Macromolecules **1991,** *24,* 1549–1553 **1549**

Critical Dynamics of a Polymer Chain in a Grafted Monolayer

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Received July 5, 1990; Revised Manuscript Received October 22, 1990

ABSTRACT: The dynamic behavior of polymer chains grafted onto a planar inert surface and forming a monolayer is considered. It is found that the molecular weight dependence of the time of large-scale chain relaxation in a monodisperse layer is $\tau \sim N^3$, which is in accordance with the molecular dynamics data. This dependence is retained upon the wide-range variation in grafting density and solvent quality. It is shown that anomalous chain relaxation is due to the critical slowing-down near the coil–stretch transition point. Analogy with a macromolecule in an elongational flow is established and analyzed. Polydispersity of chains forming the layer affects dramatically their global relaxation times.

Polymer chains sufficiently densely grafted by one end to a planar inert surface or to a liquid–liquid interface are known to form a monolayer.[1–15] The surface grafting density ρ, i.e., the number of chains per unit surface, should be sufficiently large for the neighboring chains to overlap: $\rho \gg 1/R^2$, where R^2 is the mean-square radius of gyration of an isolated chain in solution. At present the equilibrium properties of these monolayers (or "brushes") have been well studied both experimentally[1–3] and theoretically.[4–15] However, the dynamic properties of chains in a monolayer have been investigated quite insufficiently. The times of large-scale chain relaxation in a grafted layer for the case of a good solvent have been obtained in ref 15 by a direct molecular dynamics simulation of brushes with different grafting densities ρ and different polymerization indexes N. The variation of relaxation time with N and ρ turned out to be poorly explained in the framework of conventional models. The aim of the present paper is to develop a simple theory describing the dynamic behavior of macromolecules in a grafted brush and, taking this as a starting point, to reveal the critical character of chain behavior resulting from the coil–stretch transition.

Equilibrium Structure of the Monolayer

The equilibrium properties of the monolayer are determined by the number of chain segments N, the grafting density ρ, and the solvent quality. They are described by the analytical self-consistent field theory.[6–14] In further discussion only the case of long ($N \gg 1$) flexible chains will be considered. In the case of a good solvent the segment density profile $\rho(x)$ decreases parabolically with increasing distance from the grafting plane, $\varphi(x) = \varphi_0(1 - x^2/H^2)$, and the mean height H of the monolayer boundary is proportional to the contour length of the chain, $H = (2/\pi)^{2/3}(\rho a^2)^{1/3}aN$, where a is the segment length. The density of free ends is given by $g(x_N) = 3x_N(H^2 - x_N^2)^{1/2}/H^2$, where x_N is the height of the terminal Nth segment above the plane. The above relationships are asymptotic under the conditions $N \gg 1$ and $1 \gg \rho \gg 1/R^2$.

The mean-square fluctuations of the chain free end in the grafted brush are equal to $\langle \delta x_N^2 \rangle^{1/2} = 0.23H$ and are thus proportional to the chain contour length $L = aN$. Here, $\delta x = x - \langle x \rangle$.

The predictions of the self-consistent field theory have been verified by the dynamic simulation of a grafted brush.[15] Interactions between chain segments corresponded to the case of a good solvent, and hydrodynamic interactions were not taken into account. The average equilibrium characteristics obtained (segment density profile, average chain size, and the density of free ends) are in good agreement with the theory.

Furthermore, relaxation times τ have also been calculated for the square end-to-end distance h^2, the square radius of gyration R^2, and their normal components h_x^2 and R_x^2. The authors of ref 15 explained the obtained dependence of these relaxation times on N and ρ on the basis of the blob picture of the grafted layer. In the framework of these concepts, the large-scale relaxation time should scale as $\tau \sim N^2\rho^{-1/6}$. However, the fit of the simulation data to the power law dependence $\tau \sim N^\alpha\rho^\beta$ yielded the values of $\alpha = 2.4$–3.1 and $\beta = 0.8$–1.1, which are in poor agreement with the blob model predictions $\alpha = 2$ and $\beta = -1/6$.

Description of Large-Scale Chain Relaxation in a Monolayer

The relaxation of the end-to-end chain distance is usually well described by a simple dumbbell model.[16] For a free-draining chain, the friction coefficient in the dumbbell model is $\zeta = \zeta_0 N$, where ζ_0 is the segment friction coefficient. Hence, the problem of the end-to-end distance relaxation reduces to that of the motion of a Brownian particle with the diffusion coefficient $D_{\text{dumb}} = \zeta_0^{-1}N^{-1}$ in the effective external potential $U(x)$ related to the equilibrium distribution density of the end-to-end distances $g(x) \sim \exp(-U(x))$. (Energy is expressed in kT units.) Since we are mostly interested in the behavior of the h_x component perpendicular to the grafting plane, only a one-dimensional model is considered here for simplicity.

The characteristic relaxation time τ of the correlation function of the Brownian particle's coordinate $\langle \delta x(0)\, \delta x(t) \rangle \langle \delta x^2 \rangle^{-1}$ is proportional to the time of diffusion displacement over a distance on the order of the of mean-square fluctuation in the potential field $U(x)$: $\tau \sim D_{\text{dumb}}^{-1}\langle \delta x^2 \rangle$. For the chain in a grafted brush immersed in a good solvent we have $\langle \delta x^2 \rangle \sim N^2a^2(\rho a^2)^{2/3}$, which gives

$$\tau \sim N^3(\rho a^2)^{2/3}a^2\zeta_0 \qquad (1)$$

The $\tau \sim N^3$ scaling is known for the global relaxation time of highly entangled polymers in a melt or in a lattice of obstacles. Still it is rather unusual for a Gaussian chain

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0024-9297/91/2224-1549$02.50/0

in an external field, which is the background model of the self-consistent theory of grafted brushes. In order to realize better the unusual character of this relaxational behavior, we consider two simple systems: a free Gaussian chain and a chain confined in a tube. For the case of a free Gaussian chain we have $\langle \delta x^2 \rangle = Na^2$ and $\tau \sim N^2 a^2 \zeta_0$ in accordance with the well-known results of Kuhn and Rouse.

The chain in the narrow cylindrical tube with diameter $d \ll R$ in a good solvent can be considered as a one-dimensional sequence of blobs[17,18] of size d, their number being $n_b \sim N(d/a)^{-5/3}$. The chain size in this case is $R_{\text{tube}} \sim n_b d \sim L(d/a)^{-2/3}$, while its mean-square fluctuation can be estimated as $\langle \delta R_{\text{tube}}^2 \rangle \sim dn_b^2 \sim N(d/a)^{1/3}a$, which is consistent with the Monte Carlo data.[18] Hence, we obtain the relaxation time $\tau \sim N^2(d/a)^{1/3}a^2\zeta_0$.

An analogy between a chain in a tube and a chain in a grafted brush was derived from the blob picture of the brush.[4,5] It follows naturally from the very idea of the layer being formed by densely packed blobs and is formally based on the similarity of expressions for the free energy and for the longitudinal chain size provided the tube diameter is taken equal to the average distance between the neighboring grafting points $d \sim \rho^{-1/2}$. However, this analogy appears to be highly misleading when applied to the dynamic behavior of the chain in a monolayer. It gives

$$\tau \sim N^2(\rho a^2)^{-1/6}a^2\zeta_0 \qquad (2)$$

which coincides with the basic formula having been used in ref 15 to interpret the molecular dynamics results.

It is clear that although the size of the chain in a tube is proportional to N and thus may be much greater than the average size of a Gaussian coil, both these systems have size fluctuations of the order of $N^{1/2}$. The chain in a grafted layer belongs to another class of fluctuational behavior, its fluctuations being anomalously large and proportional to N. This leads to two different types of relaxational behavior described by eqs 1 and 2.

Comparison with the Computer Simulation Data

To illustrate the correspondence between the computer simulation results and two different theoretical predictions (eqs 1 and 2), the molecular dynamics data[15] for the relaxation times $\tau(R_x)$ and $\tau(h_x)$ are plotted versus chain overlapping parameter $N^{6/5}\rho$ being normalized to $N^2\rho^{-1/6}$ in Figure 1a and to $N^3\rho^{2/3}$ in Figure 1b. It is clear from Figure 1a that eq 2 predicting $\tau/(N^2\rho^{-1/6})$ = const is not supported by the simulation data. On the other hand, Figure 1b shows that $\tau/(N^3\rho^{2/3})$ is nearly constant. The lowest point in Figure 1b corresponds to the longest stimulated chains ($N = 100$) for which the statistical error was at maximum. Deviations from the asymptotic value on the left side of Figure 1b corresponding to small $N^{6/5}\rho$ are due to the fact that the monolayer is not yet well formed. A certain increase in τ at large $N^{6/5}\rho$ is possibly due to the increase in local viscosity with ρ, which might be considerable in dense enough layers but is not taken into account by eq 1.

A direct calculation of local viscosity dependence on ρ might be of interest and could be accomplished by simulating the dynamics of a small probe molecule.

In contrast to eq 2 for a blob model, eq 1 gives the increase in relaxation time with grafting density ρ which was observed in the simulation. A slightly stronger dependence $\tau \sim \rho^{\beta}$ with $\beta = 0.8$–1.1 obtained in the simulation as compared to the present theory ($\beta = 2/3$) is likely to be due to the change in local viscosity discussed above. The dependence $\tau \sim N^{\alpha}$ with $\alpha = 2.3$–3.1 reported in ref 15 is in a fairly good agreement with eq 1 even though it covers data for monolayers differing greatly in the degree of chain overlapping ($N^{6/5}\rho = 0.4$–22). For the case $\rho = 0.1$, the layers were completely formed for all chain lengths considered, and the corresponding value $\alpha = 2.9$–3.1 agrees with eq 1 even better.

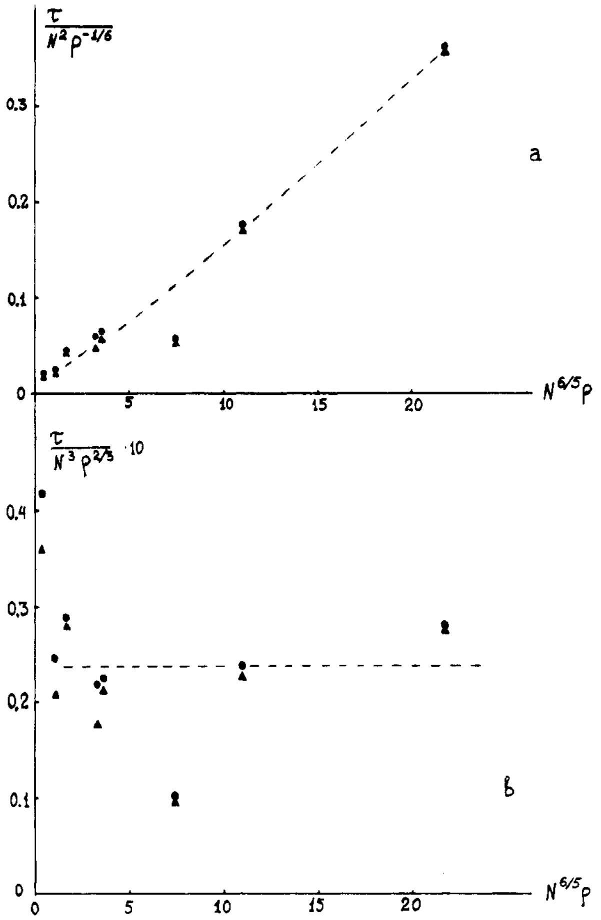

Figure 1. Relaxation times τ for the normal component of the chain radius of gyration R_x (●) and the end-to-end distance h_x (▲) versus degree of chain overlapping $\rho N^{6/5}$. The computer simulation data of ref 15 are scaled (a) by $N^2\rho^{-1/6}$ in accordance with eq 2 and (b) by $N^3\rho^{2/3}$ in accordance with eq 1.

Critical Features of Chain Behavior

As we have seen, eq 1 gives a good description of the large-scale chain relaxation in a grafted layer whereas the blob model, implying Gaussian type fluctuations of the end-to-end distance, fails. A natural question arises about the origin of the anomalously high chain fluctuations in a grafted brush. Usually, large fluctuations are characteristic of a system near a second-order phase transition point. We will show that chain behavior in a grafted layer corresponds to the vicinity of a coil–stretch transition.

Analogy with a Macromolecule in a Longitudinal Flow. According to refs 6–10, the chain in a layer is affected by a self-consistent potential $\mu(x)$ which is due to the interaction between neighboring chains

$$\mu(x) = \frac{1}{2}\left(\frac{\pi H}{2aN}\right)^2 - \frac{\pi^2}{8a^2N^2}x^2, \quad 0 \le x \le H \qquad (3)$$

The parabolic dependence of the stretching potential $\mu(x)$ leads to a straightforward analogy with a free-draining chain in a longitudinal extensional flow (see ref 19 and references therein). The latter system is well-known to undergo a coil–stretch transition with *increasing flow rate*. For small flow rates, the chain is a slightly deformed coil.

At the critical flow rate, the linear elasticity of the softest deformational mode is completely compensated for by the external field. At a flow rate sufficiently higher than the critical value, the chain is stretched nearly to its contour length, the extending force being balanced by essentially nonlinear elasticity. The critical value of the flow rate scales as N^{-2} for an ideal chain.

The important fact is that the magnitude of the self-consistent potential $\mu(x)$ in the grafted brush, i.e., the factor $\pi^2/(8a^2N^2)$, exactly equals the critical value[20] for chain elongation! This means that each chain in the brush is just in the middle of the coil–stretch transition, which gives at least a formal explanation for the anomalous amplitude of the end-to-end distance fluctuations.

For a macromolecule in a longitudinal flow, the parameter governing the coil–stretch transition is the flow rate, which can be easily changed in the experiment. The magnitude of the self-consistent potential in the brush is determined by the length of the constituent chains and is thus fixed. However, we can still follow the coil–stretch transition of a brush chain in a different way.

Short-Chain Behavior in the Brush. Let us consider a monolayer formed by chains of length $L_N = aN$ which contains a small fraction of "admixture" chains of smaller length $L_K = aK$. The grafting density of short admixture chains should satisfy the condition $\rho_K R_K^2 \ll 1$. Since each short chain is surrounded by the longer main chains of the layer, it may be considered to be located in the external field $\mu(x)$. Shorter chains being less easily deformed, the stretching field will appear subcritical to them. This means that by increasing the molecular weight of admixture chains (by "growing" them) we can follow the coil–stretch transition as $K \rightarrow N$. That will correspond to an extensional flow experiment with a fixed flow rate and varying molecular weight of the specimens investigated.

To make the above argument more rigorous, we calculate the free energy $F(x_K)$ of the short chain as a function of its end coordinate x_K following the approach reported in refs 21 and 10. The local chain stretching $E(x,x_K) = \mathrm{d}x/\mathrm{d}n$ is introduced, n being the coordinate along the chain contour. The total free energy $F(x_K)$ is assumed to be a sum $F = F_{\mathrm{el}} + F_{\mathrm{int}}$, where the elastic stretching energy is $F_{\mathrm{el}} = (1/2)\int_0^{x_K}\mathrm{d}x\, E(x,x_K)$, and the interaction energy of the chain in the field is $F_{\mathrm{int}} = \int_0^K \mu(x(n))\,\mathrm{d}n = \int_0^{x_K}\mu(x)\,E(x,x_K)^{-1}\,\mathrm{d}x$. The function $E(x,x_K)$ is determined by minimization of the functional $F(x_K)$ at fixed x_K with the additional constraint $\int_0^K \mathrm{d}n = \int_0^{x_K} E(x,x_K)^{-1}\,\mathrm{d}x = K$ and is given by

$$E(x,x_K) = \frac{\pi}{2N}\left(\frac{x_K^{\,2}}{\sin^2(\pi K/2N)} - x^2\right)^{1/2} \qquad (4)$$

Since $E(x,x_K)$ is known, the free energy can be easily calculated to give

$$F(x_K) = \frac{K}{2}\left(\frac{\pi H}{2aN}\right)^2 + \pi\frac{\cot(\pi K/2N)}{4a^2N}x^2, \quad 0 \le x_K \le H \qquad (5)$$

At $x_K > H$, the free energy increases very rapidly and therefore the chain may be virtually considered to be confined in a box of width H. (One should bear in mind that H is much greater than the size of an isolated coil.)

As it has been shown in ref 8, the potential $\mu(x)$ given by eq 3 is not completely self-consistent. It represents rather the main term, while the total potential has the form $\mu_{\mathrm{tot}} = \mu + N^{-1}\delta\mu$, the correction term being smaller by a factor of order N^{-1}. The correction term makes the free energy of the chain in a monodisperse brush consistent with the equilibrium distribution density of free ends, $g(x_N)$.

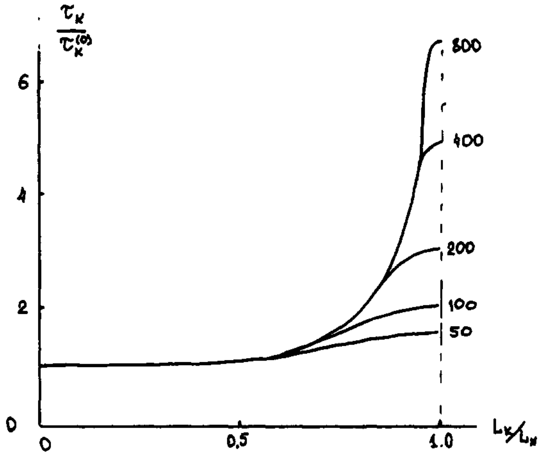

Figure 2. Relaxation time τ_K of a short admixture chain in a monodisperse brush normalized to the same value for an isolated chain $\tau_K^{(0)}$ versus the contour length ratio L_K/L_N. The length of the main chains L_N is given in the figure. Grafting density is taken to be $\rho = 0.1$.

The corresponding correction to the free energy of the admixture chain, $\delta F(x_K)$, can be calculated to a first approximation with the aid of the zero-order approximation for $E(x,x_K)$ given by eq 5. It is clear from eq 5 that the main term of the free energy at $x_K \sim H$ normally is of order N. The correction term δF is of order unity, and we know that in the limiting case $K = N$ it transforms into $\delta F(x_N) = -\log(g(x_N))$.

The term depending quadratically on x_K in eq 5 decreases with increasing K and vanishes at $K = N$. It remains large compared to the correction term $\delta F(x_K)$ under the condition $(\pi H^2/4Na^2)\cot(\pi K/2N) \gg 1$, or, with parameter $\lambda = (N - K)/N$ introduced, $\lambda \gg N^{-1}(\rho a^2)^{-2/3}$. Under this condition we obtain

$$\langle x_K\rangle = \frac{2}{\pi}aN^{1/2}(\tan(\pi K/2N))^{1/2} \qquad (6)$$

$$\langle \delta x_K^{\,2}\rangle = \frac{2}{\pi}\left(1 - \frac{2}{\pi}\right)a^2N\tan(\pi K/2N) \qquad (7)$$

(The average normal component of the end-to-end distance $\langle x_K\rangle$ is nonzero since the chain can find itself only in the half-space with $x \ge 0$.) It follows from eqs 6 and 7 that if the admixture chains are much shorter than the main chains ($K \ll N$), they form coils with mean size $\langle x_K\rangle \simeq (2/\pi)^{1/2}aK^{1/2}$ and size dispersion $\langle \delta x_K^2\rangle \simeq (1 - 2/\pi)a^2K$. As the length L_K of an admixture chain approaches L_N the deformation of the coil increases. The relative difference of chain lengths λ being in the range $1 \gg \lambda \gg N^{-1}(\rho a^2)^{-2/3}$), the average size and size fluctuations of admixture chains increase dramatically according to the power laws $\langle x_K\rangle \sim \langle x_K\rangle_0\lambda^{-1/2}$ and $\langle \delta x_K^2\rangle \sim \langle \delta x_K\rangle_0\lambda^{-1}$ (subscript zero denotes an unperturbed value in the absence of a stretching field). Finally, when L_K is very close to L_N, so that $\lambda \ll N^{-1}(\rho a^2)^{-2/3}$, the correction term of the free energy $\delta F(x_K)$ becomes dominant, limiting the increase in $\langle x_K\rangle$ and $\langle \delta x_K^2\rangle$ by the values of order H and H^2, respectively.

The increase in fluctuations with $L_K \rightarrow L_N$ is directly manifested in an increase in large-scale relaxation times of admixture chains in accordance with the equation $\tau_K \sim \langle \delta x_K^2\rangle \zeta_K$; see Figure 2. This phenomenon (critical slowing-down) is well-known for the systems approaching a second-order phase transition point.

Discussion

Comparison with the Mean Field Theory of Second-Order Phase Transitions. The nonequilibrium free energy of an admixture chain $F(x_K)$ for small $\lambda = (N - K)/N$ can be presented in the form

$$F(\eta)/K = F_0 + A_0\lambda\eta^2 + K^{-1}\delta F(\eta) \qquad (8)$$

where $\eta = x_K/L_K$ is the parameter of chain stretching and F_0 and A_0 are constants of order unity. Only the main terms in powers of λ are retained. Equation 8 bears a close resemblance to the well-known mean field free energy expansion for a system in the vicinity of a second-order phase transition[22]

$$F(\eta)/N = F_0 + A_0\lambda\eta^2 + B\eta^4 + ... \qquad (9)$$

where η is the order parameter and $\lambda = (T - T_c)/T_c$ is the relative deviation from the critical temperature.

We conclude that the coil–stretch transition of an admixture chain in the grafted brush will become a phase transition in the limit $K \rightarrow \infty$, $N \rightarrow \infty$, ρ = const, with the precritical behavior exactly coinciding with the mean field behavior of the system undergoing a second-order phase transition. In particular, the index γ describing the divergence of fluctuations $\langle \delta\eta^2 \rangle \sim \lambda^{-\gamma}$ has its mean field value $\gamma = 1$. For finite K and N, at $\lambda \sim N^{-1}(\rho a^2)^{-2/3}$, we have a crossover from regular power-law fluctuation growth to saturation. This implies that a monodisperse brush with finite N and $\lambda = 0$ is analogous to a macroscopic (infinite) system in the subcritical regime with $(T - T_c)/T_c \sim N^{-1}(\rho a^2)^{-2/3}$.

Nonparabolic Corrections to the Self-Consistent Potential and Density Profile. There is, however, a certain difference between the standard critical behavior of a system described by the mean field free energy expansion (9) and the chain behavior described by eq 8. In the former case, the amplitude of fluctuations at the critical point ($\lambda = 0$) is determined by the $B\eta^4$ term, which leads to $\langle \delta\eta^2 \rangle^{1/2}{}_{\text{crit}} \sim N^{-1/4}$. An ideal free-draining chain with finite extensibility in a longitudinal flow gives an example of exactly this type of behavior. It can be easily shown for a dumbbell model with either Langevin or FENE elasticity[23] that free energy expansion in terms of $\eta = x_N/L$ has the form of eq 9, so that chain size fluctuations in the flow with critical rate value scale as $\delta x_N = N\delta\eta \sim N^{3/4}$. In the case, λ will have the meaning of the relative deviation of the flow rate from its critical value.

However, for a chain in a grafted layer, there are no nonvanishing power terms at the critical point $\lambda = 0$. Instead, we have a term $N^{-1}\delta F$ which at $\lambda = 0$ equals $N^{-1} \ln g(\eta N/H)$, limiting the fluctuations to be $\delta\eta_{\text{crit}} \sim N^0\rho^{1/3}$.

One might think that this form of free energy is due to a particular Gaussian chain model and that taking into account the finite extensibility of chains will change the N dependence of the critical fluctuations. Indeed, if any power term of the form $B\eta^{2m}$ were present in eq 8, it would be dominant at $\lambda = 0$ in the limit $N \rightarrow \infty$, leading to $\delta\eta_{\text{crit}} \sim N^{-1/(2m)}$. Surprisingly, the form of eq 8 appears to be model independent in the sense that for any reasonable type of chain elastic behavior, only the correction term $N^{-1}\delta F$ survives at $\lambda = 0$. (The particular form of this term depends, of course, on the model parameters.)

The fact stated above implies that the self-consistent field in a monodisperse layer compensates not only for linear elasticity of the chain but also for all nonlinear terms. Consequently, the potential $\mu(x)$ and the density profile $\varphi(x)$ are not parabolic but rather contain power terms of the form $B_m(x/L)^{2m}$ ($m = 2, ...$). The reason for this specific type of extensional potential to be created in a grafted layer is that a self-consistent field simply cannot be formed without chain-end fluctuations on the order of brush height $H \sim N$ (see appendix). We may thus conclude that the fluctuational behavior of chains in a monodisperse grafted layer is unique, since it requires a very special type of a stretching field.

Generalization of Results for Large-Scale Relaxation. We have seen that eq 4 gives an adequate description of the global chain relaxation in a grafted layer for the case of a good solvent. Applying the results of ref 10 where the distribution density of free ends in the monolayer $g(x_N)$ has been obtained for different solvent qualities, we calculate $\langle \delta x_N{}^2 \rangle$, which leads to

$$\tau \sim N^3(\rho a^2)a^2\zeta_0 \qquad \text{in a } \Theta \text{ solvent}$$

$$\tau \sim N^3(\rho a^2)^2a^2\zeta_0 \qquad \text{in a precipitant}$$

The time of large-scale relaxation always remains proportional to N^3 regardless of solvent quality, though the dependence of τ on ρ changes.

The simple theory presented above as well as the results of the computer simulation corresponded to the case of a free-draining chain. In real polymer systems hydrodynamic interactions can profoundly affect the large-scale relaxation times.[24] However, since the neighboring chains in a monolayer strongly overlap, the layer may be regarded as a semidilute solution with screened hydrodynamic interactions. Hence, the friction coefficient of the entire chain may be represented as $\zeta = n_b\zeta_b$, where $\zeta_b = \zeta_0\xi/a$ is the friction coefficient of a nondraining blob with the size equal to the screening length ξ. Since in good solvent[25] $\xi \sim \rho^{-1/2}$ and $n_b \sim N\xi^{-5/3}$, the total friction coefficient is $\zeta \sim N\rho^{1/3}$ and is now proportional to the average brush height. Thus taking hydrodynamic interactions into account for the case of a good solvent gives

$$\tau \sim N^3(\rho a^2)a^2\zeta_0 \qquad (10)$$

The dependence of relaxation time on grafting density is slightly modified by the presence of hydrodynamic interactions (see eq 1), but the chain length dependence remains universal.

Effect of Polydispersity. A dramatic change in the dynamic behavior of polymer chains in a brush is caused by polydispersity. It is quite clear for a special case of admixture chains discussed above. However, the results of ref 9 indicate that in the general case of a sufficiently broad continuous molecular weight distribution of grafted chains, the end-to-end distance fluctuations return to normal behavior with amplitudes of order $N^{1/2}$. Thus, a parameter characterizing the relative distribution width will control the critical chain behavior serving as an analogue of the deviation from the critical point. Even a small increase in the degree of polydispersity will cause a transition from anomalously slow relaxation with $\tau \sim N^3$ to a normal Rouse type relaxation $\tau \sim N^2$. This effect can be rigorously shown for an analytically soluble model with a particular form of continuous molecular weight distribution.[26] For a discrete type of distribution, each fraction retains the anomalous behavior. However, with total grafting density and average molecular weight being fixed, the relaxation time of chains in each fraction decreases as the number of different fractions increases and the distribution becomes more smooth.

Effect of Entanglements. The onset of reptation as a dominant mechanism of large-scale relaxation in polymer melts[27] is supposed to occur as the number of chain segments N becomes larger than $N^* \sim 10^2$. The dependence of N^* on the polymer concentration for the case of semidilute and concentrated solutions is still not clarified. It seems that brushes with moderately dense grafting ($\rho \sim 10^{-1}$) immersed in a good solvent are unlikely to manifest significant entanglement effects at least for $N \lesssim 10^3$ (this tentative estimate is based on the results of refs 28 and 29). However, for dense brushes, e.g., block copolymers in a melt, or very long chains, the effect of entanglements should be significant.

The above consideration of chain dynamics has been based on the simple formula $\tau \sim \langle \delta h^2 \rangle \zeta$, which relates relaxation time to the equilibrium mean-square fluctuation. The equilibrium characteristics certainly do not depend on the motion mechanism, but the relationship cited breaks down with the onset of reptation.

The relaxation of a highly entangled chain in a grafted layer is similar to that in the star polymer melt since the chain has only one free end and must retrace its own path in order to escape from the tube.[30,31] According to the arguments presented in ref 30 for a block copolymer melt, the relaxation time scales as $\tau \sim N^3 \exp(\alpha N)$. The prefactor N^3 is the characteristic time of Brownian motion along the tube, and the exponential factor reflects the entropic cost for double-folding the chain while retracting the path. The form of the N^3 prefactor does not depend on the equilibrium average amplitude of the free end fluctuation. We thus conclude that it is not influenced by a polydispersity effect although the fluctuational behavior changes dramatically compared to the case of a monodisperse brush.

Polydispersity and corresponding changes in the interaction potential profile $\mu(x)$ might still affect the height of the effective barrier, i.e., the value of the factor α in the exponential. However, a detailed analysis of this problem is beyond the scope of the present paper.

Acknowledgment. We are grateful to Dr. E. B. Zhulina and Dr. Yu. Ya. Gotlib for helpful discussions.

Appendix. Chain Size Fluctuations in a Planar Monodisperse Layer: General Result

We will show that the equilibrium structure of the monodisperse layer grafted onto a planar surface cannot exist without chain size fluctuations of the order N, no matter what is the particular character of the chain elasticity or of the dependence of the potential on the segment density.

In the equilibrium state the average force exerted on a given segment at a distance x from the grafting plane by its neighbors along the chain is balanced by the force due to the chain–chain interactions. The first (elastic) force is the difference in the average chain tension T at the right and left sides of the segment, $f_{\mathrm{el}} = T(x + \delta x_{\mathrm{r}}) - T(x - \delta x_{\mathrm{l}})$, where δx_{l} and δx_{r} are the distances to the left and right neighbors, respectively. In the framework of the mean field scheme the second force is $f_{\mathrm{int}} = -\mathrm{d}\mu/\mathrm{d}x$, where $\mu(x)$ is a self-consistent potential determined by the average volume fraction ρ of polymer segments at point x. The only natural assumption we need is that both $\mu(\varphi)$ and $T(E)$, where $E(x) = \mathrm{d}x/\mathrm{d}n$ is the local chain stretching, are monotonically increasing functions. This implies that the gradients $\mathrm{d}T/\mathrm{d}x$ and $\mathrm{d}E/\mathrm{d}x = (\mathrm{d}E/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}x)$ have the same sign, and so do the gradients $\mathrm{d}\varphi/\mathrm{d}x$ and $\mathrm{d}\mu/\mathrm{d}x$.

Suppose that the fluctuations of the chain end position $\langle \delta x_N^2 \rangle^{1/2}$ increase with N more slowly than N^1. Then for the rescaled coordinate $z = x/H$, $\langle \delta z_N^2 \rangle^{1/2} \rightarrow 0$ in the asymptotic limit $N \rightarrow \infty$. Since the free-end height is the same for all the chains, all of them make the same contribution to the average density, and $\varphi(x)$ is simply determined by the local chain stretching $E(x)$: $\varphi(x) \sim \rho(\mathrm{d}n/\mathrm{d}x) \sim 1/E(x)$. Hence, $\mathrm{d}\varphi/\mathrm{d}x$ and $\mathrm{d}E/\mathrm{d}x$ have opposite signs, and the same is true for $\mathrm{d}\mu/\mathrm{d}x$ and $\mathrm{d}T/\mathrm{d}x$. Consequently, the forces $f_{\mathrm{int}} = -\mathrm{d}\mu/\mathrm{d}x$ and $f_{\mathrm{el}} \sim \mathrm{d}T/\mathrm{d}x$ have the same direction and cannot balance each other! The case of a uniform stretching $T = \mathrm{const}$, $\mu = \mathrm{const}$ does not save the situation, since the condition of vanishing tension on the free end is not satisfied. And the ultimate escape $T = 0$ is unphysical because in the limit $N \rightarrow \infty$ the chains are inevitably stretched, at least to satisfy the condition of finite density.

In simple words, for the chain to be stretched by a self-consistent potential, the density should decrease with the distance from the grafting plane. In the case of essentially one-dimensional geometry and provided the chain size fluctuations are small, it implies that the local stretching of the chain should increase from the grafted end to the free one. This makes it impossible to satisfy the free-end condition.

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