RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 49, NUMBER 2 FEBRUARY 1994

# Doubly anchored nematic polymer brushes: Shear, field effects, and quasipiezoelectricity

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(Received 27 August 1993)

The shear behavior of a doubly anchored brush of liquid-crystalline polymers immersed in a nematic solvent is investigated. In such a brush the grafted polymers bridge two plates. Remarkably, the Franck nematic elasticity in this system can dominate the shear modulus. In the presence of a field the system undergoes a Fréedericksz transition modified by the bridging polymers. In particular: (i) the polymeric elasticity affects the critical field $E_c$; (ii) the shear modulus vanishes as the field approaches $E_c$; and (iii) the nematic distortion couples to a shear strain. The system exhibits quasipiezoelectricity, which is nonlinear and is not associated with any inverse effect.

PACS number(s): 64.70.Md, 61.25.Hq, 77.65.Fs

Liquid-crystalline polymers (LCP's) and their monomeric counterparts are described by a single continuum theory [1–3], differing only in the magnitude of their material constants: elastic constants, viscosities, etc. Yet, the two systems may exhibit qualitatively different phenomenology when interfaces and confinement play a role. Theoretical studies suggest a Fréedericksz-like transition may be induced by geometric confinement of solutions of LCP's in monomeric nematic fluids [4]. In marked contrast, an external field is necessary to produce a Fréedericksz transition in a pure monomeric nematic liquid crystal [1]. In this Rapid Communication we report the distinctive behavior of another system incorporating LCP's. We study nematic brushes [4] formed by terminally grafted LCP's, i.e., flat layers consisting of LCP's attached to a surface by their end groups. The polymers involved are main-chain LCP's consisting of nematogenic monomers joined by short, flexible spacer chains. Our primary interest is in "double" brushes consisting of chains with each end attached to a different surface. The brush considered is swollen by a monomeric nematic solvent subject to homeotropic anchoring conditions, i.e., the nematic director **n** at the grafting surfaces is perpendicular to the interface. Our analysis concerns the response of the nematic "double" brush to shear and to electric fields. A number of distinctive features emerge. Three regimes may be distinguished in the shear behavior. Two are due to the elasticity of the anisotropic LCP's. The third regime, which is specific to this system, is dominated by the director elasticity of the nematic solvent. This is a remarkable feature because monomeric nematics are simple fluids exhibiting no elastic response to shear, i.e., they have zero shear modulus. The Franck elasticity of nematics is due to the distortion of the director and does not respond to strains. In the double brush the nematic elasticity couples to the bridging polymers and can dominate the shear modulus. As expected, the application of an electric field gives rise to a Fréedericksz transition. However, this has two exceptional characteristics. First, in certain regimes the elasticity of the LCP's replaces the elasticity of the nematic in controlling the transition. Second, the transition is associated with shear strain. Since the shear strain of the grafting surfaces is not accompanied by a net polarization, this effect is not piezoelectric [5,6]. It is also nonlinear in the field strength and occurs only for fields above a critical field. We thus refer to it as *quasipiezoelectric.* While the response to pure shear is continuous, the Fréedericksz transition has the features of a second-order phase transition. As a result the shear modulus *vanishes* as $E^2-E_c^2$ in the vicinity of the critical field $E_c$. These distinctive effects are traceable to the coupling between the LCP's bridging the two plates and the molecular field due to the nematic order. As a result the LCP's assume anisotropic configurations [7]. Furthermore, these ellipsoidal objects align with their major axis parallel to **n**. Because the LCP's in our system bridge two mobile surfaces, the nematic distortion is coupled to the shear strain.

The system considered is of interest from a variety of perspectives. The behavior of polymer brushes under shear is a subject of current research in polymer physics [8]. The shear behavior of double brushes has been invoked in the interpretation of experiments performed using the Israelachvili force measurement apparatus. However, thus far the discussion has been confined to brushes consisting of isotropic chains. The analysis of nematic double brushes reveals qualitatively different features of interest in the design of the corresponding experiments. The relationship to lamellar mesogels [9] affords a greater potential. The double brush is an idealized elementary unit of a lamellar mesogel formed from $ABA$ triblock copolymers with a LCP $B$ block. Such mesogels are obtainable as follows: A lamellar phase of $ABA$ melt is aligned by shear and then quenched below the glass transition temperature, $T_g$, of the $A$ domains. Some of the $B$ blocks bridge different $A$ domains. Accordingly, the resulting structure is a physically cross-linked network. This thermotropic network is then swollen by a monomeric nematic solvent yielding a nematic lamellar mesogel. The distinctive behavior of nematic double

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brushes thus has a macroscopic realization in these systems. Accordingly, mesogels of this type afford an experimental system enabling the study of these effects. Furthermore, this suggests a possible strategy for the design of novel composite materials exhibiting mecano-optic and electromechanical, quasipiezoelectric effects. Finally, the structural simplicity of the nematic mesogels makes them useful as model systems for the study of liquid-crystalline networks in general [10]. Among their special features, of interest from the perspective of network elasticity, is the importance of the elasticity of the nematic solvent in determining the moduli of the nematic gel. From the liquid-crystals research perspective the interest is in the polymeric modifications of the Fréedericksz transition; in particular, the role of polymer elasticity and the coupling to the shear strain. This last point is remarkable because electromechanical effects in liquid crystals are usually due to the coexistence, at the molecular level, of shape anisotropy and dipole moment [11]. In our system the effect results from dielectric anisotropy and the coupling between the bridging chains and director field.

Before we discuss the effects themselves, it is helpful to summarize the relevant configurational features of main-chain LCP's in nematic media [4,12,7]. These reflect the coupling with the molecular field due to the nematic order. As a result the chain tends to align with **n** and vice versa. The configuration of the LCP's arises from the superposition of two contributions. Firstly, there is weak undulation due to fluctuations of the trajectory from perfect alignment with **n**. This contribution determines the chain dimension perpendicular to **n**, $R_{\perp_0}$. In a melt state $R_{\perp_0}$ may be rationalized as the result of a two-dimensional random walk of $L/l$ steps of length $l \approx kT/a_n S$ where $L$ is the length of the chain, $a_n$ is the coupling constant with the nematic field, and $S$ is the nematic order parameter. Accordingly $R_{\perp_0}^2 \approx Ll$. The second component is $n_0$ hairpin defects [13]. These abrupt reversals in the trajectory of the chain are entropically favorable but energetically penalized. The energetic penalty, due to the unfavorable orientation of the bend with respect to the nematic field, is $U_h \approx (a_n S\epsilon)^{1/2}$ where $\epsilon$ is the chain rigidity. The equilibrium number of hairpins on a LCP of length $L$ is $n_0 \approx (L/l)\exp(-U_h/kT)$. The hairpins give rise to a one-dimensional random walk along the **n** direction. The average step length is $L/n_0$ and the number of steps is $n_0$. Consequently, the chain dimension parallel to **n** is $R_{\parallel_0}^2 \approx L^2/n_0 \approx Ll\exp(U_h/kT)$. The involvement of random walks suggests that the elastic response of the LCP's is Gaussian [14]. However, in this case the elastic free energies associated with the extension of $R_\parallel$ and of $R_\perp$ are different, $F_{\rm el}(R_\parallel)/kT \approx R_\parallel^2/R_{\parallel_0}^2$; $F_{\rm el}(R_\perp)/kT \approx R_\perp^2/R_{\perp_0}^2$. Note that the elastic response of the system is very anisotropic because $R_{\parallel_0} \gg R_{\perp_0}$. Along the nematic director we have a weak "trombone" elasticity associated with the displacement of hairpins. Perpendicular to the director we find a stronger "accordion" elasticity associated with the thermal undulations. Altogether we may view the LCP's as prolate ellipsoids oriented with their major axis parallel to **n**. This and the anisotropy of the elastic response of the two axes are the two features relevant to our discussion.

For simplicity we consider the simplest possible system exhibiting the essential physics of interest. The brush is assumed to be swollen by a $\theta$ nematic solvent, i.e., the LCP's adopt meltlike configurations. We have in mind lamellar mesogels for which the hydrodynamic relaxation is very slow and the sample volume is essentially constant. Since the glassy lamellae are assumed to be perfectly rigid, the thickness of the glassy layers remains constant irrespective of the shear strain. The nematic environment is described by the standard continuum theory. To allow for the boundary conditions imposed by the homeotropic anchoring the distorted state is described by $\theta(z) = Q\sin(\pi z/H)$, where $\theta(z)$ is the angle between the director and the lamellar normal at height $0 < z < H$. $Q$ is a variational parameter serving also as an order parameter. The polymer trajectory locally follows the director field. However, it is not necessary to know the precise trajectory of the chain. In the spirit of the Alexander model [4,15] we utilize an averaged, global description of the LCP's. We also follow the "scaling" prescription and ignore all numerical prefactors. The ellipsoid LCP's are assumed to undergo uniform deformation. Consequently, their elastic free energy is determined only by $R_\parallel$ and $R_\perp$. In a nematic medium it is also necessary to allow for the spatial orientation of the ellipsoids. In the unperturbed layer the LCP's are oriented along the lamellar normal because of the homeotropic anchoring. In a sheared brush or in a distorted medium it is sufficient to characterize the overall orientation of the polymers by a uniform tilt angle $\bar\theta$. Thus, in a brush subject to shear strain $\Delta/H$ the orientation of the LCP's is specified by (see Fig. 1)

$$\Delta = R_\parallel \sin\bar\theta + R_\perp \cos\bar\theta, \quad H = R_\parallel \cos\bar\theta , \tag{1}$$

where $\bar\theta$ is the angle between the major axis of the ellipsoid and the lamellar normal and $H$ is the thickness of the layer. To relate the two descriptions we identify $\bar\theta$ with the average $\theta(z)$

$$\bar\theta = \frac{1}{H}\int_0^H \theta(z)\,dz \sim Q . \tag{2}$$

The free energy per chain consists of four terms, $F_{\rm chain} = F_{\rm dis} + F_{\rm el}(R_\parallel) + F_{\rm el}(R_\perp) + F_E$, the two elastic contributions supplemented by the distortion free energy of the nematic and the contribution of the electric field **E**. The distortion term is

$$F_{\rm dis} = (\Sigma K/2)\int_0^H (d\theta/dz)^2 dz \sim (\Sigma K/H)Q^2 ,$$

where $K$ is the nematic-elastic constant. The electric contribution is

$$F_E = -(\Sigma|\Delta\epsilon|E^2/2)\int_0^H \sin^2\theta\, dz$$

$$\sim -\Sigma|\Delta\epsilon|E^2(Q^2 - \tfrac{1}{4}Q^4) .$$

Here $\Sigma$ is the area per chain, **E** the electric field, and $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$ the dielectric anisotropy of the medium. If $\Delta\epsilon > 0$ ( $< 0$) we apply the field parallel (perpendicular) to the plates, so the field always favors alignment parallel to the plates. Strictly speaking, one should also allow for

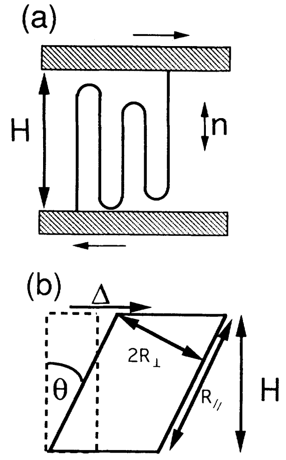

FIG. 1. A single bridging LCP undergoing shear. (a) The undistorted bridging chain in a slit imposing homeotropic anchoring. (b) The geometry before (dotted line) and after (full line) shear. The chain extension along the nematic director, **n**, is $R_\parallel = H/\cos\theta$. The shear displacement Δ consists of two terms: one is due to chain tilt, $H\tan\theta$, and the other is due to the "accordion" expansion of the chain perpendicular to **n**, $R_\perp \sin\theta$.

the flexoelectric contribution to the free energy density [1,11], $-\mathbf{P}\cdot\mathbf{E}$. Here **P**, the electric polarization of the medium due to the nematic distortion, is

$$\mathbf{P} = f_\parallel \mathbf{n}\nabla\cdot\mathbf{n} + f_\perp(\nabla\times\mathbf{n})\times\mathbf{n}$$

and $f_\parallel$ and $f_\perp$ are the flexoelectric coefficients with dimensions of electrical potential. In the following we mostly ignore this effect since the phenomena considered would occur even when both $f_\parallel$ and $f_\perp$ vanish. Altogether,

$$F_{\text{chain}}/kT = (\Sigma K/kTH)Q^2 + R_\perp^2/R_{\perp_0}^2 + R_\parallel^2/R_{\parallel_0}^2 - \Sigma|\Delta\epsilon|E^2(Q^2 - \tfrac{1}{4}Q^4) \; . \qquad (3)$$

This free energy can be expressed as a function of $\Delta, H$ and $\bar{\theta}$ by using Eqs. (1) and (2) to obtain $R_\perp$ and $R_\parallel$ in these terms. In particular, $R_\perp = (\Delta - H\tan\bar{\theta})/\cos\bar{\theta}$ and $R_\parallel = H/\cos\bar{\theta}$. Upon substituting these expressions into (3) and expanding the result around $\bar{\theta}=0$ to fourth order in $\bar{\theta}$ we find

$$F = (\mu_\parallel + \mu_\perp\delta^2) - 2\mu_\perp\delta\bar{\theta} + (\mu_\parallel + \mu_n + \mu_\perp - \sigma_E + \mu_\perp\delta^2)\bar{\theta}^2 - \tfrac{8}{3}\mu_\perp\delta\bar{\theta}^3 + (\tfrac{2}{3}\mu_\parallel + \tfrac{5}{3}\mu_\perp + \tfrac{1}{4}\sigma_E + \tfrac{2}{3}\mu_\perp\delta^2)\bar{\theta}^4 \; . \qquad (4)$$

Here $\delta = \Delta/H$ and for convenience we have written the free energy per unit volume, $F = F_{\text{chain}}/H\Sigma$, where $\Sigma H$ is the volume per chain. $F$ is expressed in terms of the moduli contributed by each component in the system [16]. There are three such moduli, two of them associated with the polymer, $\mu_\parallel = kTH/R_{\parallel_0}^2\Sigma$ and $\mu_\perp = kTH/R_{\perp_0}^2\Sigma$. The third, $\mu_n = K/H^2$, arises from the nematic solvent. These moduli are simply related to the "spring constants" determining $F_{\text{chain}}$, $\nu_n = \Sigma K/H^3$, $\nu_\parallel = kT/R_{\parallel_0}^2$, and $\nu_\perp = kT/R_{\perp_0}^2$. The symbol $\sigma_E$ in (4) is $|\Delta\epsilon|E^2$ and is proportional to the electric "Maxwell" stress [17]. In the absence of a field, minimization of (4) with respect to $\bar{\theta}$ leads to $\bar{\theta} = \delta\mu_n/(\mu_n + \mu_\parallel + \mu_\perp + \delta^2\mu_\perp)$. Upon substitution in (4) this leads to $F = \mu_\parallel + \mu_e\delta^2$ where $\mu_e$, the effective modulus, is

$$\mu_e = \mu_\perp(\mu_n + \mu_\parallel)/(\mu_n + \mu_\parallel + \mu_\perp) \; . \qquad (5)$$

In general, we always have $\mu_\perp \gg \mu_\parallel$. Three elastic regimes are now distinguishable. (i) When $\mu_\parallel \gg \mu_n$ then $\mu_e \approx \mu_\parallel$ and the elastic response is dominated by the "trombone" elasticity along the director. (ii) When $\mu_\perp \gg \mu_n \gg \mu_\parallel$ then $\mu_e \approx \mu_n$ and the nematic elasticity dominates. (iii) When $\mu_n \gg \mu_\perp$ the perpendicular "accordion" elasticity dominates and $\mu_e \approx \mu_\perp$. Note that the nematic and parallel moduli add in series, and that the compound modulus $\mu_n + \mu_\parallel$ adds to the perpendicular modulus $\mu_\perp$ in parallel. This implies that the nematic modulus dominates when it is *larger* than the parallel modulus but *smaller* than the perpendicular modulus.

To gain insight into the attainability of the various regimes we choose $H \approx R_\parallel$, $\Sigma = R_{\perp_0}^2$. This is roughly the regime expected for equilibrium diblock phases. For our theory to be valid we require lateral homogeneity, so $\Sigma$ can be no larger than $R_{\perp_0}^2$. We define $N_h = N/n_0$, which is the number of monomers between hairpins in the chain. We also set all microscopic lengths to be equal, so that $l = a$ and the nematic elastic constant is $K = kT/a$. The nematic elasticity dominates when (a) $\mu_n < \mu_\perp$ which implies $1 < N_h^{3/2}N^{-1/2}$, and (b) $\mu_n > \mu_\parallel$ which implies $N > N_h$. This last inequality is automatically true in a system with one or more hairpins. It is thus easy to satisfy $\mu_n > \mu_\parallel$. The remaining inequality $\mu_n < \mu_\perp$ depends on the number of hairpins per chain and hence on the temperature [18]. At high temperatures $N_h$ will be small and $\mu_\perp$ will be larger than $\mu_n$. The system is then dominated by the *weaker* nematic elasticity. As the temperature is increased, the number of hairpins increases, the perpendicular elasticity becomes weaker, and eventually dominates the elastic response. Finally it is important to note that the stress-induced distortion gives rise to an electric polarization

$$\mathbf{P} = -(\partial\theta/\partial z)(f_\parallel \sin^2\theta - f_\perp\cos^2\theta, 0, (f_\parallel + f_\perp)\sin\theta\cos\theta) \; .$$

**P** can have components parallel and perpendicular to the plates, but the net, or average polarization $\langle\mathbf{P}\rangle$ is zero. The net charge created on each plate, the $z$ component of **P**, is also zero.

To allow for the effect of an electric field it is necessary to use the full free energy (4), including $F_E$. Considering terms only up to second order in $\bar{\theta}$ and minimizing over $\bar{\theta}$, we find $\delta = \theta/(1+\theta^2)$. Upon substitution into (4) we obtain $F = \mu_\parallel + \mu_e\delta^2$, where the effective modulus in the presence of the field is

$$\mu_e(E) = \mu_\perp(\mu_n + \mu_\parallel - \sigma_E)/(\mu_n + \mu_\parallel + \mu_\perp - \sigma_E) \; . \qquad (6)$$

$\mu_e(E)$ specifies the location of the Fréedericksz transition and the field dependence of the shear modulus. The Fréedericksz transition occurs when $\mu_e = 0$, i.e., at $\mu_n + \mu_\parallel = \sigma_E^*$. In the absence of polymers the transition would take place at $\sigma_E^* = \mu_n$. In the presence of polymers the distortion must also overcome polymer elasticity, and the transition occurs at a higher field. The polymer elasticity never dominates the field-driven transition, since, as argued above, $\mu_n > \mu_{\parallel}$. The second important effect is the $E$ dependence of $\mu_e$. The electric stress $\sigma_E$ acts as a negative modulus. As the undistorted state approaches the transition the modulus decreases linearly with $\sigma_E$, i.e., $\mu_e \sim (E_c^2 - E^2)$. The application of a field thus softens the elasticity of the system. The field-induced displacement above the transition is also of some interest. To obtain this it is necessary to minimize the full free energy expression, (4), with respect to $\bar{\theta}$ and $\delta$. This yields $\delta \approx \sqrt{\sigma_E/\sigma_E^*} - 1$. The displacement is thus nonlinear in the field. In this respect our system differs markedly from ordinary piezoelectric materials.

In this Rapid Communication we have presented a brief study of a nematic double brush. This system exhibits four interesting and interrelated effects. The first of these is independent of any field effects, while the remaining three are field dependent. (i) The nematic elasticity can dominate the shear modulus by coupling to the bridging polymers. In marked contrast, ordinary nematic materials show no shear modulus. (ii) The modulus of the system can be softened by the application of an electric field. (iii) The system undergoes a Fréedericksz transition at a field strength which depends on the presence of bridging polymers. (iv) The material exhibits quasipiezoelectricity, in that it shears under application of a field, but only above a critical field, and then nonlinearly in the field strength. From the point of view of monomeric nematics (i) is the most unusual feature. Although monomeric nematics exhibit an elastic response this "elasticity" is due to distortions of the director field and is unrelated to the displacement of the fluid molecules. In our case the nematic and the polymer elasticities are coupled to produce a material where the nematic elastic constants affect the shear modulus. From the perspective of materials science our system shows quasipiezoelectricity, which is nonlinear and has no inverse effect.

This research was partially funded by the NSF under Grant Nos. DMR-92-57544 and DMR-91-17249. The Laboratoire de Physique de la Matière Condensée is "Unité de Recherche Associée du CNRS No. 792."

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