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Dynamic probe of the interface in lamellar forming non-linear block copolymers of the $(BA)_3B$ and $(BA)_3B(AB)_3$ type. A dielectric spectroscopy study

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Abstract

Dielectric spectroscopy is employed in lamellar forming non-linear block copolymers of the type $(BA)_3B$ and $(BA)_3B(AB)_3$ based on polyisoprene (A) and polystyrene (B), at temperatures well below the order-to-disorder transition temperature and below the glass transition temperature of the hard phase (polystyrene). We show here that dielectric spectroscopy can be used as a tool to probe the interface in ordered block copolymers with a basic triblock unit. Our estimate of the interfacial width is based on the mobility of the junction points at the interface and compares favorably with the estimated thickness from thermodynamics. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Block copolymers upon microphase separation form nanostructures whose phase and size can be controlled at the synthesis level. In contrast to macrophase separated blends, the size of the microstructures is highly coupled to the physical and chemical characteristics of the molecules. Therefore, such materials are ideal for studying chain dynamics within the restricted geometries, created by the repulsive forces between unlike molecules. The phase state of block copolymers [1] is controlled by the entropic and enthalpic contributions which scale as N^{-1} and χ (N is the total degree of polymerization and χ is the interaction parameter), respectively, the volume fraction of the A-component f, and the architecture. It is the product χN which sets the thermodynamic scale. When $\chi N < 10$, the system is in the disordered phase and the individual blocks have the unperturbed dimensions with a characteristic length scale $D \sim R_g \sim aN^{1/2}$. When $\chi N \sim 10$ (weak segregation limit (WSL)), a delicate balance between entropic and enthalpic factors produces an order-to-disorder transition (ODT). Here again the microdomain period scales as $D \sim aN^{1/2}$. When $\chi N \gg 10$ (strong segregation limit (SSL)), narrow interfaces are formed with an interfacial thickness of (in the limit of $N \to \infty$) [2]

$$\Delta_\infty = \frac{2a}{\sqrt{6\chi}}. \tag{1}$$

In this limit, the chain configurations are perturbed and the microdomain period is now

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$D \sim aN^{2/3}\chi^{1/6}$ [3]. For finite molecular weights, the interface is broader than estimated from Eq. (1) and can be approximated as [4,5]

$$\Delta \approx \Delta_\infty \left[1 + \frac{1.34}{(\chi N)^{1/3}} \right]. \quad (2)$$

From Eq. (2) we can calculate the interfacial width for a phase separated polystyrene–polyisoprene block copolymer based on the values of N, a and the measured χ (e.g., from SAXS). Mainly scattering experiments (SAXS, X-ray and neutron reflection techniques) have been employed to extract the interfacial thickness in block copolymers. In the present study we report on a completely different way of estimating the interfacial thickness. Namely, we show that dynamic techniques which are probing the local and the more important global chain dynamics can be used to provide an estimate of the "dynamic" interface in microphase separated block copolymers. We have shown recently [6] how the interfacial thickness can be obtained in triblock copolymers of the type (PS)(PI)(PS) where the junction points between PS and PI are restricted at the interface. Here we generalize these findings by employing two recently synthesized non-linear block copolymers with a basic triblock unit of the type $(PSPI)_3PS$ and $(PSPI)_3(PS)(PIPS)_3$ and dielectric spectroscopy to probe the dynamics of the junction points at the interface. We find reasonable agreement between the measured and the calculated interfacial thickness with the experiment resulting in somewhat higher values.

Table 1
Molecular characteristics of the block copolymers and homopolymers

Sample	M_n [a] (g/mol) × 10^3	M_w/M_n	wt%PS (^{1}H-NMR)
$(PSPI)_3PS$	126	1.05 [b]	58(60) [c]
$(PSPI)_3PS(PIPS)_3$	266	1.06 [b]	60(62) [c]
PS	16.7	1.02	100
PI	10.5	1.03	0

[a] Membrane osmometry in toluene at 35°C.
[b] Size exclusion chromatography in THF at 30°C.
[c] Calculated from the M_n of the precursors.

2. Experimental procedures

2.1. Samples

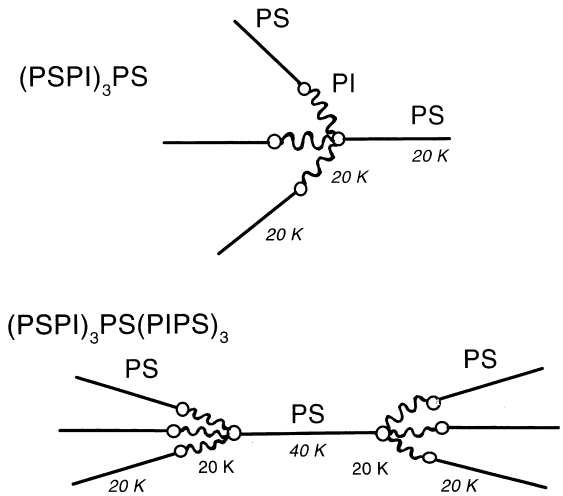
All samples were prepared by anionic polymerization and the procedure is described elsewhere in detail [7]. The molecular characteristics of the samples are given in Table 1 and their architecture in Scheme 1.

2.2. SAXS

An 18 kW rotating anode was used as the X-ray source (Rigaku) with a pinhole collimation and a two-dimensional detector (Siemens) with 512 × 512 pixels. The scattering patterns of shear oriented samples were investigated in the three principal directions. The integrated intensity in the radial direction for the $(PSPI)_3PS$ and $(PSPI)_3PS(PIPS)_3$ are shown in Fig. 1 and show the formation of lamellar structures with a period of 25.7 and 25.6 nm, respectively.

2.3. Dielectric spectroscopy

A Novocontrol BDC-S system composed of a frequency response analyzer (Solartron Schlumberger FRA 1260) and a broadband dielectric converter with an active sample cell was used to



Scheme 1.

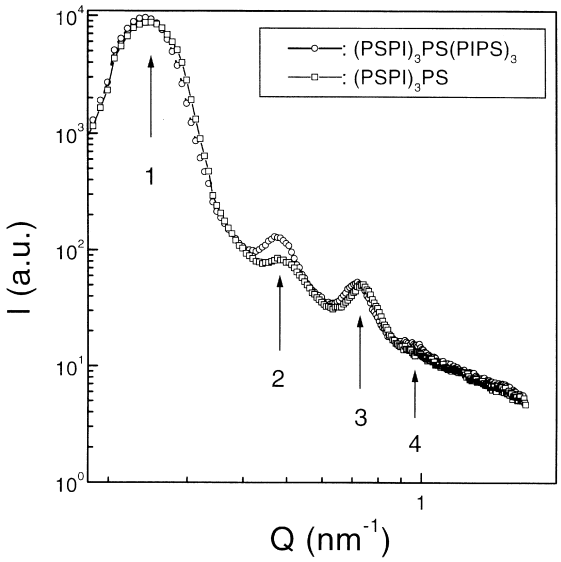


Fig. 1. Radially-averaged SAXS spectra of the two block copolymers at $T = 303$ K, indicating the formation of lamellar structures.

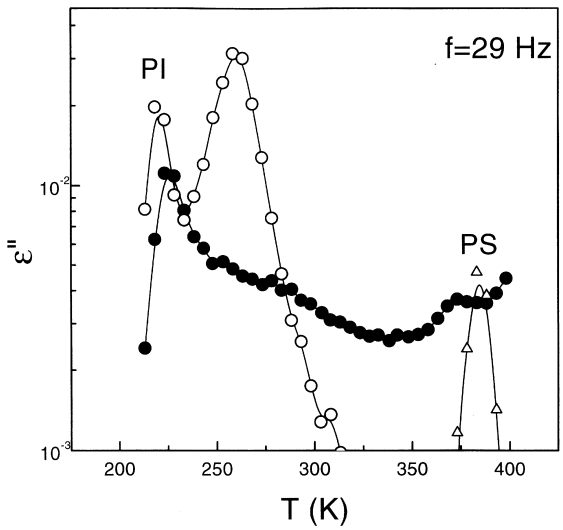


Fig. 2. Temperature dependence of the dielectric loss for the $(PSPI)_3PS$ block copolymer (●) compared to bulk PI (○) and PS (△).

measure the complex dielectric function (ε^*). Measurements were made in the frequency range 10^{-2}–10^6 Hz and over the temperature range 213–413 K with an accuracy of ±0.1 K. The resolution in tan δ was about 2×10^{-4} in the frequency range between 10^{-1} and 10^5 Hz.

2.4. Rheology

An advanced rheometric expansion system equipped with a force–rebalance transducer was used in the oscillatory mode. Isothermal frequency scans were performed for temperatures in the range 303–443 K and for frequencies $1.59 \times 10^{-3} < f < 15.9$ Hz. Strain amplitudes within the linear viscoelastic range were used.

3. Results

The dielectric loss data (ε'') from the isochronal measurements for the $(PSPI)_3PS$ are shown in Fig. 2 at $f = 29$ Hz. The corresponding data for the PI and PS homopolymers are also shown at the same frequency. Starting from low temperatures, the two peaks for the PI represent the local segmental and longest normal mode relaxation, respectively. For PS only the local segmental mode contributes to the dielectric spectrum whereas for the block copolymer three processes contribute within the T-range shown. Starting from low T we have: (i) the PI segmental mode, (ii) a very broad process relaxing in the vicinity of the normal mode process of the homopolyisoprene, (iii) a PS-like relaxation at higher T. At even higher T there is a slower process (iv) originating from the slow reorientation of the interface. Here we focus our discussion on the broad intermediate process (ii). To identify its origin we show the frequency dependence of the dielectric loss in Fig. 3 and we compare it with the bulk PI.

The normal mode process of the PI homopolymer originates from the end-to-end vector reorientations. For type-A polymer chains [8] (with dipole moments along the chain contour) the complex dielectric constant ε^* due to the normal mode process is given by

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\Delta\varepsilon} = \frac{1}{\langle r^2 \rangle} \int_0^\infty e^{-i\omega t} \left[-\frac{d\langle r(0) r(t) \rangle}{dt} \right] dt, \qquad (3)$$

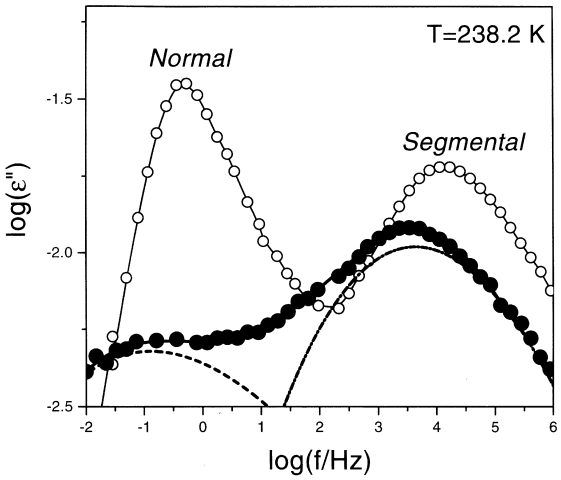
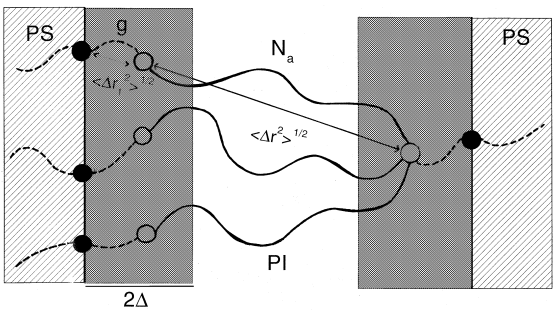


Fig. 3. Frequency dependence of the dielectric loss of $(PSPI)_3PS$ (●) compared to that of PI (○) at $T = 238.2$ K. The segmental and normal modes of PI are faster due to the shorter molecular weight of the homopolymer used for the comparison (Table 1).

where $\langle r^2 \rangle$ denotes the mean-square end-to-end distance and $\Delta\varepsilon$ is the relaxation strength of the normal mode process. It can be shown that Eq. (3) results in the following expression:

$$\Delta\varepsilon = \frac{4\pi N \mu^2 C}{3k_B T} \frac{\langle r^2 \rangle}{M}, \tag{4}$$

where N is Avogadro's number, μ is the dipole moment per contour length, C is the concentration of chains and M is the molecular weight of the chain. Eq. (4) relates the strength of the normal mode process to the relevant length scale of the motion (for junction points restricted at the interface $\langle r^2 \rangle^{1/2}$ can be replaced by $\langle \Delta r^2 \rangle^{1/2}$, see Scheme 2) and it will be used here to estimate the interfacial thickness.



Scheme 2.

For a block copolymer with an infinitely thin interface without mobility of the junction points parallel to the interface, no dielectric activity of the end-to-end vector is expected because both PI ends are effectively tethered at the glassy PS domains. However, for a finite interfacial width a process with suppressed intensity, compared to the normal mode process, is expected which arises from the mobile junction points at the interface. We show below, that the broad process in Figs. 2 and 3 of suppressed intensity which relaxes in the vicinity of the PI normal mode has all the characteristics of the junction point fluctuations within the restricted space of the interface.

In order to analyze the broad relaxation mode in Fig. 3 we have used the empirical equation of Havriliak and Negami (HN):

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\Delta\varepsilon} = \frac{1}{[1 + (i\omega\tau_{HN})^\alpha]^\gamma}, \tag{5}$$

where τ_{HN} is the characteristic relaxation time and α, γ are the shape parameters. To fit the spectra shown in Fig. 3 we have used two HN functions: the faster representing the PI segmental mode and the slower process the mobility of the junction points at the interface (normal mode-like process). Because of the broadness of the slower mode in fitting the spectra we have fixed the shape parameters for the segmental mode to the corresponding values of the bulk PI and obtained the following values: $\alpha \approx 0.3$ and $\gamma \approx 1$ for the slower mode. Because of the broadness and suppressed amplitude of this mode the uncertainty in the shape parameters is about 10% whereas for the strength about 20%. The relaxation times extracted from the fits are shown in Fig. 4 and compared with the segmental and normal mode times of a bulk PI with similar molecular weight ($M_w \sim 20\,000$) as for the PI blocks of the copolymers.

4. Discussion

A representative situation of the localization of the junction points at the interface is shown in Scheme 2. The junction points (open circles) can fluctuate within the interface (of width 2Δ) and are effectively tethered on the glassy PS blocks

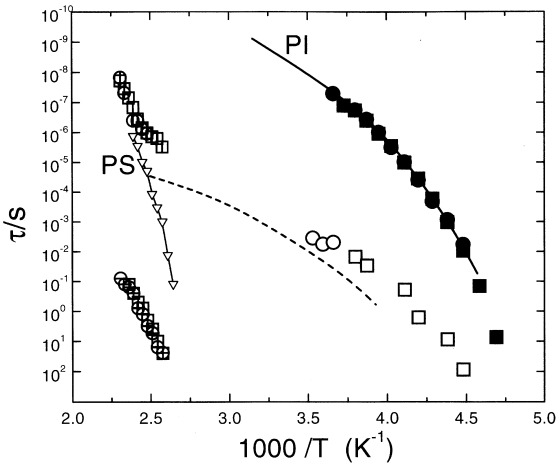


Fig. 4. Relaxation map of $(PSPI)_3PS$ (squares) and $(PSPI)_3PS(PIPS)_3$ (circles) in the usual Arrhenius representation. Filled symbols: PI segmental relaxation (DS), open symbols: PI chain mode (DS), symbols with vertical lines: PS-like process, slower process: rheology. The dielectric segmental (solid line) and normal mode (dashed line) times of homopolyisoprene are shown together with the segmental mode of bulk PS (▽).

(filled circles). There is a penetration of g PS monomers within the interface whose number is controlled by the interaction parameter ($g \sim \chi^{-1}$). Since χ is approximately 0.1, there are about 10 PS segments per PI block entering the interface. Assuming Gaussian statistics for the subchain composed of g monomers the predicted relaxation strength of this process would be $\Delta\varepsilon \sim 2\langle\Delta r_1^2\rangle = 2ga_{PS}^2$. The expectation is, therefore, that the intensity of the junction point fluctuations will only be a fraction of the intensity of a free PI chain ($\langle r^2\rangle = Na_{PI}^2$). Under the mean-field assumption of equal segment lengths ($a_{PS} \approx a_{PI}$) we obtain for the ratio of the relaxation strengths:

$$\frac{\Delta\varepsilon}{\Delta\varepsilon_N} \approx 2\frac{g}{N}. \tag{6}$$

Similarly, the dynamics of the junction point will be dominated by the PS subchain entering the interface. The slowest relaxation time can be estimated as $\tau_g \sim \zeta_{eff} g^2$, where ζ_{eff} is an effective friction coefficient at the interface. The dynamics of this Rouse subchain should be compared with the dynamics of an entangled linear or an entangled star PI chain. The ratio of the dynamics then will be

$$\frac{\tau_g}{\tau_N} \approx \left(\frac{\zeta_{eff}}{\zeta_{PI}}\right)\frac{g^2}{N^3/N_e}, \tag{7}$$

$$\frac{\tau_g}{\tau_N} \approx \left(\frac{\zeta_{eff}}{\zeta_{PI}}\right)\frac{g^2}{\left(\frac{N_a}{N_e}\right)^3 \exp\left(\nu\frac{N_a}{N_e}\right)} \tag{8}$$

for the linear and star, respectively. In Eqs. (7) and (8), N_e ($\approx$5000) is the PI entanglement molecular weight, N_a is the PI arm molecular weight, $\nu \approx 0.5$ and ζ_{PI}, ζ_{eff} are the PI and an effective "interfacial" friction coefficient, respectively. The prediction from the above equations, is that, the normal mode-like process will be faster when compared with the normal mode of a free PI chain and this effect will be amplified for the more entangled chains. This expectation for the dynamics is in qualitative agreement with the experimental finding shown in Fig. 5. However, an accurate determination of the speed-up factor is complicated by the unknown effective friction (ζ_{eff}) entering the dynamics. As for the broadening of the mode, different mechanisms can contribute: distribution in the number of segments g entering the interface, distribution in the effective friction coefficient as well as a distribution in the interfacial width. All of the above mechanisms would result in a broad dynamic process.

On the other hand, estimation of the intensity of the process is quite feasible and this permits estimation of the interfacial thickness. From the intensity of the slower process (Fig. 3) and using Eq. (4), we obtain that $\langle\Delta r_1^2\rangle^{1/2} \sim$ 5–6 nm. This value is considered here as the characteristic length of fluctuations of the junction point within the interface. The theoretical interfacial thickness can be obtained from Eq. (2). At $T = 238$ K, $\chi \sim 0.15$ ($\chi = 49/T - 0.058$, obtained for triblock copolymers [9]), with $N = 1175$ and $a = 0.68$ nm results in $\Delta \approx 1.8$ nm. Given that this estimate gives the half-width of the interface, we conclude that there is a satisfactory agreement with the experiment. In the above rough estimation we have ignored shifts of the spinodal for these star-shaped block copolymers which are expected to increase the ODT

(increasing compatibility) as compared to linear block copolymers [10].

Rheology was also employed and a master curve was constructed using the principle of time–temperature superposition. Different regimes were identified which reflect (i) the PI glass transition, (ii) the plateau caused by the entangled PI, (iii) the PS glass transition, (iv) a slower process associated with the reorientation of the interface and (v) an even slower process characteristic of ordered block copolymers. The characteristic times from (iv) are plotted in Fig. 4 together with the times from the other dielectric processes. It is worth noticing that over the T-range where DS was successful in detecting the dynamic signature of the interface, the rheological response of the system is controlled by the dynamics of the tethered PI chains (entanglement plateau).

5. Conclusions

We have shown that dielectric spectroscopy can be used as a dynamic probe of the interface in non-linear microphase separated block copolymers. The measured interfacial thickness is somewhat higher than the estimated based on thermodynamics. We should note, however, that this technique has some limitations: it can only be applied to block copolymers with a basic triblock unit where the mid-block is a type-A polymer chain and the outer blocks are glassy.

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