PHYSICAL REVIEW E, VOLUME 65, 031804

Chain segment order in ultrathin polymer films: A deuterium NMR study

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(Received 22 January 2001; published 6 March 2002)

The orientational order of monomerically thin films of polydimethylsiloxane melt deposited on the surfaces of cylindrical pores is investigated in this paper by solid-state deuterium nuclear magnetic resonance. Spectra demonstrate substantial orientation of the methyl groups by the surface. The quadrupolar splitting of the oriented film component saturates below one monomer layer, but decreases stepwise for thicker films. Comparisons of experimental and simulated spectra suggest a flat chain conformation in the first polymer monolayer.

DOI: 10.1103/PhysRevE.65.031804 PACS number(s): 82.35.Gh, 68.43.−h, 61.25.Hq, 76.60.−k

I. INTRODUCTION

Polymers at interfaces are the subject of a vast number of scientific studies due to the practical importance of surface modification by polymer films and also due to the fundamental interest of the effect of surfaces on both polymer conformation and dynamics. Insight into the related problems of wetting, polymer adsorption, and the ''collapse'' mechanism in Langmuir-Blodgett films relies on a clear picture of the microstructure and dynamics within the first few polymer monolayers. To date, a mesoscopic description of the layer in terms of loops and trains and long-range van der Waals forces dominates most discussions of thin polymer films [1], but clearly this picture is insufficient to describe the monomer-scale films often observed. Experimentally, little quantitative is known about these molecularly thin layers, whether for films formed by adsorption [2] or by spreading on liquid [3] and on solid [4] substrates. In particular, the molecular-level structure of such layers is a long-standing problem [5].

The preferred polymer for such studies has been linear polydimethylsiloxane (PDMS), a very flexible polymer often used as a model. Two features are known with certainty: (i) The thinnest layers formed are ~0.7 nm thick (~ one monomer), on both liquids [3] and solids [4]. (ii) On liquids [3], there is a transition from monomer-thick islands to thicker layers at surface concentrations $c_s \sim 0.7$ mg/m^2, corresponding to a dense monomer layer. Ellipsometry and related techniques reveal steps of discrete thickness equivalent to one to four monomer layers, again on both liquids [3] and solids [6]. Different molecular conformations have been suggested for these films [5,7], but no direct evidence is available. Reflectance infrared spectroscopy demonstrated a conformational change between layers that are one and several monomers thick on water [7]. Circular dichroism experiments [2] on adsorbed layers were consistent with a flattened, tightly bound layer coexisting with more loosely adsorbed polymer. This bimodal organization in ultrathin layers had been predicted on theoretical grounds. Both techniques give average information over all polymers in the layer, and neither gives a monomer-scale picture for any mode.

Recently [8,9], deuterium nuclear magnetic resonance (DNMR) was applied to thin polymer films, probing the orientational order of the methyl groups in linear PDMS. Uniaxial chain segment ordering was observed in a ~10 nm film of swollen brushes grafted to a solid substrate [8], and in polymer melt forming a 6–100-nm-thick liquid film on a wettable surface [9]. The latter studies, using planar solid substrates, could not be extended to monolayer films, since the number of molecules fell below the required DNMR sensitivity level. The typical sensitivity requirement is 10^{17}–10^{18} nuclei per probe; a one-monomer-thick PDMS film corresponds to 7.5×10^{18} deuterons m^{-2}, which must occupy a 0.5 cm^3 sample volume. Dispersed silica has been used to give the required high surface-to-volume ratio [10], but with unoriented surfaces. The porous substrate of choice is the Anopore membrane, which has well-oriented cylindrical pores and a 40% porosity [11]. The Anopore surface area is ~7.4 m^2/g determined by adsorption isotherms, with 99% of surface area within the pores, for ~2 m^2 per NMR sample. These Al_2O_3 membranes have been widely used to study orientational order in confined liquid crystals [12]. Their surface is naturally hydrophilic, and can provide strong PDMS adsorption [13].

Thus, this work has two major goals: (i) to take advantage the Anopore porosity and well-defined cylindrical geometry to demonstrate that previous DNMR work on polymer films can be extended to thinner films; (ii) to obtain direct information on the microstructure of molecularly thin films. Solid-state DNMR is particularly well suited to the study of conformational order and dynamics in oriented polymers, when one or more degrees of chain motion freedom are frozen, as, for example, near a glass transition or in drawn polymers [14]. Within the first adsorbed polymer monolayer, an attractive interaction between a polymer chain and the hard wall will increase the number of contacts between them, decreasing the chain mobility [6] and producing surface-induced polymer alignment. In this work, we report an investigation of the orientational order in ultrathin polymer films using the DNMR technique. DNMR probes the alignment of pendent CD_3 groups [Fig. 1(a)], which also reflects the backbone orientation to the extent that the mean angle to the backbone is known. Surface-induced order was demon-

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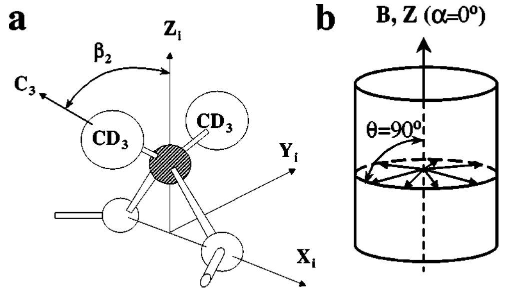

FIG. 1. (a) Simplified view of the PDMS monomer, showing the monomer molecular axes. (b) Experimental geometry. The cylinder corresponds to the membrane pore with long axis **Z**; the cylinder can be rotated, with angle α between the pore axis and the external field **B**. The arrows represent a radial distribution of the mean CD_3-rotor symmetry axis (the model in Refs. [14,17]).

strated directly through the DNMR spectra as a function of the angle α between the cylindrical pore axis **Z** and the NMR field **B** [Fig. 1(b)]. NMR spectra were also simulated and compared with experimental ones to suggest a consistent model of the conformational order and dynamics in the macromolecule.

II. EXPERIMENT

A. Sample preparation

Linear PDMS provided a model polymer system. Experiments were performed at room temperature on 98% perdeuterated PDMS (d-PDMS) with freshly prepared samples; the polymer preparation is described elsewhere [15]. The polymer has an average molecular weight $M_w = 10\,940$ g/mole, corresponding to borderline nonentangled chains [9], with a polydispersity $M_w/M_n = 1.11$. The d-PDMS films were obtained by deposition from solution onto the Anopore membrane. The membranes, with open parallel cylindrical pores of diameter 0.2 μm and length 60 μm, were cut into 4 mm × 25 mm strips and dipped for 5 min in a dilute or semidilute solution of PDMS in chloroform. Since the gyration radius for PDMS of this M_w is ~10 nm, the polymer chains can penetrate easily inside the pores. After removing the strips from the solution, the solvent was allowed to evaporate completely, leaving the pore surfaces coated with a polymer film. The surface concentration c_s varied with bulk solution concentration C_b. A parallel stack of approximately 40 strips was placed into an NMR tube 5 mm in diameter. The tube could be rotated manually within the horizontal solenoid, allowing the sample inclination α to be set with a precision of ±2° [Fig. 1(b)]. The amount of polymer could be determined by the change in strip mass and by the DNMR signal, calibrated to a known d-PDMS solution. The average surface concentration c_s is given by the total adsorbed mass divided by the surface area. The film is probably inhomogeneous, as is a spread film on water [3], but DNMR can distinguish different populations.

B. DNMR technique

DNMR spectra of d-PDMS films were obtained by a $\pi/2_x - \tau - \pi/2_y$ "solid echo" pulse sequence in a magnetic field $B = 4.7$ T at the ^{2}H Larmor frequency $\nu_L = 30.9$ MHz. The pulse length was 4 μs, the delay time τ was 100 μs, and the repetition delay was 100–300 ms. The number of acquired scans varied from 10^3 to 5×10^3 depending on the sample. Deuterium spectral line shapes are dominated by the orientation-dependent quadrupole interaction of the $I = 1$ spin. In liquids, quadrupole interactions are time averaged by rapid motion on the NMR measurement time scale, giving a single sharp isotropic peak. In contrast, when rapid motions are anisotropic, the nuclear interactions are only partially time averaged. For d-PDMS, the quadrupole coupling is preaveraged by fast methyl group rotation around the C_3-symmetry axis [see Fig. 1(a)]. Thus, DNMR probes the mean orientation of the C_3-symmetry axis of each CD_3 group. In the particular case of uniaxial motion around a macroscopic symmetry axis, the resulting line shape is a unique doublet with frequency splitting $\Delta\nu$ directly related to the angle θ between the mean symmetry axis of the CD_3 group and the spectrometer magnetic field **B**, giving

$$\Delta\nu(\theta) = \frac{3}{2}\nu_q |S| \left| \frac{3\cos^2\theta - 1}{2} \right|, \tag{1}$$

with the static quadrupole coupling constant $\nu_q \sim 100$ kHz for the CD_3 [8,9]. $|S| \equiv |P_2(\beta)|$, the second Legendre polynomial, averages ν_q for fast CD_3 group motion with angle β around the symmetry axis. S is an order parameter for the orientational order of CD_3 groups, and thus the anisotropy in chain segment reorientational motion ($0 \leqslant S \leqslant 1$).

III. RESULTS

Spectra from typical experiments are shown in Figs. 2(a)-2(b). The angle-dependent line shapes are given for adsorption from two different PDMS solutions with concentrations $C_b = 15$ and 8 mg/mL. The corresponding polymer surface concentrations are $c_s = 1.3$ and 0.8 mg/m^2. Spectral patterns depend dramatically on the deposited polymer amount. These spectral patterns can be understood by considering two different contributions: (i) liquid film yielding an isotropic central peak, and (ii) oriented film where the quadrupole splitting depends on orientation with respect to **B**. Observation of a unique doublet would mean that all CD_3 groups are equivalent and have the same mean symmetry axis.

The liquidlike film contribution increases with increasing c_s (Fig. 2). To determine the relative amount of ordered and isotropic polymer, we compared the areas under the doublets with that under the central peak, and found that the contribution from the oriented film gradually increases with the average polymer amount. For overall surface concentrations $c_s = 0.2$, 0.8, 1.3, and 3.8 mg/m^2, the oriented film contribution was 0.2, 0.7, 1.0, and 1.3 mg/m^2, respectively. These c_s can be compared to the saturation coverage of 0.7 mg/m^2 for a one-monomer-thick layer and 1.4 mg/m^2 for a two-monomer-thick layer [3]. Our DNMR results show significant orientation in two-monomer-thick films. Indeed, spin-coated films as thick as 200 nm may also possess significant order [9].

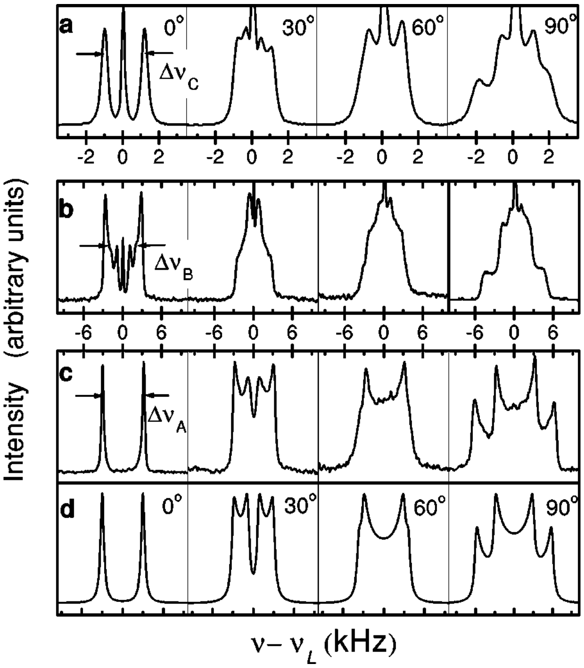

FIG. 2. Angular dependence of the DNMR spectra for different average surface concentrations c_s of adsorbed PDMS. The ratio of the area under the doublets to the total area under all peaks gives the oriented fraction. Central peaks are truncated. (a) $c_s = 1.3\ \mathrm{mg/m^2}$, oriented 75%; (b) $c_s = 0.8\ \mathrm{mg/m^2}$, oriented 89%; (c) sample prepared as in (b), then rinsed with pure solvent, leaving $c_s = 0.2\ \mathrm{mg/m^2}$; (d) spectra simulated according to the model [14,17] of a radial distribution for the mean CD_3-group symmetry axis [see Fig. 1(b)].

The quadrupole splitting $(\alpha = 0)$ of the oriented polymer decreased stepwise with increasing c_s, as shown in Fig. 3. The quadrupole splitting saturates to a value $\Delta\nu \sim 6$ kHz at low c_s. As many as three sharp doublets, corresponding to quadrupole splittings $\Delta\nu_A \sim 6$ kHz, $\Delta\nu_B \sim 4$ kHz, and $\Delta\nu_C \sim 2$ kHz, are clearly distinguished for all samples under investigation ($\alpha = 0$, Figs. 2 and 3; some doublets appear as shoulders, but the dominant peak switches between samples).

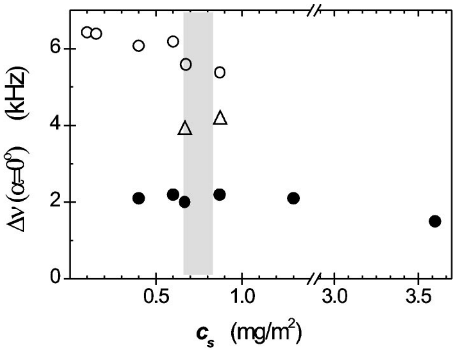

FIG. 3. Quadrupole splittings at $\alpha = 0$, as a function of c_s, for all samples, as a function of the average surface concentration. The transition from a monolayer to multilayers indicated by the shaded region, is taken from Ref. [3]. Symbols: (○) outermost peaks $\Delta\nu_A \sim 6$ kHz; (Δ) intermediate peaks $\Delta\nu_B \sim 4$ kHz; (●) innermost peaks $\Delta\nu_C \sim 2$ kHz.

The natural question arises whether these three doublets are independent, reflecting different polymer populations. To address this point, we decreased the PDMS solution concentration to $C_b = 4$ mg/mL. For this sample, which yields $c_s = 0.5\ \mathrm{mg/m^2}$ (not shown), only the splitting $\Delta\nu_A \sim 6$ kHz was well pronounced; the $\Delta\nu_C \sim 2$ kHz doublets were much weaker, while the intermediate doublets disappeared entirely. Thus, the doublets appear to correspond to different populations of aligned polymer. To remove any weakly adsorbed polymer populations [2,16], we rinsed similarly prepared strips briefly with pure solvent [Fig. 2(c), with $c_s = 0.2\ \mathrm{mg/m^2}$]. The spectra are similar to those in Fig. 2(b), but with the central part removed, leaving only the $\Delta\nu_A \sim 6$ kHz doublets.

IV. DISCUSSION

The sharp, unique doublets $\Delta\nu_A \sim 6$ kHz at $\alpha = 0$ and the increase of the maximum splitting to 12 kHz$\sim 2\Delta\nu_A$ at $\alpha = 90°$ [Fig. 2(c)] clearly demonstrates that the symmetry axis of the reorientational motion of the CD_3 groups is perpendicular to the axis of the cylindrical anopore pores. Simulated spectra, assuming a radial distribution of the mean symmetry axis [see Fig. 1(b)] [14,17], are shown on Fig. 2(d), they are in good agreement with the experimental spectra Fig. 2(c). The good agreement demonstrates a uniform distribution of symmetry axes in the plane perpendicular to the pore axes. The molecular symmetry axis of methyl groups must be aligned with respect to the cylindrical pore surface. The obvious possibility is a radial distribution of methyl mean symmetry axes shown in Fig. 1(b). The only other symmetry possible for a thin film and consistent with our spectra would be tangential circumferential [11]. This would require the symmetry axes of all pendent group motion to be constrained along the circumference with no component along the other surface direction, parallel to the axis. Such extreme anisotropy is highly unlikely. We thus conclude that the motion of PDMS segments is around the normal to the surface of pores.

A calculation [9,8] and comparison with experiment of the maximum averaged quadrupole splittings of the first polymer monolayer [Fig. 2(d) $\alpha = 90°$ spectra] suggests possible chain conformations. CD_3 groups in motion around the normal to the surface with angle β would produce the experimental symmetry axis. This gives an averaging factor $P_2(\beta)$ in Eq. (1). The angles $\beta = 60°$ or 49° give agreement with the experimental maximum quadrupolar splitting $\Delta\nu^{\max} \sim 12$ kHz. The calculated $\Delta\nu^{\max}$ is quite sensitive to the exact value chosen for β. 2β is clearly not tetrahedral [Fig. 1(a)], but may be distorted by the surface. Pendent group motion captured by β may include segment orientational fluctuations, but the spectra are not consistent with free, fast rotation of the CD_3 groups around a backbone randomly oriented on the surface, which would give spectra independent of α. The similarity of the DNMR patterns for thicker oriented films [compare Fig. 2(a) and 2(c)] demonstrates similar symmetry of methyl group motion.

Summarizing, we have shown that the first polymer layer is strongly aligned by the surface. This monolayer structure coexists with other populations, including liquid ones, that can be much more easily removed. The outer doublet [Fig. 2(c)], corresponding to the most ordered structure $|S| \approx 8 \times 10^{-2}$, remained even after an hour of rinsing. At higher surface concentrations, the freedom of pendent group motion increases stepwise, indicating stepwise reduction in the order parameter. Such striking behavior cannot be explained by mesoscopic models of loops and tails in the polymer chain, which should lead to the random collapse of the quadrupole splitting. Our data presents surprisingly well-organized structural changes in polymer films with surface concentrations. This correlates with the discrete thicknesses observed in many situations [3,6]. A well-defined doublet with $|S| \sim 10^{-3}$ persists in much thicker spin-coated polymer films [9,18].

We can speculate as to the chain conformations present. Monolayers have been suggested to be caterpillarlike, with many oxygen atoms forming hydrogen bonds with the water or oxide interface [5,7]; thicker layers may be multilayers [3,19] or helical, with several monomer groups coiling out of the interface [5,7]. For monomeric layers, our results indicate a single axis of symmetry, normal to the surface, and are inconsistent with rotation of the CD_3 groups around the backbone. This suggests that a flat chain conformation is more likely than a helix or a coil, where the orientation of the CD_3 groups varies along the polymer backbone. The similar symmetry for adsorbed layers at least two monomers thick could mean that polymer chains take similar flat conformations. These thicker layers might be multilayers, but with greater freedom of motion for the pendent groups throughout the thickness of the film. However, these DNMR results cannot rule out a helical structure with complex chain dynamics leading to the decrease in quadrupole splitting or collapse into a central peak. Figure 3 suggests at least three different, apparently discrete oriented populations of the polymer with similar symmetry with respect to the surface (Fig. 2) but different average pendent group dynamics [18]. The most ordered conformation, reflected in the largest peak splitting, disappears at surface concentrations equivalent [3] to a compact monomer-thick film.

V. CONCLUSION

In conclusion, it has been shown that the DNMR method can probe ultrathin polymer films, to below the monolayer level. DNMR investigations of the first one to three monomer layers of linear polymer have been performed for the first time, to the best of our knowledge. We have shown that the surface induces orientational order in the polymer chains for films up to at least two monomers thick on average. DNMR directly shows different macromolecular conformational dynamics depending on the polymer amount. The most probable conformation for one monolayer is a flattened structure. For thicker films, a flat conformation is also likely. Further studies at low temperatures, suppressing possible complex chain dynamics, could test this hypothesis.

Our results extend infrared dichroism results [2], which give an averaged view of polymer orientation. The advantage of NMR is that it can distinguish the degree of orientational order within different coexisting populations on the surface.

ACKNOWLEDGMENTS

The authors thank B. Zalar and R. S. Prosser for fruitful discussions and A. N. Primak for help with the modeling. NSF Grant No. DMR-9984304 is gratefully acknowledged for financial support.

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