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Nonequilibrium helical-domain morphology in diblock copolymer systems

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Abstract

A new class of domain morphologies in diblock copolymer systems, i.e. a helical domain morphology, was found in a three component mixture of polystyrene-*block*-polyisoprene diblock copolymer, homo-polystyrene, and homo-polyisoprene. An intuitive explanation of such a domain morphology is given, which predicts that this helical morphology can be observed only in a non-equilibrium state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polystyrene-*block*-polyisoprene; Helical domain; Mixture (blend) of block copolymer and homopolymer

In recent years, the self-assembling of block copolymers has attracted many theoretical and experimental interests, and many studies have been directed to explore the spontaneously formed structures and their phase transition behaviors [1–4]. Typical examples of these structures are the spheres, the cylinders, the double gyroid networks, and the lamellae in neat diblock (A-*b*-B) and triblock (A-*b*-B-*b*-A) copolymers, where A and B are polymer chains comprised of A and B monomeric units, respectively [1–6]. Even large variety of morphologies is found in the A-*b*-B-*b*-C type linear triblock copolymers systems where C is a subchain composed of C monomeric units [3,5,7].

In this Communication, we report a new possible class of the microdomain structures for A-*b*-B type diblock copolymers, i.e. a helical-domain morphology, which has not been observed so far. This new domain morphology was found for the polystyrene-*block*-polyisoprene (SI) diblock copolymer dissolved in a mixed 'solvent' of homo-polystyrene (HS) and homo-polyisoprene (HI). The mixed solvent HS/HI undergoes macrophase separation, and the helical domains are found in the HS-rich phase. Recently, a computer simulation on the long A-*b*-B block copolymer domains in a disordered matrix of short A-*b*-B block copolymer predicted helical-domain morphology as a non-equilibrium state [8]. As will be discussed later, this simulation system is essentially the same as the above-mentioned experimental system. Therefore, we confirm that the helical morphology can be categorized as a new class of domain morphologies in diblock copolymer systems but only as a non-equilibrium state. Despite of the fact that morphology is non-equilibrium and lacks reproducibility at this moment, owing to a very subtle balance of physical forces encountered in the system as will be detailed below, existence of the special morphology itself experimentally leaves no room for doubt and moreover is quite interesting, which would be anticipated to stimulate further studies in our community.

It should be noted that another helical-domain structure has been observed in an A-*b*-B-*b*-C type triblock copolymer melt [9] (A, B and C corresponding to polystyrene (PS), polybutadiene (PB), and poly(methyl methacrylate) (PMMA), respectively). In this case, the helical morphology is regarded as an equilibrium state that originates from the complex architecture of the triblock copolymer chain. Therefore, the origin and the nature of the observed helical domains in the diblock and the triblock copolymers are essentially different.

The system reported here is a ternary mixture of block

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copolymer SI, homopolymer HS, and homopolymer HI. The number-average molecular weight (M_n) and the heterogeneity index (M_w/M_n) of the SI block copolymer equal to 1.0×10^5 and 1.16, respectively, where M_w is the weight-average molecular weight. The composition of this block copolymer is almost symmetric with the weight (volume) fraction of PS block chain 0.5 (0.46). The molecular weights of the homopolymers are $M_n = 3.3 \times 10^4$ and $M_w/M_n = 1.05$ for HS, and $M_n = 3.3 \times 10^4$ and $M_w/M_n = 1.18$ for HI, respectively.

A ternary mixture of SI/HS/HI having a composition of 15/42.5/42.5 in wt% was dissolved in toluene to form a 5 wt% polymer solution. 0.5 wt% of antioxidant (Irganox 1010, Ciba-Geigy Group) was added to the solution to prevent the thermal degradation of the film specimens during the following annealing process. The slow evaporation process of the solvent lasted over 2 weeks under ambient temperature. The film specimens were further dried and annealed at 150°C under vacuum for 24 h. The morphologies of the solution-cast films were investigated under transmission electron microscopy (TEM). Ultrathin sections (~50 nm) of the film specimens were obtained using a Reichert ultramicrotome operated at −100°C. The ultrathin sections were then exposed to OsO_4 vapor for 1 h for a selective staining of PI microdomains. The stained sections were observed with a Hitachi H-600S TEM operated at 100 keV.

The TEM investigation on the films of the ternary mixtures showed a macroscopic phase separation between the HI-rich phase on the top of the film and the HS-rich phase on the bottom. In the HI-rich phase, bimolecular vesicles [10] composed of PS block chains in the matrix of HI are found. On the other hand, bimolecular vesicles composed of PI block chains in the matrix of HS are found in the HS-rich phase, as will be detailed elsewhere [11]. The helical-domain morphology was found only in the HS-rich phase, and was not observed in the HI-rich phase. Thus, the system where we can find helical morphology is basically a binary mixture of SI/HS. This situation may be due to the slight asymmetry in stiffness of the chain or conformational asymmetry [12]. Thus, the formation of the helical morphology should be attributed to the subtle balance of a set of parameters such as molecular weights of each block in the block copolymer, molecular weights of homopolymer and the segmental interaction parameter between the two polymers.

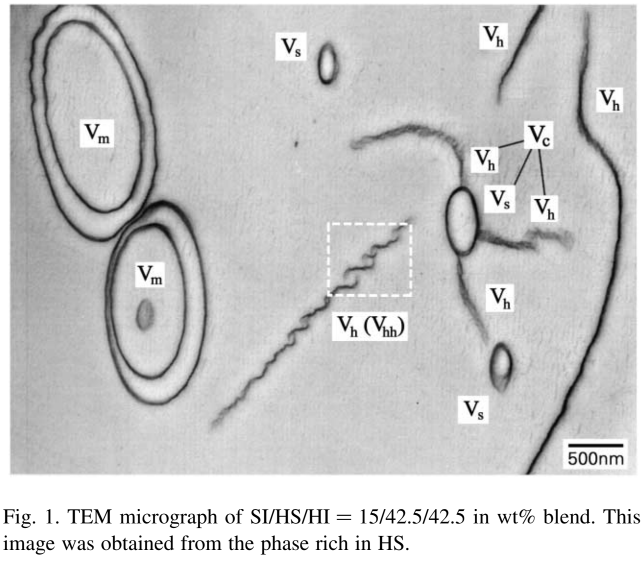

Fig. 1. TEM micrograph of SI/HS/HI = 15/42.5/42.5 in wt% blend. This image was obtained from the phase rich in HS.

Fig. 1 shows a low magnification TEM for the HS-rich phase where the PI microdomains having a dark contrast are seen to exist in the HS matrix having a bright contrast. Concerning this micrograph, it is worthwhile to point out the following. The PI block chains self-assemble themselves into multi- (or onion-ring-type) vesicles as shown in the images denoted by V_m, single vesicles as shown in the image V_s, a strand or strands of vesicles as shown in the images denoted by V_h, and a complex vesicle as shown in the image V_c which is composed of three V_hs emanating from a single V_s.

The vesicles formed by the PI blocks labeled as V_m, V_s, V_h and V_c are expected to be bimolecular vesicles as schematically shown later in Fig. 3a. The vesicles denoted as V_m and V_s are parts of spherical vesicles in the ultrathin sections of ~50 nm thickness and are composed of the bimolecular sheets or lamellae aligned perpendicularly to the ultrathin sections. The V_ms having a sharp dark contrast are flat lamellae perpendicularly aligned to the surfaces of the ultrathin sections and are running across this section. On the other hand, the parts of V_m, V_s and V_h with a gray contrast are the lamellae that are tilted to the section or those that are only partly incorporated in the section. The three V_hs that belong to the V_c (i.e. the three V_hs emanating from the V_s) and the V_h at around the center of Fig. 1 (designated further by V_{hh} for distinction) have some fine structures. The width of these vesicles are somewhat larger than the other vesicles, and therefore they have gray contrast compared to the others with dark contrast. A close observation of these images revealed that these V_hs have a helical-domain structure as shown in Fig. 2 below.

Fig. 2 shows an enlarged TEM of a part of V_{hh} as shown by the region enclosed by the square drawn in bright broken lines in Fig. 1. The figure clearly shows the vesicle is twisted into a helix. The vesicle is best interpreted as a ribbon-shaped lamella, which has a lateral width much narrower than the size along ribbon axis. Moreover, we can find a trend that a set of the two ribbon-shaped lamellae forms a double helix. The repeat distance of the helix is about twice as large as the width of the helix. Whether the helix is single- or double-stranded is a subject for future works.

Below, we offer a qualitative explanation of the helical domain found in our experiment. For a more quantitative argument of this intuitive idea, the readers should refer our forthcoming paper [8]. Each domain of the microphase separated block copolymer can be identified with a polymer brush grafted to the interface. It is well known that there

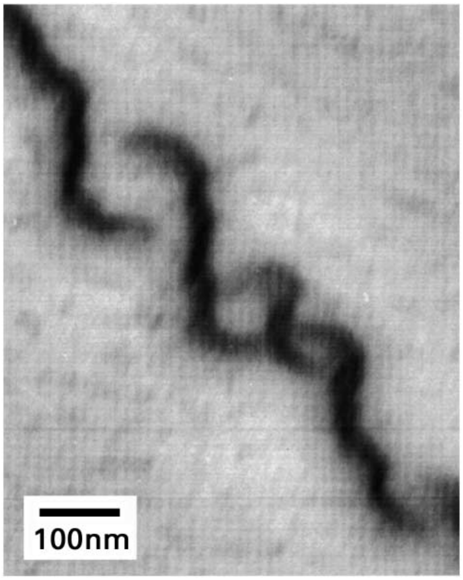

Fig. 2. Enlarged TEM micrograph of a part of the region enclosed by the bright broken line in Fig. 1.

exist two characteristic regimes for the brush depending on the ratio *r* between the molecular weight of HS, a kind of a 'solvent molecule', to that of the polymer composing the brush, i.e. the dry brush regime ($r \geq 1$) and the wet brush regime ($r \ll 1$) [10,13,14]. The interaction between two wet brushes is usually repulsive, while that between dry brushes exhibit an attractive part upon contact. Using such a character of the interaction between brushes, the stability of the helical domain can be understood as follows.

In the present experiment, the ratio *r* of the molecular weight of HS (solvent) to that of the PS block chain (brush) is equal to 0.66, which is in the crossover regime between the dry and wet brush regimes [10,13,14]. As is shown schematically in Fig. 3a, in the dry brush regime, the bimolecular layer of PI blocks form lamellae with its thickness essentially identical to that of the PI lamellae in the neat SI block copolymer used in the mixture [13,15]. In this case, the HSs are basically excluded from the PS domains composed of the PS block chains grafted to the interface (dry PS brushes), and they localize around the middle of the PS domains [13,15]. The brush–brush interactions are, therefore, screened by the intervening HS layer, and the conformation of SI block is essentially the same as that in the neat block copolymer microdomains. On the other hand, in the wet-brush regime. HSs swell the PS brushes so that the effective volume occupied by a single PS-block chain becomes much larger than that by single PI-block chains. This swelling causes the morphological transition from the lamellae to hexagonal cylinders, as shown schematically in Fig. 3c [14]. The conformation of SI block chains is strongly altered from that in the neat block copolymer system due to the swelling by HSs, and the brush–brush interactions become important opposite to the dry brush case.

In the system, we studied here, the HS chains do not wet the PS blocks. Thus, the behavior of the PS blocks must be similar to that in the lamellar case shown in Fig. 3a. The most important nature of the present helical case is the fact that the block copolymer domain is isolated and elongated in the HS matrix due to some reasons, for example, the flow and/or deformation encountered in solvent evaporation

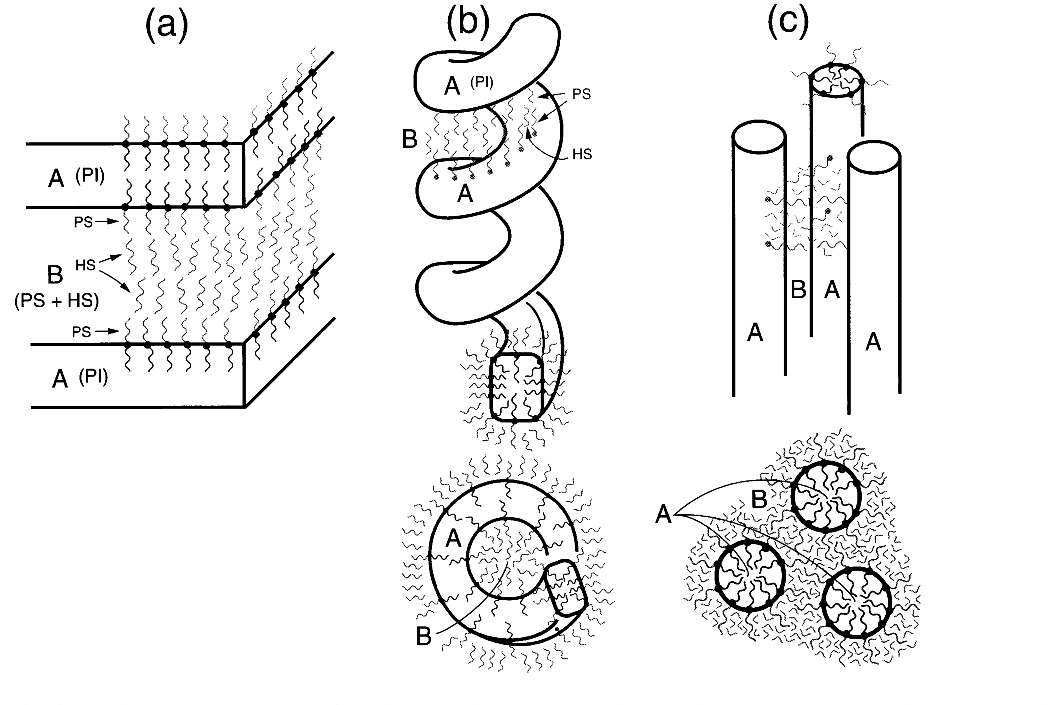

Fig. 3. Schematic model of self-assembled structure in SI/HS mixture in (a) dry brush regime, (b) intermediate regime between dry brush regime and wet brush regime, and (c) wet brush regime.

process. In such a case, the block copolymer domain tends to have a ribbon or cylindrical shape. Then, the attractive interaction between the dry PS brushes deforms this ribbon into a helical structure so that the preferable contacts between the dry PS brushes are increased (Fig. 3b). The double-helix domain structure actually observed in the experiment is reasonable in terms of lowering free energy cost for twisting the domains by increasing helical pitch, while maintaining the brush–brush interactions. The large helical pitch may make the brush–brush distance too far for their interactions, which may be circumvented by another intervening helix. The system observed in the present study shows both single- and multi-lamellar vesicles (V_ms and V_ss in Fig. 1) as well as more or less straight ribbons and helical ribbons (V_hs and V_{hh} in Fig. 1). Such a coexistence of these different types of domains can be attributed to the fact that the system is inhomogeneous and non-equilibrium and is sensitive to subtle perturbations encountered in its self-organization process. The intuitive discussions presented here should be formulated in a more quantitative manner by calculating the free energy of the helical domains where the conformational entropy of the SI blocks and HS chains as well as the interaction energy between styrene and isoprene segments are taken into account. Such a quantitative analysis will be presented in our separate paper [8].

A similar helical-domain structure has also been obtained in 3D computer simulations on a mixture of slightly asymmetric long A-*b*-B and symmetric short A-*b*-B block copolymers, designated $(\text{A-}b\text{-B})_\alpha$ and $(\text{A-}b\text{-B})_\beta$ having total degree of polymerization N_α and N_β, respectively [8,16]. The values of $\chi_{AB}N_\alpha$ and $\chi_{AB}N_\beta$ are set 50.0 and 6.0, so that $(\text{A-}b\text{-B})_\alpha$ is in the ordered lamellar state while $(\text{A-}b\text{-B})_\beta$ is in the disordered state. This means that the short $(\text{A-}b\text{-B})_\beta$ block copolymer chains do not form microphase separated domains and act as a non-selective 'solvent' for the long $(\text{A-}b\text{-B})_\alpha$ block copolymers. Because the short block copolymers act as a non-selective solvent, the interactions between the short block copolymer and each of the subchains of the long block copolymer are equally repulsive. Thus, the short $(\text{A-}b\text{-B})_\beta$ chains are excluded from the domain formed by the long $(\text{A-}b\text{-B})_\alpha$ block copolymer, which leads to the similar situation described in Fig. 3b. The only difference between this simulation system and the experimental system is whether the matrix polymer (i.e. HS or $(\text{A-}b\text{-B})_\beta$) is a selective solvent (experiment) or a non-selective solvent (simulation). It is obvious that this difference does not affect the conclusion of the intuitive argument on the helical domains described in the previous paragraphs.

Now, we compare the helical-domain morphology in our PS-*b*-PI/HS system with that in the PS-*b*-PB-*b*-PMMA triblock polymer melt studied by Krappe et al. [9]. In the latter triblock system, the weight fractions of A (PS), B (PB) and C (PMMA) block chains, denoted as ϕ_A, ϕ_B and ϕ_C, are $\phi_A = 0.26$, $\phi_B = 0.12$ and $\phi_C = 0.62$, respectively. In such a case, a cylindrical domains of A and B subchains embedded in the C-matrix are expected. If $\phi_B < \phi_A$, a fine structure can be observed inside such cylinders, i.e. the A-cylinders surrounded by B-cylindrical shells. In the system studied by Krappe et al. [9], however, ϕ_B is so small that B component cannot enclose the A-cylinder as a shell but just decorates the A-cylinders forming a helical domain around it.

As is similar to our diblock copolymer system, the helical structure in triblock copolymer system is also formed as a result of a competition between the elastic energy associated with the chain deformation and the interfacial energy. The main difference between the helical domains in diblock and triblock copolymer systems is the following. In the triblock copolymer case, the helical domains can be in equilibrium because the component of the cylindrical domains (PS + PB) are connected to the matrix component (PMMA) by a chemical bonding, and therefore, the cylindrical domains are stable in the PMMA matrix. In our diblock copolymer case, however, such a stabilization mechanism cannot be effective because the block copolymer (SI) can exclude the matrix component (HS) and form a stable lamellar or ribbon-like (or cylindrical) structures by themselves. When the isolated ribbon-like or cylindrical domains are formed, they are essentially unstable, being transformed to the helical domain. We can, therefore, conclude that the physics underlying in the two systems is substantially different. This problem will be discussed in more detail elsewhere [16].

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