

Chain-segment order and dynamics in a grafted polymer melt: A deuterium NMR study

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The dynamics of polymer chains grafted on solid substrates is investigated, using deuterium NMR. The experiments are performed on perdeuterated polydimethylsiloxane melts end grafted on porous or planar silica. The method consists in observing how nuclear interactions are time averaged by the molecular motions. One of the main results of this NMR study is that the chain segments exhibit uniaxial reorientations around the direction normal to the solid-polymer interface. Studies versus layer thickness demonstrate that this motional uniaxiality is due to the squeezing of the chains and characterized by a negative order parameter. The orientational fluctuations of segments are preferentially parallel to the grafting plane throughout the whole layer. This implies that orientational correlations take place between chain segments. [S1063-651X(97)08210-X]

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I. INTRODUCTION

Among the numerous polymer systems, polymers at interfaces are the object of considerable interest for both practical and fundamental reasons [1,2]. This novel class of materials abounds in varied configurations and properties, depending essentially on the polymer surface density, the nature of the substrate, and occasionally on the affinity of the polymer with the surrounding solvent. One of the most explored systems is the so-called “polymer brush” made of flexible polymer chains grafted on a solid substrate. A lot of work has been done with these kinds of systems, in the regime of high grafting density, and the investigations were mainly focused on the structure of the layer and on the segment concentration profile within the interface, [3,4]. On the other hand, the studies of chain dynamics in these systems remain very limited although it is especially important to understand how the motions of polymer chains are modified by the grafting on a solid surface. Additionally the knowledge of chain dynamics in grafted polymers may provide essential data for the understanding of surface properties like wetting, adhesion, and rheology for such nanolayers.

In this context we are currently developing deuterium NMR (²H NMR) in order to get some information about the local dynamics—i.e., dynamics at the segmental level—of such confined polymer systems. In a recent paper, we have already shown the feasibility of this NMR method for the study of grafted polymer melts and we have reported the first observation of uniaxial segmental motions around the normal to the grafting plane [5]. What is the origin of such anisotropic dynamics? Several interpretations can be suggested: a grafting effect (the chains being stretched perpendicularly to the surface), a squeezing effect in a layer thinner than the unperturbed radius of gyration (which would impose a parallel orientation), adsorption, etc. The aim of this paper is to give an unambiguous answer to this question. For that purpose, we need to fully characterize the local order exhibited by the grafted chains. In particular, it appears essential to

determine how the anisotropy of the segmental dynamics is affected by the grafting density.

Since the NMR approach has been briefly recalled in Ref. [5] (see also references therein), additional concepts of this technique will be detailed in Sec. II. As samples, we used grafted poly(dimethylsiloxane) (PDMS) melts. They were prepared either on flat surfaces, which allows us to keep track of the orientation of the substrate (oriented sample), or on porous silica (unoriented sample)—see Sec. III. The analysis of the ²H NMR response—nuclear relaxation functions and spectra line shapes—obtained with these two kinds of samples is presented in Sec. IV. In particular, it is shown that for porous silica, the response is dominated by the presence of residual nuclear interactions related to the anisotropy of segmental reorientations around the normal to the substrate. Furthermore, the distribution of orientational order is derived from the ²H NMR spectra. It appears that this order distribution is well centered around a mean value which depends on the thickness of the grafted layer (at fixed molecular weight). The discussion of these results (Sec. V) leads us to conclude that the order parameter must be negative, the chain segment fluctuations being preferentially parallel to the surface of the grafting substrate.

II. ²H NMR BACKGROUND AND ORIENTATIONAL ORDER

The basic concepts of ²H NMR in anisotropic fluids have been developed in numerous references [6,7]. Only elementary results relevant for our purpose are recalled herein. Due to its nonzero electric quadrupolar moment, the deuterium (²H) nucleus possesses an electrostatic energy in the nonuniform electric field of the C—D bond. This nuclear quadrupolar interaction is a second-order tensor affixed to the molecule; it is expressed by the instantaneous Hamiltonian [8]

$$H_q = \nu_q P_2(\Theta) (3I_z^2 - 2). \quad (1)$$

I_z is the usual spin operator ($I^2 = 1$, so the effect of H_q is to give a doublet of resonance lines). ν_q , the static quadrupolar interaction constant, is of the order of 200 KHz. Θ is the

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instantaneous angle between the C—D bond and the steady magnetic field \mathbf{B} , and $P_2(\Theta)$ denotes the second Legendre polynomial:

$$P_2(\Theta) = \frac{1}{2}(3 \cos^2 \Theta - 1). \quad (2)$$

In the presence of molecular motions, a *temporal* average over fast segmental reorientations with respect to the inverse spectral width in the rigid lattice limit (10^{-6} – 10^{-5} s) must be taken in Eq. (1), leading to an averaged quadrupolar interaction Δ' given by

$$\Delta' = \nu_q \overline{|P_2(\Theta)|}. \quad (3)$$

Throughout the paper, overbars will denote temporal averages taken over rapid molecular motion. Note that Δ' is independent of the value of \mathbf{B} .

Within this framework, and in the case of fast intrachain motions, the time evolution of the transverse magnetization for a deuterium nucleus may be written in the very simple form

$$M_+(t) = M_0 e^{-t/T_2} \cos \Delta' t. \quad (4)$$

If the motions of the C—D bond are isotropic (isotropic liquid), Δ' reduces to zero, and the transverse magnetic relaxation function is exponential with a relaxation time T_2 . After Fourier transforming, the spectrum is a Lorentzian line of linewidth $(\pi T_2)^{-1}$. On the other hand, if the motions are anisotropic, the fluctuations no longer average the interaction Δ' to zero. This leads to a modulation of the transverse relaxation function, corresponding in the frequency domain to a doublet of Lorentzian lines symmetric relative to the Larmor frequency, and characterized by a splitting Δ' .

In the case of a nonuniform system, i.e., containing C—D bond with distinct average axis and/or orientation degrees, there is one such doublet for each C—D bond (with a distinct orientation), and the resulting spectrum is the superposition of all these doublets. This *ensemble* average is denoted by angular brackets:

$$M_+(t) = M_0 \langle e^{-t/T_2} \cos \Delta' t \rangle. \quad (5)$$

The T_2 term (related to the fluctuating part of the Hamiltonian H_q) leads to a homogeneous broadening of the NMR line and can be viewed as an irreversible contribution to the relaxation. Unlike this contribution, the residual nuclear interaction corresponding to Δ' , even though it may be very weak compared to a true solid system, leads to a coherent or time reversible evolution which can be refocused by an appropriate pulse sequence (see Sec. III F). The resulting spectrum is inhomogeneously broadened by this interaction.

The two different averages described above must be clearly distinguished. First, the quadrupolar interaction for each nucleus is time averaged by fluctuations faster than 10^{-6} – 10^{-5} s, leading to Eq. (4). Then, the relaxation function $M_+(t)$ is integrated over all the nuclei present in the system, which leads to Eq. (5). The second step vanishes in a uniform uniaxial fluid system, wherein the motions of all C—D bonds consist of fast reorientational fluctuations around the same symmetry axis; in other words, all microscopic axes coincide with a macroscopic one, denoted by the

unit vector \mathbf{n} . In that case, the resulting spectrum is a unique doublet whose splitting Δ' may be expressed in frequency units as

$$\Delta' = \nu_q |P_2(\Omega)| \overline{|P_2(\theta)|}, \quad (6)$$

where Ω is the angle between the symmetry axis \mathbf{n} and the magnetic field \mathbf{B} , and θ is the instantaneous angle between the C—D bond and \mathbf{n} . The $P_2(\Omega)$ dependence may thus be used as a crucial test for the uniaxial character of the molecular motions. $\overline{|P_2(\theta)|}$ is the mean degree of orientational order, i.e., the so-called order parameter S ($-0.5 \leq S \leq 1$) which characterizes the anisotropy of the chain segment reorientational motions. Equation (6) may also be written in terms of an effective interaction Δ :

$$\Delta' = |P_2(\Omega)| \Delta, \quad (7)$$

with

$$\Delta = \nu_q \overline{|P_2(\theta)|} = \nu_q |S|.$$

III. EXPERIMENT

A. Polymer

The ^2H NMR experiments were carried out on perdeuterated poly(dimethylsiloxane) chains (PDMS(D); $[\text{O-Si}(\text{CD}_3)_2]_n$). The polymers have been synthesized via anionic polymerization in a mixture of tetrahydrofuran and benzene [9]. Their characteristics (molecular weight and polydispersity, determined by gel permeation chromatography) are reported in Table I. They were terminated by a reactive end group, either dimethylchlorosilane or dimethylsilane. Both can covalently bind the polymer to the silica substrates we have used (see below).

B. Substrates

For the NMR experiments, the substrate is either a porous silica (CPG 4000, from FLUKA) or a stack of glass slides (AF 45 from SCHOTT), as described in Ref. [5]. The porous silica has a specific surface area of $1.8 \text{ m}^2/\text{cm}^3$ as determined by neutron scattering and the pores have a diameter of about 400 nm (with a narrow pore size distribution, as checked by scanning electron microscopy).

We also used silicium wafers for simple experiments (measurement of the amount of grafted polymer by ellipsometry, for instance).

C. Grafting process

To attach the polymer to the above-mentioned substrates, we used two different strategies: we could graft the polymer (terminated by a dimethylchlorosilane group) directly onto the bare silica surface (scheme a, Fig. 1). But in most cases, we preferred to attach the polymer after having modified the silica surface (scheme b, Fig. 1), in order to reduce the adsorption of the polymer backbone. In the latter case, the polymer must be terminated by a dimethylsilane end group.

TABLE I. Characteristics of the grafted melts. Monodomains M_i are made of parallel glass slides (see text). M_w is the polymer molecular weight; R_g is the radius of gyration of the corresponding free chains in melt. I_w is the polydispersity $I_w = M_w/M_n$. The silica surface is used either as received—untreated surface (subscript $i = u$)—or after modification—treated surface (subscript $i = t$), in order to reduce the polymer adsorption (see text). h is the measured thickness of the polymer layer and D the calculated average distance between grafting points.

Samples	M_w (g mol ⁻¹)	I_w	R_g (Å)	Surface	h (Å)	D (Å)
Monodomains						
M_u	71 000	1.10	152	untreated	80.0	38.0
M_t	101 000	1.05	182	vinylated	140.0	35.0
Porous silica						
P_u	71 000	1.10	152	untreated	75.5	39.5
P_t^1	77 500	1.04	153	vinylated	150.0	28.2
P_t^2	77 500	1.04	153	vinylated	89.0	36.6
P_t^3	77 500	1.04	153	vinylated	21.5	74.5
P_t^4	101 000	1.05	182	vinylated	179.0	30.5

1. Modification of the substrate surface

Two different small molecules were used to passivate the silica surface: vinyltrimethylchlorosilane—VDMS (purchased from Aldrich)—or vinyl-tri(dimethylsiloxane)-dimethylchlorosilane—VTDMS—synthesized according to the method of Suzuki [10]. Thanks to their chlorosilane end group, these molecules can react with the silanol groups of the silica surface (see Fig. 2) which are thought to be responsible for most of the adsorption of the PDMS onto the silica.

The porous silica that has to be modified is used as received, without any cleaning procedure. The glass slides (or the silicium wafers) are cleaned by conventional methods [11]. The silicium wafers have an oxide layer of about 20 Å, as measured by ellipsometry.

We first wet the silica surface with heptane (containing 10% of triethylamine—TEA—final volume fraction) and let the TEA adsorb for approximately 5 min. We then introduce the short chlorosilane (10%—final volume fraction) and homogenize the reaction medium. A white ammonium salt is

immediately formed. The reaction is allowed to proceed for 2 h, at 100 °C, in a sealed reactor. The substrate is then rinsed thoroughly, first with a 50/50 mixture of dichloromethane and methanol, then with pure methanol and last with pure dichloromethane (or toluene). Finally, the substrate is dried (in a vacuum oven for the porous silica, under an argon stream for the slides).

2. Grafting of the polymer

(i) Grafting of the dimethylchlorosilane-terminated PDMS onto the bare silica: This polymer is grafted onto the bare silica (CPG: used as received; glass slides: cleaned as indicated above) in melt, at 110 °C, in a sealed reactor, for at least 24 h. The excess of free polymer (the chains which have not reacted) is eliminated by thoroughly rinsing the substrate with dichloromethane (a good solvent for PDMS).

(ii) Grafting of the dimethylsilane-terminated PDMS onto the modified silica: This polymer is grafted onto the “vinyl” modified silica via a hydrosilylation reaction. The polymer is

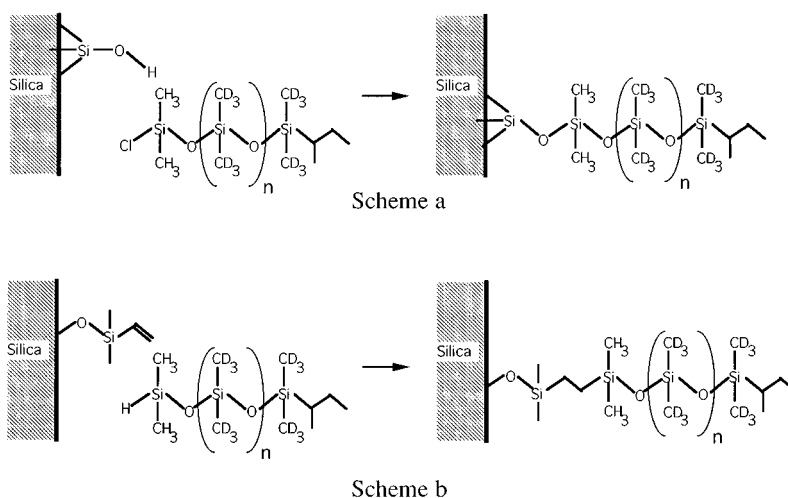


FIG. 1. Scheme a: Grafting of the dimethylchlorosilane-terminated PDMS on the bare silica surface. Scheme b: Grafting of the dimethylsilane-terminated PDMS on the “vinylated” silica. “Vinylated” surface means silica surface modified either by vinyltrimethylsiloxane groups or by vinyl-tetra(dimethylsiloxane) groups—see Fig. 2.

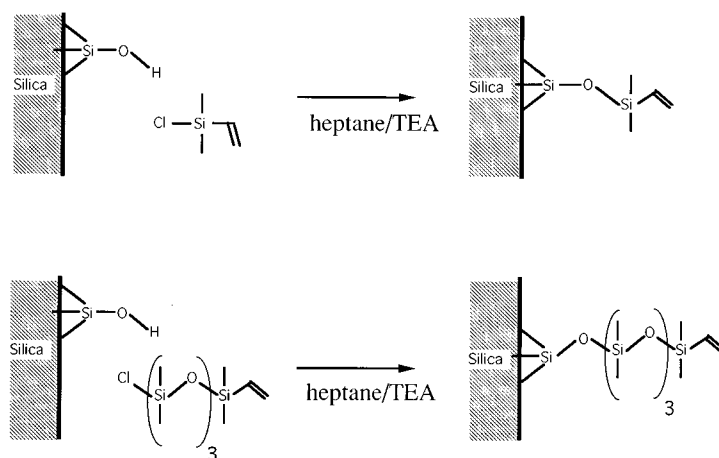


FIG. 2. Modification of the silica surface by vinyltrimethylchlorosilane (top) or by vinyl-tri(dimethylsiloxane)-dimethylchlorosilane (bottom).

used either in solution in rigorously dried toluene or in heptane, at a concentration c_b . In a few cases, we also performed this reaction in melt ($c_b = 100\%$). It has been shown that c_b is a convenient parameter to control the grafting density [12]. As a catalyst for hydrosilylation, we used the dichloro-dicyclo-octadienylplatinum complex. A typical amount is $5 \mu\text{l}$ of a 0.5 mg/ml solution in dichloromethane for 0.1 g of polymer ($M_w = 71.000 \text{ g/mol}$). When the grafting reaction is performed in melt (for the CPG and the glass slides), the corresponding amount of catalyst and the polymer are first mixed in dichloromethane and the solvent is evaporated. The grafting reaction is allowed to proceed for 24 to 48 h in a sealed reactor. As above, the chains which have not reacted are removed by thoroughly rinsing the substrate with dichloromethane. We checked that under these conditions, the polymer has the same characteristics after the treatment as before.

D. Determination of the amount of grafted polymer

For the different samples used in the NMR study, the amount h of grafted polymer together with the corresponding average distance D between grafting points are reported in Table I.

For porous silica (CPG), h has been determined by small angle neutron scattering (SANS), a well-suited technique for characterizing a polymer interface in a porous medium [13]. For the purpose of this study, we used this technique only to determine the amount of polymer per unit area $h = \int \Phi(z) dz$, where $\Phi(z)$ is the average polymer volume fraction at the distance z from the solid surface. As a solvent, we used methanol (more precisely, mixtures of perdeuterated methanol and regular methanol) in which the polymer layer is almost fully collapsed (methanol is a very poor solvent for PDMS). By adjusting the fraction of deuterated methanol, we can contrast match the silica, so that the scattering comes only from the polymer interface. We remind the reader that h is obtained, under this condition of contrast match, by extrapolating $q^2 I(q)$ at $q \approx 0$. q is the scattering vector and $I(q)$ the scattering intensity. This is formally equivalent to a Guinier plot. The extrapolation gives access to h without any

assumption about the exact shape of the polymer density profile $\Phi(z)$.

For the glass slides, h has been determined by x-ray reflectivity. This technique allows us to accurately measure the thickness of the dried grafted PDMS film.

From h , it is straightforward to calculate the amount of polymer per unit area Γ . If h is expressed in \AA , Γ is obtained in mg/m^2 using the following relationship:

$$\Gamma (\text{in mg/m}^2) = [h (\text{in \AA})] \times 0.1 \times [d (\text{in g/cm}^3)],$$

where d is the density of the polymer [0.98 g/cm^3 for PDMS (H)]. Finally, knowing the molecular weight of the polymer M_w , the distance between grafting points D expressed in \AA and the grafting density σ can be calculated from Γ :

$$D = \left(\frac{[\Gamma (\text{in mg/m}^2)] \times 6.023}{M_w} \right)^{-1/2} (\text{in \AA}),$$

$$\sigma = \left(\frac{a}{D} \right)^2,$$

where a is a monomer size (typically 5\AA for PDMS).

E. Effect of the surface treatment (on the PDMS adsorption)

We used an unlabeled PDMS melt ($M_w = 120.000 \text{ g/mol}$, polydispersity index: 1.04) to check the effect of the surface pretreatment. This polymer is either terminated by a dimethylsilane end group which can attach the polymer covalently to the surface or by a trimethylsilane which is unreactive. This latter polymer allows us to determine the amount of PDMS which is purely adsorbed. We used the same substrates as for the NMR experiments (CPG, modified by VDMS) and measured the amount of polymer that remained attached to the silica by SANS, as explained in the preceding section. The results obtained with the reactive polymer are given in Table II. When the surface is pretreated, h includes the thin ‘‘vinyl’’ layer (of the order of a few \AA thick).

It turns out that the amount of polymer which is purely adsorbed onto the bare silica is 38.6\AA , as estimated with the

TABLE II. Effect of the surface treatment on the PDMS adsorption. Comparison between the bare surface and the vinyltrimethylsiloxane modified silica. The same PDMS and the same reaction conditions have been used for the grafting except for the catalyst.

Surface	Catalyst	h (Å)
Untreated	No	85.6
Untreated	Yes	197.1
Vinyltrimethylsiloxane	No	18.1
Vinyltrimethylsiloxane	Yes	205.5

unreactive polymer. Therefore we can conclude that the SiH terminated polymer not only adsorbs onto the silica surface but it can also readily react with this surface, yielding covalently bound chains. It appears also that the platinum complex has a catalytic effect onto this reaction.

The “vinylated” surface (VTMDS treated) turns out to be well protected against the PDMS adsorption and it can be used to efficiently graft the polymer. The VTDMS treated surface has similar properties. The adsorbed amount is even lower, as checked by ellipsometry with silicium wafers.

F. Apparatus and NMR techniques

Most of the NMR experiments were performed on a Bruker CXP-90 spectrometer operating at 13 MHz, using a conventional electromagnet locked at 2 T. Each spectrum was obtained by fast Fourier transforming the averaged FID occurring after a $\pi/2$ rf pulse. The line broadening related to the magnetic field inhomogeneity $\Delta B/B$ was estimated to be less than 10 Hz ($\Delta B/B \leq 10^{-6}$) over the volume of the porous silica (~ 0.5 cm³) and about 20 Hz over the volume of the planar slides (~ 2.2 cm³). For the grafted slides, high magnetic field (10 T) spectra were also obtained with a Bruker MSL-400 pulsed NMR spectrometer operating at 65 MHz. In that case, the magnetic field inhomogeneity was 0.3×10^{-6} over the volume of the sample.

The present study was done at room temperature, i.e., well above the glass transition temperature T_g of PDMS ($T_g = -120$ °C). The weakness of the NMR signal due to the small amount of polymer is one of the main difficulties of this study, especially for the experiments performed on planar substrates. In order to increase the amount of polymer inside the NMR coil, we packed 50 parallel and equidistant slides in a cylindrical rack exactly as described in Ref. [5]. The orientation of the slides with respect to the magnetic field was adjusted with a goniometer with an angular accuracy of $\pm 1^\circ$. To improve the signal to noise ratio, the number of scans was increased up to 10^5 for the grafted slides, corresponding to an acquisition time of 24 h.

In order to distinguish the T_2 part of the transverse relaxation from the coherent contribution, it is suitable to use the two following spin echo sequences: the Hahn pulse sequence Σ_1 ($\pi/2_x, \tau, \pi_y$) leads to the usual spin echo decay $M_+(t)$ [see Eq. (5)] and gives access to the whole FID. The modified pulse sequence Σ_2 ($\pi/2_x, \tau, \pi/2_y$) refocuses the contribution of residual nuclear interactions and gives rise to a pseudosolid echo. We denote the amplitude decay of this pseudosolid echo by $M_e(t)$. It corresponds to the sole T_2

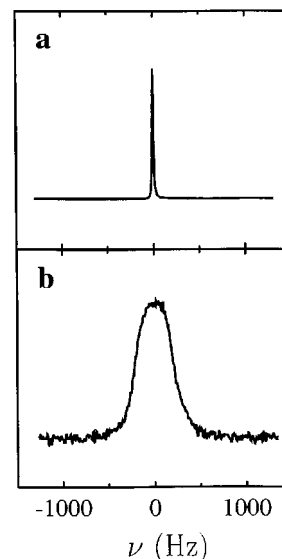


FIG. 3. (a) ^2H NMR spectrum of free perdeuterated PDMS chains ($M_w=71\,000$), in melt. (b) ^2H NMR spectrum of perdeuterated PDMS chains ($M_w=71\,000$) grafted on porous silica (sample P_u in Table I).

term in Eq. (5). In ordinary liquids ($\Delta' = 0$), the ratio $\psi(2\tau) = M_e(2\tau)/M_+(2\tau)$ must be equal to one-half whereas it is expected to be always higher in anisotropic fluids.

The transverse relaxation measurements were performed at 13 MHz and the $\pi/2$ duration was 4 μs . Because of the weak signal of deuterium nucleus and the small amount of polymer grafted onto porous silica, the echo signal was averaged on 10^3 scans. The spectrometer phases were properly adjusted and a phase cycling was used during the averaging process.

IV. EXPERIMENTAL RESULTS

A. Ungrafted melt

Figure 3(a) shows the ^2H NMR spectrum obtained on a regular (ungrafted) PDMS (D) melt ($M_w=71\,000$ g/mol). Its liquidlike line shape and the small half-height linewidth ($\delta\nu \sim 30$ Hz) are characteristic of strong time averaging process of quadrupolar interactions by rapid isotropic motions ($\tau\nu_q < 1$). The isotropic character of molecular motions is corroborated by the absence of any pseudosolid echo after the pulse sequence Σ_2 [see Fig. 4(a)]. Moreover, for this melt, the ratio $\psi(2\tau) = M_e(2\tau)/M_+(2\tau)$ is always equal to one-half as in ordinary liquids. For such a molecular weight, the lifetime of chain entanglements in PDMS is short enough compared to ^2H NMR time scales. Therefore no residual interactions resulting from entanglement constraints can affect the evolution of the spin relaxation. However, the transverse relaxation function $M_+(t)$ is characterized mainly by two (or more) relaxation times (see Fig. 5). This multiexponential character of $M_+(t)$ is related to the nonuniform mobility that long polymer chains exhibit in the molten state [14]. Besides, we checked that for a deuterated melt of low molecular weight ($M_w=3000$ g/mol), the transverse relaxation function observed in the same conditions is not affected by the chains autodiffusion.

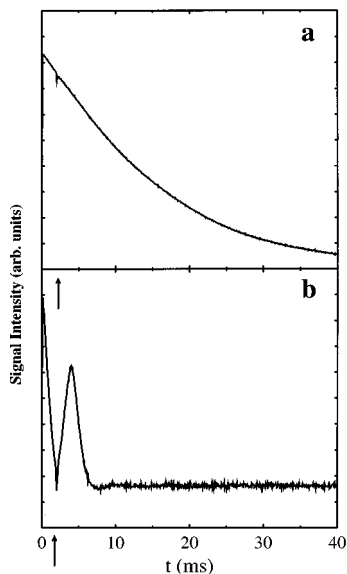


FIG. 4. (a) No echo is observable on a regular PDMS melt ($M_w = 71\,000$) after a $\Sigma_2(\pi/2|_x, \pi/2|_y)$ pulse sequence. (b) Pseudosolid echo observed on a grafted PDMS melt (sample P_u in Table I) after the same pulse sequence (arrows indicate pulse time).

B. Melt grafted on untreated surfaces

1. Porous system

Unlike the regular melt, the ^2H NMR spectrum obtained on the grafted porous medium (sample P_u in Table I) exhibits a broad non-Lorentzian line shape [Fig. 3(b)], the half-height linewidth $\delta\nu$ being about 400 Hz. In addition, a well-

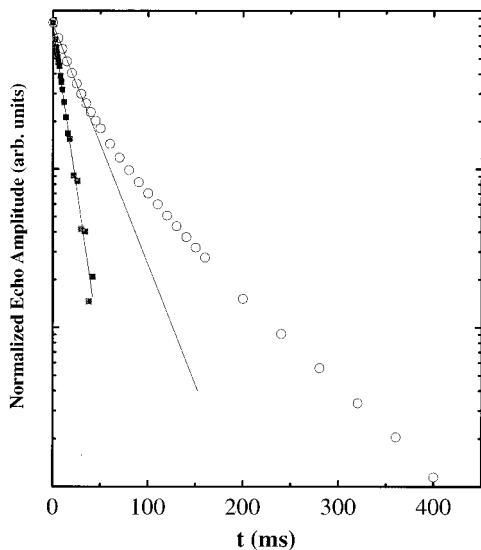


FIG. 5. Semilog plot of the echo amplitude (a.u.) measured at the maximum as a function of the time interval τ between the pulses of the sequence Σ_1 [open circles (O)] or the sequence Σ_2 [filled squares (■)]. Open circles are relative to a PDMS melt ($M_w = 71\,000$): a multiexponential decrease is observed and the full line gives access to the extreme values of the relaxation time T_2 ($79 \leq T_2 \leq 31$ ms). Filled squares are relative to a PDMS melt ($M_w = 71\,000$) grafted on porous silica (sample P_u in Table I): a single exponential is observed over two decades and the decay corresponds to a relaxation time T_2 of 10.6 ms.

shaped pseudosolid echo [Fig. 4(b)] is obtained as a response to the pulse sequence Σ_2 . Both features show that quadrupolar interactions are only partially averaged by molecular reorientations faster than 10^{-5} – 10^{-6} s. To distinguish this coherent contribution from the incoherent one, T_2 has been measured using the Σ_2 pulse sequence. The result is reported in Fig. 5 (filled squares). It turns out that the echo amplitude decay is a single exponential, and the relaxation time T_2 ($T_2 = 10.5$ ms) corresponds to a homogeneous line broadening ($1/\pi T_2 \sim 30$ Hz) much smaller than the observed spectral width ($\delta\nu \sim 400$ Hz). This proves that the incomplete time averaging of nuclear interactions due to anisotropic motions is the dominant contribution to the line broadening of the NMR spectrum (inhomogeneous broadening).

Moreover, the absence of narrow line at the top of the spectrum, together with the existence of a pseudosolid echo remaining at long delay times ($\tau \geq 10$ ms—data not shown) prove that only anisotropic motions take place within the layer on the time scale henceforth defined by the inverse width of the observed spectrum (10^{-3} s). In order to characterize more precisely this anisotropy, we have used macroscopically oriented samples (monodomains) for which the direction of the interface relative to the steady magnetic field \mathbf{B} is well defined.

2. Monodomains

We used the same monodomain (called M_u in Table I) as in Ref. [5]. We point out that this sample has the same characteristics as those of the porous medium (P_u) of the preceding section, so that the experimental results obtained on both samples can be compared.

The ^2H NMR spectrum obtained for the monodomain M_u at 10 T is reported in Fig. 6(a) (solid line). The most striking feature is that a well-resolved doublet structure appears. Moreover, as reported in Ref. [5], the doublet spacing depends on the angle Ω and its variation is accurately fitted by the $P_2(\Omega)$ function given by Eq. (6). This result demonstrates that the motions of chain segments are uniaxial around the normal \mathbf{n} to the grafting plane. The mean degree of orientational order S can be easily deduced from the observed doublet spacing ($\Delta' = 360 \pm 20$ Hz for $\Omega = 90^\circ$) using Eq. (6). Taking into account the chemical configuration of the PDMS monomer [15], the mean degree of order for segments connecting two adjacent oxygen atoms along the PDMS backbone is $|S| \cong 2.3 \times 10^{-2}$.

Moreover each component of the doublet exhibits a broad linewidth—half-height linewidth $\delta\nu \sim 200$ Hz—which is dominated by the distribution of residual quadrupolar interactions rather than by the intrinsic width $1/\pi T_2$, as already shown with the porous medium ($1/\pi T_2 \sim 30$ Hz) [16]. This is corroborated by the observation that the linewidth of each doublet component reproduces the $P_2(\Omega)$ dependence as Ω departs from the magic angle (see Ref. [5]). Therefore the segmental order is not uniform along the grafted chains and an order distribution $P(S)$ —i.e., a distribution of doublets $P(\Delta)$ —has to be introduced.

Since the dynamics along the chains is characterized by a single time T_2 , the general expression for the relaxation function [Eq. (5)] can be simplified as follows:

$$M_+(t) = M_0 e^{-t/T_2} \langle \cos \Delta' t \rangle. \quad (8)$$

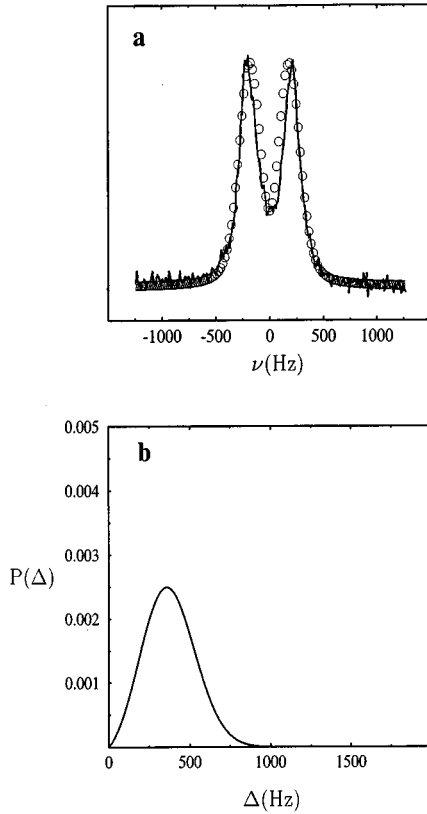


FIG. 6. Sample M_u —see Table I (monodomain, untreated surface, $M_w=71\,000$, $h=80\text{ \AA}$). (a) ^2H NMR spectrum. The spectrum was obtained at 65 MHz. The normal to the slides was perpendicular to the spectrometer magnetic field ($\Omega=90^\circ$). The number of scans was 5×10^4 , corresponding to an accumulation time of 12 h. The open circles correspond to the NMR spectrum computed according to Eq. (9) for the order distribution $P(\Delta)$ shown in (b) ($\Delta_0=260\text{ Hz}$ and $\sigma=187\text{ Hz}$).

Introducing an order distribution $P(\Delta)$ as previously explained, the transverse relaxation function is rewritten as follows:

$$M_+(t) = M_0 e^{-t/T_2} \int \cos[\nu_q |P_2(\Omega)| \Delta t] P(\Delta) d\Delta, \quad (9)$$

where the ensemble average is now explicitly accounted for by the integral over the order distribution.

By assuming a particular shape for $P(\Delta)$, for instance,

$$P(\Delta) \propto |\Delta| e^{-(\Delta-\Delta_0)^2/2\sigma^2}, \quad (10)$$

we can try to fit the experimental spectra with only two adjustable parameters Δ_0 and σ . Obviously this choice for $P(\Delta)$ is not unique, but it is justified *a posteriori* by the quality of the fits (see below). Note, however, that a pure Gaussian function would not be appropriate since it would introduce an isotropic contribution to the relaxation function which would appear as a narrow line at the top of the spectrum.

Figure 6(a) shows the result of such analysis for the spectrum obtained with the monodomain M_u at $\Omega=90^\circ$. The corresponding distribution $P(\Delta)$ is plotted in Fig. 6(b). It has

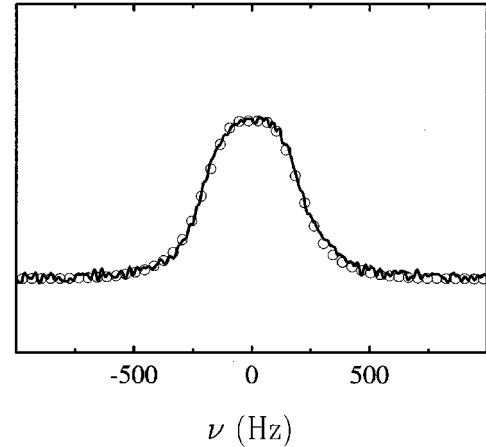


FIG. 7. ^2H NMR spectrum of perdeuterated PDMS chains ($M_w=71\,000$) grafted on porous silica (sample P_u in Table I): the experimental data are the same as for Fig. 3(b). The open circles correspond to the fit according to Eq. (11), using the order distribution shown in Fig. 6(b) determined for the monodomain M_u .

to be mentioned that the value for T_2 , previously measured with the porous sample, was used to fit the spectrum obtained with this monodomain [17].

3. Orientational order and powder spectra

For porous silica, the normal to the interface, which must be a local axis of uniaxiality for the chain segments, is randomly oriented. Therefore the resulting spectrum is expected to be a superposition of doublets $\Delta'(\Omega)$, averaged over all the orientations of the normal \mathbf{n} to the substrate. Calling $M_p(t)$ the relaxation function of the porous medium, we have

$$M_p(t) = \int_0^\pi M_+(\Omega, t) \sin\Omega d\Omega, \quad (11)$$

where $M_+(\Omega, t)$ is given by Eq. (9).

We have already determined $M_+(\Omega, t)$ for the monodomain M_u . Since the porous sample P_u has almost the same characteristics as M_u , we can check whether Eq. (11) allows us to reproduce the data obtained for P_u . The result is shown in Fig. 7 and it appears that the computed spectrum fits the data very well.

In the case of a much narrower distribution $P(\Delta)$, the powder spectrum would exhibit a structured Pake pattern characterized by a doublet spacing exactly equal to the splitting which would be obtained with a similar monodomain at $\Omega=90^\circ$. In our case, although the order distribution prevents any structure from appearing, the overall half-height line broadening ($\delta\nu=400\text{ Hz}$) appears to be close to the splitting ($\Delta'=360\text{ Hz}$) observed on the spectrum obtained with the monodomain at $\Omega=90^\circ$ [Fig. 6(a)]. This shows that the porous sample can be used to determine the mean degree of segmental order S within the layer. This provides us with a method that is more straightforward and less time consuming than the use of monodomains. In particular, it has allowed us to systematically study the influence of various parameters

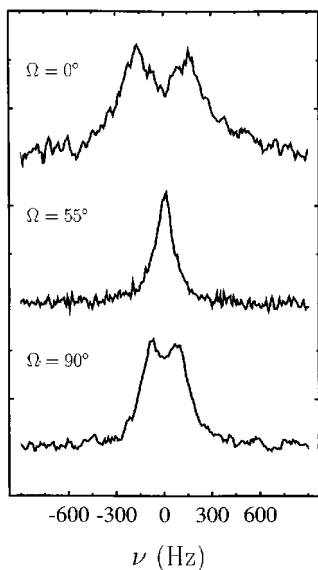


FIG. 8. ^2H NMR spectra of perdeuterated PDMS chains ($M_w = 101\,000$) end grafted on treated silica slides (sample M_t in Table I). Spectra were obtained at 13 MHz for different values of the angle Ω between the normal n to the slides and the spectrometer magnetic field \mathbf{B} . The number of scans for $\Omega = 0^\circ$ is typically 10^5 .

(e.g., grafting density) on the segment dynamics in these grafted layers in order to determine the origin of the observed anisotropy.

C. Melt grafted on treated surfaces

The results discussed so far were obtained with untreated surfaces. It is, however, well known that PDMS strongly adsorbs on bare silica surface. Therefore it was essential to determine whether such adsorption is at the origin of the observed anisotropy [18]. For this purpose, we have extended our investigations to samples where the silica surface was modified to suppress adsorption (see Sec. III E).

1. Uniaxiality

Figure 8 shows spectra obtained on the monodomain (M_t) for various angles Ω . As for the monodomain studied in the preceding section whose surface was untreated (M_u), the spectrum is still composed of a doublet whose spacing Δ' depends on Ω , with a pronounced narrowing effect at $\Omega = 55^\circ$. Again, Δ' varies with Ω according to the $|P_2(\Omega)|$ function quoted in Eq. (6). This result shows that the polymer layers grafted on pretreated surfaces exhibit the same type of uniaxial dynamics as melts grafted on untreated surfaces.

The procedure developed previously can be used to derive the order distribution $P(\Delta)$ for the sample M_t . The distribution $P(\Delta)$ and the fit of the spectrum obtained at 65 MHz are reported in Fig. 9. If we compare the two oriented samples (M_u and M_t), we can observe that their order distribution differs in the mean value of the effective residual interaction Δ [see Figs. 6(b) and 9(b)]. We do not believe that this difference is due to the effect of the surface pretreatment but rather to the grafting density which is not the same for both samples. This latter parameter seems to be the most impor-

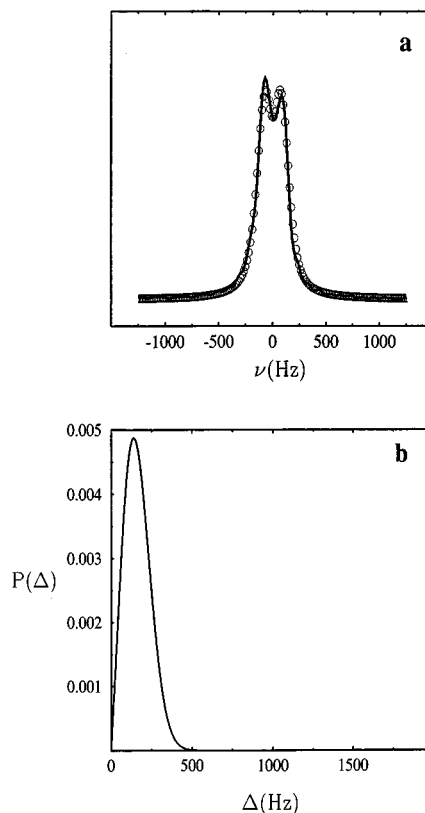


FIG. 9. Sample M_t —see Table I (monodomain, treated surface, $M_w = 101\,000$, $h = 140 \text{ \AA}$). (a) ^2H NMR spectrum. The experimental conditions are similar to those used to obtain the spectrum shown in Fig. 6(a). The open circles correspond to the NMR spectrum computed according to Eq. (9) for the order distribution $P(\Delta)$ shown in (b) ($\Delta_0 = 50 \text{ Hz}$ and $\sigma = 112 \text{ Hz}$).

tant for the mean degree of orientation, as we will see subsequently.

2. Effect of surface treatment

It has already been mentioned that the surface treatment has no effect on the uniaxial character of segmental motions. Thus polymer adsorption does not seem to play a crucial role in the molecular ordering. This is confirmed by the two samples P_t^2 and P_u , which have very similar characteristics (see Table I), the nature of their surface excepted (P_u : bare silica surface; P_t^2 : vinyl dimethylsiloxane modified silica). The NMR spectra of these two samples are similar [see Figs. 3(b) and 10 for $D = 36.6 \text{ \AA}$] and the T_2 values are very close. The line shape and linewidth are identical, indicating that the order distribution is the same for both samples. Moreover, it is important to point out that the ratio of NMR signal intensities—obtained under the same experimental conditions for both samples—is equal to the ratio of the amount of polymer per unit area Γ . This indicates that even in the presence of chain adsorption, the proportion of chain segments which are tightly bound to the grafting plane is not appreciable.

3. Effect of grafting density

To study the effect of the grafting density σ , we used a set of samples (P_t^1 , P_t^2 , P_t^3 in Table I) which differ only in their average distance D between grafting points.

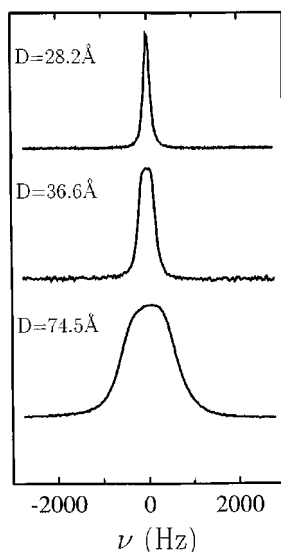


FIG. 10. ^2H NMR spectra for the samples P_t^1 , P_t^2 , and P_t^3 . These samples differ only in the average distance between grafting points D ($28 \text{ \AA} < D < 75 \text{ \AA}$).

As before (see Sec. IV B), the relaxation function of each of these three samples shows a well-defined pseudosolid echo after the pulse sequence Σ_2 and is characterized by one single relaxation time T_2 over two decades ($5 \text{ ms} \leq T_2 \leq 15 \text{ ms}$). Moreover, it appears that T_2 is a slightly increasing function of the grafting density.

The corresponding spectra are given in Fig. 10. These are unstructured powder spectra, and their line broadening—much higher than $1/\pi T_2$ —is dominated by the residual interactions effect. The effect of grafting density is clearly evident: the spectral linewidth $\delta\nu$ —i.e., the average order S —increases (from 100 Hz to 1.25 kHz) as the average distance D between grafting points increases (from 28.2 to 74.5 Å). Figure 11 shows that $\delta\nu$ increases with D in a nearly quadratic way. This variation was rather unexpected and is opposite to that calculated in the case of a strong lateral packing of polymer chains [19].

V. DISCUSSION

These experiments demonstrate that the dynamics of polymer chains in grafted layers differs strongly from the

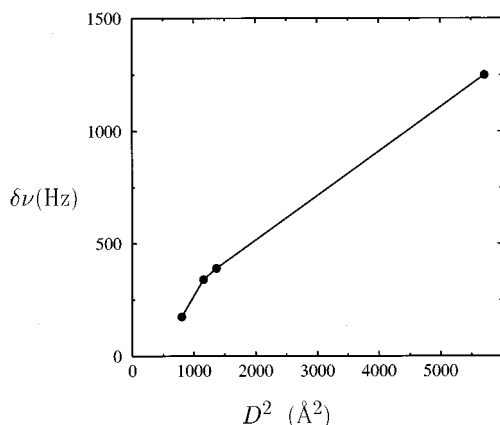


FIG. 11. Half-height linewidth of spectra shown in Fig. 10 versus D^2 .

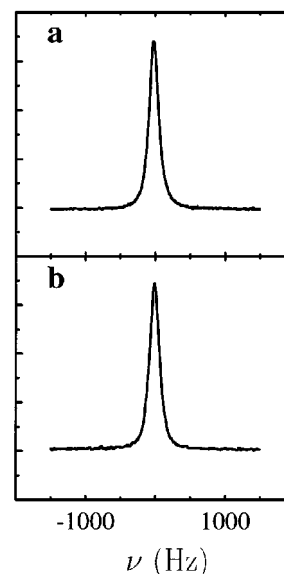


FIG. 12. ^2H NMR powder spectra of samples P_t^4 and P_t^1 obtained under the same experimental conditions.

bulk. Clearly, grafted chains exhibit uniaxial behavior, indicating they are submitted to constraints.

We observed that the relaxation function $M_e(t)$ of an end-grafted polymer is a single exponential, contrary to the corresponding polymer melt (of the same molecular weight) which exhibits a broad distribution of relaxation times. This indicates that the grafting makes slow intrachain motions more uniform along the chains. More precisely, the grafting must restrict the reconfiguration of polymer chains; in particular, the diffusion and the disentanglement process must be suppressed. Thus the apparent heterogeneity in the large scale motions (involving large subchain parts), leading to a broad distribution of relaxation times for the melt, is strongly reduced or even cancelled for the grafted chains [20]. Furthermore, it appears that this single decay time T_2 is smaller than the shortest relaxation time of the corresponding free melt (see Fig. 5). This is related to low frequency dynamics appearing because of constraints which induce motional restrictions. The variation of T_2 versus the grafting density σ suggests that the stretching cannot be the main source of constraints. This variation can, however, be explained if the chains are considered as squeezed between the polymer-air and polymer-silica interfaces; the larger the area per chain, the stronger the confinement would be.

The other important difference with respect to the bulk is the strong anisotropy of the segmental dynamics. It exhibits a clear uniaxial character, as demonstrated by the spectra observed on the monodomains: the chain segments are forced to reorient around the normal to the solid surface. Again, two types of interpretation could be proposed: either the segments tend to be perpendicular to the surface because the grafting induces interchain steric repulsion or, on the contrary, they tend to be parallel because the chains would be squeezed (the role of the adsorption has been shown to be marginal). The fact that the thickness of the layer is in any case not larger than the unperturbed radius of gyration R_g would favor the second explanation [21]. But it is the grafting density dependence which allows us to conclude: we

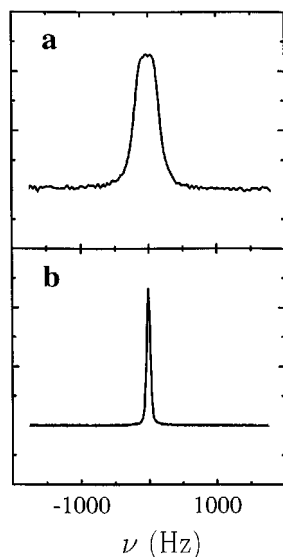


FIG. 13. ^2H NMR spectra of perdeuterated PDMS chains grafted on treated porous silica (sample P_t^2): (a) without solvent, (b) immersed in acetone.

observed that the larger the area per chain (i.e., the thinner the film) the stronger the anisotropy. Therefore the main cause of the uniaxial dynamics is the squeezing of the polymer between the silica and air surfaces. These confined chains must have an average anisotropic conformation with an oblate character relative to the silica surface. As a consequence of this confinement, the observed order parameter is *negative* [22] and describes segmental reorientational fluctuations which are uniplanar (parallel to the grafting plane), the orientational diffusion around the normal \mathbf{n} being isotropic. In the absence of such isotropic component, we would observe a bidimensional powder spectrum [23] typical of a random uniplanar distribution of chains (or subchains) lying on the grafting plane.

Since it appears that the squeezing is responsible for the anisotropy of the chain dynamics, the relevant parameter which has to be considered is the squeezing ratio h/R_g instead of the grafting density [24]. There must be a one-to-one correspondence between this ratio and the value of the degree of order. Indeed, in Fig. 12 we obtained exactly the same spectrum for two different samples (P_t^4 and P_t^1 in Table I), but with the same squeezing ratio ($h/R_g = 0.98$). This point is also confirmed by the spectra obtained with samples M_t and P_t^2 : we measured a residual nuclear interaction of 112 and 420 Hz, respectively; their grafting density is about the same ($D = 35$ and 36.6 Å, respectively) but their squeezing ratio is different ($h/R_g = 0.77$ and 0.58 , respectively). The same argument also explains the difference in the splitting observed for the two monodomains M_t and M_u (see Figs. 6 and 9).

To measure a positive order parameter in these grafted melts would require achieving a much higher grafting density. Indeed, we observed with two samples which had a squeezing ratio greater than one ($h/R_g = 1.2$) that the line-width increases again with h/R_g (spectra not shown). However, it also appears that for these two samples, the order distribution is much broader. Further investigations are

needed to confirm that S would change its sign around $h/R_g = 1$.

If we keep the molecular weight constant, there are two ways to vary the squeezing ratio: either by changing the grafting density, as discussed above, or by swelling the polymer layer. We report some data here that were obtained with sample P_t^2 immersed in acetone. Acetone is a poor solvent for PDMS with an equilibrium volume fraction of about 34% [12]. In such a solvent, the grafted layers have a density profile which is not far from a step as in air (with two well-defined interfaces). Therefore we can consider that h/R_g increases by a factor of 52% in acetone. The ^2H NMR spectra are shown in Fig. 13. In the presence of acetone, the spectrum gets narrower ($\delta\nu \sim 60$ Hz instead of 420 Hz in air). This tells us that the segmental motions are slightly anisotropic, indicating that the PDMS grafted chains of sample P_t^2 are almost isotropic in acetone. This result is consistent with our analysis, namely, that the observed anisotropy is due to the squeezing effect. If we go to much better solvent than acetone, we should observe an inversion of the sign of the order parameter because it has been proved by SANS that similar grafted chains in good solvents are strongly stretched [3]. This is indeed what we observed and more details will be published elsewhere.

It is remarkable that the ^2H NMR response of oriented samples appears under the form of one single and resolved doublet structure. This is due to the order distribution $P(\Delta)$ which is rather well centered around a mean value. It would be tempting to derive from $P(\Delta)$ the profile $S(z)$ along the normal to the surface within the layer. However, such an operation is not easy: there is no one-to-one correspondence between $P(\Delta)$ and $S(z)$, unless we make assumptions which are difficult to justify. A proper experimental method would require the use of labeled block copolymers. Nevertheless, we can propose a scheme for $S(z)$ that accounts for the main three features of $P(\Delta)$ [see Figs. 6(b) and 9(b)], namely, $P(\Delta)$ exhibits a rather well-defined peak which corresponds to the observed doublet spacing; there is no isotropic component and lastly, there is a small fraction of strongly oriented segments [the tail of $P(\Delta)$]. We can suppose that at both interfaces, the segments are strongly ordered ($S < 0$) while the rest of the layer has on average the same degree of anisotropy, characterized by a lower value for $|S|$. It is widely recognized that an impenetrable wall induces a strong orientation of the segments which are close to the wall [25], the lower limit being perfect in plane alignment ($S = -0.5$). This steric effect is believed to be of rather short range, typically a few persistence lengths (i.e., a few monomers for PDMS). In our case, we observe segments far away from the surfaces still exhibit a uniaxial dynamics $|S| \neq 0$. We believe this is related to the effect of the surfaces (density-conformation couplings, as described in Ref. [26]), enhanced by some additional short-range orientational interactions between chain segments. These interactions correlate the orientational fluctuations of segments belonging to neighboring chains and so contribute to make more uniform the segmental ordering within the layer. Such effects of orientational correlations, already observed on various other cases of confined polymers (uniaxially strained networks, for instance), are known to depend on the local density of chain segments [26]. This appears to be confirmed by the experi-

ment done in the presence of acetone: although the squeezing ratio is lower than one ($h/R_g=0.88$), the linewidth ($\delta\nu=60$ Hz) is much smaller than for the sample P_1^1 ($\delta\nu=160$ Hz) observed in air (characterized by a squeezing ratio $h/R_g=0.98$).

Finally, the above-mentioned segmental order may be the source of peculiar properties exhibited by constrained (i.e., very thin) polymer films, like unusual glass transition temperature or rate of crystallization [27]. It might also be relevant for the autophobic behavior [28].

VI. CONCLUDING REMARKS

Aspects of molecular dynamics in end-grafted polymer melts are revealed by this NMR study. In particular, it is clearly shown that the polymer segment dynamics exhibits collective uniaxial fluctuations. They are described by a negative order parameter and a high degree of anisotropy ($|S|\approx 10^{-2}$), because the chains are constrained within a layer thinner than their radius of gyration. There must be a

quite homogeneous orientational field describing the order S , induced by the squeezing and by the surfaces, although we do not know which effect is predominant.

We are currently developing several ^2H NMR studies which might be very useful in gaining more information about the segment dynamics in confined polymer films. One consists in looking at free polymer films thinner than the unperturbed radius of gyration. Another crucial investigation consists in observing grafted layers in good solvent where the chains are strongly stretched. We have already anticipated that the order parameter must change its sign, but how is the order distribution affected?

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- [1] S. T. Milner, *Science* **251**, 905 (1991).
- [2] G. J. Fleer *et al.*, *Polymers at Interfaces* (Chapman and Hall, Cambridge, England, 1993).
- [3] P. Auroy, Y. Mir, and L. Auvray, *Phys. Rev. Lett.* **66**, 719 (1991); P. Auroy, L. Auvray, and L. Léger, *Physica A* **172**, 269 (1991).
- [4] A. Karim *et al.*, *Phys. Rev. Lett.* **73**, 3407 (1994).
- [5] M. Zeghal, P. Auroy, and B. Deloche, *Phys. Rev. Lett.* **75**, 2140 (1995).
- [6] E. T. Samulski, *Polymer* **26**, 177 (1985).
- [7] J. P. Cohen-Addad, *J. Chem. Phys.* **60**, 2440 (1974). The quadrupolar Hamiltonian is analogous to the dipolar Hamiltonian of a proton pair. The relaxation function for a deuterium nucleus is written in the same way as developed in this reference.
- [8] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
- [9] B. Momper, Th. Wagner, U. Maschke, M. Ballauff, and E. W. Fischer, *Polymer Commun.* **31**, 186 (1990).
- [10] T. Suzuki, *Polymer* **30**, 333 (1989).
- [11] W. Kern, *J. Electrochem. Soc.* **137**, 1887 (1990).
- [12] P. Auroy, L. Auvray, and L. Léger, *Macromolecules* **24**, 5158 (1991).
- [13] P. Auroy, L. Auvray, and L. Léger, *J. Phys. Condens. Matter* **2**, SA317 (1990).
- [14] J. P. Cohen Addad and R. Dupeyre, *Macromolecules* **18**, 1101 (1985); M. G. Brereton, I. M. Ward, N. Boden, and P. Wright, *ibid.* **24**, 2068 (1991).
- [15] H. Toriumi, B. Deloche, J. Herz, and E. T. Samulski, *Macromolecules* **18**, 305 (1985).
- [16] Since the T_1 value is not affected by the grafting ($T_1=180$ ms), the main contribution to the transverse relaxation time T_2 measured on grafted polymer chains comes from low frequency motions. Under these conditions, it is possible to compare the homogeneous broadening of spectra obtained for different Larmor frequency values.
- [17] The field inhomogeneity was taken into account to fit the experimental spectra obtained with monodomains.
- [18] T. Cosgrove and P. C. Griffiths, *Adv. Colloid Interface Sci.* **42**, 175 (1992).
- [19] P. G. de Gennes, *Phys. Lett.* **47A**, 123 (1974).
- [20] At this point, it is relevant to refer to the work of Fredrickson and collaborators [G. Fredrickson *et al.*, *Macromolecules* **25**, 2882 (1992)] who showed theoretically that there exists a selected wavelength for the deformation of a polymer brush (long-range fluctuations are suppressed by grafting as are very short-range deformations by capillary).
- [21] The absolute value of R_g is somewhat arbitrary. In melt, we have $R_g=aN^{1/2}$ where a is a monomer size. In this paper, we took $a=5$ Å, which may be overestimated. Experimentally, R_g has been determined in θ solvent: $R_g=0.256M_w^{0.5}$, i.e., $R_g=2.28N^{0.5}$. This uncertainty does not affect qualitatively our conclusions. It may, however, change the value of the threshold h/R_g below which the chains are squeezed.
- [22] It may be noted that the value of the order parameter S which is directly worked out from the doublet spacing is surprisingly high for flexible polymer chains. Typical value is $S=-2.3\times 10^{-2}$ —sample M_u , Fig. 6. Copolymer blocks or stretched networks give rise to an order parameter S in the range of 10^{-3} . See S. Valic *et al.*, *Polymer* **36**, 3041 (1995).
- [23] H. W. Spiess, in *Advances in Polymer Science*, edited by G. Zachmann (Springer-Verlag, Berlin, 1985), Vol. 66, pp. 23–58.
- [24] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979); D. Ausserré, *J. Phys. (France)* **50**, 3021 (1989).
- [25] G. Brinke, D. Ausserré, and G. Hadziioannou, *J. Chem. Phys.* **89**, 4374 (1988); A. Yethiraj, *ibid.* **101**, 2489 (1994); D. C. Morse and G. M. Fredrickson, *Phys. Rev. Lett.* **73**, 3235 (1994).

- [26] P. Sotta, B. Deloche, and J. Herz, *Polymer* **29**, 1171 (1987).
- [27] C. W. Frank, V. Rao, M. M. Despotopoulou, R. F. W. Pease, W. D. Hinsberg, R. D. Miller, and J. F. Rabolt, *Science* **273**, 912 (1996).
- [28] L. Leibler, A. Ajdari, A. Mourran, G. Coulon, and D. Chatenay, in *Ordering in Macromolecular Systems*, edited by A. Teramoto, K. Kobayashi, and T. Norisuje (Springer-Verlag, Berlin, 1994), pp. 301–311.