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Architecture Influence on the Orientational Phase Behavior of the AB Block Copolymer Melts under Shear Flow

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Recently, Fredrickson has formulated a theory describing the reorientation of the lamellar phase in steady shear flow.[1] He started with a phenomenological Landau−Brazovskii Hamiltonian

$$H[\psi] = \frac{1}{2}\int_q [\tau + (q - q_0)^2]\psi(\mathbf{q})\,\psi(-\mathbf{q}) + \frac{1}{3!}\int_{q1}\int_{q2}\int_{q3}\xi(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\,\psi(\mathbf{q}_1)\,\psi(\mathbf{q}_2)\,\psi(\mathbf{q}_3) + \frac{1}{4!}\int_{q1}\int_{q2}\int_{q3}\int_{q4}\bar{\lambda}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)\,\psi(\mathbf{q}_1)\,\psi(\mathbf{q}_2)\,\psi(\mathbf{q}_3)\,\psi(\mathbf{q}_4) \quad (1)$$

where the local deviation of the density of one component from its average value plays a role of the order parameter $\psi(\mathbf{r})$. As the next step, he supposed that the order parameter dynamics is governed by a simple Langevine (or Fokker−Planck) equation describing a relaxation due to diffusion and a convection associated with an applied shear. With the help of the approximation

$$\xi(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = \xi\delta(\hat{\mathbf{q}}_1 + \hat{\mathbf{q}}_2 + \hat{\mathbf{q}}_3)$$
$$\bar{\lambda}(\mathbf{q}_1,\mathbf{q}_2,-\mathbf{q}_1,-\mathbf{q}_2) = \lambda[1 - \beta(\hat{\mathbf{q}}_1\cdot\hat{\mathbf{q}}_2)^2], \quad \beta \ll 1 \quad (2)$$

where $\hat{\mathbf{q}} = \mathbf{q}/q$ denotes the unit vector in the direction of $\mathbf{q}$, and all $\mathbf{q}$-vectors have the same modulus q_0, Fredrickson has shown that the effective steady-state thermodynamical potential has the following form:

$$\Phi_{\mathrm{lam}} = \Phi^{(0)}_{\mathrm{lam}} + \beta\Phi^{(1)}_{\mathrm{lam}}F(D)\cos(\theta), \qquad F(D) = \begin{cases} -D^2, & D \to 0 \\ D^{-1/3}, & D \to \infty \end{cases} \quad (3)$$

where D denotes the shear rate, the angle θ determines the orientation of the lamellae ($\theta = 0$ corresponds to the parallel lamellae), and $\Phi^{(0)}_{\mathrm{lam}}$ denotes the orientation-independent part of the potential Φ_{lam}. Equation 3 predicts the parallel lamellae to be stable at low and the perpendicular lamellae at high shear rates. The additional assumption about the order parameter dependency of the viscosity of the system in the form

$$\eta(\mathbf{r}) = \eta_0 + \eta_1\psi(\mathbf{r}) \quad (4)$$

allowed Fredrickson to predict a low-temperature region of stability for the parallel lamellae in the limit of high shear rates.

We applied a similar formalism to the reorientational transitions occurring in the hexagonal phase.[2] Analogously to (3), we obtained the following equation

$$\Phi_{\mathrm{hex}} = \Phi^{(0)}_{\mathrm{hex}} + \beta^3\Phi^{(1)}_{\mathrm{hex}}F(D)\cos(6\theta) \quad (5)$$

where the angle θ determines the orientation of the hexagonal lattice ($\theta = 0$ corresponds to the parallel orientation in real space). The summary of the orientational behavior of the lamellar and hexagonal phases is shown in Figure 1. Similar phase diagrams (without orientations) were presented by Cates and Milner,[3] Marques and Cates,[4] Fredrickson,[1] and Muthukumar.[5] These phase diagrams are in a qualitative agreement with experimental observations for the lamellar[6,7] and hexagonal[8,9] phases. The theory, however, fails to predict additional transition from the perpendicular to parallel orientation at very high shear rates[10,11] for reasons discussed in ref 12. Recent observations of a high-shear rate disordered state in symmetric pentablocks by Vigild et al.[13] also cannot be explained within this approach.

In this paper we want to outline the role of the parameter β in the discussed theories. As it was noticed in ref 2, since all the quantities are evaluated as series in β, the angle-dependent part of the thermodynamical potential Φ is proportional to β^n, where n depends on the symmetry of the phase (see eqs 3 and 5, for example). Moreover, the phase behavior presented in Figure 1 is based on the assumption that $\beta > 0$; for $\beta < 0$ we should swap the phases in Figure 1, so that the regions previously occupied by the parallel phase will now belong to the perpendicular one, and vice versa (see eqs 3 and 5). Finally, the very procedure of the expanding physical quantities in series in β could become invalid if β is not small. Therefore, even the qualitative prediction of the orientational behavior for real system requires the knowledge of β.

In the works[1,2] the assumption $\beta \ll 1$ was based on the observation that Leibler's calculations[14] for diblock molecules show a weak angle dependence of the fourth-order vertex function $\bar{\lambda}$. The same reasoning gives $\beta > 0$. Neither sign nor absolute value of β is known for other architectures. It is, however, possible to connect the phenomenological parameter β with microscopic properties of the system and calculate its value for different compositions and architectures of the molecules. Such a possibility is based on the mean-field calculations of the fourth-order vertex function $\bar{\lambda}$. Recently, we have shown how to generalize Leibler's approach for an arbitrary topology of the AB block copolymer molecules in melt.[15] In the following we assume that we know the exact function $\bar{\lambda}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$ with $q_i = q_0$. We want to use this information to extract β and λ. Since $\bar{\lambda}(\hat{\mathbf{q}}_1,-\hat{\mathbf{q}}_1,\hat{\mathbf{q}}_2,-\hat{\mathbf{q}}_2)$ from (2) depends only on the angle ϕ between $\hat{\mathbf{q}}_1$ and $\hat{\mathbf{q}}_2$, we expand it in the Legendre polynomials

$$\bar{\lambda}(\hat{\mathbf{q}}_1,-\hat{\mathbf{q}}_1,\hat{\mathbf{q}}_2,-\hat{\mathbf{q}}_2) = \sum_{n=0}^{\infty} c_n P_n[\cos\phi] = c_0 + c_2\frac{1}{2}(3\cos\phi^2 - 1)\ \ldots \quad (6)$$

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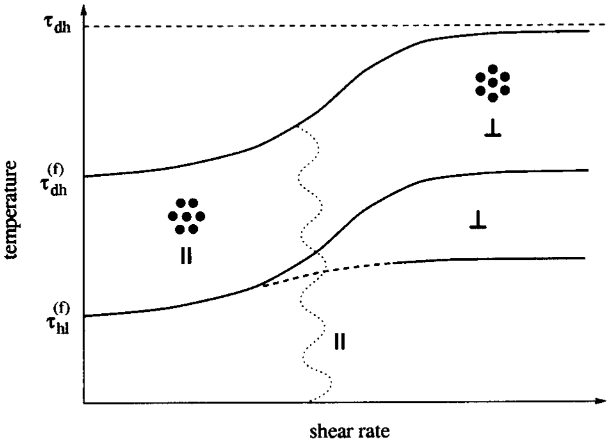

Figure 1. Summary of the orientational behavior for the hexagonal and lamellar phases of AB block copolymer melts subjected to Couette shear flow. Note that, depending on parameters, there also could be a direct transition from disorder to the lamellar phase.[4,5] At zero shear rate the disorder–hexagonal (dh) and hexagonal–lamellae (hl) transition temperatures take the values $\tau_{dh}^{(f)}$ and $\tau_{hl}^{(f)}$ predicted by the fluctuation theory.[19] At low shear rates the transition temperatures behave as $\sim D^2$ while at high shear rates as $\sim D^{-1/3}$.[1–5] The wavy line marks a crossover from the low to high shear behavior. In the limit $D \to \infty$, the transition temperatures reach their mean-field values: $\tau_{dh} = 4\xi^2/(45\bar{\lambda})$ and $\tau_{hl} = -(7 + 3\sqrt{6})\xi^2/(5\bar{\lambda})$.[4] The presented orientations correspond to diblock copolymer melts. Other architectures are predicted to have the reverse phase diagram with the perpendicular and parallel phases swapped ($\parallel \to \perp$).

where $\cos\phi = \hat{\mathbf{q}}_1 \cdot \hat{\mathbf{q}}_2$, and the term with $n = 1$ vanishes because of the symmetry of the $(\hat{\mathbf{q}}_1, -\hat{\mathbf{q}}_1, \hat{\mathbf{q}}_2, -\hat{\mathbf{q}}_2)$-star. Comparison of (2) with (6) gives

$$\lambda = c_0 - \frac{1}{2}c_2, \quad \beta = \frac{3c_2}{2c_0 - c_2} \tag{7}$$

where

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

$$c_2 = \frac{5}{2}\int_0^2 \mathrm{d}h\, \bar{\lambda}(h,0)\left[1 + \frac{3h}{2}\left(\frac{h}{4} - 1\right)\right] \tag{8}$$

Here we adopted Leibler's notation[14] and introduced the angle variables h_1 and h_2: $(\hat{\mathbf{q}}_1 + \hat{\mathbf{q}}_2)^2 = h_1$ and $(\hat{\mathbf{q}}_1 + \hat{\mathbf{q}}_4)^2 = h_2$. With the help of this notation $\bar{\lambda}(\hat{\mathbf{q}}_1, -\hat{\mathbf{q}}_1, \hat{\mathbf{q}}_2, -\hat{\mathbf{q}}_2) = \bar{\lambda}(0,h)$.

It should be mentioned that similar expansions as in eq 6 were utilized before.[16,17] However, they were never used to study the reorientational transitions.

Now we apply eqs 7 and 8 to specific systems. We start with $-(AB)_n-$ polyblock molecules (Figure 2). The simplest case ($n = 1$) represents a diblock molecule. In the limit $f \to 0$ (or $f \to 1$) the molecule reduces to a homopolymer, forming a Gaussian coil with a uniform spacial distribution of the monomers. Therefore, the angle dependency of $\bar{\lambda}$ should vanish and $\beta \to 0$. As the composition f increases, both A and B parts of the molecule form Gaussian coils with a tendency toward mutual spacial separation. Obviously, this tendency reaches its maximum at $f = 0.5$. The positive sign of β can be understood as following. In such a dumbell-like molecule the monomeric density is mostly modulated along the line connecting the centers of mass of two blobs. So, the $\phi = 0$ case in eq 6 corresponds to the most probable configuration and, therefore, gives the lowest contribution to the free energy. Since $\bar{\lambda} = \lambda(1 - \beta\cos^2\phi)$, it follows that $\beta > 0$. However, since the dumbell-like structure is only *a tendency*, the difference between $\phi = 0$ and $\phi = \pi/2$ directions is small. That is why $\max(\beta) \approx 0.1$ is a small number.

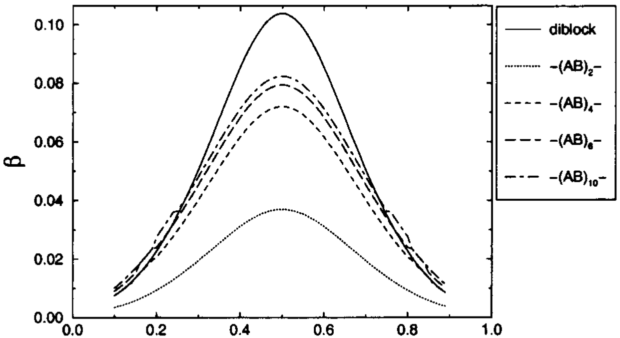

Figure 2. Compositional dependence of β for $-(AB)_n-$ polyblocks. Here f is the total content of the A component in the molecule. All blocks of the same type have equal lengths. Small deviations from smooth curves are caused by numerical evaluation of the integrals in eq 8.

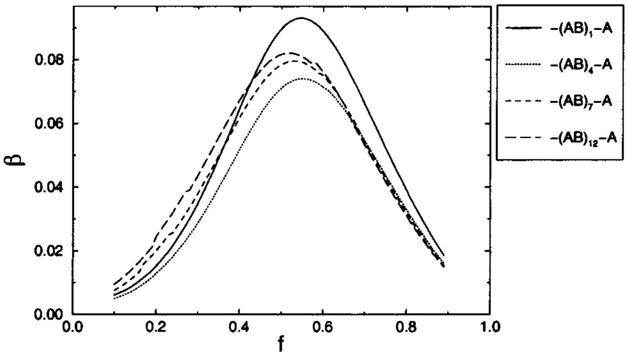

Figure 3. Compositional dependence of β for $-(AB)_n-A$ polyblocks.

As the number of blocks n in the $-(AB)_n-$ molecule increases, $\beta(f)$ keeps its shape but not the absolute value. The $-(AB)_2-$ molecule can be understood as a modification of the diblock molecule, where the junction point has been replaced by another diblock molecule. In such a molecule the monomers are distributed more homogeneously than in a diblock molecule. Therefore, the general behavior of β for $-(AB)_2-$ system remains diblocklike, while the maximum value of β is scaled down. For large n, the effect of the middle blocks is averaged out, and the molecules can be imagined as two end blocks attached to a homopolymer blob. This system behaves very similar to the diblock one with the max(β) value approaching its diblock value from below.

The next example is $-(AB)_n-A$ polyblock (Figure 3). This system behaves very similar to the previous one, with a triblock instead of diblock molecule playing the role of a reference system. The asymmetry of the curves $\beta(f)$ originates from the different numbers of A and B blocks in the molecule. The position of the maximum of these curves can be estimated as a composition at which the total volume of $n + 1$ A Gaussian coils is equal to that of n B ones, so that

$$(n + 1)\left(\frac{f_{\max}}{n + 1}\right)^{3/2} = n\left(\frac{1 - f_{\max}}{n}\right)^{3/2}$$

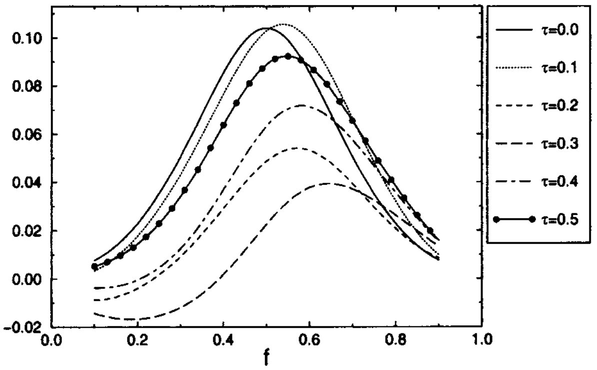

Figure 4. Compositional dependence of β for ABA triblock copolymers with nonequal A blocks: $L_A^{(1)} = \tau fN$ and $L_A^{(2)} = (1 - \tau)fN$.

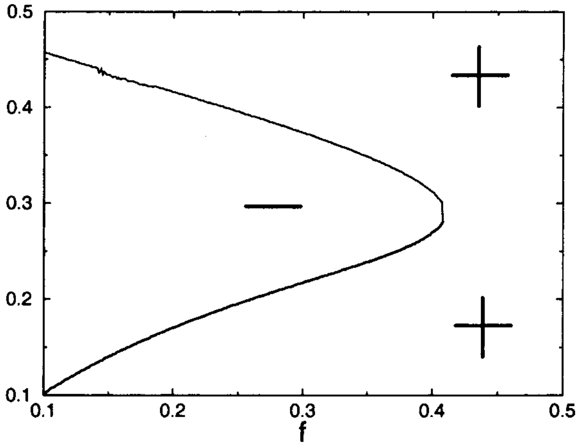

Figure 5. Sign of β as a function of the compositional parameters (f, τ). (Despite the fact that $\beta = 0$ on the line separating positive and negative regions, the orientational behavior does not disappear. One needs to take the next term in the expansion (6). However, the corresponding constant is very small, and the final orientation will more probably be determined by external factors (interactions with shear cell boundaries and so on).)

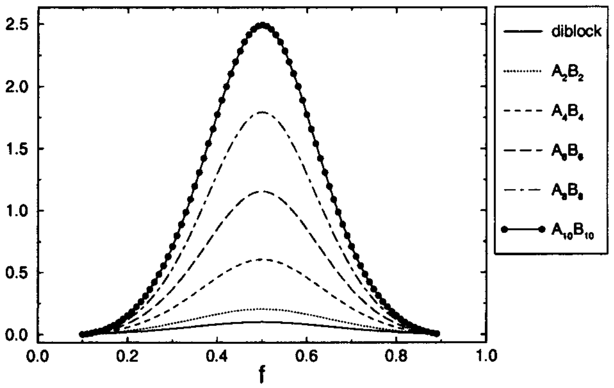

Figure 6. Compositional dependence of β for homopolymer stars A_nB_n.

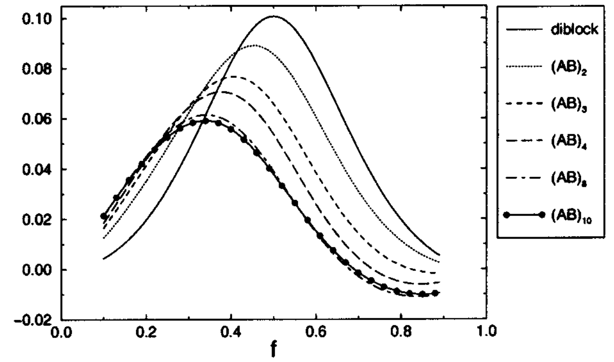

Figure 7. Compositional dependence of β for diblock stars $(AB)_n$.

Here we have ignored all surface contributions. For the triblock molecules the above equation gives $f_{\max} = 0.56$, which is the exact position. For higher n, $f_{\max}$ is slightly underestimated. However, it correctly tends to limit $f_{\max} \to 0.5$ as $n \to \infty$.

In the previous examples we kept all lengths of the A as well as B blocks equal. If we relax this condition, the behavior of β changes drastically. We illustrate this with the help of an ABA triblock molecule with nonequal A blocks (Figure 4). Let f be the total content of the A component and $L_A^{(1)} = \tau fN$, $L_A^{(2)} = (1 - \tau)fN$ be the lengths of two A blocks. Figure 4 shows that the shape of the curve $\beta(f)$ still resembles the diblock one. However, for relatively small f there are such values of τ that β changes its sign. This region of (f, τ) parameters is shown in Figure 5. The appearance of this region is connected with a change of the molecular conformation. When $\tau = 0$, the system occupies the discussed dumbell-like state. When we add a small A block (τ is small but nonzero), it tries to coalesce with the other A block in order to increase the number of favorable contacts. However, the entropy penalty for such a coalescence is big, and the molecular conformation is described by a perturbed dumbell. With the further increase of τ, the second A block moves toward the first one. At some values of τ the most probable configuration corresponds to $\phi = \pi/2$ and β changes its sign. (The most probable conformation gives the smallest contribution to the free energy, and $\bar{\lambda} = \lambda(1 - \beta \cos^2 \phi)$.) With further increase of τ the system comes back close to the dumbell-like structure, as two A blocks are very close, and β becomes positive again. This effect can be observed only at relatively small compositions. At large f the entropy contribution from the B-block conformation is small, and system occupies the dumbell conformation for all τ.

The change of sign of β modifies the orientational behavior. In the region of molecular parameters (f, τ), denoted by "−" in Figure 5, the orientational phase diagram will be the same as in Figure 1 with the perpendicular and parallel phases swapped. The same effect can be observed for other polyblocks, provided that there is an asymmetry in the lengths of blocks of the same type.

Now we switch to another type of system and consider homopolymer stars A_nB_n (each arm of this star is a homopolymer). As was shown by Dobrynin and Erukhimovich,[18] for $\bar{\lambda}(0, 0)$ becomes negative for $n > 5$, while $\bar{\lambda}(0, h \neq 0)$ is positive and large. Therefore, such a system shows a strong angle dependence, and β should be large. Indeed, as is shown in Figure 6, for $n > 5$, β becomes larger than unity. Such a behavior is caused by the collapse of the arms of the same type. The monomers are nearly collected along $\phi = 0$ line, and the molecule can be imagined as a sharp dumbell. This effect is absent for the diblock stars $(AB)_n$ (Figure 7), since the interaction-induced tendency toward the separation between A and B components and the entropy-induced tendency toward uniform spacial distribution of the monomers are separated. With increasing n, the arms of such a molecule tend to fill space uniformly. Therefore, the angle dependence of β diminishes as n

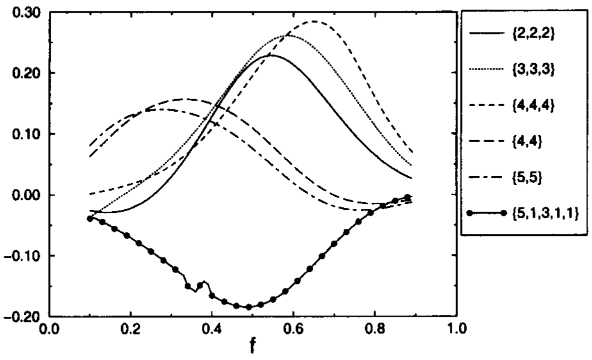

Figure 8. Compositional dependence of β for several dendrimeric structures.

$\to \infty$. The asymmetry of the curves is caused by the topologically different conditions of A and B blocks.

Finally, in Figure 8 we present the composition dependence of β for several dendrimeric systems. We use the notation of ref 2 and describe the molecular architecture by a vector $\{n_1, n_2, ...\}$. The ith element of this vector defines the number of blocks (A-blocks if i is odd and B otherwise) originated from *each* block in the $(i - 1)$th generation. Thus, for example, the {2, 2} dendrimer is equivalent to the H-shaped copolymer. Moreover, here we have assumed that all A as well as B blocks are of the same lengths. Figure 8 shows that β behavior of such complicated structures incorporates all previously discussed features: the shape of the curves resembles the diblock one, β can grow larger that the diblock maximum value $\approx$0.1, it can change sign, and, finally, there can be structures with totally reverse phase behavior (for {5,1,3,1,1} dendrimer in Figure 8, $\beta < 0$ for all f).

In conclusion, we want to emphasize the architecture influence on the predictions of the reorientational transition theory, formulated in refs 1 and 2. The phase diagrams predicted in these works are specific for the diblock copolymers and are not necessarily the same for other architectures. Some systems even exhibit different types of orientational behavior depending on composition and length ratios of blocks. Thus, the ABA triblocks show the reverse type of behavior at low content of A component and asymmetry parameter $\tau = 0.1-0.45$ and the diblocklike behavior for the rest of parameter ranges. We are not aware of any experimental conformation of this result, which could be very confusing for experimentalists. To avoid misinterpretations of experimental data, the application of the reorientational theory to a particular system should be accompanied by calculation of the parameter β. Such a calculation checks whether the theory is applicable to the system in question (β should be small: $|\beta| \ll 1$) and determines the type of behavior: the diblocklike or reverse one.

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