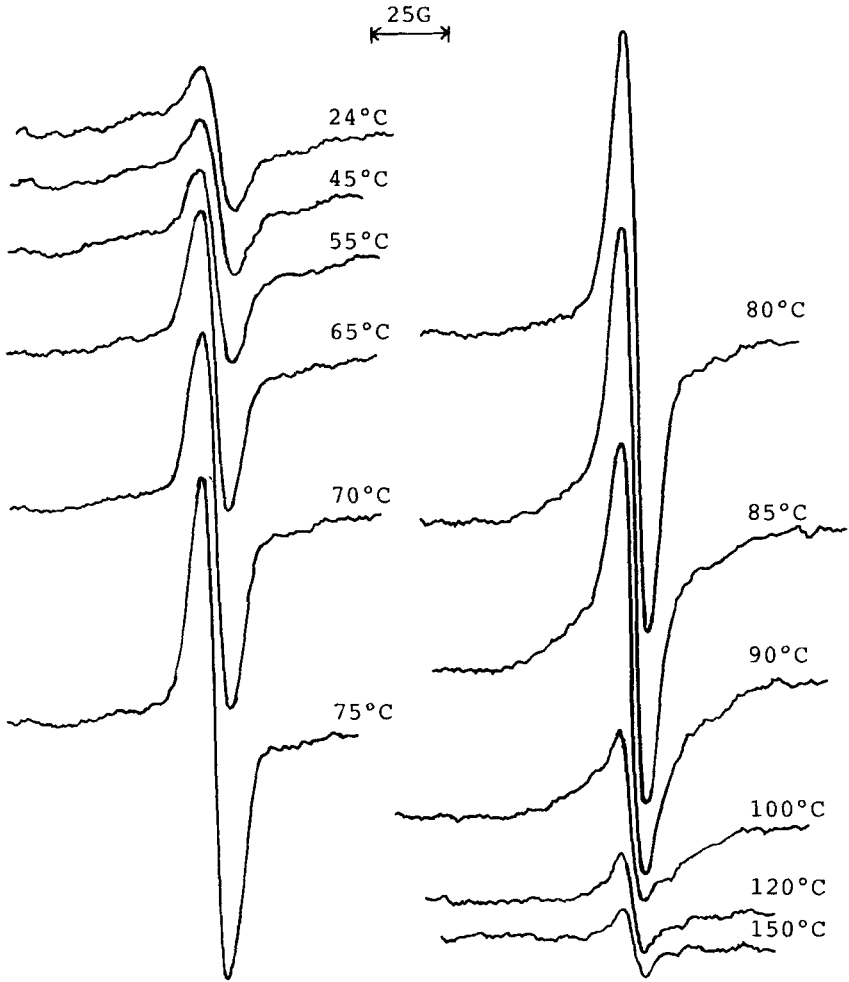


FIG. 11. ESR spectral change with temperature observed for the phase-separated polymer obtained in the curing reaction of BAPM with St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system.

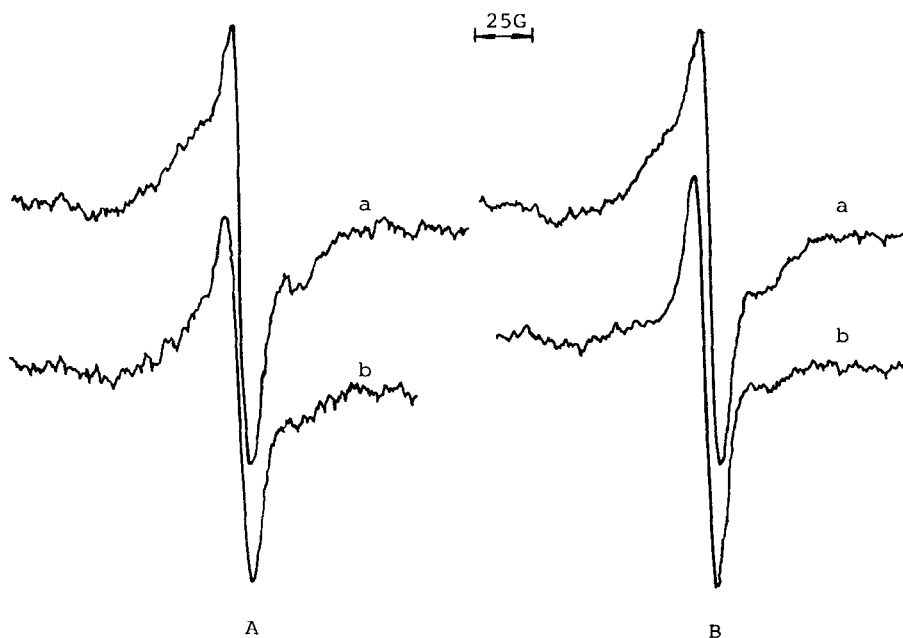


FIG. 12. ESR spectral change with treatment at -3°C observed in the cured polymer obtained by the copolymerization of BAPM and St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system at room temperature for a week; (B) before (a) and after (b) treatment at room temperature for a day without cooling, and (A) before (a) and after (b) cooling at -3°C for 1 day.

TEM Examination

In order to further confirm the above conclusion about phase separation, the cured polymer was examined by TEM. Figure 15 shows TEM photographs of two samples with different thermal histories. The untreated cured polymer clearly has a phase-separated structure (A). On the other hand, no phase separation was observed in the heated sample (B).

Some results have been reported about phase separations in crosslinked

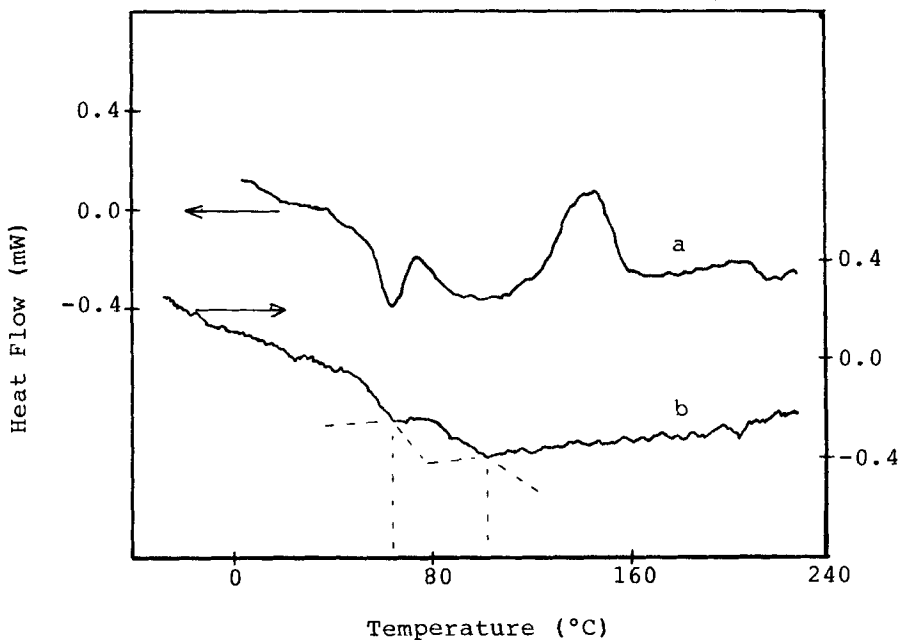


FIG. 13. DSC curves of the cured polymer obtained by the copolymerization of BAPM, MMA, and St (65:17.5:17.5 w/w/w) with the DMA (0.1 wt%)/BPO (2 wt%) initiator system at room temperature for 1.5 months: (a) first run, (b) second run. The sample was not extracted before DSC measurement; heating rate $10^{\circ}\text{C}/\text{min}$.

polymers where “sea-island” (8–16 nm diameter) structures were observed [3]. Such phase separations are transparent to visible light and not detectable by DSC or TMA. As shown in Fig. 15, a fiber-shaped phase separation of much larger size was observed in the cured polymer from BAPM and styrene. Further studies will be conducted in order to clarify the formation of such structures of phase separation.

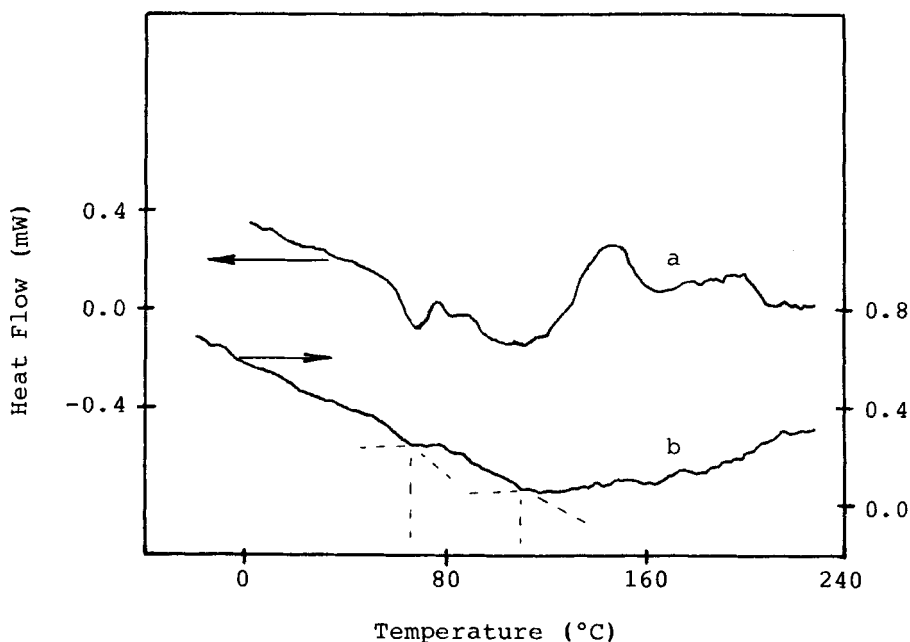
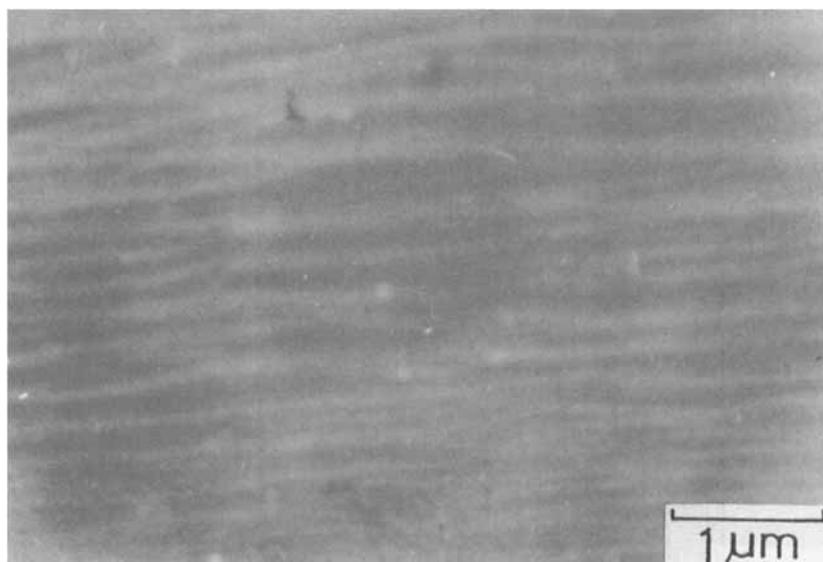


FIG. 14. DSC curves of the cured polymer obtained by the copolymerization of BAPM and St (65:35 w/w) with the DMA (0.1 wt%)/BPO (2 wt%) initiator system at room temperature for 1.5 months: (a) first run, (b) second run. The sample was not extracted before DSC measurement; heating rate $10^{\circ}\text{C}/\text{min}$.

CONCLUSION

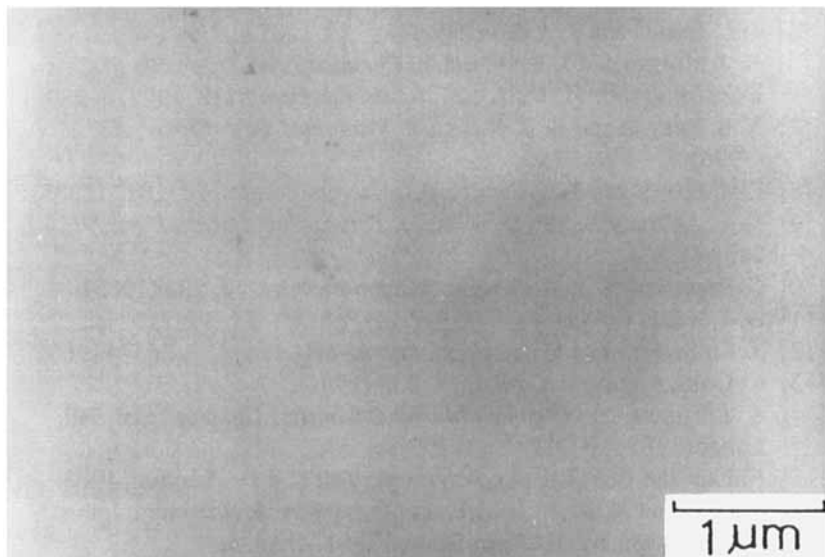
In the curing reaction of BAPM with vinyl monomers initiated with radical initiators, the copolymerization process (up to 65% conversion) can be successfully analyzed by the Mayo-Lewis integral equation for homogeneous copolymerization. The reaction system contains long-lived polymer radicals, the ESR spectra of which give important information on the curing reaction.



A

FIG. 15. TEM photographs of the polymer obtained by the copolymerization of BAPM and St (65:35 w/w) with the CoN (0.12 wt%)/HCH (2 wt%) initiator system at room temperature: (A) without thermal treatment, (B) heated at 150 °C for 3 h.

The resulting polymer cured at room temperature has a phase-separated structure. Phase separation into fiberlike shapes is accelerated by treatment at -3 °C. However, heating above 150 °C destroys the organized structure and it cannot be regenerated.



B

FIG. 15. (continued)

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