Chain Segment Order in Polymer Thin Films on a Nonadsorbing Surface: A NMR Study

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The dynamics of polydimethylsiloxane chains confined between air and a solid, wettable, and nonadsorbing surface is investigated using deuterium NMR. Chain segments in such molten films undergo uniaxial reorientations around the normal to the surfaces. The influence of the film thickness proves this dynamic uniaxiality involves rapid segment diffusion between both surfaces which impose a high degree of planar orientation. This segmental ordering is observed over a thickness range which depends on the degree of chain entanglements.

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Polymers at interfaces are the subject of intense scientific studies for both practical and fundamental reasons as, for instance, the treatment of surfaces, the elaboration of nanomaterials, or the statistical physics of confined polymers [1]. Various microscopic models have been proposed to describe the different ways to confine a polymer chain near an interface. These models are indeed necessary to account for some of the macroscopic properties due to the polymer interfaces. However, structural studies are not sufficient and obtaining data on chain dynamics appears to be essential for a deeper understanding of polymer film properties: how does the presence of a solid surface affect the dynamics of molten polymer chains? Does the confinement between two interfaces affect chain diffusion? These basic questions regarding the dynamical behavior are relevant for a better knowledge of surface properties as lubrication, wetting, adhesion, etc. However, the number of studies which really address these questions is quite limited [2–5]. In addition, most of them focused on either adsorbed [2–6] or grafted [7] polymers which are confined to a thin layer by a specific interaction with a given surface. In this Letter, we take advantage of the development of the deuterium NMR (D-NMR) to investigate the dynamical behavior of a polymer melt forming a liquid film of typically 100 Å thickness on a wettable and nonadsorbing substrate. The influence of the surfaces is therefore the simplest and the weakest one can think of: they can be viewed as completely neutral but impenetrable boundaries. Despite the absence of specific interactions, it is shown that these surfaces deeply modify the free polymer chain dynamics: it appears to be anisotropic, due to some ordering induced by the surfaces.

Experiments were performed at room temperature on perdeuterated polydimethylsiloxane [PDMS(D)], synthesized via anionic polymerization in a mixture of tetrahydrofuran and benzene. The two polymers of this study have an average molecular weight $M_W = 1.6 \times 10^4$ and 10^5 g/mol, respectively, with a polydispersity equal to 1.04 in both cases. The PDMS average molecular weight M_e between entanglements is about 2.4×10^4 g/mol [8].

The PDMS(D) films are obtained by spin coating. The substrates consist of silicon wafers (diameter ~13 mm) covered by a thin layer (thickness ~150 Å) of end-grafted polystyrene (PS, $M_W \sim 3 \times 10^4$ g/mol) [9]—see Fig. 1. This PS brush can be considered as a flat, impenetrable, and passive wall for the free PDMS chains: indeed, the PS grafted layer has a low roughness (less than 8 Å for the PS-air interface). Because of the strong incompatibility between PS and PDMS, the PS-PDMS interface is very thin (of the order of 3 Å, as checked by neutron reflectivity); finally, the PS layer completely prevents the adsorption of PDMS since the films can be removed easily and totally by immersing the wafers in toluene (in practice, the grafted substrate can be reused tens of time). The thickness of the PDMS film was controlled by the PDMS concentration of the solution used for spin coating and measured by ellipsometry with a lateral resolution of 10–30 μm and a thickness accuracy of about 1 Å. Heptane was chosen as the solvent: it is a selective solvent for PDMS, quite volatile (but not too much to avoid Marangoni instabilities), and of low surface tension (~17 mN/m). These features favor the formation of smooth, homogeneous, and defect-free PDMS films on the PS brush substrates using the spin-coating technique [10]. At room temperature, PDMS is liquid, whereas PS is in the glassy state.

In order to be sure that the PDMS totally wets the PS substrate and forms stable films, we have observed the spreading of a small PDMS(D) melt droplet ($M_W = 1.6 \times 10^4$ g/mol, typical volume of the droplet: $\sim 5 \times 10^{-7}$ cm^3) deposited on a PS brush and measured its shape

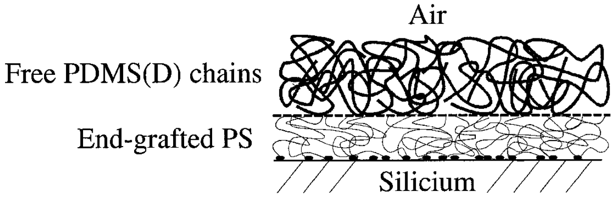

FIG. 1. Scheme of a PDMS film spin coated on a PS layer grafted onto a silicon wafer.

as a function of time with a microscope. We observed that the drop spreads on the PS surface and evolves slowly towards a van der Waals pancake. During most of this evolution, the droplet shape remains a perfect spherical cap, characterized by a dynamical contact angle $\theta(t)$ and a radius $R(t)$ [$\theta(t \sim 0)$ is of the order of a few degrees]. We observed that $R(t)$ increases with time according to the Tanner law [11]. Experimentally, we found $R(t) \sim t^{0.104}$ as shown on Fig. 2. This is characteristic of the capillary regime. These observations show that, despite the strong incompatibility between PS and PDMS, PDMS completely wets the PS brush. This is due to the large difference in the interfacial energy with air of the two polymers (~21 mN/m for PDMS and ~40 mN/m for PS). Thus, the PDMS films formed on the PS surface are *thermodynamically stable,* whatever the preparation method.

Deuterium NMR in condensed matter is much more specific and sensitive than proton NMR since it involves nuclei which are independent from each other in first approximation (whereas protons are coupled together via their dipolar field). The main nuclear interaction that we have to consider with deuteron is a quadrupolar coupling whose unique axis is oriented along a given C-D bond. The basic approach used here consists in studying how these quadrupolar interactions are time averaged by rapid molecular motions [7]. The D-NMR spectrum of a simple liquid is a single narrow line since the interactions are time averaged to zero by rapid isotropic motions. On the contrary, when rapid motions are anisotropic, the nuclear interactions are only partially time 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 Δ, in frequency units, is given by

$$\Delta \sim \nu_q \left| \frac{3\cos^2\Omega - 1}{2} \right| \left| \overline{\frac{3\cos^2\theta(t) - 1}{2}} \right| \qquad (1)$$

where ν_q denotes the static quadrupolar coupling ($\nu_q \sim 100$ kHz). Ω and θ are the angles between the symmetry axis of the system with respect to the applied magnetic field B and the C-D bond, respectively. Equation (1) is essential and deserves to be discussed. The first factor, which depends on the geometry of the experiment, provides us with a crucial test of uniaxiality, because Ω can be varied by changing the sample orientation. The second factor depends on molecular dynamics, and the overbar denotes a time average over motions faster than the characteristic D-NMR time $\nu_q^{-1} \sim 10^{-5}$ s. This factor represents the degree S of orientational order of the C-D bond with respect to the symmetry axis. Hence, the D-NMR technique allows us to monitor molecular motions via individual segment reorientation, and a measurement of the splitting Δ gives direct access to the order S. In fact, for PDMS(D), the preaveraging of the quadrupolar coupling by fast methyl group rotation should be taken into account. Then D-NMR effectively probes the mean orientation of the C_3-symmetry axis of each CD_3 group [12]: Eq. (1) remains valid if ν_q denotes the quadrupolar coupling of a rotating methyl group, and the second factor represents the mean degree of order of the molecular C_3-axis relative to the macroscopic symmetry axis of the system.

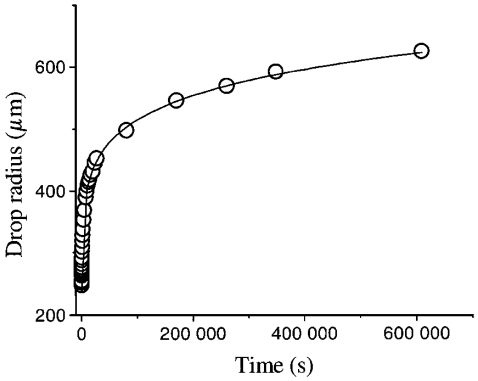

FIG. 2. Time evolution of a PDMS drop radius $R(t)$ (molecular weight $M_W = 1.6 \times 10^4$ g/mol) deposited on a PS brush. The solid line is a fit with a power law: $R(t) \sim t^{0.104}$.

D-NMR experiments were carried out on thin films of PDMS(D) spin coated from a PDMS(D) solution onto the grafted wafers as described above. In order to increase the NMR signal, we have prepared 20 wafers with the same film thickness h (±5%) and stack them parallel and regularly spaced in a cylindrical rack, introduced inside the NMR coil. Measurements were performed with a Bruker AM 400 spectrometer operating at 62 MHz. Each spectrum was obtained by Fourier transforming the averaged free induction decay. In order to improve the signal-to-noise ratio, the number of scans was increased up to 5×10^4 which corresponds to an acquisition time of about 14 h.

Figure 3 shows D-NMR spectra of a PDMS(D) melt ($M_W = 10^5$) in the bulk and of 80 Å thick film. The presence of a well-defined doublet structure in the latter case shows that the chain segment dynamics is not isotropic as in the bulk. Moreover, as shown in Fig. 4, we have observed that the doublet spacing Δ varies as the $|(3\cos^2\Omega - 1)/2|$ function of the angle Ω between the normal N to the wafers and the magnetic field B. The doublet structure ($\Delta \neq 0$), together with the angular dependence $\Delta(\Omega)$, proves that the observed nuclear interactions are time averaged along the normal N by rapid and anisotropic motions: the orientational fluctuations of segments are *uniaxial* around the N axis over a time Δ^{-1}. The observation of a unique doublet means that all chain segments exhibit the same dynamical behavior. This dynamic uniaxiality is characterized by the degree of order S deduced from Eq. (1) [with $\nu_q \sim 175$ kHz for methyl deuterons in PDMS(D)] and from the observed splitting Δ ($\Delta = 550 \pm 4$ Hz for $h = 80$ Å in Fig. 3): taking into account the internal motions and structure of the PDMS(D) monomers [12], $|S|$ is equal to a few 10^{-3}.

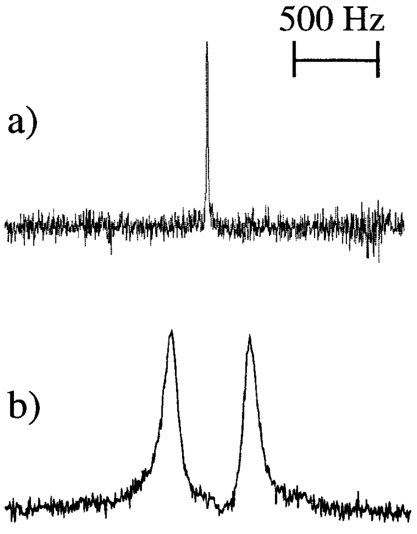

FIG. 3. The 62 MHz D-NMR spectra of a PDMS(D) melt (molecular weight $M_W = 10^5$ g/mol) (a) in the bulk; (b) in a spin-coated film (thickness $h = 80$ Å; angle $\Omega = 0°$).

Such a degree of order is rather high for chains as flexible as the PDMS ones (persistence length of a few Å). Thus it corresponds to a quite strongly constrained polymer [13]. Moreover, for linear chains confined in such thin films, it is reasonable to assume that the degree of order S is negative and thus corresponds to segmental orientational fluctuations which are preferentially parallel to the surface of the wafers, i.e., perpendicular to the symmetry axis N.

In order to understand the origin of this orientational order in a better way, we determined how the splitting Δ depends on the molecular parameters, namely, film thickness and chain molecular weight. Systematic data as a function of the thickness h are reported in Fig. 5. Surprisingly, for films of low molecular weight ($M_W = 1.6 \times 10^4$), the order [$\Delta \neq 0$ and its angular dependence $\Delta(\Omega)$] appears over a wide range of thickness h ($80 \leq h \leq 3000$ Å); in particular, it is still observable for $h \sim 30R_G$ (R_G being the unperturbed radius of gyration in the melt). Moreover, Δ, and thus S, decreases with h as $\Delta(h) \sim h^{-1}$. For longer chains ($M_W = 10^5$), the same dependence $\Delta(h)$ is also observed for $h < 250$ Å; for higher values of h, however, the splitting Δ drops abruptly and is equal to zero for $h > 350$ Å: the spectrum is then reduced to a narrow line (half-height linewidth $\delta \sim 40$ Hz), independent of the angle Ω.

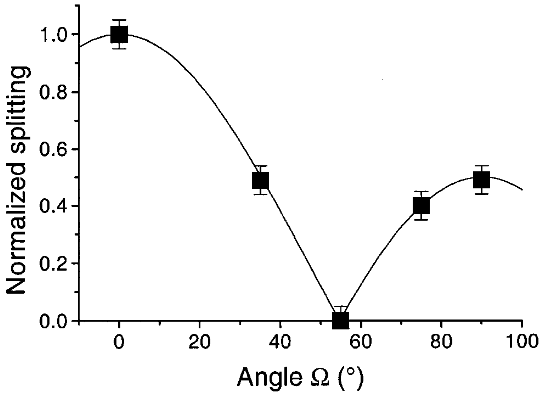

FIG. 4. Variation of the normalized splitting versus Ω. The solid line is the $|P_2(\cos\Omega)|$ function.

The nonzero order ($\Delta \neq 0$) observed for h much higher than R_G and the fact that it is independent of M_W at fixed h ($h < 250$ Å) prove that the segmental ordering is not due to a mere squeezing effect between both planar interfaces (polymer-solid and polymer-air interfaces): the ratio h/R_G is not the relevant parameter to analyze the observed ordering process. However, the $\Delta(h) \sim h^{-1}$ variation suggests that interfaces play an important role in the orientation process, because h^{-1} is proportional to the fraction of segments in contact with the surfaces. It is well known from various theoretical studies [14] that an impenetrable wall (even nonadsorbing) can induce a strong ordering of the chain segments which are close to the surface, the lower limit being a perfect in-plane alignment ($S_1 = -0.5$): such an ordering effect is believed to be short range, typically over a distance ξ of a few persistence lengths (i.e., a few monomers for PDMS). This would mean that in our experiments, we should observe two coexisting populations: a rather small fraction $\sim\xi/h$ of segments (close to the interfaces) exhibiting uniaxial dynamics ($S \neq 0$) and a majority having an isotropic liquidlike behavior ($S = 0$). Experimentally, this is not the case: all the segments exhibit the same anisotropic dynamics (see Fig. 3). Clearly, to understand the orientation process induced by the interfaces, we also have to consider the free chain (or segment) diffusion inside the film.

For chains sufficiently short to be nonentangled ($M_W = 1.6 \times 10^4 < M_e$), rapid segmental diffusion throughout

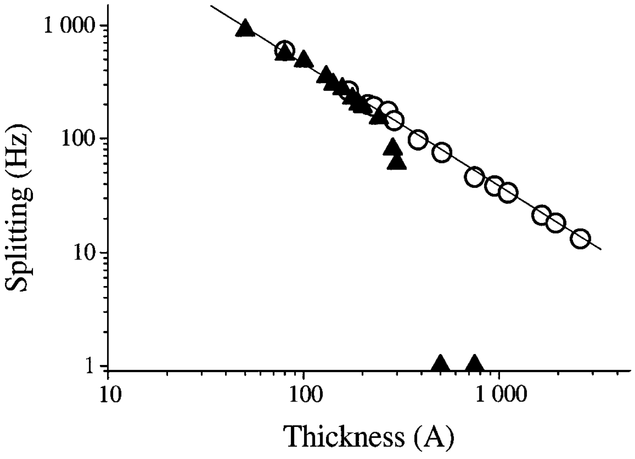

FIG. 5. Log-Log plot of the variation of the splitting Δ as a function of the film thickness h for two molecular weights M_W of PDMS(D). (▲) $M_W = 10^5$; (○) $M_W = 1.6 \times 10^4$ g/mol. The solid line represents a fit with a power law: $\Delta(h) \sim h^{-1}$.

the film occurs. Thus, the dynamics remains uniaxial over the time Δ^{-1}. Indeed, each segment probes sites of various degree of orientation over this characteristic time and acquires thus a mean order parameter $\langle S \rangle$. This average is performed over all the probed orientations. Assuming that the ordering is localized at the surfaces, it is expected that $\langle S(h) \rangle \sim h^{-1}$ and thus a decreasing function of the sample thickness. For instance, it is straightforward to show that $\langle S \rangle \sim (2\xi)/h$ in the presence of a rapid exchange between both populations of chain segments quoted above.

For long entangled chains ($M_W = 10^5 > M_e$), this model remains essentially valid as long as the film thickness h is smaller than a mean distance L. This characteristic length L is associated with the diffusion process through entangled chains: typically $L \sim (D\Delta^{-1})^{1/2}$ where D is a diffusion coefficient of chain segments. For $h < L$, the dynamics is restricted to chain reconfigurations controlled by the local (segmental) diffusion, which is independent of the molecular weight (as observed in Fig. 5). On the contrary, for $h > L$, most of the segments of entangled chains cannot diffuse throughout the film and so cannot reveal the anisotropy induced by the surfaces: the diffusion process leading to a mean order $\langle S \rangle$ does not take place any more in this regime. The (small) fraction of segments in the close vicinity of the surfaces may be highly oriented ($S \sim S_1$) but, due to entanglements, their dynamics may not be uniaxial; in any case, the NMR signal from these surface layers alone would be too small to be observed.

This interpretation in terms of surface-induced order and diffusion accounts rather well for the observations. However, for entangled chains, the change between the surface sensitive and the bulklike regimes is observed to occur over a narrow range of thickness (<100 Å). Nevertheless, the threshold distance L between both regimes, as defined above by the diffusion process, must increase as the entangled polymer size N decreases: for instance, the length $L(N)$ is expected to depend on N^{-1} if the reptation model is valid in polymer films [5]. Further experiments as a function of N would precise the $L(N)$ dependence and so the scaling law $D(N)$ for the self-diffusion of chains in polymer thin films.

These results show that, due to interfaces, chain dynamics in a polymer film is quite different from that in a regular melt, even in the absence of specific interactions imposed by the surfaces. The uniaxial chain segment ordering has to be considered in the analysis of surface properties of polymers and in polymer processing using thin films. Extension of this NMR approach to ultrathin polymer films may provide a relevant way to observe the glassy behavior, which would be induced either by specific monomer-surface interactions (as predicted by Ref. [15]) or by the slowing down of long range chain motions (as considered in Ref. [16]).

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