Microgelation in the Curing Reaction of Unsaturated Polyester Resins

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SYNOPSIS

A series of unsaturated polyesters were synthesized with various chemical structures and molecular weights. These unsaturated polyesters were used to study the curing reaction with styrene by using gel permeation chromatography and differential scanning calorimetry. The variation of the size of microgel particles during the curing reaction in unsaturated polyester–styrene resins was studied by using gel permeation chromatography. The size and structure of the microgels depend strongly on the polymer chain length and the number of vinyl groups on each unsaturated polyester chain. Using the differential scanning calorimetric method, the conversion of styrene and polyester vinyl groups during the reaction was measured. The experimental results of this study revealed that microgel formation has a great effect on the curing reaction of unsaturated polyester resins. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Unsaturated polyester resin is one of the most widely used thermoset resins in polymeric composites because of their good mechanical properties and relatively inexpensive price. With the addition of fillers and glass fibers, the resins are processed over a wide temperature range to form sheet-molding compounds (SMC), bulk-molding compounds (BMC), resin transfer molding compounds, pultrusion, etc.

The curing reaction of unsaturated polyester resin is a free-radical cross-linking copolymerization between the styrene $C=C$ double bonds and the unsaturated polyester $C=C$ double bonds. The reaction process results in a network formation through the connection of adjacent monomeric molecules. Several researchers have studied the cross-linking reaction mechanism of free-radical copolymerization of monovinyl and multivinyl components. Horie and co-workers[1,2] studied the reaction of unsaturated polyester–styrene copolymerization. Their experimental results revealed that the network formation

from highly unsaturated polyesters led to an earlier onset of gelation and a decrease of final conversion. Horie et al. attributed this phenomenon to chain segmental immobility in a cross-link network, and a diffusion-controlled termination step in the curing reaction extended the whole range of conversion.

Dusek et al.[3-6] found that the Flory–Stockmayer theory[7] of cross-linking or the theory of branching processes based on treelike representation of chemical structures yields reasonable results for the copolymerization of monovinyl and divinyl components, only if the content of the divinyl component is very low, and, also, if a perturbation correction for cyclization is used. Their results of the study of the pregel chain polymerization of ethylene dimethacrylate in the presence of various amounts of diluent suggested the occurrence of cyclization and the formation of compact microgel-like particles even at the very beginning of polymerization. Lee and co-workers observed similar results in unsaturated polyester sheet-molding compounds,[8-11] the polyurethane–polyester interpenetrating polymer network,[12] and the unsaturated polyester–styrene system.[13,14] They found that gel conversions of unsaturated polyester resins were much higher than those predicted by the classical Flory–Stockmayer theory.[7]

They attributed the reason for the discrepancy from the theory to the existence of the intramolecular cyclization reaction between unsaturated polyester and styrene vinyls. The competition between intermolecular (network formation) and intramolecular (cyclization) cross-linkings caused the delay in gelation. Hild and Okasha[15,16] attributed the delay of gelation to the reduction of reactivity of polyester vinyls as the reaction proceeds.[15,16] As a result, the maximum network density could not be reached. Minnema and Staverman[17] attributed this phenomenon to the shielding of the pendant vinyl groups in the intramolecular cyclization cross-linkings.

Yang and Lee[14] investigated the size and shape of microgel particles of the cured unsaturated polyester resins by scanning electron microscopy (SEM). They found that the network structure can be coral-like or flakelike depending on the concentration and type of polyester resins in the reacting system. However, the study of the variation of the size of microgel particles during the curing reaction has not been reported. In this work, a series of unsaturated polyester resins with different chemical structures were studied by observing the variation of the sizes of microgel particles during the curing reaction using gel permeation chromatography (GPC). The conversion for the curing reaction of unsaturated polyesters with styrene monomer was measured by differential scanning calorimetry (DSC). The cyclization and microgel gelation mechanisms of free-radical polymerization were used to explain the experimental results. To our knowledge, this is the first article that demonstrates the evidence of the shrinkage of microgels during the curing reaction of unsaturated polyester resins by GPC. The shrinkage of microgels is due to the intramolecular cross-linking reaction of unsaturated polyesters with styrene.

EXPERIMENTAL

Materials

1. Unsaturated polyester: Five unsaturated polyester resins were prepared by the conventional condensation method from phthalic anhydride (PAN), maleic anhydride (MAN), and 1,2-propylene glycol (PG). The reaction was carried out under a nitrogen atmosphere. The reaction temperature was increased by stepwise control as follows: 140°C/2 h, 160°C/2 h, 180°C/2 h, and 200°C/2 h, and finally keep at 200°C for several hours until the acid value of each sample reached the value as shown in Table I. The polyester product was then cooled down to 100°C and mixed with the styrene monomer (the weight ratio of polyester to the styrene monomer is 68.5/31.5) containing 0.1% by weight of the hydroquinone inhibitor. The resin was then cooled to room temperature immediately. The molar ratio of the final compositions of the solid polyesters were determined from NMR. The acid values of the solid polyesters were determined by a titration method that has been described elsewhere.[18] The molecular weight distribution of the solid polyester was determined by GPC at 25°C. THF was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co.) were used in the linear calibration method. Table I summarizes the chemical compositions, acid values, and molecular weight distributions of the five unsaturated polyester resins used in this study.

2. Initiator: The peroxide initiator was *tert*-butyl peroxybenzoate from Akzo Chemie Co. with a purity of 98% and an active oxygen content of 8.07%.

Table I   The Composition of Samples

	Sample				
	1	2	3	4	5
PAN	1.0	1.0	1.0	1.0	1.67
MAN	1.67	1.67	1.67	1.0	1.0
1,2-PG	2.94	2.94	2.94	2.2	2.94
M_n	1575	1815	2185	2033	2070
M_w/M_n	1.57	1.55	1.74	1.67	1.66
Acid value (mg KOH/g)	62	46	30.8	33.3	32.1
MAN/PAN	1.67	1.67	1.67	1.00	0.60

PAN = phthalic anhydride; MAN = maleic anhydride; 1,2-PG = 1,2 propylene glycol.

3. Styrene: The styrene monomer (purchased from Aldrich Chemical Co. with a purity of 99%) was purified by distillation several times very carefully before mixing with the unsaturated polyester.

Instrumentation

1. Differential scanning calorimeter (DSC): A DuPont 910 DSC was applied to investigate the exothermic reaction of curing. Hermetic DSC pans were used to minimize losses of volatile materials (such as the styrene monomer) during the heating of the sample in the DSC cell. The size of the sample ranged from 6 to 10 mg. A small sample size was required to achieve isothermal operation during cure.

2. Gel permeation chromatograph (GPC): Waters Model 746 GPC with μ-Styragel columns and an RI detector was used to investigate the variation of the particle size of the microgel formation during the early stage of the curing reaction of unsaturated polyester resins. The unsaturated polyester resins were mixed with 1 wt % of *tert*-butyl peroxybenzoate initiator. The curing reactions proceeded in a DSC cell at a temperature of 110°C and the reactions were stopped at 3, 5, 7, 9, 12, and 15 min time intervals by cooling the samples to room temperature. The samples were then dissolved into THF and filtered through a 0.5 μm FHLP Millipore filter before GPC analysis. THF was also used as the mobile phase in the GPC analysis. Since we were in the initial period of the curing reaction, the microgel particles could be dissolved in THF. Although the curing reaction was close to gelation, a small amount of large particles might be found that were due to the formation of a macro network structure [see Fig. 7(d) description below]. These large particles were not dissolved in THF and were filtered by the Millipore filter. Hence, our GPC results showed only the size distribution of primary polyesters and microgel coils.

RESULTS AND DISCUSSION

Isothermal reaction heats, obtained using DSC techniques, are often used to estimate the degree of conversion. In the use of DSC for studying the isothermal curing kinetics of thermosetting resins,[19] one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of curing α (or the extent of reaction) of the sample at that time, and then one relates the rate of curing, $d\alpha/dt$, to the rate of heat generated, dQ/dt, by

$$\frac{d\alpha}{dt} = \frac{1}{Q_{tot}} \frac{dQ}{dt} \tag{1}$$

Integrating eq. (1) with time, one obtains the relative degree of cure, α:

$$\alpha = \frac{1}{Q_{tot}} \int_0^t \left[\frac{dQ}{dt}\right]_T dt \tag{2}$$

In eqs. (1) and (2), the total heat of the curing reaction (Q_{tot}) is given by

$$Q_{tot} = Q_t + Q_r \tag{3}$$

where Q_t is the heat generated during the isothermal DSC runs at 110°C, and Q_r, the residual heat that is released when the sample is heated to 220°C at a heating rate of 10°C/min after the completion of an isothermal curing reaction at 110°C. In all the curing reactions, we defined the gel conversion, α_{gel}, as being the conversion, α, at the initial inflection of the curing profile α vs. curing time. This definition of α_{gel} may not be the true gelation but is close to gelation.

The unsaturated polyesters used in this work consist of maleic anhydride (MAN), phthalic anhydride (PAN), and propylene glycol (PG) with various molar ratios and molecular weights. MAN provides vinyl groups to the polyester resin, while PG and PAN serve as chain extenders. The aromatic ring structure of the PAN makes the chain more rigid and more compatible with the styrene monomer. The vinyl contents of unsaturated polyesters for samples 1–3 were very close, but with variation in polyester molecular weights. The polyester molecular weights for samples 3–5 were very close, but with various degrees of polyester unsaturation. From Table I, one may conclude that the polyester molecular chain of sample 3 has the highest degree of unsaturation per polyester molecular chain. In addition, because of the highest content of aliphatic MAN (which has a poor compatibility with styrene) per polyester molecular chain for sample 3, the compatibility of polyester with the styrene monomer for sample 3 is the worst of all samples. Also, from Table

I, we found that sample 1 has the highest acid value and the smallest polyester molecular weight.

To study the effect of unsaturated polyester molecular weight on the curing reaction of the unsaturated polyester–styrene system, the DSC curing profiles of samples 1–3, which have same polyester vinyl contents but different polyester molecular weights, were plotted together. Figure 1 shows the plots of curing rate $d\alpha/dt$ vs. curing time of samples 1–3 obtained from the DSC measurements. The curing temperature was carried out isothermally at 110°C. The plots of conversion α vs. curing time for samples 1–3 obtained from the DSC measurements are shown in Figure 2. For unsaturated polyester–styrene systems that have same polyester vinyl contents, the onset of gelation is earlier for samples with lower polyester molecular weight. The gel conversion, α_{gel}, is higher and the final conversion, α_f, is lower for resins with higher polyester molecular weights. The maximum curing rate, $(d\alpha/dt)_{max}$, which is the peak of the $d\alpha/dt$ vs. the curing time curve, as shown in Figure 1, increases as the molecular weight of unsaturated polyester increases. The values of gel conversions, α_{gel}, maximum curing rate, $(d\alpha/dt)_{max}$, and final conversions, α_f, for samples 1–3 are summarized in Table II.

Typical changes in the rate of cure of unsaturated polyesters with styrene for samples 1–3 over the whole range of conversion are shown in Figure 3, in which it is apparent that almost over the whole range of conversion the curing reaction rate is higher for the unsaturated polyester–styrene system with the higher polyester molecular weight. Since all these three samples possessed the same polyester vinyl contents, the increase in unsaturated polyester molecular weight led to an increase in the cross-linking density of the cured polymer. The increase in cross-linking density resulted in an increase in autoacceleration of the rate of the curing reaction, which led to a sharper increase and a sharper decrease of the curing reaction rate and an increase of $(d\alpha/dt)_{max}$ as shown in Figure 1. The increase in cross-linking density also caused an increase in the curing reaction rate over the whole range of conversion, as shown in Figure 3. It provides evidence supporting diffusion-controlled termination in this curing reaction.

To study the effect of unsaturation on the curing reaction of the unsaturated polyester–styrene system, the DSC curing profiles of samples 3–5 were plotted by grouping the same polyester molecular weights but different degrees of polyester unsatu-
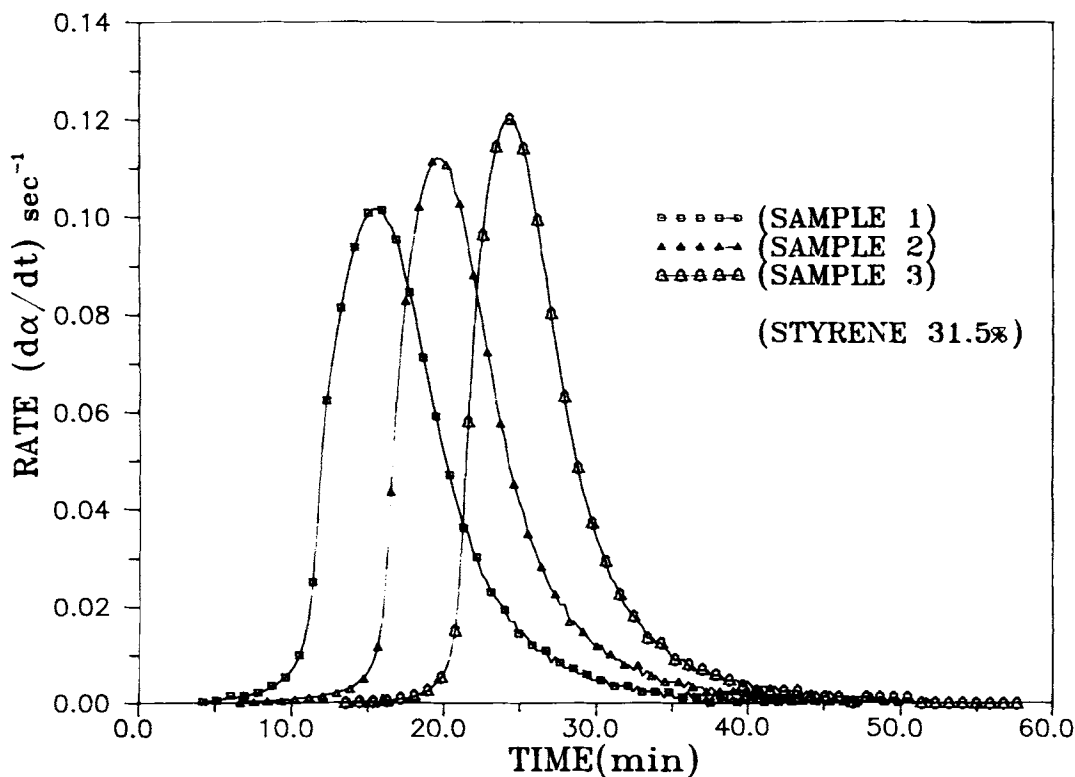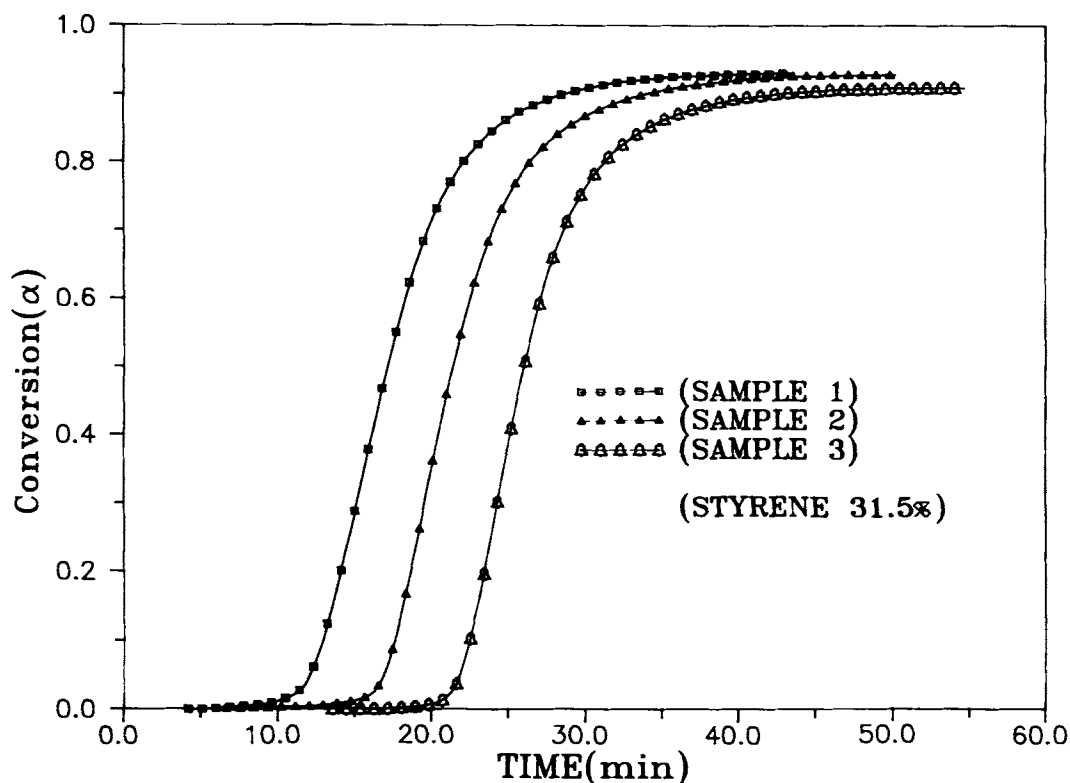

Figure 1   Curing rate $d\alpha/dt$ vs. curing time obtained from DSC measurements: (□) sample 1; (△) sample 2, (⬙) sample 3.

Figure 2   Conversion α vs. curing time obtained from DSC measurements: ($\square$) sample 1; ($\triangle$) sample 2; ($\triangle$) sample 3.

ration. Figure 4 shows the plots of the curing rate $d\alpha/dt$ vs. the curing time for samples 3–5 obtained from the DSC measurements. The curing temperature was carried out isothermally at 110°C. The plots of conversion α vs. curing time for samples 3–5 obtained from the DSC measurements are shown in Figure 5. From these DSC data, it is apparent that for unsaturated polyester resins that have same polyester molecular weights but various degrees of polyester unsaturation the gelation is earlier for samples with a lower degree of polyester unsaturation. The gel conversion, α_{gel}, is higher and the final conversion, α_f, is lower for the sample with the

higher degree of polyester unsaturation. The maximum curing reaction rate, $(d\alpha/dt)_{max}$, which is the peak of the $d\alpha/dt$ vs. the curing time curve, as shown in Figure 4, increases as the degree of polyester unsaturation increases. The values of gel conversion, α_{gel}, final conversion, α_f, and the maximum curing rate, $(d\alpha/dt)_{max}$, are also shown in Table II.

The changes in rate of cure, $d\alpha/dt$, of unsaturated polyester with styrene for samples 3–5 over the whole range of conversion, α, are shown in Figure 6. It is apparent that almost over the whole range of conversion the curing reaction rate is higher for the unsaturated polyester–styrene system with the

Table II   Curing Properties of Unsaturated Polyester

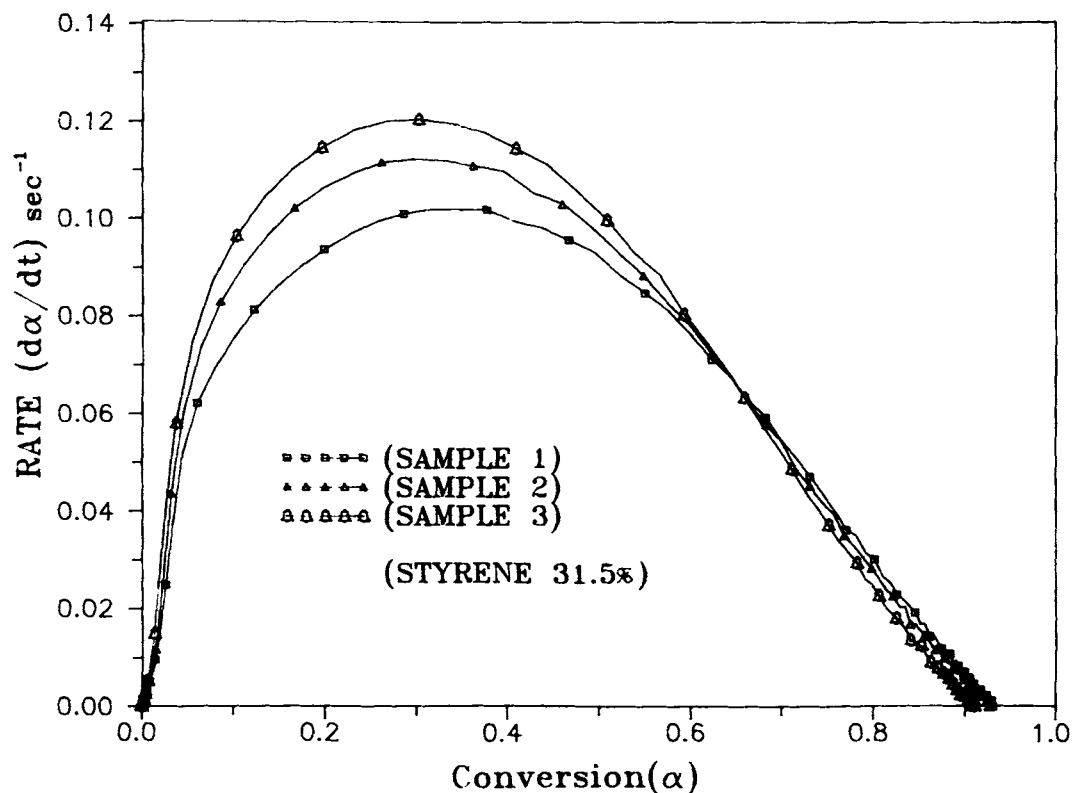|	Sample				
	1	2	3	4	5
α_{gel} (%)	3.75	3.99	4.42	3.99	3.63
α_f (%)	93.0	92.8	91.0	91.9	92.8
$(d\alpha/dt)_{max}$ (s^{-1})	0.102	0.112	0.120	0.096	0.081

Figure 3   Change in rate of cure against conversion for the curing reaction of unsaturated polyesters with styrene: (□) sample 1; (△) sample 2; (◿) sample 3.
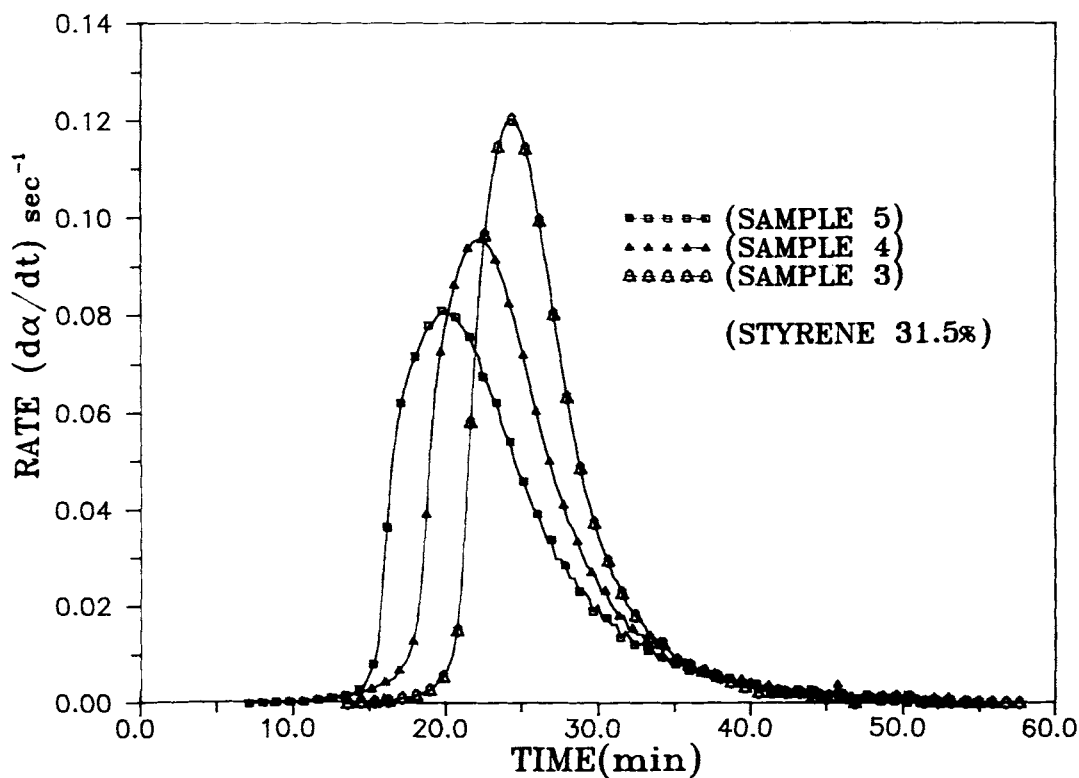

Figure 4   Curing rate $d\alpha/dt$ vs. curing time obtained from DSC measurements: (◿) sample 3; (△) sample 4; (□) sample 5.
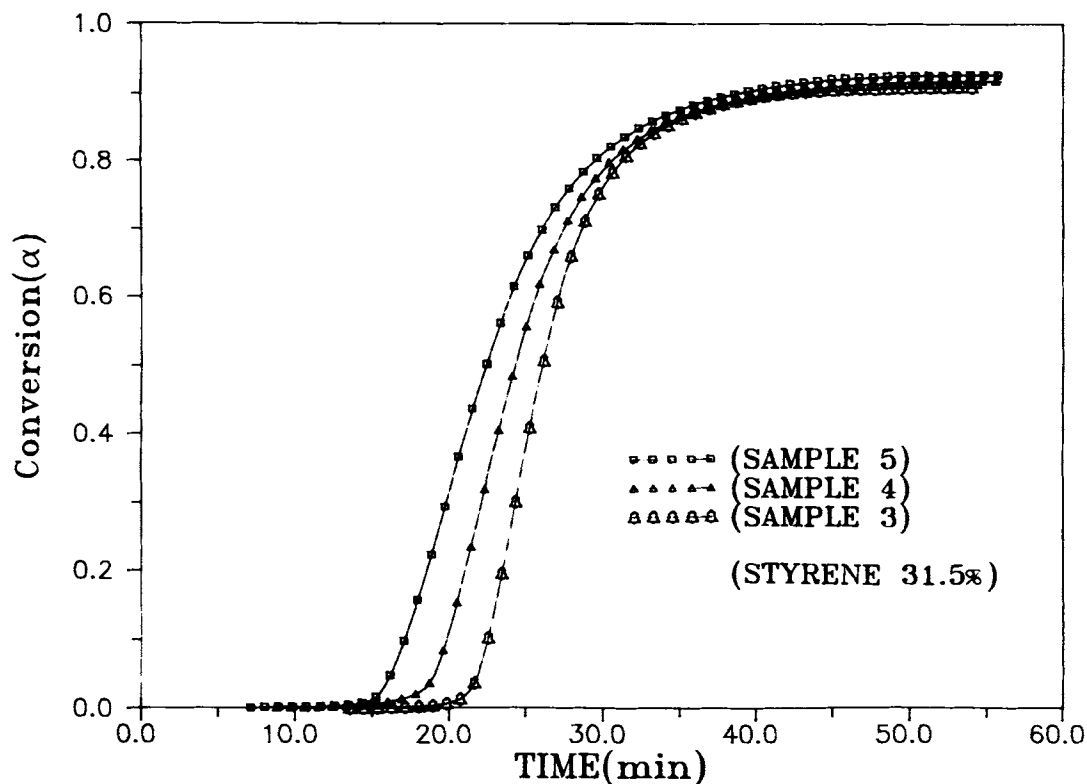
Figure 5 Conversion α vs. curing time obtained from DSC measurements: ($\triangle$) sample 3; ($\triangle$) sample 4; ($\square$) sample 5.
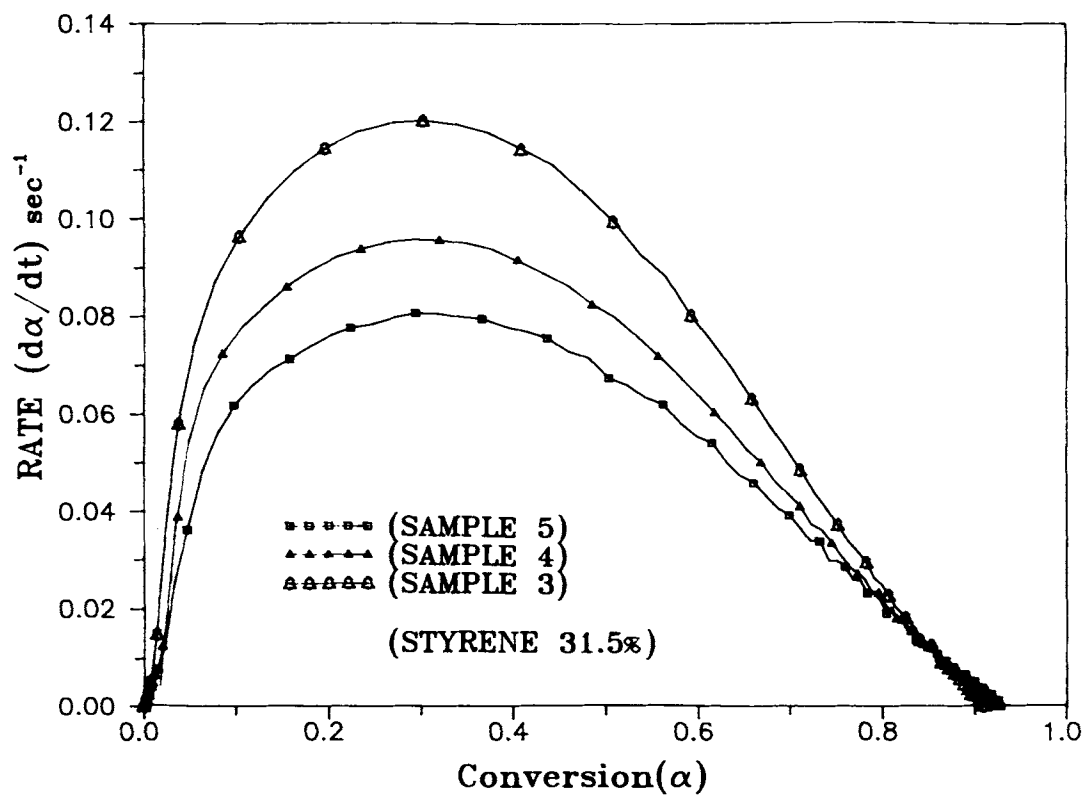

Figure 6 Change in rate of cure against conversion for curing reaction of unsaturated polyester with styrene: ($\triangle$) sample 3; ($\triangle$) sample 4; ($\square$) sample 5.

higher polyester vinyl content. Since all these samples possessed the same polyester molecular weights, the increase in polyester unsaturation led to an increase in cross-linking density of the cured polymer. The increase in cross-linking density resulted in an increase in autoacceleration of the rate of the curing reaction, which led to a sharper increase and a sharper decrease of the curing reaction rate and an increase of $(d\alpha/dt)_{max}$ (Fig. 4). As shown in Figure 6, the increase in cross-linking density also causes an increase in the curing reaction rate over the whole range of conversion, indicating diffusion-controlled termination in this curing reaction.

There are three possible chemical reactions for the curing reaction of unsaturated polyesters with styrene: styrene to styrene, styrene to the polyester $C=C$ bond, and the polyester $C=C$ bond to the polyester $C=C$ bond. Yang and Lee[14] classified these reactions into four types: (1) intermolecular cross-linking with or without linking through styrene monomers; (2) intramolecular cross-linking with or without linking through styrene monomers; (3) branching on the polyester molecule by styrene; and (4) free styrene homopolymerization. Reaction (1) tends to form a macroscopic network through the connection of adjacent polyester molecules; reaction (2) increases the cross-linking density and reduces the size of polyester coil, but does not contribute to the macroscopic network formation; reaction (3) consumes cross-linking units and may slightly increase the polymer coil size, but has little effect on the network formation; and reaction (4) produces a soluble segment that does not participate in the polymer network. Although all reactions affect the curing kinetics, only the first two contribute to network formation.

Before reaction, the mixture of the unsaturated polyester and styrene system may be pictured as many coiled unsaturated polyester chains swelled in the styrene monomer. The coiled size of unsaturated polyesters depends on the unsaturated polyester molecular chain length, chain stiffness, concentration of unsaturated polyester chains, and compatibility of unsaturated polyesters with the styrene monomer. Chemical reaction between the vinyl groups originated from unsaturated polyesters and from the styrene monomer may occur inside, outside, or at the surface of the coils. When the reaction starts, the initiators decompose and form free radicals to initiate polymerization that link adjacent unsaturated polyesters and form primary polymer chains through connecting styrene monomers by both inter- and intramolecular reactions. At the coil surface, the intermolecular cross-linking reaction

occurs, which increases the polymer coil size. Inside the coils, the reaction proceeds through the intramolecular cyclization, which does not increase the polymer coil size. Instead, the polyester coils may be tightened up to form the so-called microgel structure.[13,14,17,20-22] This phenomenon was first claimed by Minnema and Staverman in monovinyl–divinyl copolymerization.[17] Because of the high cross-linking of the microgel, the free radicals on the polymer end are likely to be trapped in the microgels. This causes the diffusion-controlled termination reaction. As the polymerization proceeds, the concentration of the microgels increases continuously, leading to macrogelation in the curing system. The curing reaction microgel gelation mechanism of unsaturated polyesters with styrene can be pictured as shown in Figure 7.

For unsaturated polyester resins with a fixed ester vinyl group (i.e., MAN) concentration, the increase of unsaturated polyester molecular weight results in an increase in the vinyl group (i.e., MAN) content per polyester molecular chain. Because of poor compatibility of MAN with the styrene monomer, the increase in the polyester molecular chain length results in an increase in the tendency for polyester molecular chains to form coils in the styrene monomer. The phenomena of a higher degree of unsaturation per polyester molecular chain and a greater tendency for polyester chains to form coils in the styrene monomer cause an increase in the chance for unsaturated polyesters to proceed to a intramolecular cross-linking reaction with the styrene monomer and to form the microgels. Hence, we may conclude that at a fixed ester vinyl group concentration the unsaturated polyester–styrene system with higher polyester molecular weight has a greater tendency to form microgel particles.

For unsaturated polyester resins with a fixed polyester molecular weight, the increase of polyester unsaturation (i.e., increase aliphatic MAN content in the chemical structure of unsaturated polyesters) results in a decrease of the compatibility of unsaturated polyesters with the styrene monomer. The lower the compatibility of unsaturated polyesters with the styrene monomer, the greater the tendency for the unsaturated polyester molecules to shrink and form coils in styrene. The phenomena of a higher degree of polyester unsaturation and a greater tendency for unsaturated polyesters to form coils in the styrene monomer cause an increase in the chance for unsaturated polyesters to proceed to an intramolecular cross-linking reaction with the styrene monomer and to form the microgels. We may conclude that for unsaturated polyester–styrene systems
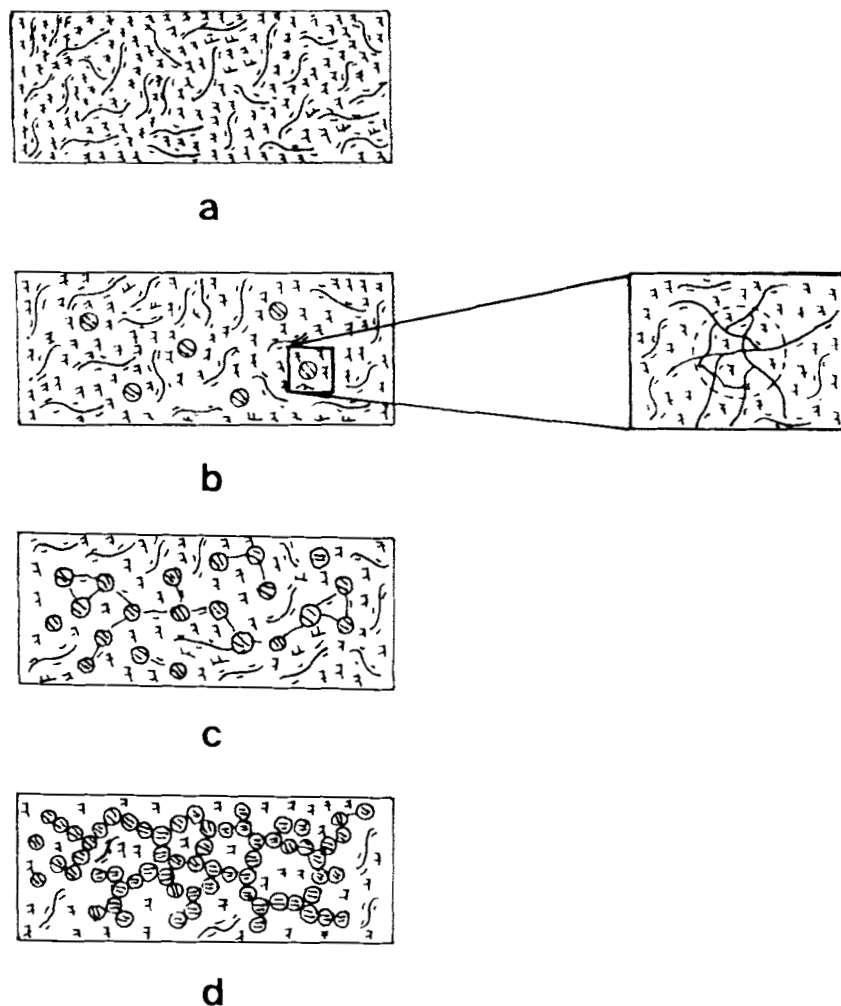
Figure 7   The curing mechanism of unsaturated polyesters: (a) the beginning of the curing reaction; (b) microgel formation due to the intramolecular cross-linking reaction; (c) intermolecular cross-linking reaction between the microgel particles; (d) macrogelation.

with a fixed polyester molecular weight the resin with a higher degree of polyester unsaturation has a greater tendency to form microgel particles.

From the above discussion, we know that either an increase in the degree of polyester unsaturation or an increase in polyester molecular weight causes an increase in the chance for unsaturated polyesters to proceed to an intramolecular cross-linking reaction for the formation of microgel particles. Many pendant vinyl groups may be trapped inside the microgels, which reduce the effective concentration of polyester vinyls for a further intermolecular cross-linking reaction. Such an effect has been known as the "molecular shielding" effect,[17] which leads to a higher gel conversion, α_{gel}, and a lower final conversion, α_f, of the curing reaction.

The phenomenon of intramolecular cross-linking

cyclization and the intermolecular cross-linking reaction of unsaturated polyester coils in the styrene monomer can be investigated from the variation of the polymer particle size during the curing reaction by GPC. In regard to the use of GPC to investigate the microgel formation during curing of unsaturated polyester resins, the relative amount of particles was plotted against the retention time in the chromatogram. Since the retention time is inversely proportional to the particle size, the shorter retention time corresponds to a larger particle size.

The GPC distribution curves of microgel particles at various degrees of conversion for samples 1–3 are shown in Figure 8. These samples have the same degrees of polyester unsaturation but different polyester molecular weights before the curing reaction. For the unsaturated polyester sample 1, which has
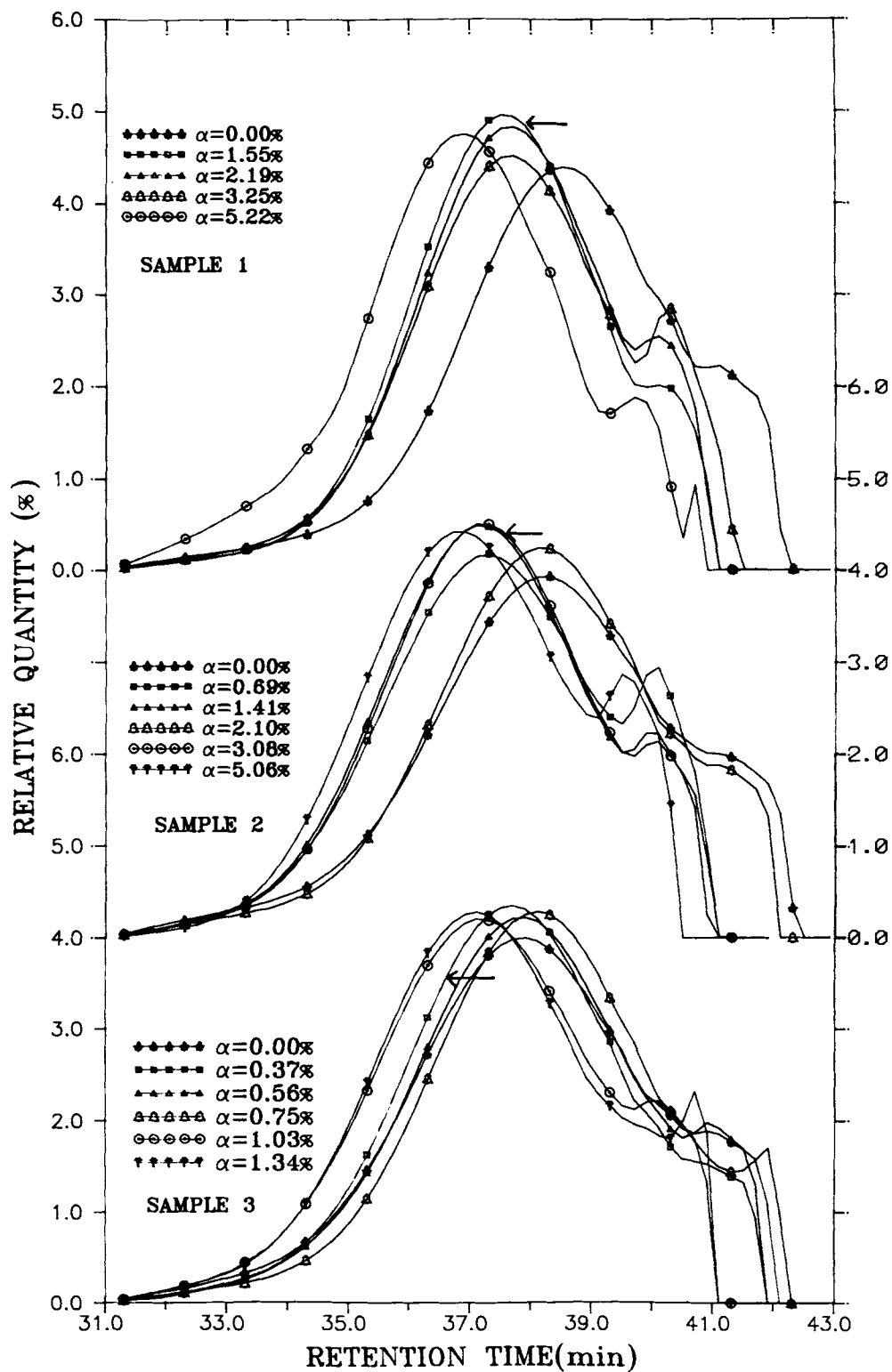
Figure 8 The GPC curves of samples 1–3 cured at 110°C with various degrees of conversion. The arrows indicate the microgel shrinkage due to intramolecular cross-linking reactions.

the smallest polyester molecular weight, as shown in the upper part of Figure 8, the particle size of the polymer microgels increases as the curing reaction proceeds. However, at a conversion of $\alpha = 2.2\%$, the particle size of the microgels is smaller than that of the microgels at a conversion of $\alpha = 1.55\%$. For the unsaturated polyester resin sample 2, which has a polyester molecular weight larger than that of sample 1 but smaller than that of sample 3, as shown in the middle part of Figure 8, the microgel particles grow as the curing reaction proceeds but shrink at a conversion of $\alpha = 1.41\%$. For the unsaturated polyester sample 3, which has the highest polymer molecular weight, as shown in the lower part of Figure 8, the microgel particles grow as the curing reaction proceeds but shrink at a conversion of $\alpha = 0.37\%$. The shrinkage of the microgel particles is due to the intramolecular cross-linking cyclizations as indicated in the (b) stage of Figure 7. After the (b)-stage curing reaction, an intermolecular reaction between the microgel particles occurs and the microgel particle size increases as the curing reaction proceeds. This behavior is shown in the (c)-stage of Figure 7.

Obviously, GPC experimental results gave evidence of the intramolecular and intermolecular microgel gelation mechanism. Also from Figure 8, we found that at a fixed ester vinyl group concentration the growing microgel particles of resins with higher unsaturated polyester molecular weights shrink at a lower conversion during the curing reaction, which means that more intramolecular cyclization occurs for resins with higher unsaturated polyester molecular weight and more ester vinyl groups are buried in the microgel particles for resins with higher unsaturated polyester molecular weight. These GPC experimental results were consistent with DSC curing experimental results showing the delay of gelation in the early stage of the curing reaction, higher gel conversion, α_{gel}, higher $(d\alpha/dt)_{max}$ value, and lower final conversion, α_f, for the unsaturated polyester–styrene system with a higher unsaturated polyester molecular weight.

The GPC distribution curves of microgel particles at various degrees of conversion for samples 3–5 are shown in Figure 9. These samples had the same polyester molecular weights but different degrees of polyester unsaturation. For the unsaturated polyester sample 3, which has the highest degree of polyester unsaturation, as shown in the lower part of Figure 9, the growing microgel particles shrink at a conversion of $\alpha = 0.37\%$ during the curing reaction. For the unsaturated polyester sample 4, which has a degree of polyester unsaturation lower than that

of sample 3 but higher than that of sample 5, as shown in the middle part of Figure 9, the growing microgel particles shrink at a conversion of $\alpha = 0.48\%$ during the curing reaction. For the unsaturated polyester sample 5, possessing the lowest degree of polyester unsaturation, as shown in the upper part of Figure 9, the growing microgel particles shrink at a conversion of $\alpha = 1.42\%$ during the curing reaction.

From these GPC experimental results, we may conclude that at a fixed unsaturated polyester molecular weight the growing microgel particles of resins with higher degrees of polyester unsaturation shrink at a lower conversion during the curing reaction. These experimental results showed that unsaturated polyesters with a higher degree of unsaturation (i.e., higher MAN/PAN molar ratio of unsaturated polyester backbone) have a greater tendency to form coils in the styrene monomer and more chances to proceed to an intramolecular cyclization to form "microgels," which reduces the effective concentration of polyester vinyls for the further intermolecular cross-linking reaction. These GPC experimental results were consistent with the DSC curing experimental results, which show the delay of gelation, higher gel conversion, α_{gel}, and lower final conversion, α_f, for the unsaturated polyester resins with a higher degree of polyester unsaturation.

Yang and Lee[13] studied the curing kinetics of styrene/unsaturated polyester (copolyester of isophthalic acid, fumaric acid, and propylene glycol) with various degrees of polyester unsaturation using a Fourier transform infrared spectrometer and a rheometer. They found that unsaturated polyesters with the higher degree of unsaturation reacted with a slower curing rate. Evidently, the unsaturated polyester chains with a higher degree of polyester unsaturation (with higher aliphatic fumaric acid concentration and lower aromatic isophthalic acid concentration) tend to form tighter coils in styrene, which facilitates intramolecular cyclizations, producing highly cross-linked microgels in slowing down the gelation of the curing reaction. This phenomenon is consistent with the results of our present work.

CONCLUSIONS

The GPC experimental results showed evidence of the shrinkage of unsaturated polyester microgels at the beginning of the curing reaction, which is due to the polymer intramolecular cyclization cross-
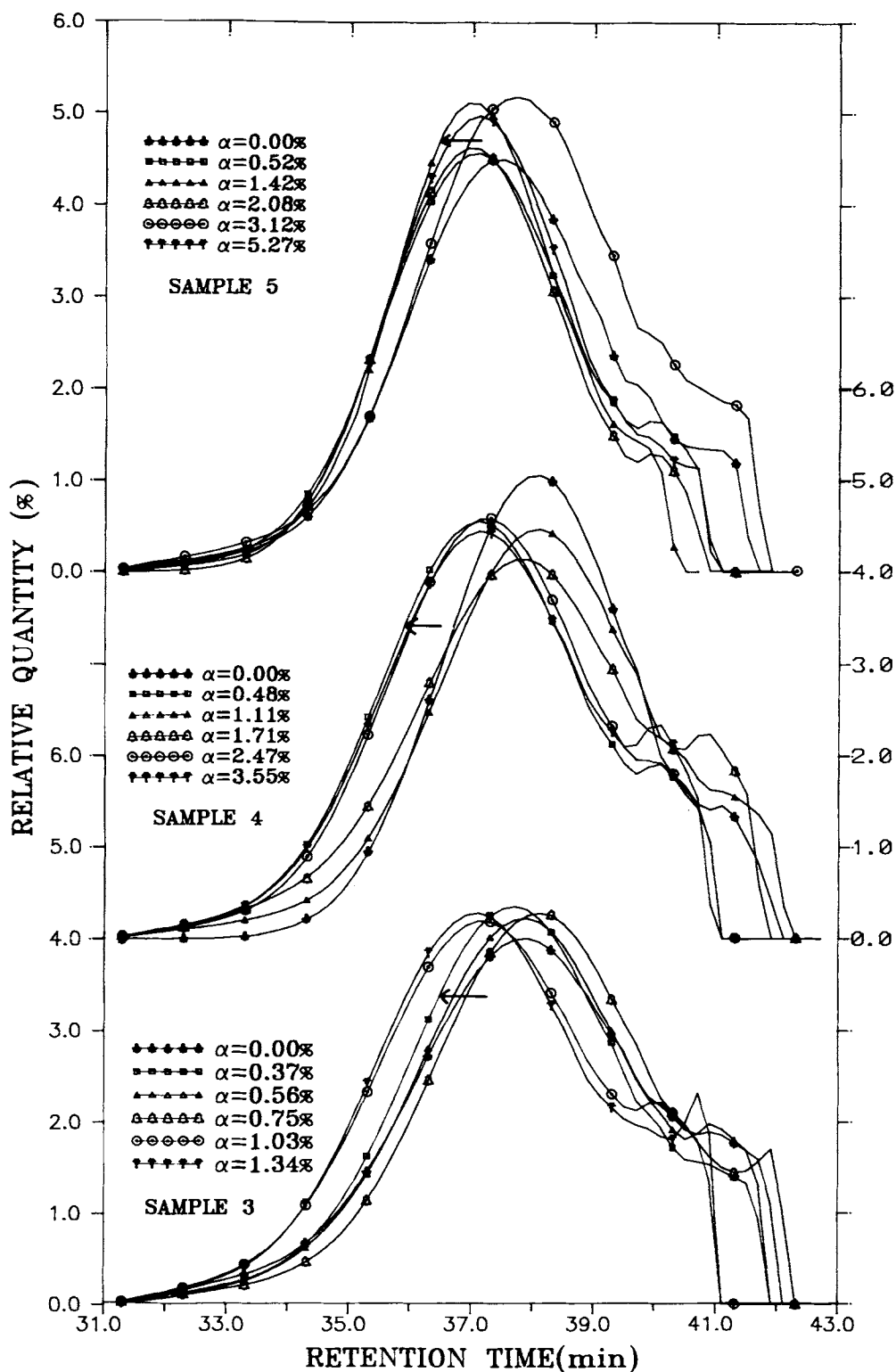
Figure 9 The GPC curves of samples 3–5 cured at 110°C with various degrees of conversion. The arrows indicate the microgel shrinkage due to intramolecular cross-linking reactions.

linking reaction. The formation of microgel particles has been found to be the key feature of the styrene–unsaturated polyester copolymerization. For unsaturated polyester resins with a fixed degree of polyester unsaturation, the resin with a lower polyester molecular weight cured with a shorter gelation time. Increase in the polyester molecular weight facilitates the unsaturated polyesters to form coils in the styrene monomer, leading to an intramolecular cross-linking reaction that causes a delay of gelation. For unsaturated polyester resins with a fixed polyester molecular weight, the gelation time of the resin with a lower degree of polyester unsaturation was shorter in the curing reaction. The higher molar ratio of MAN/PAN in unsaturated polyester molecular chains would make the molecular chains more flexible and less compatible with the styrene monomer in which the unsaturated polyester molecules form coils easily. Furthermore, a higher degree of polyester unsaturation favored unsaturated polyester chains to proceed to intramolecular cyclization reactions. Intramolecular cyclization enhances the microgel formation and, in turn, reduces the size of the microgels and makes them more compact. Many pendant polyester $C = C$ bonds may be trapped in the compact microgels that reduce the effective vinyls and cause the delay of gelation, higher gel conversion, and lower final conversion.

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