Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yang, J. F. and Yu, T. L.(1994) 'The Curing Reaction of Isocyanate-Thickened Unsaturated Polyester Resin', Journal of Macromolecular Science, Part A, 31: 4, 427 — 438

To link to this Article: DOI: 10.1080/10601329409351529

URL: http://dx.doi.org/10.1080/10601329409351529

J.M.S.—PURE APPL. CHEM., A31(4), pp. 427–438 (1994)

THE CURING REACTION OF ISOCYANATE-THICKENED UNSATURATED POLYESTER RESIN

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Key Words: Unsaturated polyester; Isocyanate; Thickening; DSC

ABSTRACT

The unsaturated polyester (UPE, copolyester of isophthalic acid, fumaric acid, and propylene glycol) was thickened with an isocyanate-terminated saturated aliphatic polyester, i.e., polycaprolactone diol (PE-di-OL), through the reaction of an isocyanate group with the hydroxyl group of the UPE. The curing reaction of the thickened UPE with styrene was studied by using differential scanning calorimetry. The variation in the size of the microgel during the curing reaction of thickened UPE was investigated by using gel permeation chromatography. The experimental data show that for a UPE system thickened with an isocyanate-terminated saturated aliphatic polyester, the curing reaction rate at lower conversion decreases as the chain length of the saturated aliphatic polyester increases. The experimental results are explained on the basis of microgel formation.

INTRODUCTION

Sheet and bulk molding compounds (SMC and BMC) have found many applications in automotive and appliance components. One of the major problems of processing SMC and BMC is the control of viscosity during both preparation and storage. The SMC and BMC can be properly utilized only when the mixture of unsaturated polyester (UPE) resin, monomer, filler, catalyst, and mold release agent are thickened sufficiently to yield a tack-free sheet. It should be stiff enough to permit easy handling and molding without glass fiber-resin separation. The two most commonly used methods for thickening of sheet and bulk molding compounds are: 1) the reaction of the Group IIA metal oxides and hydroxides [such as MgO, CaO, $Mg(OH)_2$, $Ca(OH)_2$, etc.] with carboxylic acid end groups of UPE [1-10] and 2) the reaction of isocyanate with the terminal hydroxyl groups of UPE [11-13].

Another problem in processing BMC and SMC arises from shrinkage which prevails in the high degree of polymerization shrinkage of UPE. Several workers have reported dilatometric measurements of the amount of shrinkage. In general, 7% volume shrinkage occurs during the cure of most unsaturated polyesters [14]. When fillers and fibrous reinforcements are included in an unsaturated polyester formulation, the amount of shrinkage is reduced but not totally eliminated. In order to control polymerization shrinkage and to improve properties, low profile additives are included in SMC or BMC formulations. These low profile additives are generally specific thermoplastics such as poly(vinyl acetate), poly(methyl methacrylate), polystyrene, and saturated aliphatic polyester.

In the present work, isocyanate-terminated saturated aliphatic polyesters were prepared by reacting the diisocyanate compound with a hydroxyl-terminated saturated aliphatic polyester. The UPE resin was thickened by the incorporation of an isocyanate-terminated saturated polyester. The saturated aliphatic polyester acts as a low profile additive. The isocyanate-terminated saturated aliphatic polyester is a low profile thickening agent for BMC and SMC. The advantage of combining an unsaturated polyester and polyurethane has been reported [15-21]. The UPE provides rigidity and thermal resistance, while polyurethane imparts toughness and low profile character. The purpose of this work was to investigate the effect of thickening by isocyanate-terminated saturated aliphatic polyesters on the curing reactions of UPE resins.

EXPERIMENTAL

Materials

1. Unsaturated polyester: Unsaturated polyester resin (UPE) was prepared by a conventional condensation method from isophthalic acid (IPA), fumaric acid (FA), and propylene glycol (PG). The reaction was carried out under nitrogen atmosphere. The reaction temperature was increased by stepwise control as follows: 140°C/2 hours, 160°C/2 hours, 180°C/2 hours, 200°C/2 hours, and 220°C/2 hours. The polyester product was cooled down to 120°C and mixed with styrene monomer (the weight ratio of polyester to styrene monomer is 70/30) containing 0.1% of hydroquinone inhibitor. The resin was then cooled to room temperature immediately. The mole ratio of the final composition of the solid polyester determined from NMR was IPA/FA/PG = 1.0/1.67/3.23 with a mole 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 gel permeation chromatography (GPC) was found to be 1800 with a

TABLE 1. The Composition (wt%) of Samples[a]

Sample	UPE	PE-di-OL-530	PE-di-OL-1250	TDI	Styrene
1	70	–	–	–	30
2	58.3	6.9	–	4.8	30
3	57.6	–	8.2	4.2	30

[a] UPE = unsaturated polyester. PE-di-OL-530 = poly(caprolactone)-di-ol (MW = 530). PE-di-OL-1250 = poly(caprolactone)-di-ol (MW = 1250). TDI = toluene-di-isocyanate.

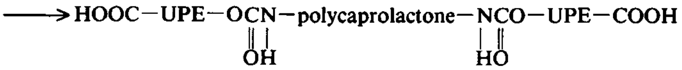
dispersion of $M_w/M_n = 4.3$ at 25°C. THF was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co.) were used in the linear calibration method.

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%.
3. Hydroxyl-terminated saturated polyester: Poly(caprolactone) diol (PE-di-OL) with weight-average molecular weights of 530 and 1250 purchased from Aldrich Chemical Co. were used as low profile additives in this study.
4. Isocyanate: The thickening agent was toluene-2,4-di-isocyanate (TDI) purchased from Riedel-de Haen AG, Germany, with a purity of 95%.
5. Styrene: Styrene monomer (purchased from Aldrich Chemical Co. with a purity of 99%) was purified by distillation several times very carefully before mixing with toluene-di-isocyanate.
6. Preparation of the isocyanate thickened unsaturated polyester resin (UPE): The isocyanate-terminated saturated polyester was prepared at room temperature by mixing TDI with PE-di-OL with a NCO/OH mole ratio of 2.0/1.0, and 30% by weight of styrene. The reaction time was about 1 hour in the presence of 1% of di-butyl-tin-dilaurate catalyst so that all the OH group of the saturated polyester was reacted completely with the isocyanate (NCO). The UPE was then mixed with this isocyanate-terminated PE-di-OL in 30% by weight of styrene monomer at room temperature for 1 hour. The UPE was thickened through the reaction between the hydroxyl group of UPE and the isocyanate group of the isocyanate-terminated PE-di-OL. In this reaction series, styrene monomer was used as diluent and later as the crosslinking agent for UPE. Table 1 lists the compositions of the samples used in this study.

The chemical reactions for preparing the thickened unsaturated polyester are shown by

$$\text{HO—polycaprolactone—OH} + 2\text{OCN—R—NCO} \longrightarrow \text{OCN—polycaprolactone—NCO}$$

$$\text{OCN—polycaprolactone—NCO} + 2\text{HO—UPE—COOH}$$



$$\longrightarrow \mathrm{HOOC{-}UPE{-}}\underset{\mathrm{O\,H}}{\mathrm{OCN}}\mathrm{{-}polycaprolactone{-}}\underset{\mathrm{H\,O}}{\mathrm{NCO}}\mathrm{{-}UPE{-}COOH}$$

Instrumentation

1. Differential Scanning Calorimeter (DSC): A Du Pont 910 DSC was used 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 ranged from 6 to 10 mg. A small sample size was required in order to achieve isothermal operation during cure.
2. Gel Permeation Chromatograph (GPC): Waters model 746 GPC with μ-styragel columns and RI detector was used to investigate the variation of the particle sizes of microgel formation during the curing reaction of UPE. The thickened or the unthickened unsaturated polyester resins were mixed with 1% *tert*-butyl peroxy benzoate initiator and cured at 110°C. The curing reaction was stopped after 3, 5, 7, and 9 minute intervals by cooling the samples to room temperature. The samples were then dissolved individually in THF which was also used as the mobile phase for GPC analysis.

RESULTS AND DISCUSSION

In the use of DSC for studying the isothermal curing kinetics of thermosetting resins [22], 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

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

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

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

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

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

where Q_t is the heat generated during the isothermal DSC runs at 110°C, and Q_r is the residual heat that is released when the 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.

Figure 1 shows plots of the curing rate $d\alpha/dt$ vs the curing time obtained from the DSC measurement for Samples 1-3. The curing temperature is 110°C. The plots of conversion α vs curing time for Samples 1-3 obtained from the DSC measurements are shown in Fig. 2.

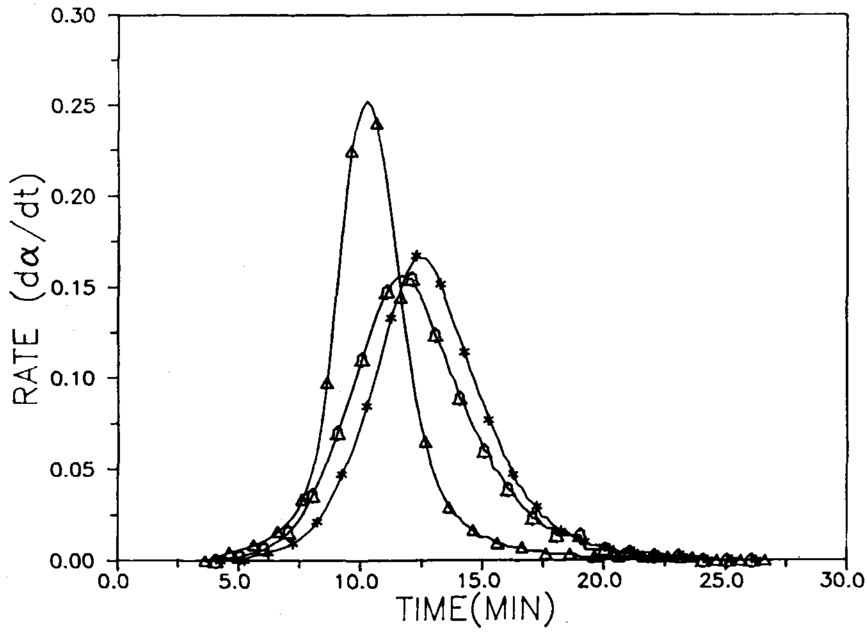


FIG. 1. Curing rate $d\alpha/dt$ vs curing time from DSC measurements: (△) Sample 1, (○) Sample 2, (∗) Sample 3.

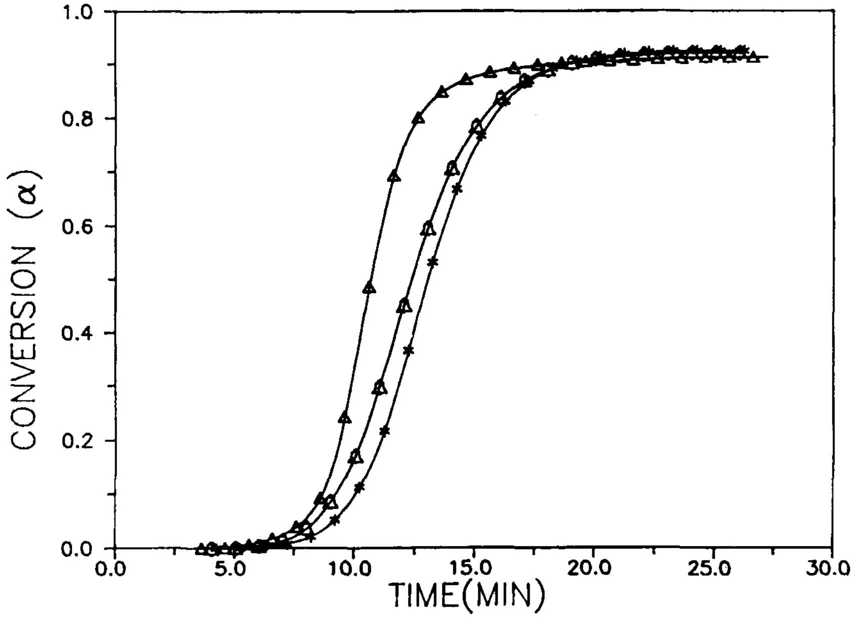


FIG. 2. Conversion α vs curing time obtained from DSC measurements: (△) Sample 1, (○) Sample 2, (∗) Sample 3.

The curing reaction of UPE with styrene is a free radical chain growth polymerization. One of the typical equations to describe the kinetics of unsaturated polyester was developed by Kamal [23] as follows:

$$(d\alpha)/(dt) = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (m + n = 2) \qquad (4)$$

where K_1, K_2, m, and n are constants.

The plots of the experimental data together with the least-squares fit of Eq. (4) for Samples 1-3 are shown in Figs. 3-5. The parameters K_1, K_2, m, and n obtained from least-squares fitting of the DSC experimental data to Eq. (4) are given in Table 2. The experimental data were found to agree with the predicted results given by Eq. (4) up to 50% conversion. When conversion exceeds 50%, the propagation reaction between styrene vinyl and ester vinyl groups becomes a diffusion-controlled process, which leads to a large deviation between the empirical and the predicted curves.

From Figs. 1 and 2 we found that the curing rate decreases as the chain length of the PE-di-OL increases. The fitting parameters K_2 and m of Eq. (4) decrease as the chain length of PE-di-OL increases. One may explain that the lower reaction rate for UPE thickened with a longer saturated aliphatic polyester is due to the lower concentration of ester vinyl groups for the UPE thickened with long isocyanate-terminated saturated aliphatic polyester. On the other hand, the experimental phenomena can also be explained by the microgel gelation mechanism proposed by Yang and Lee and their coworkers [24-26] which will be summarized in the following paragraphs.

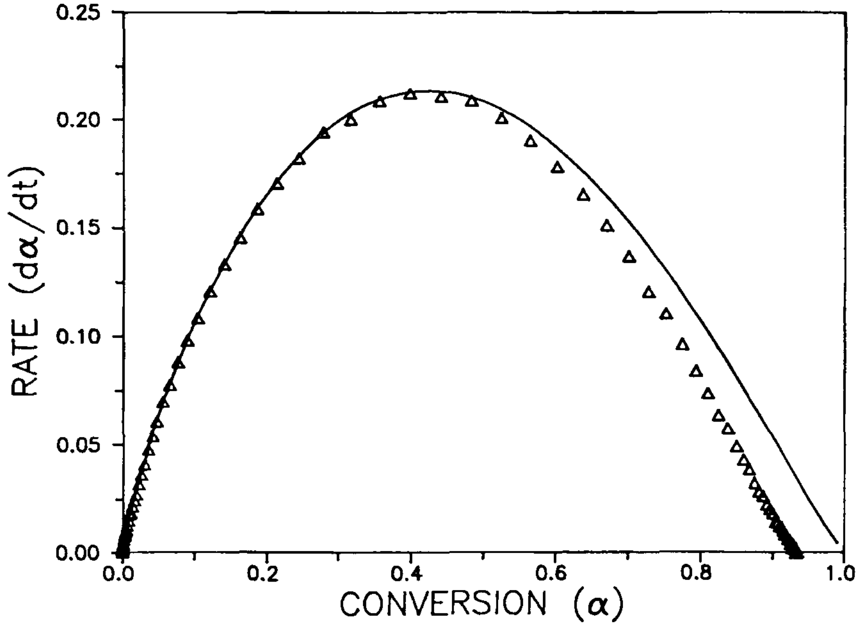


FIG. 3. DSC experimental data of Sample 1 together with the theoretical fit of Eq. (4): (△) DSC data, (——) curve based on Eq. (4).

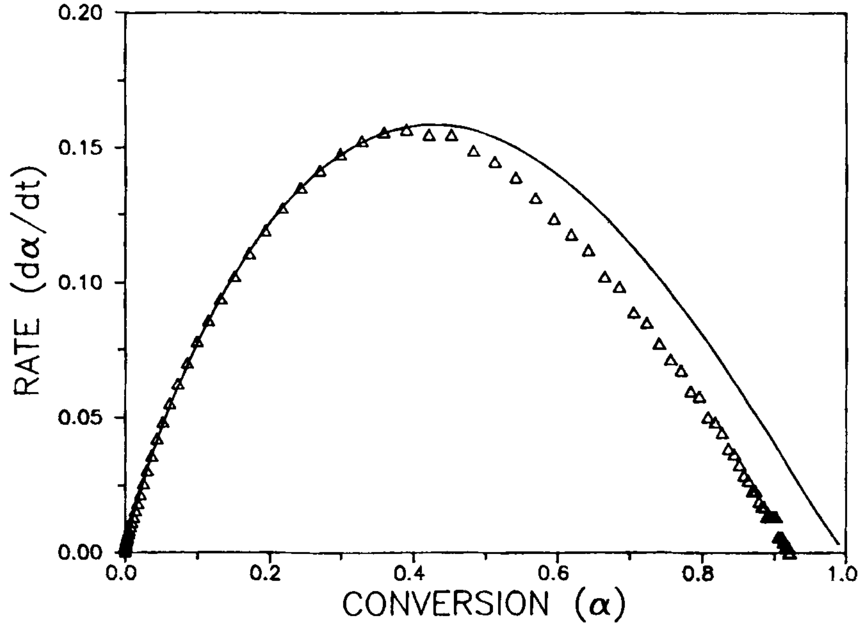


FIG. 4. Plot of DSC experimental data of Sample 2 together with the theoretical fit of Eq. (4): (△) DSC data, (—) curve based on Eq. (4).

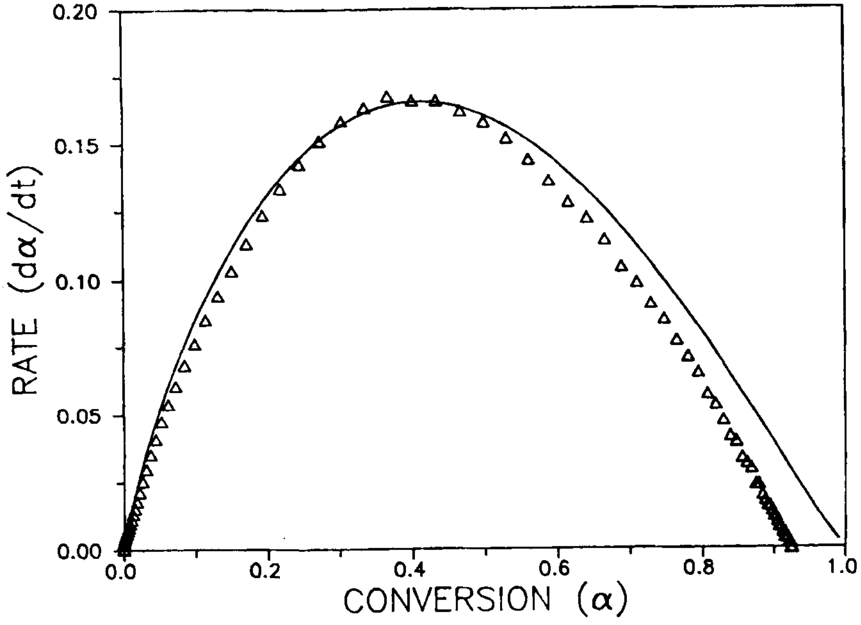


FIG. 5. DSC experimental data of Sample 3 together with the theoretical fit of Eq. (4): (△) DSC data, (—) curve based on Eq. (4).

TABLE 2. The Curing Kinetic Parameters of Kamal's Model Eq. (4)

Sample	K_1	K_2	m	n
1	0.001192	0.83	0.90	1.10
2	0.000815	0.64	0.85	1.15
3	0.000311	0.62	0.82	1.18

For a mixture of UPE and styrene, the system may be pictured as many coiled polyester chains swelled in styrene monomer. The coiled size depends on molecular chain length, chain stiffness, concentration of polyester chains, and compatibility of polyester with styrene monomer. Chemical reaction between the vinyl groups originating from the ester and also from styrene may occur inside, outside, and at the surface of the coils. Before the reaction the system contains styrene monomers, unsaturated polyester molecules, and inhibitors. When the reaction starts, the initiators decompose and form free radicals which trigger polymerization. At the very beginning of the reaction, most of the free radicals formed from the initiators are immediately consumed by the inhibitors. After the inhibitors are all consumed by the initiators, the initiators continuously decompose to create free radials which link adjacent unsaturated polyesters and form primary polymer chains through connecting styrene monomers by both inter- and intramolecular reactions. The intermolecular crosslinking reaction occurs at the coil surface, and this increases the polymer coil size. Inside the coil the reaction proceeds through intramolecular cyclization which does not increase the molecular weight. Instead the polyester coils may tighten up and form the so-called "microgel" structure [24–28]. Many pendant vinyl groups may be buried inside the microgels, which reduces the effective concentration of polyester vinyls for further intermolecular crosslinking reactions [29–36]. Thus, the curing reaction rate is reduced by the retarding effect of intramolecular cyclization. The curing reaction microgel mechanism of UPE can be pictured as shown in Fig. 6.

The compatibility of ingredients in thickening is another factor influencing the rate of curing. The polycaprolactone-diol is an aliphatic polyester; the unsaturated polyester is an aromatic polyester. The compatibility between aliphatic polyester and styrene monomer is smaller than that between aromatic polyester and styrene monomer. Due to the unfavorable compatibility of aliphatic polyester with styrene monomer, the UPE chain molecule tends to shrink when it is thickened with long PE-di-OL chain molecule. The UPE chain, after thickening with long aliphatic polyester, tends to form spherical-type structures due to the intramolecular crosslinking among the pendant C=C bonds of the saturated polyester molecules. Thus, the curing reaction rate at lower conversion of thickened UPE decreases with the chain length of saturated aliphatic polyester-diol.

With the use of GPC to investigate microgel formation during curing of UPE, 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, a shorter retention time corresponds to a larger particle size. For unthickened UPE Sample 1 with a 30% by weight of styrene monomer content, as shown in the lower

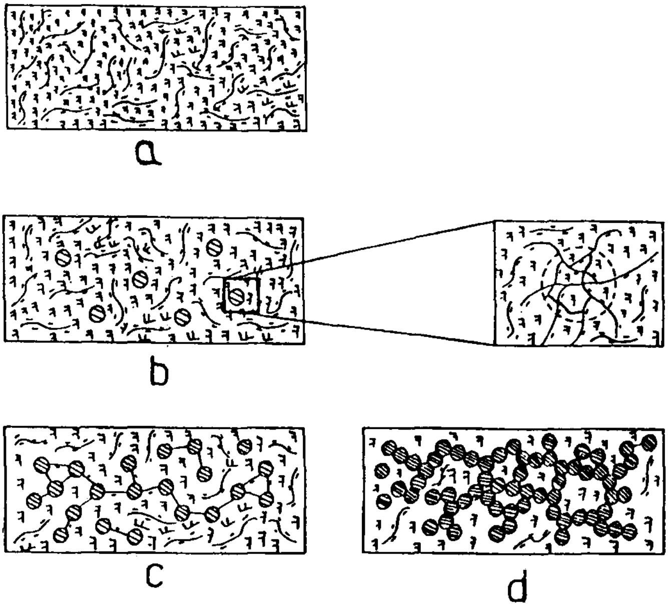


FIG. 6. The curing mechanism of unsaturated polyester. (a) The beginning of the curing reaction. (b) Microgel formation due to intramolecular crosslinking reaction. (c) Intermolecular crosslinking reaction between the microgel particles. (d) Gelation.

part of Fig. 7, the particle size of the polymer chain increases as the curing reaction proceeds. However, at a curing time of 5 minutes, the particle size of the microgel is smaller than that from a 3-minutes curing. For UPE thickened with PE-di-OL-530, as seen from the middle part in Fig. 7, the microgel particles shrink at a curing time of 5 minutes. The microgel particles of unsaturated polyester thickened with PE-di-OL-1250, as shown in the upper part of Fig. 7, shrink at a curing time of 3 minutes. The shrinkage of the microgel particles is due to the intramolecular crosslinking reactions as indicated in the (b) stage of Fig. 6. After the (b)-stage curing reaction, an intermolecular reaction between the microgel particles commences and the microgel particle size increases as the curing reaction proceeds. This behavior is shown in the (c) stage of Fig. 6. Thus, the results of GPC measurements support the intermolecular and intramolecular (cyclization) crosslinking microgelation mechanism of the microgelation of UPE thickened with saturated aliphatic polyester during curing.

Yang and Lee [36] studied the curing kinetics of styrene/UPE (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 has a slower reaction rate at lower conversion. Evidently UPE chains with a higher degree of unsaturation (with a higher aliphatic fumaric acid concentration and a lower aromatic isophthalic acid concentration) tend to form tighter coils in styrene, which facilitates intramolecular cyclizations, thereby producing highly crosslinked microgels. Many pendant vinyl groups are buried in the microgel particles, which reduces the effective vinyl concentration and therefore slows down the

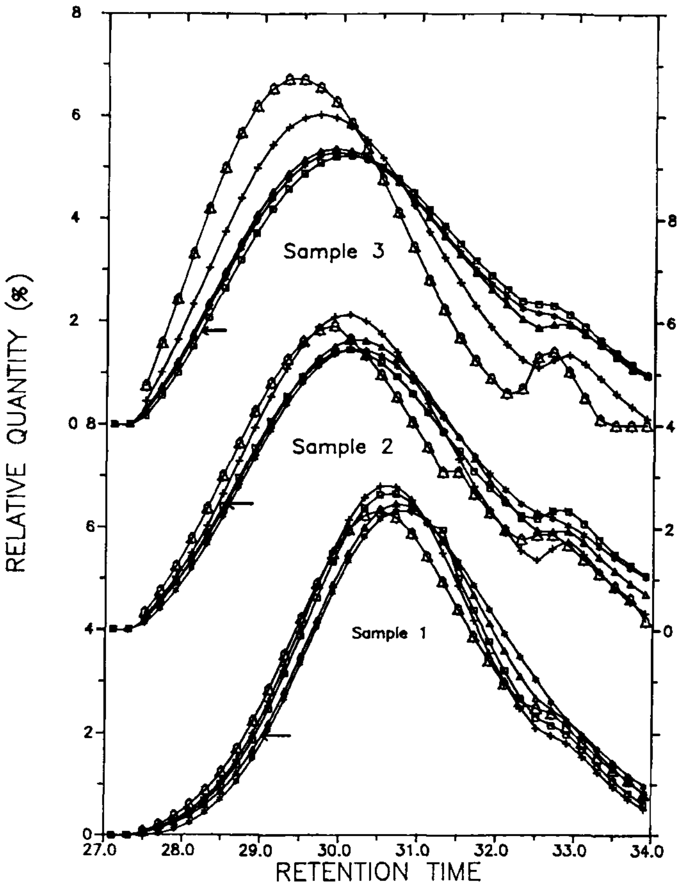


FIG. 7. The GPC curves of Samples 1-3 cured at 110°C with various curing times. Curing times in minutes: (*) 0, (□) 3, (△) 5, (+) 7, (○) 9. The arrows indicate the microgel shrinkage due to the intramolecular crosslinking reactions.

overall reaction rate. This phenomenon is consistent with the results of our present work.

CONCLUSIONS

The formation of microgel particles is the key feature of styrene-unsaturated polyester copolymerization. As an unsaturated polyester of aromatic origin is thickened with a saturated aliphatic polyester-diol, the compatibility between the polyester system and the styrene monomer decreases. The longer the saturated aliphatic polyester chain length, the worse is the compatibility, and this favors an intramolecular reaction during curing. Because intramolecular cyclization enhances microgel formation, many pendant polyester C=C bonds may be trapped in the compact microgels and become a permanent residue which causes the delay of gelation inside the system.

ACKNOWLEDGMENT

The authors would like to thank the National Science Foundation of the Republic of China for research support through Grant NSC-82-0405-E-155.

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Received April 23, 1993
Revision received July 16, 1993