Dynamic Light Scattering from Sol−Gel Transition of Unsaturated Polyester Resins

H. L. Lin,[†] T. L. Yu,*,[†] and C. H. Cheng[‡]

Department of Chemical Engineering, Yuan-Ze University, Taoyuan, Nei-Li, Taiwan 32026, and Department of Chemistry, National Tsing-Hua University, Hsinchu, Taiwan 30043

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ABSTRACT: We report the measurements of dynamic light scattering (DLS) and dynamic viscoelasticity on an unsaturated polyester/styrene system at various degrees of curing through sol−gel transition. The measurements have been carried out with both polarized and depolarized scattered light. The degrees of conversion at various curing stages were measured by differential scanning calorimetry (DSC). The experimental results indicated that the depolarized DLS correlation functions were independent of the degree of curing. The polarized DLS data revealed two modes of relaxation before gelation but only one mode of relaxation after gelation. The correlation function of polarized DLS varied with degrees of curing and approached that of depolarized DLS after gelation. Both the DLS and viscoelastic measurements showed the divergence of relaxation times at gelation, indicating the consistency of these two measurements for defining gelation.

Introduction

Unsaturated polyester (UPE) resin is one of the most important thermoset resins for composite materials due to its cheap price and high performance when manufactured with glass fibers or carbon fibers, etc. The resin is a mixture of UPE and styrene in which the UPE is a low molecular weight polymer ($M_w = 2000{\sim}10\,000$) with four to six C=C bonds per molecule, and the styrene monomer acts as both a cross-linker and a solvent. The concentration of UPE in most commercial resins is around 65∼75 wt %. The curing reaction of UPE resin is a free radical polymerization. The curing kinetics and microgelation of UPE resins in the early stages of the curing reaction have been reported by several researchers.[1−6] Three reactions may happen in the curing of UPE with styrene: (1) the reaction between the vinyl groups of UPE and styrene, (2) the reaction between the vinyl groups of styrene molecules; and (3) the reaction among the vinyl groups of UPEs. Due to the slow reaction rate of reaction 3, it is believed that the curing reaction of UPE resin is dominated by reactions 1 and 2. The cross-link reaction caused the system to gel at the early stage of curing.

Recently, experiment and theory[7−22] indicate that the gel point of the cross-link reaction can be defined by dynamic measurements. Several theoretical analyses have developed expressions for the frequency dependence of G', G'', and the complex viscosity, η^*, at the gel point,[7−12,17,18,23] using the fractal scaling concept to define the gel network structure. The results of investigation indicate that at the sol−gel transition point:

$$G'(\omega) = A\omega^n \tag{1}$$

$$G''(\omega) = B\omega^n \tag{2}$$

and

$$\tan \delta = G''(\omega)/G'(\omega) = B/A = \tan (n\pi/2) \tag{3}$$

where A and B are related to the material strength factor of the gel.[7] The exponent n is determined by the fractal dimension of the network, the stoichiometry of the gel,[14,23] and the strength of the hydrodynamic interaction between the polymer chain segments.[12,18,24]

It was shown by dynamic light scattering (DLS) measurements on solutions of polydisperse polyurethane clusters that the profile of the homodyne autocorrelation function, $g^2(t)$, changes with increasing concentration from a stretched exponential function to a power law.[25] The sol−gel transition for a dilute polymer solution near the overlap concentration was experimentally studied by Martin and Wilcoxon[10] (silica gels), Lang and Burchard[13] (polysaccharides), and Fang et al.[26] (methacrylate and ethylene dimethacrylate copolymer in butyl acetate). In the silica gel,[10] the long-time tail of the correlation functions measured prior to the gel point can be described by a stretched exponential, $g^1(t) = \exp[-(t/\tau_s)^b]$, with $b = 0.33 \pm 0.03$. The power-law time decay (5 decades) of the intensity autocorrelation function, $g^1(t) = t^{-\phi}$, $\phi = 0.13 \pm 0.02$, and a critical slowing of the average relaxation time have been observed as the gel point is approached. In the polysaccharides,[13] the corresponding exponent $\phi = 0.17 \pm 0.01$ was found for a thermal reversible gelling system. A simple cluster diffusion model of the dynamics has been proposed that relies on the concept of size-dependent viscosity, the hyperscaling form of the size distribution, and the screening of the scattering intensity.

There has been considerable activity directed to an understanding of DLS from polymer−diluent systems and from bulk polymers.[27] In bulk system it is well established that the primary α-relaxation dominates the correlation function, which displays a very broad non-exponential decay. The DLS from a bulk system is due to a localized main-chain motion. In the presence of a solvent, however, the dynamics become more complex

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* To whom correspondence should be addressed: Tel (03) 4638800, ext 553; FAX (03) 4559373; Email cetlyu@saturn.yzu.edu.tw.

[†] Yuan-Ze University.

[‡] National Tsing-Hua University.

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and also reflect contributions from the concentration fluctuations, in addition to the longitudinal density and the local anisotropy fluctuation determined by segmental motions. Thus, on the other hand, concentration, density, and optical anisotropy fluctuations are present in the polarized (V_V) correlation function, while, on the other hand, anisotropy fluctuations due to segmental reorientationl relaxation are observed in the depolarized (V_H) DLS experiment. The density and orientational scattering are scattering vector q-independent since they do not reflect translational diffusion processes.[28] Concentration fluctuations relax by cooperative diffusion, i.e., by local swelling and deswelling of the highly entangled transient network. If the relaxation rate of the concentration fluctuations is appreciably slower than that of orientational and density fluctuations, it is q^2-dependent.[29] Brown and Nicolai.[29] carried out DLS experiments on the concentrated polystyrene solutions and indicated that when the relaxation rate of the concentration fluctuations approaches the reorientational relaxation rate, the concentration fluctuations becomes q-independent; i.e., they become rate-determined by the polymer backbone mobility. With a small molecule solvent, however, a part of the concentration fluctuations relaxes faster than the orientational relaxation, i.e., the diffusion occurs in the free volume within the "frozen" network.

In the literature most papers cover DLS of the sol−gel transition of dilute polymer solutions near the overlap concentration. In the present study, we reported the results of dynamic light scattering (DLS) and dynamic viscoelastic measurements in the vicinity of the sol−gel transition during the curing of UPE/styrene system. The degree of curing at each stage of curing was measured by differential scanning calorimetry (DSC). Owing to the high transparency of UPE resin, it is easy to perform light scattering experiments on this curing system. The degrees of conversion of the partially cured resins in the present study were around 0.0∼9.0%; thus the concentrations of these partially cured resins were around 70∼80 wt %. Hence all of these resins were high-concentration polymer-rich solutions.

Experimental Section

Materials: (1) Unsaturated Polyester. UPE resin (Eterset 2821) was obtained from Eternal Chemical Co., Ltd, Taiwan. The mole ratio in the composition of the solid polyester determined from NMR was isophthalic acid/fumaric acid/1,2-propylene glycol = 1.0/1.68/3.22, with a mole ratio of 1.20 for OH/COOH and an acid value of 30.0 mg of KOH/g of solid resin. The number-average molecular weight (M_n) of the polyester determined by GPC was found to be 1850, with a polydispersity $M_w/M_n = 4.2$ at 25 °C. Tetrahydrofuran (THF) was used as the mobile phase, and narrow MWD polystyrene standards (Aldrich Chemical Co.) were used in the linear method of calibration.

(2) Styrene. Styrene monomer (Aldrich Chemical Co.) with a purity of 99% was purified by distillation several times very carefully before it was mixed with UPE.

(3) Initiator. The peroxide initiator was *tert*-butyl peroxybenzoate (Akzo Chemie Co.) with a purity of 98% and an active oxygen content of 8.1%.

(4) Sample Preparation. The UPE resin, which contained ∼30 wt % styrene as obtained from the manufacturer, was dissolved in acetone and diluted to a solution containing approximately 10 mg/mL UPE. The solution was filtered through a Millipore filter (pore size 0.45 μm, FLHP). The acetone and styrene monomer was then evaporated under vacuum at room temperature for 1 day and then at 60 °C for 2 h. The UPE was then mixed with a solution of styrene and initiator; thus the final resin had a UPE/styrene/initiator weight ratio of 70/30/1. Before mixing, the solution of styrene containing initiator was also filtered through a Millipore filter (pore size 0.45 μm, FLHP). The solution for curing study was then transferred to a clean light scattering cell and sealed. Seven sample solutions were prepared and cured at 105 °C and the reaction was stopped by cooling to 5 °C at curing times varying from 0 to 25 min. Thus samples with various degrees of curing (α = 0.0%, 0.7%, 1.5%, 3.7%, 7.0%, 7.8%, and 9.0% measured by nonisothermal DSC scans) were obtained. At least three sample tubes were prepared for each degree of conversion. One tube was used for DLS measurements and the other two tubes were used for nonisothermal DSC and dynamic viscoelastic measurements.

Instrumentation: (1) Dynamic Light Scattering and Data Analysis. A Brookhaven goniometer with BI2030AT correlator was used for DLS measurements. The measurements were carried out at scattering angles of 90°, 70°, and 50° at 25.0 ± 0.5 °C. The laser was an He−Ne ion (633 nm, Spectra Physics model) and operated at a power of 10 mW. The Brookhaven BI2030AT is a digital multi-τ sample time correlator with 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)-2^n, where n = 0, 1, 2, ..., 8. The only restriction is that successive n's must be equal to or greater than the previous n. The correlation functions were normalized with a measured baseline and the decay time distributions were calculated from DLS correlation functions by using the exponential sampling technique.[30] The simulation software was provided by Brookhaven Co.

(2) Dynamic Viscoelastic Properties Measurements. Dynamic viscoelastic measurements were carried out under 10% strain at 25 ± 0.5 °C with a cone and plate geometry rheometer (Rheometric RDS-7000, plate diameter 50 mm, cone angle 0.04 rad). At a given time interval a frequency sweep extended from 0.1 to 100 rad/s.

(3) Differential Scanning Calorimetry. Nonisothermal DSC scan with a heating rate of 10 °C/min from room temperature to 250 °C was carried out by Du Pont 2100 DSC to measure the degree of conversion of each partially cured resin. The calorimeter was previously calibrated with indium standard. Hermetic cells were used for sample preparation to avoid the evaporation of styrene monomer during the DSC scan. In all cases a sample of approximately 10 mg was used. In the use of DSC for determining the degree of curing of partially cured UPE resins,[31] one assumes that the amount of heat generated (ΔH_r) due to nonisothermal heating is directly proportional to the amount of C=C bonds reacted during DSC scan. Thus the amount of reacted C=C bonds of the partially cured resin before DSC scan is proportional to $\Delta H_u - \Delta H_r$, where ΔH_u is the heat generated by a nonisothermal DSC scan for a totally uncured resin (i.e., the UPE samples prepared as described in the sample preparation section but without being cured at 105 °C). The degree of conversion α for each partially cured resin can be obtained from

$$\alpha = 1 - \Delta H_r/\Delta H_u \tag{4}$$

The isothermal DSC scan for an uncured resin was also carried out at 105 °C for 60 min. After completion of the isothermal scan, the sample was heated from 105 to 250 °C with a heating rate of 10 °C/min. The degree of conversions for an isothermal curing at 105 °C with various curing times were then calculated from[31]

$$\alpha(t) = \frac{\Delta H_{iso}(t)}{\Delta H_{iso} + \Delta H_{noniso}} \tag{5}$$

where $\Delta H_{iso}(t)$ is the heat released from initial to a curing time t, ΔH_{iso} is the total heat released during isothermal curing at 105 °C, and ΔH_{noniso} is the heat released while the sample was

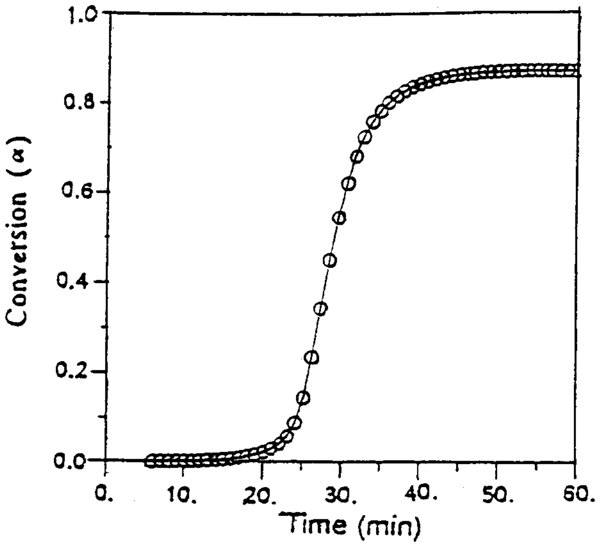

Figure 1. DSC isothermal curing of UPE resin at 105 °C.

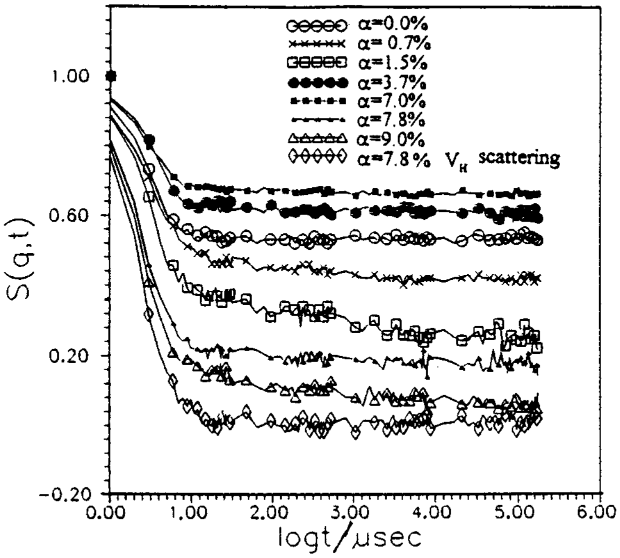

Figure 2. Autocorrelation functions of V_v scattering at $\theta = 90°$ for UPE/styrene at various degree of curing.

heated from 105 to 230 °C after completion of the isothermal curing at 105 °C.

Results and Discussion

The DSC conversion α vs curing time for isothermal curing reaction at 105 °C is shown in Figure 1. The gel point of the curing reaction can be obtained from the inflection point of α vs curing time curve. After the inflection point, the conversion α increased dramatically with reaction time. The experimental data indicated that UPE/styrene gelled at a conversion $\alpha_{gel} \sim 7.8\%$. The curing rate was slow at conversion $\alpha < \alpha_{gel}$ but increased rapidly for $\alpha > \alpha_{gel}$. Most of the researchers attributed the behavior of the rapid increase in curing reaction rate for $\alpha > \alpha_{gel}$ to the increase of the viscosity after gelation that led to a diffusion-controlled termination.[32]

The polarized autocorrelation functions $S(q,t)$ at the scattering angle $\theta = 90°$ taken prior to and after gelation at various degrees of curing are plotted semilogarithmically in Figure 2. The degree of conversion, α, of each partially cured resin was determined by a nonisothermal DSC scan and eq 4. For the reason of easy visual investigation of the variation of correlation function with degree of curing, all of the intensity correlation functions $I(q,t)$ were normalized according to

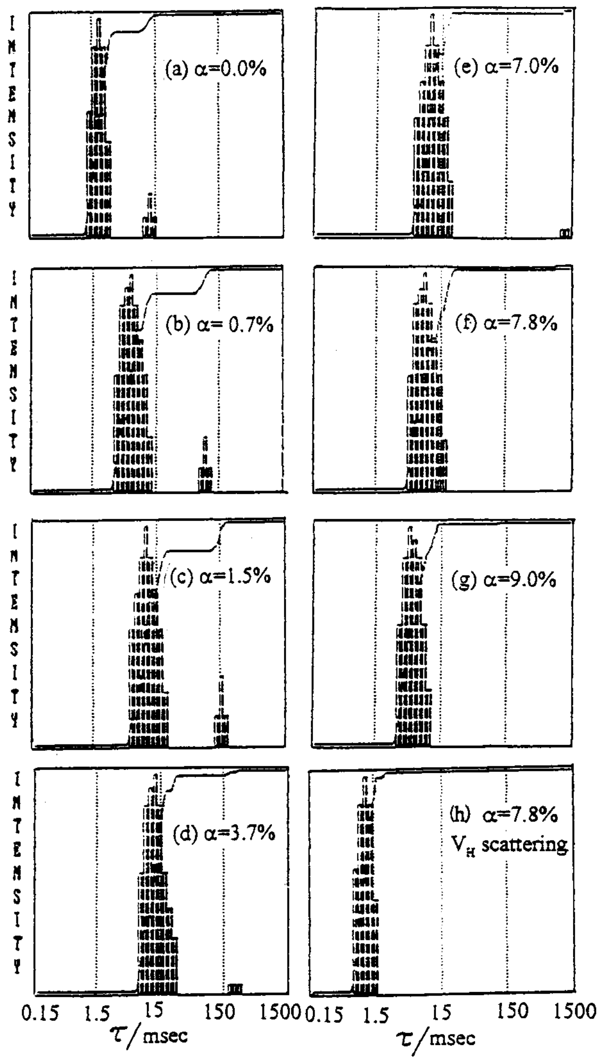

Figure 3. (a−g) Decay time distributions of V_v scattering at $\theta = 90°$ for UPE/styrene at various degrees of conversion. (h) Decay time distribution of V_H scattering at $\theta = 90°$ for UPE/styrene at a conversion $\alpha = 7.8\%$ (intensity and integration curves).

Table 1. DLS ($\theta = 90°$) Average Fast Mode Relaxation Time, Slow Mode Relaxation Time, and Amplitude of Fast Mode of V_v Scattering

conversion α (%)	τ_f (ms)	τ_s (ms)	A_f
0.0	3.3	13.7	92
0.7	8.4	132	89
1.5	14.2	160	87
3.7	15.4	314	97
7.0	14.7	1421	99
7.8	12.0		100
9.0	8.0		100
V_H scattering	1.4 ms (average)		

$$S(q,t) = \frac{I(q,t) - B}{I(q,0) - B} \tag{6}$$

where $I(q,t)$ is the autocorrelation function of the scattered intensity, $I(q,t) = \langle I(0)I(t)\rangle$, and B is the baseline. The distributions of the decay times were calculated from the correlation functions, which were normalized by measured baseline with an exponential sampling technique.[30] The decay time distributions of polarized

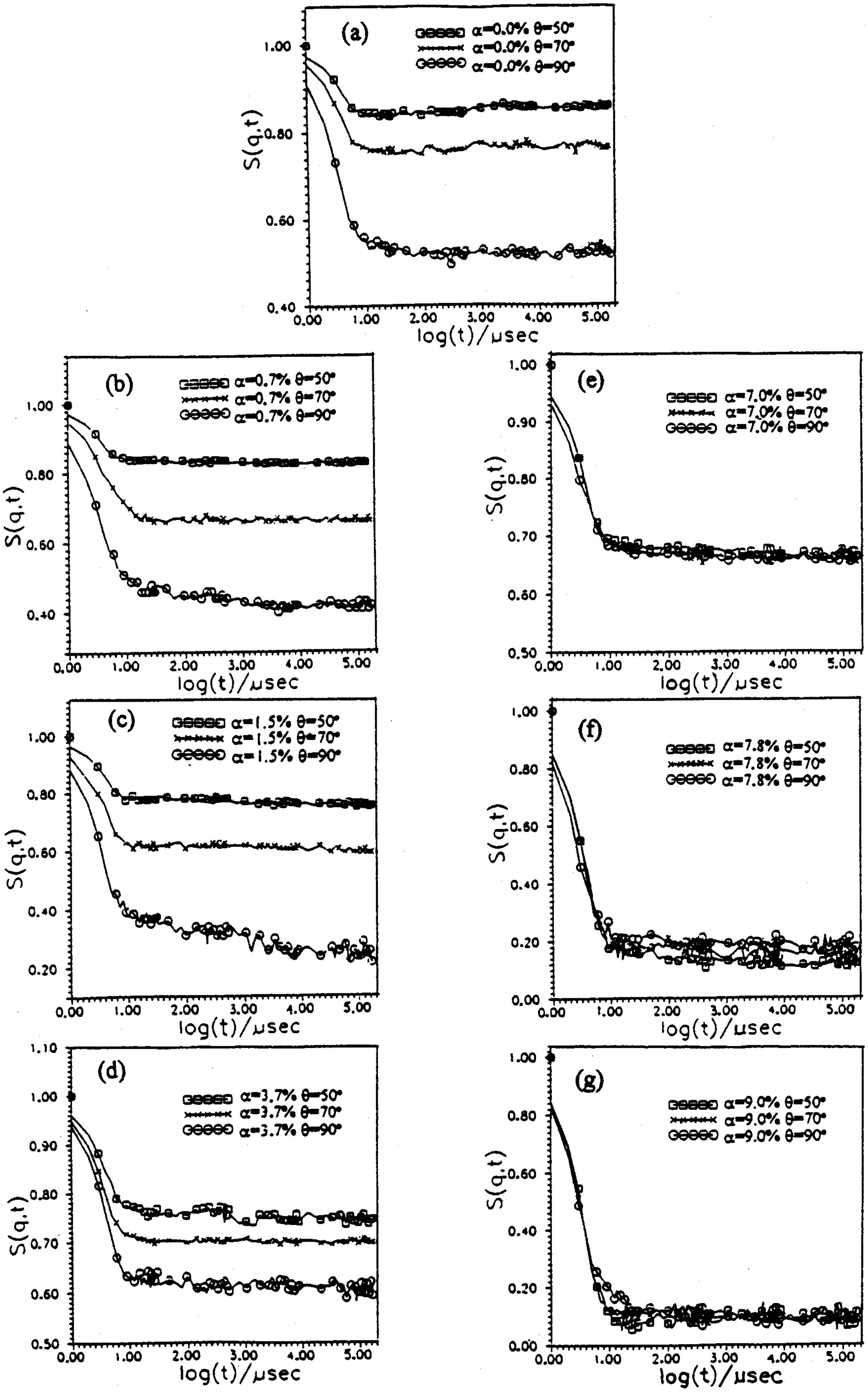

Figure 4. Autocorrelation functions of V_v scattering at various scattering angles. Scattering angle $\theta = 90°, 70°$, and $50°$. (a) $\alpha = 0.0\%$; (b) $\alpha = 0.7\%$; (c) $\alpha = 1.5\%$; (d) $\alpha = 3.7\%$; (e) $\alpha = 7.0\%$; (f) $\alpha = 7.8\%$; (g) $\alpha = 9.0\%$

DLS at a scattering angle of 90° for partially cured resins are shown in Figure 3, and the corresponding average relaxation times and fast mode amplitudes are summarized in Table 1. These polarized DLS experimental data revealed two relaxation modes prior to gelation, while only one relaxation mode was observed after gelation. To check the scattering vector q-dependency of the polarized scattering autocorrelation functions, we plotted the autocorrelation functions, $S(q,t)$, of the same degree of curing but different scattering angles in one graph. These plots are shown in Figure 4a–g for degree of curing at $\alpha = 0.0\%$, 0.7%, 1.5%, 3.7%, 7.0%, 7.8%, and 9.0% respectively. As shown in Figure 4a–g, the polarized correlation functions are q-dependent before gelation and q-independent after gelation. These results suggested that before gelation, concentration, density, and optical anisotropy fluctuations were present in the polarized light scattering, but after gelation, only density and optical anisotropy fluctuations were present in the polarized light scattering.

Upon careful examination of the decay time distributions at various degrees of conversions shown in Figure 3 and Table 1, we found that fast mode relaxation time increased from $\alpha = 0.0\%$ to $\alpha = 3.7\%$ and slow mode relaxation time increased from $\alpha = 0.0\%$ to $\alpha = 7.0\%$ with increasing conversion. However, the amplitude of the fast mode, A_f ($A_f + A_s = 1$, where A_s is the amplitude of the slow mode), decreased from $\alpha = 0.0\%$ to 1.5% and then increased from $\alpha = 1.5\%$ to 7.0%. After α was larger than 7.0%, only the fast relaxation mode was observed. Owing to the high polydispersity of UPE ($M_w/M_n = 4.2$), we believed that a small amount of UPE had been reacted with styrene monomer as resin was received from the manufacturer. The reacted UPE/styrene molecular chains resulted in a DLS slow-mode relaxation while the primary UPE molecules and the molecular chains between two neighboring entanglements or cross-links led to a fast-mode DLS relaxation. In the initial stage of curing, the reaction of UPE with styrene resulted in increases in both polymer chain length and concentration and a decrease in styrene monomer concentration, which led to an increase of slow-mode amplitude, A_s, as α increased from 0.0% to 1.5%. Since the partially cured system was a high-concentration polymer solution, the molecular diffusion was controlled by the frictional coefficient, which depends on the average free volume in the system. The increases of τ_f from $\alpha = 0.0\%$ to 3.7% and τ_s from $\alpha = 0.0\%$ to 7.0% with increasing conversion are ascribable to the fact that the system free volume decreases in which large-scale motion of the chains is highly inhibited owing to the decrease in free volume. As the curing reaction proceeded, more and more polymer molecular chains entangled and cross-linked, which caused an increase in fast-mode amplitude A_f and a decrease in τ_f with increasing α as α was higher than 3.7%. Similar results were also observed by Brillouin light scattering for polystyrene ($M_w \sim 2.35 \times 10^4$)/toluene solutions by Brown and Johnsen.[33] Their data indicated that the cooperative diffusion coefficient D_c ($\sim 1/\tau_f$) decreased with polymer concentration at polymer concentrations higher than 0.5.

As the conversion of the curing system $\alpha \geq 7.0\%$, at which the system was closed to gelation, polarized DLS data revealed only one fast relaxation mode, which corresponds to the motion of molecular chains between two neighboring cross-links. The molecular chain length between two neighboring cross-links decreased with increasing conversion and resulted in a decrease in τ_f as conversion α was higher than 7.0%

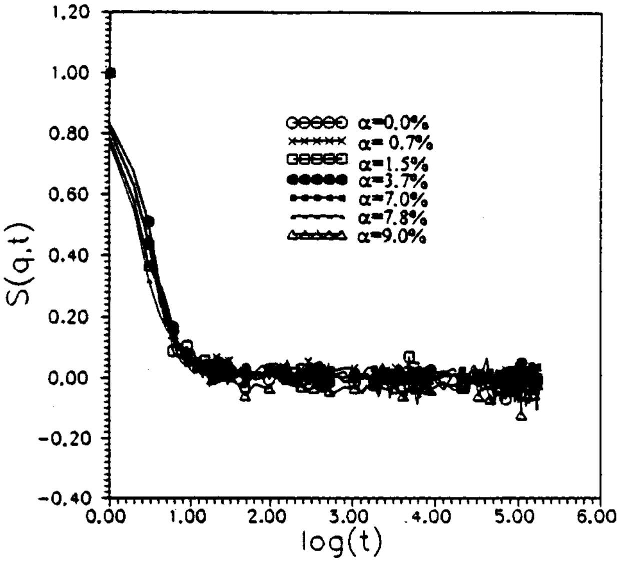

Figure 5. Autocorrelation functions of V_H scattering at a scattering angle $\theta = 90°$ with various degree of curing.

In contrast to V_v scattering, only optical anisotropy fluctuation due to segmental reorientational relaxation are observed in depolarized (V_H) DLS.[29] Figure 5 shows the autocorrelation functions, $S(q,t)$, of depolarized dynamic light scattering from the partially cured resins before and after gelation at a scattering angle $\theta = 90°$. As shown in Figure 5, all of the autocorrelation functions are merged together suggesting that the correlation functions due to segmental reorientational relaxation are independent of the degree of curing.

To observe the variation of concentration fluctuations with respect to the segmental reorientation fluctuations during curing, the autocorrelation function of V_H scattering and its decay time distribution at gelation ($\alpha = 7.8\%$) are plotted in Figure 2 and Figure 3h, respectively, together with those of V_v scattering at various degree of curing. The average relaxation time is also listed in Table 1. As shown in Figure 2, at low conversions the shape of the V_v scattering correlation function was quite different from that of the V_H scattering correlation function. However, as the curing conversion α was close to α_{gel} the correlation function of V_v scattering became close to that of V_H scattering. These results suggest that the contribution of concentration fluctuations to V_v scattering decreases with increasing conversion and after gelation most of the V_v scattering is due to the fluctuations of density and segmental reorientation.

It has been shown that the gel point can be precisely identified and located by monitoring the dynamic viscoelastic parameters throughout the reaction.[7,9,34–36] At the gel point the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ are congruent over the whole spectrum of frequencies and proportional to the frequency $\sim\omega^n$ with exponent n ranging from 0.5 to 0.8. The representation of log $G'(\omega)$ and log $G''(\omega)$ versus log ω at different stages of curing reaction is shown in Figure 6. It can be seen that the crossover between G' and G'' takes place at the critical conversion $\alpha \sim 7.8\%$ independently of the frequency applied. In the initial stage of the curing reaction G'' is greater than G', pointing the liquid nature of the medium. Beyond the gel point ($\alpha = 9.0\%$), G'

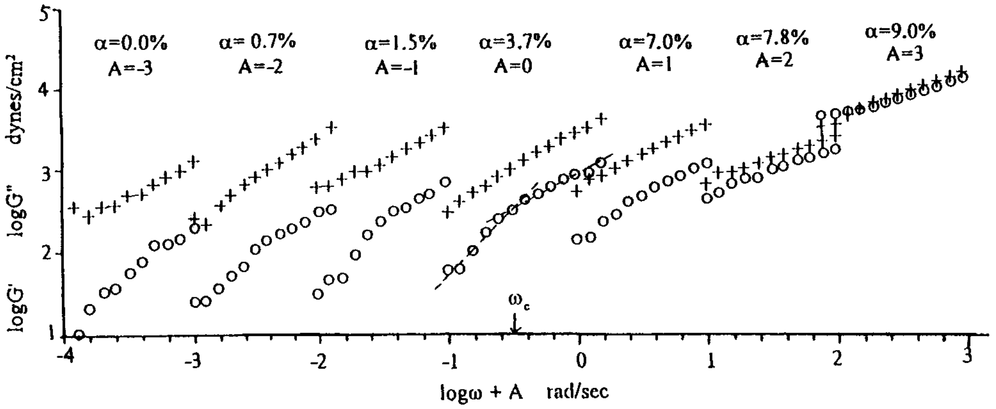

Figure 6. Log $G'(\omega)$ and log $G''(\omega)$ vs log ω at various degrees of curing. (○) $G'(\omega)$; (+) $G''(\omega)$.

Table 2. Parameters of Viscoelastic Properties

α (%)	log ω_c (rad/s)	exponent of G' at low frequency	exponent of G' at high frequency	exponent of G'' at low frequency
0.0	−0.36	1.73	0.69	0.88
0.7	−0.40	1.63	0.66	0.96
1.5	−0.43	1.72	0.81	0.84
3.7	−0.50	1.56	0.66	0.84
7.0	−0.57	1.41	0.69	0.78
7.8	−∞	0.59	0.59	0.59
9.0	−0.76	0.16	0.56	0.56

outweighs G'' at low-frequency region and G' levels off as the frequency decreases, indicating that the material has become a viscoelastic solid.

There are some analogies between the viscoelastic behavior presented in Figure 6 and that predicted by both the Rouse (free draining) and Zimm (dominant hydrodynamic interaction) models for solutions of linear polymers.[37] The Rouse model predicted that $G' = G'' \sim \omega^{1/2}$, while the Zimm model predicted that $G'' = 3^{1/2}G' \sim \omega^{2/3}$ in the high-frequency plateau region. Both Rouse and Zimm models predicted that $G' \sim \omega^2$ and $G'' \sim \omega^1$ in the liquid-type response low-frequency region. In cross-linking reactions, the critical frequency ω_c, defining the boundary between the liquid-type response and plateau regions, tends toward zero as the reaction proceeds toward gelation. We define the critical frequency, ω_c, as the frequency at which G' inflects. A typical example for defining ω_c is shown by the dashed lines in Figure 6 with a conversion $\alpha = 3.7\%$. This frequency, ω_c, decreases as the curing reaction proceeds and eventually reaches 0 at gel point. The values of ω_c are summarized in Table 2. Unfortunately, owing to the limitations of the instrument we did not do the rheological measurements at high frequency, which prevented accurate determination of the exponent n of G'' at high-frequency region. The exponents of G' in low- and high-frequency regions and G'' in the low-frequency region are also summarized in Table 2.

As shown in Figure 6 and Table 2, the exponents of G' in low- and high-frequency regions and G'' in the low-frequency region were around ~1.70, ~0.70, and ~0.90, respectively, as the degree of conversion $\alpha < 3.7\%$, which were close to the Zimm model predictions for linear polymer solutions. As the conversion $\alpha \geq 3.7\%$, both the exponents of G' and G'' at low-frequency regions decreased. At the gel point ($\alpha = 7.8\%$), the exponents n of G' and G'' were equal and around ~0.59, which was close to the high-frequency region in the Rouse model ($G' = G'' \sim \omega^{1/2}$) extends through the frequency range. The change from Zimm-like behavior to Rouse-like behavior suggested the transition from coillike microgel particles to chain-overlap-like macrogelation as the degree of conversion α increased and approached gelation. From the analogy between a solution of linear macromolecules and a cross-linking medium, the transition from liquid to solid can be depicted as a stage at which the response of an infinite molecule over the whole frequency spectrum is limited to short-range motions (short with respect to the dimensions of the molecule). Similar exponent of $n \sim 0.5$ was also reported for polyurethanes[35,38] and epoxy resins under stoichiometric conditions.[11]

The behavior of DLS correlation functions of polymer solutions corresponds to the relaxation contributed from osmotic modulus M_π and longitudinal modulus $M(t)$ [where $M(t) = K(t) + 4G(t)/3$, $K(t)$ is the time-dependent bulk modulus, and $G(t)$ is the time-dependent shear modulus]. However, the viscoelastic property corresponds to the relaxation of shear modulus $G(t)$. The relaxation times of these two measurements may be different from each other; however, it is interesting to compare the relaxation times obtained from these two measurements as the conversion of UPE/styrene system closes to gelation. Gelation of macromolecular systems is known as a typical phenomenon defined by the condition that the second moment of the cluster size distribution diverges.[39] This definition is equivalent to the divergences of M_w and of the static correlation length ζ, i.e., $M_w \rightarrow \infty$ and $\zeta \rightarrow \infty$, where ζ is proportional to the z-average of the root-mean-square radius of gyration of the formed clusters. In the present study, the gelation ofthe UPE/styrene system can be defined as the divergence of the slow-mode relaxation time, i.e., $\tau_s \rightarrow \infty$, of the polarized DLS correlation function, which corresponds to the critical frequency ω_c, while G' crossover with G'' is zero, i.e., $\omega_c = 0$. The infinite relaxation time of τ_s leads to the disappear of slow mode relaxation in DLS autocorrelation function after gelation.

Conclusion

In this study, we present V_v and V_H dynamic light scattering and dynamic viscoelasticity data of UPE/styrene in the vicinity of sol−gel transition. The autocorrelation functions of the V_v scattering are q-dependent before gelation and q-independent after gelation. The autocorrelation functions of V_H scattering are independent of the degree of curing; however, those of V_v scattering varied with the degree of curing. Before gelation the decay behaviors of autocorrelation functions of V_v and V_H scatterings were quite different. As the curing reaction approached gelation, the decay behavior of the V_v scattering varied and approached that of V_H scattering. The experimental results suggested that before gelation, concentration fluctuations dominated the V_v scattering, while after gelation, density and segmental reorientation dominated the V_v scattering. The dynamic viscoelastic data shows that the curing system changes from Zimm model-like behavior to Rouse-like behavior as the curing reaction proceeds from low conversion to gelation. Both the DLS and viscoelastic measurements demonstrated the behavior of divergence of relaxation time at gelation.

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