2-fold axis of symmetry between the methyl groups that makes them rigorously equivalent.[18]

In principle, if the 4 and 4′ carbons are nonequivalent, the 3 and 3′ carbons should also be nonequivalent. In practice the distance of the 3 and 3′ carbons from the methyl groups and the adjacent aromatic rings means that they are relatively insensitive to the effect of these groups. In the model compound the planar carbonate group is oriented close to the perpendicular with respect to the aromatic rings. Thus it affects the environment of the 3 and 3′ carbons equally. The absence of splitting for the 3 and 3′ carbons in the spectrum of the polymer is an indication that the carbonate group in the polymer is oriented well out of the plane of the adjacent ring in the polymer, as it is in the model compound.

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(19) Ideally, one would like to observe that the 4 and 4′ carbons of the model compound give NMR signals separated to about the same degree as the signals in the polymer. Unfortunately, the presence of the aromatic rings on the ends of the model compound leads to a very complicated NMR spectrum in the aromatic region. The signals from the 4 and 4′ carbons have not yet been identified.

Communications to the Editor

Slowing Down of Polymer Diffusion near a Wall

The theory of polymers confined to narrow slits and pores has been considered by several authors, and it appears that both the static and the dynamic aspects of the phenomena are well understood.[1–3] Attempts have been made to apply the predictions of the scaling theory to experiments on polymer diffusion through porous media.[4]

The situation is very different when one considers the behavior of polymers in solution near a single repulsive (i.e., impenetrable, nonadsorbing) wall. While the static aspects of the theory have been worked out (for semidilute solutions) and self-similar polymer density profiles have been predicted,[5,6] to the best of our knowledge, the problem of polymer diffusion near an interface has not been previously considered, presumably because there were no experimental techniques that could be used for studying wall depletion layers in dilute polymer solutions. The situation has changed now with the introduction of evanescent wave methods[7,8] that can detect variations of polymer density profiles on scales smaller than polymer dimensions. These techniques have been recently applied to the study of flow effects on wall depletion,[9] a question that has been also studied theoretically by the present author.[10] Slowing down of polymer diffusion near a wall was observed by forced Rayleigh scattering in the evanescent wave mode.[11] In this paper, we study the problem of polymer diffusion in solution, near a repulsive wall.

Consider a polymer of N monomers of size a such that away from the interface its bulk radius of gyration is $R_B \simeq aN^{\nu}$ where ν is the Flory exponent.[3] The bulk diffusion coefficient is given by

$$D_B \simeq k_B T/\eta_s R_B \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature, and η_s the solvent viscosity (numerical factors are suppressed in our notation). This expression takes into account hydrodynamic interactions between the monomers, due to which the polymer diffuses as a nondraining sphere of radius R_B. Now, let us assume that the polymer is placed in solution at a distance z from a wall. As long as this distance is much larger than polymer dimensions, the polymer diffusion coefficient remains unaffected by the presence of a wall. When R_B/z becomes of the order of, but larger than, unity, the polymer mobility is affected by the presence of the wall, an effect that has been studied in the context of hydrodynamics of rigid bodies.[12] In the latter case, the friction coefficient diverges when the distance from the wall approaches the dimensions of the rigid object, and thus the mobility in the plane parallel to the wall vanishes. No such singular behavior is expected for the flexible polymer.

The z-dependence of the polymer diffusion coefficient describing its two-dimensional mobility in the plane z = constant can be obtained by the following scaling argu-

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ment. When $z = R_B$ we expect that the diffusion coefficient is given by eq 1. Let us examine the limit when the center of mass of the polymer approaches the wall, $z \rightarrow a$. Subject to the above constraint, the polymer can only execute two-dimensional diffusion on the wall. Although at first glance one might expect that hydrodynamic interactions between monomers moving on the wall can still take place through the surrounding solvent, this would violate the no-slip boundary condition for the solvent since the fluid would have a nonvanishing velocity at the wall. We conclude that hydrodynamic interactions are screened in this limit and thus

$$D_W \simeq k_B T/\eta_s N \qquad (2)$$

which is the Rouse result (independent of the dimensionality of space). Although the above conjecture can be criticized on the grounds that the no-slip boundary condition need not hold on a microscopic scale, this kind of criticism applies equally well to the notion of hydrodynamic interactions between polymer segments since the use of the Oseen tensor in the derivation of eq 1 is based on the assumption that macroscopic hydrodynamics can be applied to intrapolymer length scales.[3]

Since the limiting behaviors of the diffusion coefficient at $z/R_B \rightarrow 1$ and $z/R_B \rightarrow 0$ are known, we proceed in the standard fashion[6] by writing $D(z)$ in the scaling form

$$D(z) \simeq D_B(z/R_B)^X \qquad z \leq R_B \qquad (3)$$

Notice that this form automatically satisfies $D(R_B) = D_B$ as required; demanding that the 2D result (eq 2) is obtained as $z \rightarrow a$ gives the exponent

$$X = 1/\nu - 1 \qquad (4)$$

which is 1 and $^2/_3$ for Θ and good solvent, respectively. Thus, the z-dependent diffusion coefficient is given by

$$D(z) \simeq D_B(z/R_B)^{1/\nu-1} \qquad (5)$$

and we predict that, as the polymer approaches the wall, its diffusion is drastically slowed down. Furthermore, notice that

$$D_B/D_W \simeq (R_B/a)^{1/\nu-1} = N^{1-\nu} \qquad (6)$$

i.e., the slowing down increases with the molecular weight and decreases with the quality of solvent. This result is identical with the one obtained for one-dimensional diffusion of polymers in pores,[1-3] if one replaces z by the pore size.

What is the physical mechanism behind the above effect? It has been shown that when a polymer is confined between two parallel planes such that the distance between them is smaller than its radius of gyration, the hydrodynamic interactions are screened and the polymer behaves as a free-draining object.[1-3] The situation is more complicated in the presence of a single wall where one might expect that the hydrodynamic disturbances produced by the motions of the polymer segments near a wall can still propagate through the free half-space. Note, however, that regardless of the magnitude and direction of the velocity of a segment located at a distance z from the wall, the hydrodynamic disturbance produced by its motion has to decay at the wall, in order to satisfy the no-slip boundary condition. This means that hydrodynamic interaction is screened on distances larger than z, and consequently the mobility (inverse friction coefficient) of a monomer at $\vec{r}$, such that $(\vec{r})_z = z$ is its distance from the wall, is obtained by averaging the screened Oseen tensor with respect to the polymer distribution. The assertion that the hydrodynamic screening length is given by the distance from the wall, z, is further supported by the fact that z is the static correlation length for the polymers near a wall,[4,5] and according to the dynamic scaling hypothesis,[3] the static and dynamic correlation lengths should be proportional to each other. Thus, the mobility of a monomer situated at a distance z from the wall is

$$\mu(z) = \frac{1}{\eta_s}\sum_n \left\langle \frac{1}{|r - r_n|} e^{-|r-r_n|/z} \right\rangle \qquad (7)$$

The sum is evaluated in the standard manner;[13] the bulk of the contribution comes from $n_z \simeq (z/a)^{1/\nu}$ monomers separated by distance z from the labeled one, each one contributing a factor of $1/z$. This gives

$$\mu(z) \simeq n_z/\eta_s z = z^{1/\nu-1}/\eta_s \qquad (8)$$

Using the observation that when the center of mass of the polymer is at a distance $z < R_B$ from the wall, the width of the polymer polymer distribution along the direction perpendicular to the wall is of order z (rather than R_B), we conclude that the diffusion coefficient for the polymer is given by

$$D(z) = \mu(z)KT/N \simeq k_B T/\eta_s R_B(z/R_B)^{1/\nu-1} \qquad (9)$$

where we have used $N \simeq (R_B/a)^{1/\nu}$. This agrees with our scaling result, eq 5.

What happens in more concentrated solutions? A trivial generalization of the above arguments to the dynamics of concentration fluctuations in the semidilute regime ($c \gg c^*$ where c^* is the overlap concentration) suggests that the cooperative diffusion coefficient becomes a function of the distance from the wall; i.e.

$$D_{\text{coop}}(z) \simeq k_B T/\eta_s \xi (z/\xi)^{1/\nu-1} \qquad (10)$$

where ξ is the static correlation length.[3] However, since the hydrodynamic interactions are screened on scales larger than ξ, the tracer diffusion coefficient is not strongly affected by hydrodynamic interaction and thus should not vary with the distance to the wall.

Finally, we comment on the experimental significance of our results. The screening of hydrodynamic interactions takes place in a narrow region (comparable to polymer dimensions) near a nonadsorbing wall where there is only a small probability to find a polymer. However, there is still a macroscopically large number of polymers in this region, and experiments are difficult but possible. In fact, our initial interest in this problem was stimulated by recent measurements of polymer concentration profiles in the wall depletion region using evanescent wave-induced fluorescence in equilibrium[7] and in the presence of flow.[9] Contrary to the results of ref 9, our Brownian dynamics simulations have shown that shear produces thinning of the depletion layer,[10] and a possible origin of the discrepancy was thought to be the neglect of hydrodynamic interactions in the simulation. The present results indicate that hydrodynamic interactions do not play an important role in this problem, and the reason for the discrepancy remains unknown.

A direct albeit only qualitative observation of the slowing down of polymer diffusion by forced Rayleigh scattering in the evanescent wave mode was made by varying the penetration depth of the evanescent wave into the polymer solution.[11] It is hoped that the present work will stimulate more quantitative studies of this problem.

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Transformation of *Valonia* Cellulose Crystals by an Alkaline Hydrothermal Treatment

Even though cellulose has been one of the most studied polymers, its crystalline structure remains only partially understood. As early as 1937, the work of Meyer and Misch[1] led to the proposal that native cellulose or cellulose I was crystallized in a two-chain monoclinic unit cell, each of the chains being positioned on one of the monoclinic 2-fold screw axes. This structure was questioned in 1958 when Honjo and Watanabe[2] started to investigate the highly crystalline *Valonia* cellulose by electron diffraction analysis. Their diagrams contained a series of extra reflections, which could not be accounted for by the two-chain monoclinic unit cell, but required a larger eight chain cell. The occurrence of "extra" reflections was confirmed by X-ray diffraction analysis[3,4] but, to date, the exact significance of such reflections remains to be determined. At any rate, *Valonia* cellulose I is the widely accepted native cellulose standard, having the highest crystallinity and perfection. The more common celluloses, being of lower crystallinity than *Valonia*, display diffraction spectra that are not as well-defined. For most of them (in particular for ramie and cotton cellulose), the extra reflections of Honjo and Watanabe are not resolved. Thus, the two-chain monoclinic cell seems acceptable for such samples.

The debate on the crystal structure of native cellulose has been revived recently when the first CP/MAS ^{13}C NMR spectra of cellulose became available.[5] Atalla and VanderHart[6,7] were the first to analyze in detail such spectra. From their work came the new proposal that each native cellulose was a composite of two different crystalline modifications, namely Iα and Iβ. In such a scheme, *Valonia* and bacterial cellulose would be rich in Iα, whereas ramie and cotton cellulose would be dominated by Iβ.[8] Pure Iβ cellulose was isolated from animal cellulose.[9] On the other hand, no pure Iα has been found or prepared so far.

In the two-phase model Iα/Iβ, Iβ is the most stable form. In particular, it is invariably obtained from *Valonia* cellulose after either a selective swelling of cellulose[10] or an acetylation treatment followed by saponification.[11] Quite recently, it was discovered by Horii et al.[12,13] that well-resolved Iβ ^{13}C NMR spectra could be obtained when *Valonia* cellulose was subjected to a hydrothermal annealing. In such spectra, a well-resolved multiplicity of two was found for the signals of the carbon atoms at C1, C4, and C6 of the glucose moieties. This is opposed to the initial *Valonia* spectra where at least three signals were observed for these carbons. The multiplicity of 2 for the carbon atoms in the annealed *Valonia* samples indicates that in the corresponding "annealed" unit cell there are only two glucose residues that are magnetically nonequivalent. Therefore, the corresponding crystal structure should be simpler than that of the unannealed sample. To test this hypothesis, we have compared the diffraction diagrams of *Valonia* cellulose before and after hydrothermal annealing. This report confirms unambiguously that there is indeed a substantial modification of the diffraction diagram of such cellulose when an hydrothermal annealing treatment is applied. This modification is not due to any loss in crystalline perfection but to a solid-state transformation.

In order to study the hydrothermal treatment of *Valonia* cellulose, purified vesicles of *Valonia macrophysa* were introduced in glass vessels containing a solution of 0.1 N NaOH in water. The vessels were tightly sealed, and each of them was subjected to annealing. For this, they were inserted in an autoclave, which was immersed in an oil bath where the temperture could be set in the range 220-260 °C. After 30 min at a given temperature, the autoclave was cooled under tap water and the vessel opened. The resulting annealed *Valonia* vesicles were then thoroughly washed with distilled water and delaminated under a stereomicroscope. Thin cellulose layers were floated off and mounted on carbon-coated grids. In other experiments the specimen was mounted across the holes of gold-sputtered micronet grids. The grids were observed with a JEM-2000 EXII electron microscope operated at 200 kV. A number of electron diffraction diagrams were recorded on never observed areas of the specimen ranging from 1 to 4 μm in diameter. These diagrams were obtained with various electron doses but never exceeding 300 electrons/nm^2 for the recording (this dose is half of the dose that leads to total disappearance of the electron diffraction diagram). Calibration of the diffraction diagrams was performed with the gold diffraction ring d_{111} = 0.235 nm. The unit cell refinements were obtained after a computer least-square fitting, using d spacings measured from each single reflection.

The above hydrothermal annealing treatment had no effect on the physical appearance of the *Valonia* fragments, which could be delaminated with equal ease in