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Mesoscopic Patterns of Block and Graft Copolymers in Condensed Systems

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SUMMARY: Equilibrium structures of two kinds of two-component copolymers with equivalent chemical contents but with different chain architectures in bulk were compared. They are BAB triblock copolymers and AB_2 star-branched graft copolymers. These copolymers have been confirmed to show quite different morphological change with composition. Deformation manner of B block chains of lamellar microphase-separated BAB triblock copolymers depend on B contents, however, the volumes of the deformed coils are always kept constant to have those of the unperturbed chains irrespective of their architectures. The observed polystyrene/poly(2-vinylpyridine) interfacial thickness is fairly thin though it is much thicker than the theoretically-predicted one.

Introduction

Block and graft copolymers with incompatible components are known for forming microphase-separated structures in concentrated solutions or in bulk [1-3]. Their multiphase structures are fascinating research objectives not only in academic field because they change their morphologies sensitively depending on molecular parameters such as molecular weights [4-9], compositions [7, 8] and molecular architectures [9-11] but in application field because the polymers with highly-ordered mesoscopic structures could become high-performance functional materials.

The symmetric AB diblock copolymers are well-known for forming alternating lamellar structures with very simple interface. The interface tends to curve if the content of either A or B become small. Consequently such asymmetric molecules form cylindrical or spherical structures whose isolated microdomains are composed of minor components. Thus the morphological transitions with compositions proposed by Molau [1] have long been believed as equilibrium phase diagram. However, ordered bicontinuous [12, 13] and tricontinuous structures [14, 15] were discovered and reported for two- and three-component copolymers.

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It is essential to investigate size and shape of molecules as well as morphological features to understand satisfactorily these multi-phase structures at the molecular level. Small angle neutron scattering (SANS) is a suitable technique that enables us to obtain these molecular information of the component polymer chains in bulk by using deuterium-labeled samples. Another useful neutron scattering method which can be applied to multiphase polymeric material is a neutron reflectivity (NR) measurement. Surfaces and interfaces of thin films can be observed with high accuracy by this method making use of deuterium/proton strong contrast against neutron.

Morphological features of one block and one graft copolymers were compared at the molecular level focusing principally on the difference in chain architectures in this article. Since the self-assembled ordered structures can be affected sensitively by the molecular parameters mentioned above, it is quite important to use polymer samples with well-defined structures to get definite conclusions. Careful determination of the molecular parameters is also necessary to lead successful work. Therefore, the preparation and characterization methods will be introduced briefly 16). Successively some details of morphological studies on two kinds of copolymers will be described. Then SANS was performed to investigate molecular conformations of block and graft chains in lamellar microphase-separated structures and their results were discussed in conjunction with those on lamellar microdomain spacings since they are directly related to chain dimensions in the longitudinal direction. Finally, microphase-separated interfaces will be described.

Preparation and Characterization of Samples

The samples were prepared by anionic polymerization methods in glass apparatuses under high vacuum. Two kinds of copolymer molecules with different chain architectures were obtained. They are PSP triblock copolymers 17) and SP_2 star-branched graft copolymers 10), where S and P denote polystyrene and poly(2-vinylpyridine), respectively. PSP triblock copolymers were synthesized from dipotassium salt of α-methylstyrene tetramer by two step reactions, while SP_2 graft copolymers were prepared by coupling reactions among a polystyrene chain having two bromomethyl groups on one end and two poly (2-vinylpyridine)s with living end. Deuterium-labeled samples were also prepared by using perdeuterated styrene monomer to perform neutron scattering experiments 17).

Number-averaged molecular weights of samples and also those of precursors were measured by a membrane osmometer of Hewlett Packard type 502 and molecular weight distributions were determined by gel-permeation chromatograph of Tosoh type 8020 equipped with two GMH_{XL} columns whereas compositions of copolymers were measured by pyrolysis-gas chromatography. It was confirmed that all the samples have molecular weights and compositions as designed and also confirmed that they have fairly narrow molecular weight distributions, i.e., $M_w/M_n < 1.1$.

Equilibrium Structures

Equilibrium morphology was observed by compensatively combining reciprocal lattice space information studied by small angle X-ray scattering (SAXS) with one in real space obtained by transmission electron microscopy (TEM). Computer simulations were also performed to convince such a complicated structure as three-dimensionally periodic co-continuous structures. Sample films were prepared by solvent casting procedure from dilute solutions of tetrahydrofuran, which is a common good solvent for three component polymers. Films were well annealed at above 150 °C for longer than a week to realize equilibrium structures.

Figure 1 compares phase diagrams of two different copolymers obtained by morphological observations [18]. Firstly, if we look at the diagram of PSP triblock copolymers at the top, one easily notices this diagram is asymmetric. This fact is somewhat strange considering that the segment lengths of two component polymers are similar. The reason for the asymmetry could be strongly related to the conformation of the middle block, polystyrene, as will be discussed later. Bicontinuous structure has never been observed for PSP so far.

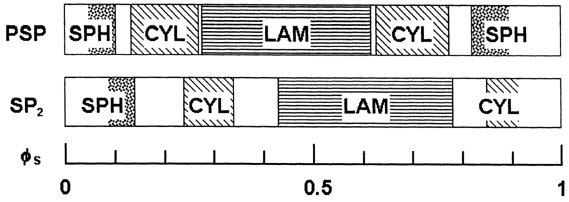

Fig. 1. Composition dependence of equilibrium microphase-separated structures for two copolymers. The horizontal axis denotes the volume fraction of polystyrene phase. SPH, CYL and LAM denote spherical, cylindrical and lamellar structures.

If the phase diagram of SP_2 is compared with that of PSP, it is quite distinct that the compositions where phase transitions occur are shifted pretty much to higher φ_s side for SP_2 when polystyrene, the grafted chain, is the major component [10, 18]. This result is quite naturally explained, comparing the conformational features between a block copolymer and a graft copolymer though the explanation is somewhat qualitative. Namely lateral total size of P chain in SP_2, whose center is actually anchored at the domain boundary, must be considerably larger than that of a regular block chain with the same molecular weight. Therefore, P chain of a graft copolymer may have a role to make the P phase convex to keep an entropic free energy balance between an S graft chain and a total P chain.

Chain Conformations of Block Polymers in Lamellar Structures

The repeating distance of self-organized structures of copolymers depends directly on the chain dimension of copolymers. Lamellar microdomain size can be easily predicted by theoretical consideration under thermodynamic equilibrium in the strong segregation regime.

Several different theories are known and most of them predict the following relationship with respect to AB diblock copolymer as

$$D \propto M^{2/3} \qquad (1)$$

where D denotes the microdomain spacing and M is the total molecular weight of the copolymer [4, 5]. Experimental data of the present PSP and SP_2 copolymers estimated by SAXS were compared in Figure 2 [6, 17, 19]. The solid line was drawn by the least square method for the data of SP diblock copolymer and its slope is 0.64. The open circles are for PSP molecules and these are replotted against $M_n / 2$ as filled circles. The magnitudes of the filled circles as well as their slope are similar to those of the diblocks. This fact means that the constitutive chain length of PSP triblock copolymers, which determines the repeating distance, should not be M but M / 2 [17]. Alternatively, the squares are for SP_2 graft copolymers. Again the slope of SP_2 graft copolymer data is almost the same as that of SP block copolymer data, however, the magnitude of the former is apparently smaller than that of the latter. This

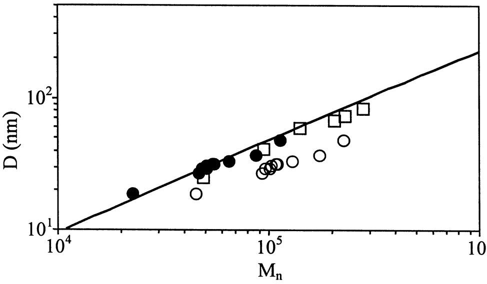

Fig. 2. Double logarithmic plots of lamellar domain spacings vs. total molecular weights of copolymers. The open and the closed circles are the data for PSP triblock copolymers, the latter being plotted against M / 2, while the squares are the data for SP_2 graft copolymers. The solid line is the experimentally-obtained one for SP diblock copolymer.

difference can be qualitatively explained by considering the difference in chain architectures between block copolymers and graft copolymers [19)].

The exponent of M in the D-M relationship in equation (1) and the experimental data in Figure 2 indicate the expansion of block polymer chain in the longitudinal direction due to the segregation power. This elongation is, in principle, independent of the lateral dimension and no theories have predicted the lateral sizes of block chains. Therefore, it is very valuable to measure the chain dimensions in both directions to understand microphase-separated structures at the molecular level. Neutron scattering experiments enables us to realize such objective. Fortunately, lamellar phases can be aligned parallel to film surfaces with very high degree of orientation if films are cast from solutions on certain substrates. This feature has been utilized cleverly in performing neutron scattering experiments as schematically shown in Figure 3.

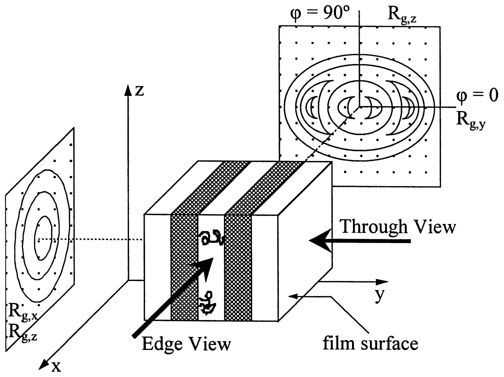

Fig. 3. Schematics of SANS measurements. The geometrical relationships among neutron beams, lamellar orientation and two-dimensional detector.

Sample films were obtained by blending deuterium-labeled and unlabeled polymers prior to casting. The lateral ($R_{g,x}$) component of the radii of gyration of polystyrene middle blocks were estimated from the through view data while longitudinal ($R_{g,y}$) component from edge-view data since the segmental distribution could be actually projected on two-dimensional position-sensitive detector in SANS experiments [17)].

They were plotted against the volume fraction of polystyrene, φ_S, in Figure 4 [20)]. The solid transverse line represents the dimension of the unperturbed chain. It is apparent that the middle block chains of PSP triblock copolymers are deformed irrespective of their volume fractions, however, the degree of deformation, i.e., the difference in the magnitude of $R_{g,x}$ and $R_{g,y}$ is getting less with increasing φ_S. One should remind that the middle blocks of two component triblock copolymers have either loop type or bridge type conformation in microphase-separated bulk. The lateral dimension of the loop chain could be larger than that of the bridge one. This leads to the good reason for speculating that the fraction of the bridge type conformation would decrease with increasing φ_S.

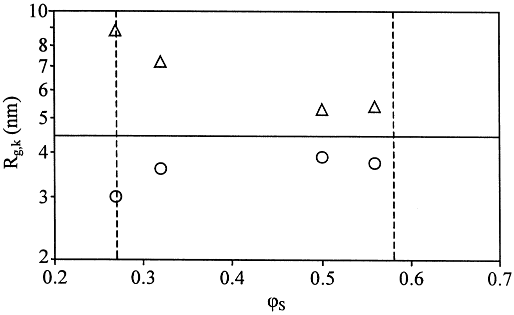

Fig. 4. Reduced radii of gyration of S blocks in PSP triblock copolymers as a function of polystyrene volume fraction. The circles are lateral dimensions ($R_{g,x}$) and the triangles are the longitudinal ones ($R_{g,y}$). The vertical two broken lines indicate the composition limits of lamellar region.

The volumes occupied by each block chain in bulk were quantitatively estimated by using the measured $R_{g,k}$ (k = x, y or z). Comparing V_b ($R_{g,x} \cdot R_{g,y} \cdot R_{g,z}$) with V_u ($= R_{g,k0}{}^3$), it has been confirmed that the volumes of the deformed chains were kept constant irrespective of the degree of deformation of the middle blocks [17, 20]. The conservation of volume in lamellar structure has also been observed for SP diblock copolymer system earlier [21]. This "volume conservation" principle must be a universal and essential feature for deformed block chains in confined space.

Polymer / Polymer Interfacial Thickness

Interfacial thickness of inter-microdomain is one of the important indication which characterizes microphase-separated structure [22]. Neutron reflectivity measurements were performed to investigate the interfacial structures with high accuracy by using deuterium-labeled samples at the ultra-thin film state [23, 24]. Ultra-thin films for NR were obtained by spin coating from dilute solutions of PSP triblock copolymer samples on one-side polished silicon wafers. All the samples used have alternating lamellar structures in bulk. As-cast thin films with less lamellar orientation were well-annealed in vacuum so as to get equilibrium structure whose lamellae are highly oriented parallel to the surface of silicon wafers. Specular reflections, in which the incident angle is equal to the reflected angle, were measured to get the scattering length density profile in the depth(z) direction [25]. Figure 5 shows an example of reflectivity data as a function of momentum transfer q_z ($= 4\pi \sin\theta/\lambda$) in z-direction obtained from a 2-vinylpyridine-styrene-d_8-2-vinylpyridine triblock copolymer [26]. The solid line expresses the calculated reflectivity by using the scattering length density profile shown in the inlet figure. An error function was assumed to represent the interfacial profile, and the thickness of the interface defined as $1 / (\varphi_i / dz)_{\varphi i = 0.5}$ of the error function was determined to be 3.2 nm. This experimentally-observed value is apparently larger than the theoretically-predicted one, 1.7 nm, for interface of the constituent homopolymers with infinite molecular weight proposed by Helfand-Wasserman [4]. This discrepancy could be explained by considering two contributions which play roles to broaden interfacial area; one is chain connectivity and the other is long range fluctuation of interfacial region which would have the dominant effect [27]. Interfacial thickness of SP diblock were also measured and it was found that there is no essential difference between diblock- and triblock copolymers.

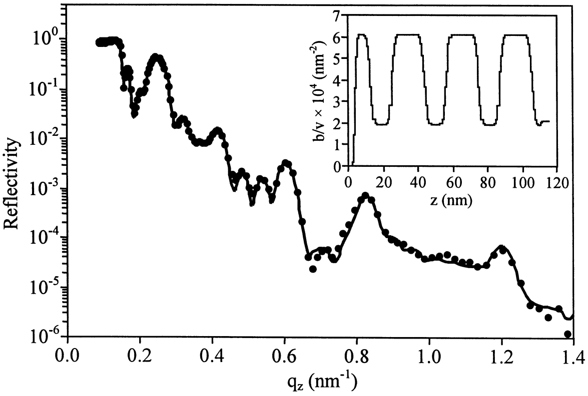

Fig. 5. Specular reflectivity profile of poly(2-vinylpyridine-styrene-d_8-*b*-2-vinylpyridine) (PS_DP). The total molecular weight is 94k and φ_s is 0.59. The solid line is the best-calculated reflectivity corresponding to the b/v profile shown in the inlet.

Summary

Equilibrium structures of two copolymers with different chain architectures were compared. The phase diagram of PSP triblock copolymers is fairly asymmetric. This is attributed to the chain conformations of middle blocks of triblock copolymers. That is, the middle block tends to deform less with increasing its volume fraction probably due to the contribution of the loop conformation and this might lead to structural phase transition from lamellar to cylinder at lower φ_s. Phase diagram of SP_2 is quite different from that of PSP especially at higher φ_s region, namely transitions of SP_2 takes place at much higher φ_s than PSP because of the asymmetric nature of SP_2 at the interface.

Lamellar microdomain spacings of two kinds of two-component copolymers, that is, PSP and SP_2, have been determined to be scaled as $M^{2/3}$ where M is the total molecular weight of copolymers. On the other hand, it was clarified that block and graft chains were shrunk in the lateral direction to compensate the elongation so as to keep their volumes constant irrespective of their chain architectures. This volume conservation principle must be a universal and essential feature of block and graft chains.

Polystyrene/poly(2-vinylpyridine) interfacial thickness of the present two-component block copolymers was measured by specular neutron reflectivity and it has been turned out to be fairly thin but experimentally-observed value is much thicker than theoretically-predicted one.

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