Interplay of Electrohydrodynamic Structure Formation and Microphase Alignment in Lamellar Block Copolymers — Supplementary Information

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We discuss the stability of a toroidal undulation in terms of the the free energy difference for a ring-array of isolated drops with respect to a toroidal rim

$$\Delta G_{tot} = \Delta G_\gamma + \Delta G_E + \Delta G_I. \tag{1}$$

The first term is the surface tension contribution G_γ. A toroidal undulation tends to break up into smaller isolated volumes with the same overall volume V but with a reduced polymer-air surface area A, driven by the surface tension γ_{PS}. A toroidal undulation is formed by the nucleation of a central column in a film with initial thickness z_0, with a modulation amplitude δ, wave vector q (i.e. wavelength $\lambda = 2\pi/q$) at the radius $r = k\lambda$ ($k = 0, 1, 2, ...$). Assuming a sinusoidal modulation in the cylindrical coordinates, the local film height is

$$z = z_0 + \delta\cos(qr). \tag{2}$$

The surface free energy per volume of the toroid is

$$G_\gamma = \gamma_{PS}\frac{A}{V} = \gamma_{PS}\iint r\,\mathrm{d}\theta\mathrm{d}s \Big/ \iiint r\,\mathrm{d}\theta\mathrm{d}r\mathrm{d}z. \tag{3}$$

Since λ is the intrinsic wavelength of the instability, we assume that the secondary instability along the torus decays with the same mode. This gives rise to $2\pi r \approx 6m\lambda$ ($m = 0, 1, 2, ...$), which is in line with previous experimental results [1]. ΔG_γ arises from the difference in A of the two conformations (toroid *vs.* isolated volumes).

The second term in Eq. (1) is the electrostatic energy contribution. For simplicity, we consider a homogeneous layered system subjected to a fixed voltage, i.e. at very early and very late stages of the instability. The electric field energy per volume is

$$G_E = -\frac{1}{2}C_{\mathrm{vol}}U^2, \tag{4}$$

where U is the voltage applied, C_{vol} is the per volume capacitance, which depends on (1) the polymer/air arrangement within the capacitor gap and (2) the alignment of the block-copolymer morphology within respect to the field lines. The minus sign stems from the orientation dependence of the depolarization field, which results from the surface charges of a dielectric body in an electric field.

For an initial homopolymer/air double-layer with film thickness h, dielectric constant ϵ_p, air layer thickness $d-h$, and dielectric constant ϵ_{air}, the capacitance per volume of a capacitor with area A is given by the capacitances of the two individual layers in series

$$C_{\mathrm{vol}} = \frac{1}{V}\left(\frac{h}{\epsilon_0\epsilon_{\mathrm{p}}A} + \frac{d-h}{\epsilon_0\epsilon_{\mathrm{air}}A}\right)^{-1}, \tag{5}$$

with ϵ_0 the vacuum permittivity. The instability proceeds to form plugs spanning the two electrodes (spaced at a distance d), covering an area A_{p}. The capacitance is then calculated by the a parallel configuration of air and polymer filled capacitors

$$C_{\mathrm{vol}} = \frac{1}{V}\left(\frac{\epsilon_0\epsilon_{\mathrm{p}}A_{\mathrm{p}}}{d} + \frac{\epsilon_0\epsilon_{\mathrm{air}}(A-A_{\mathrm{p}})}{d}\right). \tag{6}$$

EHD instabilities of BCP films and the break-up of BCP containing structures are more complex because the alignment of the BCP lamellae with repeat to the electric field lines gives rise to additional capacitance terms. Since spin-cast PS-*b*-PMMA films are typically not (or only partially) micro-phase separated, the average of the PS and PMMA dielectric constants was used. This is electrostatically identical the effective dielectric constant of the final, electrode-spanning state of the BCP, where the lamellae are aligned along the electric field lines. The expression $\epsilon_{\mathrm{p}} = (\epsilon_{\mathrm{PS}} + \epsilon_{\mathrm{PMMA}})/2$ was therefore used for both the initial and final expressions of G_{E}.

The third term in Eq. (1) arises from the internal energy of the micro-phase-separated block copolymer melt. It has two contributions, $G_{\mathrm{I}} = G_{\gamma_{\mathrm{I}}} + G_{\mathrm{el}}$, quantifying the balance between interfacial energy of the two polymer blocks and the elastic energy of deforming the lamellar stack, respectively [2]. Here, we use an Alexander-de Gennes type scaling relationship for the change in BCP internal energy arising from a deformation of the lamellar microphase morphology [3–6]. Per unit volume

$$G_{\gamma_{\mathrm{I}}} = 2\frac{\gamma_I}{D} \tag{7}$$

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and

$$G_{\mathrm{el}} = \frac{3}{2}\frac{k_{\mathrm{B}}T}{N\nu}\sum_i\left[\left(\frac{D_i}{D_{i,0}}\right)^2+\left(\frac{D_{i,0}}{D_i}\right)^2-2\right] = 3\frac{k_BT}{N\nu}\left(\frac{D^2}{2Na^2}+\frac{2Na^2}{D^2}-2\right), \quad (8)$$

where γ_{I} is the PS-PMMA interfacial tension and D is lamellar spacing consisting of the sum of PS and PMMA lamellar thicknesses, D_{PS} and D_{PMMA}, respectively (parameterized by the index i). For BCPs with symmetric blocks, $D_{\mathrm{PS}} = D_{\mathrm{PMMA}} = D/2$. $D_{i,0}$ refers to the equilibrated, undeformed chains with Gaussian end-to-end distances $D_{i,0} = a\sqrt{N/2}$. N is the total degree of polymerisation of the BCP ($N_{\mathrm{PS}} \approx N_{\mathrm{PMMA}} \approx N/2$) and $a \approx a_{\mathrm{PS}} \approx a_{\mathrm{PMMA}}$ is the Kuhn segment length. $N\nu$ is the volume of a BCP coil, with ν the monomer volume. For our system, $a = 0.52 \pm 0.05\,\mathrm{nm}$ and $\nu \approx 100\,\mathrm{Å}^3$ [7]. k_{B} is Boltzmann's constant and T is the temperature.

The internal energy difference was calculated by comparing the lamellar spacing in different confinement situations. In our case, the average lamellar spacing in the innermost columns (R_0) is as high as $1.47D_{\mathrm{eq}}$, dropping to around $1.37D_{\mathrm{eq}}$ for R_1 (Fig. 3d), where D_{eq} is the equilibrium lamellar spacing.

The value of ΔG_{tot} was calculated for the two conformations shown in the inset in Fig. 4b, (1) the transition of a supported rim to a ring of supported drops, and (2) and electrode-spanning, fully formed ring plug compared to a ring of cylindrical plugs.

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