# **Disjoining Pressures and Ordering in Thin Liquid Films Containing Charged Diblock Copolymers Adsorbed at the Interfaces**

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We report force measurements in thin liquid films containing charged diblock copolymers (poly(tertbutylstyrene)-poly(styrenesulfonate)) adsorbed at the film surfaces. Although the film surfaces are likely to be covered by copolymer layers with a brush structure, the observed features, both film ordering and force ranges, cannot be explained within the framework of interacting or overlapping brushes. Under compression, the films show stratified structures with layers of constant thickness (~45 nm). These films share some similarities with surfactant films where free homopolyelectrolyte chains are confined, but they are far less sensitive to addition of salt. The changes observed when the polymer mass and concentration are varied can be attributed to viscosity variations. The strong asymmetry of the diblock copolymers used here, resulting in poor surface anchoring, is probably the reason for the above peculiar features.

#### **I. Introduction**

The behavior of polyelectrolyte solutions is less well understood than that of neutral polymer solutions. The long-range nature of the electrostatic interactions and the large number of degrees of freedom of the counterions pose serious problems when theoretical modeling is attempted. Recent theoretical progress<sup>1</sup> and development of numerical simulations<sup>2</sup> provide evidence for many different types of behavior, according to polymer and added electrolyte concentrations. The field is nowadays very active, due to numerous practical applications of these polymers (thickening agents and responsive gels, among others).<sup>3</sup> In particular, due to the large osmotic pressure created by the polymer counterions, polyelectrolyte gels have remarkable swelling properties (their volume can change by several orders of magnitude, a behavior used for instance in the disposable diaper industry).

Besides the studies in bulk, there are also studies of polyelectrolytes at interfaces  $^{\rm 4-5}$  and of their interaction with other structures (like for instance intercalation in surfactant lamellar phases<sup>6</sup>). Indeed, such polyelectrolyte

layers exist in many biological systems and govern important mechanical or transfer functions.<sup>7</sup> Also, polyelectrolytes are often added in surfactant formulations to improve foam stability, but the way they act or organize themselves in foam films is still not completely understood.8

Related to these interfacial issues, diblock copolymers, charged or not, have lately drawn much scientific interest. These polymers are made of two distinct hydrophilic and hydrophobic polymeric parts (for charged systems, the polyelectrolyte part is the hydrophilic one). Copolymers can self-assemble in solution and form many structures as surfactants.<sup>9</sup> It is possible to control their adsorption at interfaces and for instance obtain "brushes" in which the chains are almost completely elongated and normal to the surface. Once grafted onto colloidal particle surfaces, charged brushes are predicted to be highly efficient to stabilize the colloidal suspension, because they are thick and less sensitive to salt addition than classical charged surfaces. P. Pincus<sup>10</sup> showed that this is due to the large number of counterions trapped in a polyelectrolyte brush and that the disjoining pressure (force per unit area between two surfaces) is high and affected by salt only at high salinities. These charged hairy particles are therefore interesting for practical applications. Similarly, the foaming and emulsification properties of copolymer solutions are expected to be unusual (thin films stable up to high disjoining pressures).

The theoretical predictions on charged brushes were recently extended, and a large number of different new

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regimes were predicted.<sup>11</sup> Meanwhile, experiments on charged brushes remained scarce, mainly because these brushes are not so easy to build. It is indeed difficult to adsorb or graft these charged copolymers at surfaces because of the large electrostatic repulsion between the chains. Copolymers of poly(styrenesulfonate) (PSS) with hydrophobic anchors have been synthesized and adsorbed on mica surfaces, to determine the forces between approaching surfaces with a surface force apparatus (SFA).<sup>12</sup> Copolymer adsorption was done in the presence of excess salt, to screen the repulsions between adjacent chains; after rinsing with pure water, an adsorbed layer was formed. In a later experiment, neutral polystyrene was grafted onto porous silica, and sulfonation was performed afterward.<sup>13</sup> Somewhat higher grafting densities were obtained in this way. It was thus shown that the layers shrink upon addition of salt above some threshold in concentration but never collapse even at very high ionic strength. Besides brushes adsorbed on solid surfaces, experiments have also been recently performed directly on liquid interfaces. Note that using Langmuir-Blodgett transfer techniques, it has been possible to study the same annealed polyelectrolyte brushes (polystyrene-poly-(acrylic acid)) both on liquid interfaces and on Si wafers, at different grafting densities.<sup>14</sup> Studies on single brushes deposited at the surface of water have confirmed the results of modest brush shrinkage at high salinities, together with the predictions for the dependence of the polymer layer thickness with  $\Sigma$ , the area per polymer molecule at the surface: *h* is independent of  $\Sigma$  in pure water, and  $h \sim \Sigma^{-1/3}$  in the presence of salt.<sup>15</sup> The transition between the two regimes occurs when  $c_s$  approaches the ionic concentration in the brush. Experiments on freestanding films formed from copolymer solutions gave similar results, when varying  $c_{\rm s}$ .<sup>16</sup> Also, in relation to these structure studies at liquid interfaces, a buckling instability has lately been observed in charged diblock copolymer films.17

With the exception of ref 12, in the above experiments the force between surfaces was not measured. Very recently, force measurements have been performed on thin liquid film containing poly(ethylethylene)—poly(styrene sulfonic acid) charged diblock copolymers (respectively, 144 and 136 monomers for each part) with the thin film balance technique.<sup>18</sup> The measured forces are screened electrostatic forces as for the more classical surfactant films, and the films rupture before brushes come into

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In the present paper, we report experiments performed with a thin film balance as in ref 18 and charged diblock copolymers of different chain lengths. Their lengths are larger than in ref 18, and the copolymers are more asymmetric. The film structures and their variations with copolymer concentration or added salt differ from the ones seen in ref 18. We will discuss the film behavior within the framework of overlapping or nonoverlapping brushes and show that none of them apply here. One has to go beyond that picture to explain, at least partially, the observed features.

#### **II. Experimental Setup and Materials**

Experiments were performed with the "thin film balance method". In this method, a horizontal liquid film is formed on a hole drilled in a porous glass disk, enclosed into a pressurecontrolled box, with the help of a precise screw-driven syringe pump (pressure controlled within  $\pm 3$  Pa); the gas pressure is measured with a pressure sensor (from MKS). The liquid solution is placed in a container below the film holder inside the box, to maintain the humidity level. The temperature is also held constant with water circulation inside the double wall of the box. The evolution of the film thickness *h* with applied pressure is monitored with video interferometry (with an accuracy of  $\pm 2$  nm). Different film holders were built and used for the different copolymer solutions, to get reproducible results and avoid any mixing artifacts. Usually, after a transient drainage period, the film thickness comes to an equilibrium when the applied pressure  $\Pi$  is balanced by the repulsion between film surfaces.<sup>1</sup>

The samples used are aqueous solutions of four copolymers made of sodium poly(styrenesulfonate) units and poly(tertbutylstyrene) (PtBS) units. Copolymers A, B, C, and D have (150-10), (211-13), (404-25), and (757-27) PSS-PtBS units, respectively. In the following, we call N the number of PSS monomers. The polydispersity is low  $(M_w/M_n$  is of the order of 1.04,  $M_{\rm w}$  being the weight-average and  $M_{\rm n}$  the number-average molecular weights). The synthesis is described elsewhere.<sup>20</sup> For the copolymers B, C, and D, the sulfonation degree of the polyelectrolyte part is close to 90%, while it is only 50% for copolymer A. Due to the small size of the hydrophobic portion, the polymers are soluble in water and form micelles above a critical micellar concentration (cmc), which was measured of order  $10^{-6}\,\mathrm{wt}$  % for the (404–25) copolymer. The size of micelles does not depend on polymer concentration in the dilute regime.<sup>21</sup> Salts, sodium and calcium chloride, are from Prolabo.

In our experiments, before applying a first pressure step, a large drop of the solution is held in the hole for at least  $t_0 = 30$  min, allowing completion of the adsorption of the copolymers at each interface. It appears that  $t_0$  is typically the time needed for obtaining reproducible results: after such a delay, the film always behaves the same; before  $t_0$ , the film is less stable and can break very fast.

#### **III. Results**

**1. Disjoining Pressure Variations with Polymer Concentration.** We have measured the disjoining pressure isotherms at different concentrations for the films made with aqueous solutions of the four copolymers (Figure 1).

(a) Copolymers A and B. The behavior of samples A and B is similar with respect to the thickness range and concentration dependence (Figure 1a,b). They both show

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**Figure 1.** Disjoining pressures vs film thickness for different copolymer lengths and different concentrations: (a) sample A (N=150); (b) sample B (N=210); (c) sample C (N=410); (d) sample D (N=720).

the same thickness jump, say J1, at  $\Pi_0$  (disjoining pressure where the film is formed);  $\Delta h = h_{\text{form}} - h_{\text{eq}} \sim 48 \pm 3$  nm. Here,  $h_{\rm form}$  is the thickness at the film formation, and  $h_{\rm eq}$ is the first equilibrium and stable thickness reached after initial drainage and jumps. Note that these results are widely reproducible (provided that the glass frits are well cleaned) and that  $\Pi_0$  is the most fluctuating measurement  $(200 \pm 30 \text{ Pa})$ , depending on the size of the drop held initially in the hole. The thickness jump is seen both in the film center thickness variation and in the overall film image. Similar jumps are observed with films made from surfactant solutions containing micelles,  $\Delta h$  being in this case roughly equal to the mean distance between the micelles.<sup>22</sup> For the two copolymers, the minimum concentration to form a stable film is  $c_{\rm p} \sim 0.8$  g/L. At larger concentration  $c_{\rm p}$  and after the first jump, one observes a continuous decrease of thickness with increasing  $\Pi$ , roughly down to the same minimum  $h_{\min}$  (~40 ± 3 nm). At still higher concentration, a second thickness jump (J2) occurs at intermediate pressures, directly bringing the film down to  $h_{\min}$  and often inducing the rupture of the film. The pressure at which J2 occurs increases with  $c_{\rm p}$ , but  $h_{\rm min}$  remains roughly the same. We must emphasize that the jump J2 has peculiar properties: it is not seen in each experiment, and it is not a "complete" thickness transition. This means that, surprisingly, a circular domain of thickness  $h_{\min}$  can remain in apparent equilibrium in a thicker film (its radius does not increase with time as in the stratification process of films made with micellar solutions). Occasionally, the film can be further compressed with the two thicknesses coexisting

(b) Copolymers C and D. Copolymers C and D have different behaviors than copolymers A and B:  $h_{\text{form}}$  is larger and increases with N and concentration (Figure 1c,d). However, there are also jumps at  $\Pi_0$ ; a typical one is shown in Figure 2, where one can see thinner domains appearing in the film, expanding, and finally covering the whole film. Lowering  $c_p$  makes the films initially thinner and the jumps shorter. Strikingly, at low  $c_p$  one recovers a behavior close to that of copolymers A and B, with a jump of the same amplitude as J1 at  $\Pi_0$ . Another jump with the same features as J2 can also be seen. In the following, we call this typical disjoining pressure curve (with J1 and J2) the "minimal" curve. The range of copolymer concentration which can be studied depends on *N*. This is related to the solution viscosities which for a given concentration  $c_p$  are higher for larger *N*. For this reason, we could not form films of copolymer D for  $c_p = 4$  g/L, although the films are stable for smaller  $c_p$  than those for other polymers.

Figure 1 shows that the range of pressures observed is similar for copolymers A and C and for copolymers B and D. This grouping is in contrast with that for film structure and thickness: similar for copolymers A and B and for copolymers C and D. Therefore, no obvious correlation can be made between  $\Pi$  and *N*.

**2. Salt Effects.** We have also studied the effect of salt addition. Figure 3a–c shows the disjoining pressure curves for solutions of 4 g/L of copolymer B with different amounts of added NaCl and CaCl<sub>2</sub>. The basic features of the minimal curve are still observed. The initial jump at  $\Pi_0$  is always observed, but its size  $\Delta h$  and the resulting equilibrium thickness  $h_{eq}$  vary with the salt concentration  $c_s$  (Figure 3c). In Figure 3a, the disjoining pressure curves after the jump J1 are shown: the larger  $c_s$ , the thinner the film at  $\Pi_0$  and the steeper the slope. Note that, surprisingly, at high  $\Pi$  it is the film with the largest  $c_s$  which is thicker. We want to emphasize that these salt effects occur at already relatively high concentration ( $c_s > 0.12$  M).

As can be seen in Figure 4a–c, salt effects are observed at lower  $c_s$  for copolymer C than for copolymer B. There are still some jumps at  $\Pi_0$ , but again the  $\Delta h$  and  $h_{eq}$  are salt dependent (Figure 4b,c). Nevertheless, one can see that for the C copolymer,  $\Delta h$  and  $h_{eq}$  have roughly only two possible values (~45 ± 3 and ~92 ± 3 nm) whatever  $c_s$  and  $c_p$ . A striking feature, shown in Figure 4c, is that the values found for  $\Delta h$  and  $h_{eq}$  when varying  $c_p$  without adding salt are quite similar. Also, as when lowering  $c_p$ , a minimal type behavior is recovered at sufficiently high salt concentrations. It turns out that for copolymers C and D increasing  $c_s$  or decreasing  $c_p$  acts initially in the same way.

**3. Dynamics.** For all the copolymers, when the pressure is changed, the equilibrium thickness is reached very fast, in a few seconds (Figure 5). When the pressure is brought back to its initial value, the film response is again very fast: the thickness returns to its initial value, meaning that the process is fully reversible. This is in contrast with earlier measurements of surface forces between mica plates with the same polymers.<sup>12</sup> This rapid equilibration kinetics is also observed when salt is added. Of course, with fluid surfaces, the polymer is free to move. However, thin film balance studies of films formed from polystyrene sulfonate homopolymer solutions of comparable molecular weights (stabilized by small amounts of surfactants) showed that the equilibrium state is reached much more slowly, a few tens of minutes instead of less than 1 min here.<sup>8,23</sup>

**4. Main Parameters of Analysis.** From the above observations, it turns out that  $\Delta h$  and  $h_{eq}$  are the parameters which are changing the most significantly with  $c_p$  and  $c_s$ . They are plotted in Figure 6 for copolymer D.

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**Figure 2.** Typical images of the film during a thickness jump,  $\Delta h = 88$  nm (N = 410,  $c_p = 4$  g/L). The film is seen from above, and its diameter is around 1 mm.

As for the other polymers, only a few well-defined values are observed, some of them being equal to those seen for copolymer C. Consequently, we have summarized in Figure 7 the whole set of observed thicknesses while changing  $c_p$  or  $c_s$  for all the copolymers. We must make two remarks: (1) For clarity of the figure, the behaviors at high salinities ( $c_s$  more than 0.15 M) are not shown (they correspond to the changes in the minimal curve seen in Figure 3c). (2) Obviously, for each *N*, the whole set of thicknesses shown in Figure 7 is not always detected; our purpose here is to gather all these h values in a single plot to see how they depend on N (dependence with  $c_p$  or  $c_s$  is shown in the previous figures). We have also included measurements made with the same copolymers (PtBS-PSS, and with other *N*) on vertical standing films.<sup>24</sup> In the vertical films, the equilibrium thickness was measured by light scattering, and the hydrostatic pressure was on the order of a few hundred pascals (a few centimeters of water). One can see that these different measurements are in agreement with ours and that finally all the points fall on a set of horizontal dashed lines. All these h values are multiples of  $\sim$ 45 nm (even  $h_{\min}$  falls in that frame). The minimal behavior is represented by the two jumps J1 and J2 and by the dashed region where the pressure increases. Note that the maximum observed thickness is linear in N(and it extrapolates to the border of the dashed region when N = 0).

### **IV. Discussion**

1. Thicknesses. All the measurements described above are not easy to rationalize. Because earlier measurements done with vertical films made with solutions of the same

polymers seemed to be consistent with a double-brush structure,<sup>16,24</sup> the first obvious framework for analyzing our results is that of the interaction of brushes adsorbed on each interface. Before compressing the film, we have indeed allowed enough time for the adsorption of the brushes at the surfaces (30' min, see section III.3).

One of the features expected in that case is a linear variation of thickness with N when the brushes come into contact. This is somewhat in agreement with our data (Figure 7), at least for the longer chains at the highest concentrations. Let us estimate the thickness corresponding to a double brush,  $h_{\rm B} = 2 a N A^{1/2}$ . Considering the picture of Manning condensation,  $^{25}$  f is an effective degree of charge of the chain:  $f = a/l_{\rm B}$ , where *a* is the average distance between monomers and  $I_{\rm B}$  is the Bjerrum length; here, *a* = 2.5 Å and  $l_{\rm B}$  = 7 Å, so then  $f \sim 0.3$ . This leads to  $h_{\rm B}$  = 43, 60, 116, and 207 nm for copolymers A, B, C, and D, respectively. To compare to the calculated values, one can also report scattering measurements on micellar solutions of these same copolymers, from which the corona radius R' of the micelles can be extracted (2R' thus corresponds to the double-brush thickness).<sup>26</sup> One finds that 2R' =82.5, 132, and 220 nm for copolymers B, C, and D, respectively. These two sets of thicknesses are close, providing us with a reasonable estimation of the doublebrush thickness. It turns out that our measurements fall in the same range. Another point in relative agreement with that double-brush picture is the salt effects seen for

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**Figure 3.** Salt effects on thin films of copolymer B. (a)  $\Pi(h)$  curves at various NaCl concentrations. Dashed lines correspond to power-law fits. (b) Effects of the valency of salt cations. Exponential fits are represented by dashed lines. (c) Initial jump size  $\Delta h$  and resulting equilibrium thickness  $h_{eq}$  vs NaCl concentration.

copolymer B: salt acts on the structure only at high concentration, and the dependence is not too different from the expected power law with a  $^{-1}$ <sub>3</sub> exponent (Figure 3c).<sup>10</sup> We do not observe any concentration dependence for copolymers A and B, a feature also consistent with the charged double-brush picture. Thus, at first sight, the behavior of the films is consistent with that of a double brush.

However, most of the other observed features cannot be interpreted within the brush framework. We observe for instance strong concentration effects for copolymers C and D, and at low  $c_p$  the first equilibrium thicknesses  $h_{eq}$  are close to those of only a *single* elongated brush, meaning a complete chain interpenetration, a phenomenon hard to conceive. Moreover, in this polymer concentration range, this equilibrium thickness is independent of the polymer length *N*. Also, salt effects for copolymers C and D are seen at low  $c_s$  and are not consistent with the brush picture. More important, the initial jumps seen at  $\Pi_0$  cannot either be included in the brush picture.

For comparison, the behavior of the copolymers of v.Klitzing et al.<sup>18</sup> is very different, although copolymers A and B have similar PSS chain lengths. In ref 18, no interpenetration of the brushes is seen and the initial film thickness is at least twice that of the double-brush  $h_{\rm B}$ . Our films initially thin down to equilibrium thicknesses



**Figure 4.** Salt effects on thin films of copolymer C. (a) Disjoining pressures at various salt concentrations. (b) Initial jump size  $\Delta h$  vs salt concentration. For comparison, the initial jump size vs copolymer concentration is also shown. (c) As in (b),  $h_{eq}$  vs salt and copolymer concentration.



**Figure 5.** Typical trace record of the reflected light intensity  $I_r$  (related to *h*) together with the applied pressure record. A sharp pressure variation produces a transient thickness variation, the new equilibrium being reached quickly, within a few seconds.

close to  $h_{\rm B}$  and can never be stabilized at larger *h*. Moreover, in ref 18 the film behavior depends on polymer concentration: at high concentration, a thickness jump brings the film down to an  $h_{\rm eq}$  smaller than the one at low concentration and is attributed to the presence of micelles



**Figure 6.** Initial jump sizes  $\Delta h$  and resulting equilibrium thickness  $h_{eq}$  vs concentration of copolymer D. Note that at the higher concentrations, two different jump sizes are detected.



**Figure 7.** Summary of all the thicknesses measured with the TFB apparatus for all the copolymers used. Note that we compile here all the results from Figures 1-5: for one *N*, all the reported thicknesses are not seen in each experiment; only some are seen depending on  $c_p$  or  $c_s$ . Open symbols correspond to previous measurements (ref 24). All the measurements roughly fall on periodic thickness (dashed horizontal lines). The lower solid horizontal line is the limit thickness where all the films break. The dashed area represents the thickness range where the pressure increases in the minimal curve. J1 and J2 are the two jumps always detected for all systems.

at high concentrations (which shrink the two brushes at the interfaces because of the increase in ionic strength). Here, we do not see such a behavior: the amplitude of the jumps is much smaller than the micelle diameter, of the order of  $h_{\rm B}$  (except for copolymer A). So, our films do not behave as nonoverlapping brushes either, and the jumps cannot be related to the expulsion of micelles as in ref 18.

**2. Disjoining Pressures.** Let us now discuss the shape of the curve  $\Pi(h)$ , as well as its amplitude. This can only be tested in the branch of the minimal curve between J1 and J2, since it is the only thickness range where repulsive forces are observed.

First, let us recall the theoretical predictions for the surface forces in interacting brushes. Since the midplane between surfaces is a symmetry plane on which the electric field vanishes, the only contribution to the pressure across this plane arises from the mixing entropy of the counterions.<sup>10</sup> Without salt, when brushes do not overlap the disjoining pressure varies as  $h^{-2}$  since the system is

equivalent to two charged planes facing each other (all the counterions are trapped in the brushes). In practice, there are always residual ions, coming from the free polymers in solution, and a screened Debye law should be observed instead (see below). When chains begin overlapping, the pressure is due to the mixing of the counterion atmospheres within the brushes. According to Pincus,<sup>10</sup> the disjoining pressure is then the osmotic pressure of the counterions:

$$\Pi(h) = fc_{\rm m}k_{\rm b}T$$

where  $c_{\rm m}$  is the monomer concentration in the brush, *f* is the fraction of free counterions which are not condensed ( $f \sim 0.3$ ),  $k_{\rm b}$  is the Boltzmann constant, and *T* is the absolute temperature. Assuming a homogeneous monomer density in the brush,

$$c_{\rm m} = 2N/(\Sigma h)$$

one gets

$$\Pi(h) = 2fNk_{\rm b}T/(\Sigma h) \sim h^{-1} \tag{1}$$

In the presence of salt and if the brushes overlap, the disjoining pressure is predicted to be rather salt insensitive and to be still given by the same equation.

Following these predictions, we have fitted the experimental curves obtained at different  $c_s$  by a power law,  $\Pi(h) \sim h^{-\alpha}$  (Figure 3a). Because of very small ranges in h and  $\Pi$  (less than a decade for both), one can always obtain reasonable fits, but the curves can be fitted by exponential curves as well (see afterward). When  $c_s$ increases from 0 to 0.7 M,  $\alpha$  increases from 1.7 to almost 5. Although these values should be considered as approximate, they deviate significantly from the prediction for overlapping brushes ( $\alpha = 1$ ).

If the brushes were not overlapping, we should observe instead a screened electrostatic repulsion between the interfaces as in the copolymer films of v.Klitzing et al.<sup>18</sup> The experimental curves have also been fitted with a screened interaction:  $\Pi(h) \sim e^{-\kappa h}$  where  $\kappa^{-1}$  is the Debye screening length (Figure 3b).<sup>22</sup> Again, because of the limited thickness range tested, reasonable fits can be obtained. With no added salt, we get  $\kappa^{-1} \sim 33$  nm, while the value calculated from the actual bulk ionic concentration is smaller (4 nm for copolymer B at 4 g/L). The apparent screening lengths are much too large in the presence of salt: for instance, we find  $\kappa^{-1} \sim 10$  nm at 0.7 M of NaCl or for 0.3 M of CaCl<sub>2</sub> (instead of 0.4 nm). Thus, the picture of nonoverlapping brushes is not in agreement with our results either.

If we admit that the brushes are overlapping, the magnitude of the disjoining pressures should be given by eq 1 and depend on the surface coverage  $\Sigma$  which therefore needs to be estimated. The surface tension of the copolymer solutions does not change with copolymer concentration  $c_p$  around cmc and starts decreasing only well above cmc,<sup>27</sup> presumably when  $c_p$  is high enough to screen the repulsive interactions between chains. This prevents us from using the Gibbs formula to evaluate the amount of polymer adsorbed at the surface since in the range of concentration where this work was performed both free chains and micelles coexist. On the other hand, X-ray reflectivity measurements on copolymer layers at the surface of water<sup>27</sup> or on free-standing films<sup>16</sup> showed that within

<sup>(27)</sup> Fontaine, P.; Daillant, J.; Guenoun, P.; Alba, M.; Braslau, A.; Mays, J. W.; Petit, J. M.; Rieutord, F. *J. Phys. II France* **1997**, *7*, 401.

experimental error, the scattering length density was close to that of pure water; no information about polymer adsorbed amount could therefore be extracted from these data. Experiments with poly(styrenesulfonate)-poly-(ethylethylene) copolymers with larger hydrophobic anchors, insoluble in water, allowed the determination of the surface tension variation with the amount of polymer spread.<sup>15</sup> It was shown that the surface tension was independent of the anchor and essentially controlled by the electrostatic repulsion between charged chains. Consequently, we will in the following assume that the area per chain  $\Sigma$  is comparable to the area of the insoluble polymers leading to a similar surface tension decrease (surface pressure  $\pi_{\rm S}$ ), that is,  $\Sigma \sim 10 \text{ nm}^2$  (here  $\pi_{\rm S} \sim 10$ mN/m). Thus, assuming a homogeneous monomer density in the brush, one has  $c = 2N/(\Sigma h)$ . With  $f \sim 0.3$  and using  $\Sigma \sim 10 \text{ nm}^2$ , N = 211 for copolymer B, and  $h/2 \sim 30 \text{ nm}$ (an average value taken from Figure 3a), one gets  $\Pi \sim 10^6$ Pa, a value a few orders of magnitude larger than the experimental ones. However, this value can be overestimated for the following reasons:

The actual number of condensed counterions along the chains can be smaller than in the Manning picture. However, for the discrepancy to be resolved, only a tiny fraction (of order  $10^{-4}$ ) of counterions should be free. This is far beyond the theoretical estimations.<sup>28</sup>

The simple picture of a perfect gas of counterions may fail in such dense media, and counterion-induced attractions between chains have even been predicted.<sup>29</sup> Such corrections induce negative contributions to the pressure and could lead to smaller pressures, but once again not sufficient for our films.

Thus, whatever improvement of the theory is considered, it cannot account for the small disjoining pressures measured. The forces measured between solid surfaces with the same systems<sup>12</sup> are also much smaller than predicted. These forces F can be transformed into disjoining pressures within the framework of the Langbein approximation<sup>30</sup> which states that  $F/(2\pi R) = h\Pi$  where R is the radius of curvature of the mica sheets used for the adsorption of the polymer. Typically, one finds that  $\Pi \sim 8 \times 10^3$  Pa for  $h \sim 40$  nm, a value again smaller than  $2NfkTI\Sigma h$ , although larger than ours (in these experiments,  $\Sigma$  was of order 40 nm<sup>2</sup>).

The film properties cannot therefore be understood in terms of brushes, either overlapping or nonoverlapping (though we recall that when formed, the film surfaces are covered by copolymer brushes, as it must be, regarding previous experiments on single air–water interfaces $^{15,17}$ ). The evolution of the brushes may arise from the weakness of the hydrophobic anchors at the interface, too small to be in contact and form a resistant glassy layer (the PtBS glass transition temperature is around room temperature for the molecular weights used here). This is a direct consequence of the strong asymmetry of the molecule (large PSS part, small PtBS one). If the molecule is not strongly anchored at the interface, it may be removed from the interface during film drainage leading to an increase of  $\Sigma$ . The disjoining pressure can therefore no longer be predicted because the variation of  $\Sigma$  is unknown.

The actual polymer concentration at the surface could become very low, to give the measured disjoining pressures.

In the experiments of ref 18, the hydrophobic anchors are larger and also below the glass transition. It is therefore possible that the surfaces are covered by glassy layers and are more resistant to drainage than in our case.

**3. Stratification.** The stratification process remains to be clarified since it is also different from what has been observed in ref 18. For this purpose, we will first describe the different stratification processes already observed in thin liquid films.

(a) Micellar Stratification. The observation of jumps in the film thickness is a classical observation in soap films made with surfactant solutions above cmc.<sup>22</sup> These jumps are induced by a stratification into micelle layers and correspond to their expulsion layer by layer. Here, this picture does not fit well: the size of the jumps is smaller than micelle sizes and does not increase with *N*, and only the number of jumps changes with salt or concentration while the jump size remains constant (~45 nm). Moreover, in this framework, the repulsive disjoining pressure should be a screened electrostatic repulsion between the interfaces. We have already seen that this is not the case. Thus, the picture of micellar stratification with two adsorbed brushes on each interface does not seem to be in agreement with our results, contrary to those of ref 18.

(b) Mixed Surfactant-Polyelectrolyte Films. Our results share similarities with those for liquid films made of mixed surfactant and polyelectrolyte solutions.<sup>8,19,23,31</sup> If the surfactant bears a charge opposite to that of the polymer, mixed surface layers are formed. When the surfactant concentration is small enough so that there are no surfactant-polymer complexes in the bulk, thickness jumps have been observed (often a few consecutive jumps are seen at  $\Pi_0$ ) whose size is in exact correspondence with the mesh size of the polymeric network in the bulk solution. However, it is still not clear how the chains are packed in these films and how they are expelled during film thinning. Addition of salt is known to destroy the network and indeed suppresses the stratification. With our diblock copolymers, salt reduces the number of jumps but only makes the stratification steps shrink slightly at high salt concentration (Figure 3c).

For surfactant/polyelectrolyte films, the size of the jumps is related to the mesh size and depends on the polyelectrolyte concentration  $c_p$  as  $c_p^{-1/2}$ : the more concentrated the solution, the smaller the jump. This is clearly not what we see here. Also, in the surfactant/polyelectrolyte films, there is no dependence with the polymer length (or molecular weight), and the films are never thicker than 100 nm. So we can hardly relate the stratification that we observe to a hypothetical network of PSS chains (here hydrophobically modified) formed in the thin films between the adsorbed brushes.

**4. Tentative Picture.** Perhaps the clue is the formation of a local polymer network. The thickness jumps corresponding to layers of roughly the same size, there could be a local lamellar arrangement of the chains with a layer thickness  $h_0$ . Recently, theoretical studies on the confinement of copolymer melt have discussed such structures.<sup>32</sup> Such a structure needs available free chains in the film volume; as stated before, there are actually free chains at

<sup>(28)</sup> Ray, J.; Manning, G. S. *Langmuir* **1994**, *10*, 2450. Gonzalez-Mozuelos, P.; Olvera de la Cruz, M. *J. Chem. Phys.* **1995**, *103*, 3145. Nyquist, R.; Ha, B. Y.; Liu, A. *Macromolecules* **1999**, *32*, 3481.

<sup>(29)</sup> For instance see: Borue, V. Y.; Erukhimovich, I. Y. *Macromolecules* **1988**, *21*, 3240. Grønbech-Jensen, N.; Mashl, R. J.; Bruinsma, R. F.; Gelbart, W. M. *Phys. Rev. Lett.* **1997**, *78*, 2477.

<sup>(30)</sup> Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992; p 159.

<sup>(31)</sup> Kolaric, B.; Jaeger, W.; Klitzing, R. v. J. Phys. Chem. B 2000, 104, 5096.

<sup>(32)</sup> Tsori, Y.; Andelman, D. *EuroPhys. Lett.* **2001**, *53*(6), 722. Tsori, Y.; Andelman, D. Cond-mat/0103250 2001.

the investigated concentrations, and one can also say that other free chains could come from the initial brushes (due to the weak anchoring).

The length  $h_0$  must have the peculiar characteristic of being weakly dependent on added salt and polymer concentration. This feature is reminiscent of the basic properties of charged brushes whose extension is independent of added salt (up to some threshold) and of chain density. Moreover, it has been shown that charged brushes are made of quite extended chains.<sup>33</sup> A possibility is then that the stacking of layers behaves locally as brushlike arrangements of typical size  $h_0$ . Such a size of order 45 nm is fully compatible with previous results demonstrating a rodlike behavior of the chains down to a scale (in wavevector) of q = 0.15 nm<sup>-1</sup>.<sup>33</sup> Upon compression, since the overlap pressure of the counterions is huge (see eq 1), layers get expulsed from the film. This keeps the pressure unchanged up to a thickness  $h_{eq}$  where the adsorbed chains (maybe brushlike in some cases) are compressed. Then, chains are probably expelled from the surface, increasing the area per chain during the compression.

Another important issue deals with viscosity: increasing salt and/or decreasing copolymer concentration have the same effect on the layering, because these variations both strongly reduce the viscosity. Viscous losses are an important issue in our technique, since they control the drainage of the film and thus the path towards equilibrium. The more viscous the solution, the more layers can stand in the film and the longer the drainage rates. The initially more viscous solutions are affected by smaller amounts of salt in agreement with our results for copolymer C. Once all the solutions have low viscosities, close to that of water, the minimal curve is recovered, without most of the layers which have not been able to stand in the film. Accounting for such viscosity effects clearly sheds light on the unusual layering behavior of the films.

## **V. Conclusions**

We have measured disjoining pressures in films made from charged copolymer solutions and their variations

(33) Guenoun, P.; Muller, F.; Delsanti, M.; Auvray, L.; Chen, Y. J.; Mays, J. W.; Tirrell, M. *Phys. Rev. Lett.* **1998**, *81*, 3872. with concentration, chain length, and added salt. Earlier experiments showed that these films have initially the configuration of a double brush. However, the theoretically predicted high disjoining pressures have not been measured. The analysis suggests that the brush structure is changed upon compression, probably because of a weak anchoring at the surfaces, a consequence of the asymmetry of the studied copolymers, which would not allow the formation of a glassy layer at the surface of the initial brush. The actual structure shares some similarities with that of confined homopolyelectrolyte solutions, but the fact that the chains have a hydrophobic end and that they are partly adsorbed at the film surfaces changes the ordering. The films appear structured in layers of constant thickness comparable to some local persistence length, and the characteristic thicknesses are much more insensitive to changes (in salt and polymer concentration) than those of confined homopolyelectrolyte solutions. We have also found that the viscosity plays an important role and that salt acts first by lowering the bulk viscosity before shrinking the layers. Although the films are very stable at low pressures, they rupture under moderate compressions. There are still many unsolved questions regarding thin liquid films filled with polyelectrolyte chains (adsorbed or not), one of the most mysterious being the origin of the low disjoining pressures always observed.

We plan to study other copolymers with different asymmetry between the two parts of the molecule to validate the hypothesis made in the present paper. We also plan to perform spectroscopy measurements (Raman and PM-IRRAS) in order to get information on the orientation of the chain segments in the film and at the surfaces of the solutions.

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