

# Effects of Low-Profile Additives on the Curing Reaction of Unsaturated Polyester Resins

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## SYNOPSIS

The effect of low-profile additives (LPA), i.e., poly(vinyl acetate) (PVAC) and poly(methyl methacrylate) (PMMA), on the curing reaction of unsaturated polyester (UPE) resins was studied by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). The curing reaction profiles were determined by DSC, while GPC was used to investigate the variation of the sizes of microgel particles during the early stage of curing reaction in UPE-styrene resins. The DSC experimental results indicated that the curing reaction rate decreased as the concentration of LPA increased. At a fixed LPA concentration, the curing reaction rate was slower for resins mixed with LPA possessing worse compatibility with UPE resins. During the early stage of curing reaction, the size and structure of the UPE microgels formation strongly depended on the concentration of LPA and also on the compatibility of the components in the curing system. The experimental results of this study revealed that the concentration of LPA and the compatibility of LPA with UPE resins had a strong influence on the polyester microgel formation and the curing behavior.

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## INTRODUCTION

In recent years, glass-fiber-reinforced unsaturated polyester (UPE) molding compounds have received an increasing interest in industry. The advantages for the composite materials are: high strength, dimensional stability, low weight, good corrosion properties, and cheap price.<sup>1</sup> UPE molding compounds such as sheet molding compounds (SMC), bulk molding compounds (BMC), and thick molding compounds (TMC), etc., have been formulated to meet the requirements of specific applications in industry. The composition of these compounds are: UPE resin, low-profile additives (LPA), catalyst, mold-release agent, pigments, inorganic fillers, glass-fiber reinforcement, etc.

LPAs are used in UPE molding compounds formulations to improve surface quality of the molded part, and to compensate for resin shrinkage. Poly(vinyl acetate) (PVAC) and poly(methyl

methacrylate) (PMMA) are widely used as LPAs, particularly in SMC and BMC formulations.<sup>2</sup> Although there are many explanations for the observed phenomena,<sup>3-9</sup> it is generally agreed that a major factor for the low-profile behavior is the formation of a two-phase structure between LPA and UPE resins. Phase separation occurs at the very beginning of the reaction.<sup>3,5,8,9</sup>

The curing reaction mechanism of UPE-styrene resins has been reported by several researchers. It is a free radical copolymerization of ester vinyl and styrene vinyl groups. Horie and co-workers<sup>10-12</sup> carried out an experimental study of UPE-styrene copolymerizations, and found that the network formation due to the existence of highly unsaturated vinyls in polyesters led to an earlier onset of the gelation and a decrease of final conversion. They attributed this phenomenon to chain segmental immobility in a crosslink network. Dusek et al.<sup>13-16</sup> found that the Flory-Stockmayer theory<sup>17</sup> of crosslinking or the theory of branching processes based on treelike representation of chemical structures, yields reasonable results for copolymerization of monovinyl and divinyl components, only if the con-

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tent of divinyl component was very low and also a perturbation correction for cyclization was 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 microgellike particles even at the very beginning of polymerization. Lee and co-workers<sup>18-21</sup> observed similar results in UPE sheet molding compounds,<sup>18,19</sup> a polyurethane-polyester interpenetrating polymer network,<sup>20</sup> and a UPE-styrene system.<sup>21</sup> They found that the gel conversions of UPE resins were much higher than those predicted by the classical Flory-Stockmayer theory.<sup>17</sup> They attributed the reason for the discrepancy from the theory to the existence of intramolecular cyclization reaction between UPE and styrene vinyls. The competition between intermolecular (network formation) and intramolecular (cyclization) crosslinkings caused the delay in gelation. Hild and Okasha<sup>22,23</sup> attributed the delay of gelation to the reduction of reactivity of polyester vinyls as the reaction proceeds. Thus, the maximum network density could not be reached. Minnema et al.<sup>24</sup> attributed this phenomenon to the shielding of the pendant vinyl groups in the intramolecular cyclization crosslinkings. Yang and Lee<sup>25</sup> investigated the size and shape of microgel particles of the cured UPE resins by scanning electron microscopy (SEM). They found that the network structure can be coral like or flake like, depending on the concentration and type of UPE resins in the reacting system.

In a recent work,<sup>26</sup> we studied the curing behavior of UPE-styrene systems by using differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). The variation of the sizes of polyester microgel formation during the initial period of curing reaction was investigated by GPC. The conversions in the curing reaction of UPE with styrene monomer were determined by DSC. Our experimental results indicated that the polyester molecular chain lengths and the degree of unsaturation per polyester molecular chain had a great influence on the microgel formation. Yang and Lee<sup>20,21,25</sup> pointed out that the intramolecular reaction (cyclization) and intermolecular reaction (network formation) in the early stage of curing reaction were the key feature of the gelation of UPE resins. Our GPC results demonstrated the phenomenon of the shrinkage of polyester microgel coils during the early stage of curing reaction. The experimental results provided the evidence of intramolecular cyclization as mentioned by Yang and Lee.<sup>20,21,25</sup>

Several researchers<sup>27-33</sup> have reported the effects of LPAs on the curing kinetics of a UPE-styrene system. Kubota<sup>27</sup> found a very small effect of an LPA (cellulose acetate butyrate) on the cure kinetics. Han and co-workers<sup>28-32</sup> reported lower reaction rates and final degree of cure when using an LPA. A decrease in the final conversion was also reported by Kiaee et al.<sup>4</sup> The curing reaction of UPE-styrene in the presence of LPA is an inhomogeneous free radical chain growth crosslinking copolymerization. The three major reactions (styrene-polyester vinylene, styrene-styrene, and polyester vinylene-polyester vinylene) in LPA modified resins are the same as those in pure styrene-UPE copolymerization. However, the polyester microgel structure formation and curing behavior are strongly affected by the compatibility of LPA and UPE resin.

In the present work, we studied curing reactions of UPE-styrene in the presence of thermoplastics LPAs by DSC and GPC. The curing reaction profiles were investigated by DSC and the variation of the sizes of UPE microgel coils before macrogelation was investigated by GPC. Two LPAs (PMMA and PVAC) were used in this study, which have different compatibility with UPE resins. The compatibility of PMMA with UPE resins was worse than that of PVAC with UPE resins. Lem and Han<sup>29</sup> reported that a UPE-PVAC system, forming an optically homogeneous solution before curing began, exhibited a phase separation as curing progresses beyond the incipient gel point, while the UPE-PMMA system, forming an optically heterogeneous solution before curing began, exhibited shear-thinning behavior during cure before the incipient gel point was reached. As reported in recent articles,<sup>25,26</sup> we know that intramolecular cyclization and microgel formation had a great effect on the curing reaction of unsaturated polyester resins. The main purpose of this work was to study the effects of the concentration of LPA and the effect of the compatibility of LPA with UPE resins on the microgel formation during the early stage of curing reaction.

## EXPERIMENTAL

### Materials

#### *Unsaturated Polyester*

Unsaturated polyester resin was prepared in a nitrogen atmosphere by a conventional condensation method from isophthalic acid (IPA), fumaric acid

(FA), and propylene glycol (PG). The reaction temperature was increased by stepwise control as following: 140°C/2 h, 160°C/2 h, 180°C/2 h, 200°C/2 h, and 220°C/2 h. The polyester product was then cooled down to 100°C and mixed with styrene monomer in a weight ratio 70 : 30 of polyester to styrene monomer containing 0.1% of hydroquinone inhibitor. The resin was then cooled to room temperature immediately. The mol ratio of the final composition of the solid polyester determined from NMR was IPA/FA/PG = 1.0/1.67/3.23 with a mol ratio of 1.21 for OH/COOH and an acid value of 30.0 mg KOH/g of solid resin. The number average molecular weight of the polyester determined by GPC was found to be 1,800, with a dispersity of  $M_w/M_n = 4.3$  at 25°C. THF was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co.) were used in the linear method of calibration.

### Initiator

The peroxide initiator was *tert*-butyl peroxybenzoate (Akzo Chemie Co.), with a purity of 98% and an active oxygen content of 8.07%.

### Low Profile Thermoplastics

Polymethylmethacrylate (PMMA) ( $M_n = 1.77 \times 10^5$  and  $M_w/M_n = 2.05$ ) and polyvinylacetate (PVAC) ( $M_n = 8.6 \times 10^4$  and  $M_w/M_n = 2.45$ ) purchased from Aldrich Chemical Co. were used in this study without further purification.

### Styrene

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

### Instrumentation

#### Differential Scanning Calorimeter (DSC)

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

### Gel Permeation Chromatograph (GPC)

Waters model 746 GPC with  $\mu$ -styragel columns (pore sizes were  $10^3$  Å,  $10^4$  Å, and  $10^5$  Å) and RI detector was used to investigate the variation of the particle size of microgel formation during the curing reaction of UPE resins. The UPE resins with LPAs were mixed with 1% of *tert*-butyl peroxy benzoate initiator. The curing reactions were proceeded in a DSC cell at 110°C and were stopped at 2, 3, 6, 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  $\mu$ m FHL P Millipore filter before GPC analysis. THF was also used as the mobile phase in GPC analysis. In the early stage of curing reaction, the microgels formed before macrogelation could be dissolved in THF. Although the curing reaction was close to gelation, a small amount of large particles might be formed that were due to the macro network formation shown in Fig. 8(d) in the text). These large particles were removed by Millipore filter. Hence, our GPC distribution curves showed the size distribution of LPA, primary UPE, and partially cured UPE microgels.

## RESULTS AND DISCUSSION

In the use of DSC for studying the isothermal curing kinetics of thermosetting resins, one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of curing  $\alpha$  (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:<sup>33</sup>

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \frac{dQ}{dt} \quad (1)$$

Integrating eq. (1) with time, one obtains the relative degree of cure,  $\alpha$ ,

$$\alpha = \frac{1}{Q_{\text{tot}}} \int_0^t \left( \frac{dQ}{dt} \right)_T dt \quad (2)$$

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

$$Q_{\text{tot}} = Q_{\text{iso}} + Q_r \quad (3)$$

where  $Q_{\text{iso}}$  is the heat generated during the isothermal DSC runs, at 110°C and  $Q_r$  the residual heat

that is released when sample is heated to 220°C at a heating rate of 5°C/min after the completion of an isothermal curing reaction at 110°C. In this study, we define the gel conversion,  $\alpha_{gel}$ , as the conversion at the initial inflection of conversion profile  $\alpha$  vs. curing time. This approximate definition is close to the extent of actual gel conversion.

Figure 1 is the plots of curing rate  $d\alpha/dt$  vs. curing time obtained from the DSC measurements at 110°C for UPE resins mixed with LPA in the order of 0%, 5%, 10%, and 15% by weight of PVAC. Table I summarizes the heat of isothermal curing reaction,  $Q_{iso}$ , and residual heat,  $Q_r$ , for UPE resins with 0%, 5%, 10%, and 15% of PVAC cured at 110°C. Figure 2 shows the curing profiles of conversion  $\alpha$  vs. curing time for UPE resins mixed with 0%, 5%, 10%, and 15% PVAC. Table II lists the onset of cure time,  $t_{onset}$ , cure time at the maximum of curing rate  $d\alpha/dt$ ,  $t_{peak}$ , gel conversion,  $\alpha_{gel}$ , and final conversion,  $\alpha_f$ . From these data, we found that  $t_{onset}$ ,  $t_{peak}$ , and  $\alpha_{gel}$  increased in proportional to the concentration of PVAC, while the final conversion  $\alpha_f$  decreased with increasing concentration of PVAC.

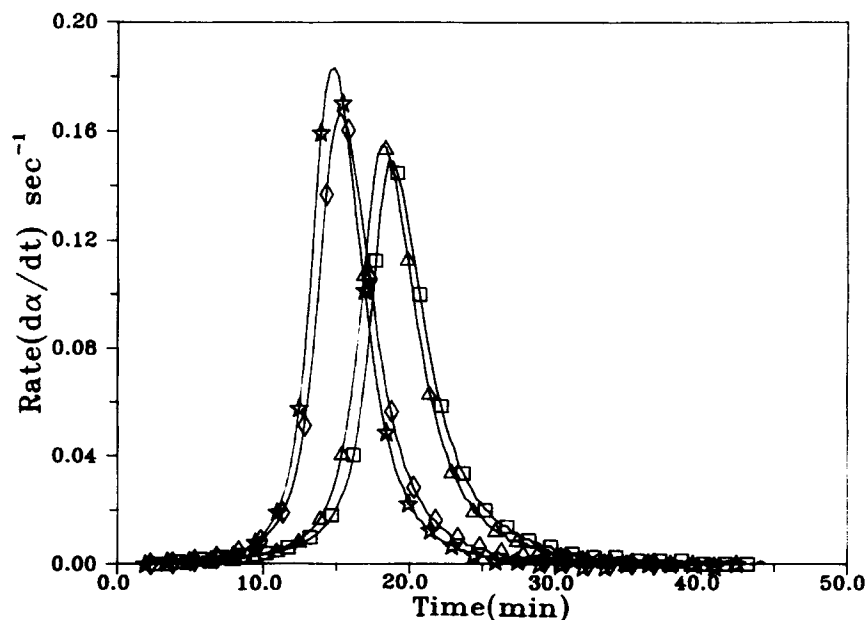
Similar experiment results were obtained from the DSC measurements at 110°C for UPE resins mixed with weight percentage for PMMA in 0%, 5%, 10%, and 15%. Table III summarizes the heat of isothermal curing reaction,  $Q_{iso}$ , and residual heat,  $Q_r$ , of UPE resins with 0%, 5%, 10%, and 15% of PMMA. Table IV lists the onset of cure time,  $t_{onset}$ ,

**Table I** Curing Heat for UPE Resins Modified with PVAC

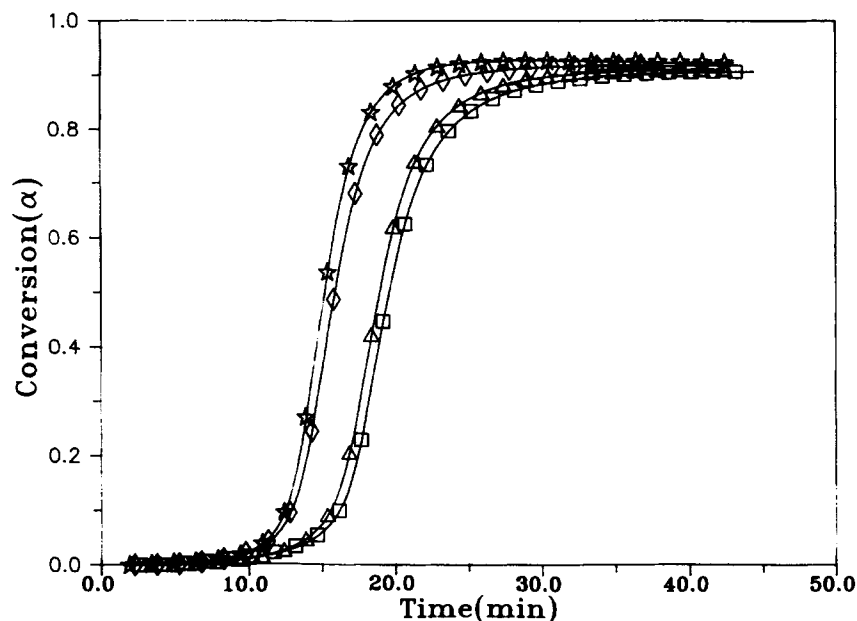
PVAC wt %	$Q_{iso}$ (J/g)	$Q_r$ (J/g)
0.0	280.2	23.4
5.0	273.2	24.3
10.0	250.6	24.5
15.0	242.7	25.2

cure time at the maximum of curing rate  $d\alpha/dt$ ,  $t_{peak}$ , gel conversion,  $\alpha_{gel}$ , and final conversion,  $\alpha_f$ . Similar effect of PMMA as that of PVAC on the curing reaction of UPE-styrene were found from these experimental results. The  $t_{onset}$ ,  $t_{peak}$ , and  $\alpha_{gel}$ , increased and  $\alpha_f$  decreased as the concentration of PMMA increased.

It may be interesting to study the influence of the compatibility of LPA with UPE resins on the curing reaction of UPE-styrene. The compatibility between the LPA and the uncured resin was tested by mixing them with a shaker until well mixed and then keeping the mixture in an undisturbed location. If the LPA is not compatible with the resin, the mixture tends to separate into two layers. Our test results showed that the PVAC was compatible with the resins, while the mixture of PMMA with UPE resin tended to separate into two layers shortly after mixing. Thus, PVAC has a better compatibility with the UPE resins than PMMA does. From DSC experi-



**Figure 1** Curing rate  $d\alpha/dt$  vs. curing time from DSC measurements. (Star) 0% PVAC; (diamond) 5% PVAC; (triangle) 10% PVAC; (square) 15% PVAC.



**Figure 2** Conversion  $\alpha$  vs. curing time obtained from DSC measurements. (Star) 0% PVAC; (diamond) 5% PVAC; (triangle) 10% PVAC; (square) 15% PVAC.

mental results (Tables II and IV), it is obvious that at a fixed LPA concentration the curing reaction rates of UPE resins in the presence of PVAC are faster than that of UPE resins in the presence of PMMA.

It is known that the curing reaction of styrene with UPE is a free radical chain growth crosslinking copolymerization of styrene and polyester vinyls. Three major reactions are: styrene–polyester vinyl, styrene–styrene vinyl, and polyester vinyl–polyester vinyl. Yang and Lee<sup>20,21</sup> classified the curing reaction of UPE–styrene system into four types: (1) intermolecular crosslinking with or without linking through styrene monomers; (2) intramolecular crosslinking with or without linking through styrene monomers; (3) chain 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

crosslinking density and reduces the sizes of polyester coils, but does not contribute to the macroscopic network formation; reaction (3) consumes crosslinking units and may slightly increase the polymer coil sizes, but has little effect on the network formation; 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 the network formation. The intramolecular crosslinking reaction resulted in the retardation of gelation by reducing the polyester coil sizes. The shrinkage of polyester coils due to intramolecular crosslinking reaction had been observed by GPC in our previous work.<sup>26</sup>

In the presence of LPA, the three major reactions of UPE–styrene copolymerization are the same as those in pure UPE–styrene system. The curing structure of UPE with styrene in the presence of LPA system may be pictured as many coiled UPE chains swelled in the mixture of LPA and styrene

**Table II** Curing Parameters for UPE Resins Modified with PVAC

PVAC wt %	$t_{\text{onset}}$ (min)	$t_{\text{peak}}$ (min)	$\alpha_{\text{gel}}$	$\alpha_f$
0.0	11.67	14.54	0.096	0.923
5.0	12.08	15.08	0.097	0.918
10.0	14.95	17.99	0.101	0.911
15.0	15.61	18.45	0.116	0.906

**Table III** Curing Heat for UPE Resins Modified with PMMA

PMMA wt %	$Q_{\text{iso}}$ (J/g)	$Q_r$ (J/g)
0.0	280.2	23.4
5.0	273.6	26.1
10.0	257.2	26.1
15.0	248.1	27.9

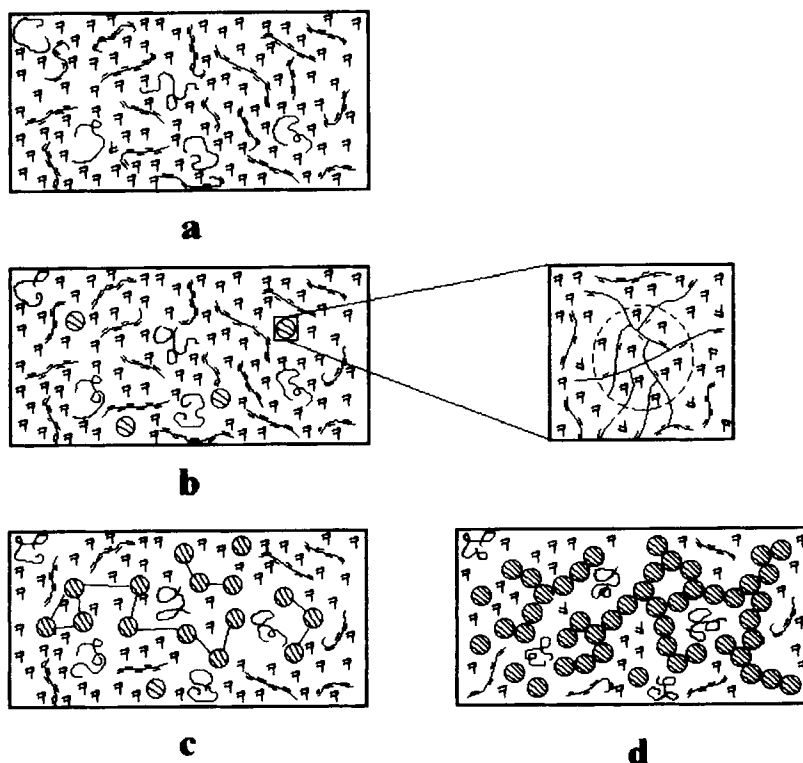
**Table IV Curing Parameters for UPE Resins Modified with PMMA**

PMMA wt %	$t_{\text{onset}}$ (min)	$t_{\text{peak}}$ (min)	$\alpha_{\text{gel}}$	$\alpha_f$
0.0	11.67	14.54	0.096	0.923
5.0	16.65	19.51	0.098	0.913
10.0	20.51	23.67	0.112	0.908
15.0	21.57	24.97	0.118	0.899

monomer. The sizes of polyester coils depend on the UPE molecular chain lengths, chain stiffness, concentration of UPE chains, concentration of LPA, and compatibility of UPE resins with LPA. Chemical reaction between the vinyl groups originated from UPEs and from styrene monomer may occur inside, outside, or at the surface of the coils. When the reaction starts, the initiators decompose to form free radicals initiating polymerization, which link adjacent UPE chains through connecting styrene monomers by both inter- and intramolecular reactions. At the coil surface, there happens the inter-

molecular crosslinking reaction, 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 "micro-gel" structure.<sup>16,24,25,35-36</sup> This phenomenon was first claimed by Minnema and Staverman<sup>24</sup> in monovinyl-divinyl copolymerization and was investigated by GPC in our previous work.<sup>26</sup> Because of the high crosslinking of the microgels, the free radicals 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 coupled with microgel gelation mechanism of UPE-styrene in the presence of LPA can be pictured, as shown in Figure 3.

Our experimental results indicated that the curing reaction of UPE with styrene was retarded by LPA. Thus, the curing reaction rate decreased as the concentration of LPA increased. The reason for this phenomenon could be due to the lower concentra-



**Figure 3** The curing mechanism of unsaturated polyester. (a) The beginning of the curing reaction; (b) Microgel formation due to intramolecular crosslinking reaction; (c) Intermolecular crosslinking reaction between the microgel particles; (d) Gelation. (—) Styrene; (—) UPE; (⊗) LPA.

tions of polyester and styrene vinyl groups. The other reason could be due to the higher viscosity of the system upon increasing concentration of LPAs. However, one may explain this behavior by using the intermolecular (network formation)–intramolecular (cyclization) reactions and microgel formation mechanism. For UPE resins mixed with LPAs, the thermoplastics LPA may be considered as a diluent. Increase of the diluent concentration favors UPE to proceed intramolecular crosslinking reaction with styrene monomer and microgel formation.

For UPE resins with a fixed LPA concentration, the worse compatibility of LPA with UPEs and styrene monomer results in a higher tendency for the UPE molecules to shrink and form coils in a mixture of LPA and styrene monomer, which causes an increase in chance for UPEs to proceed intramolecular crosslinking reaction with styrene monomer and form microgels. The compatibility of UPE resins with PMMA is worse than that with PVAC; thus, in comparing the influence of these two LPAs, the UPE molecules have more tendency to proceed intramolecular reaction and form microgels in the presence of PMMA.

From the above discussions, we may conclude that either to increase the LPA concentration or to decrease the compatibility of UPE resins with LPA results in an increase of intramolecular reaction and microgels formation during curing. Many pendant vinyl groups may be trapped inside the microgels, which reduce the effective concentration of polyester vinyls for further intermolecular crosslinking reaction. Such an effect has been known as “molecular shielding” effect,<sup>24</sup> which causes a retardation of the curing reaction and leads to a higher gel conversion,  $\alpha_{\text{gel}}$ .

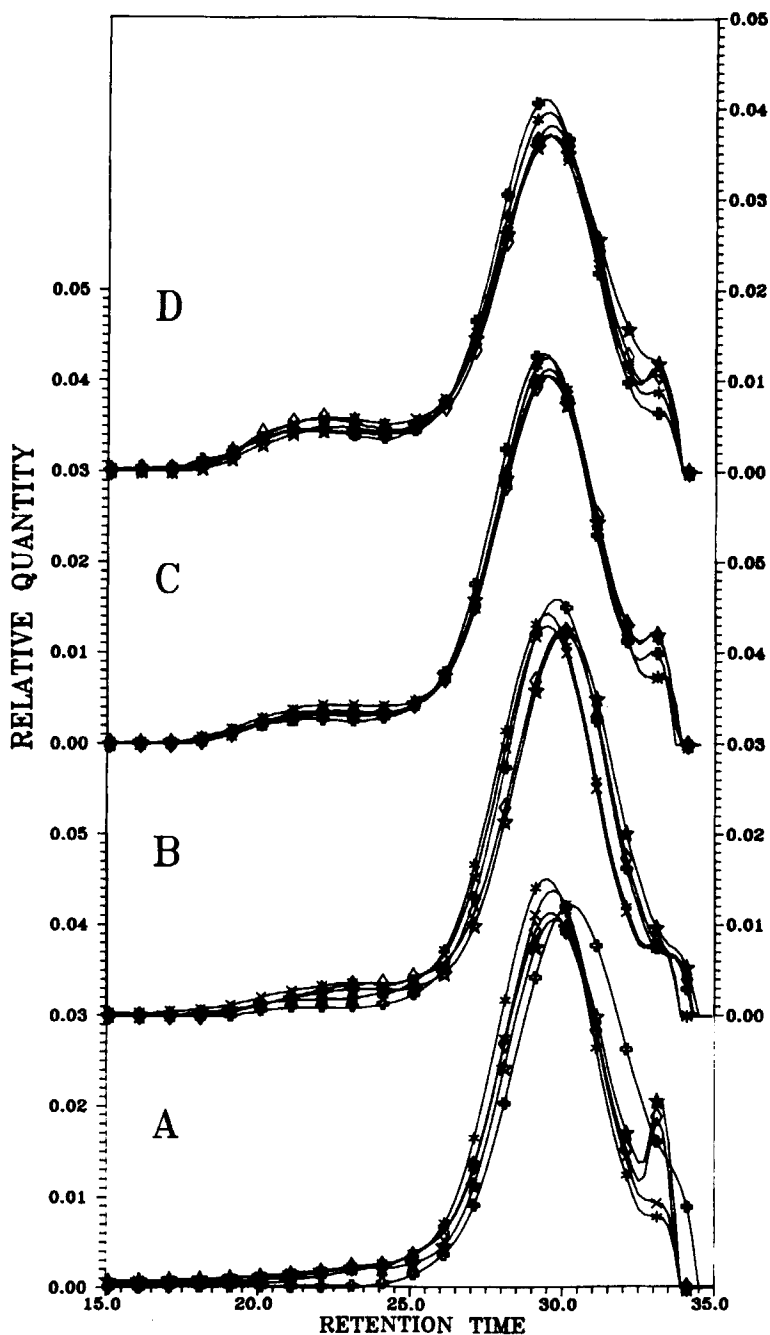
The phenomenon of intramolecular crosslinking cyclization and intermolecular crosslinking reaction of UPE coils in the mixture of LPA and styrene monomer can be investigated from the variation of the polymer particle sizes by GPC. On the use of GPC to investigate the microgel formation during curing, the relative amount of particles was plotted against retention time in the chromatogram. Because the retention time is inversely proportional to the particle size, the shorter retention time corresponds to larger particle size.

Figure 4 shows the GPC distribution curves of partially cured UPE coils for pure UPE resin [Fig. 4(A)], UPE resin mixed with 5% of PVAC [Fig. 4(B)], UPE resin mixed with 10% of PVAC [Fig.

4(C)], and UPE resin mixed with 15% of PVAC [Fig. 4(D)], which were cured at 110°C with various curing times. Figure 5 shows the GPC distribution curves of partially cured UPE coils of pure UPE resin [Fig. 5(A)], UPE resin mixed with 5% PMMA [Fig. 5(B)], UPE resin mixed with 10% PMMA [Fig. 5(C)], and UPE resin mixed with 15% PMMA [Fig. 5(D)] cured at 110°C with various curing times. The X-axis of Figures 4 and 5 is the retention time of GPC that corresponds to the particle sizes of the components in the curing system. The Y-axis is the relative quantity of the particles. All of the GPC distribution curves in Figures 4 and 5 are normalized to 1. The small peaks at the shorter retention time in Figures 4 and 5 are the size distribution of LPA with a small amount of partially cured UPEs; and the big peaks at the longer retention time are the size distribution of partially cured UPEs and primary UPEs. In order to observe the variation of the sizes of UPE microgel coils during the curing reaction, the GPC distribution curves of uncured resins (at curing time of 0 min) were subtracted from those of the partially cured resins. Thus, the size distribution of LPA was subtracted from GPC curves, and only the variation of size distributions of partially cured UPE coils were observed. These plots are shown in Figures 6, 7, and 8 for pure UPE resin and UPE resins mixed with PVAC and PMMA, respectively.

For pure UPE resin without LPA, as shown in Figures 4(A) and 6, the particle sizes of the microgel coils increased as the curing reaction proceeded. However, at a curing time of 3 min (Fig. 6) the positive peak area at the retention time of 25 ~ 30 min decreased while a small positive peak at the retention time of 32.5 ~ 33.5 min appeared, indicating that the smaller particle size of the microgels than that at a curing time of 2 min. After 3 min, the particle size of microgels increased as the curing reaction proceeded.

For UPE resin mixed with 5% of PVAC [Figs. 4(B) and 7(a)], we found that at the curing time of 3 min the peak at the retention time of 30.5; ~ 34.5 min had a largest positive area, while the peak at the retention time of 16.0 min; ~ 25.5 min had a smallest positive area, showing the presence of smallest particle size of microgels at the curing time of 3 min. The microgel coils of partially cured UPE resins in the presence of 10% PVAC [Figs. 4(C) and 7(b)] shrunk at the curing time of 3 ~ 6 min. However, at a curing time of 7 min, the sizes of the microgel coils increased. Similarly, the microgel coils of partially cured UPE mixed with 15%



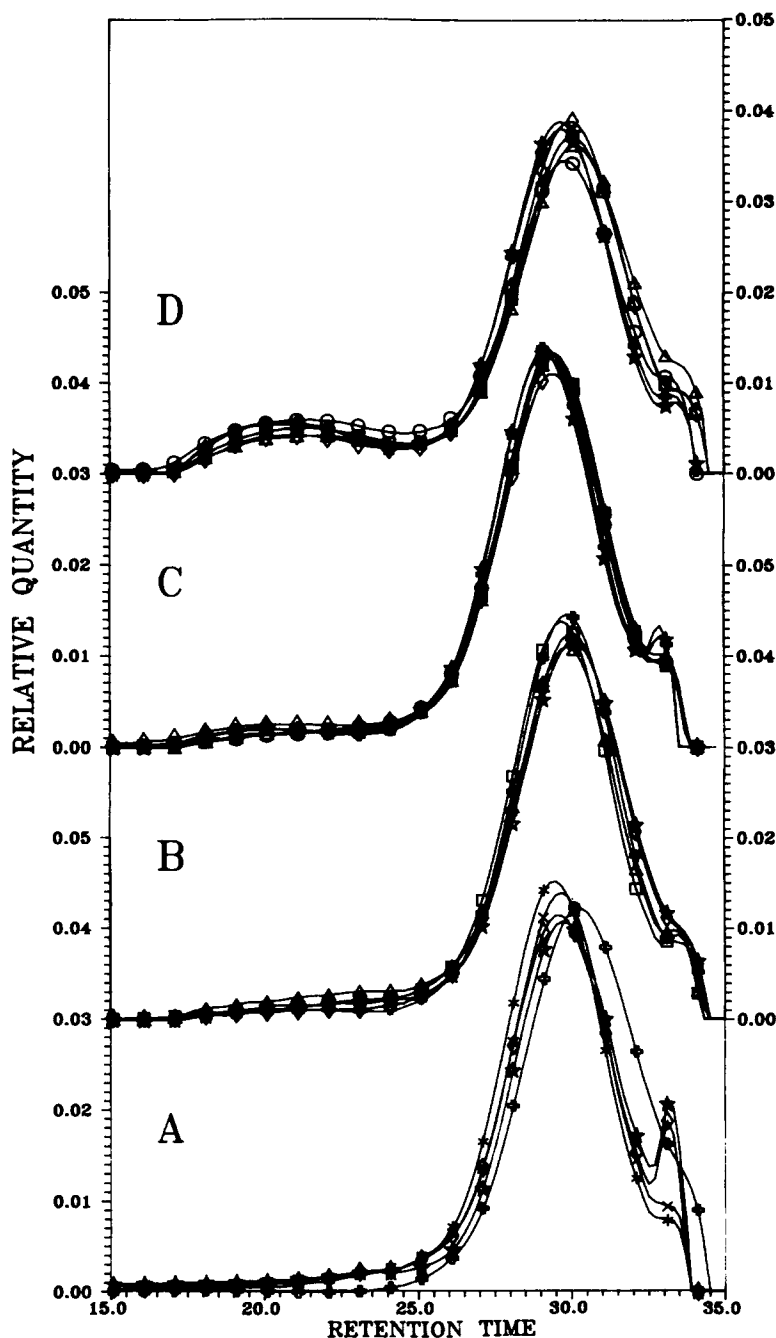
**Figure 4** The GPC distribution curves of unsaturated polyester resins with various PVAC concentrations of PVAC at various curing times. The curing temperature was  $110^{\circ}\text{C}$ . All of these distribution curves are normalized to one. (A) Pure UPE resin. (B) UPE resin mixed with 5% PVAC. (C) UPE resin mixed with 10% PVAC. (D) UPE resin mixed with 15% PVAC. Curing time: (cross) 0 min; (asterisk) 2 min; (star) 3 min; (diamond) 6 min; (X) 7 min.

PVAC [Figs. 4(D) and 7(c)] shrunk at curing time 2 ~ 6 min, and at the curing time of 7 min, the sizes of microgel coils increased.

For sample of UPE mixed with 5% PMMA [Figs. 5(B) and 8(a)], we found that the partially

cured UPE microgel particles shrunk at the curing time of 3 ~ 6 min. After 9 min of curing reaction, the sizes of partially cured UPE coils increased. The microgel particles of partially cured UPE in the presence of 10% PMMA [Figs. 5(C) and

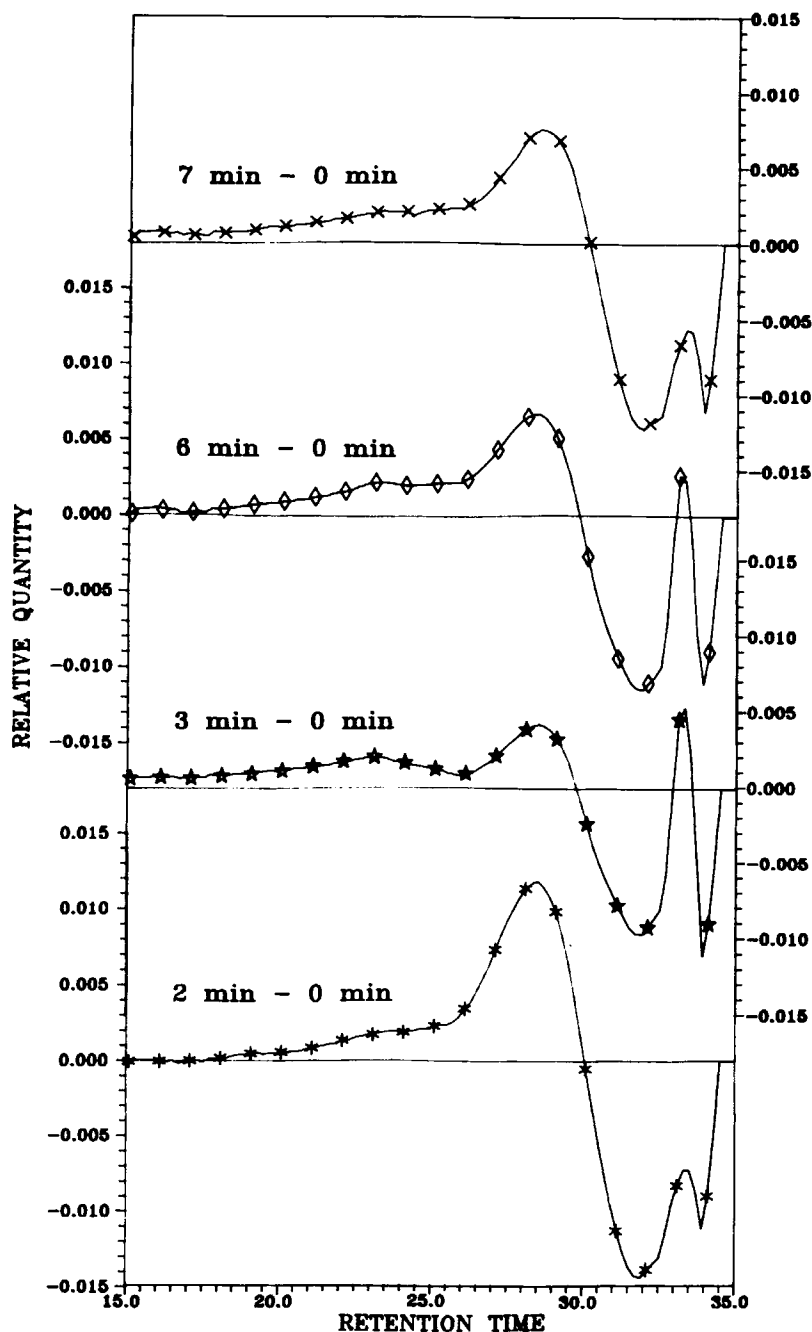




**Figure 5** The GPC distribution curves of unsaturated polyester resins with various concentrations of PMMA at various curing times. The curing temperature was 110°C. All of these distribution curves are normalized to one. (A) Pure UPE resin. (B) UPE resin mixed with 5% PMMA. (C) UPE resin mixed with 10% PMMA. (D) UPE resin mixed with 15% PMMA. Curing time: (cross) 0 min; (asterisk) 2 min; (star) 3 min; (diamond) 6 min; (X) 7 min; (triangle) 9 min; (square) 12 min; (circle) 15 min.

8(b)] shrunk at the curing time of 6 ~ 12 min. However, at the curing time of 15 min, the sizes of the UPE coils increased. Similarly, the microgel particles of partially cured UPE in the presence

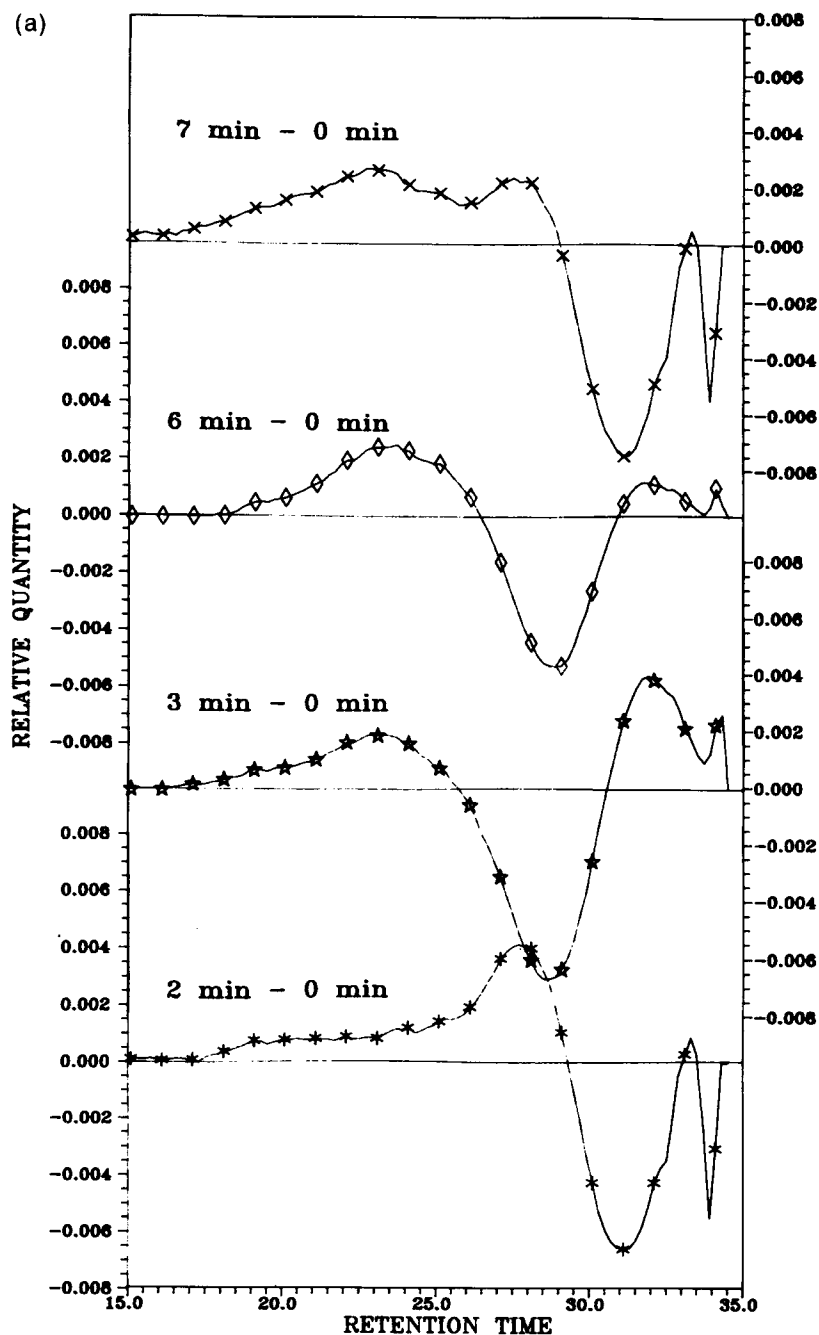
of 15% PMMA [Figs. 5(D) and 8(c)] shrunk at the curing time of 6 ~ 12 min. At the curing time of 15 min, the sizes of the UPE microgel coils increased.



**Figure 6** The variation of the coil sizes of partially cured UPE resins with 0% LPA, which were obtained by subtracting the GPC distribution curve of uncured resin (curing time 0 min) from those of partially cured resins (curing times are indicated in the figure).

The shrinkage of the microgel particles is due to the intramolecular crosslinking reactions, as shown in the b-stage of Figure 3. After the b-stage curing reaction, intermolecular reaction between the microgel particles happens, and the microgel particle size increases as the curing reaction proceeds. This behavior is shown in the

c-stage of Figure 3. From Figures 6, 7, and 8, we also noticed that either to increase the concentration of LPA or to decrease the compatibility of LPA with UPE resin resulted in an increase of the degree of shrinkage of microgel coils. The poor compatibility of LPA with UPE leads to the compactness of UPE coils in the mixture



**Figure 7** The variation of the coil sizes of partially cured UPE resins with PVAC, which were obtained by subtracting the GPC distribution curve of uncured resin (curing time 0 min) from those of partially cured resins (curing times are indicated in the figure). (a) UPE resin mixed with 5% PVAC. (b) UPE resin mixed with 10% PVAC. (c) UPE resin mixed with 15% PVAC.

of styrene and LPA, which favors UPE resins to proceed intramolecular cyclization reaction and causes the shrinkage of microgels. Similarly, increase the concentration of LPA also leads the UPE coils to be isolated and more compact in the mixture of styrene and LPA.

This phenomenon also leads to an increase in the tendency for UPE to proceed intramolecular cyclization.

Obviously, the results of our GPC measurements support the intermolecular (network formation) and intramolecular (cyclization) crosslinking microgelation

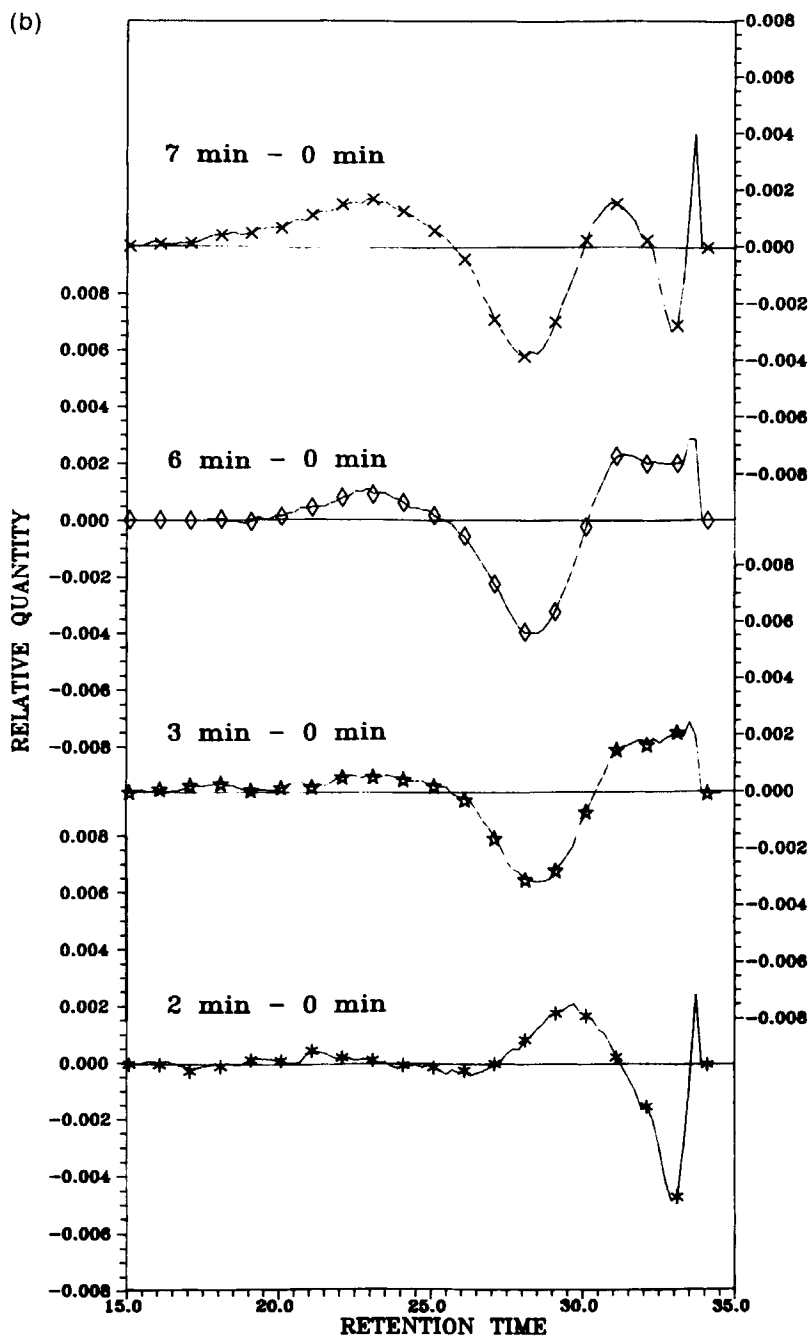


Figure 7 (Continued from the previous page)

mechanism for the curing reaction of the UPE-styrene system. Yang and Lee<sup>21</sup> studied the curing kinetics of UPE-styrene (with UPE the copolyester of isophthalic acid, fumaric acid, and propylene glycol) with various degrees of unsaturation for the UPE. They found that UPE with a higher degree of unsaturation had a slower reaction rate at lower conversion. In our previous work,<sup>26</sup> we studied the curing kinetics of the UPE-

styrene system (with UPE the copolyester of phthalic anhydride, fumaric acid, and propylene glycol) with various degrees of polyester unsaturation and molecular chain lengths by DSC and GPC. The experimental results indicated that the curing reaction rate was slower for UPE with a higher degree of unsaturation per UPE molecular chain or a longer molecular chain length. Evidently, the UPE chains with a higher degree of

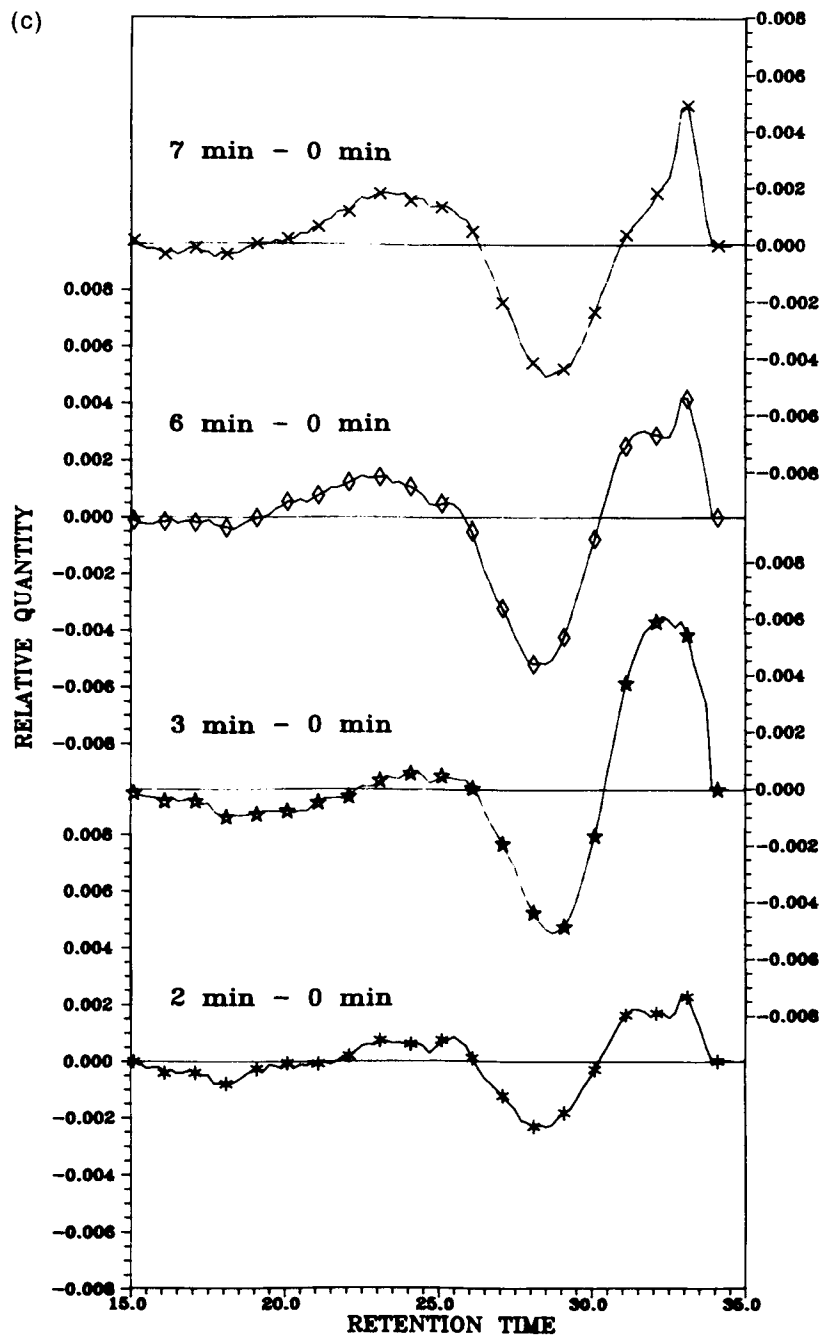


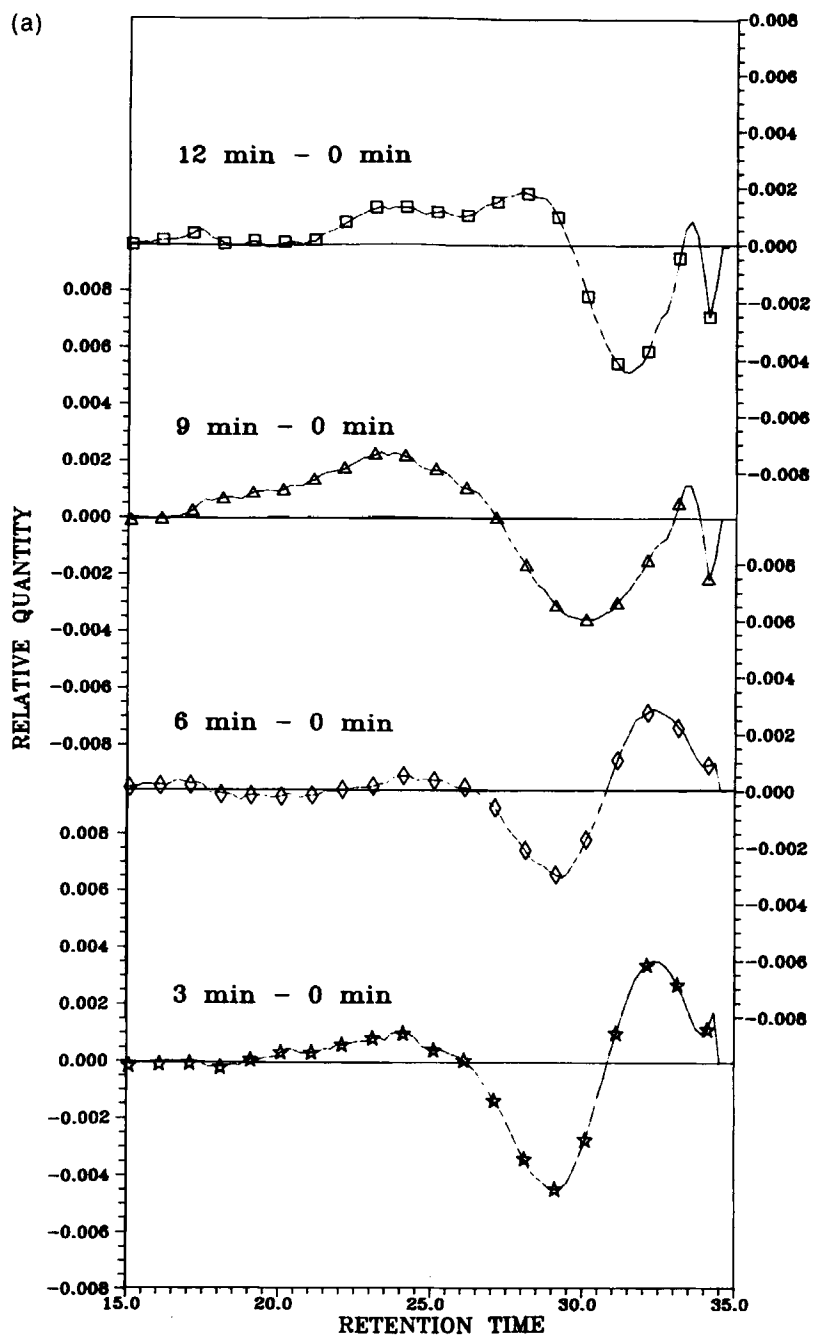
Figure 7 (Continued from the previous page)

unsaturation (with higher aliphatic fumaric acid concentration and lower aromatic isophthalic acid concentration) or a higher molecular chain length has more tendency to proceed intramolecular cyclization, which causes the formation of highly crosslinked microgels. Many pendant vinyl groups are buried in the microgel particles, which reduces the effective vinyl concentration and slowing down the overall reaction

rate. This phenomenon has been in consistent with the results of the present work.

## CONCLUSIONS

The GPC experimental results showed the evidence of the shrinkage of UPE microgels at the early stage



**Figure 8** The variation of the coil sizes of partially cured UPE resins with PMMA, which were obtained by subtracting the GPC distribution curve of uncured resin (curing time 0 min) from those of partially cured resins (curing times are indicated in the figure). (a) UPE resin mixed with 5% PMMA. (b) UPE resin mixed with 10% PMMA. (c) UPE resin mixed with 15% PMMA.

of curing reaction involving the polymer intramolecular cyclization crosslinking process. The formation of microgel particles has been found to be the key feature of the UPE-styrene copolymerization. For UPE resins mixed with LPA, the curing

reaction rate of UPE with styrene decreased as the concentration of LPA increased. Increase of the LPA concentration facilitates the UPEs to form coils in the styrene monomer and to undergo an intramolecular crosslinking reaction, which causes a delay

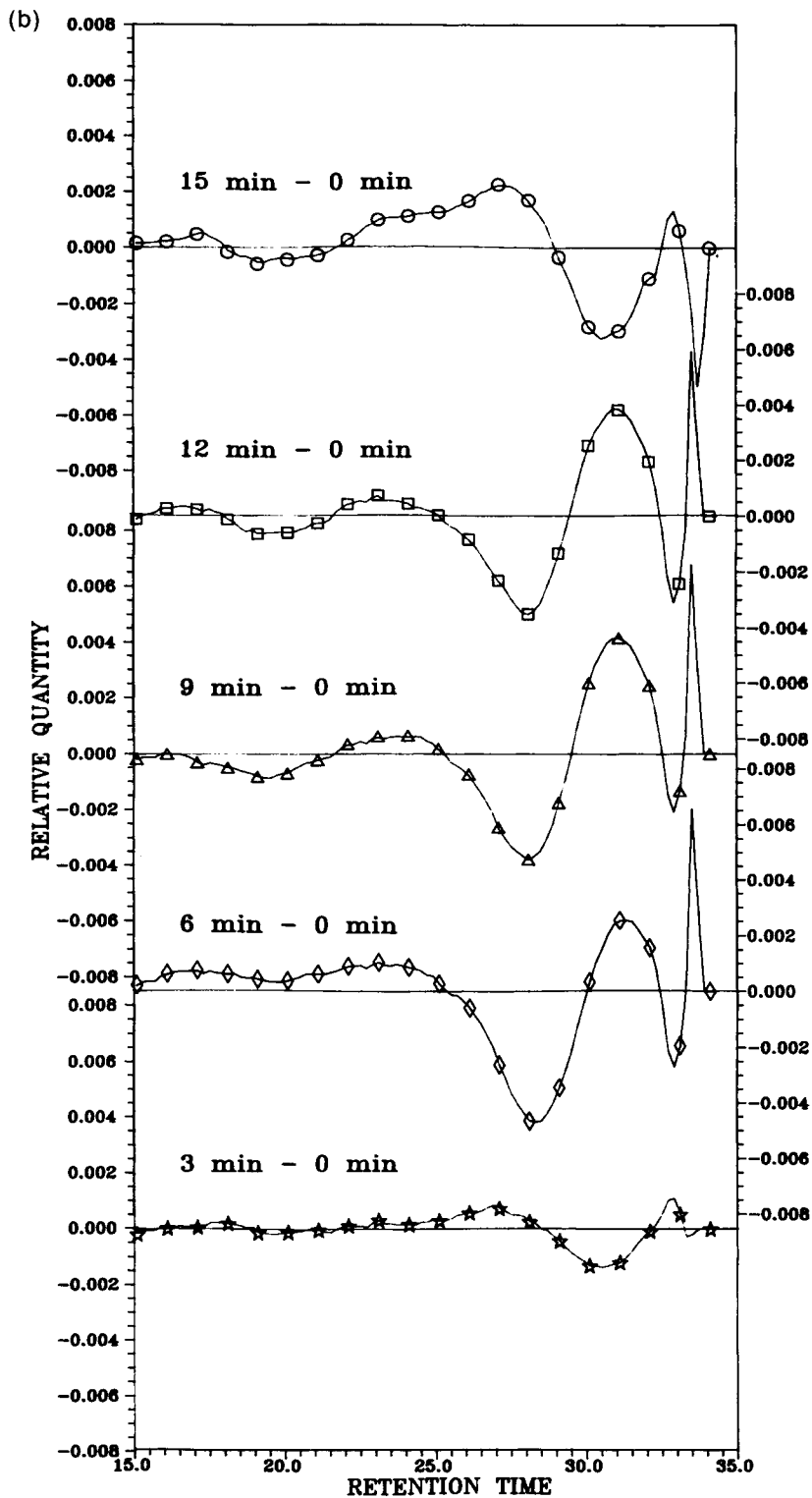


Figure 8 (Continued from the previous page)

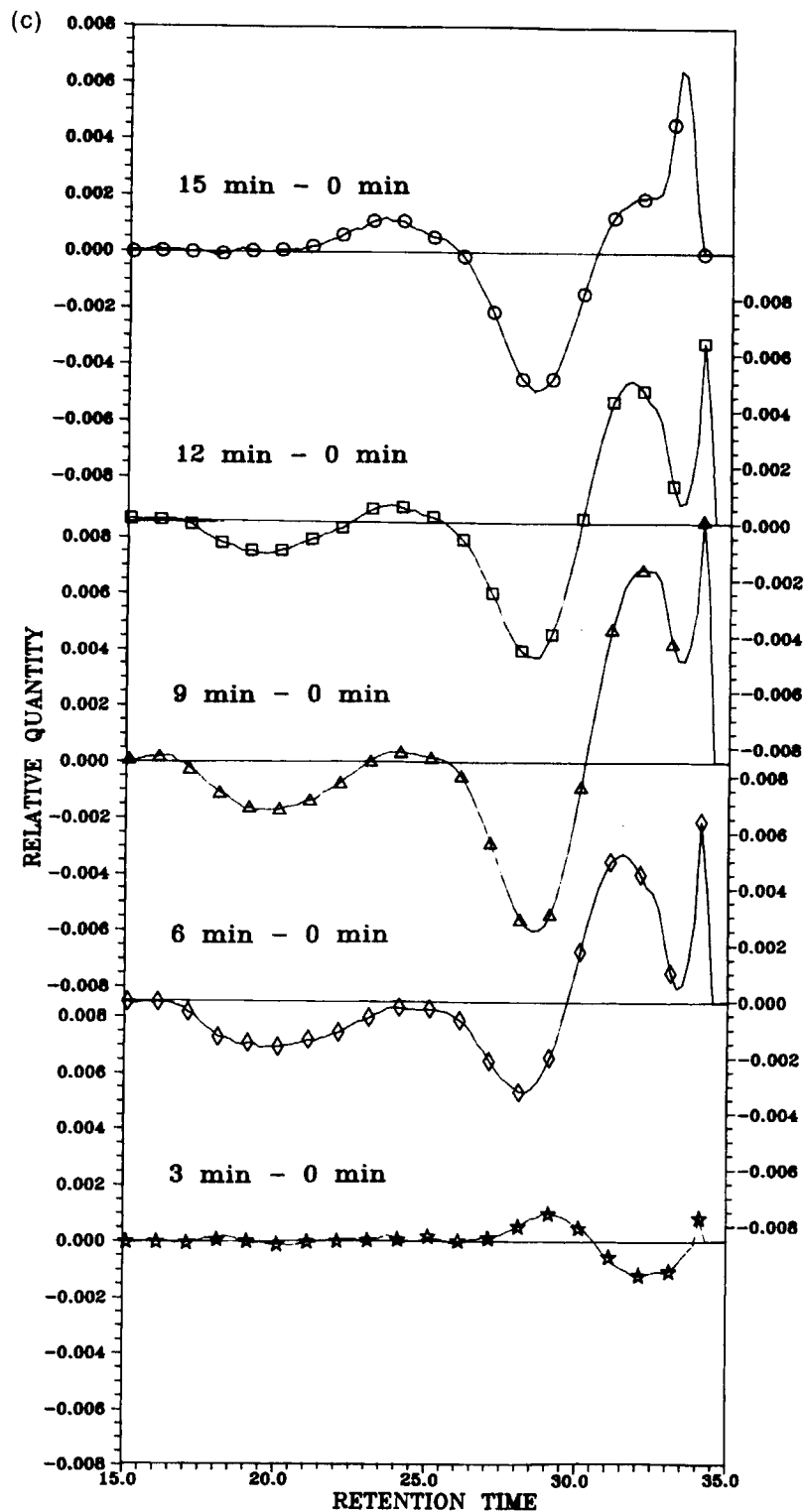


Figure 8 (Continued from the previous page)



of gelation. With a fixed LPA concentration, the compatibility of UPE with LPA is the key role on the curing reaction of UPE–styrene system. The worse the compatibility of UPE with LPAs, the slower the curing reaction rate. The poor compatibility of UPE with LPA could favor UPE chains to proceed intramolecular cyclization reactions. Intramolecular cyclization enhances the microgel formation which, in turn, reduces the size of the microgels to be more compact in the mixture of styrene and LPA. Many pendant polyester C—C bonds may be trapped in the compact microgels, retarding the effective vinyls for further intermolecular reaction and causing the delay of gelation for higher gel conversion.

## REFERENCES

1. G. Lubin, Ed., in *Handbook of Fiber Glass and Advanced Plastics Composites*, Van Nostrand Reinhold, New York, 1969.
2. R. Burns, in *Polyester Molding Compounds*, Marcel Dekker, New York, 1982.
3. C. B. Bucknall, P. Davies, and I. K. Partridge, *Polymer*, **26**, 109 (1985).
4. L. Kiaee, Y. S. Yang, and L. J. Lee, *43rd Annual Conf., Composite Inst., The Soc. Plast. Indus. Inc.*, February 1–5 (1988).
5. C. P. Hsu, M. Kinkelaar, P. Hu, and L. J. Lee, *Polym. Eng. Sci.*, **31**, 1450 (1991).
6. C. Lucas, J. Borrajo, and R. J. J. Williams, *Polymer*, **34**, 1886 (1993).
7. C. D. Han and K-W Lem, *J. Appl. Polym. Sci.*, **28**, 743 (1983).
8. L. Suspene, D. Fourquier, and Y. S. Yang, *Polymer*, **32**, 1593 (1991).
9. C. B. Bucknall, I. K. Partridge, and M. J. Phillips, *Polymer*, **32**, 786 (1991).
10. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci.*, **A-1**(7), 2561 (1969).
11. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci.*, **A-1**(8), 2839 (1970).
12. K. Horie, A. Otagawa, M. Muraoka, and I. Mita, *J. Polym. Sci., Polym. Chem. Ed.*, **53**, 445, (1975).
13. K. Dusek and M. Havsky, *J. Polym. Sci.*, **53**, 57 (1975).
14. K. Dusek and M. Havsky, *J. Polym. Sci.*, **53**, 75 (1975).
15. H. Galina, K. Dusek, Z. Tuzan, M. Bohanneky, and J. Stock, *Eur. Polym. J.*, **16**, 1043, (1980).
16. K. Dusek and J. Spevacek, *Polymer*, **21**, 750 (1980).
17. P. J. Flory, in *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
18. L. J. Lee, *Polym. Eng. Sci.*, **21**, 483 (1981).
19. Y. J. Huang and L. J. Lee, *AIChE J.*, **31**, 1585 (1985).
20. Y. S. Yang and L. J. Lee, *Macromolecules*, **20**, 1490 (1987).
21. Y. S. Yang and L. J. Lee, *Polym. Proc. Eng.*, **5**, 327 (1988).
22. G. Hild and R. Okasha, *Macromol. Chem.*, **186**, 93 (1985).
23. G. Hild and R. Okasha, *Macromol. Chem.*, **186**, 389 (1985).
24. L. Minnema and A. J. Staverman, *J. Polym. Sci.*, **29**, 281 (1958).
25. Y. S. Yang and L. J. Lee, *Polymer*, **29**, 1793 (1988).
26. S. B. Liu, J. L. Liu, and T. L. Yu, *J. Appl. Polym. Sci.*, **53**, 1165 (1994).
27. H. Kubota, *J. Appl. Polym. Sci.*, **19**, 2279 (1975).
28. K. W. Lem and C. D. Han, *J. Appl. Polym. Sci.*, **28**, 3185 (1983).
29. K. W. Lem and C. D. Han, *J. Appl. Polym. Sci.*, **28**, 3207 (1983).
30. K. W. Lem and C. D. Han, *Polym. Eng. Sci.*, **24**, 175 (1984).
31. D. S. Lee and C. D. Han, *Polym. Compos.*, **8**, 133 (1987).
32. D. S. Lee and C. D. Han, *Polym. Eng. Sci.*, **27**, 964 (1987).
33. E. A. Turi, in *Thermal Characterization of Polymeric Materials*, Academic Press, New York, 1981.
34. S. V. Muzumdar and L. J. Lee, *Polym. Eng. Sci.*, **31**, 1647 (1991).
35. Y. S. Yang and L. Suspene, *Polym. Eng. Sci.*, **31**, 321 (1991).
36. K. Dusek, H. Galina, and J. Mikes, *Polym. Bull.*, **3**, 19 (1980).

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