

Various Thermodynamic Factors in Designing Nanostructured Materials from Block Copolymers

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Introduction

Studies on various behavior of block copolymers have drawn tremendous interest from the polymer circle, because those materials exhibit nanoscale self-assembly behavior to form useful nanomaterials. Here, we discuss various thermodynamic factors that affect the design of nanomaterials based on block copolymers. It is well known from the seminal work by Leibler that the copolymer phase behavior is determined by composition ϕ , Kuhn segmental length N , and the ubiquitous phenomenological parameter called Flory's χ . Nanostructures found in A-B diblock copolymers include classical ones such as body centered cubic spheres, hexagonal cylinders, lamellae, and complex ones such as hexagonally perforated layers, gyroid networks according to given ϕ and $N\chi$. The increase of components in A-B-C triblock copolymers of course increases the number of nanostructures with core-shell and decorative structures and also introduces the latest orthorhombic triply connected networks.

However, the recent discovery of self-assembly upon heating, rarely observed immiscibility loops, and baroplasticity addresses a clear need for further microscopic interpretation of such χ . Employing a molecular model of perturbed hard sphere chains in a continuum, the molecular factors such as self and cross-interactions, the amount of free space in domains, and directional interactions is incorporated in χ . It is shown that not only typical self-assembly upon cooling, but also that upon heating, loops, pressure effects are all described through this unified way. The proper choice of molecular parameters is thus shown to control the fabrication windows and to help to design block copolymer nanomaterials at aimed purposes.

Theoretical

Here, we go beyond Leibler's Landau theory for block copolymers with the help of a microscopic model for copolymer chains to suggest the molecular view of the control parameter in designing nanomaterials based on those materials. Let us begin with the system description. The system of interest consists of A-B diblock copolymers with N_A monomers of A type and N_B monomers of B type to have the overall size $N (=N_A+N_B)$. Copolymer chains are assumed as hard sphere chains with perturbed intermonomer interactions. All the monomers in the system are assumed to have the identical diameter σ . The $\phi_A = N_A/N$ defines a volume fraction of A monomers on the copolymer chains. The system is allowed to be compressible. We denote as η_f the fraction of free volume in the system, and as $\eta = 1 - \eta_f$ the total packing density that is the fraction of volume occupied by all the monomers present.

The Landau analysis is a useful tool to probe weakly phase segregating block copolymer systems in a mean-field situation. The difference ΔF in free energies between ordered and disordered states is expanded as a power series in the order parameters, $\psi_1(\mathbf{r}) (= 1/2\eta(\langle \eta_A(\mathbf{r}) - \eta_A \rangle - \langle \eta_B(\mathbf{r}) - \eta_B \rangle))$ and $\psi_2(\mathbf{r}) (= -\langle \eta_f(\mathbf{r}) - \eta_f \rangle)$, where $\eta_A(\mathbf{r})$ and $\eta_f(\mathbf{r})$ are respectively the local packing density of *i*-monomers and the local free volume fraction, and the brackets indicate the thermal average of the difference between the local and the global values. The ΔF is then rewritten as a power series in the Fourier-transformed $\psi_1(\mathbf{q})$ and $\psi_2(\mathbf{q})$, with the *m*th-order vertex functions $\Gamma_{i,j}^{(m)}$ as its coefficients. After $\psi_1(\mathbf{q})$ is written in polar form, a minimization procedure leads to a Landau free energy expansion in only $\psi_1(\mathbf{q})$ with effective vertex terms as its coefficients at a characteristic wavenumber q^* . The effective quadratic coefficient Γ_2 can be shown that $\Gamma_2 = \eta[2\chi_s - 2\chi_F]$, where χ_s is given from the correlation functions S_{ij}^0 of noninteracting Gaussian A-B copolymers as $\Sigma \eta_i S_{ij}^0 / \det(S_{ij}^0)$, and χ_F is an effective Flory-type interaction parameter and subdivided into $\chi_F = \chi_{app} + \chi_{comp}$. The former is the density-dependent exchange energy term as $\chi_{app} \propto [\epsilon_{11} + \epsilon_{22}$

$- 2\epsilon_{12}]$, where ϵ_{ij} is Lennard-Jones-type *i,j*-contact interaction parameter. The latter is given as $\chi_{comp} = \Gamma_{12}^2 / 2\eta \Gamma_{22}$, where Γ_{12} represents the disparity in equation-of-state properties between constituents and its bulk thermodynamic analogue would be $\partial P / \partial \phi$.

Discussion

Self and cross interactions. The widely used equilibrium phase diagram for A-B nanostructures is given in Figure 1, where only the classical morphologies are shown. Other complex morphologies should be placed at a proper composition and segregation level. Let us consider a real system with finite compressibility. In the simplest situation, the self-interactions are the same for both components as $\epsilon_{11} = \epsilon_{22}$. This case includes the incompressible system studied by Leibler as its limit. The phase diagram is exactly identical to Figure 1 except the Flory χ is replaced with the theoretical χ_F that is density dependent. The distribution and the fraction of free space is determined by the given continuum model. If there is a disparity in equation-of-state properties between block components as $\epsilon_{11} > \epsilon_{22}$, then the mean-field phase diagram reveals a drastic changes as in Figure 2. The continuous point present in Figure 1 and thus the Ising-character disappear due to the preference of free space distribution to a component with weaker self interactions or lesser binding energies. The presence of free space and its preference yields the profound effects on morphology development during processing, where pressure is normally exerted to the molten materials. As is seen in Figure 3, the disparity in self interactions could yield diversified pressure responses such as pressure-induced ordering (barotropicity) and disordering (baroplasticity), or revealing both together. This compelling pressure dependence of block copolymers originates in the competing responses of χ_{app} and χ_{comp} to pressure, where the former increases upon pressurization due to the increased density and the latter decreases due to the suppressed equation-of-state property disparity. In particular, the baroplastic materials can offer the facilitated fabrication from low temperature processing because of the relieved elastic resistance upon disordering. Real examples for each case of materials are polystyrene-*b*-polybutadiene, polystyrene-*b*-polyisoprene, polystyrene-*b*-poly(methyl methacrylate) for barotropicity; polystyrene-*b*-poly(*n*-hexyl methacrylate), polystyrene-*b*-poly(2-ethyl hexyl acrylate) for baroplasticity. For the mixed behavior of barotropicity and baroplasticity, poly(ethylene-propylene)-*b*-poly(dimethyl siloxane) and poly(ethylene-ethylene)-*b*-poly(dimethyl siloxane) reveal such a peculiar behavior.

Directional interactions. Another important design parameter is the directional interactions between dissimilar monomers such as hydrogen bonding or weaker dipole-dipole interactions. The presence of directional interactions can yield self-assembly upon heating or even an immiscibility loop with typical self-assembly upon cooling on top of the loop, as seen in Figure 4. These materials can be used as high temperature adhesives and sensor materials.

Theoretically, directional interactions can be incorporated in the above procedure by taking the cross-interaction parameter to be modified to have free energy-like character. The ϵ_{ij} per one cross-contact is replaced with $\epsilon_{ij} + \delta\epsilon - kT \ln[\theta/(1+d)]$, where $\delta\epsilon$ is the energy increment due to the directional interactions and θ the fraction of the total number of cross-contacts that are directional. The symbol *d* denotes the ratio of the statistical degeneracies of nonpolar and directional interactions. Examples for the copolymers with directional interactions are the homologous series of polystyrene-*b*-poly(*n*-alkyl methacrylates) from ethyl to *n*-pentyl side groups.

Polystyrene(1)-*b*-poly(*n*-pentyl methacrylate)(2), which is characterized with the molecular parameter set of $\epsilon_{22}/\epsilon_{11} = 0.9$, $\epsilon_{12} = 0.98318(\epsilon_{11}\epsilon_{22})^{1/2}$, and $\delta\epsilon/\epsilon_{11} = 0.18$, exhibit the loop with an enormous pressure sensitivity, as seen in Figure 5. In this figure, concentration fluctuation (Hartree) corrections are considered. This type of material can thus be used as pressure sensors. Other homologous copolymers may also possess the loop character, but the upper transition is considered to be usually inaccessible due to thermal degradation.

External Fields. The application of external fields such as surface, electrical, and magnetic fields is also important in controlling and designing block copolymer based nanomaterials, because it can yield the directed self-assembly. Those fields reduce defects and thus increase grain sizes large enough to be used for microelectronics.

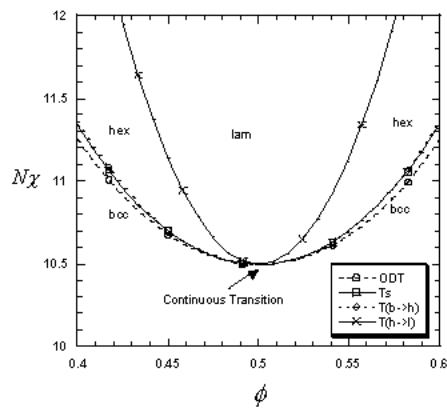


Figure 1. Mean-field phase diagram for A-B block copolymer melts, where there is no disparity in equation-of-state properties.

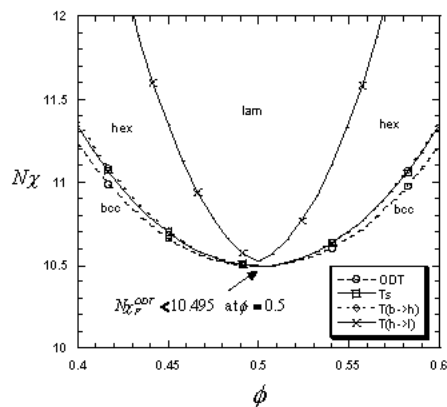


Figure 2. Mean-field phase diagram for A-B block copolymer melts, where there is a disparity in equation-of-state properties.

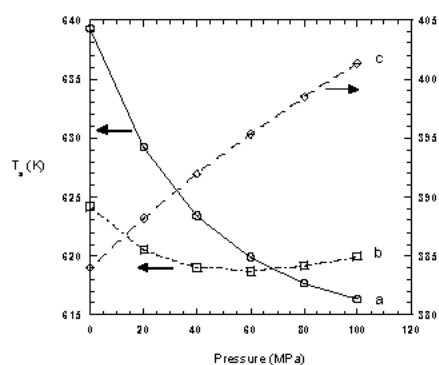


Figure 3. Changes of ordering transition up on pressurization.

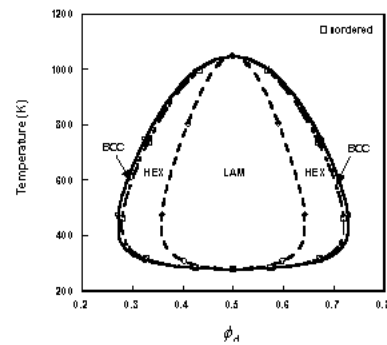


Figure 4. Classical phase diagram for A-B with directional interactions.

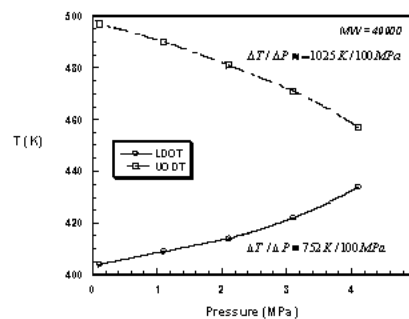


Figure 5. Pressure responses of lamellar ordering temperatures for the loop-forming symmetric Polystyrene-b-poly(n-pentyl methacrylate).

Conclusions

We have discussed various thermodynamic factors in designing nanostructured materials based on block copolymers. In Flory or Leibler picture, those are ϕ and $N\chi_F$. Using a microscopic model for block copolymers, Flory-type effective χ_F was interpreted as a compendium of various molecular factors to understand the diversified self-assembly behavior. By controlling the difference in self-interactions or the directional interactions between dissimilar species, block copolymer nanomaterials were shown to have desired sensitivity to thermodynamic conditions with desired nanostructures in a general temperature-pressure-composition window. Such understanding will prove useful in designing those nanomaterials and applying them to a number of applications.

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