Free-Standing Black Films of Polymers: A Model of Charged Brushes in Interaction

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Free-standing black films drawn from a diblock copolymer aqueous solution were studied by x-ray reflectivity. Because of the hydrophilic part of the copolymer which is a highly charged polyelectrolyte (NaPSS), such films behave as two opposing charged brushes. Above a determined threshold the thickness of the double brush decreases slowly as electrolyte is added. These results are in good agreement with recent mean-field theories.

The understanding of interactions between two charged layers of end-grafted polymers [1] is important for the control of colloidal interactions in polar solvents. The use of charged macromolecules modifies the force balance between the two surfaces through a combination of electrostatic and entropic interactions. In particular, the disjoining pressure between the grafted surfaces should be much less sensitive to Debye screening by the addition of electrolyte than with simply charged surfaces. A great number of theoretical papers deal with the interactions between neutral brushes [2–4], but only a few recent papers are devoted to polyelectrolyte brush theory [5] and interactions between two polyelectrolyte brushes [6,7]. However, Pincus [7] has recently pointed out the reduced sensitivity to added electrolyte of the interactions between two brushes, a result which could be of practical interest. A few force machine experiments (force measurements between polymers adsorbed on mica), coupled with adsorption studies on various surfaces, have been carried out [1,8,9]. Neutron experiments on polyelectrolytes end-grafted on porous silica are also in progress [10]. We present here a new experimental configuration which is able to test the situation depicted above. Diblock copolyelectrolytes in aqueous solution can behave as surfactants, leading to the possibility of free-standing films. In the following, we discuss why such films are made of end-grafted chains and we compare x-ray reflectivity measurements to recent models describing the action of electrolyte on charged brushes.

Free amphiphilic films are simple and well-defined systems with two opposite amphiphilic layers surrounding a water layer at the center (Fig. 1). Such films are drawn from a solution by means of a plane vertical frame. The black films are the final stages of the thinning due to the draining of water [11]. The Newton black film (NBF) is the thinnest form of black films [12], and x-ray reflectivity experiments have recently given a very accurate structural picture of the NBF made of SDS (sodium dodecyl sulphate) and NaCl [13]. The NBF is a bilayer of soap without any liquid water in it except a hydration layer of the polar heads. The same generic features

have been observed with highly different surfactants. It thus appears that a free black film probed by a reflectivity experiment is a model system for the study of interactions within an amphiphilic bilayer. The copolymer used in this study is a diblock copolyelectrolyte of poly(tert-butylstyrene)/sodium polystyrene sulfonate (PtBS/NaPSS) with an $M_W = 2000$ molecular weight for the PtBS block and $M_W = 45000$ molecular weight for the PSS block, synthesized by anionic polymerization [14] with a sulfonation level of PSS of about 90%. The total polydispersity is small ($M_W/M_N = 1.05$) and is estimated by combined chromatography and NMR data. The results are virtually identical to that anticipated based upon the composition of reactants. The hydrophobic part (PtBS) is small (13 monomers) in comparison with the hydrophilic part PSS (211 monomers) in order to solubilize this compound in water solution where it self-associates in the form of micelles [15]. All experiments have been carried out at a constant polymer concentration (3 g/l) above the critical micellar concentration. This ensures a constant surface concentration even when electrolyte is added as checked by surface tension measurements [15]. The
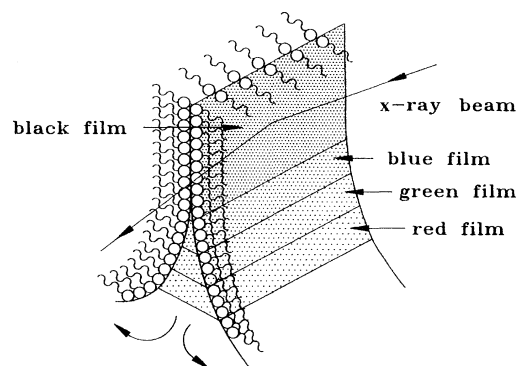

FIG. 1. Typical aspect of a free suspended film of a surfactant solution during its draining. The x-ray beam probes the sample where it is homogeneous and of thickness smaller than the wavelength of visible light (black film). Below this zone, thicker colored zones can be observed.

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water used in this study is from a milli-Q system and its conductivity is less than 18 MΩ/cm.

All reflectivity experiments on the free films have been performed using a four-circle diffractometer for vertical surfaces which has been described in detail elsewhere [16]. A conventional, fine-focus copper tube is used as an x-ray source. The monochromator is a Si(111) crystal which selects the Cu $K\alpha_1$ line ($\lambda = 1.5405$ Å). A low divergence (≈ 0.15 mrad) of the beam is obtained by means of a small vertical slit (100 μm) placed at a distance of 40 cm from the source. A perpendicular horizontal slit (600 μm) is used to limit the height of the illuminated area on the film. The reflected beam is detected by a scintillation counter placed behind an analysis slit (250 μm) at a distance 40 cm from the center of the diffractometer. The incident and reflected beams pass through vacuum flight paths. A new experimental procedure has been used which consists of drawing the films using a flat rectangular metallic frame with a bevelled edge (Fig. 2). The frame is cleaned before each experiment with two dilute acid solutions (10% nitric acid + 1.2% hydrofluoric acid for etching the frame and 10% nitric acid for passivation) and then rinsed with distilled water. The film is drawn in an airtight cell with two sealed Kapton windows in order to maintain a saturated vapor atmosphere. At last the temperature is regulated (± 0.1 °C) around room temperature. Under these conditions we obtain free films stable during hours or days. Another delicate and important point in order to obtain accurate reflectivity measurements is the alignment of the free film with respect to the beam. The film surface must be parallel to and centered within the beam sheet. In order to easily position the film one must take into account that the film equilibrates behind the external plane of the frame and parallel to it. In a first step the frame is aligned in the beam before any film is drawn. In a second step, the film is drawn on the frame and the reflectivity

signal is recovered by moving the frame forward by a small distance (≈ 100 μm). Moreover, the width of the frame is sufficiently large to allow reflectivity measurements at extreme grazing incidence, and the minimum incident angle (10 mrad) is only limited by the size of the lateral meniscus. The maximum illuminated area of the film is about 0.5 cm^2. In the following we report the behavior of black films of polymer as a function of added salt concentration (NaCl from Fluka, purity better than 99.5%).

Two typical reflectivity profiles exhibiting many distinct interference fringes (Kiessig fringes) are reported in Fig. 3. The analysis of the reflectivity profiles can be performed rigorously through the use of an optical formalism, valid at all angles [17]. This method takes into account the multiple reflections and the interfacial roughness [18]. At all salt concentrations, a model of a single homogeneous slab of definite thickness, roughness, and electron density is sufficient to give a reasonable account of the experimental data (Fig. 3). This demonstrates that no appreciable density gradient exists within the film. In particular, the hydrophobic zone of the PtBS groups is not detectable. For all salt concentrations, roughness varies from 1.5 to 2 Å $\pm$ 0.5 Å, and the electron density is expressed through the refractive index $1 - \delta$ where δ varies from 2.0 to 3.7 $\pm$ 0.2 $\times$ 10^{-6}. No systematic variation is observed with the salt concentration. However, several features of the fits, such as a lower contrast at large angles, a small deviation in the spacing, or a low value of the density, suggest that inhomogeneities of thickness could be present along the vertical of the film. These inhomogeneities have been estimated for each data set and never exceed 50 Å over 600 μm of height. Error bars on the thickness have been calculated from these estimations.
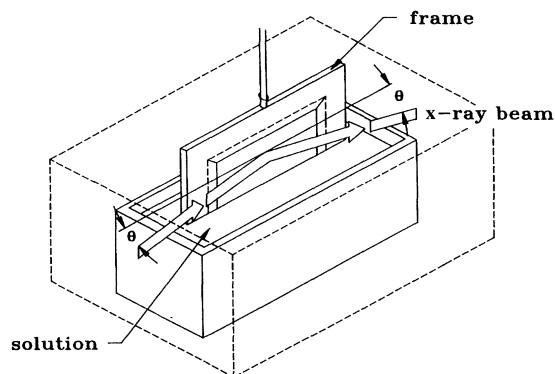

FIG. 2. Schematic of the setup installed at the center of the diffractometer. A metallic frame is immersed in the polymer solution and is then drawn up to form the film suspended on the central part of the frame. The film is then illuminated by the x-ray beam.
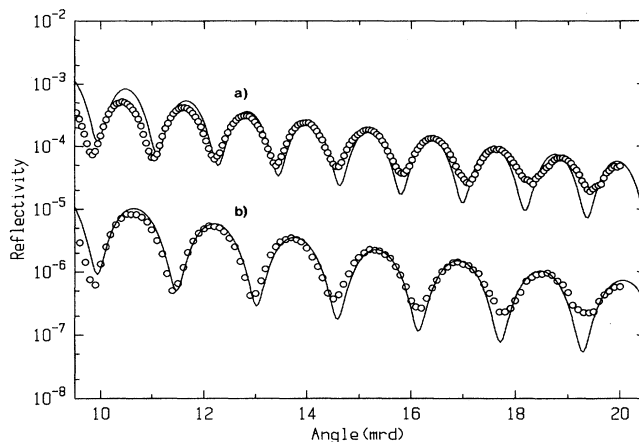

FIG. 3. Two examples of Kiessig fringes; (a) $n_S = 0.2M$ and (b) $n_S = 0.5M$, where for clarity the reflectivity has been multiplied by 10^{-2} in case (b). For each curve, the best simulation is drawn by a continuous line. Parameters of the fits are (a) $2L^* = 642$ Å, $\delta = 3.3 \times 10^{-6}$, $\sigma = 1.5$ Å and (b) $2L^* = 484$ Å, $\delta = 3.7 \times 10^{-6}$, $\sigma = 2.0$ Å.

We have reported in Fig. 4 the thickness of the film as a function of the salt concentration. Two distinct regimes are evidenced: at low electrolyte concentration $n_S < n_0$ where $n_0 \approx 0.1M$, the thickness $2L^*$ is nearly constant and for higher concentration $n_S > n_0$ the thickness is a decreasing function of the added salt.

The existence of the free film implies a lowering of the surface tension connected with some organization of the chains at the surface. The adsorption of the charged chains of NaPSS is ruled out since polyelectrolytes hardly adsorb on a neutral surface [4] in the absence of salt. The other situation is a structure of NaPSS chains which are terminally attached to the air by the hydrophobic moiety. In the following we will then compare our results to the simplest relevant model: two end-grafted brushes in contact (Fig. 5). This model has been recently studied [7,19] and only the electrostatic interactions are considered here in the framework of a mean-field approach. The equilibrium thickness L of the charged blocks is obtained by balancing the osmotic pressure of the counterions (neutralizing the brushes) against the entropic polymer elasticity which tends to contract the chains. The typical distance between chains, d, is assumed to be fixed. This is a nontrivial assumption with respect to the experiment. We first consider the situation in the absence of added salt where the Na^+ counterions are only due to the dissociation of the polyelectrolyte. Defining ξ as the scale over which a test charge is neutralized within the brush, a force balance leads to $L \approx f^{1/2} Na$ when $\xi \ll L$. Throughout this Letter the symbol "$\approx$" means "equal within a numerical factor of order 1." Here f is the fraction of charged monomers and $a = 2.5$ Å [4] is the monomer dimension. The NaPSS is fully dissociated in water, but, if we assume that the model of Manning condensation holds [20], there is only one monomer charged over a Bjerrum length scale (7 Å for water, $1 = e^2/k_BT$ is the Bjerrum length) which gives $f \approx \frac{1}{3}$. When a concentration n_S of electrolyte associ-
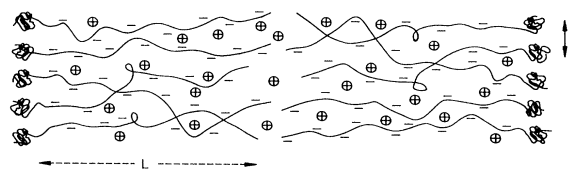
FIG. 5. Model of the diblock film where the collapsed PtBS blocks are on the sides of the scheme and the PSS chains extend over a distance $2L$ in the middle. Each chain is separated by a typical distance d. Counterions ($\oplus$) are represented within and in between the chains.

ated with a Debye length κ_S^{-1} is added to the solution, two regimes can occur. If $\kappa_S \xi \leq 1$ the salt contribution is weak and the blocks keep their extension L. If $\kappa_S \xi \geq 1$, the quantity of counterions in the film is modified by the added electrolyte and the balance of forces yields [7] $L \approx (fa/d)^{2/3}(1/4n_S)^{1/3}N$.

Our results agree well with the above scheme (Fig. 4). According to the model, the crossover concentration $n_0 \approx 0.1M$ corresponds to $\kappa_S \xi \approx 1$. One finds $\xi \approx 14$ Å, a value which fulfills $\xi \ll L$. It is then justified to check the equality $L \approx f^{1/2} Na$ in the regime $n_S < n_0$. Subtracting the extension (7 Å) of the monomers of PtBS which are in a collapsed molten state, we find $L = 333 \pm 3$ Å. This is in good agreement with the scaling prediction which gives $L = 304$ Å since $L \approx f^{1/2} Na$ holds only to within a numerical factor of order 1. At higher salt concentrations the slope of the curve reported in Fig. 4 in a log-log scale is -0.31 ± 0.06; this value is in good agreement with that expected by Pincus ($-\frac{1}{3}$) when one takes into account the only four data points which can be reasonably chosen as being in the asymptotic regime. The good agreement with the model is not sufficient to fully elucidate the structure. In particular, more work is needed in order to check if the spacing d between polymer chains stays constant as suggested by the results. Other reorganizations of the structure can also be imagined and compared to the results.

Comparable behaviors have been studied by various techniques in similar or slightly different systems. Charged star polymers have been shown to contract very weakly with added salt [21], but large constraints probably originate from the geometry. Adsorbed layers and micelles made of the same diblock PtBS/NaPSS also shrink with added salt. Preliminary results are compatible with a $\frac{1}{3}$ power law for the adsorption situation [8,9] and with a smaller exponent for micelles [15]. Interestingly, scaling theories [22] give a different answer $L \approx n_S^{-2/3}$ in the case of end-grafted brushes. However, this discrepancy can originate from the generic difficulty that scaling theories have in describing polyelectrolytes.

In conclusion, our experimental results are in good agreement with recent theoretical predictions describing two opposite polyelectrolytic brushes. The electrolyte plays a central role in determining the brush structure only
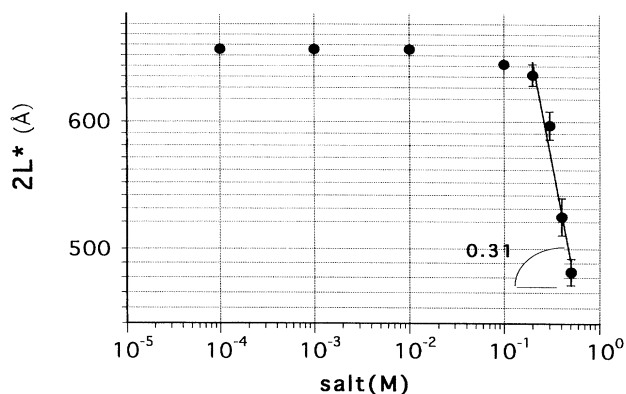

FIG. 4. Evolution of the length $2L^*$ versus the quantity of added salt in a log-log plot. The straight line is the best slope (0.31) passing through the last four data points.

when its concentration is sufficiently large that the corresponding Debye length κ_S^{-1} becomes comparable to the neutralization length ξ. We are able to demonstrate the salt concentration of crossover between the two regimes, which is important for the elucidation of colloidal stabilization phenomena. We believe that this way of probing polymeric interfaces by x-ray reflectivity on free films can be applied to many different systems. In particular, more complicated bilayers such as mixed systems of polymers and surfactants can be studied.

[1] S. S. Patel and M. Tirrell, Annu. Rev. Phys. Chem. **40**, 597–635 (1989).

[2] S. Alexander, J. Phys. (Paris) **38**, 983 (1977).

[3] P. G. de Gennes, Macromolecules **15**, 492–500 (1982).

[4] G. J. Fleer et al., *Polymers at Interfaces* (Chapman and Hall, London, 1993).

[5] S. Misra, S. Varanasi, and P. P. Varanasi, Macromolecules **22**, 4173 (1989).

[6] S. J. Miklavic and S. Marcelja, J. Phys. Chem. **92**, 6718–6722 (1988).

[7] P. Pincus, Macromolecules **24**, 2912–2919 (1991).

[8] H. Watanabe, S. S. Patel, J. F. Argillier, E. E. Parsonage, J. Mays, N. Dan-Brandon, and M. Tirrell, Mater. Res. Soc. Symp. Proc. **249**, 255 (1992).

[9] C. Amiel, M. Sikka, J. W. Schneider, J. W. Mays, and M. Tirrell (to be published).

[10] P. Auroy and L. Auvray (private communication).

[11] I. Newton, *Optiks Book II* (Smith and Watford, London, 1704), Pt. I.

[12] T. Kolarov, R. Cohen, and D. Exerowa, Colloids Surfaces **42**, 49 (1989), and references therein.

[13] O. Belorgey and J. J. Benattar, Phys. Rev. Lett. **66**, 313 (1991).

[14] P. L. Valint and J. Bock, Macromolecules **21**, 175 (1988).

[15] P. Guenoun, J. Mays, H. T. Davis, and M. Tirrell (to be published).

[16] J. J. Benattar, L. Bosio, J. Daillant, and F. Rieutord, Analysis **17**, 34 (1989).

[17] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, London, 1984), 6th ed., pp. 51–60; F. Abelès, Ann. Phys. (Paris) **5**, 596 (1950).

[18] J. Penfold and R. K. Thomas, J. Phys. Condens. Matter **2**, 1369–1412 (1990).

[19] J. Wittmer and J. F. Joanny, Macromolecules **26**, 2691 (1993).

[20] G. S. Manning, J. Chem. Phys. **51**, 924 (1969).

[21] J. Mays, Polymer Commun. **31**, 170 (1990).

[22] N. Dan and M. Tirrell, Macromolecules **26**, 4310 (1993).