Microgelation of Unsaturated Polyester Resins in the Presence of Poly(vinyl acetate) by Static and Dynamic Light Scattering

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ABSTRACT: The partially cured unsaturated polyester (UPE)/styrene resins with various degrees of conversion lower than gel conversion blended with PVAc and 2-fluorotoluene solvent were investigated using both static and dynamic light scattering (SLS and DLS). The solvent (i.e., 2-fluorotoluene) is isorefractive with PVAc; thus, one *sees* only primary and partially cured UPEs in light-scattering experiments. DLS was used to follow the variations of primary UPE and UPE microgel particle sizes, and SLS was used to follow the variations of UPE molecular weight, second virial coefficient (A_2), anisosymmetry (ρ_v), and differential index refraction (dn/dC) with degree of UPE conversion and PVAc concentration. The experimental data showed that, at a fixed degree of UPE/styrene conversion, increasing PVAc concentration in the UPE/styrene system caused decreases in dn/dC, A_2, ρ_v, and particle sizes of UPE microgels. These results suggest that mixing PVAc into UPE/styrene resins causes an increase in the compactness of UPE coils and favors intramolecular UPE/styrene cyclization in the early stage of curing. Thus A_2, ρ_v, and particle sizes of microgels decreased with increasing PVAc concentration. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1439–1449, 2001

Key words: unsaturated polyester; poly(vinyl acetate); static light scattering; dynamic light scattering; differential scanning calorimetry

INTRODUCTION

Low-profile additives (LPAs) are used in unsaturated polyester (UPE) resin formulations to improve the surface of molding compounds, compensating for resin shrinkage. Poly(vinyl acetate) (PVAc) is widely used as an LPA, particularly in sheet molding compound (SMC) and bulk molding compound (BMC) formulations. It is generally agreed that a major factor for the low-profile behavior is the result of the formation of a two-phase structure between LPA and UPE resins.[1–5]

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. Both inter- and intramolecular crosslinking reactions may happen as copolymerization proceeds. The intermolecular crosslinking reaction causes an increase in polyester coil sizes and favors earlier gelation, whereas the intramolecular crosslinking reaction leads to a reduction of the polyester coil size, thus retarding gelation. The reaction mechanism with microgel formation of UPE with styrene can be pictured as shown in Figure 1.[4] Before curing, we may picture the mixture of UPEs and styrene as many coiled polyes-
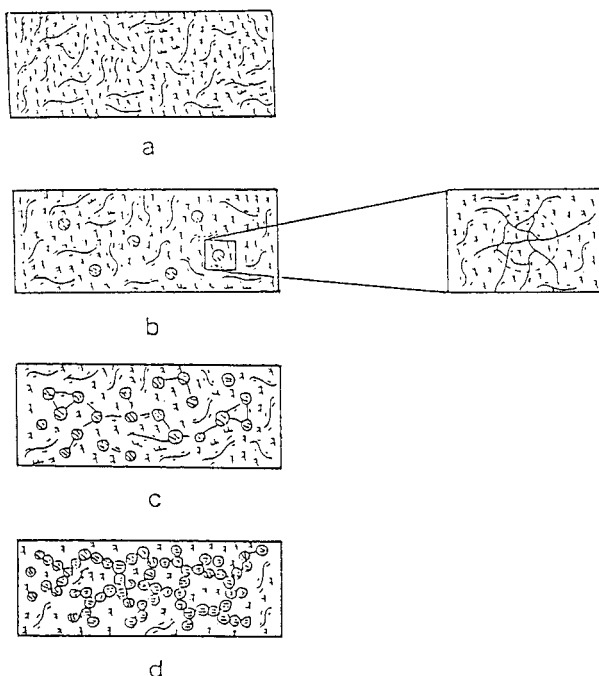
Figure 1 The curing mechanism of unsaturated polyesters. (a) Beginning of the curing reaction; (b) microgel formation resulting from intramolecular crosslinking reaction; (c) intermolecular crosslinking reaction between the microgel particles; (d) macrogelation.

ter chains swollen in styrene. The size of UPE coils depends on 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 tightens the polymer and forms the so-called "micro-gel" structure [Fig. 1(b)].[6–11] As the polymerization proceeds, the concentration of the microgels increases continuously, leading not only to intermolecular crosslinking reactions among the microgel particles [Fig. 1(c)] but also to macrogelation in the curing system [Fig. 1(d)]. The microgel formation mechanism of the UPE/styrene curing reaction was previously confirmed by light-scattering[11–15] and gel permeation chromatography (GPC)[16,17] measurements.

In the presence of LPA, the reactions between styrene and polyester vinyls are the same as

those in a pure UPE/styrene system, although the course of chain growth and network formation might be different from those of a pure UPE/styrene system. The curing structure of UPE may be pictured as consisting of many coiled UPE chains swelled in the mixture of LPA and styrene monomer. The sizes of UPE coils depend not only on molecular chain length, chain stiffness, and concentration of UPE, but also on concentration of LPA and compatibility of UPE with LPA. The effects of LPAs on the curing kinetics of styrene/UPE were previously reported.[15,17–21] Kubota[18] found a very small effect of an LPA (cellulose acetate butyrate) on the curing kinetics. Lem and Han[19,20] reported lower reaction rates and a final degree of curing in using an LPA. A decrease in the final degree of curing of UPE/styrene, resulting from the presence of LPA, was also reported by Lee and coworkers.[21] Williams and coworkers[22] reported that, when the ratio of styrene to UPE unsaturation was kept constant, PVAc did not have any effect on curing kinetics. However, the lower compatibility of LPA with UPE caused a microgel formation at a lower degree of conversion and thus led to a higher gel conversion and a lower final conversion.[15,17]

Recently, substantial progress has been made in understanding the dynamic light scattering (DLS) and static light scattering (SLS) from ternary mixtures made of two polymers and a solvent. The solvents were chosen to mask one of these two polymers,[15,23–27] hence one "sees" only one polymer, thus making data interpretation simpler. It is known that increasing the LPA concentration in UPE/styrene resins facilitated the UPEs to form coils in the styrene monomer and to undergo an intramolecular crosslinking reaction, which caused a delay of gelation.[15,17–21] In this study, the partially cured UPE resins, after evacuating of residual styrene monomer, were blended with PVAc and diluted with 2-fluorotoluene, which was isorefractive with PVAc; thus, PVAc was masked and one "sees" only primary and partially cured UPEs. The variations of UPE coil size, depolarization ratio (ρ_v), molecular weight (M_w), and second virial coefficient (A_2) with UPE conversion in different PVAc concentrations were investigated using SLS and DLS. ρ_v is an indicator of the shape and anisotropy of polymer in solvent and A_2 is an indicator of the compatibility between UPE and the PVAc/solvent system. By measuring ρ_v and A_2, we were able to follow the changes of shape and anisotropy of UPE molecules and the compatibility of UPE with

PVAc versus UPE conversion. Based on the experimental results, the effect of PVAc on the conformation of UPE microgel particles was discussed.

EXPERIMENTAL

Materials

UPE resin was purchased from Eternal Chemical Co. (Taiwan). The weight ratio of unsaturated polyester to styrene of the resin was around 67/33. The solid polyester, determined from NMR in our lab, composed of isophthalic acid/fumaric acid/1,2-propanediol $= 1.0/1.7/3.3$ (molar ratio). It had a molar ratio of OH/COOH $= 1.22$ and an acid value of 31.5 mg KOH/g. The number-average molecular weight (M_n) of the polyester determined by GPC at 25°C was found to be 1700, with a polydispersity $M_w/M_n = 4.0$. Tetrahydrofuran (THF) was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co., Milwaukee, WI) were used in the linear calibration method.

The peroxide initiator was *tert*-butyl peroxybenzoate (Akzo Chemie Co., Deventer, Netherlands) with a purity of 98% and an active oxygen content of 8.07%. Styrene monomer (Aldrich) with a purity of 99% was purified by very careful distillation several times before mixing with UPE. Poly(vinyl acetate) (Aldrich) with $M_n = 8.6 \times 10^4$ and $M_w/M_n = 2.45$ was used without further purification. 2-Fluorotoluene, an isorefractive solvent of PVAc (Tokyo Kasei Kogyo Co., Japan), was used without further purification in the light-scattering study.

Instrumentation

Differential Scanning Calorimeter (DSC)

A Du Pont 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 styrene monomer) during heating of sample in the DSC cell. The size of sample was in the range from about 6 to 10 mg. A small sample size was required to achieve isothermal operation during curing.

Dynamic Light Scattering (DLS)

A Brookhaven goniometer (Brookhaven Instruments, Holtsville, NY) with 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 ± 0.5°C. The laser was a 10-mW He-Ne (633 nm) Spectra Physics model (Mountain View, CA). The Brookhaven BI2030AT is a multi-τ 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 $n = 0, 1, 2,. . ., 8$. The only restriction is that successive values of n must be equal to or greater than the previous n. The particle size distribution was calculated from DLS correlation functions by using the Exponential Sampling software (Brookhaven Instruments).

Static Light Scattering (SLS)

The same instrument used for DLS measurements was used to carry out SLS measurements. ρ_v, A_2, and 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) 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.[28] All of the dn/dC data were measured at both 436 and 546 nm. The value at 633 nm was determined by linear interpolation.

Intrinsic Viscosity

Intrinsic viscosity of PVAc in 2-fluorotoluene was determined on dilute solutions at 25°C by a Ubbelohde viscometer with a flow time of about 100 s for fluorotoluene. $[\eta] = 0.735$ dL/g was obtained. Thus the overlap concentration $C^* \sim 1/[\eta]$,[29] of PVAc in fluorotoluene was around 1.36 wt %.

Sample Preparation

In preparing the partially cured UPE/styrene resins, the resins were mixed with 1 wt % of *tert*-butyl peroxybenzoate initiator. The curing reaction proceeded at 100°C in a closed container, and

was stopped at intervals of 0, 4, 7, 12, 14, 20 min by cooling the samples to a temperature of 5°C.

Degree of Conversion of Partially Cured Resins

The degree of conversion 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).[30]

$$\alpha(t) = 1 - H(t)/H(t = 0) \qquad (1)$$

where $H(t)$ is the heat released from a nonisothermal DSC scan for a partially cured resin with a curing time t, and $H(t = 0)$ is the heat released from a nonisothermal DSC scan for an uncured resin, that is, resin with a curing time $t = 0$. Figure 2(a,b) shows the nonisothermal DSC scanning curves for styrene/UPE cured at 100°C with curing times of 0 and 34 min, respectively; the corresponding degrees of conversion calculated from eq. (1) are 0.0 and 9.2%, respectively.

Light-Scattering Samples

Partially cured styrene/UPE resins with $\alpha = 0.0$, 1.65, 3.02, 5.44, 7.55, and 9.20 were used to prepare light-scattering samples. Three solutions of partially cured UPE/2-fluorotoluene/PVAc systems were prepared. The first two systems had PVAc concentrations of 0.0 and 0.5 wt %, which were below the overlap concentration of PVAc. The other system had a PVAc concentration of 5.0 wt %, which was higher than the overlap concentration of PVAc.

The light-scattering samples containing 0.0 and 0.5 wt % of PVAc were prepared by dissolving the partially cured resins into 0.0 and 0.5 wt % PVAc/2-fluorotoluene solutions, respectively, and diluted to UPE concentrations of 2, 4, 6, 8, and 10 mg/mL. The solutions were then filtered through a 0.5-μm FHLP 02500 Millipore filter (Millipore, Bedford, MA) into light-scattering tubes.

For partially cured UPE/2-fluorotoluene solutions containing 5 wt % of PVAc (PVAC concentration was higher than its overlap concentration C*) were prepared according to the following procedure. PVAc was first dissolved into acetone and diluted to 1 wt %. The dilute PVAc/acetone solution was filtered through a 0.5-μm FHLP Millipore filter, after which PVAc was precipitated by adding distilled water into solution. The precipitated PVAc was then separated from the solvent
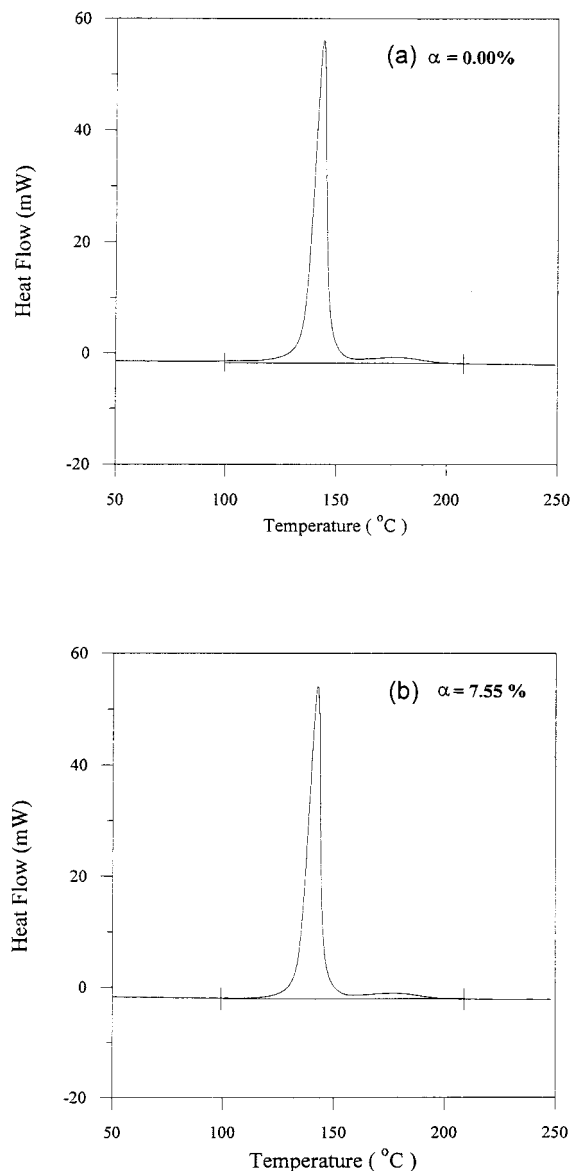

Figure 2 Nonisothermal DSC scans. (a) Styrene/UPE without curing; (b) styrene/UPE cured at 100°C for 34 min.

and dried at about 80–90°C for 1 day in a vacuum oven. Distilled water was filtered through a 0.45-μm HWAP Millipore filter before it was mixed into PVAc/acetone solution. The partially cured UPE resins were mixed with fluorotoluene and diluted to concentrations of 2, 4, 6, 8, and 10 mg/mL. These solutions were then filtered through a 0.5-μm FHLP 02500 Millipore filter into light-scattering tubes and mixed with 5 wt % of PVAc, which was purified as described earlier. These solutions were used for SLS measurements. The solutions with a UPE concentration of 2 mg/mL were used for DLS measurements.

Refractive Index Increment (dn/dC)

The same samples for light-scattering measurements were used for refractive index increment measurements. The refractive index increments of partially cured UPE/2-fluorotoluene solutions containing 0.0, 0.5, and 5.0 wt % of PVAc were measured against 2-fluorotoluene, 0.5 wt % PVAc/2-fluorotolune, and 5 wt % PVAc/2-fluorotoluene solutions, respectively.

RESULTS AND DISCUSSION

DSC Study

For studying the isothermal curing kinetics of thermosetting resins by DSC,[30] one assumes that the amount of heat generated as a result of the curing reaction is directly proportional to the degree of conversion α (or the extent of reaction) of the sample at that time, and then one relates the rate of conversion $d\alpha/dt$ to the rate of heat generated dH/dt by[30]:

$$\frac{d\alpha}{dt} = \frac{1}{H_{tot}} \frac{dH}{dt} \tag{2}$$

Integrating eq. (2) with time, one obtains the relative degree of conversion α,

$$\alpha(t) = \frac{1}{H_{tot}} \int_0^t \left[\frac{dH}{dt} \right]_T dt \tag{3}$$

where the subscript T indicates isothermal curing reaction.

In eqs. (2) and (3), the total heat of the curing reaction (H_{tot}) is given by

$$H_{tot} = H_t + H_r \tag{4}$$

where H_t is the heat generated during the isothermal runs at 100°C, and H_r is the residual heat 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 100°C.

The DSC isothermal curing profiles measured at 100°C for UPE/styrene blended with 0.0, 0.5, and 5.0 wt % of PVAc are shown in Figure 3. Table I lists the onset of cure time t_{onset}, gel time t_{gel}, gel conversion α_{gel}, and final conversion α_f of these three curing systems. In this study, we define t_{gel} and α_{gel} as the t and α, respectively, at the
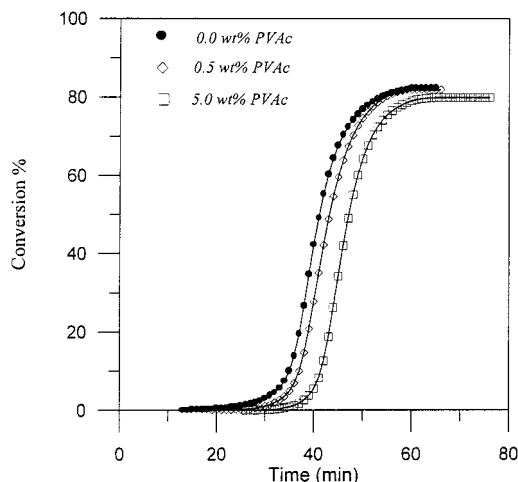

Figure 3 Isothermal DSC curing profiles at 100°C for UPE/styrene blended with 0.0, 0.5, and 5 wt % of PVAc.

initial inflection of $\alpha(t)$ versus t curve. This approximate definition may not be the *true* gel point but is close to the *actual* gel point. α_f is defined as $\alpha(t)$ at $t \rightarrow \infty$. From these data, we found that t_{onset}, t_{gel}, and α_{gel} increased, whereas α_f decreased, with increasing PVAc concentration. It is obvious that the presence of PVAc retarded the curing reaction of UPE resins. One of the reasons for the retardation of curing reaction is that the concentration of UPE and styrene vinyl decreases, whereas the concentration of PVAc increases. Another reason is that the excluded-volume effect of PVAc reduced the UPE coil sizes and increased the chance for the UPE intramolecular crosslink reaction to proceed and form more compact microgels [Fig. 1(b)]. The compactness of UPE microgels and separation of microgel particles from each other by PVAc decreased the chance for the UPE intermicrogel crosslink reaction to proceed [Fig. 1(c)]. Thus, t_{gel} and α_{gel} increased with increasing PVAc concentration.[15,17]

SLS measurements were used to follow the variations of dn/dC, ρ_v, and A_2 with UPE conver-

Table I   Curing Parameters of UPE/Styrene/PVAc Systems

PVAc Concentration (wt %)	t_{onset} (min)	t_{gel} (min)	α_{gel} (%)	α_f (%)
0.0	13	36	13.9	83.4
0.5	19	38	14.6	82.7
5.0	26	43	18.8	80.5

sion in different fixed PVAc concentrations. The light-scattering samples with various concentrations of partially cured UPE/styrene resins were prepared by mixing partially cured resins with 0.0 wt % PVAc/2-fluorotoluene, 0.5 wt % PVAc/2-fluorotoluene, and 5 wt %/2-fluorotoluene solutions. Before mixing, the UPE/styrene resin was cured at various reaction times without the presence of PVAc to obtain resins with various degrees of conversion and then the residual styrene monomer was evaporated from the partially cured resins at room temperature under vacuum. The DSC data of UPE/styrene with 0.0 wt % of PVAc indicated $\alpha_{gel} = 13.9\%$ (Table I). Thus, all of the SLS and DLS samples were prepared using the partially cured UPE/styrene resins with $\alpha < 13.9\%$.

SLS Study

The intensity of the scattered light from a polymer solution is given by the equation[31,32]

$$KC/\Delta R_\theta = 1/M_w + 2A_2C + \cdots \quad (5)$$

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

$$K = 4\pi^2 n_o^2 (dn/dC)^2/(\lambda^4 N_A) \quad (6)$$

where n_o is the refractive index of the solvent (i.e., 2-fluorotoluene in this study); dn/dC is the differential index of refraction; N_A is the Avogadro's number; and λ is the wavelength of incident radiation *in vacuo*. Debye plots were constructed to extrapolate to zero concentration in eq. (5).

The dn/dC values for partially cured UPE resins with various degrees of conversion in 2-fluorotoluene, 2-fluorotoluene/0.5 wt % PVAc, and 2-fluorotoluene/5.0 wt % PVAc solutions are listed in Table II. The measurements were made using 2-fluorotoluene/PVAc mixtures as solvents. We also carried out a refractive index increment measurement of PVAc in 2-fluorotoluene, obtaining a very small $dn/dC \sim 2.0 \times 10^{-4}$ mL/g. Because PVAc has a refractive index close to that of 2-fluorotoluene, the dn/dC of UPE//PVAc/2-fluorotoluene solutions was mainly contributed from the refractive difference between UPE and 2-fluorotoluene. For UPE/PVAc/2-fluorotoluene solutions

Table II dn/dC (10^{-2} mL/g) of UPE in 2-Fluorotoluene/PVAc Solutions

UPE Conversion (%)	PVAc Concentration		
	0.0 wt %	0.5 wt %	5.0 wt %
0.0	5.82	5.70	5.59
1.65	6.13	6.01	5.80
3.02	6.49	6.24	5.03
5.44	5.63	5.51	5.30
7.55	6.20	6.21	6.04
9.20	6.38	6.28	6.15

with the same degree of UPE conversion, Table II demonstrated that dn/dC decreased with increasing PVAc concentration. Table II also showed that, at a fixed PVAc concentration, dn/dC increased in the initial stage of curing and decreased at α values of about 5.44, 5.44, and 3.02%, then increased with increasing α for UPE resins blended with 0.0, 0.5, and 5.0 wt % PVAc/2-fluorotoluene solutions, respectively. More detailed discussion of the variation of dn/dC with α is shown below.

For many large and flexible polymers, the effects of depolarization are negligible and, as a result, 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 that are defined as follows[31]:

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

where the subscript v indicates measurements involving a vertically polarized incident light, H is the horizontally scattered light, and V is the vertically scattered light. For partially cured UPEs with short molecular chains, the effects of depolarization are not negligible. The data of ρ_v versus α for 2 mg/mL partially cured UPE resins in 2-fluorotoluene, 0.5 wt % PVAc/2-fluorotoluene, and 5.0 wt % PVAc/2-fluorotoluene solutions are summarized in Table III. For UPE/PVAc/2-fluorotoluene solutions with the same degree of UPE conversion, Table III demonstrated that ρ_v decreased with increasing PVAc concentration. Table III also showed that, at a fixed PVAc concentration, ρ_v increased in the initial stage of curing

Table III ρ_v **of UPE in 2-Fluorotoluene/PVAc Solutions**

UPE Conversion (%)	PVAc Concentration		
	0.0 wt %	0.5 wt %	5.0 wt %
0.0	0.300	0.228	0.0445
1.65	0.328	0.262	0.0643
3.02	0.358	0.313	0.0356
5.44	0.264	0.218	0.0403
7.55	0.310	0.283	0.0680
9.20	0.342	0.315	0.0615

Figure 4 Debye plot of partially cured UPE resins in 2-fluorotoluene at a scattering angle $\theta = 90°$. ($\bullet$) $\alpha = 0.0\%$; ($\diamond$) $\alpha = 1.65\%$; ($\blacktriangle$) $\alpha = 3.20\%$; ($\square$) $\alpha = 5.44\%$; ($\star$) $\alpha = 7.55\%$; ($\hollowstar$) $\alpha = 9.20\%$.

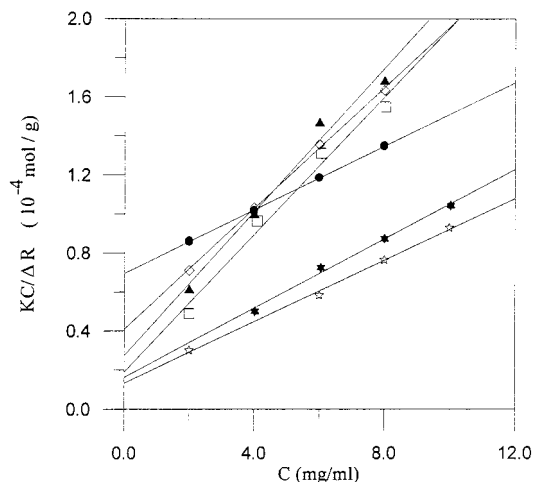and decreased at α values of about 5.44, 5.44, and 3.02%, then increased with increasing α for UPE resins blended with 0.0, 0.5, and 5.0 wt % PVAc/2-fluorotoluene solutions, respectively.

Concerning SLS measurements of the partially cured UPE/2-fluorotoluene solutions with linearly polarized incident light perpendicular to the scattering 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[31]:

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

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

The Debye plots of the partially cured UPE resins in 4-fluorotoluene without PVAc at a scattering angle $\theta = 90°$ are shown in Figure 4. In Figure 4 all the values of ΔR_θ were corrected by dividing 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 UPE and A_2 of solutions were obtained from the intercepts and slopes, respectively, from the plots of Figure 4 by using eq. (5). Similar Debye plots of partially cured UPEs in 0.5 and 5.0 wt % PVAc/2-fluorotoluene solutions were also obtained. The variations of M_w and A_2 are plotted against α and shown in Figures 5 and 6, respectively. Figure 5 showed that the M_w of partially cured UPE increased with increasing α. For UPE/PVAc/2-fluorotoluene solutions with the same degree of UPE conversion, Figure 6 demonstrated that A_2 decreased with increasing PVAc concentration. At a fixed PVAc concentration, Figure 6 showed that A_2 increased in the initial stage of curing and reached a maximum at α values of 3.02, 5.44, and 3.02%, then decreased with increasing α for UPE resins blended with 0.0, 0.5, and 5.0 wt % PVAc/2-fluorotoluene solutions, respectively.

The SLS data revealed that A_2 increased in the early stage of curing then decreased at higher conversions as α increased. The variation of A_2 with α of partially cured UPE can be explained using solubility parameters of unreacted UPE (UPE with C=C bonds), reacted UPE (with C=C bonds of UPE being reacted to C—C bonds), PVAc, styrene(C=C—ϕ), reacted styrene (C—C—ϕ), and 4-fluorotoluene. We calculated solubility parameters using the Fabor method.[33] The solubility parameters of these compounds are
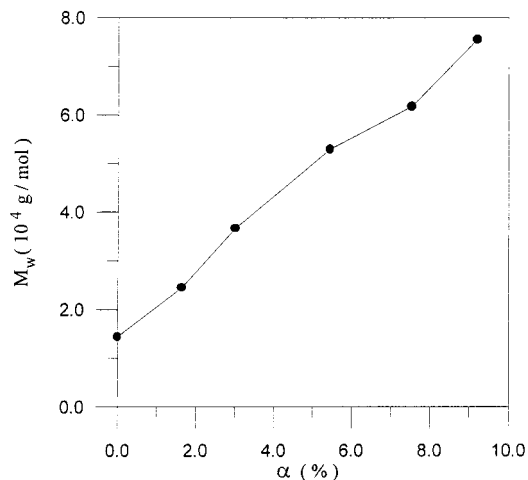
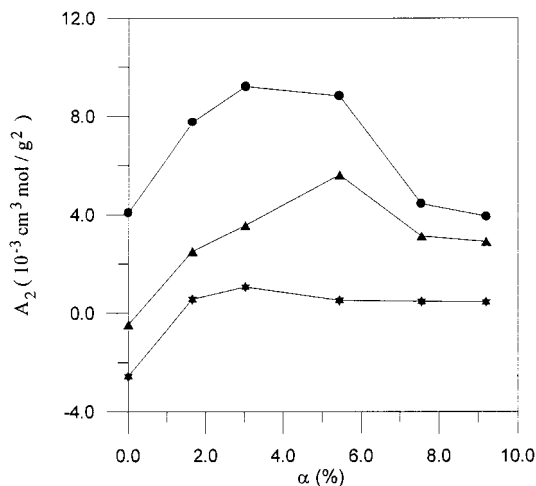**Figure 5** Variation of M_w of partially cured UPE with degree of conversion α.

Figure 6 Variations of A_2 of partially cured UPEs with degree of conversion α in 2-fluorotoluene, 0.5 wt % PVAc/2-fluorotoluene, and 5.0 wt % PAVc/2-fluorotoluene solutions. (●) 0.0 wt % PVAc; (▲) 0.5 wt % PVAc; (★) 5.0 wt % PVAc.

summarized in Table IV. The curing reaction of UPE with styrene causes C=C double bonds of UPE and styrene to be reacted into C—C single bonds. In Table V, we summarized the solubility parameter differences of unreacted and reacted styrene and UPE with other components. As shown in Table V, the solubility parameter differences of reacted styrene with other components are almost smaller than those of unreacted styrene with other components, indicating that reacted styrene is more compatible with other components in the curing system than unreacted styrene. However, the solubility parameter differences of reacted UPE with other components are greater than those of unreacted UPE with other components, suggesting that reacted UPE is less compatible than unreacted UPE with other components in the curing system. At lower UPE conversions, self-polymerization of styrene monomer and reaction of styrene with UPE increases the solubility of partially cured UPE resins with PVAc/2-fluorotoluene solutions. However at higher UPE conversion, a greater number of UPE C=C bonds reacted and crosslink density increased with increasing α. Thus the solubility of partially cured UPE resins with PVAc/2-fluorotoluene solutions decreased with increasing α at higher conversion. The variation of A_2 with α was quite consistent with that predicted from solubility parameters.

DLS Study

The DLS measurements were also carried out at a scattering angle $\theta = 90°$ for partially cured resins with a concentration of 2 mg/ml. DLS particle-size distribution curves of UPE microgels in 5.0 wt % PVAc/2-fluorotoluene solution are shown in Figure 7. Similar results of partially cured UPE in 0.0 and 0.5 wt % PVAc/2-fluorotoluene solutions are also obtained. All of 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 of partially cured UPE resins at various conversions in 0.0, 0.5, and 5.0 wt % PVAc/2-fluorotoluene solutions are summarized in Table VI. In Table VI, D_1 and D_2 are the average particle sizes and V_1 and V_2 are the volume fractions of primary and partially cured UPE coils, respectively. As shown in Table VI, both D_1 and D_2 decreased with increasing PVAc concentration. These results suggest that increasing PVAc concentration reduced the free volume of the curing system, leading UPE coils to become more compact and facilitating the UPE coils intramolecular crosslinking reaction to proceed [Fig. 1(b)]. These results could be used to explain why the gelation of UPE/styrene was retarded by the presence of PVAc and both the gel conversion (α_{gel}) and gel time (t_{gel}) increased with increasing PVAc concentration (Fig. 3 and Table I). Table VI also showed that both the size D_2 and volume fraction V_2 of partially cured UPE coils increased with increasing α in the early stage of curing and decreased at $\alpha \sim 5.44\%$ [corresponding to the microgel formation shown in Fig. 1(b)] for partially cured UPE in PVAc/2-fluorotoluene solutions. After α

Table IV   Solubility Parameters of Various Compounds

Compounds	Solubility Parameter ρ $(J^{1/2}/cm^{3/2})$
Unreacted UPE (C=C)	24.0
Reacted UPE (C—C)	28.3
PVAc	21.6
Styrene (C=C—ϕ)	18.9
Reacted styrene (C—C—ϕ)	21.6
2-Fluorotoluene	19.8

Table V   Solubility Parameter Differences of Styrene and UPE with Other Components Before and After Reaction

Before Reaction[a] ρ $(A - B)$ (J$^{1/2}$/cm$^{3/2}$)	After Reaction[a] ρ $(A - B)$ (J$^{1/2}$/cm$^{3/2}$)
Styrene $-$ unUPE $= -5.1$	restyrene $-$ unUPE $= -2.4$
Styrene $-$ PVAc $= -2.7$	restyrene $-$ PVAc $= 0$
Styrene $-$ fluorotoluene $= -0.9$	restyrene $-$ fluorotoluene $= 1.8$
Styrene $-$ reUPE $= -9.4$	restyrene $-$ reUPE $= -6.7$
unUPE $-$ PVAc $= 2.4$	reUPE $-$ PVAc $= 6.7$
unUPE $-$ fluorotoluene $= 4.2$	reUPE $-$ fluorotoluene $= 8.5$
unUPE $-$ restyrene $= 2.4$	reUPE $-$ restyrene $= 6.7$
unUPE $-$ styrene $= 5.1$	reUPE $-$ styrene $= 9.4$

[a] un = unreacted; re = reacted.

$> 5.04\%$, both D_2 and V_2 increased with increasing α [corresponding to the crosslink reaction shown in Fig. 1(c)].
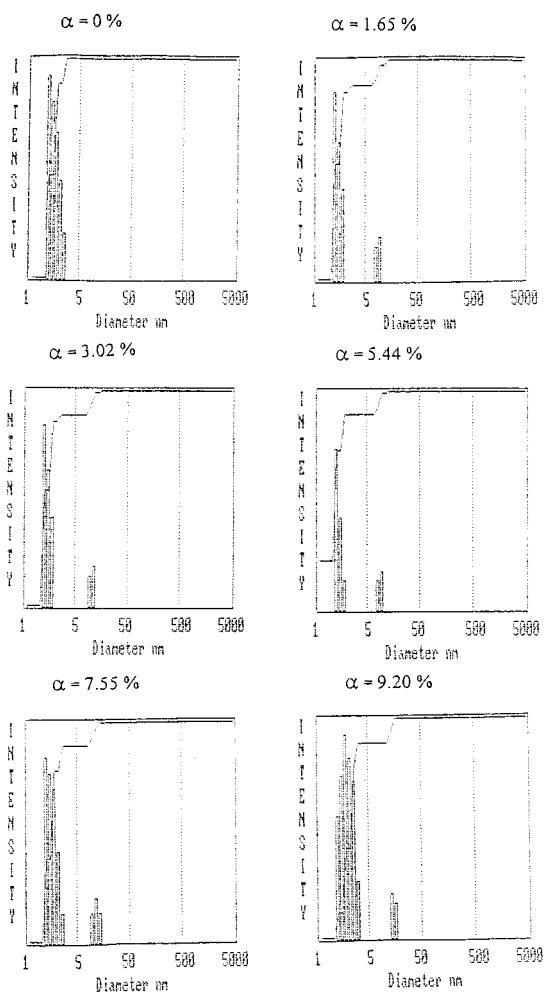

Figure 7   DLS particle size distributions of partially cured UPE resins in 5.0 wt % PVAC/ 2-fluorotoluene at various degrees of conversion α.

Discussion

Effect of Degree of UPE Conversion on UPE/PVAc/2-Fluorotoluene Solution Properties

An inspection of the dn/dC and ρ_v values shown in Tables II and III, respectively, reveals that the trend of dn/dC and ρ_v is similar to that of D_2. Both dn/dC and ρ_v increased with increasing α in the early stage of curing and then decreased at a conversion of α values of about 5.44, 5.44, and 3.02% for partially cured UPE in 0.0, 0.5, and 5.0 wt % PVAc/2-fluorotoluene solutions, respec-

Table VI   DLS Data of Partially Cured UPE in Various Concentrations of PVAc/2-Fluorotoluene Solutions

Conversion (%)	D_1 (nm)	D_2 (nm)	V_1 (%)	V_2 (%)
	0.0 wt % PVAc			
0.0	3.8	0	100	0
1.65	3.5	22	90	10
3.02	4.6	28	89	11
5.44	4.4	20	90	10
7.55	4.1	27	89	11
9.20	5.3	38	87	13
	0.5 wt % PVAc			
0.0	2.9	0	100	0
1.65	2.4	16	91	9
3.02	2.5	18	90	10
5.44	2.4	14	91	9
7.55	3.3	21	90	10
9.20	3.9	28	88	12
	5.0 wt % PVAc			
0.0	2.5	0	100	0
1.65	2.2	14	88	12
3.02	2.1	16	90	10
5.44	2.2	11	89	11
7.55	2.7	18	89	11
9.20	3.3	21	88	12

tively. After α was higher than 5.44, 5.44, and 3.02%, both dn/dC and ρ_v increased with increasing α. ρ_v is a function of particle shape and anisotropy in solvent. This permits one to follow changes in polymer shape and anisotropy.[15,20] Obviously, the more anisometric the shape of a particle, the larger the optical anisotropy that can be expected; indeed, appreciable depolarization of scattered light, because of the solute, has been observed as rodlike particles.[15,20] On the other hand, for polymers with conformation of some sort of coils in solution, the depolarization of scattered light is quite low.[15,20]

The low-molecular-weight primary UPE was synthesized from aromatic isophthalic acid and aliphatic fumaric acid and 1,2-propanediol, and thus the partially cured UPE molecules at lower conversions behaved more or less like rigid rods in PVAc/2-fluorotoluene solutions. The present experimental data showed that, before gelation, ρ_v had the lowest value as conversions approached α values of about 5.44, 5.44, and 3.02%, respectively, for partially cured UPE in 0.0, 0.5, and, 5.0 wt % of PVAc/2-fluorotoluene solutions. In this study, the partially cured UPE/styrene resins were prepared without the presence of PVAc. DLS data (Table VI) showed that UPE microgels had the smallest sizes (D_2) at α = 5.44%. In a previous study,[15] we prepared various degrees of conversion of partially cured UPE by curing the UPE/styrene resin in the presence of various concentrations of PVAc. Using DLS, we showed that the conversion corresponding to the smallest microgel sizes (D_2) decreased with increasing PVAc content. The smaller values of dn/dC, ρ_v, and D_2 indicated the formation of less anisometric UPE microgels as a result of the intramolecular crosslinking reactions inside the UPE coils, as shown in Figure 1(b). The second virial coefficient A_2 increased with increasing α at lower conversion, then decreased as α values were greater than 5.44, 5.44, and 3.02%, respectively, for partially cured UPE resins in 0.0, 0.5 and 5.0 wt % of PVAc/2-fluorotoluene solutions (Fig. 6). The increases of dn/dC, ρ_v, and D_2 and also the decrease of A_2 with increasing α at higher α values indicated the occurrence of intermolecular crosslinking reactions among microgel particles [Fig. 1(c)]. The crosslink reaction of intermicrogel particles increased the sizes and anisotropy of microgel particles and also reduced the compatibility between the partially cured UPE molecules and PVAc/2-fluorotoluene solutions.

Effect of PVAc Concentration on Properties of UPE/PVAc/2-Fluorotoluene Solutions

A careful examination of the data of dn/dC, ρ_v, A_2, and D_2 revealed that, at the same UPE conversion, all of these data values exhibited a similar dependence on PVAc concentration, that is, dn/dC, ρ_v, A_2, and D_2 decreased with increasing PVAc concentration. Replacing low-molecular-weight 2-fluorotoluene with high-molecular-weight PVAc in UPE/2-fluorotoluene solutions increased the excluded volume of polymers. The A_2 decreased with increasing PVAc concentration (or with decreasing 2-fluorotoluene concentration). As a result of the increase in the excluded volume of polymers, the sizes of UPE microgels (D_2) and primary UPE molecules (D_1) decreased, whereas PVAc concentration increased. The shrinkage of sizes of UPE microgels and primary molecules caused a change of molecular conformation from rod to coil. Thus, the anisosymmetry (ρ_v) and differential index of refraction (dn/dC) decreased with increasing PVAc content. The resulting increase in PVAc concentration leads to enhancement of compactness of UPE coils, favoring intramolecular cyclization of UPE resins and causing the shrinkage of microgels. Increasing PVAc concentration could also lead the UPE coils to be more isolated and more compact in the solutions, thus increasing the tendency to intramolecular cyclization and causing the delay of gelation, as shown in Figure 3 and Table I.

CONCLUSIONS

By following the variations of differential index of refraction (dn/dC), anisosymmetry (ρ_v), UPE microgel particle size (D_2), and second virial coefficient (A_2) with the degree of curing, we demonstrated the formation of microgels resulting from intramolecular crosslinking reactions inside the UPE coils in the early stage of curing. At a fixed UPE conversion, dn/dC, ρ_v, A_2, and D_2 decreased with increasing PVAc concentration. These results suggest that replacing low-molecular-weight 2-fluorotoluene with high-molecular-weight PVAc in UPE/2-fluorotoluene solutions caused an increase in excluded volume of polymers, leading to reductions of UPE microgel particle sizes and compatibility between UPE and PVAc/2-fluorotoluene solutions. The reduction of UPE microgel particle sizes also led to the de-

creases in anisosymmetry and differential index of refraction of UPE in the solution.

REFERENCES

1. Bucknall, C. B.; Davies, P.; Partridge, I. K. Polymer 1985, 26, 109.
2. Bucknall, C. B.; Partridge, I. K.; Phillips, M. J. Polymer 1991, 32, 786.
3. Bucknall, C. B.; Partridge, I. K.; Phillips, M. J. Polymer 1991, 32, 636.
4. Hsu, C. P.; Kinkelaar, M.; Hu, P.; Lee, L. J. Polym Eng Sci 1991, 31, 1450.
5. Hsieh, Y. N.; Yu, T. L. J Appl Polym Sci 1999, 73, 2413.
6. Dusek, K.; Galina, H.; Mikes, J. Polym Bull (Berlin) 1980, 3, 19.
7. Hild, G.; Okasha, R. Macromol Chem 1985, 186, 93.
8. Hild, G.; Okasha, R. Macromol Chem 1985, 186, 389.
9. Yang, Y. S.; Suspene, L. Polym Eng Sci 1991, 31, 321.
10. Muzumdar, S. V.; Lee, L. J. Polym Eng Sci 1991, 31, 1647.
11. Liu, S. B.; Yu, T. L. Macromol Chem Phys 1995, 196, 1307.
12. Hsu, C. P.; Lee, L. J. Polymer 1993, 34, 4496.
13. Chiu, Y. Y.; Lee, L. J. J Polym Sci Polym Chem Ed 1995, 33, 257.
14. Chen, J. S.; Yu, T. L. J Appl Polym Sci 1998, 69, 871.
15. Sun, B.; Yu, T. L. Macromol Chem Phys 1996, 197, 275.
16. Liu, S. B.; Liu, J. L.; Yu, T. L. J Appl Polym Sci 1994, 53, 1165.
17. Sun, B.; Yu, T. L. J Appl Polym Sci 1995, 57, 7.
18. Kubota, H. J Appl Polym Sci 1975, 19, 2279.
19. Lem, K. W.; Han, C. D. J Appl Polym Sci 1983, 28, 3185.
20. Lem, K. W.; Han, C. D. Polym Eng Sci 1984, 24, 175.
21. Kiaee, L.; Yang, Y. S.; Lee, L. J. Presented at the 43rd Annual Conference, Composite Institute, The Society of the Plastic Industry, Inc., Cincinnati, OH, February 1–5, 1988.
22. Lucas, J. C.; Borrajo, J.; Williams, R. J. J. Polymer 1993, 34, 1886.
23. Wheeler, L. M.; Lodge, T. P. Macromolecules 1989, 22, 3399.
24. Benmouna, M.; Benoit, H.; Dual, M.; Akcasu, Z. A. Macromolecules 1987, 20, 1107.
25. Benmouna, M.; Seils, J.; Meier, G.; Patkowski, A.; Fisher, E. W. Macromolecules 1993, 26, 668.
26. Roy, F.; Joanny, J. F. Macromolecules 1992, 25, 4612.
27. Seils, J.; Benmouna, M.; Patkowski, A.; Fisher, E. W. Macromolecules 1994, 27, 5043.
28. Operation Manual for Differential Refractometer Model RF-600; C. N. Wood Manufacturing Company: Newton, PA.
29. (a) Yu, T. L.; Reihanian, R.; Southwick, J. G.; Jamieson, A. M. J Macromol Sci Phys Ed 1980, B18, 777. (b) Bercea, M.; Ioan, C.; Ioan, S.; Simionescu, B. C.; Simionesu, C. I. Prog Polym Sci 1999, 24, 379.
30. Turi, E. A. Thermal Characterization of Polymeric Materials; Academic Press: New York, 1981.
31. (a) Instruction Manual for Model BI-2030AT Digital Correlator; Brookhaven Instruments Corp.: New York, 1986. (b) Huglin, M. B. in Light Scattering from Polymer Solutions; Huglin, M. B., Ed.; Academic Press: London, 1972; Chapter 6.
32. Chu, B. Laser Light Scattering, 2nd ed., Academic Press: San Diego, CA, 1991.
33. Van Krevelen, D. W.; Hoftyzen, P. J. in Properties of Polymers; Elsevier Scientific Publishers: Amsterdam/New York, 1976; Chapter 7.