Local Uniaxial Order in a Grafted Polymer Melt via Deuterium NMR

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Dynamics of end-grafted polymer chains on a solid substrate are investigated by deuterium NMR, which is sensitive to the anisotropy of molecular motions. The experiments are performed on a perdeuterated polydimethylsiloxane melt grafted on planar silica slides. The NMR spectra show clearly that chain segments undergo uniaxial reorientations around the normal to the interface. This local order reveals the existence of orientational correlations between chain segments. The corresponding degree of anisotropy is much higher than in other lamellar systems such as block copolymers.

Grafted polymer layers on a solid substrate are a novel class of polymeric systems which attract considerable current interest [1,2]. Until now a lot of work has been done in the regime of high grafting density, and was mainly devoted to the study of polymer layer structure and to the determination of the segment concentration profile within the layers [3,4]. On the other hand, relatively little is known about chain dynamics in these systems. Furthermore, it is fundamental to know how the high grafting density affects the segmental motions and the average chain conformations in order to have a better comprehension of physical properties such as wetting and adhesion for such monolayers. For that reason we are currently developing deuterium NMR (^{2}H-NMR) in these confined polymeric systems. Indeed, according to recent studies of strained polymer networks [5] and organized block copolymers [6], ^{2}H-NMR is known to be well adapted and extremely sensitive to detecting anisotropy in molecular motions. In this Letter we demonstrate the feasibility of this NMR approach on polymer nanolayers, and we report the first direct measurements of chain segment ordering in these systems. In practice, ^{2}H-NMR experiments were performed on end-grafted deuterated polydimethylsiloxane in the melt state. Clearly, for a high grafting density, the ^{2}H-NMR spectra reveal a uniaxial segmental order. Such a local order implies that the segments between chains are correlated in the orientation.

The substrate we used was a flat silica slide. Experiments were performed on perdeuterated polydimethylsiloxane chains (PDMS-D; $[OSi(CD_3)2]_n$) synthesized via anionic polymerization ($M_n = 71\,000$, $M_w/M_n = 1.11$). The chains carry at one end a monochlorosilane group, which can strongly react with the silanol groups on the silica surface. The grafting reaction consists of immersing the slide in the reactive polymer melt, heating the system to 100 °C under a controlled atmosphere, and then thoroughly rinsing with toluene to get rid of free chains [7]. X-ray reflectivity experiments performed on such treated slides show that the thickness (h) of the grafted polymer is 80 Å. This value is close to the radius

of gyration R_g for the PDMS chains of the corresponding ungrafted melt ($R_g \approx 70$ Å). The mean distance (D) between adjacent grafting junctions is 40 Å, indicating that the grafted chains are in the so-called "brush" regime in which they overlap each other [Fig. 1(a)].

The ^{2}H-NMR approach consists of studying how nuclear (quadrupolar) interactions attached to a C-D bond are time averaged by molecular motions. The ^{2}H-NMR 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 [8]. On the other hand,
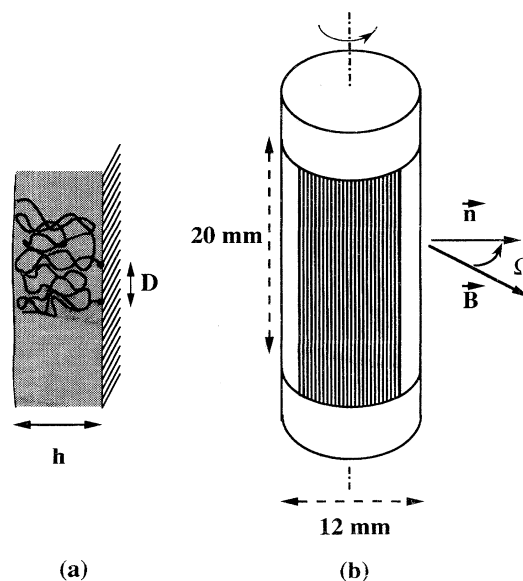

FIG. 1. (a) Schematic representation of polymer chains grafted on a planar slide. The layer thickness and the mean distance between the grafting sites are denoted by h and D, respectively. (b) Scheme of the sample holder. Fifty planar silica slides (thickness of 0.1 mm) are stacked in a cylindrical rack. The distance between the slides is 0.1 mm. The rack is introduced into the NMR coil. The angle Ω between the normal **n** to the slides and the spectrometer magnetic field **B** can be adjusted.

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 liquidlike NMR line into a doublet whose splitting is, in frequency units [9],

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

where ν_q denotes the static quadrupolar coupling constant ($\nu_q \sim 200$ kHz). Ω and θ in the second Legendre polynomial P_2 are the angles between the symmetry axis of the system with respect to the magnetic field B and the C-D bond, respectively. Equation (1) is fundamental and deserves to be discussed. The $|P_2(\cos\Omega)|$ term, which depends only on the geometry of the experiment, allows us to check the uniaxial character of the molecular motions. Varying Ω by rotating the sample provides us with a crucial test of the uniaxiality. The second factor $\overline{P_2[\cos\theta(t)]}$ depends only on molecular dynamics. The overbar denotes a time average over the motions faster than the characteristic ^{2}H-NMR time ν_q^{-1}. Thus $\overline{P_2[\cos\theta(t)]}$ is the mean degree of the orientational order S of the C-D bond with respect to the symmetry axis. Hence, this NMR approach allows us to monitor molecular motions through individual segment reorientations, and a measurement of the splitting $\Delta\nu$ gives direct access to S.

The small size of the signal is inherently one of the main difficulties of this NMR experiment performed on flat substrates. In order to increase the amount of polymer inside the NMR coil, we have packed fifty parallel and equidistant slides in a specially designed cylindrical rack, as schematized in Fig. 1(b). Measurements were carried out at room temperature, well above the glass transition temperature of PDMS ($T_g = -120\,°\mathrm{C}$). ^{2}H-NMR experiments were performed on a Bruker CXP 90 spectrometer operating at 13 MHz, with a conventional electromagnet locked at 2 T and producing a magnetic field $\mathbf{B}$ in the horizontal plane. The cylindrical rack may be turned around its vertical axis inside the NMR coil allowing us to vary Ω, the angle between $\mathbf{B}$ ad the normal $\mathbf{n}$ to the slides [Fig. 1(b)]. The magnetic field inhomogeneity $\Delta B/B$ is estimated to be $\sim 10^{-5}$ over the volume of the sample (2.2 cm^3). Each spectrum was obtained by Fourier transforming the averaged free induction decay (FID). In order to improve the signal to noise ratio, the number of scans was increased up to 10^5, corresponding to a maximum acquisition time of 24 h. The filter width was limited to 3×10^4 Hz, and the FID was treated by exponential multiplication (line broadening parameter <10 Hz).

Figure 2 shows that the ^{2}H-NMR spectra observed for $\Omega \neq 55°$ are composed of a resolved doublet whose spacing $\Delta\nu$ depends strongly on the angle Ω. A very pronounced narrowing effect occurs around $\Omega = 55°$, the magic angle which cancels the $|P_2(\cos\Omega)|$ function. As indicated in Fig. 3(a), the angular variation of the doublet spacing $\Delta\nu(\Omega)$ accurately reproduces the $|P_2(\cos\Omega)|$
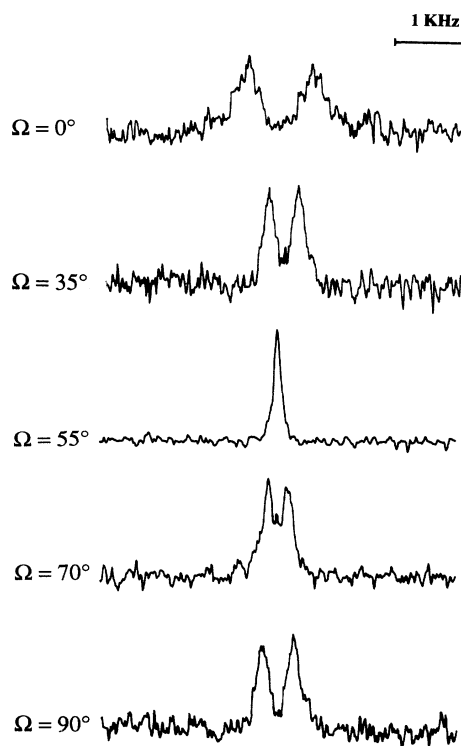

FIG. 2. ^{2}H-NMR spectra of perdeuterated polydimethylsiloxane chains ($M_n = 71\,000$) end grafted on planar silica slides. Spectra were obtained for different values of the angle Ω between the normal to the slides and the spectrometer magnetic field. Variation of signal-to-noise ratio between spectra results from the line shape spreading as Ω varies, each spectrum being normalized with respect to the maximum intensity.

variation given in Eq. (1), showing the uniaxial character of the molecular motions around the normal $\mathbf{n}$. The line shape at the magic angle is typical of an isotropic liquid, broadened by the static field inhomogeneity.

The doublet structure ($\Delta\nu \neq 0$) together with the angular dependence $\Delta\nu(\Omega)$ demonstrate that the observed nuclear interactions (quadrupolar tensors) are time averaged along $\mathbf{n}$, the normal to the slides. In other words, due to orientational fluctuations of chain segments around $\mathbf{n}$, a residual nuclear interaction $\Delta\nu$ is observed along this direction: $\mathbf{n}$ is a uniaxial symmetry axis for the segment motions over a time longer than $\Delta\nu^{-1}$. The appearance of a single and resolved doublet means that such uniaxial dynamics, characterized by the degree of order $S = \overline{P_2[\cos\theta(t)]}$ of chain segments, are well defined through the layer. The value for S may be deduced from Eq. (1) (with $\nu_q = 175$ kHz for PDMS methyl group) and from the observed splitting $\Delta\nu$ ($\Delta\nu = 450 \pm 50$ Hz for $\Omega = 90°$). Taking into account the chemical configurations of the PDMS monomer [10], the degree of order of the segment connecting two adjacent oxygen atoms of
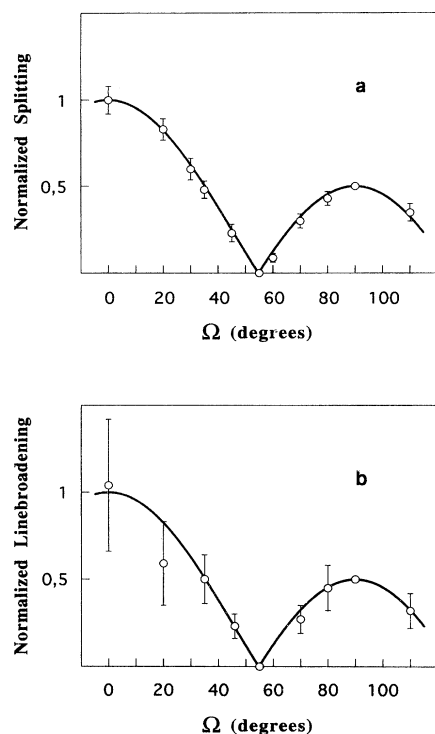
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FIG. 3. (a) Variation of the normalized splitting $\frac{1}{2}\Delta\nu(\Omega)/\Delta\nu(90°)$ versus the angle Ω. (b) Variation of the normalized line broadening $\frac{1}{2}[\delta\nu(\Omega) - \delta\nu(55°)]/[\delta\nu(90°) - \delta\nu(55°)]$ versus the angle Ω. In both cases, the curve represents the function $|P_2(\cos\Omega)|$.

the chain backbone is $S = 2.3 \times 10^{-2}$. This local uniaxial order appears well defined in the limit of the observed linewidth of the doublet components. Moreover, it is noticeable on spectra that the observed half-height linewidth $\delta\nu$ of the doublet components depends also on the angle Ω and reproduces the $|P_2(\cos\Omega)|$ curve within the error bars [Fig. 3(b)]. This implies that the line broadening, which occurs when Ω varies, comes from a distribution $P(\Delta)$ of doublets, related to a nonuniform segmental orientation along the chain. Furthermore, the absence of any central component on the spectrum at $\Omega = 0°$ shows that there are no isotropic segmental reorientations on the ^{2}H-NMR time scale. Finally, the uniaxial character of the dynamics is directly and unambiguously observable on the present spectra because we have used a macroscopically oriented sample similar to a monodomain characterized by its normal n. In contrast, other NMR studies performed on porous silica give access to an unstructured powder spectrum related to the random angular distribution of n [11].

The main result of this experiment is that we obtain the typical response of a uniaxial fluid. The observed motional uniaxiality is likely related to the dense anisotropic

confinement of the chains. The packing of the chains, arising from the high grafting density, restricts their conformations and forces them to span the layer along the normal to the interface. A simple way to visualize the chains' behavior is to consider that the reorientational motions take place through an anisotropic fluid medium made of partially aligned chains along the direction normal to the planar substrate. This kind of organization appears typical of tethered flexible molecules as in block copolymers or in lipid water systems. This has already been analyzed by de Gennes [12] using a general argument based on the flux conservation of the local stretching vector. It is shown that the order S would increase strongly with grafting density. However, in the present system, the local anisotropy of the chains does not necessarily correspond to a strong elongation of their end-to-end vectors, since the observed thickness of the polymer layer is close to the value of the radius of gyration R_g for chains in the regular melt. Moreover, in addition to the chain anchoring, the thin film geometry—or in other words the proximity of the chain segments to the impenetrable wall—may also have a crucial contribution to the local dynamical fluctuations around the normal n. In that case the segmental order, and its dependence on the grafting density, would differ from that corresponding to the case quoted above and discussed in Ref. [12]. Whatever the origin and the nature of the internal constraint are, it appears that the observed segmental ordering is not a single chain process, but instead involves orientational correlations due to interactions between chain segments. The cooperative effect of these interactions between neighboring chains may be analyzed in terms of a weak self-consistent orientational field describing the local order S [13]. These intersegmental orientational couplings can be screened in the presence of solvent molecules. Indeed, at a sufficiently high degree of dilution, the ^{2}H-NMR spectrum of the swollen brush shows a single line, typical of isotropic dynamics [14].

Another striking feature of these results is the magnitude of the order S ($S = 2.3 \times 10^{-2}$). Indeed, this value is much higher (more than 1 order of magnitude) than those found in other dense anisotropic polymer systems made of conventional monomers, i.e., monomers devoid of nematogenic groups. For instance, the maximum splitting observed with a uniaxially deformed PDMS network ($M = 25\,000$ between junctions) is equal to 90 Hz ($S = 2.3 \times 10^{-3}$) for a relative elongation of 120% [5]. This face may strengthen the idea of strong local constraints occurring within the polymer layers. Additionally, a splitting of 28 Hz ($S < 10^{-3}$) is observed on diblock copolymers in the lamellar phase, characterized by a higher chain packing at the interface than in the grafted PDMS layers considered here [15]. However, diblock copolymers and grafted layers are not closely comparable. In particular, the nature of the interfaces involved in these systems is different. More precisely, the polymer-

polymer interfaces of the diblock copolymer mesophases present a greater number of configurations for the chains then the sharp polymer-silica or polymer-air interfaces.

The present NMR study clearly shows that a grafted melt exhibits a pronounced motional uniaxiality at the chain segment level. This new experimental result concerning polymer dynamics suggests it would be relevant to study how the local order varies with the molecular parameters, chain molecular weight, and grafting density. In addition, it would be of interest to measure the order S for ungrafted polymer layers. Nevertheless, the present results imply that diffusion of homopolymer free chains inside the grafted layer would be prevented by a loss of entropy, due to the orientational correlations. This may be related to some recent observations on dewetting of polymer layers coated by homopolymer melts [16,17].

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