Polymer Vol. 37 No. 25, pp. 5743–5746, 1996

0032-3861/96/$15.00 + 0.00

S0032-3861(96)00564-2

A new depolarized mode in a binary polymer blend in the critical region

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(Revised 10 May 1996)

The critical dynamics of a low molecular weight binary polymer blend of polystyrene and polyisoprene is studied near the critical point by dynamic light scattering. Fast and slow modes are observed in the polarized mode in accordance with previous experiments in similar low molecular weight binary polymer blend melts. A new mode is detected in the depolarized dynamic light scattering experiment that displays very weak q^2-dependence. The intensity of the new depolarized mode becomes zero at high temperatures and gains considerable intensity as the critical point is approached. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer blends; polystyrene; polyisoprene)

Introduction

Polymer melts and blends have been studied extensively over many years. Although polymers of different chemical nature are generally very incompatible due to the very small entropy gain of such mixtures as opposed to the entropy gain in mixtures of small molecules, there is a large practical interest in mixing polymers to get new materials, sometimes with exciting new features. The critical dynamics of binary mixtures of simple liquids has been studied in great detail[1,2], however the critical dynamics of binary polymer mixtures is a subject that is relatively new. Recent experiments[3–8] have indicated new phenomena associated with the critical dynamics of polymer-blend mixtures. In a previous dynamic light scattering study by Hair *et al.*[3] in a polymer blend of deuterated polystyrene and polybutadiene, two diffusive relaxation modes were observed that were interpreted in terms of a coupling between order–parameter relaxation and thermal diffusion modes. In contrast to these observations, Bates *et al.*[4] found only one single exponential decay for a polymer blend of polyisoprene (PI) and poly(ethylene–propylene). Polymer blends are supposed to behave in a mean field manner as long as the number of chain segments is sufficiently large[9–12].

The objective of the present investigation is to consider the critical dynamics of relatively low molecular weight polymer blends of polystyrene (PS) and PI in comparison with the previous reported experiments and to extend the current study to depolarized measurements as well, since both components of the polymer blend contain anisotropic segments.

Experimental

Three narrow molecular weight distribution samples ($M_W/M_N < 1.1$) of PI, $M_W = 1030$ and $M_W = 2350$, and PS $M_W = 1700$, were used with PS volume fractions $f_{PS} = 0.45$ and 0.6 for the low M_W PI and $f_{PS} = 0.45$ for the higher M_W PI. More details about the present blends can be found in *Table 1* and in a recent publication[13]. Mixtures of varying composition were prepared. The samples were sealed in a cylindrical light scattering cell and scattered light was collected at various scattering angles varying between 45 and 150°. Two scattering geometries (VV and VH; V = vertical and H = horizontal) were used by choosing the polarization of the scattered light, whereas the polarization of the incident beam was always perpendicular (V) with respect to the scattering plane. Photon correlation spectroscopy was employed to measure the autocorrelation functions of both the polarized, $G_{VV}(q, t)$, and the depolarized light scattering intensity, $G_{VH}(q, t)$, with an ALV-5000 digital correlator over the time scale of 10^{-7} to 10^3 s. The samples were filtered very carefully through a 0.22 mm filter from Millipore.

Results and discussion

Typical correlation functions in the VV geometry are shown in *Figure 1a* at various temperatures. The measured correlation functions in this configuration show a nearly exponential behaviour. The two well separated processes can be fitted with a double Kohlrausch–Williams–Watts (KWW) function:

$$G_{VV}(q,t) = \alpha_f \exp[-(t/\tau_f)^{\beta_f}] + \alpha_s \exp[-(t/\tau_s)^{\beta_s}] \quad (1)$$

treating α_f, α_s, β_f, β_s, τ_f, τ_s as adjustable parameters for the fast and slow modes respectively. From the measured correlation functions we identify both the fast and the slow modes with their corresponding relaxation rates and diffusion coefficients defined respectively by the relations $\Gamma_f = 1/\tau_f$, $D_f = 1/\tau_f q^2$, and $\Gamma_s = 1/\tau_s$, $D_s = 1/\tau_s q^2$. *Figure 1b* displays the typical decrease for D_f as the critical point, T_c is approached. Results from the fit to the KWW function, for β_f and the total average intensity $\langle I_{VV} \rangle$ are shown for several temperatures in *Tables 2–4*. It is evident that two relaxation processes are present at temperatures far above the critical point, however close to T_c the faster process dominates. The presence of these two modes confirm the reported dynamic light scattering (DLS) measurements by Hair *et al.* and it is in marked contrast to the behaviour

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Table 1 Molecular characteristics

Blend	f_{PS}	$T_{g,PS}$(K)	$T_{g,PI}$(K)	$T_{g,blend}$
PS(M_W = 1700)/PI(M_W = 1030)	0.45	320	208	257
PS(M_W = 1700)/PI(M_W = 1030)	0.6	320	208	272
PS(M_W = 1700)/PI(M_W = 2350)	0.6	320	212	277

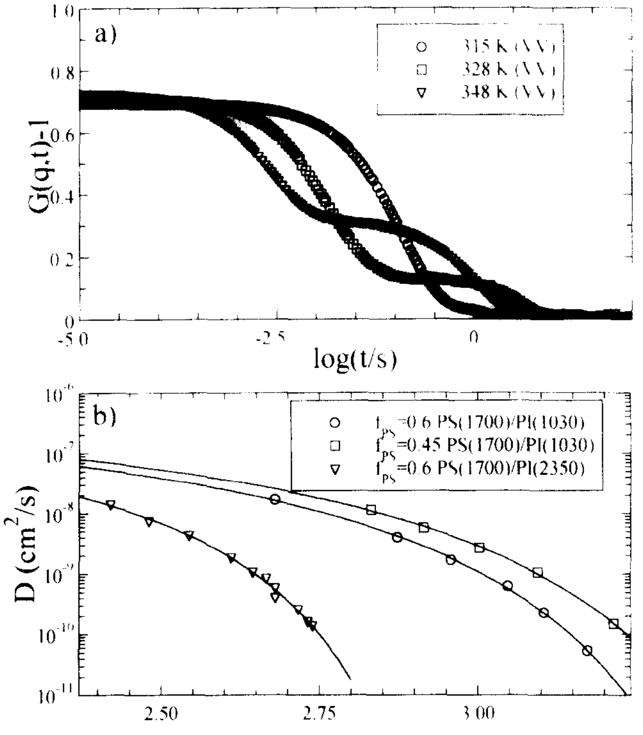

Figure 1 (a) The measured correlation functions show nearly exponential behaviour for the low M_W(= 1030) PI/PS blend with $f_{PS} = 0.6$. (b) The increase in D_f as $T \to T_c$ for the three different polymer blends

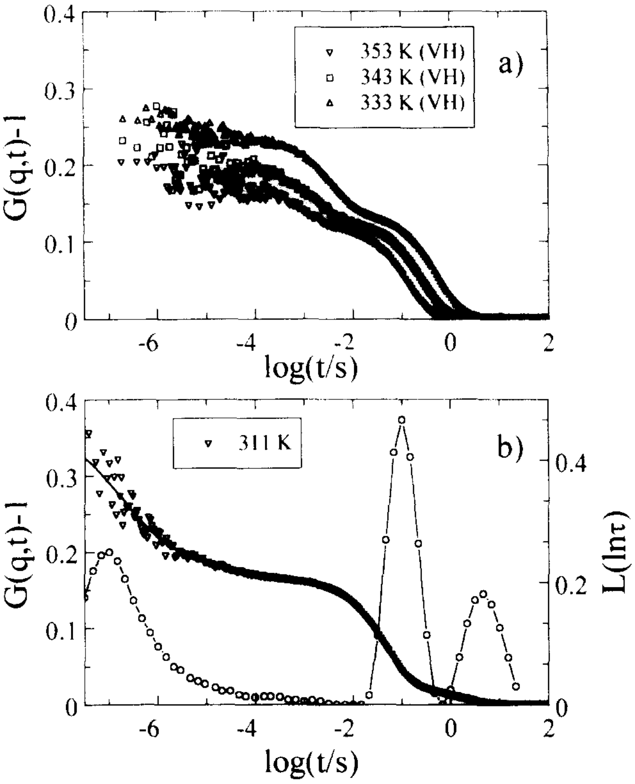

Figure 2 (a) Depolarized experimental correlation functions for the low M_W(= 1030) PI/PS blend with $f_{PS} = 0.45$ at several temperatures. (b) The faster segmental process, the new VH process and a slower process for the same blend near the critical point. The right Y-axis contains also the distribution of retardation times $L(\ln\tau)$ by making use of the inverse Laplace transform of the time correlation function. The three peaks correspond to the previously mentioned three processes

reported in ref. 4. For a given temperature from the different experimental correlation functions at different scattering angles it is verified that both modes are diffusive in nature, i.e. q^2-dependent ($q = (4\pi n/\lambda)\sin(\theta/2)$) (see *Figure 3b* for the VV experiment). The slow mode at temperatures far above the critical point might be associated to the slow process in one-component glass-forming systems arising from 'long range density fluctuations'[14]. According to Fischer *et al.*[14] the observed new ultraslow hydrodynamic mode ($\Gamma \sim q^2$) is caused by long density fluctuations indicating a nonhomogeneous distribution of free volume. The redistribution of free volume in space causes the new ultraslow mode. Fischer introduced a tentative qualitative model which describes the long range density fluctuations as a result of the coexistence of molecules with two different dynamic states which show up in the Fabry–Perot and Raman spectroscopy.

In the photon correlation experiments in the depolarized mode it was totally unexpected to observe a new relaxation mode in the VH scattering geometry in addition to the faster segmental mode. This new mode was observed for the first time five years ago, however it was not reported until now due to fact that there was no theoretical explanation for its existence. In a homodyne experiment the desired normalized field correlation function $g(t)$ is related to $G(t)$ by:

$$G(q,t) = A[1 + f^*|\alpha g(q,t)|^2] \tag{2}$$

where A is the baseline measured at long log times, f^* is the instrumental factor calculated by means of a standard PS/CCl$_4$ dilute solution, and α is the fraction of the total depolarized scattering intensity arising from fluctuations in the optical anisotropy with correlation times longer than 10^{-7} s. In principle both local segmental orientation fluctuations and overall molecular orientation can modulate the depolarized Rayleigh scattering from bulk polymers consisting of optically anisotropic segments[15]:

$$C_{VH}(q,t) = \left\langle \sum_{ij} \alpha_{yz}(j,t)\alpha_{yz}(i,0)\exp\{iq[r_j(t) - r_i(0)]\} \right\rangle \tag{3}$$

where $\alpha_{yz}(j,t)$ is the yz component of the laboratory fixed polarizability tensor of the jth segment at $rj(t)$ and $\langle\ \rangle$ denotes a statistical average. The present polymer

Table 2 Relaxation characteristics for the VV and VH experiments

VV experiment PS(M_W = 1700)/PI(M_W = 1030) f_{PS} = 0.45			VH experiment PS(M_W = 1700)/PI(M_W = 1030) f_{PS} = 0.45		
T(K)	β_f	$\langle I_{VV}\rangle$ (kHz)	T(K)	β_f	$\langle I_{VH}\rangle$ (kHz)
38	1.00	334	38	0.98	3.4
40	1.00	168	40	0.99	2.9
50	0.95	134	50	0.78	1.0
60	0.95	91	60	0.82	0.82
70	0.94	90	70	0.75	0.83
80	0.96	94	80	0.67	0.84

Table 3 Relaxation characteristics for the VV and VH experiments

VV experiment PS(M_W = 1700)/PI(M_W = 23501030) f_{PS} = 0.6			VH experiment PS(M_W = 1700)/PI(M_W = 1030) f_{PS} = 0.6		
T(K)	β_f	$\langle I_{VV}\rangle$ (kHz)	T(K)	β_f	$\langle I_{VH}\rangle$ (kHz)
-	-	-	38	0.87	2.6
42	1.0	119.5	42	0.88	1.1
49	0.94	58.3	49	0.86	0.7
55	0.95	57.4	55	0.83	1.6
65	0.94	53.1	65	0.86	1.3
75	0.96	42.2	75	0.83	1.2
100	0.94	36.9	100	0.79	1.1

Table 4 Relaxation characteristics for the VV and VH experiments

VV experiment PS(M_W = 1700)/PI(M_W = 2350) f_{PS} = 0.6			VH experiment PS(M_W = 1700)/PI(M_W = 2350) f_{PS} = 0.6		
T(K)	β_f	$\langle I_{VV}\rangle$ (kHz)	T(K)	β_f	$\langle I_{VH}\rangle$ (kHz)
92	1.00	552	92	0.96	11.7
95	0.96	338	95	0.92	9.2
100	1.00	250	100	0.90	3.9
110	0.95	172	110	0.86	3.3
120	1.00	152	120	0.82	3.0
130	0.91	148	130	0.72	2.4
140	0.90	129	140	0.67	2.0

blends are composed from optically anisotropic polymers since the values of the optical anisotropies per monomer of the two homopolymers in solution are $\langle\gamma^2\rangle_{PS} = 38\text{Å}$ and $\langle\gamma^2\rangle_{PI} = 11\text{Å}$[16]. *Figure 2a* displays an experimental correlation function near the critical point at 311 K where the segmental mode which is VH active is observed as expected, together with the new depolarized mode. The experimental correlation function is further analysed by making use of the inverse Laplace transform[17] of the time correlation function:

$$G(q,t) = \int_{-\infty}^{\infty} L(\ln\tau)\exp(-t/\tau)d\ln\tau \qquad (4)$$

where $L(\ln\tau)$ is the distribution of retardation times. The retardation time spectrum that is also shown in *Figure 2b* shows very clearly three peaks. The faster one corresponds to the peak of segmental dynamics in the blend, the intermediate peak corresponds to the new depolarized mode and there is also a slower peak of lower intensity. Far above the critical point the local segmental dynamics becomes very fast and lie outside the window of our correlator, so only the new depolarized mode and the slower mode are observed. In *Figure 2a* one can see that the intensity of the faster of the two remaining processes that is identified with the new depolarized mode is losing intensity as the temperature increases from 33 to 353 K. Most interesting is the dramatic difference in the absolute intensity I_X of this mode relative to the intensity of neat toluene I_{tol} (as can be inferred from *Figure 2b* and *Figure 3a*), that nearly goes to 0 at high temperatures far above T_c for all three polymer blends. However its intensity grows remarkably as one approaches the critical point (see *Figure 2b*). Results for the VH experiment from the fit to the KWW function, for β_f of the new depolarized mode and the total average depolarized intensity $\langle I_{VH}\rangle$ are shown for several temperatures in *Tables 2–4*.

The present experimental findings of the VH experiment can be explained with a new theory for polymer blends developed by Likhtman and Semenov[18]. They show that as the critical point is approached the dominant contribution to the VH scattering comes

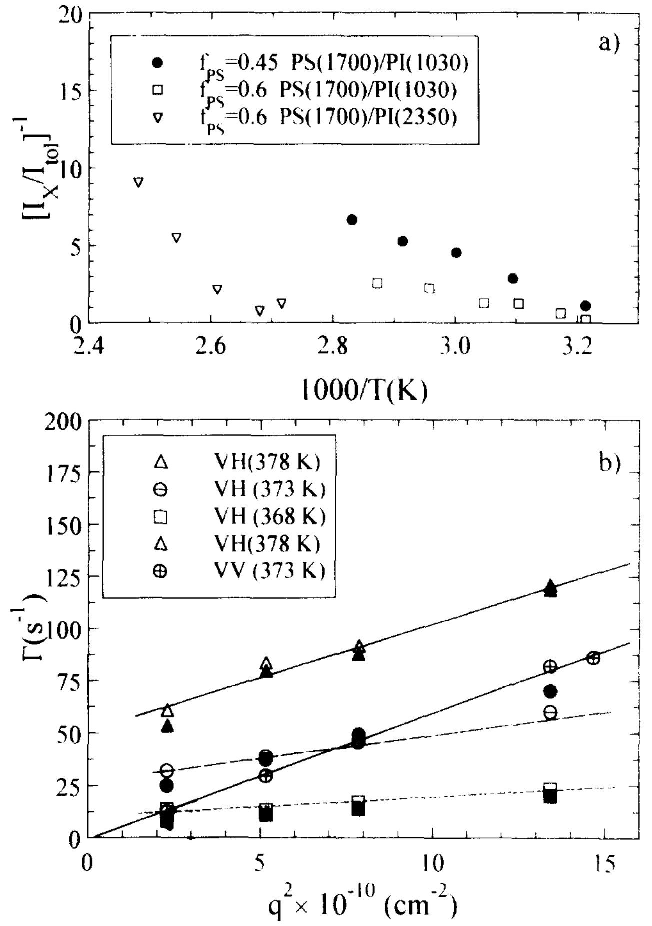

Figure 3 (a) The absolute intensity I_X of the new depolarized mode relative to the neat toluene intensity. (b) q-dependent measurements of the new VH mode for the higher M_w(= 2350) PS/PI blend with $f_{PS} = 0.6$ at 368, 373 and 378 K. For comparison we show the q^2-dependence of the fast diffusive mode at 373 K. There is satisfactory agreement between the experimental (open symbols) and theoretical values (filled symbols)

from composition fluctuation induced double scattering. It is well known that single scattering from composition fluctuations is isotropic in nature, whereas multiple scattered light includes both VV and VH components. The q-dependent measurements of this VH mode gave the dependence shown in *Figure 3b*. For comparison we show the q^2-dependence of the fast diffusive mode at 373 K. The observed finite slope of the VH data can be related to the theoretical prediction by Likhtman and Semenov[18]

$$\frac{1}{\tau_{VH}} = 4Dq_0^2\left(1 - \cos\frac{\theta}{2}\right)^{\frac{1}{2}} \qquad (5)$$

where $q_0 = 2\pi n/\lambda$ and $D = 1/\tau_{VV}q^2$. *Figure 3b* shows the truly satisfactory agreement between the experimental (open symbols) and theoretical values (filled symbols) for the PS(M_W = 1700)/PI(M_W = 2350) blend at three different temperatures, 368, 373 and 378 K. Furthermore, Likhtman and Semenov predict a departure from simple exponential decay far from the critical point. An inspection of *Tables 2–4* shows that the β parameter of all blends in the VH experiment indeed decreases with increasing temperature, in agreement with the theoretical prediction. A detailed account of the experimental procedures and data and comparison with the newly developed theory will be reported elsewhere[19].

Conclusions

The critical dynamics of a low molecular weight binary polymer blends studied near the critical point by polarized and depolarized dynamic light scattering continues to generate interest. The study described above clearly illustrates that essentially two diffusive decay rates are observed in the VV configuration, however close to the critical point the faster rate dominates in accordance with previous experiments in similar low molecular weight binary polymer blend melts. The new depolarized mode displays very weak q^2-dependence, its intensity vanishes at temperatures far above the critical point, but becomes very strong close to the critical point.

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