Scattering studies of novel degradable block copolymers of strong segregation class

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Abstract

We have investigated microdomain structures of novel block copolymers, poly(p-tert-pentyl oxyvinylbebzene-b-p-vinylphenol) and poly(p-tert-pentyl oxyvinylbebzene-b-p-vinylphenol-b-p-tert-pentyl oxyvinylbebzene) with small-angle X-ray scattering (SAXS). We analyzed SAXS profiles of the block copolymers in their ordered state with paracrystal theory, and found that the block copolymers formed the lamella structures in the order of 1 nm with long-range order. We estimated the lower-limit size of the microdomain structure by analyzing the order–disorder transition of the block copolymer solutions and explored that we can attain 7.6 nm by decreasing the molecular weight of block copolymers.

Keywords: Microphase separation; Order–disorder transition; Small-angle X-ray scattering; Paracrystal theory; Lamellar structures

1. Introduction

Block copolymers are polymers where different kinds of polymers are connected by colavolent bonds and exhibit a phase transition from a disorder state, where each component in block copolymers is well mixed homogeneously, to an ordered state, where the block copolymers form long-range ordered periodical structure, with increasing segregation power between constituent polymers. This phase transition is called order–disorder transition (ODT). In the ordered state, the block copolymers show the variety of morphologies with long-range order, thus the block copolymers is one of the promising materials in the field of nano-technologies [1–3]. As typical block copolymers, poly(styrene-b-isoprene), poly(styrene-b-butadiene), and poly(styrene-b-methyl methacrylate) are used widely. The size of the periodical structures of those diblock polymers is in the order of 10–100 nm. On the other hand, the block copolymers forming the ordered structure in the order of 1 nm has been desired for the application of electrical devices. It is impossible to make the well-ordered structure in the order of 1 nm with those polymers at low molecular weight since the segregation power between the constituent polymers is not strong enough to form the periodic structure in the order of 1 nm so that those block copolymers are in their disordered state. We thus need to make new block copolymers having strong segregation power between constituent polymers to form the microdomains in the order of 1 nm. Moreover, for practical application such as photolithography, one component of block copolymers is desired to be degradable by etching while the other has resistance to etching. In order to fulfill the conditions described above, we have selected poly-p-tert-pentyl oxyvinylbebzene (POVB) and poly-p-vinylphenol (VP) as constituent polymers of block copolymers. POVB (Fig. 1(a)) is known as one of photo resist materials and is degraded with ultraviolet (UV) etching. On the other hand, VP (Fig. 1(b)) is insensitive to UV, and OH group in VP is expected to cause strong segregation power to POVB. With this pair, we can expect that the microdomain structures in the order of 1 nm with long-range order.

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Therefore, we prepared novel block copolymers with this pair and studied their morphologies and phase behaviors. In this paper, we report the scattering studies of block copolymers consisting of POVB and VB. We studied bulk state and solutions of the block copolymers with small-angle X-ray scattering (SAXS). In bulk state, we characterized the ordered structure of the block copolymers by fitting their scattering profiles with paracrystal theory. We measured the ODT behaviors of block copolymer solutions and obtained segregation power between POVB and VB by fitting the scattering profiles in disordered state with those calculated with random phase approximation (RPA). With obtained segregation power, we estimated how small we can attain microdomain structures.

2. Experimental methods

2.1. Samples

We used a diblock copolymer POVB-b-VP (POVB-VP) and a triblock copolymer POVB-b-VP-b-POVB (POVB-VP-POVB). The characteristics of the samples used here are listed in Table 1. The samples were synthesized by living anionic polymerization method. We prepared the bulk specimen by solvent casting method from propylene glycol methyl ethyl acetate (PEGMEA) solution. In order to estimate the segregation power, we need to bring the block copolymers into their disordered state. However, it is impossible to bring the used block copolymers into their disordered state in bulk state without degradation of polymers by heating samples since the segregation power between POVB and VP is too strong. Thus we prepared POVB-VP/PEGMEA and POVB-VP-POVB/PEGMEA solutions to reduce the segregation power and measured the ODT behaviors of the solutions. The concentration of POVB-VP and POVB-VP-POVB used here was, respectively, 51.1% and 67.9% by weight.

2.2. SAXS

SAXS experiments for the block polymers in bulk at room temperature were conducted at the BL45XU, Spring-8 [4]. We used the CCD camera with Image-Intensifier [5]. The X-ray wavelength $\lambda$ was 0.11 nm. The measuring time for each sample was 2 s. All scattered intensity profiles were corrected for background and then circularly averaged for further analyses.

For the determination of the ODT temperature of the POVB-VP/PEGMEA solutions, we used the in-house SAXS instrument. The in-house SAXS apparatus consists of an 18-KW rotating anode X-ray generator, a graphite crystal for monochromatization, a 1.8 m camera, and a one-dimensional position-sensitive proportional counter. The detail of the apparatus was described elsewhere [6]. The Cu K\alpha line ($\lambda = 0.154$ nm) was used. The SAXS measurement was performed in a cooling cycle. At each temperature, we annealed the samples for 30 min, and measured SAXS profile at 1 h. The obtained SAXS profiles were corrected for smearing effects of slit-width and slit-height, absorption and air scattering as background as described elsewhere [6].

3. Experimental results

3.1. Ordered structure of bulk samples

Figs. 2 and 3 show the SAXS profiles for the bulk samples of POVB-VP and POVB-VP-POVB. In the figures, $q$ is the magnitude of scattering vector defined by

$$q = (4\pi/\lambda) \sin \theta,$$

where $\lambda$ and $2\theta$ are the wavelength of the incident beam and scattering angle, respectively. Both SAXS profiles show the higher-order distinct peaks, indicating that the samples are in ordered state. As indicated by arrows in Figs. 2 and 3, the relative peak position of higher-order peaks to the first-order peak becomes integer. Thus, the ordered structures of the block copolymers in bulk are lamella structures. In order to characterize the lamella structures of the block copolymers, we analyzed the SAXS profiles with the paracrystal model. According to previous works [7], the scattering profiles of lamellar structures can be well described by the extension of the one-dimensional paracrystal theories by Hoseman and Bagchi [8], and Blundell [9]. The scattered intensity $I_p(q)$ per single lamellar assembly along the normal direction to the lamella interfaces is given by

$$I_p(q) \equiv \langle |f|^2 \rangle - |\langle f \rangle|^2 + |\langle f \rangle|^2(Z + I_c/N).$$
deviation. According to Hosemann–Bagchi paracrystal

\[ f = \langle \sin(qL_A/2) / (qL_A/2) \rangle \exp(-t_1^2/4\pi), \]

where \( L_A \) is the average thickness of POVB domain, \( t_1 \) the interfacial thickness of domains. \( Z \) is the lattice factor characterizing the spatial distribution of the centers of plates statistically. Angular bracket in Eq. (2) corresponds to an average of \( f \) or \(|f|^2\) with respect to a distribution function \( P_L(L_A) \) for \( L_A \),

\[ P_L(L_A) = (2\pi \sigma_L^2)^{-1/2} \exp\left[-(L_A - \bar{L}_A)^2/2\sigma_L^2\right], \]

where \( \bar{L}_A \) and \( \sigma_L \) are the average thickness and its standard deviation. According to Hosemann–Bagchi paracrystal distance statistics, \( Z \) is described by

\[ Z = (1 - |F|^2)/(1 - 2|F| \cos(q\bar{D}) + |F|^2). \]

In Eq. (5), \( \bar{D} \) is the average spacing, and \( |F| \) is given by

\[ |F| = \exp(-q^2\bar{D}^2/2), \]

where \( q \) is so-called Hosemann’s \( g \)-factor characterizing the lattice distortion and is expressed by

\[ g = \Delta D / \bar{D} \]

with \( \Delta D \) the standard deviation of \( D \). The distribution of \( D \) is assumed to be Gaussian function given by

\[ P_D(D) = (2\pi D^2)^{-1/2} \exp[-(D - \bar{D})/2\Delta D^2]. \]

\( I_c \) is the zeroth-order scattered intensity and is expressed by

\[ I_c(q) = \left\{ -2|F| \left[ 1 - |F|^2 \right] \cos(q\bar{D}) - 2|F| \\
- |F|^N \cos((N + 1)q\bar{D}) + 2|F|^{N+1} \cos(Nq\bar{D}) \\
- |F|^{N+2} \cos((N + 1)q\bar{D}) / [1 - 2|F| \cos(q\bar{D}) + |F|^2] \right\}, \]

where \( N \) is the number of plates in one assembly. If \( N \) is large, \( I_c \) is important around \( q = 0 \). \( N \) is assumed to have the following distribution:

\[ P_N(N) = \exp\left[-(N - \bar{N})^2/2\sigma_N^2\right] \times \left\{ \sum_{N=1}^{2\bar{N}+1} \exp\left[-(N - \bar{N})^2/2\sigma_N^2\right] \right\}^{-1} \]

with \( \bar{N} \) and \( \sigma_N \) are the average number of \( N \) and its standard deviation, respectively. It should be noted that the volume fraction \( \phi_{POVA} \) of POVA is given by

\[ \phi = \bar{L}_A / \bar{D}. \]

In the case that the lateral persistence length \( W \) of lamellae is much larger than an average lamellar microdomain spacing \( D \), the observed scattered intensity \( J(q) \) is given by

\[ J(q) = q^{-n} I_p(q), \]

where \( q^{-n} \) is so-called Lorentz factor associated with the orientation distribution of the assembly of plates. Here we set \( n = 1 \), assuming that the normal direction of lamellar plates is restricted within the plane normal to the incident beam but randomly distributed in the plane.

We can thus determine the parameters \( \bar{D}, g, \bar{L}_A, \sigma_L, t_1, \bar{N}, \) and \( \sigma_N \) by fitting experimental results with theoretical calculation. The solid curves represent the best-fitted
results calculated by paracrystal theory. The calculated results can well express the experimental results and yield parameters listed in Table 2. First, we shall compare the parameters of the diblock copolymer, POVB-VP with those of the triblock copolymer, POVB-VP-POVB. The average domain spacing of POVB-VP is larger than that of POVB-VP-POVB although the values of $M_n$ are almost identical. This is because the packing of the block copolymer is different each other as discussed by Hashimoto et al. [10]. The $g$-factor, $\sigma_L$, and $t_I$ of POVB-VP-POVB are larger than those of POVB-VP, indicating that the regularity of microdomain of POVB-VP-POVB is worse than that of POVB-VP. This is because the ODT temperature of POVB-VP is higher than that of POVB-VP-POVB. This result agrees with those of the stability limits calculated with RPA [10].

Let us compare the parameters of our samples with those obtained for poly(styrene-b-isoprene) (S-I) samples (L-2: $M_n = 3.1 \times 10^4$, volume fraction of polystyrene $\phi_{PS} = 0.38$, L-7 : $M_n = 3.1 \times 10^4$, $\phi_{PS} = 0.43$) by Shibayama et al [7]. The parameters for L-2 and L-7 are also listed in Table 2. A remarkable property of POVB-VP and POVB-VP-POVB samples is that the values of $\bar{N}$ of POVB-VP and POVB-VP-POVB are much larger than those of S-I. This fact suggests that POVB-VP and POVB-VP-POVB have the potential to form well-aligned structures with large-scale area. However, the $g$-factor for our samples is worse than those of S-I, indicating that the periodicity of the domain spacing in our samples is worse than those of S-I. This may be caused by relatively wide molecular weight distribution of the samples and becomes shortcoming for the application to nano-devices. In order to reduce the distribution, we need to make more monodisperse samples. The values of $\sigma_L$ of our samples seem to be better than those of S-I. However, the values $\sigma_L = \sigma_L/\bar{D}$ reduced by the domain spacing are worse. This is also due to the polydispersity of the samples. The interfacial thickness of our samples is much thinner than those of S-I, which agrees that the segregation power between OVB and VP is much stronger than between S and I.

3.2. ODT behaviors of diblock copolymer solution

Fig. 4 shows the temperature dependence of the SAXS profiles of the POVB-VP solution. A sharp change in the profiles can be seen between 72 and 74 °C. This discontinuous change in SAXS profiles indicates that the ODT of the POVB-VP solution occurs within thin temperature range [11,12]. Fig. 5 shows the inverse peak intensity $I_m^{-1}$ and the square of half-width at half-maximum $\sigma_q^2$ plotted as a function of the inverse of temperature $1/T$ for the POVB-VP solution.
POVB-VP-POVB solution is 124 °C from the discontinuity in $I_m^{-1}$ and $\sigma_q^2$ vs. $1/T$ plots though we do not show here.

Next, we shall estimate the temperature dependence of Flory–Huggins $\chi$-parameter between POVB and VP by analyzing the scattering profiles in the disordered state with RPA theory [13]. According to RPA theory, the scattering profiles $I(q)$ of diblock copolymer in its disordered state can be described by

$$I(q) = k \left[ S(q)/W(q) - 2\chi \right]^{-1}$$  \hspace{1cm} (13)

with $k$ being contrast factor. $S(q)$ and $W(q)$ can be calculated with polymerization indices, weight fraction, statistical segment length of each component. The detail of $S(q)$ and $W(q)$ are described elsewhere [14]. We fitted the scattering profiles obtained experimentally with Eq. (13) with $k$ and $\chi$ being floating parameters. In order to estimate the $\chi$-parameter between POVB and VP, $\chi_{POVB-VP}$ from the scattering profiles of the diblock copolymer solutions, we assume the pseudo-binary approximation [15]. Under the pseudo-binary approximation, Eq. (13) is still valid for the scattering function of diblock copolymer solutions and the estimated $\chi$ value, $\chi_{\text{eff}}$, has the following relationship with $\chi_{POVB-VP}$:

$$\chi_{POVB-VP} = \phi_p^{-1} \chi_{\text{eff}}$$ \hspace{1cm} (14)

where $\phi_p$ is the volume fraction of polymer in the solution.

As shown in Fig. 6, Eq. (13) can well fit with experimental SAXS profiles in the disordered state and $\chi_{\text{eff}}$ can be estimated from the fitting. In Fig. 7, $\chi_{\text{eff}}$ is plotted as a function of $1/T$. The plot shows the linear relationship and is expressed by

$$\chi_{\text{eff}} = 0.0386 + 72.69/T$$ \hspace{1cm} (15)

Since the ODT occurs at 73 °C, the critical $\chi_N$ value of the ODT point ($\chi_N)_c$ is thus 13.42. By using Eqs. (14) and (15), we also estimated $(\chi_N)_c = 17.01$ for POVB-VP-POVB solution. Fig. 8 shows the temperature dependence of $\chi_{POVB-VP}$ estimated from $\chi_{\text{eff}}$ with Eq. (14):

$$\chi_{POVB-VP} = 0.054 + 102.85/T$$ \hspace{1cm} (16)

In Fig. 8, the temperature dependence of $\chi$ in S-I diblock copolymer $\chi_{S-I}$ expressed by

$$\chi_{S-I} = -0.0237 + 34.1/T$$ \hspace{1cm} (17)

is also plotted. $\chi_{POVB-VP}$ is almost 10 times as large as $\chi_{S-I}$ in the measured temperature range, indicating that the

Fig. 6. SAXS profiles of the POVB-VP solution in its disordered state. Solid lines indicate the fitting result with RPA theory.

Fig. 7. $\chi_{\text{eff}}$ is plotted as a function of $1/T$.

Fig. 8. $\chi_{POVB-VP}$ and $\chi_{S-I}$ are plotted as a function of $1/T$. 
segregation power between POVB and VP is much stronger than that between S and I.

Finally, we shall estimate the minimum $D$ spacing $D_{\text{min}}$ which can be attained by reducing molecular weight. By using $\chi_{\text{POVB-VP}} = 0.397$ at $27 ^\circ C$, $(\chi N)_c = 13.72$ for POVB-VP, we estimated the minimum molecular weight $M_{\text{min}} = 5990$. With similar way, $M_{\text{min}}$ is estimated to be 7430 for POVB-VP-POVB. Thus the values of $D_{\text{min}}$ for POVB-VP and POVB-VP-POVB are

$$D_{\text{min}} = 15.1 \times (5990/9000)^{0.5} = 12.3 \text{ nm for POVB-VP},$$

and

$$D_{\text{min}} = 9.75 \times (7430/10,000)^{0.5} = 8.40 \text{ nm for POVB-VP-POVB}.\quad (18)$$

Here we assume the weak segregation limit [13] where $D$ is proportional to $M^{0.5}$. The results indicate that we can form smaller microdomain structures with lower molecular weight block copolymers as described above.

4. Conclusion

We studied bulk state and solution of block copolymers with SAXS. In bulk state, we characterized the ordered structure of block copolymers by fitting the scattering profiles with paracrystal theory. Fitting results indicate that we can attain small microdomain structure in the order of 1 nm. We measured the ODT behaviors of block copolymer solutions and obtained $\chi_{\text{POVB-VP}}$ by fitting the scattering profiles in disordered state with the theoretical curves calculated with RPA. With the obtained $\chi_{\text{POVB-VP}}$, we estimated how small we can attain microdomain structures. We found that the microdomain structure with $D = 8.40 \text{ nm}$ can be formed with smaller molecular weight block copolymers than those we used here.

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