

Forced Rayleigh Scattering of Polystyrene-Polyvinylmethylether Mixtures

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Forced Rayleigh scattering measurements were made on mixtures of polystyrene (PS) labeled with a photochromic dye and polyvinylmethylether (PVME) over the range of temperature from 100° to 160° close to the phase separation temperature. The composition ratio of PS to PVME was 1/99. Time profiles of light intensity $I_d(t)$ diffracted at Bragg angles from the samples were quite anomalous. After initial decay of $I_d(t)$ to zero, $I_d(t)$ increased with time t to give a pronounced maximum, then followed by the diffusion process with a single decay rate. The results were interpreted as being due to that photobleached dye molecules enhanced aggregation of PS molecules in bulk PVME.

KEY WORDS: Forced Rayleigh Scattering/Diffusion Coefficient/ PS-PVME Mixtures/Aggregation/Photochromic Dye

INTRODUCTION

Polystyrene(PS) and polyvinylmethylether(PVME) are a typical polymer pair which are compatible at room temperature over the whole range of compositions. Their mixtures undergo phase separation at elevated temperatures with the lower critical solution temperature T_c above 100°C. A lot of experimental studies have been performed to elucidate the thermodynamic aspects of the phase transition¹⁻⁸, phase separation kinetics including spinodal decomposition^{9,10}, local chain dynamics¹¹⁻¹³, and viscoelastic properties¹⁴⁻¹⁷ of the PS-PVME mixtures. The results were compared with theoretical predictions.¹⁸⁻²²

Quite recently Shibasaki et al.²³ studied the effect of interaction between dissimilar polymer molecules on the slow chain dynamics in the concentrated dibutylphthalate solutions of PS-PVME mixtures combining flow birefringence and dynamic viscoelastic techniques. The results are consistent with their earlier conclusion¹⁷ that PS and PVME chains relax independently to each other at the long time end from the second plateau region to the terminal region. On the other hand, two experiments done recently showed that there was certain cooperativity in the orientational relaxation for polymer blends in melt.^{24,25} The effect has been tentatively explained by specific interaction named as "nematic interaction", which forces neighbouring polymer segments to orient in the same direction when strain is applied to the sample.

In order to further examine the effect on slow chain dynamics in polymer blends, we attempted forced Rayleigh scattering (FRS) measurements on mixtures composed of 1% PS labeled with a photochromic dye and 99% unlabeled PVME over the wide range of temperature and also of molecular weight of PS. The FRS technique is known

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as a unique technique to measure small values of the translational diffusion coefficient in melt. Unexpectedly, time profiles of the light intensity $I_d(t)$ diffracted from the mixtures were found quite anomalous at temperatures above 100°C. $I_d(t)$ exhibited a pronounced maximum after initial decay. In the temperature range studied, there occurred no macroscopic phase separation which might give very large scattered intensity. This paper describes preliminary results of FRS measurements on the PS-PVME mixtures along with qualitative discussion on the above-mentioned anomalous behavior.

EXPERIMENTAL

Materials

Polyvinylmethylether (PVME, Scientific Polymer Products) was purified using benzene and hexane as solvent and precipitant, respectively. Its weight average molecular weight M_w and a ratio M_w/M_n were estimated from GPC combined with low-angle light scattering measurements as 6.0×10^4 and 1.3, respectively. Three samples of narrow distribution polystyrenes (PS, Toso) with different molecular weights were used in this study. Their sample codes, M_w and M_w/M_n are listed in Table I. PS samples were labeled with a photobleachable dye of 2-nitro-4-carboxy-4'-(dimethylamino) stilbene following the labeling procedure described in an earlier paper.²⁶⁾ GPC combined with low-angle light scattering measurements showed that there was no change in either molecular weight or molecular weight distribution of the polymers during the labeling procedure. Mixtures of 1% labeled PS and 99% PVME were prepared by a freeze-drying procedure on molecularly mixed benzene solutions of weighed amounts of polymers for a week.

Methods

Dynamic viscoelastic measurements were made on the homogeneous PVME sample with a cone-and-plate type rheometer (RPX 750, Iwamoto) over a range of frequency from 10^{-2} to 1 s^{-1} . Storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, measured at temperatures from 23° to 80° were reduced to the reference temperature T_r of 60°C following the frequency-temperature superposition principle.

Forced Rayleigh scattering (FRS) measurements were performed with an instrument described elsewhere.²⁷⁾ In FRS spectroscopy, two coherent laser beams are crossed in an absorbing sample to produce an interference pattern with the fringe spacing of the order of μm . Absorption of light by dye molecules attached to polymer molecules from this interference pattern gives rise to a spatial periodicity in the

Table I Polymer Samples

Sample Code	$M_w/10^4$	M_w/M_n
PVME	6.0	1.3
F1	1.03	1.02
F4	4.39	1.01
F10	10.2	1.02

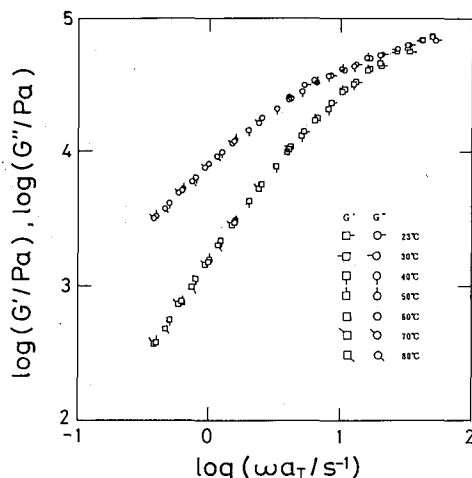


Fig. 1 G' and G'' of PVME in bulk are plotted against reduced frequency ωa_T . The reference temperature T_r is 60°C.

complex index of refraction of the sample. The time profile of the resulting optical grating is efficiently monitored by observing the light intensity I_d scattered at the Bragg angle from the sample. The intensity $I_d(t)$ diminishes with time t as the grating becomes more and more disrupted by the translational diffusive motion of polymer molecules in the system. Thus the FRS technique makes it possible to determine the diffusion coefficient of the probe chain very accurately. Mochromatic light from an Ar-ion laser ($\lambda = 488\text{nm}$) and from a He-Ne laser ($\lambda = 633\text{nm}$) was used as a writing and a reading beam, respectively. Acquisition and analysis of light intensity data, $I_d(t)$, diffracted from the mixture were handled with a homemade processor. Measurements were conducted at four temperatures of 100°, 120°, 140°, and 160°C.

RESULTS AND DISCUSSION

Viscoelastic behavior of the pure PVME sample

Figure 1 shows frequency dependences of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, of PVME in bulk. The shift factor a_T was fitted with the WLF equation (1), and the WLF coefficients C_1 and C_2 at $T_r = 60^\circ\text{C}$ were evaluated as 9.49 and 233, respectively.

$$\log a_T = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)} \quad (1)$$

At the low frequency end, $G''(\omega)$ is proportional to ω as is expected, but $G'(\omega)$ does not tend to reach the limiting slope of 2 characteristic of the terminal zone owing to the polydispersity of the sample. The steady viscosity η at the temperature where FRS measurements were made was calculated from the $G''(\omega)$ data in the figure with eq (1),

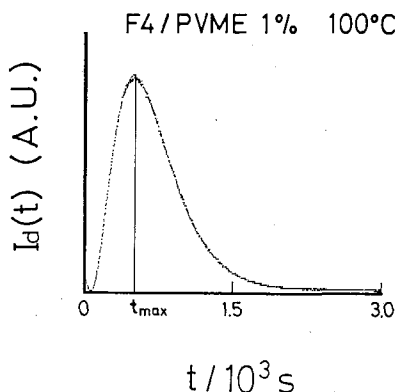


Fig. 2 A typical time profile of the light intensity $I_d(t)$ diffracted from the PS-PVME mixture.

and values estimated are tabulated in Table II.

FRS behavior of PS in the mixture

Figure 2 shows a typical time profile of the light intensity $I_d(t)$ diffracted at the Bragg angle (the grating spacing $d=4\mu\text{m}$) from the mixture of 1% PS in PVME at 100°C . The molecular weight of the PS sample is 43,900. When the sample was irradiated by the intense Ar-ion laser beam, sufficiently high scattered intensity was obtained at $t=0$. The $I_d(t)$ initially decayed down to a baseline value, then started to increase with increasing time to give a pronounced maximum at $t=t_{\text{max}}$, and again slowly decayed at the later stage. Very similar time dependence was observed for I_d of all mixtures with different M of PS as well as at different temperatures. It is to be noted here that light intensity I_s scattered from the samples before photobleaching only fluctuates around an average value of $\langle I_s \rangle$ for a long time interval even at the highest temperature of 160°C . This indicates that the unbleached mixtures with this composition (PS/PVME=1/99) may remain in the homogeneous state. Since $I_d(t)$ of the bleached samples became equal to the background value at $t \rightarrow \infty$ and the samples looked transparent by naked eyes, photobleaching of the dye molecules does not induce the macroscopic phase transformation. We also noticed that the $I_d(t)$ curve from a sample in which the dye molecules are molecularly dissolved in the PVME matrix decayed following a single exponential type of decay function without showing any maximum.

The decay of the $I_d(t)$ at the later stage could be fitted by eq (2) with a single decay rate Γ_d to all mixtures.

$$I_d(t) = \{A \exp(-\Gamma_d t) + B_1\}^2 + B_2^2 \quad (2)$$

Here A is the amplitude, and B_1 and B_2 are contributions from the coherent and incoherent background optical field, respectively. The Γ_d was estimated from a least-squares fit to an accuracy of 15%. Figure 3 shows a linear plot of Γ_d against the square of the wave vector q ($|q| = 2\pi/d$) for three mixtures at 100°C . It is seen from the figure that the straight lines connecting two points cross the origin for respective

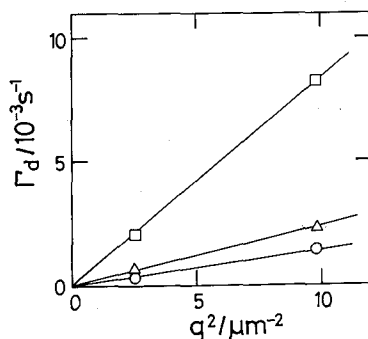


Fig. 3 The decay rate Γ_d obtained from a least-squares fit of eq (2) to the decay curve of $I_d(t)$ at the later stage is linearly plotted against the square of the wave vector q . Symbols are ($\square$) F1/PVME; ($\triangle$) F4/PVME; and ($\circ$) F10/PVME.

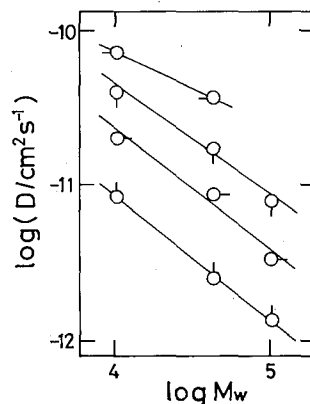


Fig. 4 The dependence of the diffusion coefficient D on PS molecular weight M at various temperatures. Symbols are ($\circ$) 100°; ($\odot$) 120°; ($\text{—}\circ$) 140°; and ($\times$) 160°C.

Table II Results of FRS measurements

D : the diffusion coefficient of PS; $t_{\max}$: elapsed time at which the maximum of the light intensity $I_d(t)$ was observed; X : the ratio of two $I_d(t)$ values at $t=t_{\max}$ and $t=0$.

Sample Code	T=100°C, $\eta_{\text{PVME}}=3500\text{p}$			T=120°C, $\eta_{\text{PVME}}=980\text{p}$		
	$D/10^{-12}\text{cm}^2\text{s}^{-1}$	$t_{\max}/\text{s}$	X	$D/10^{-12}\text{cm}^2\text{s}^{-1}$	$t_{\max}/\text{s}$	X
F 1/PVME	8.3	48	0.8	19.8	16	2.5
F 4/PVME	2.5	470	21	8.4	170	29
F10/PVME	1.34	1550	43	3.3	560	68

Sample Code	T=140°C, $\eta_{\text{PVME}}=324\text{p}$			T=160°C, $\eta_{\text{PVME}}=121\text{p}$		
	$D/10^{-12}\text{cm}^2\text{s}^{-1}$	$t_{\max}/\text{s}$	X	$D/10^{-12}\text{cm}^2\text{s}^{-1}$	$t_{\max}/\text{s}$	X
F 1/PVME	39.5	5.4	15	71	3.8	4.1
F 4/PVME	17.0	66	50	36	32	23
F10/PVME	7.8	250	63			

samples. Therefore the later stage is surely controlled by the slow diffusion process with the diffusion coefficient D which may be easily estimated as the slope of the respective straight lines ($\Gamma_d = Dq^2$). D values at different temperatures of 120°, 140° and 160°C could be estimated with the similar procedure, and are listed in Table II.

The forced fit of eq (2) to the decay curve of the $I_d(t)$ at the initial stage gave q -dependent D values, indicating that the process is not diffusion-controlled. For characterization of the anomalous time profiles of the $I_d(t)$, we picked up two quantities. One is $t_{\max}$ and the other a ratio X of two $I_d(t)$ values at $t=t_{\max}$ and $t=0$. The both quantities increased with increasing d , being the characteristic length for displacements of labeled PS molecules in the FRS measurements, and also increased with an

increase in M of PS. Table II lists values of $t_{\max}$ and X obtained at $d=4\ \mu\text{m}$. The $t_{\max}$ monotonically decreases with increasing temperature, whereas X looks to increase up to $T=140^\circ\text{C}$ and then tends to decrease with a further increase in T .

Figure 4 gives a plot of D against PS molecular weight. The M dependence of D is approximately represented by the power law,

$$D \propto M^{-\alpha} \quad (3)$$

In the T range from 100° to 140°C , the exponent α take a constant value of 0.76 ± 0.04 . We made additional FRS measurements on a PS-PVME mixture containing 1% labeled PS with $M_w=1,260,000$ at 100°C . The value of $D=1.7 \times 10^{-2} \text{cm}^2\text{s}^{-1}$ obtained is nicely located on the corresponding straight line extrapolated toward the higher molecular weight side in the figure. The exponent is smaller than unity, the value predicted for the model of the free-draining Rouse chain in the unentangled melt.

Since the molecular weight between entanglements M_e is 5,800 to PVME, the PVME chains surely form an entanglement network. Its mesh size is calculated about equal to the unperturbed radius of gyration R_g of PS with $M_w=10,000$ from empirical R_g - M_w relationships for PVME and PS.

$$R_g^2 = 1.35 \times 10^{-17} M_w \quad (\text{PVME}) \quad (4)$$

$$R_g^2 = 7.86 \times 10^{-18} M_w \quad (\text{PS}) \quad (5)$$

The molecular weight of the diffusing PS chains studied ranges from 10,300 to 102,000. Therefore the size of PS molecules is equal to or larger than the mesh size of the PVME network. According to the modern concept of entanglement dynamics,²⁸⁾ reptation of a single PS chain in the tube formed by surrounding PVME chains is expected to give the dependence of D on M like $D \propto M^{-2}$. Recent tracer diffusion study on entangled solutions of PS in dibutylphthalate has revealed that the M dependence of the tracer diffusion coefficient D_{tr}^∞ is accurately represented by the power law with the larger value of the exponent, 2.5.²⁹⁾ Therefore the diffusion process at the later stage is neither the free diffusion of the Rouse chain nor the reptation of the single chain topologically constrained in the tube.

The self diffusion coefficient D_s of the PVME chain in bulk can be roughly calculated by using the reptation theory and recent experimental results.^{30,31)} We have shown that the theoretical prediction eq (6) gives correct M/M_e dependence in the highly entangled state.³¹⁾

$$D_s \eta = (\rho R T R_g^2 / 6M) (M/M_e) \quad (6)$$

The absolute magnitude given by the theory is about five times larger than experimental values. From eqs (4) and (6) and $\eta=3.5 \times 10^3 \text{p}$, then D_s of the PVME chain with $M_w=60,000$ at $T=100^\circ\text{C}$ is calculated as $4.3 \times 10^{-11} \text{cm}^2\text{s}^{-1}$. In comparison of this value with D values tabulated in Table II, we see that D_s of the matrix PVME chain is much larger than D even for the lowest molecular weight PS molecules.

Irie and Tanaka³²⁾ found that PS with a small amount of azobenzene pendant

groups became insoluble in cyclohexane upon irradiation with ultraviolet light, while lower molecular weight azobenzene itself did not show any solubility change on photoisomerization. They showed that the formation of large precipitated particles was induced by photoisomerization of the azobenzene chromophores from the non-polar trans to the polar cis form. Deschamps and Leger³³⁾ made FRS measurements on entangled solutions of PS labeled at the chain end with one photochromic spiropyran molecule in cyclopentane. At temperatures close to the theta temperature, the diffracted light intensity continuously increased long after the exciting laser pulse stopped, and started to relax after attaining a maximum. Such an anomalous FRS signal has also been observed in the case of the concentrated solutions of PS in cyclohexane at the theta temperature.³⁴⁾ The appearance of the maximum may be ascribed to the formation of PS aggregates induced by the photoisomerization of the dye molecules.

The anomalous FRS signal observed for the PS-PVME mixtures may be explained with a similar idea. The labeled PS molecules are molecularly mixed in the PVME matrix unless they are irradiated with an exciting laser beam. As soon as the optical grating is formed in the samples due to photobleaching of the dye molecules, the unbleached PS molecules in the dark fringes of the interference pattern make diffusive motion for random spatial distribution in the samples towards the new equilibrium state. At the same time photobleaching of the dyes in the bright fringes induces aggregation of the bleached PS molecules. The phase angle of the diffractive electric field originated from the latter aggregation process is different from the first one by π . Therefore the total electric field E_T diffracted from the sample at the early stage may be expressed by two contributions with different signs, E_d from the unbleached PS and E_a from the bleached PS molecules.

$$E_T(t) = E_d(t) - E_a(t) \quad (7)$$

At $t \sim 0$, $E_d \gg E_a \sim 0$, thus the initial decay of $I_d(t)$ ($\equiv |E_T|^2$) is mainly determined by

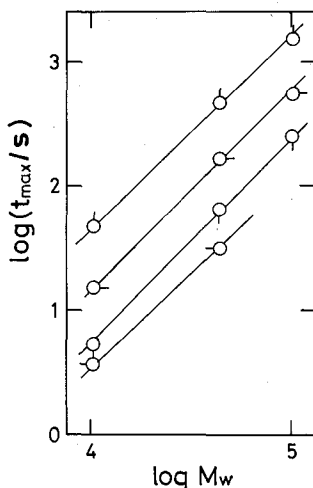


Fig. 5 The dependence of $t_{\max}$ on PS molecular weight M . Symbols are the same as in Figure 4.

the diffusion motion of unbleached PS molecules, and $I_d(t)$ becomes zero at $E_d = E_a$. On the other hand, the maximum of $I_d(t)$ can be related to the aggregation process and the $t_{\max}$ may be considered as the time needed for the formation of aggregated PS particles. As is shown in Figure 5, $t_{\max}$ is strongly dependent on PS molecular weight. If the power law is applied to the data as is expressed by the straight lines in the figure, the exponent reads as 1.6 ± 0.1 almost independent of T . The constancy of the exponent suggests that aggregation of PS molecules is not induced by macroscopic phase transformation in PS-PVME mixtures above T_c but by photobleaching of dye molecules. The magnitude of the exponent is not unreasonable if respective PS molecules were assumed to aggregate through the PVME matrix by the reptation mechanism, since $D \propto t_{\max}^{-1} \propto M^{-1.6}$.

From the above arguments, we suppose that we have observed diffusion of aggregated PS particles at the later stage. The radius a of the particles assumed as spheres is roughly estimated by applying the Einstein-Stokes formula (8) and using values of η_{PVME} and D tabulated in Table II.

$$a = (k_B T) / (6\pi\eta_{\text{PVME}}D) \quad (8)$$

The aggregation number N of PS molecules in the sphere is estimated from $N = 4\pi\rho a^3 N_a / 3M$ where ρ is the density of PS in bulk. At 140°C , N was evaluated as $2 \sim 3$, $7 \sim 8$, and 33 for $M = 1.03$, 4.39, and 10.2×10^4 , respectively. Thus N appears to increase with PS molecular weight.

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