# Thermodynamics of a Partially Swollen Polymer Brush

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ABSTRACT: Swelling initially solvent-free monolayers of anchored polymer chains with a gradually increasing amount of solvent significantly influences their thermodynamics, especially the lateral pressure. Upon increasing the amount of solvent, the lateral pressure initially increases inversely proportional to the square of the average volume fraction of the anchored chains but finally levels off to a limiting value independent of the composition. With increasing area per anchored chain the limiting value of the lateral pressure decreases, while the amount of solvent needed to reach the limiting value increases. The observed effects are in good agreement with predictions based on analytical mean field theory.

## Introduction

The concept of a polymer brush—flexible polymers terminally attached to a surface with a lateral spacing considerably less than the undisturbed coil dimensions—has been applied successfully to describe phenomena as various as morphologies of phase-separated block copolymers,[1−6] steric stabilization of colloids,[7,8] and friction reduction between solid interfaces.[9,10] Current literature concentrates mainly either on brushes composed of pure polymer melts without solvent or on completely swollen brushes in contact with an excess of a good solvent for the polymer chains. *Partially swollen brushes*, resulting from the exposure of a polymer brush to a limited amount of a good solvent, have received much less attention. However, partially swollen brushes have a considerable application potential. For example, a hygroscopic polymer brush may help liquids to spread as wetting layers instead of forming droplets[11] and thus might be used as antifogging coating; on the other hand, layers of partially swollen brushes might be very effective lubrication agents for solid/air interfaces quite similar to the lubricating properties of completely swollen brushes attached to solid/liquid interfaces.[9,10]

In melt as well as in swollen brushes, the interaction between neighboring polymers leads to a distortion of the coils, which reduces the conformational entropy. The major difference between these two systems is that in the melt case the volume fraction of chain segments on average and locally is fixed at a constant value, while in the swollen brush the average as well as the local volume fraction of chain segments results from balancing osmotic forces and polymer chain statistics. In a melt brush the volume fraction of polymer segments is unity throughout the whole brush; the height of the brush is proportional to the surface concentration $n/A$, and the free energy is proportional to $(n/A)^2$. In a completely swollen brush, the local volume fraction of polymer segments is significantly less than unity and gradually decreases from a finite value at the plane of anchoring toward zero at the top of the brush.[11−18] Upon increasing the surface concentration, solvent is “squeezed out” of the swollen brush. Thus, the average volume fraction of segments increases with increasing surfaces concentration, the height of the brush being proportional to $(n/A)^{1/3}$ and the free energy being proportional to $(n/A)^{5/3}$.

If one takes a melt brush of a given surface concentration and applies a good solvent in small increments, one can expect a transition between the two scenarios (see Figure 1): the *local* volume fraction of the polymer is less than unity and decreases with increasing distance from the plane of tethering; however, it does not decrease to zero at the top of the brush. The *average* volume fraction of polymer, on the other hand, is determined by the experimentalist, e.g., by choosing an appropriate amount of solvent applied. The height of the brush is proportional to the surface concentration and inversely proportional to the average volume fraction of the polymer.

In a previous contribution[19] we investigated the thermodynamics—more precisely, the first derivative of the free energy with respect to area—of a melt polymer brush by anchoring hydrophobic polymer chains via ionic headgroups to a water surface and analyzing the lateral pressure of the resulting monolayers.[20]

To investigate the gradual transition from a melt state to a completely swollen state and its influence on the thermodynamics of a polymer brush, we apply in the current contribution mixtures of anchored polymers and nonanchored compounds to a water surface and analyze the lateral pressures of the resulting mixed monolayers.

## Thermodynamics

To investigate the thermodynamics of a partially swollen brush, we determine and discuss in the next section the lateral pressure of mixed monolayers of anchored polymers and nonanchored compounds on a water surface. The scope of this section is to derive an expression for this lateral pressure, based on current polymer brush theories.

The lateral pressure $\Pi$ of a monolayer on a water surface is given by the difference between the first derivatives of the free energy, $F$, with respect to area, $A$, of the clean water surface and of the monolayer-covered surface.

$$\Pi = \left(\frac{\partial F}{\partial A}\right)_{\text{water/air−interface}} - \left(\frac{\partial F}{\partial A}\right)_{\text{covered surface}} \qquad (1)$$

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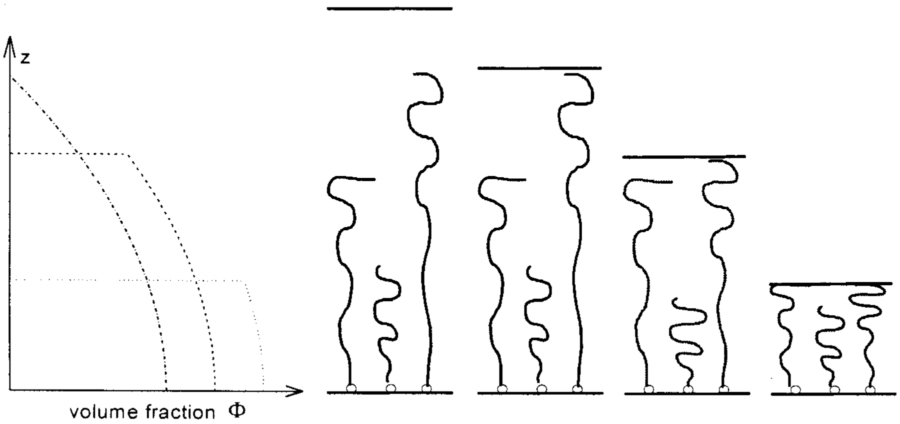


**Figure 1.** Schematic representation of the gradual transition from a nonswollen brush to a completely swollen brush accompanied by a gradual transition from a boxlike volume fraction profile of the anchored chains to a parabolic profile.

We assume that the second term of the right-hand side of eq 1 can be represented by the sum of the following three contributions: (i) the interfacial tension at the polymer/air interface, (ii) the interfacial tension at the polymer/water interface, and (iii) a contribution to the surface pressure due to an elastic stretching of the polymer chains.[21]

$$\Pi = \left(\frac{\partial F}{\partial A}\right)_{\text{water/air−interface}} - \left(\frac{\partial F}{\partial A}\right)_{\text{polymer/air−interface}} - \left(\frac{\partial F}{\partial A}\right)_{\text{water/polymer−interface}} - \left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} \quad (2)$$

In the following, the contribution to the surface pressure due to elastic stretching will be discussed first qualitatively and then refined using results based on analytical mean field theory.[11−13]

Let us first consider a brush of uniformly extended chains in which the chains are anchored to the "bottom" of the brush and all free ends are at the "top". This assumption of uniform stretching is useful to highlight the principal trends to be expected. However, since there is no driving force to fix the free ends of all chains at a certain height, it is inaccurate, and we limit us at this point to discuss only proportionalities. A much more elaborate picture has been developed by Millner, Witten, and Cates and is used for a more quantitative analysis below.

If one starts with a monolayer free of solvent and adds small amounts of a good solvent, one can expect that the solvent initially is completely absorbed by the anchored polymer. Up to a certain amount of solvent the local volume fraction of polymer chains is nonzero in the entire layer; above that point, however, the state of a completely swollen brush is reached, and further addition of solvent gives rise to an additional "layer" of pure solvent on top of the completely swollen brush. This layer does not further influence the lateral pressure.

In the first regime the volume of the layer, $hA$, is proportional to the number of chains, $n$, to the volume of a chain segment, $v_{\text{p}}$, and the number of segments per anchored chain, $N_{\text{p}}$, and is inverse proportional to the average volume fraction of the polymer, $\phi_{\text{p}}$. Thus, its height, $h$, is given by

$$h = \frac{v_{\text{p}} N_{\text{p}}}{\phi_{\text{p}}} \frac{n}{A} \quad (3)$$

For a single uniformly stretched Gaussian chain, the free energy due to the stretching is proportional to the square of the end-to-end distance[22−24] and inversely proportional to the number of segments per chain. In a first approximation, we may assume that all chains are uniformly stretched with a head-to-end distance proportional to the height $h$ and contribute equally to the free energy of the system. The free energy of the complete system, $F_{\text{elastic}}$, is thus proportional to the square of the film thickness and proportional to the number of chains, $n$, incorporated in the monolayer.

$$F_{\text{elastic}} \propto n \frac{1}{N_{\text{p}}} h^2 \quad (4)$$

Inserting eq 3 into eq 4 yields the free energy as a function of the mean volume fraction of polymer chains and the area covered by the brush:

$$F_{\text{elastic}} \propto N_{\text{p}} \phi_{\text{p}}^{-2} \frac{n^3}{A^2} \quad (5)$$

The contribution to the lateral pressure due to the stretching of the chains, $\Pi_{\text{el}}$, is given by its first derivative with respect to area:

$$-\left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} \propto N_{\text{p}} \phi_{\text{p}}^{-2} \left(\frac{n}{A}\right)^3 \quad (6)$$

Thus, in the first regime one expects that the lateral pressure increases proportional to the inverse square of the volume fraction of polymer.

However, below a certain average volume fraction of anchored chains (from here on denoted $\varphi_{\text{p}}$*), we expect that the brush reaches the state of a completely swollen brush. Further addition of solvent does not change the conformations of the chains and thus does not influence the lateral pressure. We still expect that the lateral pressure increases with increasing surface concentration of anchored chains. Furthermore, we already know that the volume fraction of polymer chains in a completely swollen brush increases with increasing surface concentration of the anchored chains.[11−13] Thus, we expect that $\varphi_{\text{p}}$* increases with increasing anchoring density.

In addition, the transition to a completely swollen brush will occur at lower degrees of swelling if the interaction between solvent and polymer chains is unfavorable. This interaction can be summarized by an

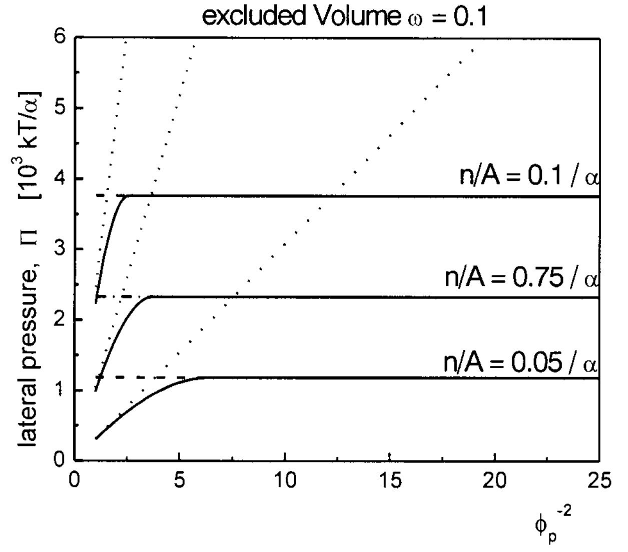


**Figure 2.** Predicted dependency of the lateral pressure of mixtures of anchored polymers and nonanchored solvent on the degree of swelling at variable area per chain but constant excluded-volume parameter.

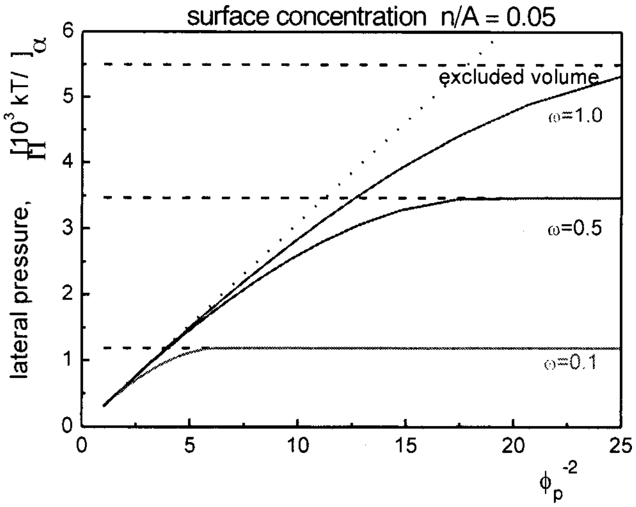


**Figure 3.** Predicted dependency of the lateral pressure of mixtures of anchored polymers and nonanchored solvent on the degree of swelling at constant area per chain but variable excluded-volume parameter.

excluded-volume parameter, $\omega$, which in the case of athermal solvents is inversely proportional to the size of the solvent molecules and decreases further in the case of unfavorable energetic interactions.

Thus, depending on the area per chain and the excluded-volume parameter, $\omega$, one expects that the elastic contribution to the lateral pressure follows initially the dotted and finally the dashed line in Figure 2 and Figure 3. It is worth noting that in the first regime of this simple scenario the polymer chains and the nonanchored solvent are completely and homogeneously mixed. Thus, as long as no solvent is expelled from the layer, the free energy of interaction between chains and solvent is independent of the area per chain and thus does not influence its first derivative, the lateral pressure.

A more detailed description based on the theory of Miller, Witten, and Cates is derived in the Appendix. This treatment describes the transition from a solvent-free layer of uniform volume fraction of polymer chains to a completely swollen brush with a local volume fraction of chains decreasing in a parabolic fashion from the plane of tethering. The intermediate volume fraction profiles can be described by truncated parabolas as depicted schematically in Figure 1. According to this description, the transition between a partially swollen and a completely swollen brush occurs at

$$\phi_p^* = \sqrt[3]{\frac{\pi^2}{4\omega/v_p}\alpha^2(A/n)^{-2}}$$

with the excluded-volume parameter $\omega$ and the chain cross-section parameter α given in the Appendix.

At volume fractions of anchored chains $\varphi_p$ larger than $\varphi_p$*, the elastic contribution to the lateral pressure is given by a sum of two terms. The first term, which is independent of the solvent quality, reflects the effects described in the simple model above. The second term is due to the changes in the shape of the volume fraction profile of the polymer chains which modifies the energetic interaction between polymer chains and solvent.

$$-\left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} = \frac{\pi^2}{4}k_B T N_p \alpha^2 \phi_p^{-2}\left(\frac{A}{n}\right)^{-3} - \frac{\pi^4}{40}k_B T N_p \alpha^4 \frac{v_p}{\omega}\phi_p^{-5}\left(\frac{A}{n}\right)^{-5} \quad \text{(A6)}$$

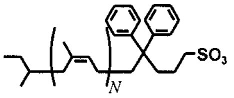
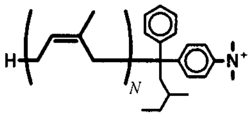
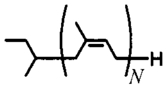
At average volume fractions $\varphi_p$ smaller than $\varphi_p$*, a completely swollen brush in coexistence with excess solvent is formed. In this regime, the elastic contribution to the lateral pressure, given by eq A8, depends on the solvent quality but is independent of $\varphi_p$.

$$-\left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} = k_B T \frac{3}{5}\left(\frac{\pi}{2}\right)^{2/3} N_p \left(\frac{\omega}{v_p}\right)^{2/3} \alpha^{2/3}(A/n)^{-5/3} \quad \text{(A8)}$$

The predictions based on eq A6 and eq A8 are depicted schematically as continuous lines in Figure 2 and Figure 3.

Let us now consider the first three terms of the right-hand side of eq 2, which will influence the experimentally accessible lateral pressure as well. The first term—the surface tension of a water surface—is independent of the area and composition of the polymer brush. The second and third term will depend on the contribution of the two components (polymer chain/solvent) to the interfacial tensions. These contributions depend on the cohesion energies of the involved molecules and on the volume fraction of segments of the polymer chain at the two interfaces. Since these volume fractions close to the interface depend on the average composition, one can in general expect that the interfacial tensions depend on the composition, too. If, however, the cohesion energies of all involved components are the same, e.g., if the anchored polymer chains are swollen with oligomers of the same chemical nature, these variations in composition will have only negligible influence on the interfacial tensions. In this case, the first three terms of the right-hand side of eq 2 are independent of the area and the average volume fraction of anchored chains and can be summarized into a single constant: the spreading coefficient of the polymer in the absence of anchoring, $\gamma$*. In this case, the lateral pressure reflects mainly changes in free energy due to changes in the

**Table 1. Characterization of the Polyisoprenes**

| name | $PI{-}SO_3^-36K$ | $PI{-}N^+12K$ | PI-0.6K |
|---|---|---|---|
| structure/polar headgroup |  |  |  |
| $M_w/M_n$ | 1.02 | 1.04 | 1.1 |
| $M_n$ (kg/mol) | 36.5 | 11.8 | 0.6 |
| av no. of repeat units, $N$ | 538 | 174 | 8.8 |

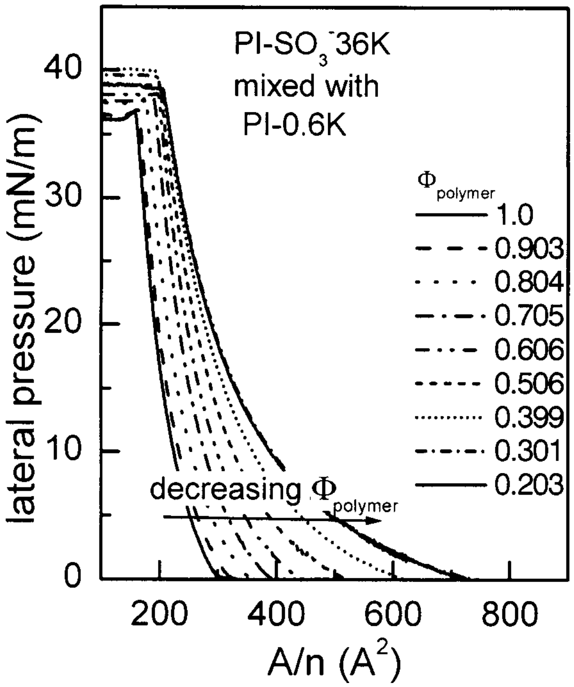


**Figure 4.** Lateral pressure/area isotherms of mixtures of anchored polyisoprene PI-SO$_3$-36K and nonanchored isoprene oligomers PI-0.6K.

conformation of the polymer chains, and eq 2 reduces to

$$\Pi = \gamma^* - \left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} \qquad (7)$$

## Experimental Section

Linear polyisoprenes with ionic headgroups have been prepared via anionic polymerization as described in ref 19 and refs 25−27. The characterization of the polymer is summarized in Table 1.

Cereclor 42 (chlorinated paraffins) was obtained from ICI Chemicals and Polymers and used as received. According to ICI specifications, the material is produced from C14−C17 paraffins and contains 41−44 wt % chlorine and has a density of 1.15−1.18 g/mL.

Trichloromethane (Aldrich, 99.99% pure), ethanol (Aldrich, 99.99+% pure) were used as received. Water (resistivity 18.2 × $10^6$ Ω·cm$^{-1}$, total dissolved organic carbon <5 ppm) was purified with an ion exchange/filter system (Millipore).

Isotherms on the surface of pure water were recorded using a 20 cm × 46 cm rectangular Langmuir trough made of poly(tetrafluoroethylene), equipped with one compression barrier and a floating barrier for the detection of the surface pressure via the Langmuir method (Lauda FW2, Germany). The monolayers were spread from chloroform solutions which contained 0.05 wt % polymer/nonvolatile compounds and 10 wt % ethanol. All isotherms were recorded at a temperature of 20 °C. The number-average molecular weight was used to calculate the mean area per anchored chain.

## Results and Discussion

As outlined above, the degree of swelling and the influence of nonanchored solvent on the lateral pressure significantly depend on the excluded-volume parameter, $\omega$. This parameter is highest for small athermal solvents and decreases with increasing solvent size or less favorable energetic interactions between the solvent and the anchored chains.

To test this prediction, we mixed anchored polyisoprenes and two different nonanchored liquids, applied these mixtures to a water surface, and determined the lateral pressures of the resulting monolayers as a function of area per chain and average volume fraction of polymer chains.

In a first series of experiments, mixtures of anchored polyisoprenes of a chain length of approximately 540 repeat units (PI-SO$_3$-36K) and nonanchored isoprene oligomers of approximately 9 repeat units (PI-0.6K) were investigated. As discussed above, in this case the involved interfacial tensions can be regarded as constant, and one can expect the lateral pressure to follow eq 7.

As can be seen from Figure 4 and Figure 5, at a given area per anchored chain, increasing the amount of nonanchored oligomers gives rise to an increased lateral pressure: The isotherms are affected down to average volume fractions of anchored chains of $\varphi_p = 0.4$; only the two isotherms at values of $\varphi_p < 0.4$ are not affected by changes in composition. In Figure 5 lateral pressures are plotted vs $\varphi_p^{-2}$ (symbols and continuous lines) and compared with the predictions based on eqs 7, A6, and A8 (dashed lines). These predictions have been calculated using an excluded-volume parameter equal to the inverse chain length of the nonanchored oligomers ($v_p/\omega$ = 8.8) and a spreading coefficient of $\gamma^* = -6$ mN/m. They represent the experimental data quite well.

We chose a size of a chain segment equal to the size of a repeat unit as defined in Table 1. We note, however, that one might as well choose a different entity as chain segment. This does not influence the total chain length or the total chain volume, $N_p v_p$, but determines the value of $N_p$, $v_p$, $\alpha$, and $\omega$ to be used in the data analysis. At first sight this seems confusing; however, $\alpha^2(v_p/\omega)$, $\alpha^2 N_p$, and $\varphi_p^*$ as well as the results presented in eqs A6 and A8 and the predictions depicted in Figure 5 are not influenced by this choice.

The spreading coefficient of $\gamma^* = -6 \times 10^{-3}$ N m$^{-1}$ assumed in Figure 5 is smaller than the value of $\gamma^* = -13 \times 10^{-3}$ N m$^{-1}$ calculated from surface tensions given in the literature. This observation has already been made earlier in the analysis of the lateral pressure of nonswollen brushes.[19] It might be due to trace impurities in the polymer that lower the surface tension of the bottom interface of the monolayer.

The swelling of polymers is influenced by the solvent size *and* the energetic interactions between chain seg-

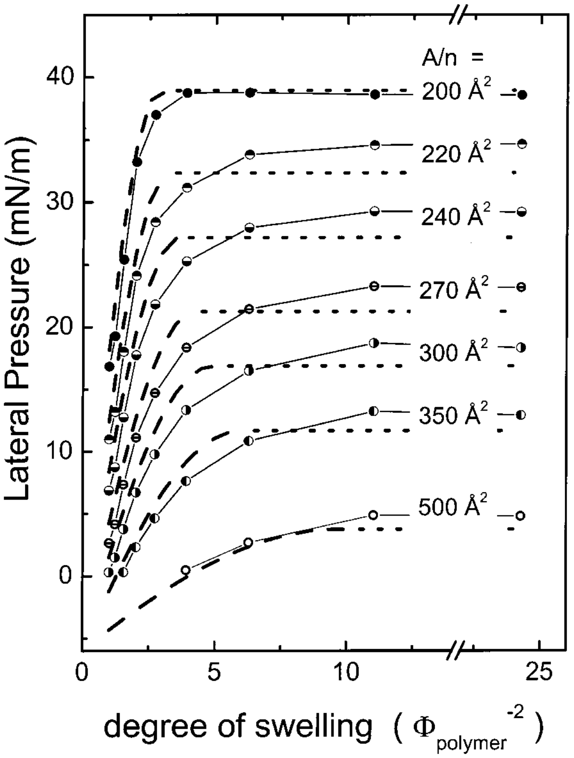


**Figure 5.** Experimentally observed dependency of the lateral pressure of anchored polyisoprene on the degree of swelling with nonanchored oligomers (symbols and continuous lines) compared to predictions based on mean field theory (dashed lines).

ments and the solvent. To illustrate the latter case, chlorinated paraffin has been used instead of isoprene oligomers as nonanchored solvent to swell monolayers of anchored polyisorene chains of 174 repeat units. The volume ratio of a chloroparaffine molecule to an anchored chain is approximately the same as in the previous example. Because of the differences in chemical structure between the polyisoprene and chlorinated paraffin, however, one can expect unfavorable energetic interactions and thus a comparatively small excluded-volume parameter.

From the isotherms in Figure 6 it is obvious that a comparatively small amount of added chlorinated paraffin gives rise to a significant increase of the lateral pressure. This effect, however, levels off at volume fractions of anchored chains $\varphi_p \leq 0.88$; the isotherm of a mixture of $\varphi_p = 0.88$ is almost identical to the isotherm at $\varphi_p = 0.59$. If the lateral pressure is replotted vs $\varphi_p^{-2}$, one observes that it initially increases with increasing degree of swelling but levels of much earlier than in the previous case (compare Figure 5 and Figure 7).

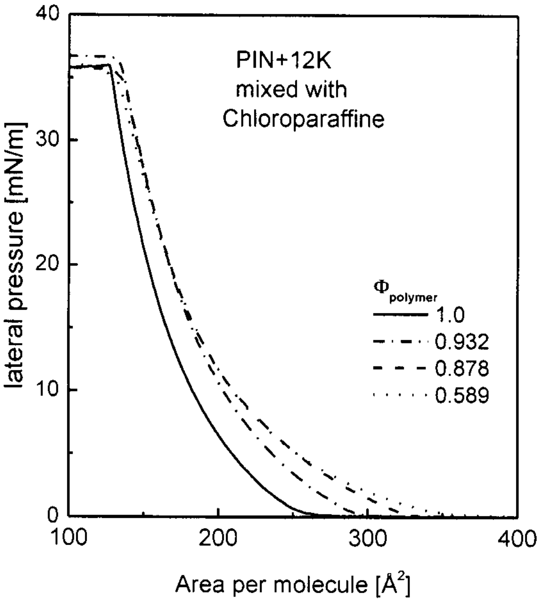


**Figure 6.** Lateral pressure/area isotherms of mixtures of anchored polyisoprene PI-N$^+$12K and chloroparaffin.

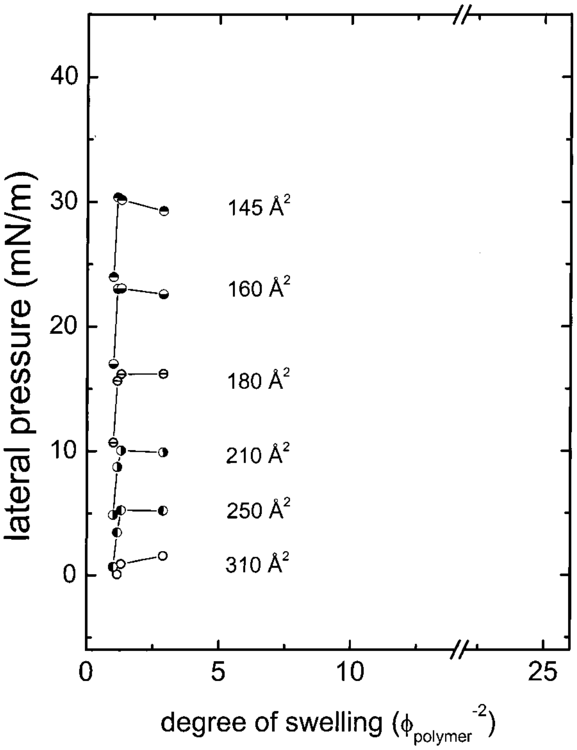


**Figure 7.** Experimentally observed dependency of the lateral pressure of anchored polyisoprene on the degree of swelling with chloroparaffin.

As pointed out in eq 2, the lateral pressure is not only given by the elastic contribution but also influenced by the surface tensions of the involved interfaces. In the case of mixtures of anchored chains and nonanchored oligomers chemically identical to the anchored chains, one can assume that these tensions are independent of the average composition. This time, however, the solvent is chemically different from the anchored chains. Thus, the interfacial tensions depend on the average composition. This dependency has not been determined, and thus no quantitative comparisons between experiment and mean field predictions have been made. Nevertheless, it is obvious from Figure 6 that swelling with chlorinated paraffin instead of nonanchored isoprene oligomers significantly limits the maximum degree of swelling of the anchored chains.

## Conclusion

It has been shown that the lateral pressure of monolayers of anchored polymers increases upon gradual addition of nonanchored solvents. The lateral pressure initially increases inversely proportional to the square of the average volume fraction of anchored chains but finally levels off to a value independent of the added amount of solvent. Oligomers of segments that are chemically identical to the polymer chains influence the lateral pressure to a larger extend than solvents with unfavorable energetic interactions with the anchored chains. The results are in reasonable agreement with analytical mean field theory.

**Acknowledgment.** The sulfonated polyisoprene was synthesized by R. Heger at the Max-Planck-Institut f. Kolloid & Grenzflächenforschung, Berlin. We thank ICI Chemicals for donating the chlorinated paraffin. The experiments were done in the Laboratory of Organic & Macromolecular Chemistry, OC3, of the University of Ulm. The support of the head of the laboratory, M. Möller, is gratefully appreciated. This work was funded by the Deutsche Forschungsgemeinschaft within the priority program “Wetting” (Project Go/693-6).

## Appendix A

The partially swollen brush considered here is equivalent to a swollen brush compressed between planar interfaces to a height, $h$. This height is smaller than the height of a completely swollen brush, $h_0$, and is given by eq 3.

As has been derived by Millner, Witten, and Cates,[12,13] the free energy per unit surface of such a brush is given by

$$\left(\frac{F}{F_0}\right)_{\text{elastic}} = \frac{5}{9}\left(\frac{h_0}{h} + \left(\frac{h}{h_0}\right)^2 - \frac{1}{5}\left(\frac{h}{h_0}\right)^5\right) \qquad \text{(A1)}$$

With the height, $h_0$, and the free energy per unit surface $F_0/A$ of a completely swollen brush given by

$$h_0 = N_{\text{p}}\left(\frac{4}{\pi^2}\,\frac{n}{A}\,\omega\,\frac{\langle r^2\rangle_0}{N_{\text{p}}}\right)^{1/3} \qquad \text{(A2)}$$

$$\left(\frac{F_0}{k_{\text{B}}TA}\right)_{\text{elastic}} = \frac{9}{10}\left(\frac{\pi}{2}\right)^{2/3} N_{\text{p}}\left(\frac{n}{A}\right)^{5/3}\omega^{2/3}\left(\frac{N_{\text{p}}}{\langle r^2\rangle_0}\right)^{1/3} \qquad \text{(A3)}$$

$\langle r^2\rangle_0$ is the mean-square end-to-end distance of the undisturbed chain; the excluded-volume parameter, $\omega$, is given by the Flory interaction parameter $\chi$, the volume of a chain segment $v_{\text{p}}$, and the volume of a solvent molecule $v_{\text{s}}$ according to $\omega = (1 - 2\chi)v_{\text{p}}^2/v_{\text{s}}$. In the case of polymer chains dissolved in chemical identical oligomers, the excluded-volume parameter is inversely proportional to $N_{\text{s}}$, the number of segments per oligomer, $\omega = v_{\text{p}}/N_{\text{s}}$.

Inserting eqs 3, A2, and A3 into eq A1, we obtain

$$(F)_{\text{elastic}} = \frac{1}{2}k_{\text{B}}TN_{\text{p}}\,\frac{\omega}{v_{\text{p}}}\,\phi_{\text{p}} + \frac{\pi^2}{8}\,k_{\text{B}}TN_{\text{p}}\alpha^2\phi_{\text{p}}^{-2}\,\frac{n^3}{A^2} - \frac{\pi^4}{160}\,k_{\text{B}}TN_{\text{p}}\alpha^4\,\frac{v_{\text{p}}}{\omega}\,\phi_{\text{p}}^{-5}\,\frac{n^5}{A^4} \qquad \text{(A4)}$$

with

$$\alpha = v_{\text{p}}/\sqrt{\langle r^2\rangle_0/N_{\text{p}}} \qquad \text{(A5)}$$

By taking the first derivative of eq A4, we obtain the contribution of the polymer brush to the lateral pressure, quoted already in the main part.

$$-\left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} = \frac{\pi^2}{4}\,k_{\text{B}}TN_{\text{p}}\alpha^2\phi_{\text{p}}^{-2}\left(\frac{A}{n}\right)^{-3} - \frac{\pi^4}{40}k_{\text{B}}TN_{\text{p}}\alpha^4\,\frac{v_{\text{p}}}{\omega}\phi_{\text{p}}^{-5}\left(\frac{A}{n}\right)^{-5} \qquad \text{(A6)}$$

The transition from the partially swollen brush as described by eq A6 to the completely swollen brush occurs at $h/h_0 = 1$. Therefore, eq A6 is valid down to an average volume fraction of

$$\phi_{\text{p}}{*} = \sqrt[3]{\frac{\pi^2}{4\omega/v_{\text{p}}}\,\alpha^2(A/n)^{-2}} \qquad \text{(A7)}$$

At average volume fractions smaller than $\varphi_{\text{p}}{*}$ the state of a completely swollen brush is reached, and the contribution to the lateral pressure is equal to $-\mathrm{d}F_0/\mathrm{d}A$, which is obtained by taking the derivative of eq A3.

$$-\left(\frac{\partial F}{\partial A}\right)_{\text{elastic}} = k_{\text{B}}T\,\frac{3}{5}\left(\frac{\pi}{2}\right)^{2/3} N_{\text{p}}\left(\frac{\omega}{v_{\text{p}}}\right)^{2/3}\alpha^{2/3}(A/n)^{-5/3} \qquad \text{(A8)}$$

## Appendix B

**Calculation of the Molecular Parameters.** $(\langle r^2\rangle_0/N_{\text{p}})^{1/2}$ was calculated from the constant $(\langle r^2\rangle_0/M)^{1/2} = 7.66 \times 10^{-11}$ m g$^{-1/2}$ mol$^{1/2}$ [28] ($M$ = molar mass of the polymer) and the molar mass of the repeat unit $m = 68$ g/mol according to $(\langle r^2\rangle_0/N_{\text{p}})^{1/2} = (\langle r^2\rangle_0/M)^{1/2}m^{1/2} = 6.32$ Å. We note, however, that the data given in the literature on $\langle r^2\rangle_0/M$ scatter by approximately 10%.

$v_{\text{p}}$ was derived from the density of the polymer, $\rho = 913$ kg m$^{-3}$,[29] and the molar mass of the repeat unit $m = 68$ g/mol and theAvogadro constant $N_{\text{A}}$ according to $v_{\text{p}} = m/(N_{\text{A}}\rho) = 123.7$ Å$^3$.

$\gamma{*} = -13 \times 10^{-3}$ N m$^{-1}$ of polyisoprene can be calculated from the surface tension of clean water according to

$$\gamma{*} = \left(\frac{\partial F}{\partial A}\right)_{\text{water/air-interface}} - \left(\frac{\partial F}{\partial A}\right)_{\text{polymer/air-interface}} - \left(\frac{\partial F}{\partial A}\right)_{\text{water/polymer-interface}}$$

with $\gamma_{\text{wa}} = 72.9 \times 10^{-3}$ N m$^{-1}$,[30] the surface tension of the polyisoprene, $\gamma_{\text{pa}} = 31 \times 10^{-3}$ N m$^{-1}$,[31] and the interfacial tension of the polymer water interface, $\gamma_{\text{wp}}{}^{\circ} = 54.7 \times 10^{-3}$ N m$^{-1}$, calculated from the contact angle between polymer and water, $\Theta = 109°$,[31] according to the Young equation[32] $\gamma_{\text{pa}} - \gamma_{\text{wp}} = \gamma_{\text{wa}}\cos\Theta$.

The average volume fraction of anchored chains was calculated from the mass and the density of polymer chains $m_{\text{p}}$ and $\rho_{\text{p}}$ and the mass and density of the nonvolatile oligomers or chlorinated paraffine $m_{\text{s}}$ and $\rho_{\text{s}}$ assuming zero partial volume of mixing according to

$$\phi_{\text{p}} = \frac{m_{\text{p}}/\rho_{\text{p}}}{m_{\text{p}}/\rho_{\text{p}} + m_{\text{s}}/\rho_{\text{s}}}$$

## References and Notes

(1) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(2) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733.
(3) Semenov, A. N. *Macromolecules* **1993**, *26*, 6617.
(4) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(5) Millner, S. T. *J. Polym. Sci., Part B* **1994**, *32*, 2743.
(6) Review article: Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(7) vandePas, J. C.; Olsthoorn, Th. M.; Schepers, F. J.; deVries, C. H. E.; Buytenhek, C. J. *Colloids Surf.* **1994**, *85*, 221.

(8) Hristova, K.; Needham, D. *Macromolecules* **1995**, *28*, 991.

(9) Klein, J. *Annu. Rev. Mater. Sci.* **1996**, *26*, 581.

(10) Klein, J.; Kumacheva, E.; Mahalu, D.; Perahia, D.; Fetters, L. J. *Nature* **1994**, *370*, 634.

(11) (a) Marko, J. F.; Johner, A.; Marques, C. M. *J. Chem. Phys.* **1993**, *99*, 8142. (b) Johner, A.; Marques, C. M. *Phys. Rev. Lett.* **1992**, *69*, 1827.

(12) (a) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610. (b) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413.

(13) Milner, S. T. *Europhys. Lett.* **1988**, *7*, 659.

(14) Wijmans, C. M.; Scheutjens, J. M. H. M.; Zhulina, E. B. *Macromolecules* **1992**, *25*, 2657.

(15) Venema, P.; Odijik, T. *J. Phys. Chem.* **1992**, *96*, 3922.

(16) Review article: Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.

(17) Kent, M. S.; Lee, L.-T.; Farnoux, B.; Rondelez, F. *Macromolecules* **1992**, *25*, 6231.

(18) Granick, S.; Herz, J. *Macromolecules* **1985**, *18*, 460.

(19) Heger, R.; Goedel, W. A. *Macromolecules* **1996**, *29*, 8912.

(20) For an introduction to the characterization and transfer of insoluble films, see: (a) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid−Gas Interfaces*; Interscience: New York, 1966. (b) Roberts, G. *Langmuir−Blodgett Films*; Plenum Press: New York, 1990. (c) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: San Diego, 1991.

(21) In this treatment we neglect contributions to the lateral pressure due to the interactions of the headgroups as well as van der Waals type interaction between the monolayer and the subphase.

(22) Treolar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, 1975; pp 56−57.

(23) deGennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; p 31.

(24) Mark, J. E.; Erman, B. *Rubberlike Elasticity a Molecular Primer*; Wiley & Sons: New York, 1988; p 30.

(25) Hshieh, H.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996; pp 283−285.

(26) Quirk, R. P.; Zhu, L.-F. *Br. Polym. J.* **1990**, *23*, 47.

(27) Quirk, R. P. *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 259.

(28) (a) Brandrup, J., Immergut, E., Eds. *Polymer Handbook*, 3rd ed. Wiley: New York, 1989; p VII/33. (b) Prud'homme, J.; Roovers, J. E. L.; Bywater, S. *Eur. Polym. J.* **1972**, *8*, 901.

(29) (a) Brandrup, J., immergut, E., Eds. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; p V/7. (b) Wood, L. A. *Rubber Chem. Technol.* **1939**, *12*, 130.

(30) Gaonkar, A. G.; Neumann, R. D. *Colloids Surf.* **1987**, *27*, 1.

(31) Lee, L. H. *J. Polym. Sci., Part A-2* **1967**, *5*, 1103.

(32) (a) Hiemenez, P. C. *Principles of Colloid & Surface Chemistry*, 2nd ed.; Marcel Dekker: New York, 1986; p 308. (b) Brezesinski, G.; Mögel, H. J. *Grenzflächen & Kolloide*; Spektrum Akademischer Verlag: Heidelberg, 1993; p 56.

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