Swelling and Shrinkage of Lamellar Domain of Conformationally Restricted Block Copolymers by Metal Chloride

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Introduction. Block copolymers show a rich variety of spatially periodic nanostructures due to their ability of molecular self-assembly[1−3] and have been widely used as nanotemplates for photonic crystals, high-density storage media, and nanoparticles.[4] It has been well-established theoretically[5−8] and verified experimentally[2,9−11] that the size of the repeating structure of a block copolymer is expressed by molecular parameters involving conformational parameters. The long period (D) of the mesophase in a diblock copolymer is given as the scaling form of $D \sim aN^{1/2}\Psi(\chi N)$, where a is the statistical segment length, N is the total number of the statistical segment, χ is the Flory−Huggins interaction parameter between segments, and the scaling function $\Psi(y)$ has the limiting values: $\Psi(y) \sim 1$ for $y \rightarrow 0$ (i.e., weak segregation limit (WSL)) and $\Psi(y) \sim y^{1/6}$ for $y \rightarrow \infty$ (i.e., strong segregation limit (SSL)). Changing the molecular weight of a block copolymer is thus a basic option for tailoring the period of nanostructure, but this often encounters laborious synthetic difficulties. As an alternative, the addition of additives such as homopolymer to a block copolymer provides a relatively simple means to control the period, but the controllability is sometimes hampered by undesirable macrophase separation.[12,13] Also, D and the order-to-disorder transition temperature (T_{ODT}) depend on microstructures in one block (for instance, 1,2 vs 1,4 addition in polydiene block[14,15]) of a block copolymer and functional groups attached to a backbone or the end of a chain.[16−18] Ikkala and co-workers[19,20] studied the mesophase transformation of polystyrene-*block*-poly(4-vinylpyridine) (PS−P4VP) by the addition of an oligomer with end-functionalized moiety, capable of forming a hydrogen bonding with the nitrogen in the pyridine ring of P4VP.

In this study, we demonstrate a simple but effective method to control the periodicity of block copolymer mesophase using a small additive that gives rise to a significant change in chain conformation of the block copolymer. This could be achieved by introducing the coordination between metal halide and a functional group, for instance, nitrogen atom, which is available in poly(vinylpyridine) (PVP). Interestingly, the type of the coordination between metal halide and nitrogen atom changes significantly with the position of nitrogen in PVP chains: intermolecular coordination for P4VP chains but intramolecular coordination for poly(2-vinylpyridine) (P2VP) chains.[21] If so, the chain conformation (and thus D) of PS-*block*-P2VP copolymer (PS−P2VP) after the coordination would be significantly different from that of PS-P4VP. This is because the chain stretching perpendicular to the lamellar layer is only expected for P2VP, not P4VP.

In this paper, we report on the change of D and T_{ODT} of PS−P2VP and PS−P4VP with amount of cadmium chloride ($CdCl_2$) by rheology, synchrotron small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). The D and T_{ODT} of P2VP coordinated with tiny amounts of $CdCl_2$ increased significantly. Furthermore, even if D was increased by ∼40%, lamellar microdomain was maintained. The experimental result is in good agreement with theoretical prediction by the mean-field theory in SSL, including the increase of chain stiffness based on the degree of the coordination. On the other hand, the D of PS−P4VP decreased with increasing amount of $CdCl_2$, which is possibly due to intermolecular coordination between P4VP chains or the nonlocal coordination of $CdCl_2$ within a P4VP chain.

Experimental Section. A symmetric PS−P2VP was synthesized by the anionic polymerization of styrene and 2-vinylpyridine monomers in THF at −78 °C under argon environment[22] by using *s*-BuLi. The weight-average molecular weight (M_w) and polydispersity index (PDI) were 19 300 and 1.06, measured by size exclusion chromatography coupled with multiangle laser light scattering. The volume fraction of PS (f) was determined to be 0.51 by ^{1}H nuclear magnetic resonance spectrometer with densities of PS, P2VP, and P4VP (1.05, 1.14, and 1.11 g/cm^3) at room temperature.

A symmetric PS−P4VP with $M_w = 23\,800$, PDI = 1.08, and $f = 0.54$ was purchased from Polymer Source. PS−P2VP (or PS−4PVP) with various amounts of $CdCl_2$ was prepared by mixing two solutions (one contained PS−P2VP (or PS−P4VP) in THF, and the other contained various amounts of $CdCl_2$ in ethanol). The molar ratio of $CdCl_2$ to 2VP was varied from 0.01 to 0.2, and thus volume fraction ($\phi_{\mathrm{CdCl_2}}$) of $CdCl_2$ in the PS−P2VP changed from 0.0023 to 0.0443. The sample for rheological measurement and synchrotron SAXS was prepared by solution casting and annealed for 2 days under vacuum at 180 °C. SAXS measurements were performed upon heating from 160 to 300 °C at a rate of 0.5 °C/min on beamlines 4C1 and 4C2 at the Pohang Light Source (Korea).[23] A flat Au mirror was used to reject higher harmonics. A 2-D CCD camera (Princeton Instruments Inc., SCX-TE/CCD-1242) was used to collect the scattered X-rays. The sample thickness was 1 mm, and the exposure time was 5 min.

An Advanced Rheometric Expansion System (ARES, TI Instruments) with 8 mm diameter parallel plates was used to determine the dynamic storage and loss moduli (G' and G'') upon heating at a heating rate of 0.5 °C/min. A strain amplitude of 0.05 and angular frequency (ω) of 0.1 rad/s, which lie in the linear viscoelasticity range, were used. The microdomains of PS−P2VP and PS−P4VP with $CdCl_2$ were investigated using TEM (Hitachi 7600) operating at 100 kV. The specimens were stained with iodine for 2 h at room temperature, which selectively stained the P2VP (or P4VP) microdomains.

Results and Discussion. Figure 1 gives temperature sweep of G' at $\omega = 0.1$ rad/s for PS−P2VP with various amounts of $CdCl_2$. A precipitous decrease in G' is referred to as T_{ODT}.[6,24−26]

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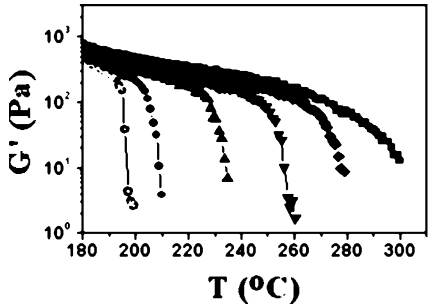

Figure 1. Temperature sweep of G' at $\omega = 0.1$ rad/s for PS−P2VP with various amounts of $CdCl_2$: (○) neat PS−P2VP, (●) PS−P2VP-[0.01], (▲) PS−P2VP[0.02], (▼) PS−P2VP[0.03], (◆) PS−P2VP[0.04], and (■) PS−P2VP[0.05]. Here, the value in the brackets after PS−P2VP represents the molar ratio of $CdCl_2$ to 2VP.

The T_{ODT} of PS−P2VP[0.01] was 208 °C, ~10 °C higher than that (198 °C) of neat PS−P2VP, even though ϕ_{CdCl_2} was very small (0.0023). Here, the value in the brackets after PS−P2VP represents the molar ratio of $CdCl_2$ to 2VP, which is the same as the number (ν) of coordinated $CdCl_2$ per 2VP monomer unit. We found that the T_{ODT} of PS−P2VP with $CdCl_2$ was thermoreversible. For instance, the difference of T_{ODT} of PS−P2VP-[0.02] measured from G' during heating and cooling cycles at a rate of 0.5 °C/min was less than 3 °C. When depolarized light scattering experiment was performed during heating and cooling cycles at a very small rate (0.5 °C/h), the T_{ODT} was essentially the same (less than 0.5 °C). The T_{ODT} of PS−P2VP with various amounts of $CdCl_2$ was also determined from plots of $1/I(q^*)$ and full width at half-maximum (fwhm) vs $1/T$ (see Figure S1 in Supporting Information). Here, $I(q^*)$ is the maximum SAXS intensity and q^* is the scattering vector corresponding to the maximum SAXS intensity. The values of T_{ODT} obtained from SAXS measurement were in good agreement with those determined from temporal change in G'.

Figure 2a gives the change of domain size ($D = 2\pi/q^*$) taken at 180 °C for PS−P2VP with ν. The D of PS−P2VP[0.2] (thus, $\phi_{CdCl_2} = 0.044$) was 20.5 nm, ~1.4 times larger than that (14.7 nm) of neat PS−P2VP. Interestingly, even for a 40% increase in D, the lamellar microdomain was maintained, as shown in the inset of Figure 2a. We found that D obtained from TEM image was consistent with that obtained from SAXS result. On the other hand, the D for PS−P4VP with $CdCl_2$ did not increase with increasing the amount of $CdCl_2$, as given in Figure 2b. Rather, D (24.4 nm) for PS−P4VP[0.1] was even smaller than that (28.7 nm) of neat PS−P4VP.

The reason that the change of D for PS−P2VP with $CdCl_2$ is different from that of PS−P4VP would be the different types of the coordination between $CdCl_2$ and nitrogen atoms in corresponding monomer units. For PS−P2VP, the coordination of $CdCl_2$ with two nitrogen atoms would be the intramolecular coordination, where $CdCl_2$ locally coordinates with two neighboring nitrogen atoms, similar to P2VP homopolymer,[21] as shown in Figure 3a. In this situation, the stretching of P2VP chains normal to the lamellar layer is much larger than that parallel to the lamellar layer; thus the D of PS−P2VP with $CdCl_2$ was larger than that of neat PS−P2VP. On the other hand, intermolecular coordination is more favorable between $CdCl_2$ and nitrogen atoms in P4VP because of difficulty in coordinating two neighboring pyridine rings in a chain, as given in Figure 3b. Thus, P4VP chains do not need to be stretched toward perpendicular to the lamellar layer, and the D of PS−P4VP with $CdCl_2$ would not increase. Furthermore, the lamellar microdomain was not well-developed for both PS−P4VP[0.05] and PS−P4VP[0.1], as shown in the inset of the TEM image given in Figure 2b. Balsara and co-workers[27,28] showed that cross-linked PS-*block*-polyisoprene copolymer did not exhibit well-ordered microdomain for the number of cross-links per block copolymer chain larger than ~3. Since the maximum number of the intermolecular bridges in PS−P4VP[0.05] was ~6, the poor ordering in the lamellar microdomains might be attributed to the fact that the intermolecular bridge acts similarly as a cross-link.

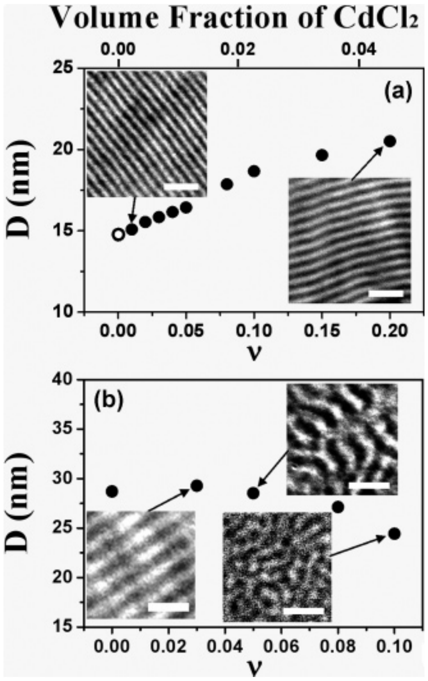

Figure 2. (a) Change of D with ν for (a) PS−P2VP and (b) PS−P4VP. Inset TEM images (scale bar = 50 nm) in (a) are PS−P2VP-[0.01] and PS−P2VP[0.2], respectively. Inset TEM images (scale bar = 50 nm) in (b) are PS−P4VP[0.03], PS−P4VP[0.05], and PS−P4VP-[0.1], respectively.

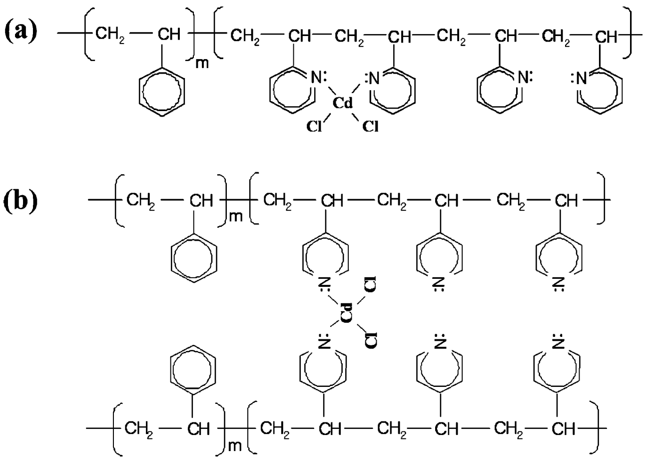

Figure 3. Two types of the coordination between $CdCl_2$ and nitrogen atoms: (a) intramolecular coordination for PS−P2VP and (b) intermolecular coordination for PS−P4VP.

The effect of chain conformation of PVP block coordinated with $CdCl_2$ on D for PS−P2VP can be theoretically analyzed as follows. We consider a melt consisting of m diblock copolymers, each with M chemical bonds consisting of M_S bonds for the PS block and M_V bonds for the P2VP block. The coarse-grained conformational statistics for i-block is specified by the Kuhn statistical length a_i and the number of the Kuhn segments $N_i = M_i b_i / a_i$, where b_i is the length of a chemical bond projected

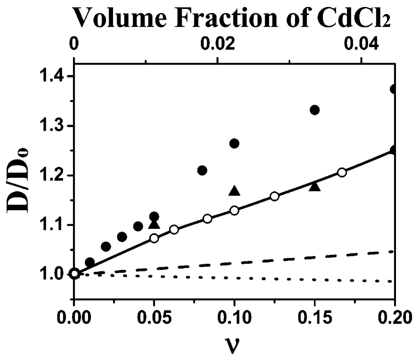

Figure 4. Plot of D/D_0 vs ν for PS−P2VP. Filled circles and triangles represent experimental values for PS−P2VP and PS−P2VP−H, respectively. The solid line connecting open circles represents theoretical values for PS−P2VP. The long-dashed and dotted lines are predicted D/D_0 by eqs 4a and 4b, respectively.

to the chain backbone direction. Taking into account the conformational asymmetry ($a_S \neq a_V$), the free energy F at a strongly segregated limit (SSL) is expressed by the sum of stretching and interfacial energy[8,29]

$$\frac{F}{mk_BT} = (\psi_S + \psi_V)\left(\frac{R}{aN^{1/2}}\right)^2 + \zeta(\chi N)^{1/2}\left(\frac{aN^{1/2}}{R}\right) \qquad (1)$$

Here R is the microdomain size (thus $D = 2R$ for lamellar microdomains), N is $N = N_S + N_V$, and a is the averaged Kuhn segment length $a = [fa_S^2 + (1 - f)a_V^2]^{1/2}$. The coefficients ψ_i and ζ depend on f, a_i, and the geometry of microstructure and can be obtained by the standard unit cell approximation.[30] The ψ_i and ζ for lamellar microdomains are given by[29]

$$\psi_S = \frac{\pi^2 f}{8}[f + (1 - f)(a_S/a_V)^{-2}],$$

$$\psi_V = \frac{\pi^2(1 - f)}{8}[(1 - f) + f(a_S/a_V)^2]$$

$$\zeta = \frac{1 + a_S/a_V}{2\sqrt{6}[(1 - f) + f(a_S/a_V)^2]^{1/2}}\left[1 + \frac{1}{3}\left(\frac{1 - a_S/a_V}{1 + a_S/a_V}\right)^2\right] \qquad (2)$$

Minimization of F with respect to R leads to the well-known scaling form for the microdomain size

$$R = \left[\frac{\zeta}{2(\psi_S + \psi_V)}\right]^{1/3} a\chi^{1/6}N^{2/3} \qquad (3)$$

Here, the principal domain spacing $D = 2R$ for lamellar phase, $D = (3\pi^4/4)^{1/6}R$ for cylindrical phase, and $D = (8\pi^2/9)^{1/6}R$ for spherical phase. We assume that the coordination of $CdCl_2$ with P2VP induces a change in Kuhn length of the P2VP block from a_V to $a_V\kappa_n$, where κ_n is the Kuhn length of a P2VP block coordinated with n $CdCl_2$ relative to that of a neat the P2VP block. This change also rescales the segment-based parameters, i.e., N, N_V, χ, and therefore alters the balance between the stretching energy and the interfacial energy, which in turn changes D. The κ_n was estimated by the rotational isomeric state (RIS) model[31] with a molecular mechanics (MM) simulation, assuming that the coordination of $CdCl_2$ with two neighboring pyridine groups took place randomly on the P2VP chains. For the RIS calculation, 100 stereosequences of Bernoullian P2VP chains with $P_m = 0.5$, i.e., a random distribution of meso and racemic dyads, were generated by Monte Carlo method, and then n $CdCl_2$ are randomly coordinated between neighboring pendant groups. The conformational property under interest (κ_n) is averaged over this sequence ensemble.

Figure 4 presents the D/D_0 as ν ($= 2n/M = [CdCl_2]/[2VP]$) for the PS−P2VP, where the filled circle symbol and the solid line connecting open circles represent the experimental and theoretically predicted values, respectively. The experimental value of D/D_0 for PS−P2VP turned out rather larger than predicted one. The discrepancy might be attributed to the fact that the SSL might not be valid for PS−P2VP due to a small degree of polymerization ($\chi N \sim 24$ at 180 °C, where χ in ref 32 is used). The predicted value resulted from the overestimation of the chain stretching term. But, the theoretically predicted D/D_0 is in good agreement with the measured one for a higher molecular weight block copolymer (PS−P2VP−H with $M_w = 196\,500$, $f = 0.54$, and $D_0 = 81.89$ nm) with $\chi N \sim 200$ at 180 °C.

On the other hand, D of the mixtures of a block copolymer (A−B) and homopolymer (A) changes differently with volume fraction of the homopolymer in the mixture (ϕ_H) depending upon solubilization type:[12,33,34]

$$D/D_0 = 1/(1 - \phi_H) \quad \text{for localized solubilization} \qquad (4a)$$

$$D/D_0 = f^{2/3}/[(1 - \phi_H)\{(1 - \phi_H)f + \phi_H\}^2]^{1/3} \quad \text{for uniform solubilization} \qquad (4b)$$

Here, f is the volume fraction of A block in A−B and D_0 is the domain spacing of neat block copolymer. When the $CdCl_2$ is assumed to act simply as a homopolymer, the predicted values of D/D_0 by eq 4a and eq 4b are given as long-dashed and dotted lines in Figure 4, respectively. Of interest in Figure 4 is that the D of PS−P2VP with $CdCl_2$ (conformationally perturbed diblock) increases much more rapidly than that of the solubilized systems. It is worth pointing out that to achieve the same swelling ($D/D_0 = 1.2−1.4$) in the solubilized systems, one type of microdomain usually changes into another based on the volume fraction.[12,33] By contrast, D in the present system increases up to 40% without undergoing any possible order-to-order transition, as confirmed experimentally given in Figure 2a. This suggests that the conformational perturbation is more advantageous for the microphase swelling than the conventional method based on the homopolymer solubilization.

In summary, the D of PS−PVP was greatly affected by the coordination type with $CdCl_2$. For PS−P4VP, the D decreased as the coordination number of $CdCl_2$ increased due to intermolecular coordination between P4VP chains or the nonlocal coordination of $CdCl_2$ within a P4VP chain. On the other hand, the chain conformation of P2VP block was greatly changed by the local intramolecular coordination. Our theoretical estimation based on RIS model also confirms that the persistence length of PS−P2VP[0.2] becomes approximately twice that of neat P2VP, which in turn results in large lamellar swelling due to the reduction of the free energy penalty associated with the chain stretching. This large increase of D for PS−P2VP by the coordination with $CdCl_2$, while maintaining the lamellar microdomains, would be an effective means to develop one-dimensional photonic band-gap materials,[35,36] because D is effectively tuned by the amount of $CdCl_2$.

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Supporting Information Available: Plots of $1/I(q^*)$ vs $1/T$ and fwhm vs $1/T$ for PS−P2VP coordinated with various amounts of

$CdCl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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