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Dynamic Structure Factor of Homogeneous Diblock Copolymers Solutions

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Summary: The dynamics of homogeneous diblock copolymer solutions in the mean field regime sensitively depends on the composition polydispersity at constant chain length polydispersity. It was observed by photon correlation spectroscopy that the decay of the order parameter fluctuations in high molecular mass diblock copolymers solutions in a common solvent can change from a pure relaxational to a pure diffusive character. A rationalization of this behavior is presented.

Prediction of the dynamic response of diblock copolymers relies on the identification of the dominant mechanisms in the relaxation of the order parameter (composition) fluctuations, $\phi_q(t)$, manifested in the intermediate scattering function (dynamic structure factor) S(q,t) of the system. The contribution of different relaxation processes can be deduced from the distribution of relaxation times L(lnτ) derived from the inverse Laplace transformation of S(q,t) measured with photon correlation spectroscopy[1] In homogeneous diblock copolymer solutions three relaxation modes can be resolved with this approach. The fastest relaxation mode is the cooperative diffusion[2], responsible for the relaxation of the concentration fluctuations and is therefore not block copolymer specific. It is the other two processes which determine the properties of S(q,t) and reflect the cleanness(polydispersity) of the diblock copolymer chains. For an ideally monodisperse diblock copolymer system[3,4]:

$$S(q,t) = S(q)\exp(-\Gamma_1 t) \qquad (1)$$

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where Γ_1 is the overall chain relaxation. The most probable $\phi_q(t)$ have wave vectors q~q* with q*R~O (1) (R being the chain radius of gyration) and hence the static structure factor S(q) peaks[5,6] at a finite q*. The presence of a finite composition polydispersity leads to an additional contribution[7,8]:

$$S(q,t) = S_1(q)\exp(-\Gamma_1 t) + S_2(q)\exp(-D_s q^2 t) \qquad (2)$$

where S_i is the structure factor of the i-th process and $D_S(=\Gamma_2/q^2)$ is identified with the chain self diffusion in the mean field regime. The contribution of the two relaxation mechanisms to the thermal decay of $\phi_q(t)$ with wavelength $2\pi/q$ is schematically shown in Fig. 1.

The chain relaxation(first term in eq. 2) can relax $\phi_q(t)$ as shown for the first(1) process in Fig. 1 and is light scattering active due to the refractive index contrast between the two blocks. Its contribution to the total S(q) is:

$$S_1(q) = \frac{1}{(F(f,q^*) - 2\chi N)(1 + (q-q^*)^2 \xi^2)} \qquad (3)$$

where N is the total number of monomers in the chain, F(f,q*) is a function of Gaussian form factors, f is the block copolymer composition and ξ is the coherence length. The $S_1(q)$ peaks[9,10] at q* and is subsequently responsible for the peak in S(q).

The self-diffusion process(2)(second term in eq. 2) relates to the exchange of two block copolymers chains. According to Fig. 1, this process would be invisible if all chains were exactly the same(monodisperse) because of the absence of composition fluctuation($\phi_q(t)$) and hence light scattering. The characteristics of this relaxation mode read[7,8]:

$$S_2 = \frac{\kappa_o}{(1 - 2\chi\kappa_o\phi^{1.6}N)} \qquad (4)$$

$\kappa_o = \langle f^2\rangle - \langle f\rangle^2$ is the composition polydispersity and ϕ the polymer volume fraction; for ideally monodisperse($\kappa_o=0$) diblocks $S_2=0$ and eq. 2 become identical with eq. 1. The effect of the composition polydispersity on the experimental S(q,t) and the

Figure Captions

Fig. 1: Composition fluctuations of wavelength 2π/q for the component A in a compositionally polydisperse diblock A-B decay via chain overall motion (1) and/or center of mass diffusion (2). The size of the boxes visualizes the different block lengths i.e. the composition polydispersity.

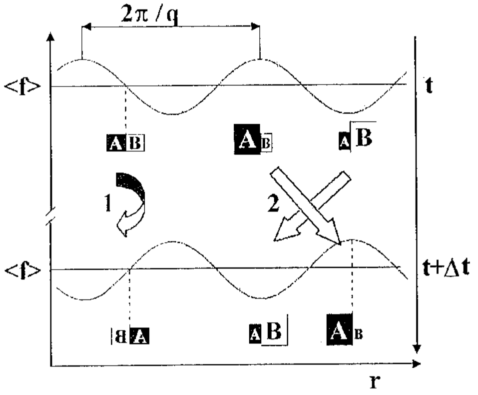
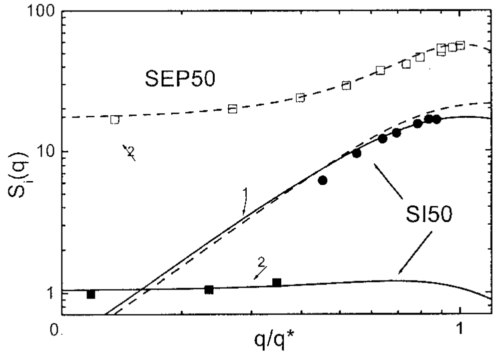


Fig. 2: Experimental and theoretical prediction(lines) for the structure factors S_i of the two process(es)(i=1,2) in eq. 2 associated with the order parameter fluctuations for 2.85 wt% SI50 (solid symbols and lines) and 2.88 wt% SEP50 (open symbols and dashed lines)(Ref. 14).



independence of the two modes in eq. 2 has been experimentally shown in several investigations[7-11] at low magnifications, i.e. $q/q^* << 1$. In this low q range, S_2 is q-independent and the self-diffusion can be readily measured even at low polydispersity since S_1, $S_2/S_1(q) \approx \kappa_o/N(qR)^2$ the relative contribution of S_2 increases with decreasing q.

With increasing magnification($q > 0.5q^*$) S_2 was found to increase with q and for polydisperse high molecular weight styrene-isoprene(SI) diblock copolymers becomes the main process of S(q,t) and peaks at q*. In a new theoretical approach[12,13] to the $\phi_q(t)$ of polydisperse diblock copolymers, S(q,t) still retains the bimodal structure of eq. 2 but the q-dependence of S_i of the two contributions has changed. This alteration depends sensitively on κ_o and the proximity to the ordering transition(ODT).

Far from ODT in the disordered homogeneous state the predicted behavior near q* was proven by examining the effect of κ_o introduced by partial hydrogenation of the SI to styrene-(ethyl-alt-propylene)(SEP). Figure 2 shows the experimental points and theoretical contributions, $S_i(q)(i=1,2)$, to the total S(q) of symmetric SI50(solid symbols) and its twin SEP50(open symbols). In SI50 with low κ_o the two contributions of eq. 2 are well described theoretically(solid lines). The weak S_2 is virtually q-independent and $S_1(q)$ is responsible for the peak in S(q). Furthermore we found that $S(q \sim q^*,t)$ exhibits a purely rexational(q independent decay rate) behavior. On the other hand, the significant increase of κ_o in SEP50 makes $S_2(q)$ the dominant contribution of S(q). Besides the expected increase of $S_2(q \rightarrow 0)$ with κ_o $S_2(q)$ increases with q and peaks at q*. Hence, $S(q \sim q^*,t)$ exhibit a purely diffusive(q^2-dependent decay rate) behavior. The theory(dashed lines) can satisfactory capture this dominant diffusive component and predicts a considerable contribution of $S_1(q \sim q^*,t)$ similar to SI50. However, this contribution can hardly be resolve experimentally.

Concluding, the dynamic structure factor of disordered diblock copolymers far from ODT and q less but near q^* sensitively depends on their composition polydispersity. In relation to monodisperse diblock copolymers, the relaxation of the composition fluctuations with the most probable wavelength($\sim 1/q^*$) can proceed via inter-diffusion and not chain overall motion. Thus the change of S(q,t) from a pure relaxational to a pure diffusive character can be controlled.

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