

Microgelation of Unsaturated Polyester Resins by Static and Dynamic Light Scattering

J. S. CHEN, T. L. YU

Department of Chemical Engineering, Yuan Ze Institute of Technology, Nei-Li, Taoyuan, Taiwan 32026

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ABSTRACT: The microgelation phenomenon during the curing of unsaturated polyester resin was investigated by both static and dynamic light scattering before gelation. The results of static light scattering revealed that the polymer molecular weight increased with degree of curing. The second virial coefficient, A_2 , decreased slowly in the initial stage of curing and decreased dramatically at a conversion around $\alpha \sim 8.7\%$, indicating a drastic decrease of compatibility between the polyesters and styrene. Two modes of the size distribution of the microgel particles during curing were observed by dynamic light scattering. The small particles consist of primary unsaturated polyester molecules. The large ones consist of microgel particles formed by linking adjacent polyester molecules. The sizes of the microgel particles increased in the initial stage of curing, then decreased slightly at a conversion of $\alpha \sim 8.7\%$, which was due to the intramolecular crosslink reaction of the microgel particles. The experimental results revealed that the compatibility between polyesters and the styrene monomer became worse as the intramolecular crosslinking reaction inside the microgel particles caused a tight packing of the micro-gel molecules. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 871–878, 1998

Key words: unsaturated polyester; static light scattering; dynamic light scattering; DSC; microgel

INTRODUCTION

Unsaturated polyester (UPE) resins are one of the most widely used thermoset polymers. In recent years, UPE resins have received increasing industrial attention for producing fiber-reinforced composites because of their good mechanical properties and relatively low price. With the addition of fillers, low-profile additives, and glass fibers, the resins are processed to form sheet-molding compounds (SMC), bulk-molding compounds (BMC), resin transfer-molding compounds (RTM), etc.

The curing reaction of UPE resins is a free-radical crosslinking copolymerization between the styrene C=C double bond and the UPE C=C double bonds. An important feature of this copolymerization is the formation of a heterogeneous structure through intramolecular reactions. Several researchers have studied the crosslinking reaction mechanism of free-radical copolymerization of monovinyl and multivinyl components. Horie and coworkers^{1,2} studied the copolymerization of UPE with styrene. Their experimental results revealed that the network formation from highly unsaturated polyesters led to an earlier onset of gelation and a decrease of the final conversion. Horie et al. attributed this phenomenon to the immobility of chain segments in a crosslink network and stated that diffusion-controlled termination extended over the whole range of conversion in the curing reaction. Horie et al.³ also inves-

Correspondence to: T. L. Yu.

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tigated the crosslinking copolymerization of methyl methacrylate with dimethacrylate in the bulk and in toluene by differential scanning calorimetry (DSC). They noticed that the polymerization proceeded heterogeneously, providing an opaque solution. Lee and coworkers observed similar results in SMC from UPE resins,⁴⁻⁷ polyurethane/UPE interpenetrating polymer networks,⁸ and UPE/styrene systems.^{9,10} They found that the conversions of UPE resins at the gel point were much higher than those predicted by the classical Flory-Stockmayer theory.¹¹ They attributed the reason for this discrepancy to the existence of intramolecular cyclization reactions between the UPE and styrene. The competition between intermolecular (network formation) and intramolecular (cyclization) crosslinking reactions caused the delay in gelation. Hild and Okasha^{12,13} attributed the delay of gelation to the reduction of activity of poly(ester vinyl)s as the reaction proceeds. As a result, the maximum network density could not be reached. Minnema and Staverman¹⁴ attributed this phenomenon to the shielding of pendant vinyl groups by intramolecular crosslinking.

The reaction of UPEs with styrene can be classified into four types¹³: (1) intermolecular crosslinking of unsaturated polyesters with or without linking through styrene monomers; (2) intramolecular crosslinking of UPE with or without linking through styrene monomers; (3) branching on the polyester molecules by styrene; and (4) free styrene homopolymerization. The curing reaction with microgel formation of UPEs with styrene can be pictured as shown in Figure 1. Before the curing reaction, we may picture the mixture of UPEs and styrene as many coiled polyester chains swollen in styrene. The size of UPE coils depends on the chain length, chain stiffness, degree of unsaturation in the polymer chains, and compatibility of the UPE with styrene [Fig. 1(a)]. When the reaction starts, the initiator decomposes and forms free radicals to initiate the polymerization which links the adjacent UPEs and forms polymer chains through connecting styrene monomers by both inter- and intramolecular reactions. At the coil surface, intermolecular crosslinking reactions take place which increase the coil size. Inside the coils, the reaction through intramolecular cyclization reactions tighten the polymer and form the so-called microgel structure [Fig. 1(b)].¹³⁻¹⁸ As the polymerization proceeds, the concentration of the microgels increases continuously, leading to intermolecular crosslinking reactions among the

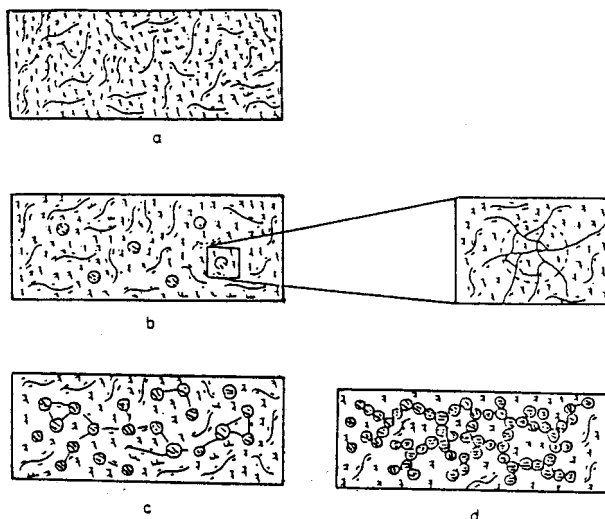


Figure 1 Curing mechanism of unsaturated polyesters: (a) beginning of the curing reaction; (b) microgel formation due to the intramolecular crosslinking reaction; (c) intermolecular crosslinking reaction between the microgel particles; (d) macrogelation.

microgel particles [Fig. 1(c)], and macrogelation in the curing system [Fig. 1(d)].

The study of the variation of the polyester coil particle size during the early stage of curing of the UPE/styrene system was first investigated using dynamic light scattering (DLS) by Hsu and Lee.¹⁹ Their results showed two modes of particle-size distribution: One mode is the distribution of the primary UPE molecules. The other mode is the distribution of reacted UPE coils which were formed by linking adjacent UPE molecules through free-radical polymerization with styrene monomers. Chiu and Lee²⁰ also showed two different-size particle groups formed from the very beginning of the reaction for the homopolymerization of ethylene glycol dimethacrylate (EGDMA). However, the results of Lee et al. did not show the phenomenon of shrinkage of reacted polymer coils which was due to the intramolecular crosslinking reactions. In recent work, we studied the curing behavior of UPE with styrene during the early stage of curing by gel permeation chromatography (GPC)²¹ and DLS.¹⁵ Our DLS results showed two modes of particle-size distribution during the early stage of curing. These experimental results also showed the shrinkage of reacted UPE coils before gelation, indicating the formation of microgel particles due to intramolecular cyclization reactions as shown in Figure 1(b). In the present work, the variation of polyester coil size, depolarization ratio (ρ_v), molecular weight

(M_w), and second virial coefficient (A_2) of the UPE/styrene system in the early stage of curing were investigated by both static light scattering (SLS) and DLS. ρ_v is an indicator of the shape and anisotropy of the polymer in solvent, and A_2 , an indicator of the compatibility between solvent and polymer. By measuring ρ_v and A_2 , we were able to follow the change of the shape and anisotropy of the UPE molecules in the styrene monomer and the compatibility of UPE with styrene during curing.

EXPERIMENTAL

Materials

UPE

UPE was prepared in a nitrogen atmosphere by the conventional condensation method from isophthalic acid (IPA), fumaric acid (FA), and 1,2-propanediol (PG). The reaction temperature was increased by a stepwise control as follows: 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 to 100°C and mixed with styrene in a weight ratio 70/30 of polyesters to styrene containing 0.1 wt % of a hydroquinone inhibitor. The resin was then cooled to room temperature immediately. The mol ratio in the final composition of the solid polyesters 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 (M_n) of the polyesters determined by GPC was found to be 1800, with a polydispersity $M_w/M_n = 4.3$ at 25°C. Tetrahydrofuran (THF) was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co., Milwaukee, WI) were used in the linear method of calibration.

Initiator

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

Styrene

The styrene monomer (Aldrich Chemical Co.) with a purity of 99% was purified by distillation several times very carefully before mixing with unsaturated polyesters.

Instrumentation

Differential Scanning Calorimeter (DSC)

A DuPont 910 DSC was applied to study the exotherms of curing. The calorimeter was previously calibrated with indium standards. Hermetic pans were used to minimize losses of volatile materials (such as the styrene monomer) during heating of the sample in the DSC cell. The size of sample was in the range from 6 to 10 mg. A small sample size was required to achieve an isothermal operation during curing.

Dynamic Light Scattering (DLS)

A Brookhaven goniometer with a BI2030AT correlator was used to investigate the variation of the polyester particle size during the curing reaction. DLS measurements were made at a scattering angle of 90° and at a temperature of $25 \pm 0.5^\circ\text{C}$. The laser was a 10 mW He—Ne (633 nm) Spectra Physics model. The Brookhaven BI2030AT is a multitaup sample time correlator with a variable sampling time increment ranging from 1 μs to 1 s. The available 128 real-time data channels are split into four groups. Each group consists of 32 equally spaced time intervals. The spacing in the first group is the normal sample time. Successive groups have sample times equal to normal $\times 2^n$, where $n = 0, 1, 2, \dots, 8$. The only restriction is that successive n 's must be equal to or greater than the previous n . The particle-size distribution was calculated from the DLS correlation functions using the Exponential Sampling software provided by Brookhaven Co.

Static Light Scattering (SLS)

The same instrument for the DLS measurements was used to carry out the SLS measurements. Depolarization ratios ρ_v , second virial coefficients A_2 , and molecular weights M_w of the partially cured resins during the early stage of curing were obtained from these measurements.

Differential Index of Refraction

A C. N. Wood (Newton, PA, USA) RF600 differential refractometer was used to determine the differential refractive index increment dn/dC , which is also referred to as the specific increment, ν . This was calibrated using aqueous NaCl solutions.²² All the dn/dC data were measured at both 436 and 546 nm. The value at 633 nm was determined by linear interpolation.

Sample Preparation

In preparing the partially cured UPE resins, the resins were mixed with 1 wt % of the *tert*-butyl peroxybenzoate initiator. The curing reaction proceeded at 100°C in a closed container and was stopped at 0-, 4-, 7-, 12-, 14-, and 20-min time intervals by cooling the samples to a temperature of 5°C.

Degree of Conversion of Partially Cured Resins

The degree of curing of each partially cured sample was determined by nonisothermal DSC measurements from room temperature to 250°C with a heating rate of 10°C/min. The conversion α was calculated from eq. (1):

$$\alpha(t) = 1 - Q(t)/Q(t = 0) \quad (1)$$

where $Q(t)$ is the heat released from the nonisothermal DSC scan for a partially cured resin with a curing time t , and $Q(t = 0)$, the heat released from the nonisothermal DSC scan for an uncured resin, that is, a resin with a curing time $t = 0$.

Light-scattering Samples

The light-scattering samples were prepared by dissolving the partially cured resins into styrene and diluting to concentrations of 2, 4, 6, and 8 mg/mL. All the solutions were filtered through a 0.5- μm FHP 02500 Millipore filter before the light-scattering measurements. These solutions

were used for the refractive index increment and SLS measurements. The solutions with a concentration of 2 mg/mL were used for the DLS measurements.

RESULTS AND DISCUSSION

For studying the isothermal curing kinetics of thermosetting resins by DSC, 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 , by²³

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \frac{dQ}{dt} \quad (2)$$

By integrating eq. (2) with the time, one obtains the relative degree of cure, α :

$$\alpha(t) = \frac{1}{Q_{\text{tot}}} \int_0^t \left[\frac{dQ}{dt} \right]_T dt \quad (3)$$

where the subscript T indicates an isothermal curing reaction. In eqs. (2) and (3), the total heat of the curing reaction (Q_{tot}) is given by

$$Q_{\text{tot}} = Q_t + Q_r \quad (4)$$

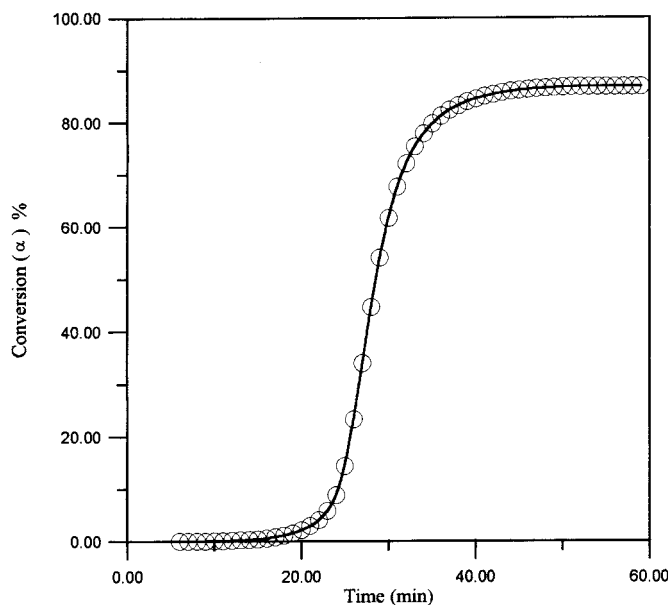


Figure 2 Isothermal DSC curing scan at 100°C.

Table I Differential Index of Refraction Depolarization Ratio and Static Light-scattering Data

Conversion (%)	dn/dc ($\times 10^2$ mL g $^{-1}$)	ρ_v	M_w ($\times 10^{-4}$ g mol $^{-1}$)	A_2 ($\times 10^3$ mL mol g $^{-2}$)
0.0	1.462	0.20	1.28	4.56
4.30	1.506	0.24	4.65	3.70
6.51	1.545	0.27	6.48	2.87
8.12	1.518	0.13	8.27	2.65
8.74	1.557	0.22	9.42	1.21
13.70	1.659	0.36	12.10	0.55

where Q_i is the heat generated during the isothermal DSC runs at 100°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 100°C.

The isothermal curing profile for the UPE/styrene system at 100°C obtained from the DSC measurement is shown in Figure 2. The result of the DSC measurement indicated an inflection around 25 min which corresponded to a conversion $\alpha \sim 15\%$. The inflection point of a DSC curing curve is close to the gel point of the curing system. Thus, all the static and dynamic light-scattering measurements were carried out at conversions with $\alpha < 15\%$.

The intensity of the scattered light from a polymer solution is given by the equation^{24,25}

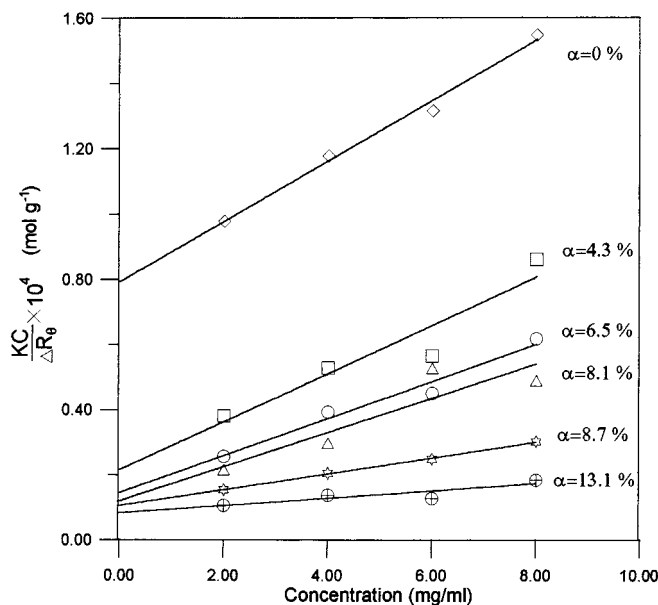
$$\frac{KC}{\Delta R_\theta} = \frac{1}{M_w} + 2A_2C + \dots \quad (5)$$

where ΔR_θ is the excess Rayleigh ratio of the solution at the scattering angle θ ; A_2 , the second virial coefficient; and C , the polymer concentration. For vertically polarized incident radiation, the optical constant, K , is given by

$$K = \frac{4\pi^2 n_0^2 (dn/dC)^2}{\lambda^4 N_A} \quad (6)$$

where n_0 is the index of refraction of the solvent, that is, styrene; N_A , Avogadro's number; λ , the wavelength of the incident radiation *in vacuo*; and dn/dC , the differential index of refraction. Debye plots were constructed to extrapolate to zero concentration in eq. (5).

The dn/dc values of the partially cured resins at various degrees of conversion are listed in Table I. For many large, flexible-chain polymers, depolarization effects are negligible, and as a result,


Figure 3 Debye plot of partially cured resins at a scattering angle $\theta = 90^\circ$.

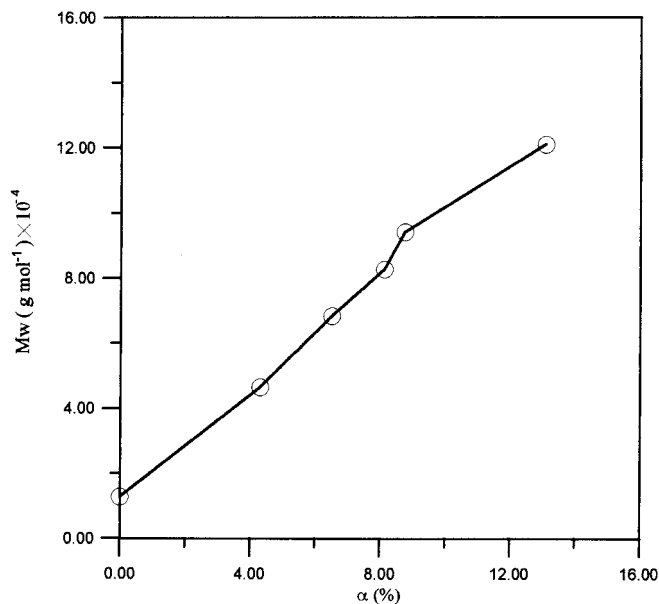


Figure 4 Variation of M_w of partially cured UPE with degree of conversion α .

no polarization corrections are necessary. M_w and A_2 are correct as calculated from eq. (5). For optically anisotropic molecules, the polarization of the scattered light has components both parallel and perpendicular to the incident polarization. Historically, the anisotropic part of the scattering was expressed using depolarization ratios which are defined as follows:

$$\rho_v = H_v(90^\circ)/V_v(90^\circ) \quad (7)$$

where the subscript v indicates measurements involving a vertically polarized incident laser light; H , the horizontally scattered light; and V , the vertically scattered light. For partially cured UPE with short polymer chains, depolarization effects are not negligible. The ρ_v values of the partially cured resins at a concentration of 2 mg/L are also listed in Table I. In the SLS measurements of the partially cured UPE solutions with linearly polarized incident light perpendicular to the scat-

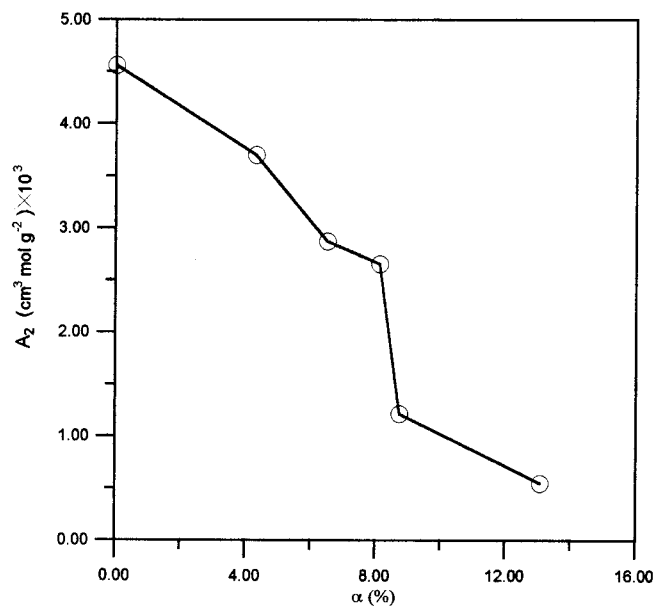


Figure 5 Variation of A_2 of partially cured UPEs and styrene with degree of conversion α .

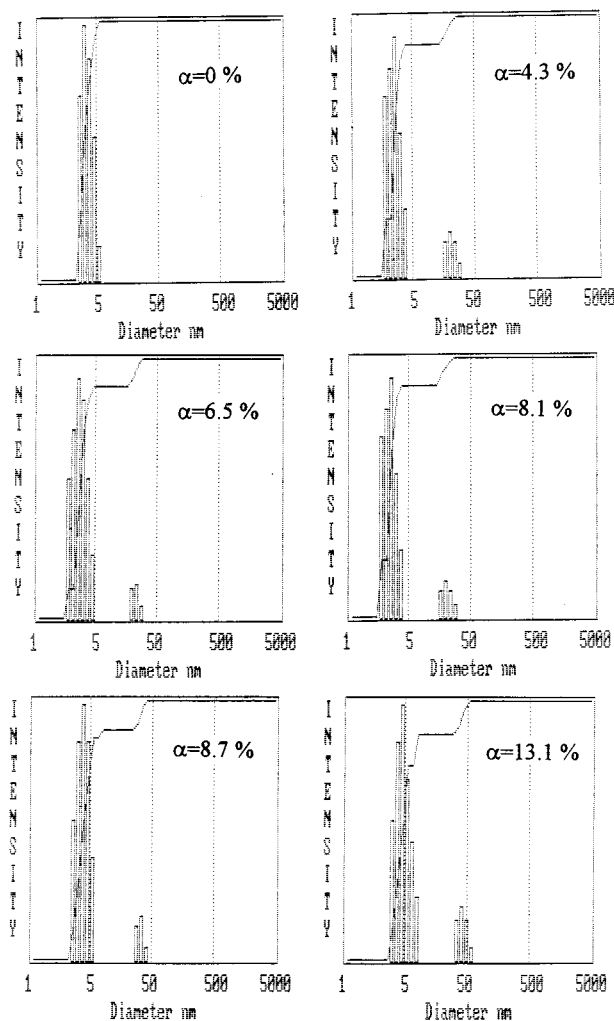


Figure 6 DLS particle-size distributions of partially cured UPE resins at various degrees of conversion α .

tering plane and no analyzer, M_w and A_2 calculated from eq. (5) should be considered apparent, but not true values. Polarization corrections for these polymers are as follows^{24,25}:

$$M_{w,app} = M_w [(3 + 3\rho_v)/(3 - 4\rho_v)] \quad (8)$$

$$A_{2,app} = A_2 [(3 + 3\rho_v)/(3 - 4\rho_v)] \quad (9)$$

The Debye plots of the partially cured resins at a scattering $\theta = 90^\circ$ are shown in Figure 3. In Figure 3, all the values of ΔR_θ were corrected by timing the raw data with the depolarization factor, that is, $(3 + 3\rho_v)/(3 - 4\rho_v)$. Thus, the M_w of the partially cured polymer and the A_2 of the partially cured solutions were obtained from the intercepts and slopes, respectively, from the plots of Figure 3 by using eq. (5). The variation of M_w

and A_2 with degree of conversion α are shown in Figures 4 and 5, respectively. The experimental data revealed that the M_w of partially cured resins increased with conversion α , while A_2 decreased slowly with conversion α in the beginning of the curing reaction, then decreased dramatically as the degree of conversion α increased from ~ 8.1 to 8.7%.

The DLS measurements were also carried out at a scattering angle $\theta = 90^\circ$ for partially cured resins with a concentration of 2 mg/mL. The DLS distribution curves of the microgel particles are shown in Figure 6. All the distribution curves have two modes of particle-size distribution. The small-size mode corresponds to the primary UPE coils. The large-size mode corresponds to the reacted UPE coils which were formed by linking adjacent polyesters through styrene monomers by free-radical polymerization. The average particle sizes and volume fractions for these two modes of size distribution of partially cured resins at various degrees of curing are shown in Table II, in which D_1 and D_2 are the average particle sizes of primary UPE and reacted UPE coils, respectively, and V_1 and V_2 are the volume fractions of primary UPE and reacted UPE coils, respectively. As shown in Table II, both the size D_2 and volume fraction V_2 of reacted UPE coils increased with conversion in the beginning of the curing reaction and slightly decreased at a conversion $\alpha \sim 8.1\%$. After conversion $\alpha > 8.1\%$, both D_2 and V_2 increased with the degree of conversion.

Inspecting the dn/dc and ρ_v values shown in Table I, a similar trend of dn/dc and ρ_v as that of D_2 was also found. Both dn/dc and ρ_v increased with the degree of conversion in the beginning of curing and then decreased at a conversion of $\alpha \sim 8.1\%$. After the conversion α was higher than 8.7%, both dn/dc and ρ_v increased with the degree of conversion. The depolarization ratio is a function of the particle shape and anisotropy in the solvent. This permits one to follow the change in polymer shape and anisotropy.^{26,27} Obviously, the

Table II Dynamic Light-scattering Data

Conversion (%)	D_1 (nm)	D_2 (nm)	V_1 (%)	V_2 (%)
0.0	4.0	0.0	100	0.0
4.30	3.7	28	89	11
6.51	3.7	31	89	11
8.12	3.7	28	90	10
8.74	4.4	43	88	12
13.70	4.8	56	87	13

more anisometric the shape of a particle, the larger the optical anisotropy can be expected, and, indeed, an appreciable depolarization of the scattered light, due to the solute, was observed as rodlike particles.^{26,27} On the other hand, with polymers assuming in solution the conformation of some sort of coils, the depolarization of scattered light is quite low.^{26,27} The low MW UPE was synthesized from aromatic isophthalic acid, aliphatic fumaric acid, and 1,2-propanediol; thus, the UPE molecules behaved more or less like rigid rods in the styrene monomer at lower conversions. The present experimental data showed that before gelation both D_2 and ρ_v had the lowest value as the degree of conversion approached to $\alpha \sim 8.1\%$. The lower value of ρ_v at a conversion $\alpha \sim 8.1\%$ suggested the formation of fewer anisometric UPE microgels due to the intramolecular crosslinking reactions inside the UPE coils as shown in Figure 1(b). As mentioned before, that the second virial coefficient A_2 decreased dramatically as the degree of conversion α increased from ~ 8.1 to $\sim 8.7\%$ suggested that intermolecular crosslinking reactions among the microgel particles caused a strong decrease in the compatibility between the UPE molecules and the styrene monomer [Fig. 1(c)].

CONCLUSIONS

By following the variation of the UPE particle size (D_2) and the depolarization ratio (ρ_v) during curing, we demonstrated the formation of microgels due to intramolecular crosslinking reactions inside the UPE coils in the early stage of curing. The variation of A_2 with the degree of conversion also revealed a strong decrease in the compatibility between the partially cured UPE and the styrene monomer as intermolecular crosslinking reactions among the microgel particles proceeded. Combining the SLS and DLS results, we clearly showed the microgelation curing mechanism of the UPE/styrene system before gelation.

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