Design of block copolymers for ordered microstructures using free energy landscapes

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Block copolymer melts assemble into various ordered structures. This is because there are various interactions between different types of monomers, and the constraint that the monomers are connected by chemical bonds. This phenomenon also occurs in gradient copolymers[1], which have a chemical distribution of the monomers along the polymer chain. The density functional theory in which the free energy is represented by a functional of the densities of each types of monomers is useful in describing phase separation phenomena. Although this theory is quite successful[2], it does not answer the question "How to generate the desired microstructure?"

In this work, we propose an idea to predict the molecular structure of the copolymer that assembles to a desired self-assembled microphase separated structure. We also propose a useful expression for the free energy functional which can be applied for any monomer distributions of gradient and block copolymers.

The free energy functional is derived by using the standard procedure of the random phase approximation(RPA).

$$F\left[\{\phi_K(\boldsymbol{r})\}\right] \sim \int d\boldsymbol{r}\cdots d\boldsymbol{r}' \Gamma^{(n)}_{K,\cdots,K'}(\boldsymbol{r},\cdots,\boldsymbol{r}') \times \delta\phi_K(\boldsymbol{r})\cdots\delta\phi_{K'}(\boldsymbol{r}'), \quad (1)$$

where $\phi_K(\boldsymbol{r})$ is the volume fraction of K-type monomer at $\boldsymbol{r}$, $K(=A,B,\cdots)$ represents the type of the monomer, $\delta\phi_K(\boldsymbol{r}) \equiv \phi_K(\boldsymbol{r}) - \bar{\phi}_K$ and $\bar{\phi}_K$ is the spatial average of $\phi_K(\boldsymbol{r})$. To calcurate the vertex functions $\Gamma^{(n)}_{K,\cdots,K'}$, we introduce the monomer distribution function $K(s)$, which gives us the probability of finding a monomer of type K at the s-th monomer of the polymer chain. We express the monomer distribution function $K(s)$ using the Fourier expansion as:

$$K(s) = \sum_p K^p \cos\left(\frac{\pi p s}{N}\right). \quad (2)$$

We expect that the asymmetry in the monomer distribution will be important for the case of asymmetric microphase separated structures. Thus we faithfully evaluate not only the second order but also the third order vertex functions in equation (1) using RPA. We approximate the higher order terms in the expansion by the entropic terms of the Flory-Huggins model.

When we specify the density fields $\delta\phi_K(\boldsymbol{r})$, the free energy can be regarded as a functional of monomer distribution functions $\{K(s)\}$. Since we express $\{K(s)\}$ in a Fourier expansion, the free energy is a function of the coefficients $\{K^p\}$. Then, we can find the copolymer that assembles to the desired structure with the coeffcients $\{K^p\}$ give the free energy minimum. This is the free energy landscape(FEL).

Figure 1 is a simple example of the FEL. Here, the target microphase separated structure is a sinusoidal profile of a lamellar phase of A-B copolymers, where A and B-domains are symmetric. In Figure 1, the free energy is negative for the polymers with the parameter $A^1 \simeq 0.5$. This is because we set the origin of the free energy to the free energy of the homogeneous state. That is, the system is more stable when it assembles into the target microphase separated structure than into homogeneous.

Since more stable microphase separated structures than the target structure can exist, we have to check the stability of our target structure. We will discuss this point at the meeting.

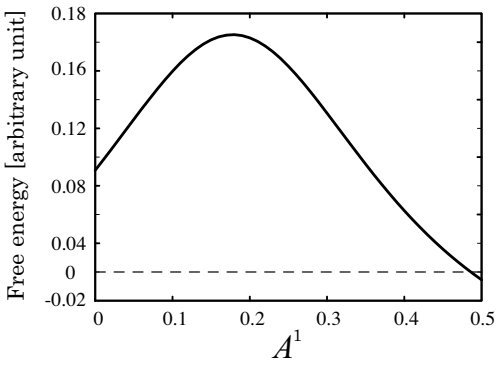

Figure 1: The FEL for the sinusoidal profile of a lamellar structure as a target microphase separated structure. The origin of the free energy is set to the free energy value of the homogeneous state. The coefficients are $A^0 = 0.5, A^1 + A^2 = 0.5, A^p = 0 (p \geq 3)$.

References

[1] A. Aksimentiev and R. Holyst, J. Chem. Phys. **111** (1999), 2329.

[2] L. Leibler, Macromolecules **13** (1980), 1602.