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Nuclear magnetic relaxation without spin diffusion in polymers at interfaces

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We consider theoretically the possibility of solid state NMR experiments with frozen linear polymer chains at interfaces. Three different cases are studied, namely, when the macromolecules are grafted on the surface, when they are adsorbed, and when they are very strongly adsorbed from a melt that is subsequently washed by a good solvent. The latter case is somewhat intermediate between the two former ones. For each case, we consider the relaxation when paramagnetic centers are located on the surface. We show that the shape of the relaxation curves depends critically on the monomer concentration profile, and exhibits characteristic power-law variations. [S1063-651X(99)04305-6]

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) has proven to be a very efficient technique for studying static and dynamic properties of polymers [1–4]. It has recently been possible to measure the fractal dimension of polymers and gels by solid state NMR. This was successfully demonstrated by Devreux [5] on silica gels, and more recently by Tabti *et al.* [6,7] on glassy frozen linear polymers. The gist of the method is to place dilute paramagnetic centers (PC's) *on* the polymer; the nuclei of the polymer become inequivalent with respect to nuclear relaxation: in a frozen gel or solution the nuclei close to the PC's relax more rapidly than those at large distances. This leads, under suitable conditions (no spin diffusion), to a nonexponential relaxation of the overall nuclear magnetization M. The fractal dimension d_f is obtained from an analysis of the relaxation curve shape and, in particular, from the short time behavior that obeys a power law $M \sim t^{\alpha}$. These experiments lead to measurements of the fractal dimensions that are in agreement with what was predicted by percolation and by the de Gennes' theory [8] for polymers. It seemed to us that it would be interesting to study the case when polymers are located at surfaces. Most of the experimental studies for the determination of polymer density profiles at interfaces were made so far by neutron reflectivity [9,10], or by neutron or x-ray scattering experiments [11]. NMR would provide an interesting independent and complementary way of probing the local chain conformations. In the following, we would like to consider the case of linear polymer chains in the vicinity of a surface. Two different cases may be discussed, concerning macromolecules that are either grafted by an end point, or adsorbed onto the surface. In each of these cases one can gain information by studying a mixture of protonated and deuterated polymers in a proton-free solvent. This allows one to consider the relaxation of only those chains that are hydrogenated. In the limit of small fractions of protonated chains, single chain behavior can be observed. By increasing the fraction of hydrogenated polymers, one crosses over to the case where all chains are identical. As we will see, one expects to get identical information from these experiments for short times, but quite different results for longer times. Let us stress that in all cases the polymers are quenched at low temperature so that their motions are frozen.

As mentioned above, polymers may be attached to a surface in two different ways: they may be grafted by one end of a monomer. They may also be adsorbed by an attractive surface. In the former case, the surface is assumed to be neutral, and for a large density of graft points, only one monomer is located on the surface. The remainder of the macromolecule adopts a stretched configuration because of the repulsion by the other chains. In the latter case, a finite fraction of the monomers is located on the surface, and the adsorbed polymer layer has a characteristic concentration profile that may be checked by NMR, as we shall discuss. In the following, we will first consider the case of a semidiluted solution. This was already discussed in [6] a slightly different way . We will then turn to surfaces. Section III discusses grafted polymers, while the case of adsorbed chains is studied in Sec. IV.

II. A REMINDER OF NUCLEAR RELAXATION OF SEMIDILUTED SOLUTIONS

We first briefly review the configuration of linear polymer chains in solution. We assume that each macromolecule is made of N monomers of size a. In a dilute solution, the various chains are far from each other. It was shown that it is possible to define a characteristic distance R, which is related to N by a fractal dimension d_f:

$$N \sim \left(\frac{R}{a}\right)^{d_f}, \tag{1}$$

where d_f is very close to 5/3 in a good solvent, and to 2 in a so-called theta solvent [12,13]. In the former, the only interaction between monomers is the excluded volume interaction, which prevents any two monomers from being on top of each other. This corresponds to a self avoiding walk. In the latter, the previous interaction is compensated by larger distance attraction, and the polymer may be considered roughly as a random walk in three-dimensional space.

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As the monomer concentration c is increased, the average distance d between polymers decreases until it becomes of the order of R. This occurs at the overlap concentration $c^{\star}$:

$$c^{\star} \sim \frac{N}{R^3} \sim N^{d_f-3} a^{-3}. \tag{2}$$

For larger concentrations, polymers overlap. This is the semidiluted regime that will be considered below. In this concentration range, $c^{\star} \ll c \ll 1$, it was shown that a second length is present, in addition to the radius R of the chains. This is the screening length ξ, and corresponds to the average distance between successive contacts of a given chain with the others [14–16]. Therefore, the solution may be described in the following way: for distances smaller than ξ, the chain has the same conformation as in a diluted solution. More precisely, excluded volume interactions are present for these small distances. For distances larger than ξ, the interaction is screened, and the chain behaves as a random walk. Both R and ξ may be obtained by scaling arguments, assuming that they are only a function of the relative concentration $c/c^{\star}$. We discuss rather the ''blob model,'' that is based on the preceding description: locally, excluded volume interactions are present. This implies that for distances smaller than or equal to ξ, one may generalize relation (1). A blob is a part of the polymer, made of g monomers, with size ξ, such that

$$g \sim \left(\frac{\xi}{a}\right)^{5/3}, \tag{3}$$

where we restricted the discussion to good solvents. Because of screening, the chain may be considered as a random walk, if one takes the blob as an elementary step unit:

$$R^2 \sim \left(\frac{N}{g}\right) \xi^2. \tag{4}$$

Because screening is local, one expects the screening length to be independent of the total chain length N. Thus, it is plausible to assume that g depends on concentration as

$$g \sim c^{\alpha}. \tag{5}$$

Finally, α is determined by continuity: at the overlap concentration, one expects g to become of the the order of the chain length N. This leads to

$$\xi \sim c^{-3/4} \tag{6}$$

and

$$R \sim N^{1/2} c^{-1/8}. \tag{7}$$

These relations were checked experimentally by small angle neutron scattering. It is important to note that in order to be able to observe the properties of a chain at distances larger than ξ, one needs to label some chains, for instance, by deuteration. When no labeling is made, one may still observe the local properties. But at larger distances, one observes a transient gel, with mesh size ξ. Therefore, such measurements would not lead to a fractal dimension equal to 2 but 3.

To show how scaling arguments can be used to predict the relaxation behavior we consider the case of a frozen semidiluted solution. This case has been studied both theoretically and experimentally in [6,7]. We shall not use the theory developed in [6] but a simplified approach, which is appropriate for describing relaxation at short time, and which correctly accounts for the power-law variation of magnetization in this regime. This approach was used in [5]. The nuclei, whose relaxation we consider, are placed in a magnetic field B_0 and have a gyromagnetic ratio γ. The dipolar coupling of a nuclear spin I to the spin S of a PC located at a distance r is proportional to r^{-3}. The fluctuations of S due either to its own spin lattice relaxation or to ''flip-flops'' between neighboring PC's give rise [17] to the relaxation of spin I at a rate W proportional to r^{-6}:

$$W = \frac{C}{r^6}. \tag{8}$$

The component of I whose relaxation is observed depends on the technique employed to ''quench'' spin diffusion. In the case of linear polymers the nuclei were irradiated by a radio-frequency field of amplitude B_1 and frequency $\omega = \omega_0 + \Delta$ where $\omega_0 = -\gamma B_0$ is the Larmor frequency. In the frame rotating at frequency ω the nuclear spins ''see'' an effective field $\mathbf{B_{eff}}$ of components $-\Delta/\gamma$ and B_1, respectively, along and perpendicular to B_0. Spin diffusion is inhibited when the angle between $\mathbf{B_{eff}}$ and $\mathbf{B_0}$ takes the ''magic angle'' value $\theta = 54.7°$. In these types of experiments one observes the component I_Z of magnetization along $\mathbf{B_{eff}}$.

The proportionality constant C depends upon the angle between $\mathbf{r}$ and the applied magnetic field $\mathbf{B_0}$ but we shall neglect this dependence in the following since it only affects the final result through a numerical factor. After a saturating pulse, which cancels the nuclear magnetization, the component I_Z of I evolves according to

$$I_Z \sim \exp\left(-\frac{Ct}{r^6}\right). \tag{9}$$

At a short time scale one can consider that each nuclear spin is relaxed by the closest PC and the relaxed magnetization M is given by

$$M(t) \sim \int_0^{+\infty} \exp\left(-\frac{Ct}{r^6}\right) \rho(r) r^2 dr, \tag{10}$$

where $\rho(r)$ is the density of nuclei around the relaxing center. The exponential term in relation (10) decreases steeply from the value 1 to zero at a distance $r(t)$ of the order $r(t) = (Ct)^{1/6}$ and we can approximate relation (10) by

$$M \sim \int_{r_0}^{r(t)} \rho(r) r^2 dr. \tag{11}$$

The magnetization is thus proportional to the number $N(t)$ of nuclei inside a sphere of radius $r(t)$. Assuming $C=1$, if $r(t)$ is smaller than the screening length ξ of the solution:

$$M(t) \sim r^{d_f} \sim t^{d_f/6} (t \ll \xi^6), \tag{12}$$

from which d_f can be deduced. Relation (12) was used to check that $d_f \simeq 5/3$ and we shall use this value in the following. For distances $r(t) > \xi$ the solution becomes homogeneous viewed from the PC's and the relaxation regime changes to

$$M(t) \sim N(\xi) \left(\frac{r}{\xi} \right)^3 \sim \xi^{d_f - 3} t^{1/2} (t \gg \xi^6). \tag{13}$$

In all that precedes we have assumed that the mean distance between PC's is larger than $(Ct)^{1/6}$ so that each nucleus can be considered relaxed by a single PC.

Remark. Case of a small fraction of protonated polymers. This case has not been studied experimentally. Since a single chain is Gaussian on a scale larger than ξ, one expects that relation (13) is replaced by

$$M(t) \sim N(\xi) \left(\frac{r}{\xi} \right)^2 \sim \xi^{d_f - 2} t^{1/3} (t \gg \xi^6). \tag{14}$$

III. GRAFTED CHAINS

Let us now consider a flat solid surface. Polymer chains are grafted by one of their end points with density $\sigma \sim d^{-2}$ where d is the average distance between graft points. The structure of the resulting layer was discussed by Alexander [18] and by de Gennes [19], and others [20–23]. We recall briefly their results. When d is larger than the radius of gyration R of a single chain, the structure of every polymer remains basically unchanged. As d becomes smaller than R, because of the excluded volume interactions between monomers, the chains adopt a stretched configuration. The width of the layer may be found by a simple scaling argument. Assuming that the radius depends only on the ratio of the radius to the distance d, we have

$$R \sim N^{3/5} f\left(\frac{N^{3/5}}{d} \right), \tag{15}$$

where the exponent 3/5 corresponds to a single polymer in a good solvent. The function $f(x)$ is unknown but has known asymptotic behavior: for large x, it has a power-law behavior, $f(x) \sim x^\alpha$, where the exponent α is determined by the condition that the polymer has an extended shape, so that its radius is proportional to N. Inserting this into relation (15) leads to

$$R \sim N\, d^{-2/3} (d \ll N^{3/5}). \tag{16}$$

This may also be described in a different way. If we consider a part of the polymer, made of n elements, this remains isotropic as long as n is small. For larger values of n, the chain realizes that other chains are grafted at a distance d and adopts an extended structure. Therefore, we may introduce blobs, made of g elements, such that

$$d \sim g^{3/5} \tag{17}$$

and the chain is a linear array of these blobs:

$$R \sim \left(\frac{N}{g} \right) d. \tag{18}$$

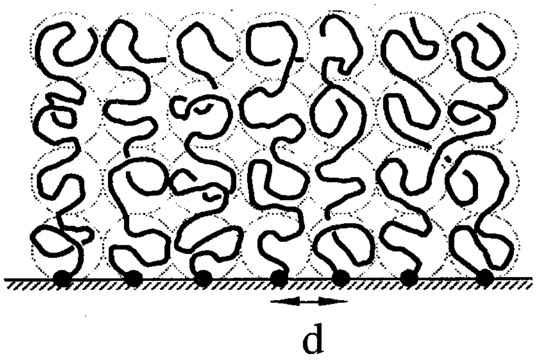

FIG. 1. Configuration of a layer of grafted polymers and visualization of blobs.

Using relations (17) and (18), one recovers Eq. (16). The corresponding configuration is shown on Fig. 1. In this Alexander-de Gennes approach, one may consider that one has a layer of constant density made of these blobs. Subsequently, it was shown by Milner, Witten, and Cates (MWC) [24] that although this simple scaling picture gives the right variations for the variables, there is a parabolic density profile extending from the surface to the outside: the local concentration at a distance x from the surface varies as

$$C(x) = C_0 - \frac{1}{2} \left(\frac{x}{R} \right)^2. \tag{19}$$

This is related to the fact that the end points are not at the outer end of the layer, but might be located anywhere in it. These results may be checked by NMR experiments. We will first consider the case when PC's are present at every graft point on the surface. For short times, when one considers monomers inside a blob, the monomers that are relaxed are localized in the first layer of blobs, along the surface. The magnetization $M(t)$ increases as

$$M(t) \sim N(t), \tag{20}$$

where the number $N(t)$ of relaxed sites is the number of monomers that are at a distance smaller than $x(t)$ such that

$$x(t) \sim t^{1/6}. \tag{21}$$

Thus, the observed magnetization is

$$M(t) \sim x^{5/3} \sim t^{5/18}. \tag{22}$$

This is identical to what is observed for short times in a semidiluted solution of chains. But the characteristic time beyond which relation (22) is no more valid is different for both cases: whereas it is determined by the concentration in bulk solutions, it is fixed by the density in graft points in the present case. The crossover time to a different relaxation corresponds to a distance on the order of the blob size here:

$$T_d \sim d^6. \tag{23}$$

For times larger than T_d, two effects have to be considered. The first one is that each monomer is interacting with more than one PC on the surface. The second one is that one has to take into account the concentration profile. We consider the first effect, and assume that the profile is constant, as in the Alexander-de Gennes approach. Then for distances larger than the blob size, every monomer is no longer interacting only with the PC that is located on the end point of the chain to which it belongs. One may consider that it is interacting with all $(x/d)^2$ PC's on the surface that are located within a distance x from its own graft point. Note that this allows the relaxation to cross over from a spherical symmetry, at the local—blob—scale to a planar symmetry for large distances. Because the relaxation rate is the sum of contributions from all PC's, the local relaxation rate is no longer proportional to x^{-6}, but to $(x/d)^2 x^{-6}$. Thus we find

$$W(x) \sim d^{-2} x^{-4} (x > d) \tag{24}$$

leading to

$$x \sim \left(\frac{t}{d^2} \right)^{1/4} (x > d), \tag{25}$$

instead of Eq. (21). In the Alexander-de Gennes scaling approach the grafted layer is assumed to be made of a constant density of blobs. This implies that the density of relaxing monomers is a constant as a function of the distance h to the wall. This in turn implies that the signal increases as

$$M(t) \sim N(d) \frac{x}{d} \sim d^{1/6} t^{1/4} (R^4 d^2 \gg t \gg T_d), \tag{26}$$

where the d-dependent prefactor ensures a smooth crossover between relations (22) and (26) for time T_d [relation (23)]. Although the constant density assumption gave the right scaling results, it was shown by MWC that a more accurate analysis leads rather to the parabolic decrease described in Eq. (19). This would lead to a different form for $t > T_d$. Indeed, Eq. (19) implies that in addition to the linear term that we just considered, there is a cubic term correction:

$$N(x) \sim x - a x^3 \tag{27}$$

leading to

$$M(t) \sim d^{1/6} (t^{1/4} - b t^{3/4}) (R^4 d^2 \gg t \gg T_d), \tag{28}$$

where the coefficient b may be directly deduced from Eq. (19). The difference between Eqs. (26) and (28) may be seen by NMR experiments on samples where all polymers are hydrogenated and all graft points are spinlabeled. Interestingly, if some of the graft points only are spinlabeled, an intermediate regime appears both because the relaxation remains related to only one graft point for intermediate times, and also because the symmetry remains spherical. Then for intermediate times, between time T_d and the time when more than a single labeled graft point come into play, one should observe a relaxation where relation (21) is valid between time and distance, and where the number of blobs increases in a three-dimensional way: for distances larger than the size of a blob, the sphere of relaxed nuclei around a given graft point contains densely packed blobs. This leads, for intermediate times, to a relaxation:

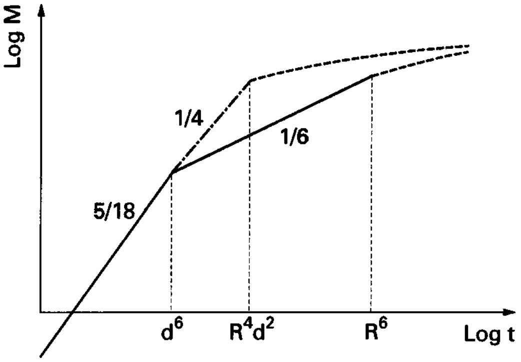

FIG. 2. Variation with time of the proton magnetization of a layer of grafted chains. Dash-dotted curve: all chains are protonated. Continuous curve: a very small proportion of the chains are protonated. In both cases the protonated chains bear a PC at the grafting end.

$$M(t) \sim N(d) \left(\frac{x}{d} \right)^3 \sim \frac{t^{1/2}}{d^{4/3}} (T_G \gg t \gg T_d), \tag{29}$$

where T_G corresponds to the characteristic time for more than one labeled point to contribute to the relaxation. If D is the distance between labeled graft points, $T_G \sim D^6$. Finally, we mention the possibility of labelling only one (very few) chains that would be hydrogenated in otherwise deuterated grafted polymers. The labeled chain is grafted by paramagnetic centers. In this case only is one able to observe the stretched nature of the grafted polymers. Apart from a normalization factor related to the fact that some chains only are relaxing, the signal has the same form as Eq. (22) for short times, smaller than T_d. For larger times, relaxation should be a purely one-dimensional phenomenon because the chain under observation is stretching outwards: the number of blobs involved in the relaxation increases then linearly for large distances, so that

$$N(t) \sim N(d) \frac{x}{d}, \tag{30}$$

with x and t still related by relation (21), leading to

$$M(t) \sim d^{2/3} t^{1/6} (R^6 \gg t \gg T_d). \tag{31}$$

Figure 2 shows a sketch of the relaxation behaviors in the case when all chains are protonated and in the case when a very small fraction of the chains are protonated. In both cases it is assumed that the PC's are borne by the protonated chains and that the concentration profile is the one predicted by the Alexander–de Gennes model.

IV. ADSORBED POLYMERS

A second way to have polymers at interfaces is to adsorb them [25–28]. Although the interaction of a monomer with a surface is usually small, the interaction of a chain may be very large. This is due to the fact that many monomers of a given polymer are located on the surface. We will be concerned only with the attractive case. Two regimes may be considered, namely, the adsorption of a single chain, and the saturation regime. This corresponds to the situation where no more polymers may be attached to the surface, for a given value of the attraction. (Note, however, that this does not imply complete coverage by monomers). We recall first the results about the adsorption of a single chain and in the plateau regime, when the surface is saturated. In the following we will consider impenetrable surfaces. A similar approach could be made for interfaces [relation (32) which would have to be changed].

Consider a chain that is attached to the surface. Every monomer is assumed to have an attractive free energy gain $kT\delta$ when localized on the wall. Because of the linear nature of the polymer, the number N_S of monomers on the surface is [29]

$$N_S \sim N^{3/5}, \tag{32}$$

where we assumed that the wall is flat and impenetrable, and that excluded volume effects are present between monomers. Note that the latter relation is valid only in the isotropic case, when the polymer is not adsorbed. Therefore, the energy gain is $kT\delta N_S$. When this becomes larger than the thermal energy, the polymer is adsorbed on the wall, and adopts a flat configuration. The number of monomers on the surface becomes proportional to N, and may be obtained by a scaling argument [30,31] where one assumes that the variable is the relative energy gain δN_S. The same type of argument is also used to get the width D of the adsorbed polymer:

$$D \sim N^{3/5} f(\delta N^{3/5}). \tag{33}$$

Assuming that for large energies the function $f(x)$ behaves as a power law, one gets the exponent by the constraint that in this state the width D of the chain is independent of N, and depends only on δ. One gets

$$D \sim \delta^{-1}. \tag{34}$$

One may consider sequences along the chain, made of n elements. When n is small, the number of monomers on the surface is small, and the sequence is not adsorbed. When n is large, the sequence is adsorbed. The crossover corresponds to a so-called surface blob, made of g elements, such that the energy gained by the monomers on the surface just compensates the entropy loss kT:

$$\delta g^{3/5} \sim 1. \tag{35}$$

The size D of these blobs is

$$D \sim g^{3/5} \sim \delta^{-1}, \tag{36}$$

which is the width obtained above. Thus, the adsorbed chain may be considered as a two-dimensional polymer if one takes the surface blob as a unit. Its radius parallel to the plane is

$$R_{//} \sim \left(\frac{N}{g}\right)^{3/4} D \sim N^{3/4} D^{-1/4}. \tag{37}$$

If we consider a polymer solution in the presence of an attractive surface, some chains are attracted, and there is a partitioning of the macromolecules between the bulk and the surface. One may estimate by a Boltzmann weighting the relative fraction in each of the populations. As the surface interaction δ is increased, more polymers are attracted, and the surface concentration increases. Because of excluded volume effects, once the adsorbed polymers start overlapping, loops with size larger than D appear. Their size grows as the surface concentration increases. There is a plateau region, where the surface is saturated with surface blobs [30]. There is then a concentration profile between the surface, where the monomer concentration may be high, and the bulk of the solution, which may still be in a dilute regime. This is the case that we consider now. It was shown by Pincus and de Gennes [32] and by Eisenriegler *et al.* [29] that the profile is made of three regions.

The surface concentration Φ_S is the number of monomers on the surface per blob:

$$\Phi_S \sim \frac{g^{3/5}}{D^2} \sim \delta. \tag{38}$$

(i) For distances smaller than D, in the proximal region, the profile decreases as

$$\Phi(z) \sim \Phi_S \left(\frac{z}{a}\right)^{-1/3} (z < D), \tag{39}$$

where $\Phi(z)$ is the number of monomers per unit surface at a distance z from the surface;

(ii) For intermediate distances, in the central regime, $D \ll z \ll R$, the layer has a self similar behavior and Φ depends only on z:

$$\Phi(z) \sim z^{-4/3}, \tag{40}$$

where R is the isotropic radius of the polymer;

(iii) In the distal regime, for $z \gg R$, the profile decreases exponentially. Note that as δ increases, the surface concentration increases and the width of the proximal region decreases. For large attraction, when δ is of order unity, the surface concentration is unity, and the proximal layer does not exist anymore.

In what follows, we assume that PC's are localized on the surface, and we consider the relaxation of the polymers. We study the case when all polymers are equivalent.

A. The single polymer

When the surface concentration of polymers at equilibrium is very small, the equilibrium time is very long. It is more convenient to graft the appropriate amount of polymers on the surface by one of their end points. We shall consider that the grafting point bears a PC. In the single chain case, one may separate the short from the long time scales as above: for short times, relaxation occurs within a surface blob. For larger times, one is probing the long-distance arrangement of the macromolecule. The analysis of the previous section tells us that the local conformation of the polymer, inside a blob, is the same as for a free chain. Thus we expect the same type of relaxation as before, and relation (22) is valid: $M(t) \sim t^{5/18}$. The crossover time T_x, however, is related to the strength δ of the interaction. It corresponds to relaxation reaching points located at a distance on the order of the width D of the adsorbed chain. This implies

$$T_x \sim D^6 \sim \delta^{-6} (\delta N^{3/5} \gg 1). \tag{41}$$

For times larger than T_x, one probes the structure of the adsorbed chain. As discussed above, this is two-dimensional if one considers the adsorbed blob as a unit. This implies

$$M(t) \sim N(D) \left(\frac{x}{D} \right)^{4/3} \sim D^{1/3} t^{2/9} (T \gg t \gg T_x), \tag{42}$$

where we used $N(D) \sim D^{5/3}$, and we assumed that relation (21) is still valid. $T \sim R_{//}^6$ is the characteristic relaxation time for the whole chain, with $R_{//}$ given by relation (37). We turn now to the plateau regime.

B. Saturated surface

We consider now a flat surface saturated with adsorbed linear polymers. Magnetic centers are supposed to be distributed on the surface, and all chains are equivalent. For the sake of simplicity, we will assume that the attraction is high, $\delta \simeq 1$. This implies that the surface concentration is approximately unity, and that only the central regime is present, so that the profile varies as in relation (40). Let I be the average distance between PC's. As in the preceding sections, we find that two different relaxation regimes occur, depending on the distance scale that is being probed. For short distances and times, the relaxed nuclei form spherical pockets of radius $r \sim t^{1/6}$ around the PC's. The number of nuclei in these pockets is

$$N(t) \sim \int_a^r z^{-4/3} (r^2 - z^2) dz \sim r^2 \left[1 - \frac{1}{5} \left(\frac{a}{r} \right)^{1/3} \right] (t \ll I^6). \tag{43}$$

It is easy to see that the dominant contribution in $N(t)$ comes from nuclei at a distance $z \sim a$ from the surface and that the variation of $N(t)$ in this regime ($N(t) \sim t^{1/3}$) does not depend on the shape of the profile.

For large distances, every site is relaxed by several PC's, and the symmetry becomes planar, as in the grafted chain case. Then, as discussed in the grafted polymer case, the relaxation rate is proportional to x^{-4} instead of x^{-6} [see relation (24)]. The nuclei relaxed are those located between the surface and the plane at height

$$x \sim \left(\frac{t}{I^2} \right)^{1/4}. \tag{44}$$

Their number is

$$N(t) = \int_a^x z^{-4/3} dz \sim \text{const} - x^{-1/3}. \tag{45}$$

This gives a magnetization varying as

$$1 - \frac{M(t)}{M_{eq}} \sim t^{-1/12} (R^4 I^2 \gg t \gg I^6), \tag{46}$$

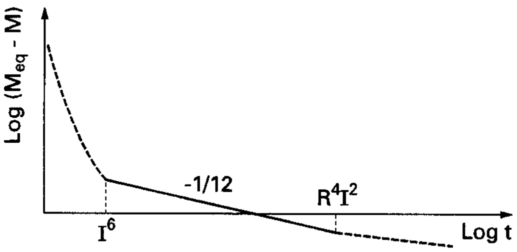

FIG. 3. Variation with time of the nuclear magnetization of an adsorbed layer of polymer chains. Paramagnetic centers are distributed on the surface with an average separation I.

where $M_{\rm eq}$ is the equilibrium magnetization. The variation of $M_{\rm eq} - M$ predicted by Eqs. (43) and (46) is shown on Fig. 3.

C. Strong adsorption

Recently, Guiselin [33] considered the case when polymer chains are strongly adsorbed on a solid surface. More precisely, he studied the case when a melt — or a semidiluted solution — is in the presence of a strongly adsorbing wall. The interaction energy δ that was considered above is assumed to be much larger than the thermal energy. This implies that whenever a monomer is in contact with the surface, it is irreversibly bound to it; then the bulk is washed by a good solvent. Because the chains are very strongly adsorbed to the wall, there results a concentration profile that is very different from the one that exists when δ is small, and was discussed above: the loop distribution is presently characteristic of a melt, and different from the previous equilibrium case. This distribution was considered by Guiselin [33,34] and by Aubouy [35]. They showed that the layer may be considered as a polydispersed brush of grafted chains. The distribution of such irreversibly adsorbed loops from a melt was shown to be:

$$S(n) \sim n^{-1/2}, \tag{47}$$

where $S(n)$ is the number per unit surface of loops with more than n monomers. Thus at a distance z from the surface, the adsorbed layer may be considered as a brush with grafting density $S(n)$, with a relation to be determined between n and z. This implies that the average distance between graft points is

$$D \sim S(n)^{-1/2}. \tag{48}$$

The local concentration $\phi(z)$ is related to the distribution:

$$\phi(z)\, dz = S(n) dn, \tag{49}$$

and, assuming that the local structure is still elongated, we have

$$z \sim \frac{n}{g} D, \tag{50}$$

implying

$$\frac{dz}{dn} \sim \frac{D}{g} \sim D^{-2/3} \sim S^{1/3}(n), \tag{51}$$

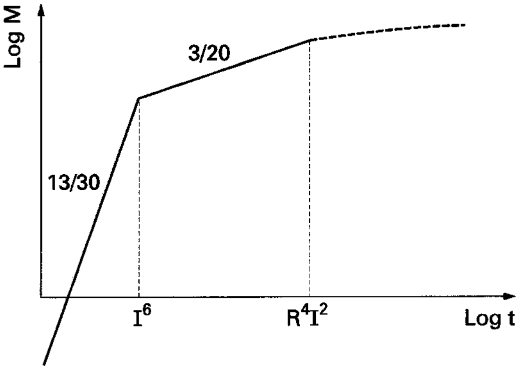

FIG. 4. Variation with time of the nuclear magnetization of an irreversibly adsorbed layer washed and placed in a good solvent. Paramagnetic centers are distributed on the surface with an average separation I.

where we used relation (48), and we assumed that the local relation between D and the number g of elements in a blob follows the conventional Flory relation. Using relations (47), (49), and (51), one gets

$$\phi(z) \sim z^{-2/5} \tag{52}$$

and the width L of the layer

$$L \sim N^{5/6}. \tag{53}$$

Thus because of the presence of a good solvent, the polymer strongly adsorbed from a melt has a width much larger than the radius of a polymer. This may be observed by NMR. In the following, we assume that all polymers are equivalent, and that PC's are present on the surface and are at an average distance I from each other. Then, as in the preceding sections, two regimes may be observed, respectively, for small and large times. For short times, $t \ll I^6$, relaxation is the sum of contributions due to a single PC and, as in the previous section, nuclei relaxed are located in a sphere of radius $r \sim t^{1/6}$; there are I^2 such spheres per unit surface and we have

$$N(t) \sim I^2 \int_0^r (r^2 - z^2)\, z^{-2/5}\, dz \sim r^{13/5}. \tag{54}$$

This leads to

$$M(t) \sim I^2\, t^{13/30} \quad (t \ll I^6). \tag{55}$$

For larger times, $t \gg I^6$, the relaxation front becomes planar and is located at a distance x from the surface given by relation (44); the relaxed number of nuclei per unit surface is

$$N(t) \sim \int_0^x z^{-2/5}\, dz \sim x^{3/5}, \tag{56}$$

and thus,

$$M(t) \sim t^{3/20}\, I^{-3/10} \quad (R^4 I^2 \gg t \gg I^6). \tag{57}$$

Note that there is an important change in the relaxation law (see Fig. 4) that depends on the density of PC's on the surface and this should be a clear signature of the particular concentration profile in the Guiselin case.

V. EXPERIMENTAL CONSIDERATIONS

We examine in turn the questions of signal-to-noise ratio, duration of the experiment, and the possible influence of residual spin diffusion due to the finite amplitude of the rf field.

A. Signal-to-noise ratio

In order to have large enough surfaces, one may use porous media, with pore size much larger than the radius of the polymer. A typical pore diameter used in such experiments is a few thousands angstroms [36], much larger than the width of the polymer layer. This implies that the surface may be considered as locally flat, as assumed above, and there is no influence of the porous medium on the NMR results. As an example we consider a layer of polydimethylsiloxane (PDMS) grafted on porous silica of specific area 2.5 $\mathrm{m}^2/\mathrm{cm}^{-3}$; the chains have a molecular weight $M \sim 65\,000$ and are grafted with a mean separation $d = 30$ Å. Protons are observed at a frequency $\nu = 100$ MHz; their number for a sample of volume $V_S = 1\ \mathrm{cm}^3$ is $N_P = 1.5 \times 10^{21}$.

To estimate the signal-to-noise ratio Ψ, we can use the standard formula [37,38],

$$\Psi = \alpha \eta M_0 (\mu_0 Q \omega_0 V_C / 4FkT_C \delta\nu)^{1/2},$$

where α is a numerical factor (~ 1), η is the ratio V_S/V_C of sample to coil volume, M_0 is the nuclear magnetization proportional to N_P/V_S, $\mu_0 = 4\pi \times 10^{-7}$, Q is the quality factor of the coil, $\omega_0 = 2\pi\nu$ is the Larmor angular frequency, F is the noise figure of the preamplifier, T_C is the temperature of the coil assumed to be room temperature, and $\delta\nu$ is the bandwidth necessary for observation of the free induction decay signal. We assume one scan acquisition and take $\delta\nu = 20$ kHz.

Taking $F = 1.5$, $V_C = 2\ \mathrm{cm}^3$, and $Q = 100$, one finds, with the above values of the other parameters, $\Psi = 1500$. This value of Ψ allows observation of relaxation over three decades.

In the case of layers adsorbed at saturation or of washed layers, one finds similar estimations for Ψ. Observation of relaxation of an adsorbed layer in the dilute regime should be much more difficult.

B. Duration of the experiment

The characteristic lengths to be measured in experiments with polymers at interfaces are significantly larger than the maximum lengths (~ 50 Å) probed in the previous experiments of NMR relaxation without spin diffusion. As a consequence it will be necessary to monitor the evolution of the nuclear magnetization over much longer times if the parameters of the experiment are not optimized. We consider the same grafted polymer as above (PDMS, $M = 65\,000$, $d = 30$ Å). Assuming (deuterated) dichloromethane as solvent this corresponds [36] to a grafted width $h \sim 300$ Å. If each grafting point bears a paramagnetic center of spin $S = \frac{1}{2}$ and Landé factor $g = 2$, the maximum measurement time will be, according to Eq. (25), of the order of

$$t_{\max} \sim \frac{h^4 d^2}{C}.$$

$t_{\max}$ should not exceed the relaxation time resulting from the combination of intrinsic relaxation due to segmental motions and parasitic relaxation. This problem was already met in [6]. Parasitic relaxation can be kept at a low level if care is taken to avoid paramagnetic impurities in particular oxygen. At liquid nitrogen temperatures the segmental motions are blocked by the frozen solvent and the associated relaxation is weak. In order to have small measurement times, one should choose conditions where C is close to its maximum value. This favors the experimental scheme where spin diffusion is inhibited by application of an rf field. Neglecting terms proportional to the spectral density of the fluctuations of the S spin at the nuclear Larmor frequency ω_0, the value of C under magic angle irradiation is equal to [39]

$$C=\frac{8}{45}S(S+1)(\gamma_e\gamma_p\hbar)^2\frac{\tau_c}{1+(\gamma_p B_{\rm eff}\tau_c)^2},$$

where τ_c is the correlation time of the fluctuations of the longitudinal component of the S spin; γ_e is the gyromagnetic factor of the S spin ($\gamma_e=1.76\times10^7\,{\rm s}^{-1}/{\rm G}$ for $g=2$), and γ_p is the gyromagnetic factor of the nuclei, here protons ($\gamma_p=2.67\times10^4\ {\rm s}^{-1}/{\rm G}$); $B_{\rm eff}=\sqrt{(3/2)}B_1$ is the effective field seen by the nuclei in the frame rotating at frequency ω_0 about the static magnetic field.

The maximum of C is obtained when $\gamma_p B_{\rm eff}\tau_c\sim1$, that is, if $B_1=10$ G for $\tau_c\sim3\times10^{-6}$ s. One has then $t_{\max}=160$ s.

C. Residual spin diffusion

Another important point is to make sure that spin diffusion is negligible over time scales of the order of $t_{\max}$. Two factors contribute in order to have a very small spin diffusion: (i) the application of an rf field ''at magic angle'' reduces the value of the spin diffusion coefficient with respect to its value D_0 in the absence of rf irradiation, (ii) the value of D_0 itself is expected to be much smaller than in a bulk polymer because of the heterogenous nature of the medium at small length scales. At length scales larger than d the grafted polymer can be considered as a homogeneous material in which it takes a time t for nuclear magnetization to diffuse over a distance r with r and t related by

$$r^2=D_0t. \tag{58}$$

The value of D_0 that should be used in Eq. (58) is the one that gives the correct diffusion time over the size of a blob. Spin diffusion proceeds via short-ranged flip flops with a rate W_{ij} that decreases with internuclear distance as $1/r_{ij}^6$. The situation here should not be confused with the somewhat similar one studied by Fischer *et al.* [40]. In their case the polymers were entangled but not frozen; at small time scales magnetization propagated most efficiently by atomic diffusion; at larger time scales this mechanism was relayed by flip flops occurring between nuclei that come one to another thanks to the atomic motions. In our case the chains are static and magnetization propagates only by flip flops: much smaller diffusion coefficients are expected. Because of the very fast variation of $W_{ij}$with r_{ij}^6, the diffusion inside a blob bears strong similarity to the problem of the random walk of a particle along a polymer coil with the possibility for the particle to use ''shortcuts'' due to the presence of loops. Accurate 2D simulations [41] have shown that the presence of shortcuts does not modify the linear nature of diffusion. Our own 3D simulations lead to the same result: this implies that diffusion on a coiled polymer does not obey the simple law (58) and that on a given length scale it proceeds more slowly than in the molten polymer. To estimate this reduction factor we shall use the experimental results of Tabti [7] who found that spin diffusion inside a polystyrene coil of extension $R\sim30$ Å corresponds to an effective $D_0\sim10^{-14}-10^{-15}\ {\rm cm}^2\,{\rm s}^{-1}$, much smaller than in rigid bulk polymers like polystyrene where $D_0\sim5\times10^{-12}{\rm cm}^2\,{\rm s}^{-1}$ [42].

Under application of an rf field ''at magic angle'' the value of D_0 is reduced to $D_{\rm res}\sim K/B_{\rm eff}$, where K is an increasing function of the magnitude of the nuclear dipolar interactions responsible for flip-flops. These interactions should not be significantly greater for protons in PDMS than for fluorine in $\rm CaF_2$ with field applied along the [100] direction. We can thus use the results of [39] where it was found $D_{\rm res}\sim0.05\,D_0$ for $B_1=10$ G. We are thus left with a residual spin diffusion $D_{\rm res}\sim5\times10^{-16}-5\times10^{-17}\ {\rm cm}^2\,{\rm s}^{-1}$ which gives a characteristic time for diffusion $t_{\rm diff}=h^2/D_{\rm res}\gtrsim1.8\times10^4$ s. This value is much larger than $t_{\max}$, which shows that spin diffusion can be kept at a negligible level.

VI. CONCLUSION

We considered the nuclear relaxation of linear polymer chains at interfaces. Paramagnetic centers are located on the surface. Polymers are either grafted or adsorbed on a solid surface. After grafting or adsorption the solution is quenched so that motions are frozen. We considered both the case when all macromolecules are similar, and when some are hydrogenated and others are deuterated. Because there is a power-law decay in the monomer concentration, we found that the relaxation is strongly nonexponential in all cases, but has power-law variation. Various relaxation regimes may be observed, depending on both the monomer concentration profile and the density of paramagnetic centers on the surface.

(1) For strong adsorption, and in the so-called Guiselin case, when the adsorption energy for each monomer is large and the bulk is washed by a good solvent after irreversible adsorption of the chains, the monomer concentration profile has a single power-law behavior. It decreases as $z^{-4/3}$ or $z^{-2/5}$, respectively, as a function of the distance z to the wall. Two time regimes may be defined. For short times, relaxation of a monomer is due to a single paramagnetic center. Because of this, the symmetry is spherical, and relation (21), $t\sim x^6$, is valid. Beyond a crossover time $T_x\sim I^6$, where I is the distance between centers on the surface, relaxation is no longer related to a single center but to many centers. Because of this, the symmetry becomes planar, and relation (21) above is replaced by $t\sim I^2x^4$. Because of this, although there is a single power-law decay for the concentration profile, two different relaxation laws are found for short and long times. We note that because of the difference in the exponents for the concentration decay in both problems, the effect is more

important in the irreversible case than in the strong adsorption case.

(2) For the case when polymers are grafted on a surface, it was shown that it is possible to define two distance ranges. For short distances, shorter than the average distance d between graft points, the chain behaves as a self-avoiding walk, with fractal dimension $d_f = 5/3$. For distances larger than d, the polymers adopt a stretched conformation because of excluded volume interactions. It is then possible to discriminate between these two regimes. It may be also possible to show that the monomer concentration profile is not flat, as assumed in the original scaling approach, but has rather a parabolic shape, as was shown by Milner, Cates, and Witten. It is possible in the latter case to also modulate the previous results either by changing the density of paramagnetic centers on the surface, as was discussed above, or by labeling some hydrogenated chains in a matrix of deuterated ones.

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