Structural Changes in Block Copolymers: Coupling of Electric Field and Mobile Ions

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(Received 26 July 2002; published 10 April 2003)

We argue that the presence of dissociated ions in block copolymers under electric fields can induce strong morphological changes and even lead to phase transitions. We investigate, in particular, diblock copolymers in the body centered cubic (bcc) phase. In pure dielectric materials (no free charges), a dielectric breakdown is expected to occur for large enough electric fields, preempting any structural phase transition. On the other hand, dissociated ions are predicted to induce a phase transition to a hexagonal array of cylinders, at fields of about 10 V/μm or even lower. The strength of this mechanism can be tuned by controlling the amount of free ions present.

DOI: 10.1103/PhysRevLett.90.145504 PACS numbers: 61.25.Hq, 61.41.+e, 64.70.Nd

Designed control of material properties in the submicrometer range has drawn considerable interest in recent years because of its importance in applications as well as in basic research. As possible applications we mention waveguides, photonic band gap materials, and dielectric mirrors [1]. Recent studies have highlighted the role of external electric fields in creating well aligned structures. An electric field was used to create an instability in polymer films, thus replicating the pattern of a master template [2]. In block copolymers, electric fields are effective in aligning microdomains in a desired direction, as has been shown experimentally [3] and theoretically [4]. For example, removal of one of the two components of a copolymer film is used to produce antireflection coatings [5]. Furthermore, diblock copolymers, such as polystyrene (PS)/polymethylmethacrylate (PMMA) in its hexagonal phase were used as a starting point to produce an array of long, aligned, and conducting nanowires [6].

A well known method to cause orientation or structural changes in heterogeneous dielectric media is based on the "dielectric mechanism." As an example, we consider a material composed of two types of microdomains having dielectric constants, ε_A and ε_B, respectively, and placed in an external electric field $\mathbf{E}$. An electrostatic energy penalty will be paid whenever a dielectric interface is oriented perpendicular to the field [7]. Thus, a state where $\nabla\varepsilon$ is perpendicular to $\mathbf{E}$ is favored. This energy cost, proportional to $(\varepsilon_A - \varepsilon_B)^2E^2$, is enhanced when the difference in polarizabilities is large. A real concern is whether this relatively weak effect (second order in E) requires high fields exceeding the typical values for dielectric breakdown of the entire film. This breakdown occurs for fields $\gtrsim 100$ V/μm in thick films of 1–3 mm, but is expected to be much smaller for thin films as considered here [8].

So far, no attention was given to the existence of free (mobile) ions inside dielectric copolymer materials. However, these ions could be found in a large amount because during anionic polymerization, the reaction is initiated by an organometallic reagent (usually butyl lithium). When monomers are eventually exhausted, each carbonionic chain neutralized with water gives rise to one neutral polymer chain and one metal hydroxide unit (usually LiOH). The use of organolithic reagents and catalysts increases even further the total amount of ions [9].

Here we argue that the presence of ions may be responsible for morphology changes and can even lead to field-induced phase transition. In practice, even when a small number of ions is present, the mechanism proposed here might be more efficient than the dielectric one as the effect is proportional to E and not E^2. Similar considerations can apply in general to any highly polarizable heterogeneous media. The new driving force is the free energy gain of free charges (dissociated ions) as they move upstream or downstream the electrostatic potential (depending on their sign). The fields needed to drive morphological changes are typically much smaller than the fields resulting from the dielectric mechanism, and their value is well below dielectric breakdown threshold. Moreover, tuning the free ion concentration offers a convenient control of these morphological changes.

Although our approach is general for phases where one component is spatially discontinuous, we concentrate as an example on PS/PMMA diblock copolymers used by several experimental groups [6]. We show that with the alternative "free ions mechanism" there is a phase transition from a body centered cubic (bcc) lattice of spherical domains to a hexagonal array of cylinders, in agreement with recent experimental findings of Russell and coworkers [10]. The resulting cylinders have smaller radius than "regular" cylinders which is advantageous in applications [5].

In an A/B diblock copolymer melt the *macroscopic* phase separation occurring for two A/B immiscible chains (or blocks) is hindered because of chain connectivity. Instead, the system undergoes a *mesoscopic* phase separation, with typical length scales of dozens of nanometers. The Flory parameter $\chi \sim T^{-1}$ characterizes the repulsion between the blocks and $f = N_A/N$ is the fraction of A monomers in a copolymer chain of $N = N_A + N_B$ monomers. The phase behavior (in mean-field theory) is given by f and the combined $N\chi$ parameter [11]. For small values of $N\chi$ (high temperature) the system is in a mixed, disordered, phase. Lowering the temperature or equivalently raising $N\chi$ above $N\chi_c \simeq 10.5$ results in a weak first-order phase transition to a lamellar phase for symmetric melts ($f = \frac{1}{2}$). An increase of $|f - \frac{1}{2}|$ changes the spontaneous curvature and induces a transition to a hexagonal phase of cylinders, a gyroid phase of cubic symmetry, or a bcc lattice of spherical domains.

The copolymer bulk free energy F_b can be written as a functional of the local order parameter $\phi(\mathbf{r}) = \phi_A(\mathbf{r}) - f$. This order parameter denotes the deviation of the A monomer volume fraction from its average value $\langle\phi_A\rangle = f$, and the free energy expression is

$$\frac{Nb^3F_b[\phi]}{k_BT} = \int d^3r\left\{\frac{1}{2}\tau\phi^2 + \frac{1}{2}h(q_0^2\phi + \nabla^2\phi)^2 + \frac{1}{6}\Lambda\phi^3 + \frac{u}{24}\phi^4\right\}. \qquad (1)$$

This and similar (mean-field) free energy forms have been used extensively in the past to describe spatially modulated phases [12] such as weakly segregated diblock copolymers [7,11,13,14], Langmuir films, and magnetic (garnet) films [15]. In Eq. (1), $\tau \sim N(\chi_c - \chi)$ is the reduced temperature and $q_0 \sim R_g^{-1}$ is the first wave number which becomes stable upon transition to the lamellar phase. The lattice periodicity $d_0 = 2\pi/q_0$ is about 10 nanometers, b is the Kuhn segment length, $h \sim R_g^4$, and the constants Λ and u are the three-point and four-point vertex functions calculated by Leibler [11] in the weak segregation limit. They depend on f and τ. The simple model, Eq. (1), is used in order to establish the new qualitative behavior due to ions (below). Functionals extending to higher segregations [16], self-consistent field studies [17], and corrections due to different monomeric volumes, dynamics, etc. [18], are available as well and could be used to further study the mobile-ion mechanism.

Contrary to lamellar or hexagonal phases where orientation by electric fields is related to a preferred spatial orientation [3–7], a bcc lattice of spheres is isotropic and no orientation is possible. On the other hand, strong enough electric fields will elongate the spheres and eventually will cause a morphological change of the bcc phase into a hexagonal array of cylinders.

Let us consider first a PS-PMMA copolymer melt in the absence of external E field. The parameters $N\chi$ and f are chosen such that the thermodynamically stable phase is a bcc stack of PMMA spheres embedded in a PS matrix. Within the single q-mode approximation employed throughout this paper (weak segregation limit), the order parameter ϕ for the bcc phase is given by $\phi^{\rm bcc}(\mathbf{r}) = A_{\rm bcc}\sum_{n=1}^{6}\cos(\mathbf{q}_n\cdot\mathbf{r})$. $A_{\rm bcc}$ is the amplitude of density modulations, and the six fundamental q modes are given by $\mathbf{q}_{1,4} = q_0(\mp 1, 0, 1)/\sqrt{2}$, $\mathbf{q}_{2,5} = q_0(1, \mp 1, 0)/\sqrt{2}$, and $\mathbf{q}_{3,6} = q_0(0, 1, \mp 1)/\sqrt{2}$. Consider now only the dielectric mechanism. We assume for simplicity that the external electric field E is applied along the $(1, 1, 1)$ direction of the lattice: $\mathbf{E} = E(1, 1, 1)$. This choice of $\mathbf{E}$ direction does not affect the magnitude of the critical field E_c [19]. As the field is turned on, the PMMA spheres elongate along the field direction, thereby reducing the component of $\nabla\varepsilon$ along $\mathbf{E}$. For sufficiently strong fields, the electrostatic energy dominates and the system is composed of cylinders oriented along the $(1, 1, 1)$ direction with dielectric interfaces parallel to E. The order parameter can now be written as a sum of two terms. The first contains the q_1, q_2, and q_3 modes and has a *hexagonal* symmetry, whereas the second contains the q_4, q_5, and q_6 modes. Hence, as a function of electric field strength the order parameter $\phi(\mathbf{r}, \mathbf{E})$ is $\phi(\mathbf{r}, \mathbf{E}) = w(E)\sum_{n=1}^{3}\cos(\mathbf{q}_n\cdot\mathbf{r}) + g(E)\sum_{m=4}^{6}\cos(\mathbf{q}_m\cdot\mathbf{r})$. For large enough field the order parameter reduces to the hexagonal one $\phi^{\rm hex}(\mathbf{r}) = A_{\rm hex}\sum_{n=1}^{3}\cos(\mathbf{q}_n\cdot\mathbf{r})$, where $A_{\rm hex}$ is the amplitude of density modulations in the hexagonal phase. Clearly, $A_{\rm hex}$ is the limit of $w(E)$ for large E fields, while $g(E)$ should vanish there.

In the weak segregation regime one can expand the electrostatic free energy per unit volume in small density variations ϕ and obtain the following form [3,7]:

$$\frac{Nb^3}{k_BT}F_{\rm dielec} = \beta\sum_q(\hat{\mathbf{q}}\cdot\mathbf{E})^2\phi_{\mathbf{q}}\phi_{-\mathbf{q}} = \beta E^2g^2, \qquad (2)$$

where $\beta = Nb^3(\varepsilon_{\rm PS} - \varepsilon_{\rm PMMA})^2/(2\bar{\varepsilon}k_BT)$ [3], the static dielectric constants of PS and PMMA for high temperatures ($> 160\,^\circ$C) are $\varepsilon_{\rm PS} \approx 2.5$ and $\varepsilon_{\rm PMMA} \approx 6$, respectively, and $\bar{\varepsilon} = f\varepsilon_{\rm PMMA} + (1 - f)\varepsilon_{\rm PS}$.

The free energy $F_b + F_{\rm el}$ [Eqs. (1) and (2)] is then minimized with respect to $w(E)$ and $g(E)$ for given parameters τ, Λ, u, and electric field E. The results of this minimization are shown in Fig. 1. When the field strength is $E = 0$, $w(0) = g(0) = A_{\rm bcc}$ and the spheres are undisturbed [Fig. 1(a)]. As E increases from zero, $w(E)$ increases monotonically while $g(E)$ decreases monotonically. At a *critical* field, $E = E_c$, $w(E)$ jumps discontinuously to $A_{\rm hex}$, while $g(E)$ jumps (down) to zero. In Fig. 1(b) the field is slightly below E_c, $E = 0.98E_c$, and the spheres are substantially elongated. For all fields $E > E_c$ the system is in a state with hexagonal symmetry [$g(E) = 0$] along the field; see Fig. 1(c). The value of E_c for PS/PMMA is estimated to be quite large [18], $E_c \approx 70$ V$/\mu$m. It is comparable to the value for dielectric breakdown and much bigger than the reported bcc to hexagonal transition fields [10].

In order to resolve the discrepancy between experiments and the dielectric mechanism, we now turn to calculate the free charge effect since ions are present in the block-copolymer melt. In PMMA the ionic solvating ability is due to $\mathrm{Li}^+ \leftarrow \mathrm{O{=}C}$ coordination bridges. Nonpolar polymers such as PS do not form coordination bridges of this type and preclude the dissociation of ionic pairs. Hence, dissociated charges are found mainly inside the PMMA-rich spherical domains, as is measured by Kim and Oh [20] and reconfirmed by our own experiments. We denote by Q the total charge of *dissociated* ions inside each PMMA spherical domain. Q is much smaller than the nominal amount of ions in the sphere. It should be emphasized that in contrast to the "leaky dielectric" model of Taylor and Melcher [21] describing the electrohydrodynamics phenomena in conducting dielectric fluids, here there is no flow of material, but rather an elastic behavior of the polymer chains.

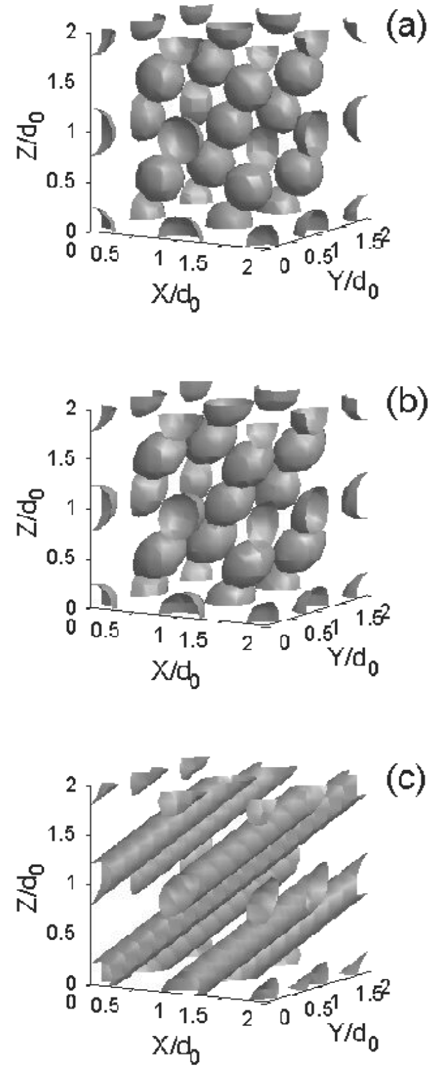

FIG. 1. Plot of the intermaterial dividing surface defined by $\phi(\mathbf{r}) = \frac{1}{2} - f$. A bcc lattice of spheres with $E = 0$ is shown in (a). In (b) the field is $E = 0.98E_c$ and the spheres are highly deformed. The system undergoes an abrupt change into a hexagonal phase of cylinders at $E = E_c$. In (c) the shown field is $E = 1.02E_c$. The chosen parameters are $f = 0.37$ and $N\chi = 12$, $N = 500$, $b = 2.5 \times 10^{-10}$ m, $\beta = 1.7 \times 10^{-17}\ \mathrm{m^2/V^2}$. Explicit dependence of τ, h, u, and Λ on $N\chi$ and f is given in Ref. [13].

We carried out dc conductivity measurements at 160 °C in pure PMMA and PS films doped with 6.6×10^{14} LiOH ions per m^3. In the PMMA sample, the integrated transient current after the voltage is applied indicates that the mobile (dissociated) ions constitute a fraction of 3×10^{-5} of the total embedded ions. The actual fraction of dissociated pairs in the PS/PMMA block copolymer system is expected to be higher because of the high doping [20]. The hazy and strongly birefringent PS sample showed no decaying currents, indicating a negligible amount of dissociated pairs. Since each spherical domain has approximately six PMMA chains, we deduced from the fraction 3×10^{-5} mentioned above that $Q \gtrsim 10^{-3}e$. In addition, from the conductivity data and charge density estimates we calculate the Li^+ mobility in PMMA to be $\mu \simeq 4.6 \times 10^5\ \mathrm{m^2/J\,sec}$.

In the presence of the E field, there is $+Q$ charge at one end of the bcc domain and $-Q$ at the other end, creating an effective dipole. The two energy contributions are the dipole-field and dipole-dipole interactions. The first contribution is the usual dipole-field interaction. The dipole moment of each bcc domain is $|\mathbf{p}| = 2QR$, where $R \approx 0.2d_0 \approx 2$ nm is the sphere radius. The dipole-field interaction energy per unit volume in the bcc phase is

$$F_{\text{d-f}}^{\text{bcc}} = -4QRE/d_0^3. \tag{3}$$

Note that this energy is linear in the field E and in the charge Q.

In the hexagonal phase the drift distance λ for dissociated ions can be very large. For an ac field of frequency w, λ is given by $\lambda = 2\pi e\mu E/w$. In a dc field ($w = 0$) this infinite length is limited by the experimental duration (dozens of seconds) or the system size, and therefore we take $\lambda \approx 1\ \mu$m (which corresponds to time scales of about 1 sec). The dipole-field interaction in the hexagonal phase is

$$F_{\text{d-f}}^{\text{hex}} = -4Q\lambda E/d_0^3 \gg F_{\text{d-f}}^{\text{bcc}}. \tag{4}$$

The ability of the charges to delocalize and diffuse in the hexagonal phase is the driving force behind this bcc to hexagonal transition [22].

The dipole-dipole interaction can be divided to interaction of the charges inside the same sphere and between neighboring spheres. Inside the same domain the interactions between charges are balanced by thermal dissociation and, therefore, affect only their number Q. Dipole-dipole interaction between adjacent domains is estimated by summing up all dipoles taken to be parallel to the field. The contribution per unit volume is $F_{\text{d-d}} \simeq 75(QR)^2[\varepsilon_{\text{eff}} d_0^6]^{-1}$ [23], where ε_{eff} is the effective dielectric constant of the compound material and is taken here to be just the average, $\bar{\varepsilon}$. This free energy contribution is positive (destabilizing the bcc phase) and quadratic in the charge Q.

We now compare the total free energy difference between the bcc and hexagonal phases. The last terms calculated, $F_{\text{d-d}}$ and $F_{\text{d-f}}^{\text{hex}} - F_{\text{d-f}}^{\text{bcc}} \approx F_{\text{d-f}}^{\text{hex}}$, need to be compared to the dielectric contribution F_{dielec} and the bare polymeric difference $\Delta F = F_b[\phi^{\text{hex}}] - F_b[\phi^{\text{bcc}}] \approx k_B T/(200Nb^3)$ (see Ref. [13]). The value of ΔF can be reduced by approaching the bcc/hex phase-transition boundary on the $N\chi$–f phase diagram. When comparing orders of magnitudes for a field $E = 6$ V/μm we see that

$$\frac{F_{\text{d-f}}^{\text{hex}}}{\Delta F} \simeq 1, \qquad \frac{F_{\text{dielec}}}{\Delta F} \simeq 6 \times 10^{-4}, \qquad \frac{F_{\text{d-d}}}{\Delta F} \simeq 5 \times 10^{-5}. \tag{5}$$

Therefore, the dominant mechanism in the bcc to hexagonal transition is the interaction of ions with the external fields, and for the above parameters it is about 10^4 stronger than the dielectric mechanism. Because $F_{\text{dielec}} \sim E^2$ [Eq. (2)] while $F_{\text{d-f}}^{\text{hex}} \sim E$, only at much higher E fields will the former dominate. The dipole-dipole interaction between domains is independent on E and is negligible.

In conclusion, we propose an alternative mechanism explaining structural changes in polarized media such as diblock copolymers. The mechanism is based on the interaction of free charges with an external field rather than on the tendency to reduce dielectric interfaces perpendicular to the field. We calculate the deformation of the bcc phase of diblock copolymers using the dielectric mechanism only, and find that the critical field for transition to a hexagonal phase is $E_c \approx 70$ V/μm. It is shown that the ions which are normally present in these materials can cause a similar structural change but with a much smaller field of order 6 V/μm. Thus, this mechanism should be the dominant one. Moreover, the strength of this mechanism can be greatly enhanced by the addition of ions. We note that there has already been some evidence that the bcc to hexagonal transition in diblock copolymers can be achieved experimentally with such small E field [10]. It will be of interest to use more refined theory and experiment to further investigate the effect of these free ions on other morphological changes and structural phase transitions in anisotropic polarizable media.

We thank T. Russell for discussions and communication of his experimental results prior to publication and T. Thurn-Albrecht for useful comments. One of us (D. A.) acknowledges support from the Israel Science Foundation under Grant No. 210/02.

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