PHOTON CORRELATION SPECTROSCOPY OF INTERACTIVE POLYMER SYSTEMS

G. FYTAS, K. CHRISSOPOULOU, S. H. ANASTASIADIS,†
D. VLASSOPOULOS and K. KARATASOS
Foundation for Research and Technology-Hellas
Institute of Electronic Structure and Laser
P.O. Box 1527, 71110 Heraklion, Crete, Greece

ABSTRACT: We present two recent applications of dynamic light scattering to study order parameter fluctuations in chemically dissimilar polymer systems: (i) Diblock copolymer solutions near the disorder to order transition with wavevectors $q \sim q^*$ at the maximum of the structure factor $S(q^*)$, (ii) Binary polymer blends near the macrophase separation temperature in the low q limit.

1. Dynamic Structure Factor of Diblock Copolymer Solutions

Diblock copolymers AB are thermodynamically single component systems with interacting chemically dissimilar blocks that unlike binary polymer blends, cannot macrophase separate. Instead these systems can self assemble at low temperature below the T_{ODT} and/or concentration above φ_{ODT} in a common solvent depending on the overall polymerization index $N=N_A+N_B$. The transition (ODT) from a disordered to an ordered state is clearly manifested in the static structure factor S(q). Since the most probable composition fluctuations $\psi_q(t)$ occur a finite $q=q^* \sim O(R^{-1})$ (R is the size of the AB chain), S(q) peaks at q^* and for a monodisperse diblock vanishes in the thermodynamic limit $q \rightarrow 0$ [1,2].

Nowadays the dynamic structure factor S(q,t) can be best studied by photon correlation spectroscopy (PCS) mainly due to its broad time range provided q^* falls within the range of the (low) light scattering q's. Hence, synthesis of very high

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† Also at University of Crete, Physics Department, 71003 Heraklion, Crete, Greece

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molecular weight AB polymers is a crucial requirement. At such high N, the measurements of S(q,t) near ODT should be performed in solution even for the case of weakly unfavorable interactions (χ) between A and B segments; it is the product χN that controls the phase morphology. For low molecular weight AB melts [3,4] near T_{ODT}, S(q,t) can be studied only at low q/q^* values i.e. far from the maximum of S(q). For symmetric AB copolymers within the mean-field approximation [2]

$$S(q) \propto N\left[F(x) - 2\chi N\right]^{-1} \qquad (1)$$

where the function F(x) is a combination of the Debye correlation functions for unperturbed Gaussian coils depending on $x=(qR)^2$. S(q) shows a maximum at x^* for which $F(x^*)=2\chi N$.

Figure 1 shows the autocorrelation function of the polarized light scattering intensity $(G_{VV}(q,t)-1)/f^* \propto |S(q,t)|^2$ (f^* is a measure of the coherence area) for a 7.1 wt% solution of styrene-isoprene diblock copolymer (SI-1M) (Table 1) in the toluene for qR=1.35 at 20°C.

TABLE 1: Molecular characteristics

Sample	$M_w(10^6)$	w_{PS}	N	f_{PS}	φ_{ODT}
SI-53 [5]	0.172	0.53	2042	0.50	0.195
SI-1M [6]	1.04	0.44	12477	0.41	0.067

The spectrum of relaxation times L(lnτ) (upper inset of Fig. 1), obtained from the inversion of the experimental $G_{VV}(q,t)$, displays a main peak at τ~0.02 s. This mode corresponds to the main relaxation of the composition fluctuations in disorder diblocks relaxing via chain reptation; for the SI-1M/toluene system, the mode is probed near the maximum of the static structure factor and, thus, it exhibits the highest intensity, I_1 [6]. The fastest weak peak of L(lnτ) at $\tau\sim3\times10^{-5}$ s, on the other hand, is due to the total concentration fluctuations decaying via cooperative diffusion and hence it is not diblock copolymer specific. Its intensity I_{coop} relative to that of the main mode, $I_{coop}/I_1 \sim g/N$ ($g\sim\varphi^{-5/4}$ is the number of monomers per blob) is expectedly small for high N's even in the absence of thermodynamic effects. The intermediate process in L(lnτ) at $\tau\sim10^{-3}$ s can be attributed to composition fluctuations relaxing via Rouse-like chain conformation

motions in times shorter than the main chain reptation process [6]. This mode can be resolved for sufficiently high N and observed by PCS due to the refractive index contrast between the two blocks, i.e. it is invisible in high MW homopolymers. No additional process is observed in the L(lnτ) of SI-1M.

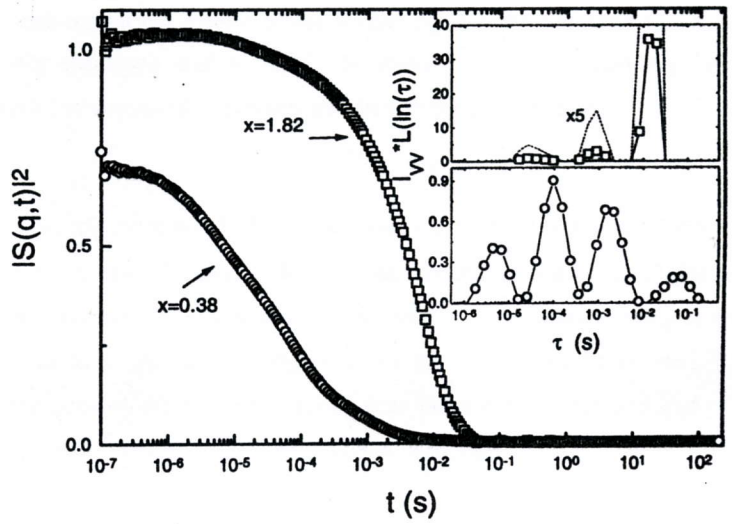

Figure 1. Concentration correlation functions at 23°C for 7.1 wt% SI-1M/toluene at $x=(qR)^2=1.82$ (□) and for 18.7 wt% SI-53/toluene at x=0.38 (O). The insets show the distribution of relaxation times L(lnτ) multiplied by the total polarized intensity normalized to that of toluene.

The behavior is modified for low MW AB with qR<1. For 18.7 wt% SI-53 (Table 1) solution in toluene, the coherent scattering function also shows three peak structure, however, the assignment is different. While the fast process corresponds, like before, to the cooperative diffusion, the intermediate peak is now the diblock copolymer mode due to chain reptation. The third peak in L(lnτ) of SI-53 corresponds to the chain self diffusion detectable due to chemistry imperfections leading to small but finite composition polydispersity in block copolymers [7,8]. This is analog to the incoherent scattering from size polydispersity of colloidal particles [9]. The polydispersity process is not observed in SI-1M since I_1 dominates the scattering for $q/q^*\cong1$ whereas I_{poly} is

more evident at $q \to 0$. The slowest weak process for SI-53/toluene is attributed to the long range density fluctuations [10]. Thus, the resolution of the relaxation processes in a dynamic light scattering experiment enables the assignment of the different contributions to the total static structure factor facilitating the comparison with theoretical predictions.

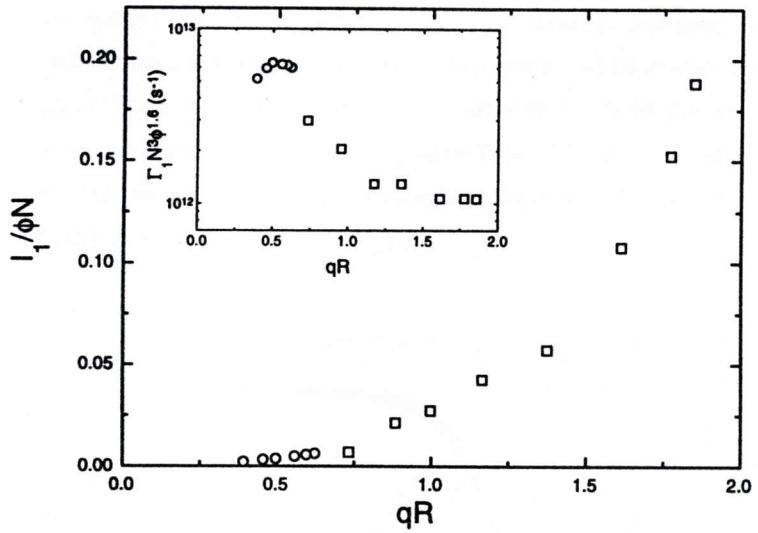

Figure 2. Intensity of the main internal copolymer mode, I_1, normalized with the total number of segments and the volume fraction of the polymer in the solution for the SI-1M/toluene (❑) and SI-53/toluene (O) as a function of qR. The insets shows the relaxation rate plotted according to Eq. (4) version qR.

Figure 2 shows the intensity of the copolymer specific mode reduced with the concentration and number of segments, $I_1(q)/\varphi N$, for the two SI copolymers covering different qR ranges. The net S(q) (free from the polydispersity contribution) becomes vanishingly small at low qR in accordance with the prediction of Eq. 1 for monodisperse diblocks.

$$S(q \to 0) \propto q^2 R^2 \qquad (2)$$

For the SI-1M, the q^* appears to fall into the highest q-range of the PCS; the S(q) of even higher MW SI clearly shifts [11] to lower q. For $q<q^*$, S(q,t) supports the theoretical prediction :

$$S(q,t) \sim S(q) \exp\left[-\Gamma_1(q)t\right] \qquad (3)$$

In the low qR limit, the collective thermal decay rate $\Gamma_1(q) \propto q^2/S(q)$ becomes q-independent and equals the inverse of the longest chain relaxation time τ_1, i.e. scales with N_e/N^3 for entangled chains (N_e is the mean number of monomers between entanglements). For entangled copolymer solutions in the low qR limit

$$\Gamma_1 \simeq \varphi^{3(1-\nu)/(3\nu-1)} N_e / N^3 \qquad (4)$$

where the scaling exponent ν=0.59 for good solvent. The effect of the proximity to the ODT in S(q,t) is expected for $q \equiv q^*$. The dramatic increase of $S(q^*)$ (Eq. 1) due to the unfavorable thermodynamic interactions should lead to significant slowing down of $\Gamma_1(q \equiv q^*)$. As shown in the inset of Figure 2 for the SI-1M, the decay rate of long wavelength composition fluctuations is about three times times faster than that of ψ_{q^*}. For the shorter SI-53, $\Gamma_1 \sim q^0$ at low qR values even near φ_{ODT}.

2. Interaction-Induced Anisotropic Light Scattering from Polymer Blends

The static structure factor of binary polymer blends A/B assumes its maximum value S(0) in the thermodynamic limit q=0 and hence S(q,t) is best studied by PCS [12]. For blends in the one phase region far above the glass transition (T_g), S(q,t) decays exponentially with $\Gamma_c = Dq^2$ where D is the interdiffusion coefficient; only very close to the critical point, T_s, (Ising regime) where $q\xi >> 1$ (ξ is the correlation length), $\Gamma \sim q^3$ [13]. In the mean field approximation, $S(0) \propto \varepsilon^{-1}$ where $\varepsilon = 1 - T_s/T$.

Such polymer mixtures near and above T_s are isotropic on macroscopic scales, and single light scattering from composition fluctuations is also isotropic. Due to the chain-like nature of macromolecules, it is conceivable, however, that instant snap-shots of the spatial order parameter (composition) fluctuations of $O(\xi)$ can be both inhomogeneous and anisotropic, i.e. not exactly spherical; light scattering from these transient anisotropic domains will be depolarized. Anisotropic scattering could also

arise from fluctuation-induced segmental orientational correlations as recently considered for short diblocks [14] near ODT; this is in fact weak (I_{VH}~$N^{-3/2}$).

The presence of dynamic depolarized light scattering from critical polymer blends already 20-30 K above T_s was recently revealed in five chemically different systems A/B. In the examined temperature region near T_s, all polymer mixtures exhibit single isotropic scattering. Figure 3 shows the polarized (VV) and depolarized (VH) intensity correlation functions $|C_{VV}(q,t)|^2=(G(q,t) - 1)/f^*$ a polystyrene (PS) / poly(methyl phenyl siloxane) (PMPS) blend (T_s=100°C) with PS volume fraction f_{PS} = 0.5, at 120°C and q=0.027 nm^{-1}.The $|C_{VV}(q,t)|^2$ exhibits two relaxation processes: a fast, which is the well-known interdiffusion [12], and a slow which will be discussed at the end of this paper. The two relaxation processes are not related with the fast segmental orientation dynamics of dense polymers near T_g, since T_g (= -3°C) of this blend is rather low. While the fast process is present in all examined blends near T_s, the slow relaxation can be hardly seen in blends far above T_g [12].

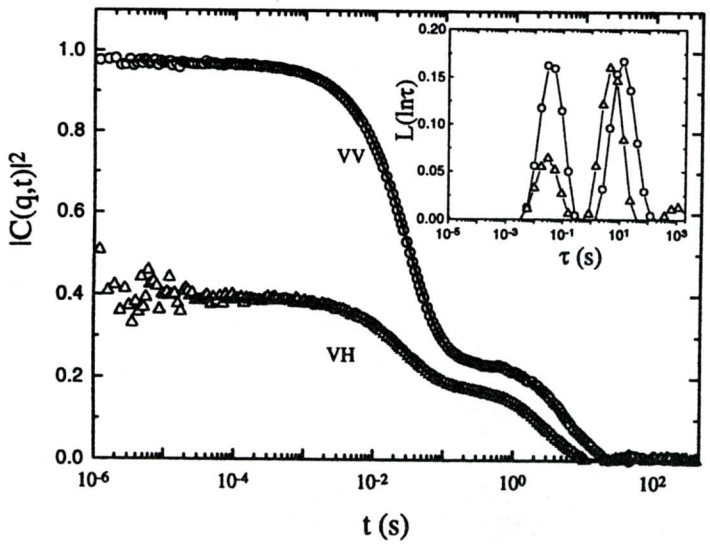

Figure 3. Correlation functions in the VV(O) and VH(Δ) geometries for a PS/PMPS blend with f_{PS}=0.5, at 120°C and q=0.027 nm^{-1}. The inset shows the corresponding distributions or relaxation times.

The fast process of $G_{VH}(q,t)$ shows the following characteristic features: (i) $C_{VH}(q,t)=[(G_{VH}(q,t)-1)/f^*]^{1/2}$ exhibits non exponential shape, $\exp[-(\Gamma t)^{\beta}]$ with $\beta\cong0.8$, (ii) the rate Γ exhibits distinctly weaker q-dependence than Γ_c of S(q,t) with a finite intercept at $q \to 0$, (iii) Γ exhibits a critical slowing down, (iv) it is an induced process with intensity $I_{VH} \propto \varepsilon^{-2}$ whereas I_{VV}~ε^{-1} and, (v) I_{VH} is essentially not related to permanent segmental optical anisotropy and observed under single VV scattering conditions. A theoretical account of this new VH process in critical blends is based on fluctuations induced second order scattering, which, while insignificant for the strong single VV scattering, provides the dominant contribution to the dynamic VH scattering intensity. A quantitative assessment of dynamic double scattering from composition fluctuations in a symmetric near critical blend (f_A=0.5, N_A=N_B=N) leads to [15] :

$$C_{VH}^{(2)}\left(\mathbf{k}_0,\mathbf{k},t\right) = I_0 k_0^4 A^4 \int d^3\mathbf{Q}\, S\left(\mathbf{k}-\mathbf{Q},t\right) S\left(\mathbf{Q}-\mathbf{k}_0,t\right) \times \left[f(\mathbf{Q})f^*(\mathbf{Q}) + f(\mathbf{Q})f^*\left(\mathbf{k}_0+\mathbf{k}-\mathbf{Q}\right)\right] \quad (5)$$

where $f(\mathbf{Q})=4\pi\,(\mathbf{Qe_0})\,(\mathbf{Qe})\,/\,[Q^2-(k_0+i/L)^2]$, $\mathbf{e_0}$ and $\mathbf{e}$ are the unit vectors for the electric field polarization of incident and scattered light, $\mathbf{k_0}$ and $\mathbf{k}$ are the corresponding wave vectors, $A=\partial n/\partial \varphi$ the refractive index increment and I_0 is the intensity of the incident beam. In the derivation of Eq. 5, it was assumed that the size of the scattering volume L is finite, i.e., $k_0L>>1$. While no optical anisotropy is explicitly assumed, formally the form anisotropy of the 3D patterns of composition fluctuations is reflected in the structure factors (in Eq. 5) which are anisotropic with respect to the orientation of Q (for fixed $\mathbf{k_0}$ and $\mathbf{k}$). Near the critical point, $S(q,t)$~$S(0)/(1+q^2\xi^2)\exp(-Dq^2t)$ and, for $k_0\xi<<1$, $C_{VH}^{(2)}(\theta,t)$ (Eq. 5) at a scattering angle θ can be approximately written as:

$$C_{VH}^{(2)}(\theta,t) \cong I_{VH}^{(2)} \exp\left(-4Dk_0^2t\right) \sinh\left(4Dk_0^2t\cos(\theta/2)\right) / 4Dk_0^2t\cos(\theta/2) \quad (6)$$

where the double scattering contribution to the VH intensity is:

$$I_{VH}^{(2)} \sim I_0 A^4 k_0^8 L\, S^2(0) \propto N^2\varepsilon^{-2} \quad (7)$$

The strong molecular weight dependence in eq. (7) is important since it makes essentially the effect polymer-specific. Further, eq. (6) can readily accommodate the

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edited by

E. R. Pike

Clerk Maxwell Professor of Theoretical Physics,
King's College,
London, U.K.

and

J. B. Abbiss

Chief Scientist,
Singular Systems,
Irvine, California, U.S.A.

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