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Phase Behavior of Ring Diblock Copolymer Melt in Equilibrium and under Shear

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The phase behavior of diblock copolymer rings did not attract as much attention as the phase behavior of their linear counterparts (see refs 1 and 2 and references therein). Recently Marko[3] considered the weak-segregation regime of the diblock copolymer ring melt and assuming Gaussian chain statistics calculated the order−disorder transition (ODT) temperature as a function of composition f (A monomer fraction). In this work, we calculate the nonlinear response properties of such a melt and obtain its phase diagram.

In Leibler's formalism[4] the random phase approximation connects the third and fourth-order vertex functions with 2-, 3-, and 4-point correlation functions of Gaussian chains. The usage of the Gaussian statistics for ring polymers is questionable (see refs 5−10 for discussion). However, the radius of gyration R_G of a ring polymer scales with the polymerization index N as almost Gaussian: $R_G \sim N^{\nu}$; $\nu = 0.4-0.45$. Also the ODT temperatures computed by Marko are in a good agreement with simulation data.[7] Therefore, we can use Gaussian statistics as a first approximation.

Marko has obtained the following equation for the probability to find two monomers separated by α and $N-\alpha$ monomers along the N-monomer ring at the positions $\mathbf{r}$ and $\mathbf{r}'$

$$P_2(\mathbf{r},\mathbf{r}',\alpha) = \frac{L(\mathbf{r}-\mathbf{r}',\alpha)L(\mathbf{r}'-\mathbf{r}, N-\alpha)}{L(\mathbf{0}, N)} \quad (1)$$

where $L(\mathbf{R}, \alpha)$ stands for the probability of a Gaussian chain segment to have its ends at positions $\mathbf{0}$ and $\mathbf{R}$

$$L(\mathbf{R}, \alpha) = \left(\frac{3}{2\pi a^2\alpha}\right)^{3/2} \exp\left(-\frac{3R^2}{2a^2\alpha}\right) \quad (2)$$

where a is a monomer size, and the radius of gyration $R_G{}^2 = Na^2/6$. The multiplier $L(\mathbf{0}, N)^{-1}$ is a normalization constant. The Fourier transform of the eq 1 is[3]

$$P_2(\mathbf{q}_1,\mathbf{q}_2,\alpha) = (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2)\exp\left[-\frac{x}{N^2}\alpha(N-\alpha)\right], \quad x = q^2R_G{}^2 \quad (3)$$

We derive similar expressions for three- and four-monomer probabilities

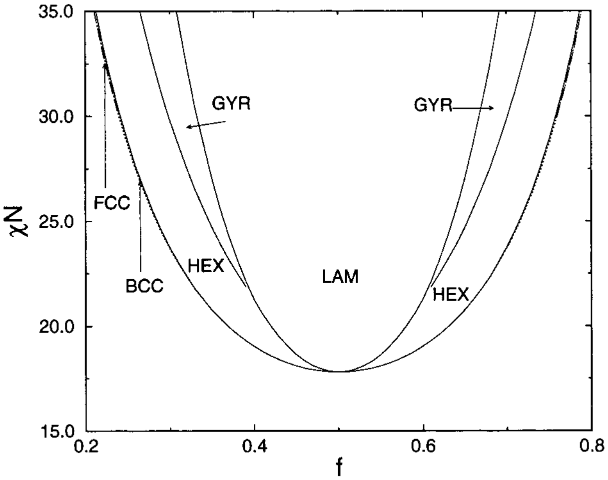

Figure 1. Phase diagram for the diblock copolymer ring. With increase of the χN parameter the following sequence of transitions takes place: DIS ↔ fcc(0.24) ↔ bcc(0.33) ↔ HEX ↔ GYR(0.39) ↔ LAM. The number in brackets indicates the compositional limit of stability of the corresponding phase.

$$P_3(\mathbf{r},\mathbf{r}',\mathbf{r}'',\alpha,\beta) = \frac{L(\mathbf{r}-\mathbf{r}',\alpha)L(\mathbf{r}'-\mathbf{r}'',\beta)L(\mathbf{r}''-\mathbf{r}, N-\alpha-\beta)}{L(\mathbf{0}, N)} \quad (4)$$

$$P_4(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''',\alpha,\beta,\gamma) = [L(\mathbf{r}-\mathbf{r}',\alpha)L(\mathbf{r}'-\mathbf{r}'',\beta)L(\mathbf{r}''-\mathbf{r}''',\gamma)L(\mathbf{r}'''-\mathbf{r}, N-\alpha-\beta-\gamma)]/L(\mathbf{0}, N) \quad (5)$$

together with their Fourier transforms

$$P_3(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\alpha,\beta) = (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3) \times \exp\left[-\frac{x}{N^2}(\alpha(N-\alpha) + h\beta(N-\alpha-\beta))\right] \quad (6)$$

$$P_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4,\alpha,\beta,\gamma) = (2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4) \exp\left[-\frac{x}{N^2}\{(N-\alpha-\gamma)(\alpha+\gamma) + h_2\alpha\gamma + h_1\beta(N-\alpha-\beta-\gamma)\}\right] \quad (7)$$

where following Leibler we assumed that all wavevectors have the same length q_*, and introduced the angle variables

$$|\mathbf{q}_3|^2 = hq_*{}^2 \quad \text{for } P_3$$

$$(\mathbf{q}_1+\mathbf{q}_2)^2 = h_1q_*{}^2 \text{ and } (\mathbf{q}_1+\mathbf{q}_4)^2 = h_2q_*{}^2 \quad \text{for } P_4$$

Expressions for the linear response functions were presented by Marko.[3] Analogous expressions for the nonlinear functions are provided in the Appendix. Once those functions are known, the vertex functions can be calculated with the help of eqs V-16 and V-17 from ref 4. The phase diagram construction is straightforward and was explained elsewhere (see ref 4 for the general method and 11 for details). The result is presented in Figure 1. The phase behavior of the ring diblock copolymer melt is almost the same as that of the linear diblocks with the transition temperatures shifted (in

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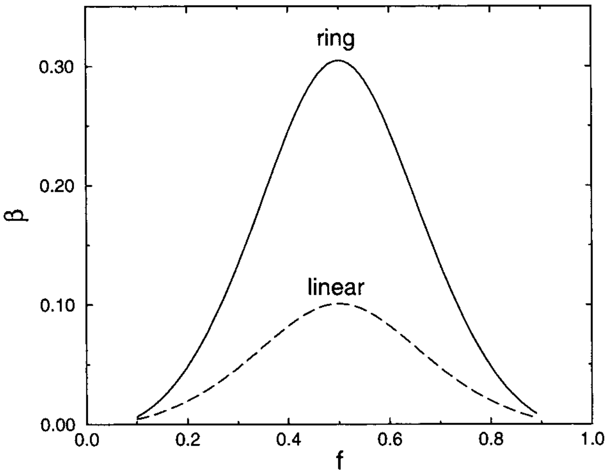

Figure 2. Parameter β as a function of composition.

agreement with 12). The only difference is a big compositional range $f = 0.33-0.67$ where the direct transition DIS → HEX occurs.

At the end, we want to discuss briefly the orientational behavior of a ring diblock copolymer melt subjected to steady shear flow. The recently developed theory for the orientational transitions in the lamellar[13] and hexagonal[14] phases shows that the nonequilibrium thermodynamic potential Φ can be written as

$$\Phi = \Phi_0 + \beta^n \Phi_1 F(D) \cos(m\theta),$$

$$F(D) = \begin{cases} -D^2, & D \to 0 \\ D^{-1/3}, & D \to \infty \end{cases} \quad (8)$$

where Φ_0 denotes the orientation-independent part, D denotes the shear rate, and n,m are symmetry-dependent integers ($n = 1$, $m = 1$ for lamellae; $n = 3$, $m = 6$ for hexagons). The potential in (8) favors the parallel orientation to be stable at low and the perpendicular one at high shear rates (see refs 13 and 14 for details). The parameter β determines the strength of the angle dependence of the fourth order vertex function: $\Gamma_4(0,h) = \lambda[1 - \beta(1 - h/2)^2]$. For the linear diblocks, β is small and positive. As we noted before,[15] if β changes sign the perpendicular and parallel orientations exchange their positions on the orientational phase diagram. This was shown to happen for some systems (ABA triblocks with nonsymmetric A blocks, for example). To check whether it happens for rings we use the obtained equation for Γ_4 to calculate β in the following way[15]

$$\beta = \frac{3c_2}{2c_0 - c_2} \quad (9)$$

where

$$c_0 = \frac{1}{2}\int_0^2 \mathrm{d}h\ \Gamma_4(h,0)$$

$$c_2 = \frac{5}{2}\int_0^2 \mathrm{d}h\ \Gamma_4(h,0)\left[1 + \frac{3h}{2}\left(\frac{h}{4} - 1\right)\right] \quad (10)$$

Figure 2 compares the compositional dependence of β for the ring diblock copolymers with that for the linear diblocks. The parameter β stays positive providing that the ring diblock melt shows the same orientational behavior as its linear counterpart. The absolute value stays small enough to justify its usage as a small parameter in perturbation theory.[13,14] However, $\max(\beta_{\text{ring}})/\max(\beta_{\text{linear}}) \approx 3$. This shows that the orientation-dependent term in eq 8 is larger for the ring diblocks. Therefore, we predict them to align better than the linear diblocks when subjected to shear.

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Appendix

Similar calculations were performed in refs 4, 16, and 11. Here we introduce the following notation:

$$T_{i_1,i_2,i_3}(\alpha,\beta) = \frac{1}{N}\int_0^{i_1}\mathrm{d}s \int_0^{i_2}\mathrm{d}s' \int_0^{i_3}\mathrm{d}s'' \exp\left[-\frac{x}{N^2}(\alpha(N - \alpha) + h\beta(N - \alpha - \beta))\right] \quad (11)$$

$$U^{i,j}_{i_1,i_2,i_3,i_4}(\alpha,\beta,\gamma) = \frac{1}{N}\int_0^{i_1}\mathrm{d}s \int_0^{i_2}\mathrm{d}s' \int_0^{i_3}\mathrm{d}s'' \int_0^{i_4}\mathrm{d}s''' \times \exp\left[-\frac{x}{N^2}\{(N - \alpha - \gamma)(\alpha + \gamma) + h_j\alpha\gamma + h_i\beta(N - \alpha - \beta - \gamma)\}\right] \quad (12)$$

The equations for the third-order functions read as follows:

$$G_{\mathrm{AAA}} = 2(2T_{f,s,s'}(s' - s'', s - s') + T_{f,s,s'}(N - s + s'', s' - s'')) \quad (13)$$

$$G_{\mathrm{AAB}} = 2T_{1-f,f,s'}(s' - s'', s + fN - s') \quad (14)$$

$$G_{\mathrm{ABA}} = G_{\mathrm{BAA}} = 2T_{1-f,f,s'}((1 - f)N - s + s'', s' - s'') \quad (15)$$

The fourth-order functions are

$$G_{\mathrm{AAAA}} = 4\sum_{i=1}^{3}\sum_{j=1}^{3}(1 - \delta_{ij})U^{i,j}_{f,s,s',s''}(s'' - s''', s' - s'', s - s') \quad (16)$$

$$G_{\mathrm{AAAB}} = G_{\mathrm{AABA}} = G_{\mathrm{ABAA}} = G_{\mathrm{BAAA}} = \sum_{i=1}^{3}\sum_{j=1}^{3}(1 - \delta_{i,j})U^{i,j}_{1-f,f,s',s''}(s'' - s''', s' - s'', s + fN - s') \quad (17)$$

$$G_{\mathrm{AABB}} = G_{\mathrm{BBAA}} = 2\sum_{i=2}^{3}U^{1,i}_{1-f,s,f,s''}(s'' - s''', fN - s'' + s', s - s') \quad (18)$$

The other functions can be obtained by exchanging A ↔ B and $f \leftrightarrow (1 - f)$. For G_{ABAB} and G_{ABBA} one needs to swap $h_1 \leftrightarrow h_3$ and $h_1 \leftrightarrow h_2$ respectively in the equation for G_{AABB}. Unfortunately, all these integrals cannot be calculated analytically and should be treated numerically.

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