Communications to the Editor

Uniaxial Dynamics in a Semicrystalline Diblock Copolymer

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Introduction. Block copolymers with lamellar morphology are subject of many theoretical and experimental studies for both fundamental and practical reasons.[1−4] In particular, these polymer systems currently attract considerable interest due to their anisotropic physical properties; the properties are significantly different in directions parallel and perpendicular to the lamellae.

Deuterium NMR (^{2}H-NMR) spectroscopy, a technique which is very sensitive to the anisotropy of molecular motions, has been recently developed in this field.[5−8] In this paper we report preliminary ^{2}H-NMR results obtained for the lamellar mesophase of a diblock copolymer exhibiting glassy and semicrystalline blocks. Specifically, the effect of crystallites on the chain segment motions in semicrystalline blocks is presented herein for the first time. Moreover, relevant information concerning the microstructure of crystalline phase is reported.

Experimental Section. The ^{2}H-NMR approach consists of studying how nuclear (quadrupolar) interactions are time averaged by rapid molecular motions.[7,9] The background of this approach is described in refs 9 and 10. The experiments are performed on a lamellar structure of polystyrene−polydimethylsiloxane (PS−PDMS) diblock copolymer slightly swollen with *n*-octane, a good and preferential solvent for PDMS blocks. We used labeled *n*-octane (C_8D_{18}) as a ^{2}H-NMR probe.

PS−PDMS diblock copolymer was synthesized by anionic polymerization in cyclohexane using *sec*-butyllithium as initiator. Weight average molecular weights (M_w) of blocks are 40 000 for PS and 51 000 for PDMS; the polydispersity index of PS chains is 1.03. A macroscopically oriented lamellar structure is prepared by flow under constraint in vacuum,[5] above the glass transition temperature (T_g) of PS. Small-angle X-ray scattering data show that the periodicity of such a lamellar structure is 618 Å. Then 9.5 wt % of *n*-octane-d_{18} is incorporated into the lamellar structure by swelling the sample in solvent vapors. Note that the *n*-octane crystallizes at 216 K, whereas the crystallization temperature (T_c) for PDMS homopolymer is 236 K.[11] More details about the sample preparation will be given elsewhere.[12]

^{2}H-NMR spectra were recorded on a Bruker CXP 90 spectrometer, operating at 13 MHz, using an electromagnet locked at 2 T. A macroscopically oriented PS−PDMS sample was cut into a parallelepiped (8 mm × 4 mm × 1 mm) and swollen by labeled solvent. The NMR tube containing the swollen sample was sealed in order to avoid the loss of solvent. The orientation of the sample relative to the spectrometer magnetic field **B** (Figure 1) was controlled by a home-made goniometer. The sample was thermostated with a Bruker variable temperature unit B-VT 1000. All NMR experiments were performed on the same sample by increasing the temperature.

Results. In Figure 2 we report ^{2}H-NMR spectra of C_8D_{18} probe molecules diffusing in the PDMS lamellae of the diblock observed at 233 K, i.e. below the crystallization temperature (T_c) for PDMS. Clearly, spectral line shapes strongly depend on Ω, the angle between the magnetic field **B** and the normal **n** to lamellae. The spectrum changes from a single line for $\Omega = 55°$ (half-height line width of 285 Hz) to a doublet structure for $\Omega \neq 55°$; the doublet spacing is reduced by a factor of 2 (from 195 to 96 Hz) as Ω varies from 0 to 90°.

For $\Omega \neq 55°$, the doublet spacing decreases as the temperature increases and an abrupt change in the spectral line width occurs just above T_c. Spectra observed below and above T_c, for $\Omega = 0°$, are reported in Figure 3: for $T > T_c$, the spectrum is a single line independent of the angle Ω. The half-height line width (140 Hz at $T = 242$ K) is reduced to 70 Hz at $T = 294$ K. Moreover, no pseudosolid echo is observable at this temperature; this confirms that the probe reorientational diffusion is isotropic at room temperature.

Finally, the integrated intensities of the spectral lines obtained for $\Omega = 55°$ above and below T_c are the same within the experimental errors. This indicates that for $T < T_c$ probe molecules are ejected from the crystallites and diffuse through the amorphous PDMS regions.

Discussion. The presence of a doublet structure in conjunction with the Ω angular dependence shows that at $T < T_c$ the observed quadrupolar interactions are no longer time averaged to zero by rapid reorientational motions of the octane molecules: the observed interactions are partially averaged along the normal **n** to the blocks lamellae. This effect is related to the anisotropic dynamics of the probe molecules, undergoing uniaxial reorientation along the sample symmetry axis as they diffuse through the amorphous parts of PDMS blocks. These uniaxial probe motions reflect the anisotropy of the PDMS chain segments fluctuations. Such uniaxial dynamics is characterized by the mean degree of orientational order (S) which may be easily deduced from the observed quadrupolar splitting[7,9] ($\Delta\nu$): S is estimated to be 10^{-3}. This value is 1 order of magnitude higher than that recently measured on an amorphous polybutadiene sequence in a lamellar diblock.[7] Note that the uniaxial character of the dynamics is clearly observable on the present spectra because a macroscopically oriented sample has been used.

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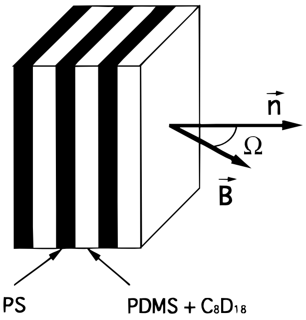

Figure 1. Schematic representation of a lamellar monodomain of diblock copolymer (slightly swollen by *n*-octane-d_{18}) placed in the spectrometer magnetic field **B**. The sample orientation is defined by Ω, the angle between **B** and the normal **n** to the layers.

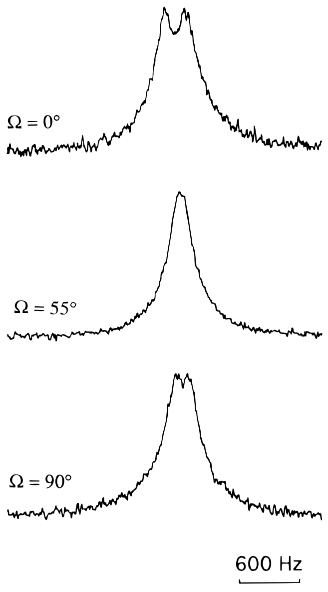

Figure 2. ^{2}H-NMR spectra of *n*-octane-d_{18} probe molecules in lamellar structure of oriented PS-PDMS, observed at 233 K for various angles Ω.

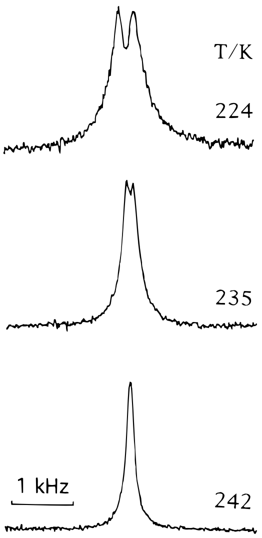

Figure 3. ^{2}H-NMR spectra of *n*-octane-d_{18} incorporated in macroscopically oriented lamellar structure of PS-PDMS, observed for $\Omega = 0°$, below and above T_c.

The observed motional uniaxiality is related to a dense anisotropic confinement of PDMS chains at low temperatures. In fact it is known that, for $T < T_c$, the PDMS crystallizes in the monoclinic system and forms folded-chain layers of well-defined thickness.[13] Here, for $T < T_c$, the amorphous PDMS chains between the glassy PS lamellae are constrained by the presence of crystallites.[11] Figure 3 shows clearly how an increase of temperature in the vicinity of T_c affects the uniaxiality of probe motions. The quadrupolar splitting $\Delta\nu$ is reduced from 240 to 95 Hz as temperature increases from 224 to 235 K and then disappears just above T_c. A high amount of crystallites at low temperatures produces strong constraints on the amorphous PDMS chains. Near T_c, the amount of crystallites drastically decreases, reducing constraints and consequently the values of splitting $\Delta\nu$ (i.e. values of order S). Above T_c, the anisotropy of probe motion disappears.

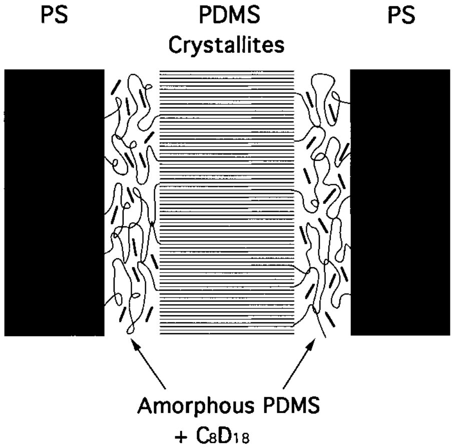

Figure 4. Schematic representation of a semicrystalline PDMS block. The dark short rodlike lines represent the octane molecules diffusing through the amorphous PDMS microdomains.

A simple interpretation of our results would be that the growth of crystalline sublayers are governed by the lamellar morphology of PS-PDMS matrix, and therefore they are parallel to the block interfaces, as schematized in Figure 4. The crystallites are supposed to growth in the central part of the PDMS domains where the dynamics of chain segments (close to chain extremities) is less restricted than in the vicinity of the PS−PDMS interface. Then the amorphous PDMS chains, placed between PDMS crystallites and glassy PS layers, exhibit anisotropic fluctuations due to strong uniaxial constraints induced by the growth of dense crystalline domains.[11,14] During the crystallization process the octane molecules are ejected from the crystallites and diffuse anisotropically through amorphous PDMS chains which are uniaxially deformed around the symmetry axis **n**. According to previous NMR data obtained on uniaxially deformed swollen polymer networks,[15,16] the observed value for the splitting $\Delta\nu$ (i.e. for the induced order parameter *S*) corresponds to a high degree of chain deformation.

X-ray scattering experiments at low temperatures and further NMR measurements are currently being developed on this system.

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