Behavior of a Nematic Liquid Near a Grafted Solid Surface

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Summary: We discuss the nematic order parameter and the polymer concentration profile for a solid surface carrying grafted chains. Different regimes are found, depending upon the polymer chain length and the grafting density. These ideas are compared with experimental results obtained with polystyrene in the presence of pentylcyanobiphenyl.

Keywords: polymer brush, liquid crystals, anchoring

Introduction

A number of experimental studies have been carried out on dilute polymer chains immersed in nematic solvents[1-2]. Conventional polymers (e.g.: polystyrene) tend to destroy the nematic order. This implies that the polymer can dissolve in the nematic phase only if it is small (degree of polymerisation N   100). This property is widely used in the preparation of PDLC's where the phase separation of a polymer and a liquid crystal is blocked at a typical micron length scale[3]. We discuss here in greater detail a situation which is richer experimentally: the polymer chains are grafted onto a solid wall and cannot escape from the nematic. We shall show that studies of the monomer concentration profiles near the wall could give us direct information on the behaviour of coils in nematic solvents.

Polymers grafted onto walls can also be useful for display applications[4]. Most liquid crystal devices are strongly dependent on certain ‘anchoring” properties of the cell wall with respect to the nematic. In general, a solid wall reacts on the direction of the nematic alignment but not very much on the magnitude of the nematic order parameter S: we discuss here how to achieve prescribed S values at an interface.

We first consider a theoretical point of view; we restrict our study to a case, **1)** without adsorption: the chains are attached by one extremity to the wall, but the rest of the chain does not stick to the wall, **2)** with no influence of the wall on the nematic order parameter: with no grafted chains, the boundary condition for S is $\partial S/\partial z=0$ on the wall, **3)** the nematic order is

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suppressed inside the chain. The Flory Huggins interaction parameter is modified by the nematic order of the solvent : $\chi = \chi_0+\chi_1 S^2$. If χ_1 is positive and of the order of unity, the nematic order is destroyed[5] in the chains, **4)** the chains are in good solvent in the isotropic phase ($\chi_0<1/2$), **5)** we consider the nematic order parameter as a scalar (instead of a traceless tensor of rank two). This amounts to neglect any spatial variation of the preferred axis, and to consider only the magnitude of the molecular alignment.

In a second part, we will describe the experimental results obtained with the system polystyrene (PS) + pentylcyanobiphenyl (5CB). This LC molecule has a nematic isotropic transition T_{NI} of 35.2°C. The (deuterated) PS chains are either free or chemically grafted to a silicon wafer[6]. Their structure (in the presence of 5CB) is determined as a function of T, using small angle neutron scattering for the mixtures of free chains and LC (§ IIa) and a combination of optical and neutron reflectivity techniques for the interfaces between grafted chains and bulk LC (§ IIb) [7-8].

Grafted chains in the isotropic phase ($T>T_{NI}$)[9-10]

If the coils are separate (low σ), each coil occupies roughly a half sphere with a radius comparable to the Flory radius $R_F=N^{3/5}a$. When the mean distance D between grafted chains becomes smaller than R_F, i.e. $D=\frac{a}{\sqrt{\sigma}}<aN^{3/5}$ or $\sigma>N^{-6/5}$, the chains become stretched.

The free energy per chain is the sum of the excluded volume interaction and the entropy contribution. In a mean field description, F_{ch} is given by: $\frac{F_{ch}}{kT}=\upsilon_0\frac{N^2}{LD^2}+\frac{3}{2}\frac{L^2}{R_0{}^2}$ (1)

$\upsilon_0 = a^3\,(1-2\,\chi_0)$ is the excluded volume between monomers and $R_0=aN^{1/2}$ the unperturbed radius of gyration.

F_{ch} is minimum for $L = Na\,(a/D)^{2/3}= Na\,\sigma^{1/3}$. This result can also be derived by a scaling argument. For $D<R_F$, the chain can be seen as a succession of blobs of size D, containing g_D monomers such as $g_D{}^{3/5}\,a = D$.

Solute chains in the nematic phase ($T<T_{NI}$)

The free energy of the pure nematic can be expended in power of S

$$\frac{F}{kT}\bigg|_{cm^3}=\frac{A}{2}\tau^*S^2+\frac{1}{3}BS^3+\frac{1}{2}K\bar{\nabla}S^2 \tag{2}$$

$\tau^*\approx\tau=\frac{T-T_{NI}}{T_{NI}}$ measures the distance to the transition and $\xi=\sqrt{\frac{K}{A\tau^*}}\approx\frac{a}{\tau^{*1/2}}$ defines the scale of variation of S (Figure 1). (2) is minimum for $S = S_0(T)$. Inside the chain, T_{NI} is decreased ($\tilde{A}=A+\chi_1\phi$, ϕ monomer volume fraction) and S=0. If the chains are smaller than

ξ, the nematic around the chain is disturbed on a length of order R ($S \approx S_0(1 - \frac{R}{r}e^{-r/\xi})$). For large chain, S is disturbed in a layer of thickness ξ. The free energy per chain is:

$$\frac{F_{ch}}{kT} = \upsilon_0 \frac{N^2}{R^3} + \frac{\tau\Delta H_0}{kT}R^3 + \int K\left|\vec{\nabla} S\right|^2 d^3r \qquad (3)$$

The second term represents the energy to form an isotropic droplet ($\tau\Delta H_0=\mu_I-\mu_N$, ΔH_0=latent heat). The last term is the elastic term associated to variations of S. After minimization of F_{ch} with respect to R, we find two regimes (Figure 1):

$$1)\ \text{if } R_0<\xi,\ \frac{F_{ch}}{kT} \approx \upsilon_0 \frac{N^2}{R^3} + KS_0^2R \text{ and } R \approx \left(\frac{\upsilon_0}{KS_0^2}\right)^{1/4} N^{1/2} \approx R_0 \qquad (4)$$

$$2)\ \text{if } R_0>\xi,\ \frac{F_{ch}}{kT} \approx \upsilon_0 \frac{N^2}{R^3} + \frac{\tau\Delta H_0}{kT}R^3 \text{ is minimum for } R \approx \xi^{1/3}a^{2/3}N^{1/3} \qquad (5)$$

Small chains are ideal ($R \approx R_0$) and large chains are collapsed ($R \approx N^{1/3}$) but still contain a large amount of solvent.

Small grafted chains in a nematic ($R_0<\xi$)

A) "N, Id" regime: separate coils with no interactions ($D>\xi$, i.e. $\sigma<\left(\frac{a}{\xi}\right)^2 = \sigma_\xi$)

At low σ, each chain occupies roughly a half sphere of radius R_0 and destroys the nematic order up to a larger distance ξ.

B) "I, Id" regime: separate coils with interactions ($\xi>D$, i.e. $\frac{\sigma}{\sigma_\xi} > 1$)

The coils act as electrical charges and $S - S_0$ is the resulting screened Coulomb potential ($S - S_0 \approx -S_0\frac{R}{r}e^{-r/\xi}$). For $D<\xi$, the distorsions due to different coils overlap and S becomes uniform parallel to the interface: $S = S(z)$. Inside the layer of thickness R occupied by the chains, $S = 0$. Outside this layer, S(z) increases on a scale ξ up to S_0. The free energy is now the sum of the excluded volume term, plus the free energy to create an isotropic layer of thickness R, plus a constant term associated with the interval (R, R+ ξ).

$$\left.\frac{F}{kT}\right|_{cm^2} \approx \upsilon_0 \frac{N^2}{R^3}\frac{\sigma}{a^2} + \frac{\tau\Delta H_0}{kT}R + \text{const.} \qquad (6)$$

F is minimum for $R^4 = N^2\frac{\upsilon_0 kT}{D^2\tau\Delta H_0}$, i.e. $R \approx N^{1/2}a\sqrt{\frac{\xi}{D}}$.

To describe the cross-over between these two regimes, we set: $R = N^{1/2}\, a\, f\left(\frac{\xi}{D}\right)$ (7)

with $f(x) = 1 (x \to 0)$ and $f(x) \approx x^{1/2}$ $(x>>1)$.

We call this regime the Isotropic Ideal regime: the fluid in contact with the wall is isotropic; the chains are ideal ($R \approx N^{1/2}$) but becoming more swollen: the interactions between chains help to destroy the nematic order inside one chain.

C) "I, Str" regime: overlapping coils

For $N^{1/2}a\sqrt{\frac{\xi}{D}} > D$, i.e. $D < \left(\xi R_0^{2}\right)^{1/3}$ or $\frac{\sigma}{\sigma_\xi} > \left(\frac{R_0}{\xi}\right)^{-4/3}$ the coils overlap directly. We must add to the free energy (1), the energy to form the isotropic phase :

$$\frac{F_{ch}}{kT} = \upsilon_0 \frac{N^2}{LD^2} + \frac{\tau \Delta H_0}{kT} LD^2 + \frac{3}{2}\frac{L^2}{R_0^{2}} \qquad (8)$$

The two last terms oppose chain extension. The balance of the two first terms leads to $\varphi = \left(\frac{\tau \Delta H_0}{kT\upsilon_0}\right)^{1/2}$ = const. This corresponds to the equilibrium between an internal osmotic pressure (due to excluded volume) and an external osmotic pressure (due to S). It leads to

$$L = \frac{N}{D^2 \varphi} = N\xi\left(\frac{a^2}{D^2}\right) \qquad (9)$$

which holds for $D > \xi^{3/4} a^{1/4}$ i.e. $\frac{\sigma}{\sigma_\xi} < \left(\frac{D}{a}\right)^{2/3}$. In this regime, called "I, wStr", the monomer volume fraction inside the brush is $\frac{a}{\xi}$.

For $D = (R_0^2 \xi)^{1/3}$, we find $L = D$: we have a smooth cross-over with the (I, I_d) regime.

The three terms of eq (8) are equal for $D^4 = \xi^3 a$. For $D<\xi^{3/4}a^{1/4}$, the elastic term becomes dominant and the effect of nematic ordering becomes negligible. As in eq. (1),

$$L = Na\,(a/D)^{2/3} = Na\,\sigma^{1/3} \qquad (10)$$

In this regime, called "I, sStr", the monomer volume fraction inside the brush is $\left(\frac{a}{D}\right)^{4/3}$.

Large grafted chains in a nematic: $R_0 > \xi$

Here, at large D, we have separate coils, of size given by eq. (5).

For $D < aN^{1/3}\left(\frac{\xi}{a}\right)^{1/3}$, the chains become stretched; the free energy per chain is given by eq. (8) and we recover the discussion of the preceeding paragraph, section C).

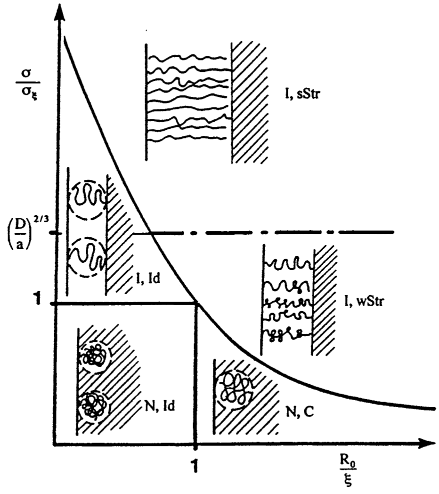

Figure 1. The 5 regimes of a grafted surface in a nematic. The region occupied by the brush is nematic or isotropic.

Free deuterated PS chains in 5CB

Far above T_{NI} (35.2°C), 5CB can be considered as a good solvent for PS. Indeed, at 90°C, PS can be easily dissolved in 5CB at any concentration. The small angle neutron scattering (SANS) intensity I(q) of dilute PS chains follows the scaling law I(q) $q^{-5/3}$ while in the semi-dilute regime, we recover the standard Orstein-Zernike behavior $I^{-1}(q) = I^{-1}(q=0)(1+q^2\zeta^2)$ (Figure 2). Both q-dependences are characteristic of a polymer in a good solvent[11]. If the

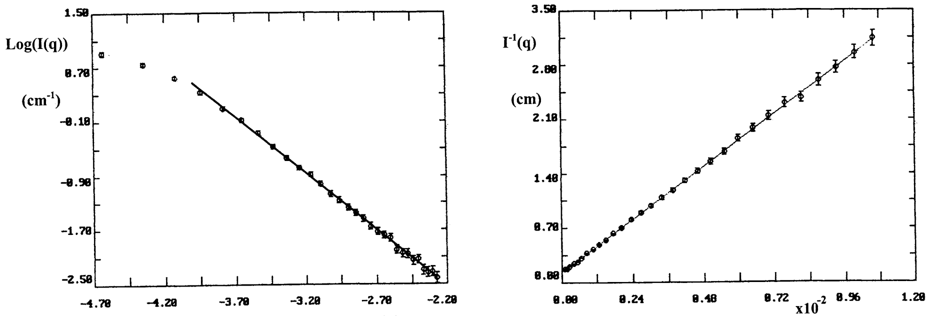

Figure 2. SANS spectra of 2 deuterated PS solutions in 5CB at 90°C. Polymer characteristics: M_w=153 400, polydispersity index=1.04. Left: dilute regime (ϕ=1%); the fit to the data (Log(I(q) vs Log(q)) gives the scaling exponent -1.66, i.e. I(q) $q^{-1.66\pm0.01}$. Right: semi-dilute regime (ϕ=5%); the fit to the data (I^{-1}(q) vs q^2) gives the screening length ζ=46.1±0.9Å.

screening length ζ (proportional to the blob size) is plotted versus ϕ (PS concentration) (Figure 3), it can be seen that it follows the scaling law $\zeta\ \ \phi^{-0.63}$, quite close to the power law characteristic of the semi-dilute regime for a polymer in good solvent ($\zeta\ \ \phi^{-0.75}$). Thus, in the absence of order correlations, i.e. far above T_{NI}, 5CB can be considered as a good solvent for PS; this is very important for the understanding of the interfacial phenomena and among the prerequisites of the theoretical description exposed above, it was the most important one.

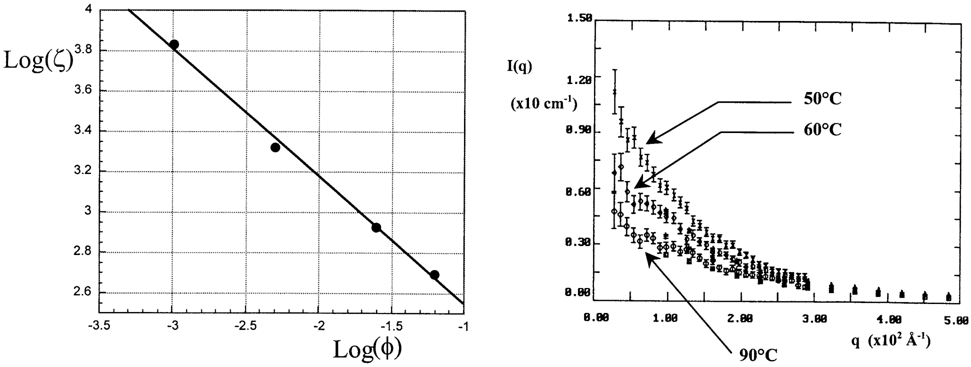

Figure 3. Left: variation of the screening length ζ with the polymer concentration in the semi-dilute regime (same polymer characteristics as for Figure 2). The solid line is a fit to the data, which yields $\zeta\ \ \phi^{-0.63\pm0.03}$. Right: Scattering intensity of a 1% PS solution in 5CB at low q, for 3 different temperatures (same polymer characteristics as for Figure 2).

When the temperature is lowered to get closer to T_{NI}, an increase of the scattering intensity at low q is observed (*cf.* Figure 3, right). This indicates that the solution is approaching a phase separation. This demixtion is due to the orientation correlations of the solvent whose range ζ_N increases as T approaches T_{NI} ($\zeta_N \propto (T-T_{NI})^{-1/2}$). These orientation correlations induce an attraction between monomers, as for a polymer chain dissolved in a solvent mixture close to a critical point[12]. This can be accounted for by an effective Flory Huggins interaction parameter $\chi_{eff} = \chi_0 + \frac{2\pi e}{a^3}\zeta_N{}^2$, where e>0 does not depend on T and has the dimension of a length.

$$\chi_{eff} = \chi_0 + \frac{T_{NI}}{T - T_{NI}}\chi_2 \qquad (\chi_2 > 0) \tag{11}$$

According to the standard (mean field) theory of phase transitions[11], it follows that the scattering intensity I(q) of **dilute** PS solutions in 5CB above T_{NI} should scale as:

$$I^{-1}(q) \propto \frac{T - T_S}{T - T_{NI}} + \frac{q^2a^2}{18}\frac{1}{\phi(1-\phi)} \tag{12}$$

T_S being the spinodal temperature, slightly higher than T_{NI}. Using equation 11, $T_S(\phi,N)$ can be calculated: $T_S(\phi,N) = T_{NI} + \dfrac{\chi_2}{\dfrac{1}{2N\phi} + \dfrac{1}{2(1-\phi)} - \chi_0}$

(13)

At $T=T_S$, the scattering intensity diverges.

This formalism accounts for the experimental data very well, as shown by Figure 4. Close to the spinodal, the PS chains are ideal, they have a gaussian statistics. An extrapolation of the scattering intensity at q=0 for different temperatures allows us to compare the data with the first term of equation 12. Again, the agreement is very good (cf. Figure 5). We did not vary the PS molecular weight (i.e. N) systematically, in the dilute regime. T_S has been determined for only 2 different polymers (at fixed ϕ): T_S is found to be higher than T_{NI} and to increase with N, in qualitative (but not quantitative) agreement with (13). If ϕ is not small (i.e. if we are not in the dilute regime), the above formalism is no longer valid. Experimentally, the scattering intensity at low q still increases when T is decreased, but I(q) does not diverge. If T is further decreased (but still above T_{NI}), a sharp up-turn of I(q) at very low q is observed (I(q) q^{-4} - Porod's law), which can be ascribed to the formation of sharp interfaces (cf. Figure 5). The phase separation does not go to completion but is frozen at a length scale of the order of 1µm; the samples turn to milky. This is due to the glassy behavior of PS at high concentration; above a certain polymer volume fraction (of the order of 60%, at room temperature), the PS chain dynamics become very slow and thus, the demixtion is nearly stopped. This property is exploited for the formation of PDLC's.

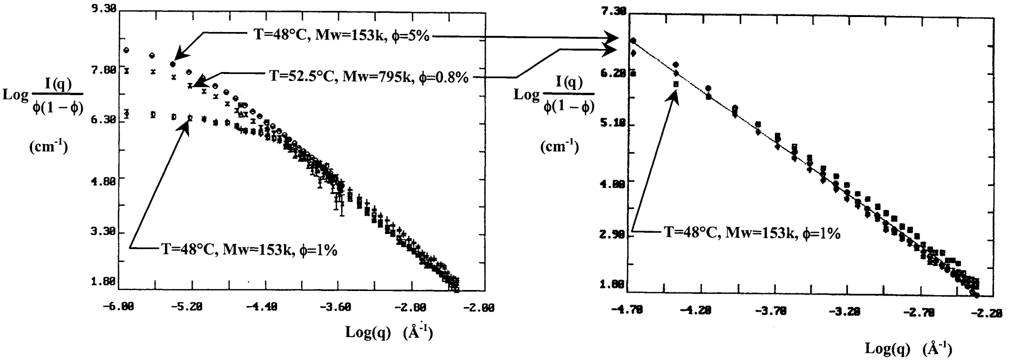

Figure 4. Scattering intensity, divided by $\phi(1-\phi)$, for 3 different PS solutions in 5CB, close to the spinodal. The right figure is a zoom of the data shown on the left, in the intermediate q-range. The solid line is a fit to the data which yields I(q) $q^{-2.00\pm0.02}$.

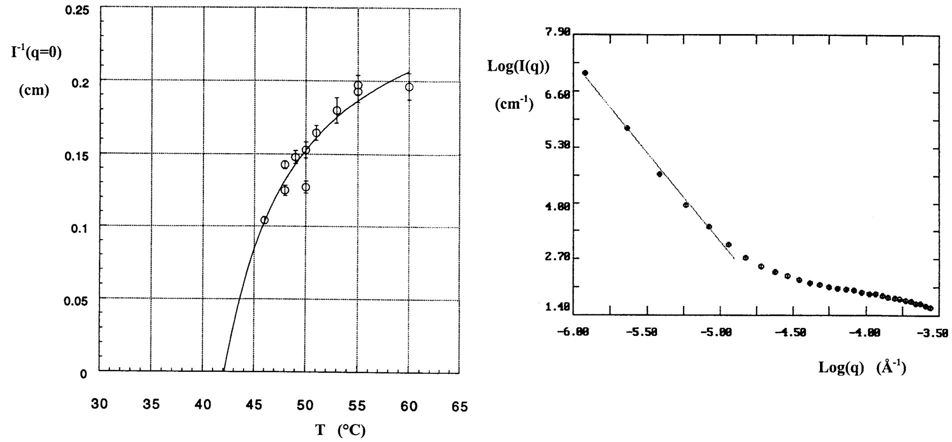

Figure 5. Left: reciprocal scattering intensity extrapolated at q=0 versus T. The solid line is a fit to the data, which yield T_S=42.1±0.5°C. Right: scattering intensity for a 30% PS solution in 5CB at 37°C (same polymer characteristics as for Figure 2). The solid line is a fit to the data which yields I(q) $q^{-4.12\pm0.15}$.

Grafted PS chains in the presence of 5CB [13]

In the isotropic state (i.e. at T above T_{NI}), a droplet of 5CB deposited onto a dry PS brush spreads. No finite equilibrium contact angle can be found. In front of the droplet edge, it can be observed that 5CB penetrates the PS brush and swells it (to reach a 5CB volume fraction of 60%, at least). The spreading laws of 5CB onto dry PS brushes are rather complicated to analyse quantitatively due to the glassy nature of PS. However, if the 5CB droplet is deposited onto a PS brush already swollen with 5CB, it spreads according to Tanner's law, characteristic of the complete wetting regime for simple liquids [14]. This behavior is consistent with the values of the surface tensions (γ_{5CB}=30dyne/cm and $\gamma_{PS}\approx$40dyne/cm at 40°C) and with the fact that above T_{NI}, as demonstrated previously, 5CB is a solvent of PS (θ solvent close to T_{NI} and good solvent, far above T_{NI}).

If T is lowered below T_{NI}, 5CB does not spread onto PS brushes anymore. A 5CB droplet deposited onto a PS brush has now a finite contact angle, whose value depends on T but not strongly on the brush characteristics. The droplet is surrounded by a wetting film, which consists of PS swollen by a certain amount of 5CB (40% at room temperature, as determined by ellispometry [8]). The droplet itself exhibits typical liquid crystalline textures when observed under polarized light (cf. Figure 6). The analysis of these textures [13,15] has allowed

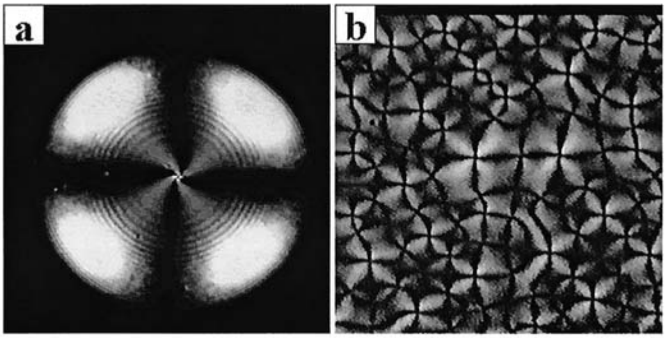

Figure 6. a) Radial texture of a 5CB droplet on grafted PS at room temperature, showing the azimuthal anchoring degeneration. b) Texture instabilities close to T_{NI}, showing memory-free anchoring.

us to characterize the anchoring of 5CB molecules at the interface between bulk 5CB and grafted PS: it is of weak energy (one order of magnitude below the anchoring at a SiO interface), conic (i.e. azimuthally degenerated and tilted - tilt angle: 72°C at room temperature) and memory free. This type of anchoring corresponds to what is expected and observed for a liquid crsytal at the nematic-isotropic interface [16]. In our case, the isotropic phase is "stabilized" by the grafted polymer; we have described this anchoring as "fluid".

A neutron reflectivity study has confirmed the homogeneous distribution of 5CB along the normal to the interface within the swollen PS brush, as shown by Figure 7.

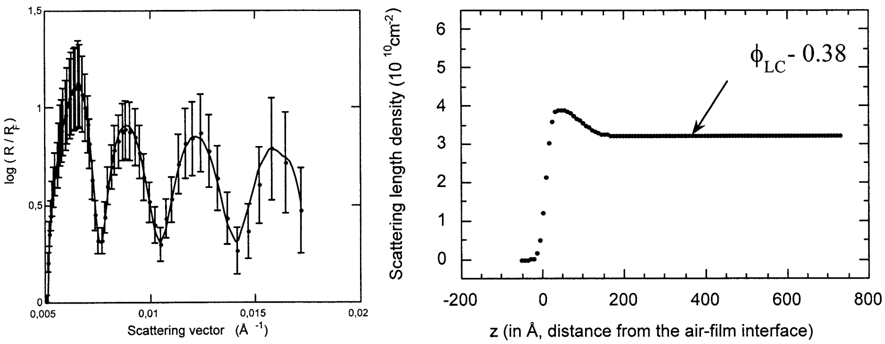

Figure 7. Neutron reflectivity study of a PS brush, saturated with 5CB molecules, at room temperature. The PS has a molecular weight of 230k g/mol and the brush has a dry thickness of 420Å. Left: measured reflectivity normalized by the Fresnel reflectivity. The solid line is a fit to the data corresponding to the scattering length density profile shown on the right. The plateau value corresponds to a 5CB volume fraction of 0.38. The (slight) enrichment in 5CB at the air film interface is due to the lower surface tension of 5CB, compared to PS.

Thus, it appears that a PS brush, within a broad range of grafting density, forms a swollen and homogeneous layer, in the presence of nematic 5CB. The LC molecules entrapped in this layer have an isotropic behavior. This corresponds to the "I,wStr" regime described in I)d.

Conclusion

Polymer brushes in the presence of a nematic solvent exhibit various structures and ordering profiles, depending upon the polymer molecular weight and the grafting density. The most interesting case (and probably the most common one) - I,wStr regime - allows the stabilization of a fluid anchoring, a key feature for the fabrication of bistable LC displays.

[1] B. Kronberg, J. Bassignana, D. Patterson, *J. Phys. Chem.* **1978**, *22*, 171.
[2] A. Dubault, C. Casagrande, M. Veyssié, *Mol. Cryst. Lett.* **1977**, *41*, 239.
[3] J.W. Doane et al. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511.
[4] Patent PCT FR 98/00909.
[5] F. Brochard, *C.R. Acad. Sc. Paris* **1980**, *290*, 485.
[6] Y. Tran, P. Auroy, *J. American Chem. Soc.* **2001**, *123*, 3644.
[7] L. Auvray, P. Auroy, in: *"Neutron, X-Ray and Light Scattering"*, P. Lindner and T. Zemb Eds, Elsevier Science Publishers B.V., 1991, 199.
[8] O. Ou-Ramdane, P. Auroy, P. Silberzan, *Phys. Rev. Lett.* **1998**, *80*, 5141.
[9] S. Alexander, *J. Phys. (Paris)* **1977**, *38*, 983.
[10] P.G. de Gennes, *Macromolecules* **1980**, *13*, 1075.
[11] P.G. de Gennes, *"Scaling Concepts in Polymer Physics"*, Cornell University Press, 1979.
[12] P.G. de Gennes, *J. Phys. Lett.* **1976**, *L59*, 37.
[13] O. Ou Ramdane, Ph.D. Thesis, Université Paris 6, 1998.
[14] P.G. de Gennes, F. Brochard-Wyart, D. Quéré, *"Gouttes, bulles, perles et ondes"*, Belin, Paris, 2002.
[15] O. Ou Ramdane et al. *Phys. Rev. Lett.* **2000**, 84, 3871.
[16] B. Jérôme, *Rep. Prog. Phys.* **1991**, *54*, 391.