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Orientational diffusion of homopolymer chains in a lamellar structure of diblock copolymer: a deuterium n.m.r. study

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Chain dynamics in lamellar microdomains of polystyrene–polybutadiene (PS–PB) diblock copolymer is investigated by deuterium nuclear magnetic resonance (n.m.r.). The experiments are performed on perdeuterated PB homopolymer chains dissolved in the PB sublayers of a macroscopically oriented PS–PB sample. The n.m.r. spectra show that homopolymer chain segments undergo uniaxial reorientations around the direction normal to the layers. This local uniaxial order implies that the PB chains of the diblock are slightly elongated and that the segments between chains are correlated in orientation.

(Keywords: block copolymers; deuterium n.m.r.; uniaxial order)

Introduction

Above a critical molecular weight, diblock copolymers exhibit microdomains due to segregation of incompatible polymer blocks[1]. The symmetry and the structure of these microdomains are now well known[2,3]. Among the various structures of the microdomains, the lamellar and hexagonal ones are inherently anisotropic and may influence molecular properties such as the chain mobility. However, very little is known about chain dynamics in microstructured block copolymers. For that reason we are presently developing deuterium nuclear magnetic resonance (^{2}H n.m.r.) in this field. Indeed, according to previous studies of anisotropic fluids, such as liquid crystals[4] or polymer networks under stress[5,6], ^{2}H n.m.r. is very sensitive to the anisotropy of molecular motions. The first tentative application of ^{2}H n.m.r. has recently been made on a lamellar structure of a polystyrene–deuterated polybutadiene diblock, showing that this technique might also be well suited for probing local order in these polymer systems[7]. Another attempt has been made using deuterated solvent as n.m.r. probe[8]. A relevant approach is to study the reorientational diffusion of homopolymer chains dissolved into the microdomains formed of the like blocks of a copolymer. In this paper we report the first observations of uniaxial chain-segment ordering carried out on deuterated polybutadiene homopolymer chains used as n.m.r. probes, incorporated in the polybutadiene sublayers of a macroscopically oriented polystyrene–polybutadiene diblock. More precisely, uniaxial orientational fluctuations of chain segments have been observed on the spectra of a homopolymer in a macroscopically oriented lamellar structure. Such a local order, which is quite similar to that observed on a homopolymer diffusing in a uniaxially strained network, reveals the existence of orientational correlations between segments of partially elongated chains.

Experimental

A symmetric polystyrene–polybutadiene (PS–PB) diblock copolymer ($M_w = 84\,000$, or $42\,000$ per sequence; $M_w/M_n = 1.03$) and a perdeuterated polybutadiene (PBD) of low molecular weight ($M_w = 4600$) were synthesized via anionic polymerization. About 10 wt% (20 wt% relative to the PB sequences) of PBD was introduced in the diblock copolymer (*Figure 1a*) by

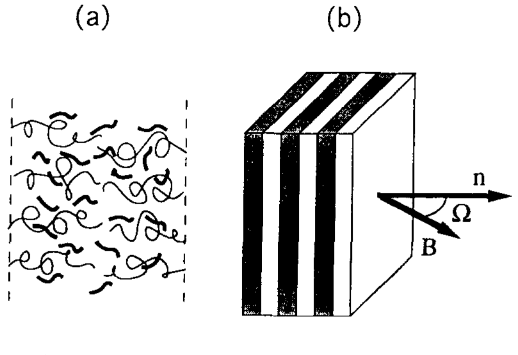

Figure 1 Schematic representation of (a) a single microdomain of a diblock copolymer–homopolymer blend, and (b) a monodomain of diblock copolymer with lamellar structure placed in the spectrometer magnetic field **B** (Ω is the angle between **B** and the normal **n** to the layers)

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dissolving the mixture in benzene. The solvent was removed by a freeze-drying process. It should be noticed that among the various swelling agents which may be used as n.m.r. probes in block copolymers, the homopolymer chains are the most selective. As in our previous work[7], the macroscopic orientation of the lamellar structure was carried out by flow under constraint, in vacuum, above the glass transition temperature (T_g) of PS. Small-angle X-ray scattering data, before and after the orientation process, show that the periodicity of such a swollen lamellar structure is 540 Å. The angular distribution which characterizes the quality of the lamellar orientation is less than 2°. Finally, the sample used in the n.m.r. experiments was cut in the shape of a parellelepiped (*Figure 1b*).

Additional ^{2}H n.m.r. experiments were performed on the same PBD chains introduced in a crosslinked PB network characterized by an average molecular weight between crosslink junctions $M_c = 40\,000$. Incorporation of homopolymer chains inside the network was realized at room temperature in a saturated atmosphere of benzene vapour. Then, the solvent was slowly removed and the sample was dried in vacuum. The concentration of homopolymer in the network is estimated to be 20 wt%.

The ^{2}H n.m.r. approach consists in studying how nuclear (quadrupolar) interactions attached to a C–D bond are time-averaged by molecular motions. The ^{2}H n.m.r. spectrum of a simple liquid is a single narrow line since the quadrupolar interactions are time-averaged to zero by the rapid isotropic molecular motions[9]. On the other hand, when fast motions are anisotropic, the nuclear interactions are only partially averaged. In the particular case of uniaxial motions around a macroscopic symmetry axis, such a residual interaction splits the liquid-like n.m.r. line into a doublet whose splitting is, in frequency units[5]:

$$\Delta\nu = (3/2)\nu_q |P_2(\cos\Omega)| \overline{P_2[\cos\theta(t)]} \qquad (1)$$

where ν_q denotes the static quadrupolar coupling constant (~ 200 kHz). The angles in the second Legendre polynomial depend on the experimental geometry and the molecular dynamics: $\theta(t)$ and Ω are the angles between the symmetry axis of the system with respect to the C–D bond and the spectrometer magnetic field **B**, respectively. The overbar denotes a time average over the motions faster than the characteristic ^{2}H n.m.r. time ν_q^{-1}. $\overline{P_2[\cos\theta(t)]}$ is the mean degree of the orientational order S of the C–D bond with respect to the symmetry axis. Hence, this n.m.r. approach allows one to monitor molecular motions through individual segment reorientation, and a measurement of the splitting $\Delta\nu$ gives direct access to S.

In order to decrease the line broadening present at room temperature, the n.m.r. experiments were performed at 100°C (just below T_g of PS, but well below the order–disorder transition temperature of the system) in vacuum. The orientation of the sample with respect to the magnetic field **B** may be fixed at different values of Ω (*Figure 1b*). ^{2}H n.m.r. spectra were obtained at 13 MHz, using a conventional electromagnet locked at 2 T. Note that for such a low value of magnetic field the effects related to the chemical shift are reduced. Each spectrum was obtained by fast Fourier transforming of the averaged free induction decay (f.i.d.). In order to improve the resolution of overlapping resonances, Gaussian multiplication was also used[10]; f.i.d. is multiplied by the function $[\exp(-at - bt^2)]$, where $a (a < 0)$ and b are two adjustable parameters.

Results and discussion

The ^{2}H n.m.r. spectra reported in *Figure 2a* clearly show that the spectral lineshape strongly depends on the angle Ω. In particular, the well pronounced narrowing effect observed for $\Omega = 55°$ yields a similar spectrum, i.e. similar lineshape and linewidth, to that obtained on PBD melt (reported in ref. 7) and on homopolymer dissolved in a relaxed network (*Figure 4*). In each case, the observed structure corresponds to the difference in chemical shifts ($\Delta\sigma = 44$ Hz, i.e. 3.38 ppm) between the two kinds of deuterons in the butadiene sequence, the most intense spectral component being associated with the methylene deuterons (CD_2 component) and the other one to the ethylene deuterons (CD component). From the spectra reported in *Figure 2b* (f.i.d. treated by Gaussian multiplication), it appears that the CD_2 component splits into a doublet structure ($\Delta\nu \neq 0$) for $\Omega \neq 55°$. Indeed, the ratio of the integrated intensities between the spectral components changes from about 1 : 2 to 1 : 1 : 1 for $\Omega = 55°$ and 90°, respectively. Moreover, the separation between the peak of the CD component and the centre of the doublet structure remains constant and equal to $\Delta\sigma$, whatever the values of $\Omega \neq 55°$ (it has been checked that for a spectrum obtained at 6.5 MHz the separation under consideration is reduced by a factor of two, whereas the doublet spacing $\Delta\nu$ remains equal to that obtained at 13 MHz). On the other hand, the doublet spacing $\Delta\nu$ depends on

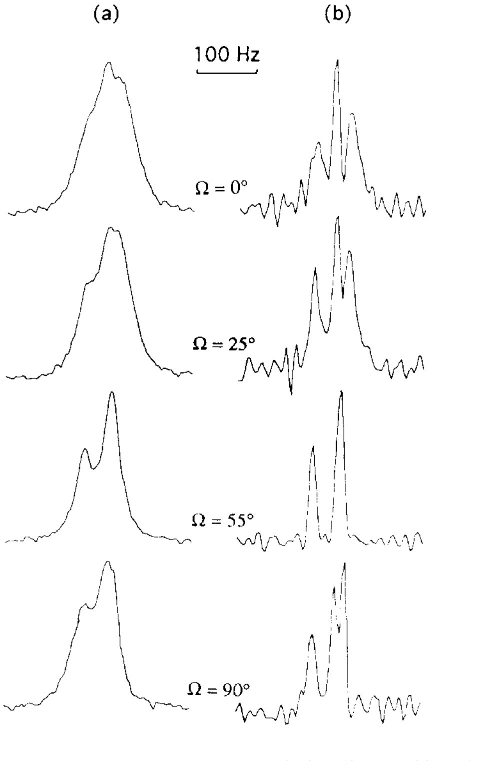

Figure 2 ^{2}H n.m.r. spectra of PBD probe chains dissolved in sublayers of oriented PS–PB, observed at 100°C for different angles Ω. (a) Spectra without treatment; (b) spectra treated by Gaussian multiplication ($a = -157.08\ \mathrm{s}^{-1}$; $b = 1452.40\ \mathrm{s}^{-2}$)

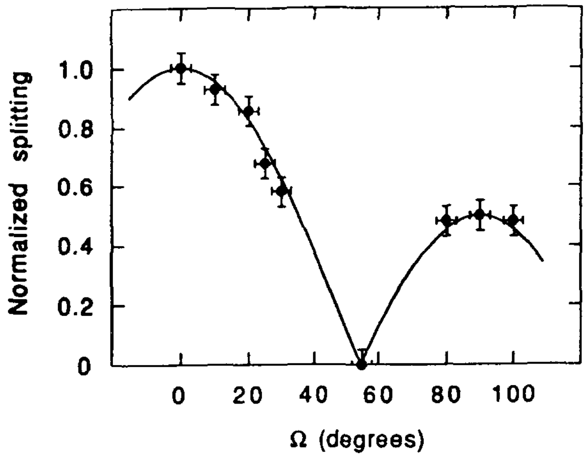

Figure 3 Variation of the normalized splitting, $[\Delta\nu(\Omega)/\Delta\nu(0^\circ)]$, as a function of the angle Ω. The curve represents the function $|P_2(\cos\Omega)|$

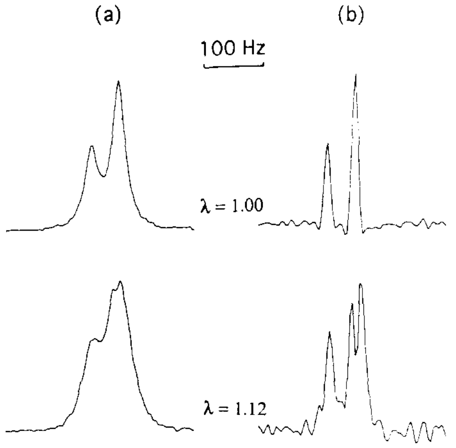

Figure 4 ^2H n.m.r. spectra of PBD chains dissolved in PB network: (a) without any treatment; (b) treated by Gaussian multiplication ($a = -157.08\,s^{-1}$; $b = 1452.40\,s^{-2}$). The network is in a relaxed state (elongation ratio $\lambda = 1$) or uniaxially elongated ($\lambda > 1$) along the direction perpendicular to the magnetic field ($\Omega = 90^\circ$). The temperature of the sample is regulated to 60°C

Ω; clearly, $\Delta\nu$ is higher for $\Omega \leq 25^\circ$ than for $\Omega = 90^\circ$, so that one component of the doublet begins to overlap with the CD component, *Figure 2b*. Concerning the angular dependence $\Delta\nu(\Omega)$ of the doublet spacing, *Figure 3* shows that it accurately reproduces the $|P_2(\cos\Omega)|$ variation given in equation (1).

The appearance of a resolved splitting ($\Delta\nu \neq 0$) together with the angular dependence $\Delta\nu(\Omega)$ show that the observed nuclear interactions are time-averaged along **n**, the normal to the lamella. Obviously this property should also be valid for the CD component of the PB sequence. In fact, this component is really composed of a doublet structure which is not resolved on the spectra shown; more details concerning this point, related to the molecular structure of PB chains[6], will be given in a forthcoming paper. Hence, our results mean that, as the PBD probe chains diffuse within the lamellar microdomains, their segments undergo uniaxial reorientational motions (changes in local conformations, larger-scale chain reorientation) on the ^2H n.m.r. timescale. More precisely, the normal **n** is a uniaxial symmetry axis for the chain dynamics over times longer than $\Delta\nu^{-1}$. Such a uniaxial dynamics is characterized by the mean degree of order S; it may be estimated to be 10^{-3} from equation (1) and from the observed splitting ($\Delta\nu = 28\,Hz$ for $\Omega = 0^\circ$). This local uniaxial order appears well defined within the limit of the observed spectral linewidth; accordingly, the degree of order S appears to be nearly uniform along the homopolymer chains, contrary to the case of the PB chains of the sequence itself[7]. Finally, the anisotropy of the segmental dynamics is clearly revealed on the present spectra because the n.m.r. experiments have been carried out on a macroscopically oriented sample; ^2H n.m.r. measurements performed on a non-oriented sample give access to a 'powder spectrum' composed of unresolved doublet structures related to a random angular distribution of the lamella[11].

The main result of this study is that the free probe chains acquire a uniaxial order at the segmental level. This order suggests that the homopolymer chains exhibit a non-random orientational conformation as they diffuse within the sublayers. This result may be consistent with the anisotropy of the radius of gyration, which has been measured by small-angle neutron scattering (SANS) on similar copolymers[12,13] and copolymer–homopolymer blends[14,15]. Indeed, the segmental order observed herein on probe chains reflects, more or less faithfully, the local order of the PB sequence itself[7]. A simple way to visualize the observed behaviour is to consider that the reorientational diffusion of the homopolymer takes place through an anisotropic fluid medium made of elongated and partially aligned chains, along the direction normal to the lamella[12]. From this point of view the observed phenomenon may be similar to that obtained on homopolymer chains inside a uniaxially strained rubber matrix, probing a uniaxial molecular field[16]. In fact, it is striking that spectra reported in *Figure 2* for $\Omega = 90^\circ$ are very similar, i.e. similar lineshape and identical splitting, to those obtained on the same free PBD chains diffusing in a PB network uniaxially deformed at an elongation ratio $\lambda = 1.12$ (*Figure 4*). Although the molecular deformation process in strained networks and copolymers is not necessarily identical, this similarity permits one to consider that the degree of chain deformation is very close in both cases. Then, under the assumption of affine deformation at the molecular level in the case of networks, the extension ratio of PB chains of the studied copolymer is close to (or higher than) 1.12. This value is in very good agreement with that deduced from the SANS experiments quoted above[14,15].

The observed order induced along homopolymer chains of low molecular weight (i.e. close to the critical entanglement molecular weight) necessarily involves short-range orientational correlations arising from interactions between chain segments. We do not know the nature of these interactions between PB chains in a copolymer, but their effects may result from a dense (lateral) packing of chains[12,13]. Then we anticipate that the observed order may depend on the local density of chain segments. Such a density–conformation coupling has already been suggested experimentally in the case of strained swollen networks[17], and theoretically in the case of polymer interfaces[18]. Finally, the presence of a quadrupolar order is very specific of the homopolymer. It shows that both extremities of the homopolymer chains dissolved in the sublayers are free and equivalent on the characteristic ^{2}H n.m.r. time scale, whereas the constraint imposed on PB copolymer chains by their junctions to the interface between microdomains introduces an asymmetry in the chain behaviour which may induce some additional dipolar effect along the chains[18]. In other words, the orientational distribution function of the free chain segments relative to the normal to the layers would depend on terms of quadrupolar symmetry only. Under these conditions, a close comparison of the dynamic behaviour of the two kinds of chains (homopolymer and copolymer chains) would be very interesting. In particular, it may yield useful information about the localization of the homopolymer chains within the copolymer lamellar structures[19]. This work is currently being developed.

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