RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 49, NUMBER 3 MARCH 1994

Cylindrical phases of isotropic diblock copolymers as giant wormlike nematic liquid crystals: Frank elasticity and Fréedericksz transitions

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(Received 22 November 1993)

Melts of unsymmetric diblock copolymers in the strong segregation limit can form a system of cylindrical micelle worms. We describe this composite material as a giant nematic phase, and calculate the Frank bend constant. As a nematic phase the giant worms are novel for three main reasons. (1) The diameter is of the order of 100 Å, i.e., about 100 times larger than ordinary nematic phases. (2) The system is self-organized and its properties can be tailored by choosing the lengths of the diblocks. (3) The system, despite its large size, exhibits a Fréedericksz transition at a critical voltage V_c comparable to that of monomeric nematic phases. We calculate how V_c depends on the microscopic diblock parameters. A macroscopic measurement of V_c allows the measurement of one of these parameters.

PACS number(s): 61.30.Gd, 62.20.Dc, 61.41.+e

Diblock copolymers are materials which consist of two different polymer chains irreversibly tethered together at one end. At high temperatures the two blocks are uniformly mixed. At low temperatures the chains are driven to phase separate for enthalpic reasons. Irreversible tethering makes macrophase separation impossible, and microphase separation into structures of the order of 100 Å is the result. The mesophases formed can be lamellae, ordered arrays of cylinders or spheres, and various bicontinuous phases [1]. They are analogous to phases formed in surfactant systems, and also to phases formed by metallic alloys, but on a much larger spatial scale. In this study we consider the case of melts of diblocks which form cylinders in the strong segregation limit. Experimentally these are readily observed and their formation is understood theoretically [2]. These cylinders consist of a nucleus formed by one of the blocks surrounded by a corona of the other block. At low temperatures a sharp interface separates the two. The chains in each region are crowded and stretch away from the interface forming a polymer brush [3]. The elasticity of ordered mesophases is currently of much interest [4] as is the effect of electric fields upon polymer phases [5,6], and nematic polymers in general [7,8]. This study combines elements of all three.

The novel aspect introduced here is to describe the cylinders as a giant nematic liquid crystal phase, with the nematic director aligned along the cylinder axes. Nematic liquids are simple ordered fluids and are interesting from a number of perspectives. In particular, they can undergo a second order distortional transition induced by external electric or magnetic fields—the Fréedericksz transition [9]. This transition is of great technological importance in display devices and enables the measurement of the Frank nematic elastic constants. Here we consider the bend geometry, where the cylinders are aligned perpendicular to two plates and a voltage is applied parallel to the plates (Fig. 1). At low voltages the anchoring and bend penalty favors alignment perpendicular to the plates. The applied field, for a system of positive dielectric anisotropy, $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} > 0$, favors alignment parallel to the plates. At a critical voltage $V_c = \pi\sqrt{K_{\text{bend}}/\epsilon_a}$ the electric field term causes a distortion and the director gains a component parallel to the plates. Here K_{bend} is the Frank bend constant. We calculate K_{bend} and in so doing calculate the persistence length of the worms. We find a critical voltage which depends weakly on the degree of polymerization N, and should be of order $N^{1/3}$ volts for randomly chosen polymers, i.e., of the same order as the critical voltage for monomeric nematic phases. It is thus readily observable in laboratory experiments and should allow the measurement of some diblock properties. When it occurs in a crosslinked diblock it should provide an interesting electromechanical effect.

We consider an isotropic diblock copolymer, consisting of fN A monomers and $(1-f)N$ B monomers, where N is the total degree of polymerization. Each block is assumed to have the same monomer statistical segment length b and the same monomer volume v. We first remind the reader of the properties of the cylindrical phase in the undistorted state [2]. The undistorted cylinders consist of a nucleus of radius R_n, of A monomers and a corona, of B monomers which extends to radius R_c.

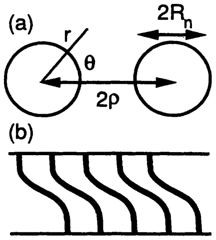

FIG. 1. (a) A cross section of the torus, showing the coordinate system used. (b) A sketch of the distorted state of the cylinders having undergone the Fréedericksz transition.

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1063-651X/94/49(3)/1811(4)/$06.00 49

By conservation of volume $R_c^2/R_n^2 = 1/f$. The free energy of a chain of N monomers is $\frac{3}{2}kTb^{-2}\int_0^N dn(d\mathbf{r}/dn)^2$ where $\mathbf{r}(n)$ is the position of the nth monomer. The free energy per unit length of any diblock micellar phase consists of three terms: (1) the energy of the stretched chains in the corona of the micelle; (2) a similar free energy for the core or nucleus; and (3) the surface free energy, so $F = F_c + F_n + F_s$. Here [2] $F_s = 2\pi\gamma R_n$, $F_c = F_s 6\ln f(12\ln f - 2\pi^2)^{-1}(R_n/R_{n0})^3$, and $F_n = F_s\pi^2(2\pi^2 - 12\ln f)^{-1}(R_n/R_{n0})^3$. The subscript 0 refers to equilibrium quantities in the unbent state. In this problem there is a constant energy scale per unit volume $2\gamma/R_{n0}$, which factors out of all the free energy expressions. The system is specified by one variable f. There is only one length scale R_{n0}, the equilibrium radius of the core, which in this paper always refers to the unbent state. By comparing the free energy of cylinders with other geometries cylinders are predicted to form when $0.12 < f < 0.28$. Note that R_{n0} itself depends on f. This dependence can be expressed explicitly as $R_{n0}^3 = L^3 4\pi^2 f^2/(\pi^2 - 6\ln f)$, where L is the thickness of the A region in a symmetric ($f = 1/2$) *lamellar* phase with the same N.

To calculate the bend energy of a cylinder it is sufficient to bend it into a torus of radius ρ (Fig. 1) [10]. Our assumptions are a subset of those used in the unbent case [2]. We assume that the chains move radially away from the cylinder axis in straight lines. We calculate the surface and nuclear energies exactly. The coronal energy is calculated using the Alexander–de Gennes approximation [11]. The nucleus may distort, a feature which significantly lowers the bending free energy. We use a coordinate system centered on the cylinder axis (Fig. 1). As a chain travels from the cylinder axis to the tip of the corona it explores a certain volume which is a function of the distance traveled, r. By elementary geometry the volume taken up by the toroidal wedge between r and $r + dr$ and θ and $\theta + d\theta$ is $dV = 2\pi(\rho - r\cos\theta)rd\theta dr$, where θ is defined in the figure. The volume is a function of θ, i.e., at $\theta = 0$ it is minimal while at $\theta = \pi$ it is maximal. This implies that the equilibrium grafting density and nuclear radius depend on θ. Knowing how dV depends on the coordinates we can calculate the coronal and nuclear stretching terms. The area perpendicular to the trajectory at a distance r is $S(r) = 2\pi(\rho - r\cos\theta)rd\theta = [(\rho/L)S_2(r) - \frac{1}{2}S_3(r)\cos\theta]d\theta$ where $S_2(r) = 2\pi rL$ and $S_3(r) = 4\pi r^2$ are the areas seen in the cylindrical and spherical case. As noted by Fredrickson [10], we can use Semenov's free energy expressions [2] for spheres and cylinders to obtain the nuclear free energy exactly. Thus we have a free energy per unit length of $dF_n = (2\pi)^{-1}[F_{n2}(r) - \frac{1}{2}\beta F_{n3}(r)\cos\theta]d\theta$ where $F_{n2} = F_{n0}\xi^4, F_{n3} = (4/5)F_{n0}\xi^5$. Here we have defined a dimensionless measure of the nuclear cross section, $\xi(\theta) \equiv R_n(\theta)/R_{n0}$, and a dimensionless curvature $\beta \equiv R_{n0}/\rho$. The nuclear free energy per unit length is then

$$F_n = F_{n0}\langle\xi^4(1 - \tfrac{2}{5}\beta\xi\cos\theta)\rangle, \qquad (1)$$

where $\langle u\rangle \equiv (2\pi)^{-1}\int_0^{2\pi} d\theta u(\theta)$. For the coronal terms there is no longer a linear dependence on $S(r)$ and we need to make an explicit calculation. The stretching energy of n_c chains is $\frac{3}{2}kTb^{-2}n_c\int_{R_n}^{R_c} dr(dr/dn)$. Now $dr/dn = (dr/dV_c)(dV_c/dn)$, where dV_c is the volume explored per chain, i.e., $dV_c = dV/n_c$ and $dV_c/dn = v$. We thus have $\frac{3}{2}kTvb^{-2}n_c^2\int_0^{R_c} dr 1/S(r)$. By volume conservation $n_c Nv = \int_{R_n}^{R_c} dr S(r)$, so

$$F_c = F_{c0}\frac{f^2}{\ln\frac{1}{\sqrt{f}}} \times \left\langle \eta^4\xi^4\left(1 - \frac{2}{3}\beta\eta\xi c\right)^2 \ln\left(\eta\frac{(1 - \beta\xi c)}{(1 - \beta\xi\eta c)}\right)\right\rangle, \qquad (2)$$

where $\eta \equiv R_c(\theta)/R_n(\theta)$ measures the coronal cross section, and $c \equiv \cos\theta$. The remaining term in the free energy is the interfacial term

$$F_s = F_{s0}\left\langle(1 - \beta\xi\cos\theta)\left[\xi^2 + \left(\frac{d\xi}{d\theta}\right)^2\right]^{1/2}\right\rangle. \qquad (3)$$

There are two further equations, the first is the relation between the nuclear radius and the coronal radius, which is obtained by calculating the volume in a toroidal wedge of size $d\theta$

$$\eta^2 - \frac{2}{3}(\cos\theta)\beta\xi\eta^3 = (1/f)\left(1 - \frac{2}{3}(\cos\theta)\beta\xi\right). \qquad (4)$$

The second gives the volume per unit length

$$V = \pi R_{n0}^2 f^{-1}\langle\xi^2(1 - \tfrac{2}{3}\beta\xi\cos\theta)\rangle. \qquad (5)$$

Equations (1)–(5) are sufficient to solve the problem. Note that for an unbent cylinder we have $\beta = 0$, $\eta = f^{-1/2}$, and $\xi = 1$, and all the free energies reduce to their equilbrium values.

We need to calculate the change in free energy per unit volume $(F_n + F_c + F_s)V^{-1}$. In bending the cylinder we allow the cross section to change, so we write $\xi(\theta) = 1 + \beta\epsilon(\theta)$. The free energies and volume per unit length in the bent case are $F_c/F_{c0} = 1 + 4\beta\langle\epsilon\rangle + \beta^2(h + g\langle c\epsilon\rangle + 6\langle\epsilon^2\rangle)$, $F_n/F_{n0} = 1 + 4\beta\langle\epsilon\rangle + \beta^2(6\langle\epsilon^2\rangle - 2\langle c\epsilon\rangle)$, $F_s/F_{s0} = 1 + \beta\langle\epsilon\rangle + \beta^2(\frac{1}{2}\langle\epsilon'^2\rangle - 2\langle c\epsilon\rangle)$, and $V/V_0 = 1 + 2\beta\langle\epsilon\rangle + \beta^2(\langle\epsilon^2\rangle - 2\langle c\epsilon\rangle)$. The total change in free energy per unit volume $(F_c + F_n + F_s)/V$ is thus

$$\beta^2 F_{s0}V_0^{-1}[(F_{c0}/F_{s0})h + \langle\tfrac{1}{2}\epsilon'^2 + \tfrac{3}{2}\epsilon^2 + E\epsilon\cos\theta\rangle]. \qquad (6)$$

Here $V_0 = \pi R_{n0}^2 f^{-1}$, $h(f) \equiv (18f\ln f)^{-1}(4f\ln f + 40f^{1/2} - 21f - 19)$, $g(f) \equiv \frac{20}{3}(\ln f)^{-1}[2 - \ln(f) - 2f^{-1/2}]$, and $E(f) = (F_{c0}/F_{s0})(2 + g) > 0$ are all positive.

First consider the case where the nucleus is undistorted, so $\epsilon(\theta) = 0$. In this case there is only one term in the free energy $\delta F = F_{c0}V_0^{-1}\beta^2 h$, which arises solely from the corona, and is always positive. Now we allow the nucleus to distort. The second term in (6), $\langle\frac{1}{2}\epsilon'^2 + \frac{3}{2}\epsilon^2 + E\epsilon\cos\theta\rangle$, then comes into play. This is exactly the action for a classical particle of displacement ϵ, with θ interpreted as time. The particle moves in an inverted parabolic potential, plus a periodic force $\cos\theta$. Physically these terms arise as follows. The kinetic energy term ϵ'^2 arises from the curvature dependence of the surface tension (3). The potential $\propto \epsilon^2$ causes resistance to growth or shrinking of the radius, since we are bending a cylinder which has the equilibrium radius. The term in $\cos\theta$ describes the angular coupling of the bend.

We now need to minimize (6) over all nuclear distortions. The Euler-Lagrange equation for $\epsilon(\theta)$ is the equation of motion for our fictitious particle, $\epsilon'' = 3\epsilon + E\cos\theta$. By inspection this has the solution $\epsilon(\theta) = -(E/4)\cos\theta$. The free energy change per unit volume upon bending is then $\delta F = V_0^{-1}\beta^2[F_{c0}h(f) - \frac{1}{16}F_{s0}E^2(f)]$. Note that by distorting the nucleus the bending energy is lowered, by a significant factor, of about 40%. However, a plot of δF shows it is always positive, i.e., the system is stable against bending deformations.

The cross section of the cylinder in the distorted state obeys the equation $r(\theta)/R_{n0} = 1 - (E/4)\beta\cos\theta$. We can compare this to the equation for a circle with unit radius and center $(x = \omega, y = 0)$, $r = 1 + \omega\cos\theta - \frac{1}{2}\omega^2\sin^2\theta$, for $\omega \ll 1$. To first order our distorted circle corresponds to an outward displacement of the cylinder axis, away from the axis of the torus, by $\frac{1}{4}R_{n0}\beta E$. This displacement is of course small compared with the imposed radius of curvature ρ; the actual radius of curvature is $\bar{\rho} = \rho(1 + \frac{1}{4}\beta^2 E)$. The cross section is still approximately circular. However, the chains no longer have purely radial trajectories with respect to this circle, and the nucleus is distorted.

When a section of an ordinary nematic fluid is bent into a torus of radius ρ the free energy per unit volume is $\frac{1}{2}K_{\mathrm{bend}}|\mathbf{n}\times(\nabla\times\mathbf{n})|^2 = 2\rho^{-1}K_{\mathrm{bend}}$. This provides the required bend constant $K_{\mathrm{bend}} = (2\pi)^{-1}f(F_{c0}h - \frac{1}{16}F_{s0}E^2)$. We note in passing that this calculation also gives us the persistence length [12] of cylindrical diblock worms in a homopolymer of large molecular weight. The result, $l_p = 4\pi(kT)^{-1}\gamma R_{n0}^3[F_{c0}/F_{s0}h - \frac{1}{16}E^2]$, can be much larger than that for a single polymer chain $l_s \sim a$, because of the N dependence of $R_{n0} \sim a(fN)^{2/3}$ [2]. The ratio of l_p to l_s should be about $(fN)^2$, which can be substantial. Indeed micrographs of such worms [13] show this large persistence length. Here we have calculated the bend constant in the regime where the worms are free to grow or shrink in radius. If this freedom is removed, as it would be at short times, the bending energy will be slightly different. We have also done this calculation and find no change to the term in β^2.

The second ingredient in the Fréedericksz transition is the dielectric anisotropy. The microphase separation and geometric organization of the two blocks induces this anisotropy. This has previously been used in the weak segregation limit of lamellar systems for alignment purposes [6]. The dielectric anisotropy of a system of cylinders of dielectric constant ϵ_c embedded in a medium of dielectric constant ϵ_m is a nontrivial problem, first solved by Lord Rayleigh [14]. The result for $f \ll 1$ is

$$\epsilon_a = \epsilon_\parallel - \epsilon_\perp = \epsilon_m f\left(\frac{\epsilon_c}{\epsilon_m} - 1 - \frac{2\Delta}{1 - f\Delta}\right), \qquad (7)$$

where $\Delta \equiv (\epsilon_c - \epsilon_m)/(\epsilon_c + \epsilon_m)$. For the diblock problem $f\Delta \ll 1$, so $\epsilon_a \approx f(\epsilon_m - \epsilon_c)^2/(\epsilon_m + \epsilon_c)$. Giant diblock micelles, unlike ordinary monomeric liquid crystals, exhibit only positive dielectric anisotropy.

The analytical form for the critical voltage V_c can be found using our expressions for K_{bend} and ϵ_a. The expression is cumbersome, but it can be well approximated by

$$V_c = [\gamma L(\epsilon_m + \epsilon_c)/(\epsilon_m - \epsilon_c)^2]^{1/2}(0.971 - 0.683f). \qquad (8)$$

To obtain an estimate of the voltage we set $\gamma = kT/a^2$, $\epsilon_m + \epsilon_c = \epsilon_0$, and $\epsilon_m - \epsilon_c = \epsilon_0$, where $a \sim 1$ Å is a monomer size and ϵ_0 is the permittivity of free space. Noting that $L \sim aN^{2/3}$ we find $V \approx N^{1/3}$ volts. The voltage depends weakly on the degree of polymerization and will vary between about 1 V for short polymers up to 100 V for the longest polymers. It is thus readily accessible in laboratory experiments and will allow measurements of microscopic diblock properties such as surface tension.

We have neglected several minor effects in this study and we list two here. (1) We have studied the distortion of a *single* cylinder. For a diblock in a homopolymer melt this is an excellent approximation. For a melt of diblocks each micelle is surrounded by six adjacent micelles, which distort the cylindrical shape to that of a hexagon. The corrections caused by this distortion have been calculated recently [15] and have been shown to be very small. This is essentially because they occur near the tip of the corona, which has a low effective grafting density and a low modulus [4]. (2) Giant micellar worms can change their morphology and even break under the influence of a strong enough field. This effect can be neglected, since at the critical field the electrical energy per unit volume is $\sim K_{\mathrm{bend}}/H^2$, whereas the other energies are of order $K_{\mathrm{bend}}/R_{n0}^2$, where H is the plate separation.

We have calculated the bend constant for the worms. For nematic phases there are two other elastic constants, splay and twist. On dimensional grounds the twist constant should be of the same form as the bend constant $K_{\mathrm{twist}} \sim \gamma R_{n0}G(f)$, where G is some well behaved function of f. The splay constant is more problematical. For infinitely long polymers splay, infinite wavelength splay is impossible because their are no chain ends [8]. For giant worms, splay is possible, by breaking the worms. In a spherically splayed geometry the area increases as r^2 and hence the number of ends created per unit volume is $\sim rdr/(r^2dr) \sim r^{-1}$. The free energy per unit volume is thus ur^{-1}, where u is a constant. For classical nematic phases the splay free energy per unit volume is $K_{\mathrm{splay}}r^{-2}$. Thus the inifinite wavelength splay constant for giant worms diverges. These elastic constants, though important for some deformations, play no part in the transition considered here [16]. We conclude by noting an interesting effect which will occur if the diblocks are permanently crosslinked in the ordered phase. The system then forms an ordered rubber in which the distortion of the director is directly related to a displacement of the cylinders. Such a rubber would show an electromechanic effect, i.e., a relative displacement of the two plates caused by the application of a field [17].

The calculation of the bending constant arose in part out of a suggestion by Matt Tirrell. The author thanks Fred MacKintosh for useful discussions. The author acknowledges partial support from the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the NSF under Grant Nos. DMR-92-57544 and DMR-91-17249.

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