Macromolecules **1993,** *26,* 6477–6482

Brush Formation from Mixtures of Short and Long End-Functionalized Chains in a Good Solvent

Eugenia Kumacheva and Jacob Klein*

Materials and Interfaces Department, Weizmann Institute of Science, Rehovot 76100, Israel

Philip Pincus

Materials Department, University of California at Santa Barbara,
Santa Barbara, California 93106

Lewis J. Fetters

Exxon Research and Engineering Company, Corporate Research,
Annandale, New Jersey 08801

Received July 8, 1993; Revised Manuscript Received September 7, 1993®

ABSTRACT: Using surface force measurements, we have determined the structure of polymer brushes formed onto mica, from dilute solutions of zwitterion-terminated polystyrene chains of molecular weights 26 500 and 375 000 in the good solvent toluene. We find that brushes of the longer amphiphiles, formed from a solution of these polymers alone, are rapidly replaced by shorter chains when the latter are added to the solution. This requires a certain minimum concentration of the shorter amphiphiles, but substantial replacement of long-by-short chains can occur even when the monomer concentrations of the shorter polymers is only (1/500) that of the longer ones. By analyzing the force profiles for the mixed brushes thus formed, we obtain a quantitative measure of their structural details. We evaluate these observations in terms of a simple scaling model for the free energy of brushes that are in equilibrium with free end-functionalized chains in solution.

I. Introduction

The structure and interactions of adsorbed polymers have been extensively studied, motivated in part by their use in stabilizing colloidal dispersions and by other practical applications, and their physics is well understood.[1–8] It has long been known that when a surface is in contact with a polydispersed solution of adsorbing polymers, the chains of higher molecular weight adhere to the surface more firmly.[9–11] In equilibrium, this results in the coverage of the surfaces by the longer polymers to the exclusion of the shorter ones.

Chains that do not adsorb along their backbones, but are anchored to a surface by one end alone, have been investigated only relatively recently.[12] At high surface coverage (where the mean interanchor spacing $s \ll R_F$, the swollen end-to-end dimension of the chains in free solution) the tethered chains are stretched normal to the surface, to form so-called polymer brushes. Surface force measurements[12] and other methods[13] have been extensively used to probe the behavior of such brushes, especially the way in which the brush height h varies with degree of polymerization (DP) N and with s. In a good solvent h is determined by the balance between the segmental repulsion between adjacent tethered chains acting to stretch them and the decrease in entropy due to such stretching. Using this idea, Alexander[14] established the basic relations for the characteristics of the brush, based on scaling considerations. He found

$$h = \text{constant} \times Na^{5/3}s^{-2/3} \tag{1}$$

As in all scaling treatments, the constant prefactor is undetermined but is expected to be of order unity. For polymer brushes this has been well confirmed by direct determinations of the brush height[13,15] and also by self-consistent mean-field calculations.[16,17] Equation 1 applies for the case where s is fixed. For the case where the chains on the surface are in equilibrium with those in the adjacent solution, the value of s itself will depend on the length (strictly, the DP) N of the chains.[15] This is because the overall stretching energy per chain must be balanced by the sticking energy Δ of the end group, where $\Delta = \gamma k_B T$ (k_B is Boltzmann's constant and T the temperature). In the language of scaling, it is then the number of "blobs" or correlation lengths per chain that remain constant as N changes. In this case one expects[15,18]

$$s \propto N^{3/5} \tag{2}$$

and therefore

$$h \propto N^{3/5} \tag{3}$$

Using surface force measurements, a comprehensive study of the height h as a function of N for end-functionalized polystyrene chains (designated PS–X(M)[19]) was carried out.[15] The relation (3) was found to hold for dense ($s \ll R_F$) brush layers formed on mica from the good solvent toluene, while the variation of s was quite close to the prediction of eq 2. This suggests that the tethered PS–X chains are indeed in equilibrium (over the incubation time of the experiments) with the free chains in the toluene solution. We note that in this system $\Delta \approx (6–8)k_B T$. The kinetics of brush formation from a solution of end-functionalized chains has been considered in detail by Ligoure and Leibler.[18]

Very recently,[20] in the course of studying forces between brushes of a PS–X(375) amphiphile formed on mica from toluene solution, we investigated the effect of adding to the solution the much shorter amphiphile PS–X(26). It was found that the longer amphiphiles were rapidly displaced from the surface by the shorter ones, which formed a brush characteristic of the PS–X(26). This showed clearly that—in contrast to *adsorbing* chains—for the case of nonadsorbing polymers with the same functional end group it is the *shorter* chains that displace longer

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® Abstract published in *Advance ACS Abstracts,* October 15, 1993.

0024-9297/93/2226-6477$04.00/0

ones from the surface. The driving force for this is the much lower free energy per unit area ΔF associated with the shorter brushes in equilibrium; a simple argument[20] indicated $\Delta F \propto -(N^{-6/5})$. This is a strong chain-length dependence, suggesting interesting strategies for tailoring the structure of brush layers; in particular, it also suggests new possible separation/fractionation techniques from solutions containing different lengths of amphiphiles.

In our earlier study,[20] the chain concentration of added shorter amphiphiles was much larger than that of the longer PS–X chains in the solution.[21] However, as a consequence of the strong N dependence of ΔF, one might expect that a brush in equilibrium with amphiphilic chains in solution will be displaced on introducing similar but shorter chains even to a much *lower* concentration. This has implications for the structure of brushes formed by self-assembly from mixed or polydispersed solutions. While the case of polydispersed or binodal brushes has been analyzed in a number of cases,[17,22,23,29b] there have been no treatments of the structure of brushes formed from a *solution* containing amphiphiles of different lengths, though in practice brushes are generally formed in precisely that way. The aim of the present work is to investigate this situation directly using surface force measurements. In section II we consider the free energy of a brush in equilibrium with a solution of end-adsorbing chains, and in sections III–V we describe the experiments and discuss the results. We conclude with some remarks on the implication of our results for the structure of polymeric brushes formed from polydispersed solutions.

II. Polymer Brushes in Equilibrium with Free End-Functionalized Chains

As already noted, a number of groups have studied theoretically the structure of polydispersed brushes.[17,22,23] The goal of this section is rather more modest, namely, to show that, for a given end-anchoring energy $\Delta = \gamma k_B T$ and nonadsorbing polymers, shorter chains will generally displace longer ones in thermodynamic equilibrium. As in the experiments, our approach is to consider a solution of end-functionalized polymer in a good solvent; the polymers are taken to be nonadsorbing on the exposed interface, while the functional ends are attracted to surface sites.

Consider a solution of such end-functionalized polymers of degree of polymerization N. The bulk solution has a chemical potential μ per monomeric unit. Adsorption of the functional ends to the surface may lead to the formation of Alexander brushes[14] ($s \ll R_F$) or of "mushrooms"[24] ($s > R_F$). The mushroom state consists of nonoverlapping polymers end-attached to the interface. We consider only the case where the bulk polymer solution is dilute, i.e., $\phi_b < \phi^*$, where ϕ is the polymer volume fraction and ϕ^* is its value at the bulk overlap concentration.[25] This is also the most common experimental situation. In semidilute solutions, $\phi_b \geq \phi^*$, the structure and energetics of the surface layers are strongly influenced by the osmotic pressure of the bulk solution which opposes stretching.[24] In order to simplify our analysis, we concentrate on the case of dilute solutions where $\mu \cong (k_B T/N) \ln \phi_b$. Assuming that the solvent is good for the polymers and that the adsorption is sufficiently strong that the coverage is in the brush regime, the free energy per molecule in the brush may be written as

$$f \cong (-\gamma + n_b + \ln \sigma) k_B T \qquad (4)$$

Here the first term is the free energy change due to the binding energy of the functional end group on the surface; the second term is the excess repulsive free energy associated with each brush molecule in the good solvent conditions, where n_b is the number of "blobs" describing the stretched chains (the brush height $h = n_b s$, where the blob size is equal to the interanchor spacing s); and the last term is the surface entropy of mixing of the end-attached polymers, where the surface density $\sigma = (a^2/s^2)$. A similar expression for the free energy per molecule in a brush, though with a somewhat different term for the stretching energy, was given by Ligoure and Leibler.[18] The number of blobs in the stretched chains is given by $n_b = N/g$, where g is the number of monomeric units within a blob. The correlations within the blobs are as in a swollen excluded-volume polymer, leading to $g \cong (s/a)^{5/3}$, where a is a monomer size.

In thermodynamic equilibrium, the chemical potential $\mu_b = N\mu$ of a chain in the bulk solution must equal the chemical potential μ_{brush} of a chain in the brush. For Z chains in the brush covering a surface area A, we have the overall brush energy $F_{\text{brush}} = Zf$. Recalling that $Z = (A/s^2)$, we evaluate $\mu_{\text{brush}} = \partial F_{\text{brush}}/\partial Z$. Finally, equating $\mu_b = \mu_{\text{brush}}$, we find for the area ($=s^2$) per chain in the brush

$$s^2 \cong a^2[(11/6)N/(\gamma + \ln[\phi_b/\sigma])]^{6/5} \qquad (5)$$

Equation 5 may be viewed as the surface-excess isotherm of the end-attached polymers. When the logarithmic term (representing the entropy cost of moving a chain from the bulk to the surface) is small compared to γ, the brush is in the "plateau" regime of the isotherm. In that case we recover the relation of eq 2. When the entropy term approaches γ, we move away from the plateau to the low-surface-coverage situation. Since $s^2 = a^2/\sigma$, eq 5 is a transcendental equation, but the logarithmic term is slowly varying and the principal behavior may be understood by treating it as a constant. In order to be self-consistent, i.e., that the surface is in the brush regime, we must have $\gamma + \ln[\phi_b/\sigma] \geq (11/6)$. This defines a critical bulk volume fraction $\Phi \cong N^{-6/5}e^{-(\gamma-(11/6))}$, below which the surface coverage is dilute. For $N \sim 10^3$ and $\gamma \sim 7$, we find $\Phi \cong 10^{-6}$, which is within the range of typical experimental parameters.[15] Thus a rather sharp change in surface coverage is expected in the vicinity of $\phi_b \cong \Phi$.

The free energy per unit area of the interface, ΔF, is then

$$\Delta F(N,\gamma) = N\mu/s^2 \cong$$
$$[(\gamma + \ln[\phi_b/\sigma])/({}^{11}/{}_{6}N)]^{6/5}(k_B T/a^2) \ln \phi_b \leq 0 \qquad (6)$$

The dominant variables which control ΔF are clearly the molecular weight of the polymer and the energy γ binding the end groups to the surface. The bulk concentration intervenes in a relatively mild logarithmic form and, provided that $\phi_b > \Phi$, may be considered as leading to weak corrections. In that case we also recover the $\Delta F(N)$ dependence announced earlier. It is clear that, if γ is fixed, e.g., by using the same functional ends on chains of different lengths, low molecular weight species are preferentially end-adsorbed over higher molecular weight molecules. For two different molecular weights $N_1 > N_2$, the longer molecules are able to displace the shorter chains only if their bulk concentration is much higher. A measure of this crossover concentration is obtained by setting $\Delta F(N_1,\gamma) = \Delta F(N_2,\gamma)$. This gives the following relation at the crossover

$$\phi_{b1}/\phi_{b2} = \exp[\beta([\alpha N_1/N_2] - 1) - \ln(\sigma_2/\sigma_1)] \qquad (7)$$

where $\alpha = (\ln \phi_{b2}/\ln \phi_{b1})^{5/6}$ and $\beta = \gamma + \ln[\phi_{b2}/\sigma_2]$. Here the subscripts ϕ_{bi} and σ_i refer to bulk and surface

Table I. Molecular Characteristics of Polystyrenes[a]

sample	M_w	M_w/M_n	R_F (Å)
PS (unfunctionalized)	1.31×10^5	1.03	335
PS-X(26)	2.65×10^4	1.02	131
PS-X(375)	3.75×10^5	1.03	620

[a] Samples were synthesized as described in ref 15. Weight- and number-average molecular weights of the PS-X were determined by light scattering and size-exclusion chromatography. R_F is the root-mean-square end-to-end dimension of the chains in toluene, given by $R_F = 0.335M^{0.586}$ (see ref 15).

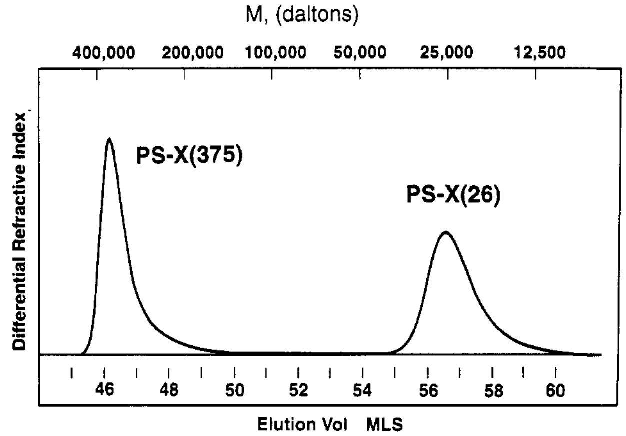

Figure 1. Size-exclusion chromatogram of the PS-X samples used in the present study. The chromatogram was obtained by injecting a solution containing a mixture of the two samples into a Waters 150C SEC equipped with a six-column Ultrastyragel set. The nominal porosity range covered was 10^2–10^6 Å.

concentrations of the species N_i. Since $\phi_{b2} < \phi_{b1}$, $\alpha > 1$, while the brush regime constraint imposes $\beta > 1$. Thus for any significant difference between the degrees of polymerization, we have

$$\phi_{b1}/\phi_{b2} \cong e^{\alpha\beta(N_1/N_2)} \qquad (\alpha,\beta > 1) \tag{8}$$

This is a sufficiently strong dependence that end-adsorbing polymers of significantly different molecular weights would hardly be expected to coexist on the surface. In practical systems the validity of these expressions is bounded by the requirement $\phi_b > \Phi$ as the low concentration limit and by $\phi_b < \phi^*$ on the high concentration side.

III. Experimental Section

The end-adsorbing polymers used in these studies were anionically-polymerized polystyrene (PS) chains terminated with the zwitterionic group $-N^+(CH_3)_2(CH_2)_3SO_3^-$ (-X). Their characteristics are given in Table I. These PS-X(M) samples were from the batches (with the same designation) used in the earlier surface force measurements and exchange studies.[15] Details of their synthesis are given in ref 15. In Figure 1 is shown the size-exclusion chromatogram of the two samples. Unfunctionalized polystyrene (designated PS, also described in Table I) was used as the control in a number of the experiments. All solvents employed were analytical or spectroscopic grade, used without further treatment. The mica used was grade 2 FS/GS, obtained from Unimica Corp. Analytical-grade sucrose was used to glue the cleaved mica sheets to the cylindrical lenses.

The experimental procedure was as follows. After cleaning, mounting, and measuring the air contact positions of the interferometric fringes, the surfaces were immersed in toluene and the force distance profiles $F(D)$ determined. The surfaces were then widely separated; some 5 mL of the toluene was withdrawn and an equal volume of polymer solution was added to establish the final concentration[26] (to within 10%) of the required polymer in the incubating bath. $F(D)$ was then measured again, generally after some 3 h. For the usual case in these experiments where the initial polymer added was the longer amphiphile PS-X(375), the shorter chains were then added using the same procedure. $F(D)$ was determined again after 2-3 h of incubation in the mixed solution and again after following overnight or longer immersion. On each introduction of polymer solution with a syringe, an aliquot of a few milliliters was repeatedly inserted and withdrawn to facilitate uniform distribution of the polymer in the bath volume. In addition, in some of the experiments the initial introduction of PS-X was preceded by adding a solution of unfunctionalized PS (Table I) to a concentration 10^{-4} g/mL in the toluene as a control: $F(D)$ profiles measured after incubating in this PS solution for some hours revealed the total absence of adsorption, as anticipated.

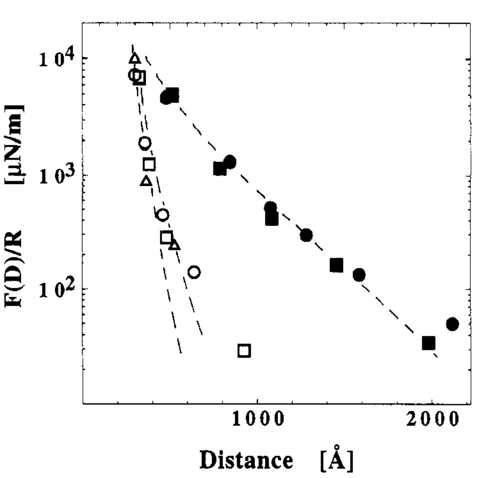

Figure 2. Force–distance $F(D)$ profiles between curved mica sheets (mean radius of curvature $R \sim 1$ cm) immersed in toluene. The data are normalized by R in the usual Derjaguin approximation, where $F(D)/2\pi R$ is the surface energy per unit area of flat parallel plates the same distance D apart: (■,●) following 3 h of incubation in a 10^{-4}-g/mL PS-X(375) solution; (○) following addition of PS-X(26) to a concentration of 10^{-4} g/mL and incubation for further 3.5 h; (△,□) following an additional 16.5 h of incubation. The broken curves are from force profiles in ref 15 for brushes formed from 10^{-4}-g/mL solutions of PS-X(26) and of PS-X(375) alone.

Experiments were carried out using two different versions of the mica surface force balance. $F(D)$ profiles from both were identical within the scatter. Results given are from two or more separate contact positions within one or more experiments.

IV. Results

Figure 2 shows the force–distance profile $F(D)$ for the interaction between mica surfaces bearing a brush of PS-X(375) (filled symbols). This profile was obtained following incubation of the surfaces to equilibrium in a 10^{-4}-g/mL solution of the amphiphile in toluene. The profile is closely similar to earlier ones obtained for this system,[15,20] as indicated by the broken lines derived from previous studies. On addition of PS-X(26) to the solution to a concentration 10^{-4} g/mL, and incubating for some hours, the force profile shifts markedly inward (Figure 1, empty symbols): the $F(D)$ profile is now close to that due to brushes formed by the shorter amphiphiles alone, reproducing the behavior previously reported.[20] The broken curves straddling the profile are from the earlier study,[20] in which the same monomer concentrations ($\phi_b \approx 10^{-4}$) of long and short end-functionalized chains were used.

The idea that brushes formed from a solution of longer end-functionalized chains should be replaced by shorter chains even from a much lower concentration of the latter was examined directly. A brush of PS-X(375) was allowed to form from a toluene solution at $\phi_b(375) = 10^{-4}$ and PS-X(26) was added to the solution to a 100-fold lower concentration, $\phi_b(26) \approx 10^{-6}$. The resulting behavior is shown in Figure 3. The filled symbols are for the PS-X(375) brush prior to addition of the shorter amphiphiles,

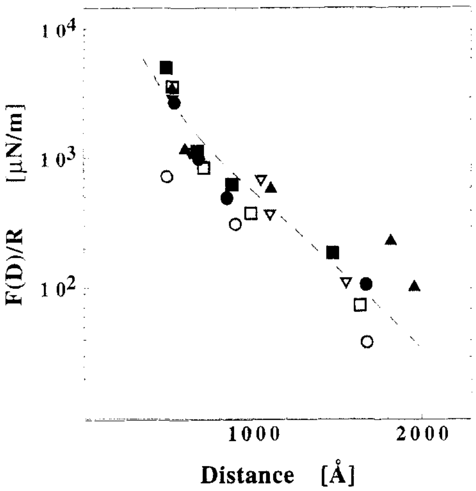

Figure 3. Force–distance profiles as in Figure 2: (■, ●,▲) following 3–4 h of incubation in a 10^{-4}-g/mL PS–X(375) solution; (□) following addition of PS–X(26) to a concentration of 10^{-6} g/mL and incubation for 3 h; (○) following incubation for an additional 3 h; (▽) following incubation for an additional 18 h. The broken curve is from Figure 2 for the brush formed from a pure 10^{-4}-g/mL PS–X(375) solution alone.

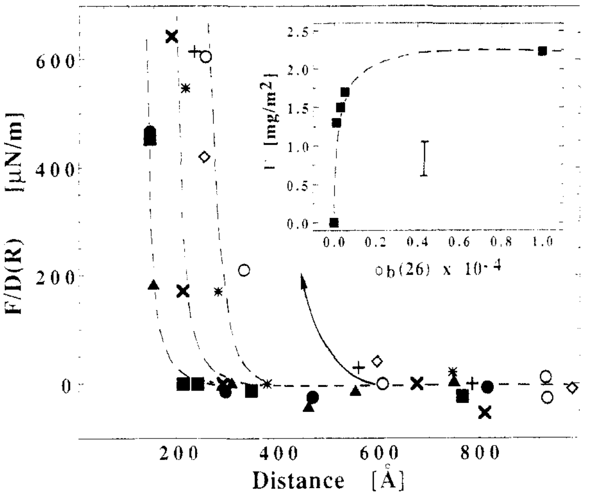

Figure 4. Force–distance profiles as in Figure 2: (■,●,▲) following 3–4 h of incubation in a 10^{-6}-g/mL PS–X(26) solution; (×,*,+) following an increase of the PS–X(26) concentration to 3×10^{-6} g/mL and a further 3–4 h of incubation; (○,◇) following an increase of the PS–X(26) concentration to 5×10^{-6} g/mL and a further 3–4 h of incubation. The inset shows the variation of the surface excess Γ(26) with volume fraction $\phi_b(26)$, estimated from the profiles as described in the text. The arrow indicates the onset of repulsion due to brushes formed from 10^{-4} g/mL PS–X(26) solution.[15,20]

while the empty symbols show the profiles after the PS–X(26) was added; varying the incubation time from 2 to 24 h led to no significant change in the force profiles. Clearly the presence of the shorter chains at a volume fraction $\phi_b(26) = 10^{-6}$ does not result in sensible displacement of the brush composed of the longer chains.

A different indication for the effect of the low bulk concentrations is provided by studies of brush formation from solutions of PS–X(26) alone. The force–distance profiles for interaction between initially bare mica surfaces that had been incubated in PS–X(26)/toluene solutions at concentrations in the range 1×10^{-6}–5×10^{-6} are shown in Figure 4. Also shown in Figure 4 schematically is the onset of repulsion due to PS–X(26) brushes formed from a 10^{-4}-g/mL solution of the amphiphile.[15,20] While the data are limited, the brush formed on the mica surfaces from the more dilute solutions is significantly shorter. We may estimate the surface excess Γ(26) of PS–X(26) from these low solution concentrations using the data of Figure 4 and the approach of ref 15. In this, the $F(D)$ profiles are used in the region of high compression to yield the local osmotic pressures due to the concentration of styrene monomers in the gap between the plates. By comparing with the osmotic pressure for a compressed brush whose adsorbance has been independently determined via refractive index measurements, the local monomer concentration and hence the specific surface excess of the PS–X chains is determined. Details of the procedure for the PS–X/mica/toluene system are given in ref 15. Applying this to the data of Figure 4, we find Γ(26) in the range 1.3–1.7 mg/m² (polymer excess/area of mica) for the range of bulk concentrations $\phi_b(26) = (1–5) \times 10^{-6}$. These data are shown in the inset to Figure 4 together with the value Γ(26) = 2.2 mg/m² at $\phi_b(26) = 10^{-4}$ deduced earlier and also from the force profile data of Figure 2.

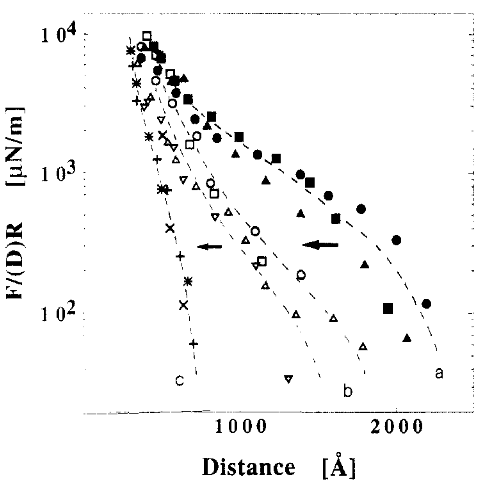

Figure 5. Force–distance profiles as in Figure 2: (■,●,▲) following 2–3 h of incubation in a 5×10^{-3}-g/mL PS–X(375) solution; (△,□) following addition of PS–X(26) to the solution to a concentration of 10^{-5} g/mL and incubation for a further 3 h; (○) following an additional 15 h of incubation; (▽) following an additional 6 h of incubation; (×) following further addition of PS–X(26) to the solution to a concentration 10^{-4} of g/mL and incubation for a further 2 h; (+) following incubation for an additional 4 h; (*) following incubation for an additional 14 h. The broken lines are a guide to the eye.

Within the limits of validity of the treatment of section II, the largest ratio of long/short chains in the mixed amphiphile solution is when the long chains are just under their overlap concentration $\phi^*(375)$, while the short chains are just above their crossover concentration Φ(26). The force profiles in Figure 5 show the results of an experiment where we attempt to attain this limiting ratio. Here solid symbols (Figure 5a) show the $F(D)$ profiles following incubation to equilibrium in a $\phi_b(375) = 5 \times 10^{-3}$ solution (compared with $\phi^*(375) \approx 10^{-2}$). The empty symbols (Figure 5b) are profiles following addition of the shorter amphiphiles to the apparatus to a concentration $\phi_b(26) = 10^{-5}$ (compared with $\Phi(26) \approx 5 \times 10^{-6}$) and incubation for 3–24 h; little additional change in the profiles is observed over this period. Finally, the crosses (Figure 5c) show the behavior following further addition of the shorter chains, to a final concentration $\phi_b(26) = 10^{-4}$, and incubation for an additional period 2–24 h; again, profiles show little significant further change within this time.

V. Discussion and Concluding Remarks

The data of Figure 2 reproduce our earlier observation[20] that, for equal monomer concentrations ($\phi_b = 10^{-4}$ for the data of Figure 2), the shorter end-functionalized chains PS–X(26) rapidly, and essentially completely, replace the longer amphiphiles PS–X(375) on the mica surface. This is consistent with the much lower free energy associated with unit area of the shorter brushes, as in eq 6. When the shorter chains are added to a 100-fold lower concentration, however, displacement of long by short chains no longer occurs. At the same time, from the relation of eq 8, one might expect such displacement whenever the ratio of short/long concentrations appreciably exceeds exp(−375/26) $\approx 10^{-6}$. The fact that it does not occur in Figure 3 even when this ratio is 10^{-2} deserves comment.

The reasons for this probably have to do with the fact, remarked on in section II, that, at sufficiently low bulk concentrations of short amphiphiles, it becomes unfavorable to remove the short chains from solution onto the surface. This is expected to occur when the value of $\ln(\phi_b/\sigma)$ approaches γ. This is approximately the same condition as having the bulk concentration of the amphiphile become comparable with Φ. For PS–X(26), we have $N \approx 250$, and for $\gamma = 6$, we find $\Phi(26) \approx 5 \times 10^{-6}$. The data of Figure 3, showing no sensible displacement of long amphiphiles by the shorter ones, were taken at $\phi_b(26) = 10^{-6} < \Phi$ and are therefore quite consistent with this expectation. The data of Figure 4, and in particular the inset which shows clearly the reduction in surface excess from its isotherm plateau value, support directly the idea that at concentrations lower than Φ there is a marked reduction in the tendency of the amphiphiles to adhere to the surface from solution.[27]

The profiles in Figure 5 are consistent with this conclusion. These show clearly that even when the concentration of shorter amphiphiles (10^{-5}) is some 500 times lower than that of the longer ones (5×10^{-3}), displacement of long by shorter chains *does* occur readily as long as the concentration of the latter is greater than the crossover concentration Φ. Since the profiles following this displacement (Figure 5b) are intermediate between those due to the pure PS–X(375) brushes and the PS–X(26) brushes, it is evident that the replacement of the longer amphiphiles is only partial. This is probably because the concentration of the shorter chains ($\phi_b(26) = 10^{-5}$) is quite close to its crossover value ($\Phi(26) \approx 5 \times 10^{-6}$), so that the limiting behavior of complete replacement suggested by the results of section II is not attained. The profiles of Figure 5 demonstrate for the first time directly how brushes consisting of chains of different lengths may be created by suitably controlling the concentration of the different amphiphiles in the solution. Finally, when the shorter chains are added to their final concentration (which at $\phi_b(26) = 10^{-4}$ is still 50 times lower than that of the longer chains), the displacement of the longer chains goes to completion, and the profiles (Figure 5c) revert to a form close to that due to the pure PS–X(26) brushes, as earlier observed.

It is of interest to estimate the surface-excess values corresponding to the force profiles of Figure 5 and to try and deduce from these a more quantitative picture of the mixed brush. Applying the procedure of the reference outlined above, we find that the adsorbance of PS–X(375) from the $\phi_b(375) = 5 \times 10^{-3}$ solution (Figure 5a) is $\Gamma(375) \approx 3.6 \pm 0.5$ mg/m^2, the adsorbance corresponding to the mixed-chain brush (Figure 5b) is $\Gamma_{\mathrm{mixed}} \approx 2.8 \pm 0.4$ mg/m^2, and the surface excess following the final displacement (Figure 5c) is $\Gamma_{5c} \approx 2.3 \pm 0.3$ mg/m^2. We note that the surface excess of the brush formed from the $\phi_b(375) = 5 \times 10^{-3}$ solution is some 10% greater than that formed from $\phi_b(375) = 10^{-4}$ solutions (see refs 15 and 20 and also Figure 2). The fact that a 50-fold increase in the amphiphile concentration results in this relatively small increase indicates that already at $\phi_b = 10^{-4}$ the adsorbance isotherm is in the plateau regime, as concluded also for the shorter chains.[27] In the mixed brush, attachment of the shorter end-functionalized chains has taken place on the mica surface, displacing some of the longer ones. To proceed, we assume (a) that chains are randomly attached on the surface and (b) that the shorter chains in the mixed brush have little effect on its overall thickness, which is then determined by the remaining long chains. This is a reasonable assumption in view of the disparity in chain lengths. Equation 1 relates the interanchor spacing s to the brush height as $s \propto h^{-3/2}$: using this relation we may estimate the value of the interanchor spacing $s_{\mathrm{mixed}}(375)$ for PS–X(375) in the mixed brush. This is done by comparing its height with the height of the pure PS–X(375) brush, for which s is known (via the surface excess), giving $s_{\mathrm{mixed}}(375) \approx 220 \pm 30$ Å. This value is much less than the swollen coil size $R_F(375) = 575$ Å (Table I), showing that the chains are considerably overlapped and that use of eq 1 is indeed self-consistent. The value of $s_{\mathrm{mixed}}(375)$ corresponds to an adsorbance of PS–X(375) in the mixed brush $\Gamma_{\mathrm{mixed}}(375) = 1.2 \pm 0.2$ mg/m^2. Thus the surface excess of the *shorter* chains is given by $\Gamma_{\mathrm{mixed}}(26) = \Gamma_{\mathrm{mixed}} - \Gamma_{\mathrm{mixed}}(375) = 1.6 \pm 0.3$ mg/m^2. The corresponding interanchor spacing of the short chains is $s_{\mathrm{mixed}}(26) \approx 52 \pm 5$ Å, significantly less than $R_F = 120$ Å for these polymers, showing that they are also in the overlap regime in the mixed brush.

The picture that emerges from the profiles in Figure 5 then is as follows. A brush of the longer chains forms from the concentrated (5×10^{-3} g/mL) PS–X(375) solution; on introducing the shorter amphiphiles to a low (10^{-5} g/mL) concentration, these penetrate the long-chain brush to attach to the surface. In this process some $^2/_3$ of the long chains in the original brush are displaced and go back into solution. The remaining long chains in the mixed brush are spaced on average some 220 Å apart on the mica and stretch some 800 Å normal to each surface. Interspersed between them with a mean spacing of some 50 Å are the shorter surface-attached amphiphiles. When the concentration of short chains in the solution is subsequently increased 10-fold, most of the remaining longer chains on the surface are displaced, and the resulting brush closely resembles one formed from an equivalent solution of PS–X(26) alone. This picture, illustrated schematically in Figure 6, and the results of Figures 3 and 4, are fully consistent with the discussion in section II, showing the importance of the crossover concentration Φ as a criterion for surface coverage and surface exchange.

A number of remarks are in order. The results of Figure 5 show that a solution of long amphiphiles containing as little as 1 part in 500 of shorter end-functionalized polymers can readily lead to brushes that are largely composed of the shorter chains. This has clear implications for fractionation and separation of amphiphiles from solutions containing mixtures of chains of different lengths. An interesting corollary concerns the polydispersity of the PS–X samples used in this and other studies, as derived from the molecular weight distribution in the size-exclusion chromatogram (SEC; Figure 1). The SEC distribution appears to include a substantial percentage of molecular weights that are much lower than the peak molecular weights M.[28] At the same time, the brushes formed from single-component PS–X(M) solutions both in this and in earlier studies are characteristic of the M values in accord with eq 1, which assumes a single-valued M. While we have not carried out a quantitative analysis of the precise brush structure expected from a polydispersed solution (such an analysis has very recently been done by: Dan,

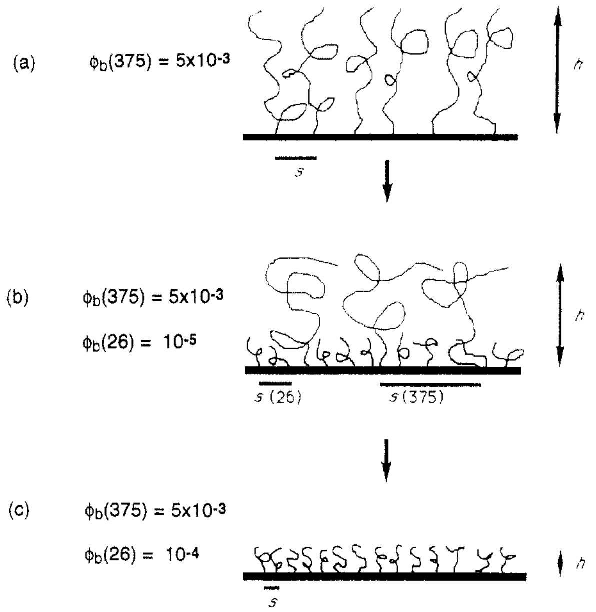

Figure 6. Schematic illustration of the progressive exchange process revealed by the profiles of Figure 5 and their analysis as described in the text. (a) Following incubation in a 5×10^{-3}-g/mL solution of PS–X(375); $s \approx 130$ Å, $h \approx 1250$ Å. (b) Following addition of PS–X(26) to a concentration of 10^{-5} g/mL; $s(26) \approx 52$ Å, $s(375) \approx 220$ Å, $h \approx 800$ Å. (c) Following a further increase of the PS–X(26) concentration to 10^{-4} g/mL; $s = 45$ Å, $h \approx 300$ Å.

N., to be published), the results of the present study—which show how readily long-by-short replacement occurs—strongly suggest that the amount of chains shorter than *M* in the PS–X(M) samples is in practice likely to be much smaller than is indicated in Figure 1.

In all cases studied of the long-chain-by-short-chain exchange, the force–distance profiles came close to their limiting already within 2–3 h of adding the amphiphiles; longer waiting times did not change the profiles significantly. This time is "rapid" in the sense that it is comparable with the construction time of brushes on bare mica from single-component PS–X solutions in similar conditions, as already noted in previous investigations.[15,18,20] In particular, the replacement time was rapid both for complete and for partial replacement and also when a partially replaced brush (Figure 5b) underwent complete replacement (Figure 5c). This suggests that "tailoring" of self-assembling brushes by judicious choice of the relative concentrations of different lengths of end-functionalized chains in solution should be readily feasible. Another implication of the rapid kinetics of the equilibration process is that, in studies of brush formation from solutions containing different lengths of end-functionalized chains, it is important to take into account the relative chain concentrations and not only their lengths. While these remarks apply for the particular set of amphiphiles studied here, for which the end-functionalization consists of a single group with a sticking energy of order (5–10)-k_BT, this value is typical for many of the other brush-forming amphiphiles (e.g., diblock copolymers) studied to date.[29,30] Finally, although we did not vary the value of this sticking energy (i.e., γ) in our experiments, it is clear from the analysis of section II that γ must provide a complementary parameter (in addition to N and ϕ_b) in controlling the characteristics of brushes formed from multicomponent solutions.

Acknowledgment. We thank the Ministry of Science, Israel, the U.S. Israel Binational Science Foundation, and the Minerva Foundation for partial support of this work and Dr. Nily Dan for useful discussions.

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