Orienting Ion-Containing Block Copolymers Using Ac Electric Fields

Yoav Tsori,* François Tournilhac, and Ludwik Leibler

Laboratoire Matière Molle & Chimie (UMR 167) ESPCI, 10 rue Vauquelin, 75231 Paris CEDEX 05, France

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ABSTRACT: We consider orientation mechanisms for block copolymers in an electric field. Theoretical and experimental studies have shown that nonuniformity of the dielectric constant gives rise to a preferred orientation of the melt with respect to the applied field. We show that the presence of ions, as found in anionically prepared copolymers, may increase the alignment effect markedly. Time-varying (ac) and static (dc) fields are considered within a unified framework. We find that orientation of block copolymers can in principle be achieved without a dielectric contrast if there is a mobility contrast. The presence of ions is especially important at small field frequencies, as is in most experiments. Unlike the no-ions case, it is found that orienting forces depend on the polymer chain lengths. The mobile-ions mechanism suggested here can be used to reduce the magnitude of orienting fields as well as to discriminate between block copolymers of different lengths.

1. Introduction

Numerous applications of ordered mesophases in soft materials have emerged in recent years. Few examples are antireflection coatings,[1] photonic band-gap materials[2] and waveguides,[3] and ordered arrays of thin metallic wires.[4] In these systems, it is crucial that the crystalline domains are oriented in a specific direction. Several techniques have been used to this end. Mechanical shear is effective in aligning bulk systems and in annealing defects.[5] Static (dc) electric fields are widely used in thin films of block copolymers (BCP) to control the film morphology.[6−10] In this paper, we focus on the alignment mechanism of a BCP melt in time-varying (ac) electric fields.

The pioneering work of Amundson and Helfand and co-workers[11,12] showed that diblock copolymers (composed of two different chemical sequences tethered at one point) in the lamellar phase can be aligned parallel to an external dc electric field. The driving force in this alignment is the "dielectric mechanism". In this mechanism, there is an electrostatic free energy penalty for having dielectric interfaces perpendicular to the external field. Thus, lamellae (or cylinders) will tend to align parallel to the field.

However, most studies to date have given little or no attention to the ions in BCP. These ions naturally exist in many polymeric systems and, in particular, in anionically prepared BCP. To see this consider a typical polymerization reaction initiated with one butyllithium (BuLi) group. At the end of polymerization and after rinsing with water, the Li and OH ions form a lithium hydroxide (LiOH) pair. Hence, unless special measures are taken (e.g., final purification by continuous methanol extraction) ions exist in abundance in the melt, i.e., one ion pair per polymer chain. Some fraction of these ions are dissociated (either thermally or because of a high polymeric solvation ability), and those positive and negative charges move under the influence of the field. This motion, in turn, changes the field and exerts forces on the melt.

This paper generalizes the results of previous studies to a BCP melt containing dissociated mobile ions in time-varying fields. As we will see below, in these systems there are strong orienting forces. Forces occur by the presence of a *conductivity* or *mobility* contrast[13] and can occur even without dielectric contrast. The details of our calculation show that in many common BCP melts and under normal circumstances the relative strength of the orienting forces due to ions leads to substantial reduction in the magnitude of external fields.[14]

2. Electric Field in the Melt

To find what are the orienting forces on the sample, we need to calculate the distribution of electric field inside a nonuniform polymer system such as block copolymers in one of the ordered phases.[15,16] It is therefore implicitly assumed that the electric field relaxes faster than any other process, thereby instantaneously adjusting to the BCP morphology. We adopt a description neglecting the microscopic polymer chemistry, architecture, etc., and focus on coarse-grained variables. These are the dielectric constant $\epsilon(\mathbf{r})$, the ionic mobility $\mu(\mathbf{r})$, number density $\rho^{\pm}(\mathbf{r})$ for the two ionic species (positively and negatively charged, respectively), and electric field $\mathbf{E}(\mathbf{r})$. The average ionic densities $\rho_0^{\pm} = \langle\rho^{\pm}(\mathbf{r})\rangle$ can be controlled by sample doping, etc. The first two quantities are material properties and are given solely as a function of the BCP density. It should be noted that the BCP melt considered by us is different from the "leaky dielectric" model of Taylor and Melcher[17] for two conducting dielectric fluids. Here the chain behavior is elastic, and there is no hydrodynamic flow. In the weak-segregation regime employed below (high temperature region of the ordered phases), the chains are weakly stretched, and it is appropriate to neglect deviations from anisotropy of the dielectric and mobility tensors and take ϵ and μ to be scalars. For example for an A/B diblock copolymer with an average fraction f of A monomers, the order parameter ϕ is defined as the deviation of the A-monomer concentration from its average value, $\phi(\mathbf{r}) = \phi_A(\mathbf{r}) - f$. For symmetric ($f = 1/2$) diblock copolymers

$$\epsilon(\mathbf{r}) = \phi(\mathbf{r})(\epsilon_A - \epsilon_B) + \epsilon_0 \qquad (1)$$

where ϵ_A and ϵ_B are the dielectric constants of the A

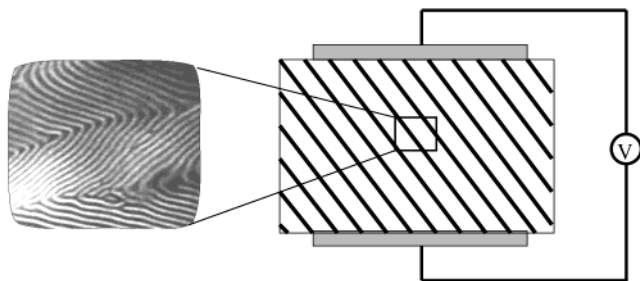* Corresponding author. E-mail: yoav.tsori@espci.fr.

Figure 1. Schematic illustration of a block copolymer melt (diagonal lines) between two flat and parallel electrodes (dark gray). Inset shows a typical morphology as revealed by transmission electron microscopy.

Table 1. Data Collected from Dc Conductivity Measurements of PMMA and PS Doped with LiOH Ions at 160°

	PMMA	PS
sample aspect	transparent	hazy
birefringence	no	strongly
no. of LiOH ions per m^3	6.6×10^{26}	6.6×10^{26}
fraction of dissociated ion pairs	3×10^{-5}	below experimental error
mobility [m^2/(J s)]	4.6×10^5	below experimental error

and B monomers, respectively, and $\epsilon_0 = {}^1/_2(\epsilon_A + \epsilon_B)$ is the material average dielectric constant. The quantities to be found are $\rho^{\pm}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$.

The BCP melt is put between two flat parallel plates connected to an oscillatory voltage supply of frequency ω, $V(t) = V_0 e^{i\omega t}$, as is schematically seen in Figure 1. The x axis is perpendicular to the plates. We concentrate on the so-called "weak-segregation" limit where the polymer density deviations from the average value are small and a linearization procedure suffices. Then our goal is to deduce what is the best orientation of the dielectric-conducting material with respect to the external field $\mathbf{E}_0$. Such a conducting system is dissipative, and hence, we look for mechanical stability instead of thermodynamic equilibrium.

There are four length scales in the system. The first is d_0, the natural crystal periodicity, $d_0 \simeq 50-200$ nm. For a weakly segregated diblock copolymer of N monomers, $d_0 \sim N^{1/2}$. The other length scale is $l_{\text{drift}} \equiv \pi e \mu E / \omega$, the drift distance an ion of charge e and mobility μ undergoes in a field E in a time equal to half of the oscillation period. We call the high-frequency regime the regime where $l_{\text{drift}} \ll d_0$; the low-frequency regime is when $l_{\text{drift}} \gg d_0$. The third length is the wavelength of light, and is given by $l_{\text{light}} = 2\pi c/(\omega \sqrt{\epsilon})$. In most circumstances l_{light} is larger than the two other lengths, $l_{\text{light}} \gg d_0$, $l_{\text{light}} \gg l_{\text{drift}}$. The last length scale is the system size L.

There are three energy scales in the system. One is the electrostatic energy stored in unit volume of the dielectric material, $U_{\text{dielec}} = \epsilon E^2$. The second is the Joule heating per unit volume in one field cycle, $U_{\text{Joule}} \equiv 2\pi E^2 \sigma / \omega$. The third energy is the thermal energy kT. As the frequency of field decreases Joule heating becomes more dominant. Table 1 shows some of the data collected by us on conductivity of poly(methyl methacrylate) (PMMA) and polystyrene (PS) doped with Li ions. These polymers constitute one of the best studied pairs in diblock copolymers. Let us estimates U_{dielec} and U_{Joule} for pure PMMA polymer. In anionically prepared polymers there is approximately one LiOH group per

chain. To evaluate how many of these ions participate in the alignment process we conducted dc conductivity measurements on pure PMMA doped with a known amount of LiOH. The samples were sandwiched between two conducting flat indium tin oxide coated glass substrates at 160 °C. Integration of the current allowed us to deduce that a fraction of 3×10^{-5} of these ions are dissociated and *mobile* in PMMA. We concluded that the mobile ion number density is $\rho_0 \simeq 3 \times 10^{22}$ m^{-3}. Li ion mobility in PMMA is $\mu_0 \simeq 4.6 \times 10^5$ m^2/(J s), giving an average conductivity $\sigma_0 = e^2 \rho_0 \mu_0 \simeq 3.5 \times 10^{-10}$ C/(m V s). For frequencies of 50 Hz, we therefore have $\sigma_0/\omega \simeq 1.1 \times 10^{-12}$ C/(m V). On the other hand, $\epsilon_{\text{PMMA}} \simeq 6(8.85 \times 10^{-12})$ C/(m V), so we find that $2\pi\sigma_0/\omega \simeq 0.13\epsilon_{\text{PMMA}}$ (or $U_{\text{Joule}}/U_{\text{dielec}} \simeq 0.13$). This estimate shows us that we should expect free ions (conductive behavior) to start playing an important role at *low* frequencies.

An important question is whether the heating caused by moving ions can cause problems in the experimental setup. The total heat created per unit time in the volume is $\sim L^3 \sigma E^2$ (L is the system size). This heat should be compared with the integrated heat flux out of the melt, $\sim L^2 \kappa \nabla T$, where κ is the heat conductivity, and the temperature gradient can be approximated by $\nabla T \simeq \Delta T/L$. In most setups the sample temperature variation is controlled to within $\Delta T \simeq 1$ K. Concentrating on PMMA where $\kappa \simeq 0.19$ W/(m K)[18] and considering a sample of size $L = 1$ cm and applied field $E = 1000$ V/cm, we find that the ratio between the heat created to the heat that can flow outside of the sample is 1.8×10^{-3}, and thus heating does not present a problem. In the case of a smaller sample of $L = 1$ μm, this ratio becomes even smaller, 1.8×10^{-7} (small samples have a large surface area).

Below we employ a formal derivation using Maxwell's equations to find the electric field distribution in non-homogeneous media. While we will be interested in relatively low frequencies relevant to experiments, the results we obtain are general. Maxwell's equations in the CGS system of units are

$$\nabla \times \mathbf{E} + \frac{1}{c}\dot{\mathbf{B}} = 0 \tag{2}$$

$$\nabla \times \mathbf{B} - \frac{\epsilon}{c}\dot{\mathbf{E}} = \frac{4\pi}{c}\mathbf{J}, \quad \mathbf{J} = e^2(\mu^+\rho^+ + \mu^-\rho^-)\,\mathbf{E} \tag{3}$$

$\mathbf{B}$ is the magnetic field, $\mathbf{J}$ is the current density, and μ^+ and μ^- are the mobilities of the positive and negative ions, respectively. The *number* densities of positive and negative ions are denoted by ρ^+ and ρ^-, respectively, all assumed monovalent. We put eq 2 into eq 3 and add two continuity equations for the positive and negative ions to have three governing equations:

$$-\nabla(\nabla\mathbf{E}) + \nabla^2\mathbf{E} - \frac{\epsilon}{c^2}\ddot{\mathbf{E}} = \frac{4\pi e^2}{c^2}[\mu_+(\dot{\rho}^+\mathbf{E} + \rho^+\dot{\mathbf{E}}) +$$
$$\mu^-(\dot{\rho}^-\mathbf{E} + \rho^-\dot{\mathbf{E}})] \tag{4}$$

$$\frac{\partial\rho^+}{\partial t} + \nabla(e\mu^+\rho^+\mathbf{E}) = 0 \tag{5}$$

$$\frac{\partial\rho^-}{\partial t} - \nabla(e\mu^-\rho^-\mathbf{E}) = 0 \tag{6}$$

We are interested in the weak-segregation regime of the phase diagram, which is the high-temperature region of the various ordered phases. The weak segrega-

tion is more relevant to experiments because the melt is not so viscous as it is for strong segregations (low temperatures). The copolymer density is slowly varying, and the interfaces between domains are smooth. As we show below, this allows to replace the complicated task of numerically solving eqs 4, 5, and 6 by an approximate analytical procedure. In this scheme, the material quantities $\epsilon(\mathbf{r})$ and $\mu(\mathbf{r})$ are given by the expansions $\epsilon = \epsilon_0 + \epsilon_1$ and $\mu^+ = \mu^- = \mu_0 + \mu_1$, with $\epsilon_1 \ll \epsilon_0$ and $\mu_1 \ll \mu_0$, where for simplicity we assume hereafter that positive and negative ions have the same mobility. The charge density and electric field can be similarly written as $\rho^\pm = \rho_0^\pm + \rho_1^\pm$ and $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1$.

The zero-order approximation of eqs 4, 5, and 6 gives the field $\mathbf{E}_0$: $\mathbf{E}_0 = \tilde{\mathbf{E}}_0 e^{ik_{\text{light}}(\omega)\mathbf{r}+i\omega t} + c.c.$, where $c.c.$ stands for the complex conjugate operation, and the k-vector obeys the dispersion relation:

$$k_{\text{light}}^2(\omega) = \frac{\epsilon_0\omega^2 - 4\pi ie^2\omega\mu_0(\rho_0^+ + \rho_0^-)}{c^2}$$
$$= \frac{\omega^2}{c^2}(\epsilon_0 - 8\pi i\sigma_0/\omega) \ll k^2 \qquad (7)$$

k_{light} is parallel to the electrodes (and perpendicular to $\mathbf{E}_0$). The second line above is correct for neutral media with $\rho_0^\pm = \rho_0$ and where the average conductivity σ_0 has been identified as $\sigma_0 = e^2\mu_0\rho_0$. In the inequality $k_{\text{light}}^2 \ll k^2$, k is inversely proportional to the characteristic BCP length scale. The inequality is valid because even at visible frequencies (e.g., red light, $f = 4.3 \times 10^{14}$ Hz), the wavelength $\lambda = 700$ nm is larger than any structure size in block copolymers ($l_{\text{light}} \gg d_0$); we are interested in much smaller frequencies.

The electric field in a conducting media decays exponentially but it can be regarded as approximately uniform (with less than 10% decrease across the sample) if $\text{Im}(k_{\text{light}})L < 0.1$, where L is the system size. Below we concentrate on two regimes: the first is where Joule heating U_{Joule} in one field cycle is larger than the energy U_{dielec} stored in the dielectric, $2\pi E^2\sigma/\omega \gg \epsilon E^2$. In this regime $\mathbf{E}_0$ is approximately uniform if $0.1c/L > \sqrt{4\pi\sigma_0\omega}$. The second regime is where $U_{\text{Joule}} \ll U_{\text{dielec}}$, and it is then required that $0.1c/L > 4\pi\sigma_0/\sqrt{\epsilon_0}$. When these requirements are met, the field is approximately uniform and $\tilde{\mathbf{E}}_0 = \mathbf{E}_0$.

We continue by writing the deviations from uniform quantities ϵ_1, μ_1, $\mathbf{E}_1$ and $\rho_1^\pm$ by using the Fourier representation

$$\epsilon_1(\mathbf{r}) = \sum_{\mathbf{k}}\epsilon_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} + c.c., \quad \mu_1(\mathbf{r}, t) = \sum_{\mathbf{k}}\mu_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} + c.c.$$

$$\mathbf{E}_1(\mathbf{r}, t) = \sum_{\mathbf{k}}\mathbf{E}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}+i\omega t} + c.c., \qquad (8)$$

$$\rho_1(\mathbf{r}, t) = \sum_{\mathbf{k}}\rho_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}+i\omega t} + c.c.$$

We are interested in a mesoscopic system where many modes participate in the sum; For an infinite system the sums over all existing k-modes become integrals. Since the electric potential has to comply with the boundary conditions on the electrodes, $\mathbf{E}_{\mathbf{k}}$ is nonzero only for a restricted set of k's obeying $kL = 2n\pi$, with integer n.

The Fourier representation of eq 8 is substituted in eqs 4, 5, and 6. After some algebra one finally has

$$\mathbf{E}_{\mathbf{k}} = \frac{C - B\mu_k\mathbf{k}\cdot\mathbf{E}_0}{k_{\text{light}}^2 - k^2}\left[\mathbf{E}_0 - \frac{\mathbf{k}\cdot\mathbf{E}_0}{k_{\text{light}}^2 + B\mu_0\mathbf{k}\cdot\mathbf{E}_0}(\mathbf{k} + B\mu_0\mathbf{E}_0)\right]$$

$$= \frac{C - B\mu_k\mathbf{k}\cdot\mathbf{E}_0}{(k_{\text{light}}^2 - k^2)(k_{\text{light}}^2 + B\mu_0\mathbf{k}\cdot\mathbf{E}_0)}[k_{\text{light}}^2\mathbf{E}_0 - \qquad (9)$$
$$(\mathbf{k}\cdot\mathbf{E}_0)\mathbf{k}]$$

with B and C given by

$$B = -\frac{8\pi e^2 i\omega\mu_0}{c^2}\frac{\omega(\rho_0^- - \rho_0^+)/e + \mu_0\mathbf{k}\cdot\mathbf{E}_0(\rho_0^+ + \rho_0^-)}{\omega^2/e^2 - (\mu_0\mathbf{k}\cdot\mathbf{E}_0)^2}$$
$$\qquad (10)$$
$$C = \frac{4\pi e^2 i\omega}{c^2}\mu_k(\rho_0^+ + \rho_0^-) - \frac{\epsilon_k\omega^2}{c^2}$$

3. Orienting with Electric Field

At this point we have the general expression for the field in the block copolymer. When there are no ions in the system, $\rho^\pm = 0$, eq 9 reduces to the expression used by Amundson and Helfand. We adhere hereafter to overall charge neutrality, $\rho_0^+ = \rho_0^- \equiv \rho_0$, and to the experimentally relevant regime where $k_{\text{light}} \ll k$, or equivalently, $l_{\text{light}} \gg d_0$. The Fourier component of the field is

$$\mathbf{E}_{\mathbf{k}} = -\frac{T\mu_k - \epsilon_k\omega^2}{T\mu_0 - \epsilon_0\omega^2}\frac{\mathbf{k}\cdot\mathbf{E}_0}{k^2}\mathbf{k}$$
$$\qquad (11)$$
$$T = 8\pi e^2 i\omega\rho_0\frac{(\omega/e)^2 + (\mu_0\mathbf{k}\cdot\mathbf{E}_0)^2}{(\omega/e)^2 - (\mu_0\mathbf{k}\cdot\mathbf{E}_0)^2}$$

Compared to the classical expression, here the ratio ϵ_k/ϵ_0 is replaced by a direction-dependent quantity (containing $\mathbf{k}\mathbf{E}_0$ via T). This fact is significant because it means that the field and the orienting force depend on the periodicity of the BCP melt, whereas in the purely dielectric case (no ions) the field depends on the direction of the wavevector $\mathbf{k}$ but not on its absolute value. Hence in contrast to previous predictions, two melts with the same chemical sequence but different chain lengths are oriented differently. For low frequencies (see below), longer polymers (smaller k's) are expected to feel a stronger aligning force than shorter polymers.

The discussion continues with two distinct cases, corresponding to low and high frequencies.

•Low-frequency limit: $\omega/e \ll \mu_0\mathbf{k}\mathbf{E}_0$ ($l_{\text{drift}} \gg d_0$). The meaning of this limit is that the drift distance an ion undergoes in the external field is much larger than any BCP length scale (crystal periodicity). In this limit, the directionality term $\mathbf{k}\mathbf{E}_0$ in T is lost and we have

$$\mathbf{E}_{\mathbf{k}} = -\frac{8\pi e^2 i\omega\rho_0\mu_k + \epsilon_k\omega^2}{8\pi e^2 i\omega\rho_0\mu_0 + \epsilon_0\omega^2}\frac{\mathbf{k}\cdot\mathbf{E}_0}{k^2}\mathbf{k} \qquad (12)$$

•High-frequency limit: $\omega/e \gg \mu_0\mathbf{k}\mathbf{E}_0$ ($l_{\text{drift}} \ll d_0$). Here the ionic drift distance in the electric field is much smaller than the BCP length scale, so charges are
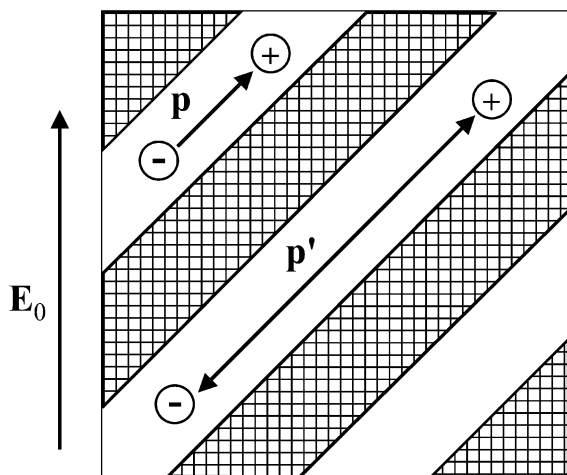
Figure 2. Illustration of lamellae in external electric field E_0. If the lamellae are tilted with respect to E_0, bound-charge dipoles such as **p** cause a torque $L = p \times E_0$. In much the same way, mobile oscillating ions create an effective dipole **p′** and contribute a torque **p′** $\times E_0$.

almost fixed in their positions. In this limit too, the directionality term kE_0 is lost, yielding E_k

$$E_k = -\frac{8\pi e^2 i\omega\rho_0\mu_k - \epsilon_k\omega^2}{8\pi e^2 i\omega\rho_0\mu_0 - \epsilon_0\omega^2} \frac{k\cdot E_0}{k^2}k \qquad (13)$$

4. Force and Torque

Systems with currents are generally dissipative and therefore the steady-state of the system is not given by free energy minimization, which is ill-defined under such circumstances. Rather, the system state is given by mechanical stability. The total torque has an effect on the dielectric material (bound charges) as well as on free charges, $L = L_{dielec} + L_{ions}$. To understand the origin of torque in a nonhomogeneous system in electric field, consider the most simple case of a lamellar system depicted in Figure 2. If the lamellae correspond to alternating stripes of high- and low-ϵ, then an induced dipole **p** is created, and a torque **p** $\times E_0$ exists. On the other hand, there could be materials where $\epsilon(\mathbf{r})$ is spatially uniform, and the stripes correspond to high and low conductivity (or mobility) regions. In an ac field, oscillating ions create an effective dipole **p′**, and a torque **p′** $\times E_0$ now exists.

We calculate first $L_{dielec} = \int \mathbf{p} \times E_0 \, d^3r$, where $\mathbf{p} = \chi(E_0 + E_1)$, and the susceptibility χ is given by $\epsilon = 1 + 4\pi\chi$. L_{dielec} can therefore be expressed as $L_{dielec} = \int \chi E_1 \times E_0 \, d^3r$. In the low-frequency limit E_1 is given by eqs 8 and 12, and the torque is

$$L_{dielec} = \sum_k \alpha(k, \omega) \frac{(k\cdot E_0)}{k^2} k \times E_0$$

$$\qquad (14)$$

$$\alpha(k, \omega) = -\frac{V}{4\pi} \frac{8\pi i\omega\sigma_0\mu_k/\mu_0 + \epsilon_k\omega^2}{8\pi i\omega\sigma_0 + \epsilon_0\omega^2}\epsilon_k^* = c.c.$$

For concreteness, we focus our attention on a simple lamellar phase in diblock copolymers, consisting of alternating planar stacks rich in A and B monomers. We see from the above expression that the torque vanishes if **k** is parallel or perpendicular to E_0. This corresponds to lamellae perpendicular or parallel to the

field, respectively. Furthermore, lamellae parallel to the field are mechanically stable while perpendicular lamellae are not.

The Helfand and Amundson expression for the torque is recovered in the absence of free ions, $\rho_0 = 0$. One has zero conductivity ($\sigma_0 = 0$) and

$$L_{dielec} = 2 \frac{V}{4\pi}\sum_k \left[-\frac{\epsilon_k\epsilon_k^*(k\cdot E_0)}{\epsilon_0} \frac{(k\cdot E_0)}{k^2}k \right] \times E_0 \qquad (15)$$

Naturally, the mobility μ does not enter into the expression.

We turn now to calculate the torque due to mobile dissociated ions. The ionic current has a component along E_0 and a component along E_1. The former does not contribute to the torque. For each mobile ion, the oscillatory motion along E_1 has an average length $\mu eE_1 2/(\omega\pi)$. The torque is hence

$$L_{ions} = \int e^2(\rho^+ + \rho^-)\mu \, 2/(\omega\pi)E_1 \times E_0 \, d^3r \qquad (16)$$

Using E_1 from eq 12 and after some algebra we find that

$$L_{ions} = \sum_k \beta(k, \omega)\frac{(k\cdot E_0)}{k^2}k \times E_0$$

$$\qquad (17)$$

$$\beta(k, \omega) = \frac{8\sigma_0 V}{\omega\pi}$$

$$\frac{-(8\pi\omega\sigma_0/\mu_0)^2\mu_k\mu_k^* - (8\pi\omega i\sigma_0/\mu_0)(\mu_k\epsilon_k^* - \mu_k^*\epsilon_k)\omega^2 - \epsilon_k\epsilon_k^*\omega^4}{(\epsilon_0\omega^2)^2 + 64\pi^2\omega^2\sigma_0^2}$$

Similar to eq 14 for the torque due to fixed dipoles, L_{ions} vanishes if the lamellae are parallel or perpendicular to E_0 (**k** perpendicular or parallel to E_0, respectively). In the $\sigma_0/\omega \gg \epsilon_0$ regime one obtains

$$L_{ions} = \frac{8\sigma_0 V}{\omega\pi}\sum_k -\frac{\mu_k\mu_k^*}{\mu_0^2}\frac{(k\cdot E_0)}{k^2}k \times E_0 \qquad (18)$$

This result is analogous to the Helfand and Amundson torque, eq 15. It is shown again that a dielectric contrast is not necessary in order to orient lamellae; a *mobility* contrast might be enough. Moreover, from the $1/\omega$ factor in the above expression, it is clear that as the field frequency is reduced the importance of conductive behavior becomes the dominant one. The expression for the total torque due to fixed and mobile charges is (eqs 14 and 17)

$$L = L_{dielec} + L_{ions} =$$

$$\sum_k [\alpha(k, \omega) + \beta(k, \omega)]\frac{(k\cdot E_0)}{k^2}k \times E_0 \qquad (19)$$

Let us compare the total torque at a frequency of 50 Hz (eq 19) to the torque due to the dielectric mechanism only, eq 15. The ratio between the torques is $L/L_{dielec} \simeq 1 + 16(\epsilon_0^2/\epsilon_k\epsilon_k^*)(\mu_k\mu_k^*/\mu_0^2)(\sigma_0/\omega\epsilon_0)$. In the special case where $\epsilon_k/\epsilon_0 \simeq \mu_k/\mu_0$ holds, we find that

$$\frac{L}{L_{dielec}} \simeq 1 + 16\frac{\sigma_0}{\omega\epsilon_0} \simeq 1.4 \qquad (20)$$

This figure emphasizes the importance of free mobile ions in orientation experiments in BCPs. The effect of ions vanishes as $\omega \to \infty$ ($L_{\text{ions}} = 0$), but for frequencies smaller than 50 Hz, the mobile ion mechanism becomes increasingly important and it may even dominate the orientation process.

5. Summary

We consider in this paper orientation of block copolymers in external electric fields. The results presented here are a generalization of previous expressions[11,12,14] for time-varying fields and for ion-containing samples. This is the realistic situation in many experiments because unless special measures are taken to extract ions, they will be found in abundance (e.g., in anionically prepared block copolymers). We show that as compared to "clean" block copolymers, the existence of dissociated mobile ions can greatly enhance orientation effects. The underlying physics in these systems is qualitatively different in several ways. First, depending on the frequency of applied field and on the mobility, ions undergo oscillatory movement with amplitude which is larger or smaller than the feature size of the underlying block copolymer crystal. This motion is associated with a force which tends to align microstructures in a specific direction. In the static case the ionic drift is related to an electrostatic potential energy gain favoring certain sample morphology.[14]

A second change from the no-ions case is that the system has currents and is dissipative. An estimate for heating shows that the sample heating should pose no real experimental concern; it should be relatively simple to control the temperature throughout the whole sample. We look at forces that generate torque on the material. It is shown that in the presence of ions these forces depend on the underlying BCP periodicity. Thus, lamellar block copolymers of certain chain lengths have different torque from the same BCP but with twice the chain lengths, in marked contrast to previous predictions.

In the high frequency domain, ions are almost immobile and contribute little to the aligning torque. On the other hand, in the low frequency domain ions exert on the system as a whole strong aligning torque. These forces can be comparable or even larger than those due to the "dielectric mechanism", as is exemplified by the ratio of the fields, eq 20. Charge accumulation at the electrodes may be a concern in static fields (or for very low frequencies), thereby reducing the field in the sample.[19] This problem can be circumvented by using high enough frequencies where the drift path of the ions l_{drift} is smaller than the system size L, or by using electrodes permeable to the ions.

It would be interesting to verify the predictions of this paper by performing an experiment in diblock copolymers with small dielectric contrast between the two blocks. In the lamellar or hexagonal mesophases, ac voltage could orient the sample even for surprisingly small fields. If the BCP is in a bcc phase of spheres we expect a phase transition from the bcc to the hexagonal phase, as predicted by us for static dc fields.[14] We hope that this paper will stimulate further experimental study of block copolymer orientation in electric fields.

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