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Collective Dynamics of Polymer Brushes

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ABSTRACT: Dynamics of poly(ethylene oxide)−polystyrene (PEO−PS) brushes with shorter anchoring PEO blocks adsorbed on a flat surface are considered theoretically. Three relaxation modes are identified: a fast cooperative (hydrodynamic) mode, a slower drag mode, and the slowest anchor-sliding mode. It is shown that the anchor mode is likely to be dominant and that it is strongly coupled to a two-dimensional microdomain structure, which is presumably formed by PEO. A scaling picture of pattern formation on the adsorbing surface is developed. The theory yields an interpretation of existing evanescent-wave dynamic light-scattering data. The PEO pattern gives rise to high scattering intensity and slow dynamics at high wavenumbers.

1. Introduction

End-grafted polymer layers are often called "brushes" when the mean distance between grafting points is smaller than the layer thickness.[1] An interest in these systems is stimulated, in part, by their possible applications for colloidal stabilization and for modification of bulk surfaces and interfaces for improved adhesion, wetting, and wear properties.[2] Polymer brushes received considerable attention recently, mostly with regard to their static properties.[3] Theoretical studies of brush dynamics (excluding simulations) are not numerous and are mostly concerned with single-chain dynamics.[4−6] Collective brush dynamics was very briefly discussed by De Gennes[1] in terms of shear and longitudinal deformation modes, the latter being governed by the cooperative diffusion constant. A simple continuum approach developed in ref 7 does not account for the brush structure in a consistent way: the continuum model (originally suggested for adsorbed layers[8]) is not exactly appropriate for brushes.

Experimentally, collective brush dynamics was recently studied using evanescent-wave dynamic light scattering, which probes brush surface waves. The brushes were formed by polystyrene, PS, chains (M = 80−500 kDa, kDa = kilodaltons) attached to a glass surface by relatively short poly(ethylene oxide), PEO, blocks.[2] It would be fair to say that there is no quantitative (or even just scaling) theory of collective brush dynamics that allows an interpretation of the experimental data.[2] Yet the problem is additionally attractive since an unusual behavior was observed: the relaxation of surface waves was found to slow as the scattering vector was increased.[2]

Hence, the aim of the present paper is to develop a theory of brush surface waves as probed by the evanescent-wave scattering technique. Collective near-equilibrium dynamics of polymer brushes is considered in section 3 following a brief discussion of their static properties in the second section. A comparison (section 4) of the theoretical results with the evanescent-wave scattering data (for the thickest polymer brush)[2] reveals a marked discrepancy. This triggers the suspicion that the original assumption of immobile anchoring blocks is incorrect. An anchor-sliding dynamical mode is then considered in section 5. We show that the interaction between the anchoring PEO blocks is likely to drive them to form a domain structure on the glass surface. It is found that the tendency for surface pattern formation (and the pattern itself) must be strongly manifested in the evanescent-wave scattering owing to the coupling between PEO and PS blocks.

2. Static Properties

Let us consider a grafted layer formed by PEO−PS diblock copolymers with the anchoring PEO blocks adsorbed on a glass surface (the PEO block is assumed to be much shorter than the PS block). The layer is swollen by toluene, a good solvent for PS. It is this model brush system that was studied in ref 2. The grafting density $\sigma = 1/s^2$ (s is the mean interanchor distance) is assumed to be high, so that PS chains are extended into the solvent.[9] The equilibrium brush structure is well-understood theoretically;[3,10] for the marginal solvent conditions the predicted brush height is

$$h_0 = \left(\frac{24}{\pi^2}\right)^{1/3} N\,(\sigma\omega a^2)^{1/3} \tag{1}$$

where N is the number of PS monomers per chain, w is the monomer interaction parameter (second virial coefficient), $a = b/\sqrt{6}$, and b is the PS statistical segment. Equation 1 is a mean-field result implying that the energy of excluded-volume interactions per unit volume is

$$\frac{k_B T}{2}\, wc^2$$

where c is the local monomer concentration. This equation is valid in the marginal solvent regime, i.e., when $w/(b^6 c) \ll 1$ ($k_B T$ is considered as the energy unit below).

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The equilibrium monomer concentration profile is parabolic[10]

$$c_0(z) = c_\mathrm{m}\,(1 - z^2/h_0^2)$$

where $c_\mathrm{m} = {}^3/_2\sigma N/h_0$ is assumed to be small (z is the distance from the grafting surface). The mean molecular field is proportional to the concentration:

$$U_0 = wc_0(z)$$

The total brush free energy is[10]

$$F_0 = \frac{9}{10}\left(\frac{\pi^2}{24}\right)^{1/3} AN\sigma\left(\frac{\sigma w}{a}\right)^{2/3} \tag{2}$$

where A is the total brush area.

Intensity of the scattered light is directly proportional to the structure factor of anchored PS chains, $S(q) = \langle\delta c_{-\mathbf{q}}\delta c_\mathbf{q}\rangle/A$, where $\mathbf{q}$ is the scattering wave vector, and

$$\delta c_\mathbf{q} = \int \delta c(\mathbf{r})\mathrm{e}^{-i\mathbf{qr}}\,\mathrm{d}^3 r$$

i.e., $\delta c_\mathbf{q}$ is the relevant Fourier component of the monomer concentration fluctuation $\delta c(\mathbf{r}) = c(\mathbf{r}) - \langle c(\mathbf{r})\rangle$, where $c(\mathbf{r})$ is the instantaneous monomer concentration and $\langle c(\mathbf{r})\rangle$ is the time-averaged concentration.

The static structure factor of a swollen polymer brush was calculated in ref 11 using a quantitative mean-field approach. According to the basic principles of statistical mechanics, the mean-square fluctuation, $S(q)$, is inversely proportional to the fluctuation free energy δF, which can be represented as a sum of three terms due to (i) monomer interactions, (ii) elongation of grafted chains, and (iii) brush/solvent surface tension. The latter contribution due to the surface tension is neglected below: the tension is small since the average monomer volume fraction is low, $\phi \equiv cv \ll 1$, where v is monomer volume.[11]

We also assume for simplicity that $\mathbf{q}$ is parallel to the anchoring surface. Note that it is a two-dimensional monomer concentration fluctuation

$$\delta\Phi(x, y) = \int \delta c(\mathbf{r})\,\mathrm{d}z \tag{3}$$

that is probed by the scattering in this case. The fluctuation also implies a waviness of the brush free surface.

The predicted structure factor is then[11] (see also Appendix A)

$$S(q) \simeq \frac{h_0}{w}\frac{Q^2}{\dfrac{36}{\pi^2} + Q^2} \tag{4}$$

where $Q = qh_0$. Equation 4 is in qualitative agreement with the results obtained earlier for dry brushes.[12,13] Note that fluctuations are suppressed in the limit $q \to 0$, i.e., $\lambda = 2\pi/q \to \infty$: the longer λ, the stronger the chain elongation in the transverse direction (i.e., parallel to $\mathbf{q}$) required in order to produce a given fluctuation amplitude.

The excess free energy associated with a prescribed concentration fluctuation $\delta\Phi(x) = \delta\Phi\cos(qx)$ is also related to the structure factor:

$$\Delta F = \frac{A}{4}\frac{1}{S(q)}|\delta\Phi|^2 \tag{5}$$

Note that eq 5 can be written as

$$\Delta F = \mathrm{const}\left[(\epsilon h_0)^2 + \frac{9}{\pi^4}(\epsilon\lambda)^2\right] \tag{6}$$

where $\epsilon \equiv (\delta\Phi)/(\sigma N)$ is the relative fluctuation amplitude and $\lambda = (2\pi)/q$ is the wavelength. This equation can be interpreted as follows: The surface deformation implies both an elongation of grafted chains (the length increment is $\sim\epsilon h_0$) and their lateral shear displacement (the free end displacement to the distance $\sim\epsilon\lambda$). The corresponding elastic energy is the sum of two terms: one for the longitudinal deformation (the first term in square brackets in eq 6) and another for the shear deformation (the second term in eq 6). Note that minimization of the total free energy $\Delta F + \int \delta\Phi U_\mathrm{ext}\,\mathrm{d}x\mathrm{d}y$ in the presence of an external field U_ext yields the correct result for the equilibrium concentration fluctuation induced by the field, i.e., precisely eq A2.

3. Collective Dynamics

The dynamic light scattering probes both the amplitude and the relaxation dynamics of the segment concentration fluctuations. The technique allows one to measure the dynamic structure factor

$$S(q, t) = \langle\delta c_{-\mathbf{q}}(0)\delta c_\mathbf{q}(t)\rangle/A$$

A useful interpretation of the structure factor follows from the fluctuation theorem:[14] Let us assume that a weak external field is applied to the system at $t = 0$. In the presence of the field (i.e., for $t > 0$) each monomer gains a potential energy $U_\mathrm{ext}(x)$ defined in eq A1. The field induces a concentration fluctuation $\delta\Phi(x, t)$ which relaxes toward the equilibrium. It is the dynamic structure factor that defines the relaxation function (for $t > 0$)

$$\delta\Phi(x, t) = [S(q, 0) - S(q, t)]\,U_\mathrm{ext}(x) \tag{7}$$

where $S(q, 0) = S(q)$ is the static structure factor (see eq 4) that is thus proportional to the amplitude of the concentration wave, $\delta\Phi = \delta\Phi(0, \infty)$, induced by the field: $S(q) = \delta\Phi/u$.

One can distinguish two basic modes of polymer dynamics: (i) a single-fluid cooperative motion of polymer segments together with the solvent and (ii) a drag motion of the segments with respect to the solvent. These modes have been originally identified by de Gennes[1] as the transverse and the longitudinal modes. Note, however, that in fact the cooperative (hydrodynamic) mode involves both transverse (shear) and longitudinal (breathing) deformation of grafted chains, and the same is true for the slower drag mode (see below).

Obviously the first mode implies much lower dissipation (the main source of dissipation is polymer/solvent friction, which is minimized in the case when polymer

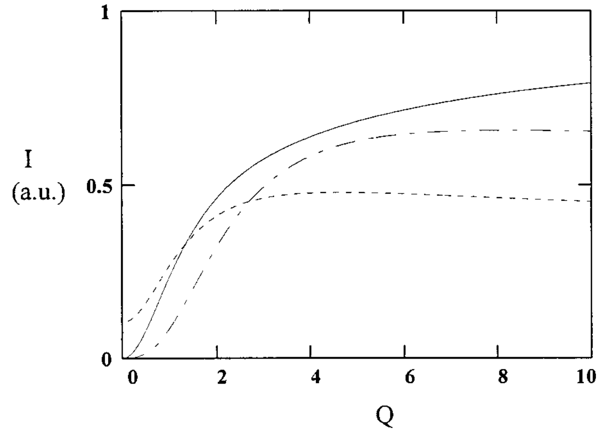

Figure 1. Fast-mode intensity I_1 as a function of the reduced wavenumber $Q = qh_0$ (solid line); the drag-mode intensity I_2 (long dashes); the relative contribution of the drag mode $I_2/(I_1 + I_2)$ (short dashes).

segments do not move with respect to the solvent); i.e., it is fast. However, this fast cooperative mode cannot provide a complete relaxation as it implies a continuous deformation of the brush, and it is restricted by the fluid incompressibility. Hence a slower drag mode considered in section 3.2. It is shown there that relaxation times (t_1 and t_2) of the two modes are well separated, so that their intensities, $I_i = (\delta\Phi_i)/u$, $i = 1, 2$, are well defined (here $\delta\Phi_i$ is the concentration wave amplitude increment during the corresponding relaxation stage). The total intensity is just the static structure factor: $I_{\text{tot}} \equiv I_1 + I_2 = S(q)$.

3.1. Fast Relaxation Mode. The intensity of the fast cooperative (hydrodynamic) process is calculated in Appendix B. The resultant wave-vector dependence of the intensity is shown in Figure 1. The intensity increases as Q^2 in the regime of low $Q = qh_0$, and it shows a plateau at high q's. The main features of the fast process are the following: (i) a relative motion of polymer segments with respect to the solvent is negligible; (ii) a continuous brush deformation is restricted by (iii) fluid incompressibility. The results obtained in Appendix B show that these conditions are in fact not too restrictive: a significant portion of the initial fluctuation relaxs during the fast process. The relative amplitude of the fast process $I_1/I_{\text{tot}} \simeq 0.896$ for long wavelengths ($Q \ll 1$); I/I_{tot} somewhat decreases down to 0.55 at higher Q's.

Let us consider the relaxation time of the fast mode in the regime $Q \ll 1$. It is shear brush deformations that are relevant in this case. The local shear strain is

$$\gamma = \frac{\mathrm{d}X}{\mathrm{d}z} = \frac{i}{q}\frac{\mathrm{d}^2Y}{\mathrm{d}z^2} \simeq \text{const}\,\frac{z+2}{(1+z)^2} \tag{8}$$

where the first equation is the definition of γ, the second equation follows from eq B2, and the third equation follows from eq B9. The corresponding elastic energy increment is defined in eq B5 where the Y-terms are negligible: $\Delta F_{\text{el}} \simeq (A/4) \int \tau\, |\gamma|^2\, \mathrm{d}z$. The dissipation rate per unit volume is $\eta^*|R(\dot\gamma e^{iqx})|^2$, where η^* is the effective viscosity considered below and $R(\dot\gamma e^{iqx})$ is the local shear rate. Hence the total dissipation rate is $D = (A/2)\eta^* \int |\dot\gamma|^2\, \mathrm{d}z$. Note that the general structure of eq B7 implies that the total free energy decrement, $-\Delta F$, is equal to the elastic energy increment ΔF_{el}. The fast-mode relaxation time t_1 can be obtained using the following obvious relation: $-\Delta F = \int D\, \mathrm{d}t$. Assuming a simple exponential relaxation, $\dot\gamma \propto e^{-t/t_1}$, we thus get

$$t_1 = \frac{\int \eta^* |\gamma|^2\, \mathrm{d}z}{\int \tau\, |\gamma|^2\, \mathrm{d}z} \tag{9}$$

Using also eq 8 and recovering the k_BT dependence, we obtain

$$t_1 \simeq 0.5\, \frac{\eta^* N b^2}{\sigma h_0 k_B T} \tag{10}$$

Equation 9 implies that the relaxation time $t_1 \sim \eta^*/E$, where $E \sim \tau$ is the shear elastic modulus of the brush, which is also proportional to concentration of *elastic blobs*, c_{el}: $E \sim c_{\text{el}}$. A grafted chain can be represented as a nearly straight sequence of elastic blobs; hence, $\xi_{\text{el}}(N/g_{\text{el}}) \sim h_0$, where $\xi_{\text{el}} = bg_{\text{el}}^{1/2}$ is the blob size and g_{el} is the number of monomers per blob. Hence $\xi_{\text{el}} \sim Nb^2/h_0$, $c_{\text{el}} \sim (\sigma N)/(h_0 g_{\text{el}}) \sim \sigma h_0/(Nb^2)$ and

$$t_1 \sim \frac{\eta^* h_0 g_{\text{el}}}{\sigma N} \tag{11}$$

Turning to the effective viscosity, we first note that the dissipation rate is due to (i) solvent viscosity, $\eta_s\dot\gamma^2$, and (ii) monomer/solvent friction, D_{ms}. The second contribution (which actually dominates the first one) is due to the fact that monomers do not exactly follow the solvent particles. Short enough parts of polymer chains (dissipation blobs) that relax a bit faster than t_1 are moving collectively, so that the typical blob/solvent velocity is $\Delta v \sim \tilde\xi\dot\gamma$, where $\tilde\xi$ is the dissipation blob size which is also equal to the typical uncertainty of blob z-coordinate due to thermal fluctuations during the time t_1. Therefore $D_{\text{ms}} \sim \tilde c\tilde\zeta(\Delta v)^2$, where $\tilde c = (\sigma N)/(h_0\tilde g)$ is concentration of dissipation blobs, $\tilde\zeta$ is the blob/solvent friction constant, and $\tilde g$ is the number of monomers per blob. Hence $D_{\text{ms}} = \eta_{\text{ms}}\dot\gamma^2$ with $\eta_{\text{ms}} \sim \tilde\zeta\, \tilde\xi^2\sigma N/(h_0\tilde g)$. At this point let us assume that $\eta_s \ll \eta_{\text{ms}}$ (this is verified below), so that $\eta^* \simeq \eta_{\text{ms}}$. On one hand, using eq 11 we get

$$t_1 \sim \tilde\zeta\, \tilde\xi^2 g_{\text{el}}/\tilde g$$

On the other hand, the blob relaxation time, $\tilde t$, is nearly the time required for the blob to diffuse to its own size, i.e.

$$\tilde t \sim \tilde\xi^2/\tilde D \sim \tilde\zeta\, \tilde\xi^2$$

(here we used Einstein's relation between the blob diffusion constant $\tilde D$ and its friction constant: $\tilde D = 1/\tilde\zeta$). Hence the condition $\tilde t \sim t_1$ requires $\tilde g \sim g_{\text{el}}$, i.e., the dissipation blob coincides with elastic blob. At this point it is easy to verify that $\eta_{\text{ms}} \gg \eta_s$: it follows from the marginal solvent condition, $w/(b^6c_{\text{m}}) \ll 1$, assumed in this study.

Therefore the fast-mode time t_1 is equal to the relaxation time of elastic blob, $t_{\text{el}} \sim \zeta_{\text{el}}\xi_{\text{el}}^2$. The elastic blob friction constant, ζ_{el}, can be estimated using the Rouse/Zimm model valid for semidilute polymer solutions: $\zeta_{\text{el}} \sim (g_{\text{el}}/g_c)\zeta_c$, where g_c is the number of monomers per concentration blob, $\zeta_c \sim \eta_s\xi_c$ is its friction constant, and $\xi_c \sim bg_c^{1/2}$ is its size. Note that elastic blobs are always larger than concentration blobs in the marginal solvent regime. By definition of the concentration blob, $g_c/\xi_c^3 \sim$ c, where $c = (\sigma N)/h_0$ is the (average) monomer concentration in the brush. So we finally arrive at the following scaling estimate for the fast-mode time

$$t_1 \sim t_{el} \sim \eta_s \sigma \left(\frac{Nb^2}{h_0}\right)^5 \qquad (12)$$

Note that t_1 is virtually N-independent since $h_0 \propto N$ for a given grafting density σ (see eq 1): $t_1 \propto N^0 \sigma^{-2/3}$. The fast mode is different from the usual cooperative diffusion process in polymer solutions (note that t_1 does not depend on q). The fast mode is associated with relaxation of elastic blobs, or, in other words, with relaxation of the elastic energy of lateral chain "polarization", the relaxation that is controlled by the friction between neighboring elastic blobs.

3.2. The Drag Mode. The drag-mode intensity $I_2 = I_{tot} - I_1$ is plotted vs q in Figure 1 ($I_{tot} = S(q)$ is the static structure factor). Note that the fast process is always dominant: the relative intensity of the slow drag mode is $I_2/I_{tot} \simeq 10.4\%$ in the low-q limit; in the experimentally relevant regime, $Q = qh_0 \sim 3$, the slow mode contribution is $I_2/I_{tot} \simeq 40\%$.

Let us consider the drag-mode relaxation time t_2 using the dissipation argument (see the previous section). For simplicity let us assume first that the solvent does not flow. The effect of solvent flow, i.e., of hydrodynamic interaction of monomers, is accounted for by a simple renormalization of monomer friction constant (see below). We also neglect any coupling between fast and slow modes. This assumption does not qualitatively affect t_2. The free energy decrement due to the relaxation process is $-\Delta F = (A/4)\delta\Phi u = (A/4)S(q)u^2$. On the other hand, the same quantity is equal to the gross dissipation: $-\Delta F = \int D\ \mathrm{d}t$, where $D = \zeta_0 \sum_{l,C} \mathbf{v}_{l,C}^2$ is the dissipation rate, ζ_0 is the monomer friction constant, and $\mathbf{v}_{l,C}$ is the monomer velocity. Assuming an exponential relaxation, $\mathbf{v}_{l,C} = (\mathrm{d}/\mathrm{d}t)\ (\mathbf{W}_{l,C} e^{-t/t_2})$, where $\mathbf{W}_{l,C}$ is the total monomer displacement during the drag process, we get

$$\int D\ \mathrm{d}t \simeq \frac{1}{2}\frac{\zeta_0}{t_2}\sum_{l,C}\mathbf{W}_{l,C}^2$$

Hence

$$t_2 \simeq \frac{2\zeta_0}{AS(q)u^2}\sum_{l,C}\mathbf{W}_{l,C}^2 \qquad (13)$$

The displacement of the lth monomer in the x-direction, $W_{x,l}$, is proportional to the lateral force, $f_x = -\ \partial U/\partial x$, as defined in eq A4. Therefore $\sum_l W_{x,l}^2 = {}^8/_{15}\ N^5 a^4 f_x^2$. Turning to displacements in z-direction, let us assume that all chains are uniformely stretched in this direction, i.e., $W_{x,l} = (\delta h/h_0) z_l$, where δh is defined in eq A5. Then $\sum_l W_{z,l}^2 = (\delta h/h_0)^2\ N[(\int z^2 c_0(z)\ \mathrm{d}z)/(\int c_0(z)\ \mathrm{d}z)] = {}^1/_{45}\ [h_0^2/(\sigma^2 N)]\ (\delta\Phi)^2$. Finally, calculating $\sum_{l,C}\mathbf{W}_{l,C}^2 = \sigma \int \mathrm{d}x\mathrm{d}y\ [\sum_l W_{x,l}^2 + \sum_l W_{z,l}^2]$ using eqs A2 and A3 and substituting the result into eq 13, we get the slow-mode relaxation time

$$t_2 \simeq \frac{4}{5}\zeta_0 a^2 N^2 \frac{1 + Q^2/54}{1 + \pi^2 Q^2/36} \qquad (14)$$

where $Q = qh_0$.

Table 1. Molecular Characteristics of PEO−PS Brushes:[2,9] Number of Monomers in PS Block (N) and in PEO Block (n), Mean Interanchor Distance ($s = 1/\sqrt{\sigma}$), and Brush thickness (h_0)

sample	N	n	s (nm)	h_0 (nm)
PEO−PS/500	4790	91	23	130
PEO−PS/184	1700	167	11	80
PEO−PS/80	730	90	7	45

The effect of hydrodynamic interactions was neglected so far. It is known that in semidilute polymer solutions these interactions are screened out on the scales larger than concentration blob size ξ_c. Hence their effect for large-scale chain dynamics is reduced to a renormalization of the monomer friction constant

$$\zeta_0 \rightarrow \zeta_0^* = \zeta_c/g_c$$

where $\zeta_c \sim \eta_s \xi_c$ is the friction constant of a concentration blob (see the previous section). Thus we get $\zeta_0^* \simeq C\eta_s c b^4$, where $c = (\sigma N)/h_0$ and C is a numerical constant. Substituting ζ_0^* for ζ_0 into eq 14, we get

$$t_2 = t_2(0)\frac{1 + Q^2/54}{1 + \pi^2 Q^2/36} \qquad (15)$$

where

$$t_2(0) = \frac{4}{30} C \frac{\eta_s}{k_B T}\frac{\sigma N}{h_0} b^6 N^2 = \left(\frac{\pi^2}{4}\right)^{1/3} C \frac{b^{16/3}\sigma^{2/3}}{w^{1/3}}\frac{\eta_s}{k_B T} N^2$$

i.e., t_2 is of the order of the Rouse/Zimm relaxation time of grafted chains. Note that the time t_2 is proportional to N^2 (since $h_0 \propto N$ if σ = const), and it has nothing to do with single-chain relaxation time $t_s \propto N^3$ predicted by Klushin and Skvortsov:[6] the single-chain relaxation is driven by the chain entropy, which is much weaker than the osmotic pressure that drives the drag relaxation process. Hence the single-chain (self-diffusion) time is much longer than the collective time t_2.

So far we assumed that the brush is unentangled. The entanglements are supposed to be important for $N > N_e(\phi)$. For the reference PEO−PS/500 brush studied in ref 2 (its parameters are quoted in Table 1), $N_e(1) \simeq 200$. The average monomer volume fraction is $\phi = (N_{v\sigma})/h_0 \simeq 1.4\%$ since the monomer volume is $v \simeq 0.17$ nm^3. Using the empirical law[16] $N_e(\phi) \simeq N_e(1)/\phi$, we get $N/N_e(\phi) \simeq 0.3$ for $\phi = 1.4\%$. Hence entanglements are indeed not important. This conclusion, however, should be taken with some reservations as the conformation of a grafted chain is different from that of a free chain in a semidilute solution. Grafted chains are stretched perpendicular to the grafting surface forming a sort of two-dimensional lattice. A lateral motion of a grafted chain is restricted by this lattice, whereas its motion in the z-direction is virtually free.

Hence in the general case a two-stage slow process is expected: Rouse/Zimm longitudinal relaxation followed by a slower lateral topological relaxation process involving an "arm retraction" mechanism in analogy with the dynamics of branched polymers.[17] The topological relaxation time should be exponentially long if the chains are strongly stretched ($h_0 \gg s$)

$$t_{top} \sim t_2 \exp(\text{const}\ h_0/s)$$

where const is expected to be small (it is inversely proportional to an effective N_e in two dimensions). For the reference PEO−PS/500 brush, $h_0/s \simeq 5$ so that it is likely that the topological slowing is not yet in effect for this brush.

4. Comparison with Experiments

Let us estimate the relaxation times t_1 and t_2 for the thickest PEO−PS/500 brush in toluene studied experimentally[2] (the reference brush). The relevant molecular parameters are $b = b_{PS} \simeq 0.7$ nm, $\eta_s \simeq 0.005$ P; other parameters are indicated in Table 1. The probed wavevector range was $q \simeq (0.025-0.04)$ nm^{-1}.

The scaling result for t_1, eq 12, is not really useful as it involves high powers and unknown numerical constants. Let us use eq 10 instead. Obviously $\eta^* > \eta_s$, hence the following inequality

$$t_1 \gtrsim 0.5 \frac{\eta_s N b^2}{\sigma h_0 k_B T} \simeq 0.5 \times 10^{-6} \text{ s}$$

The time t_1 is therefore within the experimental window (from 10^{-7} to 10^3 s)[2] although it is perhaps close to the resolution limit.

The slow-mode time is defined in eq 15. To determine the unknown constant C, we note that the self-diffusion constant, D_s, of polymer (PS) chains in unentangled marginal solution is just inversely proportional to ζ_0^*: $D_s = (k_B T)/(N\zeta_0^*) = (k_B T)/(NC\eta_s c b^4)$. Using the relevant self-diffusion data on PS/toluene solutions,[18] we get $C \simeq 16$ (note that C is supposed to be a universal number, i.e., independent of polymer/solvent pair). Thus we arrive at the following estimate for the slow-mode time in the experimental q-range ($Q = qh_0 = 3/5$):

$$t_2 \simeq (1-2) \times 10^{-5} \text{ s}$$

The predicted relaxation times are compared with the experimental data in Figure 2a. A similar comparison for wave-vector dependence of the total intensity has been performed in a previous paper.[11] The result is shown in Figure 2b (the predicted intensity $I_{tot}(q)$ essentially follows the dependence defined in eq 4). Note that the experimental q-dependence of I_{tot} is drastically different from the theoretical results: the measured intensity sharply increases in the region $Q \gtrsim 4$ where the predicted curve shows a plateau. The disagreement between theory and the experimental data on relaxation times is even more pronounced. Only one relaxation mode was observed. On one hand, the observed relaxation time is much longer than both predicted t_1 and t_2 in the whole q-range. On the other hand, the measured q-dependence of the time qualitatively disagrees with theory: experiments show collective dynamics that drastically slows at high q's while theoretical slow-mode relaxation time t_2 decreases with q. The theory involves no ad hoc assumptions that could possibly give rise to that strong disagreement. It is thus likely that the observed dynamics is due to a collective relaxation process that is entirely different from those considered above. In other words, it is a new (third) superslow relaxation mode that was observed, while the predicted two modes (fast hydrodynamic mode and slow drag mode) are just not resolved owing to some reason (it is possible that the fast-mode time is too close to the resolution limit and that the drag-mode intensity is not high enough). So, what is the nature of the new superslow process? A tentative explanation is provided in the next sections.

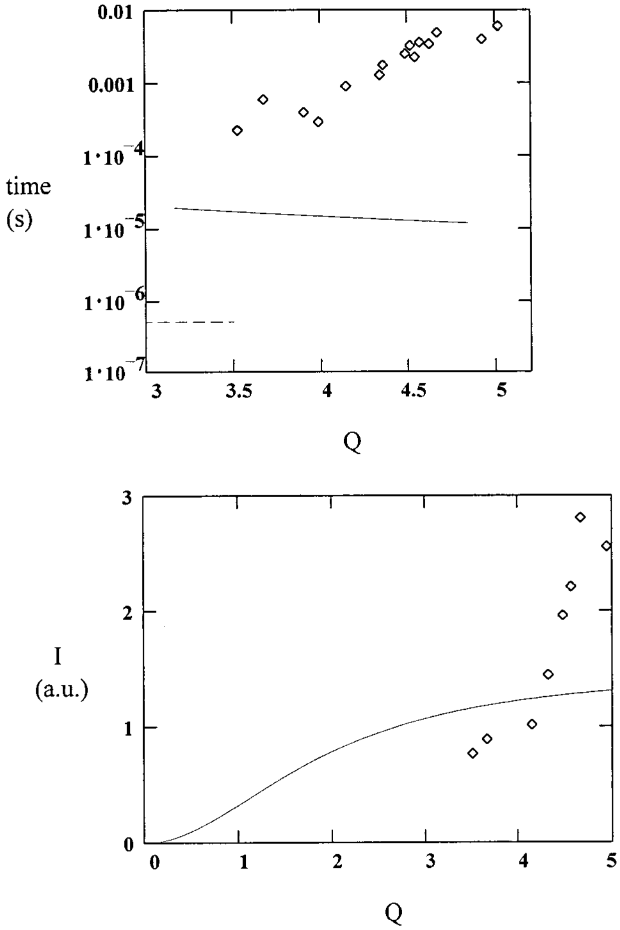

Figure 2. (a, top) Wavenumber dependence of the predicted relaxation time for the drag mode (solid line); the fast-mode relaxation time (dashes); experimental data for PEO−PS/500 brush[2] (diamonds). (b, bottom) Observed scattering intensity (diamonds) and the predicted total intensity $I_{tot} = I_1 + I_2$.

5. Anchor Mode

So far we assumed that grafted points do not move. This must be true with chemical grafting, however, not in the case of anchoring by a short block adsorbed on a surface. Clearly collective motion of anchoring blocks (PEO) must contribute to dynamical scattering giving rise to the additional anchor-sliding relaxation mode considered below.

So, let us allow for an inhomogeneous distribution of anchoring blocks: $\sigma = \sigma_0 + \delta\sigma(x)$, where σ is the two-dimensional concentration of anchoring points (i.e., number of blocks per unit area), σ_0 is the average grafting density, and $\delta\sigma$ is a small fluctuation. Excess free energy due to $\delta\sigma$ can be written as $\Delta F = \Delta F_a + \Delta F_{brush}$, where the first term accounts for free energy of PEO blocks in the adsorbed layer, and the second term is due to a redistribution of PS blocks connected to PEO.

The surface energy ΔF_a depends on interactions between PEO segments on glass surface in the presence of a solvent (toluene). The question is whether these are repulsive or attractive. Unfortunately the situation is not clear not only with regard to PEO confined on a surface but even in three dimensions (i.e., for bulk PEO solutions). While early studies[19] yield a conclusion that toluene is good for PEO, more recent experimental results[20,21] unambiguously indicate that toluene is a poor solvent for PEO. Hence there is a possibility of effective *attraction* between PEO segments also in the adsorbed layer, which can be considered a two-dimensional (2D) semidilute solution, i.e., a tendency for phase separation. In this case

$$\Delta F_{\mathrm{a}} = -\Delta\chi_2 \int (\delta\phi_2)^2 \,\mathrm{d}x\mathrm{d}y/A_0$$

where $\Delta\chi_2$ is the interaction parameter (analogous to the Flory parameter), which measures an excess of attraction over (exclude volume) repulsion between PEO segments in the adsorbed layer; $\delta\phi_2 = \phi_2 - \langle\phi_2\rangle = nA_0\delta\sigma$ is the fluctuation of the "surface fraction" of PEO defined as the product of surface area per PEO block (nA_0) and number concentration of these blocks, $\phi_2 = nA_0\sigma$; and n is the number of monomers per PEO block. The area per PEO monomer, A_0, can be estimated as d_0l_0, where $l_0 \simeq 0.45$ nm is the monomer length, $d_0 = (v_0/l_0)^{1/2}$ is its effective thickness, and $v_0 \simeq 0.07$ nm^3 is its volume: $A_0 \simeq d_0l_0 \simeq 0.175$ nm^2.

Let us calculate the brush free energy contribution, $\Delta F_{\mathrm{brush}}$, assuming a harmonic fluctuation, $\delta\sigma(x) = \delta\sigma \cos(qx)$, and also allowing for a fluctuation of the total 2D density of PS segments, $\delta\Phi(x) = \delta\Phi \cos(qx)$.

Using an argument similar to that given in Appendix A involving a weak external field $U_{\mathrm{ext}}(x) = -u \cos(qx)$, it is easy to show that the field induces the following equilibrium fluctuations: $\delta\Phi = (h_0/w)u$, $\delta\sigma = [h_0/(Nw)]u$. Taking also into account that $\Delta F_{\mathrm{brush}}$ for $\delta\sigma = 0$ is defined in eq 5 and using the argument presented just after eq 5, we get the brush free energy (including the external field term)

$$\Delta F_{\mathrm{brush}} = \frac{A}{4}\frac{w}{h_0}\{|\delta\Phi|^2 + K\,|\delta\Phi - N\delta\sigma|^2\} - \frac{A}{2}\,u\delta\Phi \tag{16}$$

where $K = (36/\pi^2)\,[1/(qh_0)^2]$. Minimizing the total energy $\Delta F = \Delta F_{\mathrm{brush}} + \Delta F_{\mathrm{a}}$ with respect to $\delta\Phi$, we obtain

$$\delta\Phi = \frac{h_0}{w}\frac{1}{1+K}\,u + \frac{K}{1+K}\,N\delta\sigma \tag{17}$$

$$\Delta F = \mathrm{const} + \frac{A}{4}\left\{\frac{w}{h_0}\left(\frac{K}{1+K} - K_{\mathrm{a}}\right)(N\delta\sigma)^2 - 2\,\frac{K}{1+K}\,uN\delta\sigma\right\} \tag{18}$$

where const does not depend on $\delta\sigma$, and

$$K_{\mathrm{a}} = \frac{48}{\pi^2}\left(\frac{R_N}{h_0}\right)^2 n\Delta\chi_2\phi_2 \tag{19}$$

Here $R_N = aN^{1/2}$ is the Gaussian size of PS blocks.

We are now in a position to calculate the anchor contribution to the dynamic structure factor considering the brush response to a weak external field applied at $t = 0$ and using the general eq 7. The field induces a tilt of PS chains with respect to the z-axis (normal to the plane). Hence a lateral elastic force acting on PEO blocks gives rise to their motion along the grafting surface. This process must be very slow owing to high friction between PEO segments and the adsorbing surface.

This friction constant is enhanced owing to attraction between PEO blocks and the adsorbing surface. In addition, an effective attraction between neighboring adsorbed PEO blocks must also result in a higher surface friction. Hence we *assume* that PEO/surface friction is higher than the corresponding PS/solvent friction; i.e., the former is the main source of dissipation for the anchor-sliding process. This conjecture is equivalent to the assumption that the PEO-sliding process is much slower than PS relaxation (i.e., both fast and drag modes considered in section 3). Thus conformations of PS chains are assumed to be nearly at equilibrium (with prescribed distribution of grafting points) during the anchor-sliding process. This justifies minimization with respect to $\delta\Phi$, which was performed in order to derive eqs 17 and 18.

The dissipation rate due to anchor sliding is

$$D = n\zeta_2 \int \sigma v_2^2 \,\mathrm{d}x\mathrm{d}y$$

where ζ_2 is the effective friction constant of PEO monomer and v_2 is the local drift velocity of PEO. The continuity equation reads $(\partial/\partial t)\delta\sigma(x, t) = -(\partial/\partial x)(\sigma v_2)$. Taking into account that $\delta\sigma(x, t) = \delta\sigma(t) \cos(qx)$ and that $\sigma \simeq \sigma_0$ is nearly constant, we get

$$D = \frac{A}{2}\,\frac{n\zeta_2}{\sigma_0 q^2}\left|\frac{\mathrm{d}(\delta\sigma)}{\mathrm{d}t}\right|^2 \tag{20}$$

Substitution of eqs 18 and 20 in the basic dissipation equation $(\mathrm{d}/\mathrm{d}t)(\Delta F) = -D$ gives

$$\left(\frac{K}{1+K} - K_{\mathrm{a}}\right)\frac{w}{h_0}\,N\delta\sigma - \frac{K}{1+K}\,u + \frac{n}{N}\,\frac{\zeta_2}{\sigma q^2}\,\frac{\mathrm{d}(\delta\sigma)}{\mathrm{d}t} = 0$$

Solving this equation, substituting the result in eq 17, and comparing the result with eq 7, we get the dynamic structure factor $S(q, t) = I_3 \exp(-t/t_3)$, where

$$I_3 = \frac{h_0}{w}\,\frac{K^2}{(1+K)\,[K - K_{\mathrm{a}}(1+K)]} \tag{21}$$

is the intensity of the anchor mode, and

$$t_3 = t_3(q) = \frac{24}{\pi^2}\,\zeta_2 a^2 nN\,\frac{1}{(qh_0)^2}\left[\frac{K}{1+K} - K_{\mathrm{a}}\right]^{-1} \tag{22}$$

is its relaxation time. In the regime $qh_0 \gg 1$, the last equation can be simplified

$$t_3 = \frac{2}{3}\,\zeta_2 a^2 nN\,\frac{1}{1 - q^2/q_0^2} \tag{23}$$

where

$$q_0 \simeq \frac{6}{\pi h_0}\,K_{\mathrm{a}}^{-1/2} \tag{24}$$

6. Discussion

Obviously both the time and the intensity defined in eqs 21 and 22 diverge as $q \rightarrow q_0$. This behavior indicates that the system is unstable with respect to fluctuations with $q \geq q_0$; i.e., it tends to form a two-dimensional microdomain structure at equilibrium. (A similar structure, but for the case of poor solvent for both blocks and chemical grafting instead of adsorption, was considered in ref 22.) Note that the theoretical approach outlined above implies a homogeneous equilibrium state; i.e., it is not applicable in the case of a microdomain structure. However, eqs 21 and 22 do capture the main qualitative features: a slowing of the relaxation process and an increase of its intensity at larger q's. These features are typical of bulk microphase-separated block copolymer systems.[23-25] It is this qualitative behavior that was observed for the reference brush.[2] Therefore, we attribute the observed behavior to a microdomain pattern formed by PEO blocks on the adsorbing surface.

Note that even for $\Delta\chi_2 = 0$ (i.e., no tendency for 2D pattern formation) the predicted intensity of the anchor-sliding mode, eq 21, is of the order of the drag-mode intensity (see section 3.2): $I_3 \sim I_2$ for $qh_0 \sim 1$. It is known[23-25] that formation of a microdomain pattern in bulk block copolymers results in strong enhancement of the scattering intensity not only at $q \sim q^*$ but also at lower q's (here q^* is the pattern primary wavenumber). In fact, the microdomain structures are never perfectly periodic in practice: the structures always incorporate defects and can be considered as polycrystalline. It is slow motions of large crystallites (grains) and intergrain boundaries that give rise to both high intensity and long relaxation times at $q < q^*$. A similar effect of a 2D pattern in the brush case must be expected. Hence the anchor-sliding mode coupled with the 2D PEO pattern is likely to provide a dominant contribution to the structure factor in a wide q range.

Let us consider the q-dependence of the measured dynamic structure factor. The pattern conjecture implies that the proper reduced variable is λ^*q since $\lambda^* = (2\pi)/q^*$ is the primary characteristic scale of the pattern. The surface microdomain structure of PEO is analyzed in Appendix D. It is shown there that λ^* scales as $\lambda^* \sim b^{1/6}n^{1/4}s^{5/6}$, where $s = \sigma_0^{-1/2}$ is the mean interanchor distance. The measured intensities and relaxation times are plotted against the reduced wavenumber $\tilde{q} = qb^{1/6}n^{1/4}s^{5/6}$ in parts a and b of Figure 3, respectively. A rather good superposition is obvious in both cases. The predicted q-dependence of the anchor relaxation time, t_3, eq 23, is also shown in Figure 3b. The fitted value of the parameter q_0 was then substituted in eq 24 in order to obtain a crude estimate of the interaction parameter $\Delta\chi_2$ using molecular characteristics of the reference brush (see Table 1) and also using eq 19. The result is $\Delta\chi_2 \sim 0.4$, i.e., $\chi_2 \simeq \Delta\chi_2 + 0.5 \sim 1$.

Note that the q-dependence of the intensity is remarkably similar to a typical scattering curve for ordered bulk block copolymers. Also the experimental curves show that the pattern wave vector corresponds to $\tilde{q} \sim 1.6$. This implies that the omitted numerical factor κ in eq D1 is $\kappa \sim 1/1.6 \sim 1$, which is consistent with $\chi_2 \sim 1$.

It is interesting to note that the observed low-q relaxation time for the brush formed by 184 kDa PS chains is about five times longer than the time for 500 kDa PS brush; i.e., a longer time corresponds to shorter chains. This result is rather unexpected, and it is certainly in contrast with the predictions for the drag-mode relaxation times (the predicted t_2 for 184 kDa is faster than t_2 for 500 kDa by a factor of 3, i.e., a normal molecular weight dependence). Note however that PEO blocks are much longer in the case of the 184 kDa brush than in the case of the 500 kDa brush. It is also important that two-dimensional concentration of PEO in the adsorbed layer is much higher (around 30%) in the case of the 184 kDa brush. Hence a higher PEO/surface friction and a slower anchor-sliding relaxation are expected for the shorter 184 kDa brush. This supports the proposed idea that the observed dynamics should be attributed to the anchor-sliding mode.

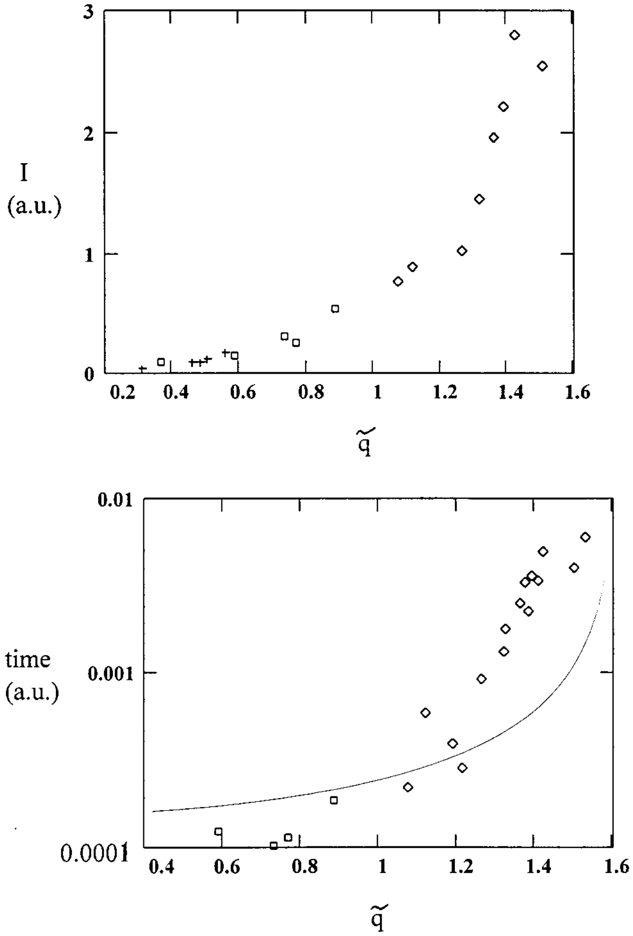

Figure 3. (a, top) Scattering intensity (arbitrary units) measured for PEO–PS/500 (diamonds), PEO–PS/184 (squares), and PEO–PS/80 brushes (pluses) as a function of reduced wavenumber $\tilde{q} = qb^{1/6}s^{5/6}n^{1/4}$. (b, bottom) Experimental relaxation times vs $\tilde{q}$ (diamonds, squares); solid curve is plotted according to eq 23 with $\tilde{q}_0 = 1.61$.

7. Conclusions

1. Collective dynamics of polymer density fluctuations in physically grafted polymer layers are considered theoretically. In particular we focus on PEO–PS brushes formed by adsorption of short PEO blocks onto a solid surface. Three relaxation modes are identified: a cooperative hydrodynamic mode (fast), a drag mode (slow), and an anchor-sliding mode (the slowest).

2. The intensities of the fast cooperative and the drag modes both increase with q. The intensities are comparable for $qh_0 \sim 1$, although the fast mode dominates in the limit $q \to 0$. The relaxation time of the fast mode is nearly equal to the elastic blob relaxation time. The drag mode is characterized by the Rouse/Zimm time for grafted chains.

3. The observed relaxation times in the whole q-range are much longer than both the fast- and the drag-mode times.

4. The observed dynamics is likely to be due to the anchor-sliding relaxation process coupled with the surface pattern formed by adsorbed PEO blocks. The driving force for the pattern formation is an effective attraction between adsorbed blocks defined by the

interaction parameter $\Delta\chi_2$. It is shown that the PEO microdomain structure is manifested in a significant increase of the scattering intensity and in a significant slowing of the dynamics in the region $q > 1/h_0$.

5. The basic wavenumber of the 2D microdomain structure is predicted to scale as $1/q^* \sim b^{1/6}n^{1/4}s^{5/6}$, where n is the number of monomers per anchoring block and s is the mean interanchor distance.

6. The measured scattering intensities for three different brushes show a master curve when plotted vs q/q^*, i.e., vs $qn^{1/4}s^{5/6}$. The same is true regarding the relaxation times.

7. The final note concerning q-dependencies of the predicted relaxation times: The fast hydrodynamic process is characterized by the elastic blob relaxation time, so its rate is assumed to be nearly q-independent. The relaxation rate of the slower drag mode somewhat increases as q is increased, thus showing a normal behavior (faster relaxation at shorter scales). On the other hand, the anchor-sliding relaxation slows as q is increased (in the region $q < q^*$) showing an anomalous behavior. This slowing is attributed to the two-dimensional microdomain pattern formed by adsorbed anchor blocks: the pattern is characterized by a highly cooperative and hence slow dynamics. As q increases toward q^*, the pattern contribution to the scattering intensity increases as well, hence a slower relaxation.

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Appendix A. Static Structure Factor

Equation 4 was derived in ref 11 using the fluctuation theorem,[14] which relates the structure factor and the susceptibility of the system to an external potential field

$$U_{\mathrm{ext}}(x) = -\mathsf{R}\,[u\mathrm{e}^{iqx}] \tag{A1}$$

where u is a small amplitude of the field and R stands for the real part. We can assume that u is real without any loss of generality since initially the system is uniform in the x-direction. The steady two-dimensional monomer concentration fluctuation $\delta\Phi$ (see eq 3) induced by the external field is proportional to its amplitude (in the limit $u \to 0$):

$$\delta\Phi = -\,S(q)U_{\mathrm{ext}} \tag{A2}$$

Note that the x-axis is chosen to be parallel to the wave vector $\mathbf{q}$, hence, no y-dependence is involved.

Let us calculate the concentration fluctuation, $\delta\Phi$. The total field experienced by the monomers is

$$U = U_{\mathrm{ext}} + U_{\mathrm{mol}}$$

where $U_{\mathrm{mol}} = wc = U_0 + w\delta c$ is the molecular field. The total field has to remain parabolic in the z-direction;[11,15] hence, δc does not depend on z, i.e., $\delta c = \delta\Phi/h_0$. Therefore $U = U_0 + (1 - (w/h_0)S(q))\, U_{\mathrm{ext}}$. The x-component of the force experienced by each monomer of a grafted chain is

$$f_{\mathrm{x}} = -\frac{\partial U}{\partial x} = -\left(1 - \frac{w}{h_0}\,S(q)\right)\frac{\partial U_{\mathrm{ext}}}{\partial x} \tag{A3}$$

The force gives rise to a monomer displacement W_x in the x-direction (note that chains are Gaussian in this direction)

$$W_{x,l} = 2a^2N^2\left(\frac{l}{N} - \frac{1}{2}\,\frac{l^2}{N^2}\right) f_x \tag{A4}$$

where l is the monomer position along the chain, $l = 0$, ..., N; $l = 0$ corresponds to the grafting end. Hence the total chain "polarization" $P \equiv \sum_l W_{x,l} = {}^2\!/_3N^3a^2f_x$. The total monomer concentration fluctuation is related to P: $\delta\Phi = -\sigma(\partial P/\partial x) = -\,{}^2\!/_3\sigma N^3a^2q^2\,(1 - (w/h_0)S(q))U_{\mathrm{ext}}$. Finally, recalling eq A2, we obtain $S(q)$, eq 4.

The brush height h is distorted by the field: $h = h_0 + \delta h$. Using the free surface condition $c(x, y, h) = 0$, we get (in the linear approximation):

$$\delta h \simeq -\,\delta c/\left(\frac{\partial c_0}{\partial z}\right)_{z=h_0} \frac{h_0}{3}\,\frac{\delta\Phi}{\sigma N} \tag{A5}$$

(note that $\delta\Phi = h_0\delta c$), i.e., the relative amplitude of the free surface wave, $\delta h/h_0$, is equal to ${}^1\!/_3$ of the relative concentration fluctuation $(\delta\Phi)/(\sigma N)$.

Appendix B. The Fast Mode: Intensity

The displacement vector of a brush element, $W = (W_x, 0, W_z)$, during the fast relaxation stage can be written as

$$W_x = \mathsf{R}\,[X(z)\mathrm{e}^{iqx}], \quad W_z = \mathsf{R}\,[Y(z)\mathrm{e}^{iqx}] \tag{B1}$$

Note that the flow is a linear response to the external field, eq A1, hence x-dependence of $\mathbf{W}$ is given by e^{iqx}. Both functions X and Y can be obtained by minimization of the free energy F in the presence of the external field. The incompressibility condition, eq C4 (see Appendix C), yields the following relation to be imposed on the X and Y functions:

$$iqX(z) + \frac{\mathrm{d}Y}{\mathrm{d}z} = 0 \tag{B2}$$

Note that both X and Y do not vanish in the general case ($q \neq 0$), thus implying simultaneous shear and elongational deformations of grafted chains. The free energy is $F = F_{\mathrm{ext}} + F_{\mathrm{osm}} + F_{\mathrm{el}}$, where $F_{\mathrm{ext}} = \int U_{\mathrm{ext}}c\, \mathrm{d}^3r$ is the external field contribution, $F_{\mathrm{osm}} = {}^1\!/_2w \int c^2\, \mathrm{d}^3r$ is osmotic energy due to monomer interactions, and F_{el} is the elastic energy due to deformation (elongation) of polymer chain trajectories induced by the field.

The monomer concentration in the vicinity of each material element is constant (recall that the flow is incompressible and that monomers do not move with respect to the flow). Hence the osmotic free energy is constant as well, and so it can be disregarded (it is not relevant for the free energy minimization). The total flux of monomers across the line $x = \text{const}$ is $J = \int (\partial W_x/\partial t)\, c_0(z)\, \mathrm{d}z$. Hence the total 2D concentration fluctuation induced during the fast relaxation stage is

$$\delta\Phi(x) = -\int \mathrm{d}t\,\frac{\partial J}{\partial x} = \int \frac{\partial W_z}{\partial z}\,c_0(z)\,\mathrm{d}z = \mathsf{R}\,[\delta\Phi_1\mathrm{e}^{iqx}]$$

where

$$\delta\Phi_1 = \int \frac{\mathrm{d}Y}{\mathrm{d}z}\,c_0(z)\,\mathrm{d}z = -\int Y\,\frac{\mathrm{d}c_0}{\mathrm{d}z}\,\mathrm{d}z \tag{B3}$$

The external field contribution is then

$$F_{\mathrm{ext}} = \frac{A}{2}\, uR \left[\int Y \frac{\mathrm{d}c_0}{\mathrm{d}z}\, \mathrm{d}z\right]$$

(it is proportional to the brush area A).

The elastic free energy is a sum including partial contributions of all segments ($l = 0, ..., N$) of all chains (labeled by C)

$$F_{\mathrm{el}} = \frac{1}{4a^2} \sum_{l,C} \left(\frac{\partial \mathbf{r}_{l,C}}{\partial l}\right)^2 \tag{B4}$$

where $\mathbf{r}_{l,C}$ is the position of the monomer (l, C). The free energy increment due to continuous deformation of the brush is (see Appendix C)

$$\Delta F_{\mathrm{el}} = \frac{A}{4} \int \left\{\tau \left(\left|\frac{\mathrm{d}X}{\mathrm{d}z}\right|^2 + \left|\frac{\mathrm{d}Y}{\mathrm{d}z}\right|^2\right) + \frac{\mathrm{d}^2\tau}{\mathrm{d}z^2} \left|Y\right|^2\right\} \mathrm{d}z \tag{B5}$$

where $\tau = \tau(z)$ is elastic contribution to the longitudinal (zz) stress in the equilibrium brush. The function $\tau(z)$ can be obtained using the condition of mechanical equilibrium

$$\frac{\partial \tau}{\partial z} - c_0(z) \frac{\partial U_0}{\partial z} = 0$$

and the free surface boundary condition, $\tau(h_0) = 0$. The result is

$$\tau = \tau_{\mathrm{m}} \left(1 - \frac{z^2}{h_0^2}\right)^2, \quad \tau_{\mathrm{m}} = \frac{w}{2} c_{\mathrm{m}}^2 = \frac{3\pi^2}{64} \frac{\sigma h_0}{Na^2} \tag{B6}$$

As mentioned above the brush state on completion of the fast relaxation process must correspond to the free energy minimum, i.e., to the minimum of $\Delta F = F_{\mathrm{ext}} + \Delta F_{\mathrm{el}}$. It is easy to show that both X and Y must be real as u is real. Hence

$$\Delta F = \frac{A}{2}\, u \int Y c_0' \,\mathrm{d}z + \frac{A}{4} \int \left\{\tau \left(\frac{1}{q^2} \mathrm{Y}''^2 + Y'^2\right) + \tau'' Y^2\right\} \mathrm{d}z \tag{B7}$$

where prime (′) denotes z-derivative, d/dz. The term $|\mathrm{d}X/\mathrm{d}z|^2$ on the right-hand side of eq B5 was substituted by $(1/q^2)|\mathrm{d}^2Y/\mathrm{d}z^2|^2$ (see eq B2). Minimization of ΔF with respect to $Y = Y(z)$ yields the following equation:

$$uc_0' + Y\tau'' - (\tau Y')' + \frac{1}{q^2} (\tau Y'')'' = 0 \tag{B8}$$

The relevant boundary condition at $z = 0$ is $Y = Y' = 0$, which follows from eq B2 and the assumption that grafted monomers do not move (i.e., $W_x = W_z = 0$ at $z = 0$). As for the other boundary (the brush free surface), it is enough to assume that $Y(z)$ is regular at $z = h_0$. Equation B8 can be solved analytically in the limit $q \to 0$ when it reduces to

$$q^2 uc_0' + (\tau Y'')'' = 0$$

The result is

$$Y = \frac{2h_0 uc_{\mathrm{m}}}{\tau_{\mathrm{m}}} \frac{1}{6} Q^2 \frac{z}{h_0} \ln\left(1 + \frac{z}{h_0}\right), \quad Q \equiv qh_0 \to 0 \tag{B9}$$

Substituting the last equation into eq B3, we get the fast-mode intensity

$$I_1 = \frac{\delta \Phi_1}{u} \simeq \frac{8h_0}{w} Q^2 \frac{1}{6} \int_0^1 Z^2 \ln(1 + Z)\, \mathrm{d}Z \simeq 0.246 Q^2 h_0/w, \quad Q \to 0$$

The total intensity in this limit is $I_{\mathrm{tot}} = S(q) \simeq (\pi^2/36)Q^2h_0/\omega$; i.e., the *relative* amplitude of the fast process is large: $I_1/I_{\mathrm{tot}} \simeq 0.896$.

In the general case, eq B8 was solved numerically. The obtained $Y(z)$ was then substituted into eq B3. The intensity of the fast mode $I_1 = \delta\Phi_1/u$ was obtained as a result.

Appendix C. Elastic Free Energy

We start with eq B4. A brush element located at $\mathbf{r} = (x, y, z)$ moves to a new location $\mathbf{r}' = (x', y', z')$ during the fast relaxation stage:

$$\mathbf{r} = (x, y, z) \to (x', y', z') = (x + W_x(\mathbf{r}), y, z + W_z(\mathbf{r}))$$

The net elastic energy increment is

$$\Delta F_{\mathrm{el}} = \frac{1}{4a^2} \sum_{l,C} \left[\left(\frac{\partial \mathbf{r}'_{l,C}}{\partial l}\right)^2 - \left(\frac{\partial \mathbf{r}_{l,C}}{\partial l}\right)^2\right] = F_1 + F_2 \tag{C1}$$

where

$$F_1 = \frac{1}{4a^2} = \int \mathrm{d}^3r \sum_{l,C} \left(\frac{\partial \mathbf{W}_{l,C}}{\partial l}\right)^2 \delta(\mathbf{r} - \mathbf{r}_{l,C})$$

$$F_2 = \frac{1}{2a^2} = \int \mathrm{d}^3r \sum_{l,C} \frac{\partial \mathbf{r}_{l,C}}{\partial l} \frac{\partial \mathbf{W}_{l,C}}{\partial l} \delta(\mathbf{r} - \mathbf{r}_{l,C})$$

and $\mathbf{W}_{l,C} = (W_x(\mathbf{r}_{l,C}), 0, W_z(\mathbf{r}_{l,C}))$. Taking into account that $\partial \mathbf{r}_{l,C}/\partial l = (0, 0, \partial z_{l,C}/\partial l)$ and $\partial \mathbf{W}_{l,C}/\partial l = (\partial z_{l,C}/\partial l)(\partial \mathbf{W}/\partial z)$ we rewrite the last equations as

$$F_1 = \frac{1}{2} \int \mathrm{d}^3r \left(\frac{\partial \mathbf{W}}{\partial z}\right)^2 \tau, \quad F_2 = \int \mathrm{d}^3r \frac{\partial W_z}{\partial z} \tau \tag{C2}$$

where $\tau = \tau(z) = (1/2a^2)\sum_{l,C} (\partial z_{l,C}/\partial l)^2\, \delta(\mathbf{r} - \mathbf{r}_{l,C})$. Note that $(1/2a^2)(\partial z_{l,C}/\partial l)$ is the local chain tension and that $(\partial z_{l,C}/\partial l)\delta\,(\mathbf{r} - \mathbf{r}_{l,C})$ is the probability that the chain segment (l, C) does contribute to the stress at the point $\mathbf{r}$. Hence τ is equal to the total elastic stress along the z-axis; the function $\tau(z)$ is calculated in Appendix B, eq B6.

The volume conservation equation (i.e., incompressibility) has the form $|\partial \mathbf{r}'/\partial \mathbf{r}| = 1$, which reduces to

$$\frac{\partial W_x}{\partial x} + \frac{\partial W_z}{\partial z} + \frac{\partial W_x}{\partial x} \frac{\partial W_x}{\partial z} - \frac{\partial W_x}{\partial z} \frac{\partial W_z}{\partial x} = 0 \tag{C3}$$

In the linear approximation this equation takes the form

$$\frac{\partial W_x}{\partial x} + \frac{\partial W_z}{\partial z} = 0 \qquad \text{(C4)}$$

Using eq C3, it is possible to show that

$$\int \mathrm{d}x\mathrm{d}y \frac{\partial W_z}{\partial z} = - \frac{\partial}{\partial z} \int \mathrm{d}x\mathrm{d}y \frac{\partial W_x}{\partial x} W_z \simeq \frac{\partial}{\partial z} \int \mathrm{d}x\mathrm{d}y\ W_z \frac{\partial W_z}{\partial z}$$

The terms that are proportional to W^3 are neglected (note that $-\ \partial W_x/\partial_z$ was substituted by $\partial W_z/\partial z$ in the last step). The last equation and eqs B1, C1, and C2 may now be used to obtain the elastic energy increment, eq B5, in which $A = \int \mathrm{d}x\mathrm{d}y$.

Appendix D. Microdomain Structure on the Adsorbing Surface

Let us estimate the wavenumber q^* corresponding to the microdomain structure (we expect that $q^* > q_0$). The driving force for the structure formation is attraction of PEO blocks reflected in positive $\Delta\chi_2$, which results in the tendency for phase separation, i.e., formation of PEO-rich domains on the adsorbing surface. The natural growth of these domains (driven by the edge tension) is restricted owing to the presence of PS blocks. The equilibrium domain size is determined by a balance of the excess (elastic) free energy $\Delta F_{\mathrm{brush}}$ and the energy ΔF_{a} due to PEO domains; it is the total excess energy $\Delta F = \Delta F_{\mathrm{brush}} + \Delta F_{\mathrm{a}}$ that should be minimized with respect to the domain size.

In order to estimate ΔF_{a}, we note that PEO segregation on the surface must be strong since $\chi_2 n \gg 1$: $\chi_2 \sim 1$ (see section 6) and $n \sim 100$ (see Table 1). Hence we expect that PEO blocks form islands on the surface with almost no PEO left outside the islands. The surface fraction covered by the islands is $\varphi = \phi_2/\phi_2^*$, where ϕ_2^* is PEO concentration inside an island (ϕ_2^* depends on χ_2, but it is virtually independent of n; it is expected that $\phi_2^* \sim 1$ for $\chi_2 \sim 1$) and $\phi_2 = \sigma_0 n A_0 \ll 1$ is the average PEO concentration. Hence φ is small, implying circular islands. The island diameter $D \sim \lambda\sqrt{\varphi}$, where $\lambda \sim 2\pi/q^*$ is the interisland distance. Neglecting any interactions between islands we represent the PEO free energy as a sum of "bulk" energy, which is proportional to the total area of islands, and the edge energy, which is proportional to their total perimeter. The bulk contribution does not depend on λ since the total area covered by islands is constant; hence, bulk energy is irrelevant. Therefore ΔF_{a} can be regarded as edge energy

$$\Delta F_{\mathrm{a}} = \beta P \sim \frac{4\beta A}{\lambda} \sqrt{\frac{\phi_2}{\phi_2^*}}$$

where $\beta = \beta(\chi_2)$ is the edge tension and $P = \pi D\{(\phi_2 A)/[\phi_2^*(\pi D^2/4)]\}$ is the total perimeter.

The brush free energy contribution cannot be calculated using eq 16, which is not valid since distribution of anchoring points is strongly inhomogeneous. Fragments of PS blocks adjacent to PEO blocks form nearly spherical shells around each PEO island. The shells are characterized by higher monomer concentration and higher chain tension than on the average over the brush. The shell size must be nearly equal to λ; i.e., the shells extend into the brush to the distance $\sim\lambda$ (see Figure 4). Hence the excess elastic/osmotic energy due to the shells is

$$\Delta F_{\mathrm{brush}} \sim \frac{\lambda}{h_0} F_0$$

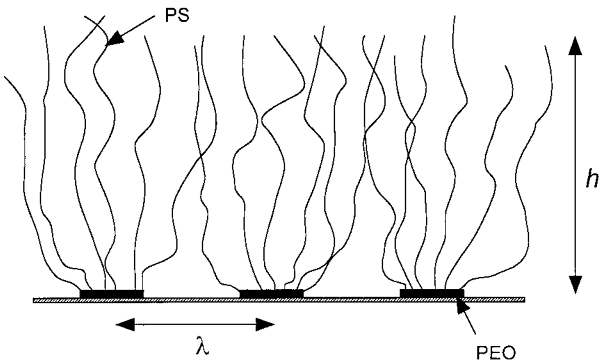

Figure 4. Sketch of a microphase-separated brush: PEO forms islands on the adsorbing surface; their ordered arrangement (2D pattern) is stabilized by interaction of PS chains attached to PEO blocks.

where F_0 is the free energy of the uniform brush defined in eq 2 and h_0 is the brush thickness, eq 1. Minimizing $\Delta F_{\mathrm{brush}} + \Delta F_{\mathrm{a}}$ with respect to λ, we get the equilibrium wavelength of the structure

$$\lambda^2 = \frac{2\pi}{q^*} = \kappa b^{1/6} n^{1/4} \sigma_0^{-5/12} \qquad \text{(D1)}$$

where $\kappa \sim \beta^{1/2} b^{1/2} w^{-1/6} A_0^{1/4} (\phi_2^*)^{-1/4}$. Note that λ^* does not depend on PS molecular weight. The reason is that the perturbation of PS blocks "trajectories" due to PEO domains is local: it extends inside the PS brush to a distance $\sim\lambda$, which is much smaller than the total brush height. Hence λ^* depends on the local degree of elongation of PS chains and their grafting density, but not on the total brush height.

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