Nanoscale manipulation of lamellar copolymers using electric fields

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Abstract. Block copolymers can self-assemble into lamellar and cylindrical phases with a fundamental period of 10–100nm. These nanoscopic phases are a basis for a great range of applications in nanotechnology. We describe how electric fields can be utilized to tune the lamellar period of copolymers that consist of liquid-crystal sub-units. Copolymers that are swollen in liquid-crystals have anisotropic chains and liquid-crystals have a dielectric anisotropy. We evaluate the critical electric field required to tilt the liquid-crystal director relative to the lamellar normal in terms of the repulsive interaction between the chemical dissimilar copolymer blocks. We show that the tilting of the liquid-crystal director can lead to an adjustment of the lamellar period with an amplitude that is proportional the chain anisotropy. This reversible tuning of the lamellar period of block copolymers can lead to interesting applications in nanotechnology.

1. Introduction

Block copolymers consists of two or more incompatible polymers that are covalently bonded together. To minimized the interfacial energy between dissimilar polymer blocks, a melt of block copolymers often self assemble into nano-periodic structures. Typical ordered phases of block copolymers include lamellar, cylindrical and cubic phases [1]. The lattice parameter of these block copolymer crystals depends on the size of the polymer chains and lies within the range of 10-100nm.

Block copolymers are important in condensed matter physics research due to their rich phase behavior. They also offer promising applications in nanotechnology due to their regular nanometer-scale patterns [2]. Research efforts in block copolymers have focused on how to direct the self-assemble process in order to obtain defect-free patterns and as well as on how to orient anisotropic block copolymer structures. Recently the has been some research efforts on how to obtain block copolymers with tunable characteristic length-scales. Such block copolymers are useful in the fabrication of sensory and display devices [3, 4].

In this article we investigate the behavior of electrically tunable block copolymers that incorporate liquid-crystals. This study is motivated by the rich coupling between the block copolymer and liquid-crystal sub-systems. There is a coupling between polymer shape and liquid-crystal order as illustrated in Fig. 1. There is also a coupling between the liquid-crystal director and the anisotropy of the block copolymer microstructure. For example when the immiscible blocks microphase separate into layers, the liquid-crystal director is coupled to the layer normal. This coupling is unique to the case liquid-crystal block copolymers since they are stretchable. It is a soft parameter for these system and it leads to novel elastic properties such as semi-soft elasticity [5]. A melt of liquid-crystal diblock copolymers can respond to relative weak electric fields compared to conventional block copolymers due to the dielectric anisotropy of the constituent liquid-crystals. Our theoretical analysis shows that the layered liquid-crystal block copolymers can exhibit unusually large electrically induced layer contractions. This behavior is desirable in the fabrication of nanotechnological devices such as broad-wavelength electrically tunable block copolymer photonic crystals.

2. Model

We consider a system of diblock copolymers with side-chain liquid crystals as illustrated in Fig. 1. We can describe this system using two fields: $\psi(\vec{r})$ and $\theta(\vec{r})$, the deviation of the local density of one block species from its spatial average and local orientation of the liquid-crystals director, respectively. The free energy describing microphase separation of the immiscible polymers in the limit of weak segregation is given as [5]

$$\begin{aligned} \frac{Na^3}{k_BT}F_{ab} &= \int d^3r\,\{\tau\psi^2+\psi^4/12+ \\ &+ \xi^2\left[q_0^2\psi+A(\theta)\partial_{xx}\psi+B(\theta)\partial_{yy}\psi+C(\theta)\partial_{xy}\psi+\partial_{zz}\psi\right]^2+ \\ &+ K_1(\nabla\cdot\mathbf{n})^2+K_3(\mathbf{n}\times\nabla\times\mathbf{n})^2+\alpha\left(\mathbf{n}\cdot\vec{\nabla}\psi\right)^2\}/2, \end{aligned} \tag{1}$$

where $d_0 = 2\pi/q_0$ is the fundamental periodicity in the system and is comparable to the polymer radius of gyration through the relation $q_0 \cong 1.95R_g^{-1}$. The parameter $\tau = 2N(\chi_c - \chi)$, measures the distance to the critical point ($\tau = 0$) in terms of the Flory-Huggins interaction parameter and $N = N_A + N_B$ is the total chain polymerization index. At the critical point $N\chi_c \approx 10.49$. In addition, a is the Kuhn statistical segment, $\xi^2 = 3c^2R_g^2/2$, $v_p = Na^3$ is the volume per unit copolymer chain c is a constant of order 1. The coefficients λ and u depend on the block ratio $f_A = N_A/N$. Below we would restrict ourselves to the case where the block ratio is symmetric $f = 1/2$. In this limit $\lambda = 0$ and the lamellar phase is the only stable ordered phase above the critical value χ_c. For convenience we set $c = u = 1$.

The nematic director $\mathbf{n} = (\cos\theta, \sin\theta, 0)$. The Frank-Oseen contribution defines the penalty for distorting the nematic director, with K_1 and K_3 being the splay and bend moduli respectively. In the microphase separated system the chain anisotropy manifest with anisotropic local density fluctuations. This is reflected by the anisotropic spatial gradients of $\psi(r)$ that are coupled to the characteristic wavenumber q_0 with $A(\theta) = \cos^2\theta + \kappa^2\sin^2\theta$, $B(\theta) = \sin^2\theta + \kappa^2\cos^2\theta$, and $C(\theta) = (\kappa^2 - 1)\sin 2\theta$. The anisotropy of the copolymer chains that is induced by the uniform orientation of the liquid-crystals is described by κ, the ratio between the long axes and the short axes of the individual block.

Finally, the last term in Eq. (1) describes the coupling of the liquid-crystal director to the anisotropy of the block copolymer microstructure. In the case of a lamellar phase, this describes the anchoring of the liquid-crystal molecule to the lamellar interface.

2.1. Electric field contribution

An applied uniform electric field will have an alignment effect on the block copolymer backbone and also on the liquid-crystals. The lamellar system has an inhomogeneous dielectric constant due to the stacking of chemically distinct polymers and is also dielectric anisotropic due to the liquid crystals. The electric field contribution to the free energy is then [6, 7],

$$\frac{Na^3}{k_BT}F_{el} = \frac{\beta}{2}\int d^3r\left(\vec{\nabla}\psi/|\vec{\nabla}\psi|\cdot\vec{E}\right)^2\psi^2 - \frac{\Omega}{2}\int(\mathbf{E}\cdot\mathbf{n})^2d^3r, \tag{2}$$

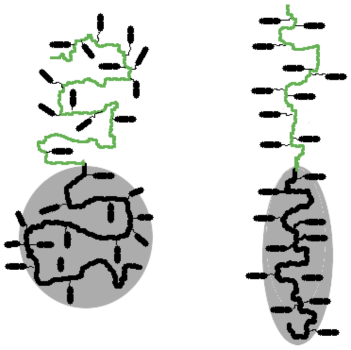

Figure 1. Schematic diagram of a liquid-crystal diblock copolymer chain. The shape of the copolymer chains depends on the orientational order of the side-chain liquid-crystals. Nematic ordering of the liquid-crystals results to stretched coils.

where $\beta = Na^3(\varepsilon_A - \varepsilon_B)^2/[k_BT(\varepsilon_A + \varepsilon_B)]$ for symmetric AB diblock copolymer, ε_A and ε_B are the dielectric constants for the A/B blocks, k_B is the Boltzmann constant , and T is the temperature of the system. This means that there is a energy cost when the dielectric interfaces are perpendicular to the electric field. We also have $\Omega = Na^3\Delta\varepsilon\varepsilon_0/(k_BT)$, where ε_0 is the permittivity of free space and $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$ is the dielectric anisotropy, the difference between the liquid-crystal dielectric constant along their long and short axes.

3. Results

To understand the effects of a uniform field on the microstructure of liquid-crystal block copolymers, we consider a lamellar phase with the liquid crystals oriented parallel to the layers as illustrated in Fig. 2. A uniform electric field points along the x-axis, $\vec{E} = E\hat{x}$, parallel to the layers. We assume that the liquid-crystals have a negative dielectric anisotropy, $\varepsilon_{\|} < \varepsilon_{\perp}$, and thus the electric field will favor a 90° reorientation of the liquid-crystal director.

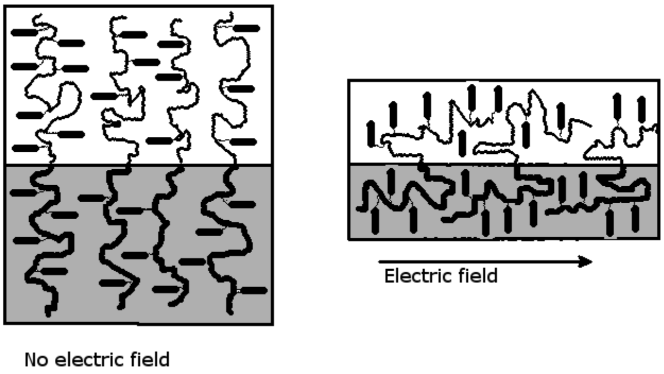

Figure 2. Schematic diagram of an electrically tunable block copolymer. The side-chain liquid-crystal molecules have a negative dielectric anisotropy, they prefer to orient perpendicular to the field. As the nematic director tilts so does the coupled anisotropic chains leading to the lamellar contraction.

3.1. Mean field Calculations

The energetics of the system are then described by the total free energy

$$\mathcal{F} = F_{ab} + F_{el}. \tag{3}$$

For a given electric field strength, E, we can find the mean field solutions of $\psi(r)$ and $\theta(r)$ that minimize the total free energy. That is we can describe the lowest energy state adopted by the system in thermodynamic equilibrium.

Within the weak segregation limit the local density profile of lamellar diblock copolymers can be approximated by a sinusoidal function [7]

$$\psi(y) = D\cos(qy), \tag{4}$$

where $2\pi/q$ is the fundamental period of the lamellae and D is the amplitude of the density modulations. The lowest energy state is obtained under the condition that the amplitude D and the characteristic wavenumber q minimize the free energy of the system. Substituting Eq. (4) into Eq. (3) we obtain the free energy per unit volume

$$f = \frac{Na^3}{k_B T}\frac{\mathcal{F}}{V} = \frac{1}{4}\left[-|\tau| + \alpha q^2 \sin^2\theta + \xi^2\left(\mathcal{B}q^2 - q_o^2\right)^2\right] D^2 + \frac{1}{64}D^4 + \frac{|\Omega|}{2}E^2\cos^2\theta. \tag{5}$$

Minimizing the above free energy density with respect to D and q, we obtain the equilibrium amplitude D_m and characteristic wavenumber q_m. In the off state ($E = 0$) we have $D_m^b = 2\sqrt{-\tau}$ and $q_m^b = q_0/\kappa$. In the on-state ($E \neq 0$)

$$D_m^a = \sqrt{8[|\tau| - \alpha q^2\sin^2\theta - \xi^2(q_0^2 - \mathcal{B}q^2)^2]} \tag{6}$$

and

$$q_m^a = \sqrt{\frac{q_0^2}{\mathcal{B}} - \frac{\alpha\sin^2\theta}{2\xi^2\mathcal{B}^2}}, \tag{7}$$

where $\mathcal{B} = \kappa^2 + (1-\kappa^2)\sin^2\theta$. The value of $\theta(\vec{r})$ that minimizes the free energy is naturally a strong function of the applied electric field. Substitute Eq. (6) and Eq (7) into Eq. (5) we obtain the free energy density as the functional of the liquid-crystal director angle, $f(\theta)$. In the small field limit θ (and $\sin(\theta)$) is small and the free energy can be expanded as follows,

$$\begin{aligned} f(\theta) &= -|\tau^2| + \frac{|\Omega|E^2}{2} + \left(2|\tau|\alpha\frac{q_0^2}{\kappa^2} - \frac{|\Omega|E^2}{2}\right)\sin^2\theta \\ &\quad + \frac{\alpha q_0^2}{\kappa^2}\left[2|\tau|(1-\kappa^{-2}) - \frac{\alpha q_0^2}{\kappa^2}\left(\frac{|\tau|}{2\xi^2 q_0^4} + 1\right)\right]\sin^4\theta + \mathcal{O}(\sin^6\theta). \end{aligned} \tag{8}$$

It can be seen in Eq. (8) that the electric fields alters the coefficient of the $\sin^2\theta$ term. The coefficient changes sign at the critical electric field

$$E_c = 2\sqrt{\frac{|\tau|\alpha}{|\Omega|}\frac{q_0}{\kappa}}. \tag{9}$$

above which it becomes energetically favorable for electric field to tilt the liquid-crystals molecules relative to block copolymer layers. When E is slightly above E_c the free energy is minimized when,

$$\sin^2\theta = \frac{(E/E_c)^2 - 1}{2(1-\kappa^{-2}) - \alpha q_0^2[1/|\tau| + 1/(2\xi^2 q_0^4)/\kappa^2]}. \tag{10}$$

A consequence of the liquid-crystal reorientation induced by the electric field is the contraction of the layer thickness. The strain associated with layer contraction is

$$\delta = \frac{t_b - t_a}{t_b} \tag{11}$$

where $t_b = 2\pi/q_m^b$ and $t_a = 2\pi/q_m^a$ are the layer width at $E < E_c$ and $E > E_c$ respectively. Utilizing Eq. (7) and Eq. (10) we can obtain the strain that is achieved at a full 90° liquid-crystal director rotation

$$\delta_{max} = 1 - \kappa^{-1}\left(1 - \frac{\alpha}{2\xi^2 q_0^2}\right)^{-1/2}. \tag{12}$$

In the limit of a soft anchoring of the liquid crystals to the lamellar surfaces, $\delta_{max} = 1 - \kappa^{-1}$. In this limit a typical value of $\kappa = 1.6$[8], this implies reversible contraction lamellar thickness of 40% can be induce by the electric field.

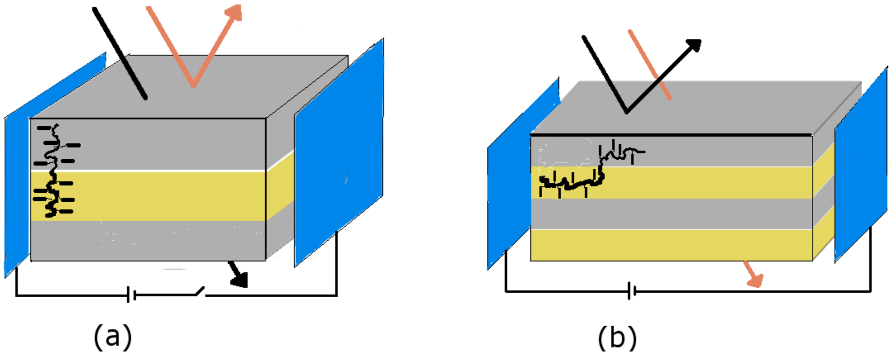

Figure 3. Schematic diagram of an electrically tunable block copolymer photonic crystal exhibiting colored stop bands. At the off-state the lamellar sample completely reflects longwavelength in the visible spectrum (infrared). (b) Contraction of the lamellar spacing leads to complete reflection of shorter wavelengths in the visible spectrum (ultraviolet).The inset diagram shows the orientation of the anisotropic copolymer chains within the lamellar structure.

3.2. Applications

The tunability of the block copolymer microstructure can lead to useful applications. For example in photonic applications. The wavelength of light, λ, that is coherently reflected by the polymer photonic crystal depends on the lamellar periodicity d_l:

$$\lambda \approx 2d_l\sqrt{n_e^2 - \sin^2\phi}$$

where n_e is the effective refractive index of the material and ϕ is the angle of incidence of light with respect to the lamellar normal. The liquid-crystal block copolymers discussed in this article can provide another option in the fabrication of electrically tunable photonic crystals with a full color display [3]. When the electrically induced liquid-crystal rotation changes d_l/n_e from $350 - 700$ nm, we can obtain a polymer photonic crystal film operating in the visible light spectrum, showing different colors depending on the electric field strength as depicted in Fig. 3.

4. Summary

In summary, we have developed a theory that describes a microstructure of weakly segregated block copolymers that incorporated liquid-crystals molecules. We have shown that the coupling of the liquid-crystals to the block copolymers backbone can lead to diblock copolymers crystals that can exhibit exceptional properties. For example a lamellar block copolymer crystal may exhibit a large electrically induced layer contractions. Such tunable block copolymer systems have a great potential in photonic applications.

Acknowledgments

The author would like to thank Ken Elder and Martin Grant for valuable discussions.

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