

# Studies on Structural Responses in Sphere-Forming Triblock Copolymers Subjected to Stress Fields

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## *Abstract*

Polymeric materials have occupied critical positions in our life. In the history of the evolution of the polymeric materials, its physical properties have been continuously developed through synthesis of new monomers, establishment of new polymerization methods, functionalization and blending of polymers. Among the polymer blend, when two or more homopolymers immiscible to each other are blended, phase separation occurs in a macroscopic scale up to several micrometers, which always imparts fragility and brittleness to the blended polymers. Block copolymer was originally proposed to solve such an issue, which is composed of immiscible homopolymers with their either ends covalently bonded to each other. Due to the covalent bonding, the block chains are no longer allowed to disperse macroscopically, which results in improvement of the miscibility. However, in case that block copolymers composed of monomer species which strongly segregate to each other, phase separation unavoidably occurs even under the constraint effect of the covalent bonding. At a glance, the strategy of block copolymer seems to fail for the case of the strong segregation. But, unique properties can be generated as a result of the formation of microphase-separated structures in a variety of its morphologies.

In the case of a diblock copolymer composed of A and B components, the phase diagram was theoretically calculated, which shows that various morphologies, such as sphere, cylinder, double-gyroid, and lamella, can be formed depending on volume fraction of A component ( $\phi$ ), degree of polymerization ( $N$ ) and Flory-Huggins's  $\chi$  parameter as shown in Fig. 1. When the diblock copolymer takes the value of  $\chi N$  as 80 as an example, the equilibrium morphology is found to vary with increasing of  $\phi$  in the order of A-spheres forming body-centered cubic (BCC) lattice, A-cylinders arranged in hexagonal lattice, alternatively-stacked A and B lamellae, B-cylinders and B-spheres. As for the case of triblock copolymers, the equilibrium morphology similarly varies as the volume fraction increases (see Fig. 2). When A and B components of an ABA-typed triblock copolymer are in glassy and rubbery states, respectively, at a given

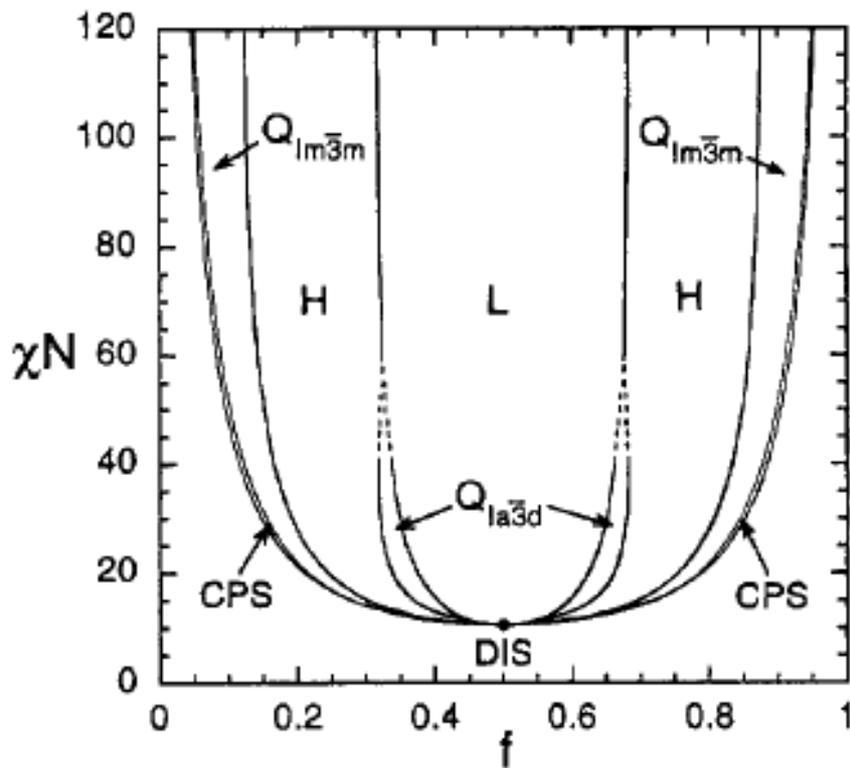


Fig. 1 Phase diagram described for diblock copolymers.

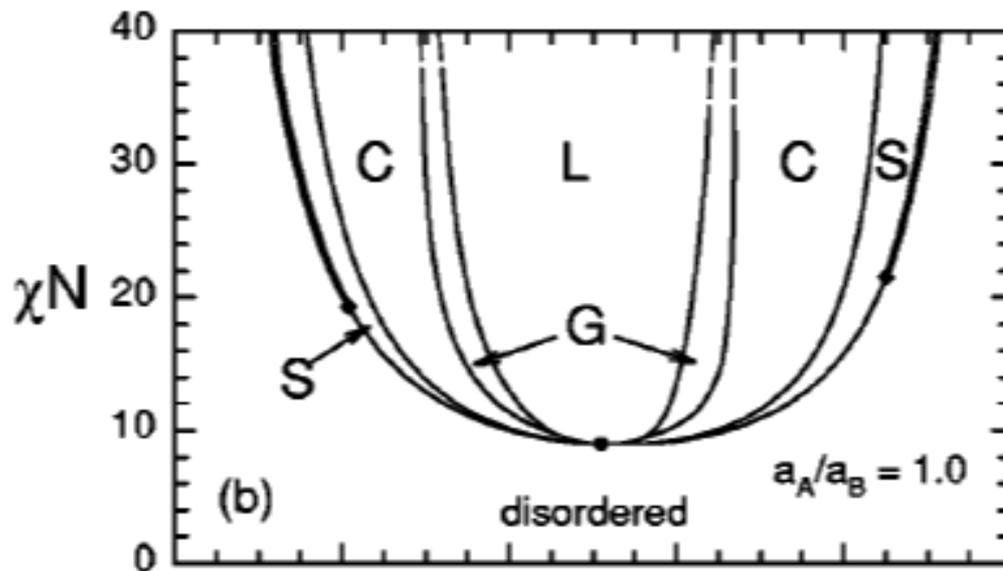


Fig. 2 Phase diagram described for ABA-type triblock copolymers with identical segmental-sizes of A and B components.

temperature, the response of the triblock copolymer film to stretching becomes elastic for A-spheres embedded in rubbery B-matrix, while it becomes brittle for B-spheres within A-matrix because the glassy A-matrix is fractured by the stretching. Therefore, the response to a physical stimulus sensitively varies with the morphology formed. Note here that the elasticity of the triblock copolymer film forming glassy A-spheres in rubbery B-matrix is specific to ABA-typed triblock copolymers due to the bridge conformation of B block chains. When the glassy spheres are interconnected by the rubbery block chains with the bridge conformation, the triblock copolymer film behaves as elastomer film because the glassy spheres play a role of physical crosslinking points for the rubbery matrix. Later on, I will discuss the details about the usability of this material. As for the case that randomly oriented A-cylinders exist in B-matrix, the triblock copolymer film exhibits an elastic property by its yield point, at which the glassy cylinders are fractured by the stretching. Beyond the yield point, the plastic property changes to a elastic one because the rubbery B block chains interconnect the fractured cylinders. It should be noted that these changes in the mechanical property are irrespective of the stretching direction because of the random orientation of cylinders. When these cylinders oriented parallel to a certain direction, the mechanical property dramatically varies depending on the angle with which the orientation direction of cylinders and the stretching direction inclined to each other. Namely, young's modulus ( $E$ ) becomes the largest when the stretching direction corresponds to the orientation direction of the glassy A-cylinders. It is needless to say that such an anisotropic mechanical-property can be directly utilized for an unique soft material having the anisotropy. Additionally, when the glassy cylinders oriented perpendicular to the film surface, the film becomes hard to be compressed but flexible in any directions parallel to the film surface. In the strategy to utilize the shape of cylinders with high aspect ratios, it is possible to use triblock copolymers as a template to fabricate an array of metallic nano-wires, which polarizes light in a variety of wavelength ranging from infrared to ultra-violet light in accordance with feature spacing of the array.

For the purpose to attain the cylinder orientation parallel to the film surface to a high extent, several kinds of external fields have been used, such as uniaxial flow and shear. In these literatures, such external fields were usually applied with strain as high as 10 to attain the high degree of cylinder orientation with the desired direction. When the uniaxial flow was applied to a triblock copolymer with random orientation of

cylinders, the cylinders might locally fracture and reconnect so as to form new cylinders aligned parallel to the flow direction. Such a reconstruction of new cylinder might demand the high strain to be applied for the complete orientation of cylinders. With respect to the cost for processing of block copolymers, the lower strain is more preferred.

Thus, I proposed an idea that the spheres transformed into cylinders oriented parallel to the flow direction, when the flow was applied to a triblock copolymer film with spherical microdomains. During the morphological transition, any fracture of cylinders must not take place. But, since the temperature at which the flow is applied should be higher than glass transition temperature ( $T_g$ ) of glassy block chains, the equilibrium morphology at the high temperature should be cylinder, and it should be sphere at room temperature before the flow application. Such a morphological transition is not the case of the sample used in this study, polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS-16) triblock copolymer used in this study. Namely, the equilibrium morphology of SEBS-16 at room temperature is cylindrical. Fig. 2 shows a phase diagram for a symmetric ABA-typed triblock copolymer, theoretically calculated by Matsen and Thompson. The vertical axis in the phase diagram is a product of  $\chi$  and total degree of polymerization, where  $\chi$  is inversely proportional to the absolute temperature in the case of SEBS-16. Therefore, to raise the temperature corresponds to a downward movement of a point along the vertical axis on the phase diagram. Since cylinder is the equilibrium morphology at room temperature for SEBS-16, increasing temperature leads to formation of sphere, which is opposite to the desired morphological transition from sphere to cylinder by a thermal annealing. This fact may suggest a necessity to use the irreversible morphological-transition from sphere to cylinder upon thermal annealing. For that purpose, to form and to vitrify the spherical microdomains with a non-equilibrated state at room temperature is required. There has been a lot of studies on microphase-separated structures in the non-equilibrated state. According to the studies, such non-equilibrium structures can be formed by evaporating the solvent which is selectively good for either constituent of block copolymers. As will be described in Chapter 1, the selectivity of the solvent plays a key role to induce the formation of non-equilibrium morphology. Sakurai et. al. reported that cylinders with their long axis oriented perpendicular to the film surface were spontaneously formed by a merely thermal annealing of the SEBS-16 as-cast film in which non-equilibrium spheres had existed. They concluded that the spontaneous

perpendicular-orientation of cylinders might be resulted from coalescence of the non-equilibrium spheres along a path parallel to the surface normal. (The path might be a trace of solvent molecules evaporating.) Therefore, I considered that the coalescence of the non-equilibrium spheres is also applicable to the case of cylinder orientation parallel to the film surface. Namely, the cylinder orientation parallel to the film surface was attempted by applying flow-field to the SEBS-16 specimen with non-equilibrium spheres to induce the directional coalescence of the spheres along the flow direction. Consequently, a high degree of cylinder orientation was successfully realized with appreciably small strains ranging from 1.5 to 4.5 as demonstrated in Chapter 1.

Among the unique methods to attain the orientation of anisotropic microdomains, Aida et. al. demonstrated the usefulness of uniaxial stretching for orientation of lamellar microdomains. Note that the sample they used was polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer. When thermally annealed under stretched state at temperatures higher than  $T_g$  of polystyrene (PS) block chains, SBS film must be fractured because the role of physical crosslinking points no longer works on, in turn the specimen totally becomes rubbery. Therefore, in their work the middle block chains, being rubbery chains, were chemically crosslinked so as not to fracture upon thermal annealing of the SBS specimen. The chemical crosslinking of the rubbery phase, however, spoils the significant advantages of thermoplastic property, such as reusability and recyclability. Therefore, I attempted to examine the potential ability of the uniaxial stretching on the cylinder orientation without chemically crosslinking of thermoplastic elastomers. I proposed an alternative idea to maintain the stretched state of the specimen without using the chemical crosslinking even at the high temperature that is to sandwich the SEBS-16 specimen with a couple of glass plates so as not to fracture during the thermal annealing. This method was applied to SEBS-16 film forming non-equilibrium spheres. Then, it can be simply expected that the non-equilibrium spheres placed in a line parallel to the stretching direction coalesce to each other by the thermal annealing, which results in the formation of cylinders oriented parallel to the stretching direction. The detailed description of the results of the attempt is demonstrated in Chapter 2.

Small-angle X-ray scattering is well known as a powerful tool to detect inhomogeneity in electron density in a length scale ranging from several nano-meters to several hundred nano-meters. Since block copolymers usually form microphase-

separated structures in characteristic length scales larger than approximately 10 nm, SAXS has been often utilized to characterize the self-assembled structures in block copolymers. Actually, to examine orientational states of cylinders or hexagonal lattice, two-dimensional SAXS (2d-SAXS) technique was utilized as shown in Chapters 1 and 2. In the course of the SAXS study of Chapter 2, the 2d-SAXS image definitely showed an elliptically-deformed particle scattering peak for the SEBS-16 specimen under the stretched state (before the thermal annealing). This finding indicates that glassy PS microdomains deformed by the stretching. At a glance, the deformation of the glassy domains is not acceptable because it has been considered that glassy substances hardly deform.

In general, young's modulus  $E$  usually takes a value of 3-4 GPa for atactic PS homopolymers even with low molecular weight. But, the value of  $E$  has been found to decrease considerably for thin or ultrathin PS film. Torres et. al. estimated  $E$  for PS homopolymers with various molecular weights and thicknesses ranging from 10 ~ 200 nm. In this work, the PS thin or ultrathin film was attached on a pre-strained substrate, and the strained state of the substrate was released, which results in wrinkling of the PS film. From the wavelength of the wrinkle and the film thickness, the value of  $E$  was estimated. They found that even for PS with high molecular weight the value of  $E$  largely decreased when the film thickness was less than 50 nm. To explain the depression of  $E$ , they assumed two-layers model, in which the value of  $E$  significantly decreased in the layer near to the free surface. As a result of model calculation, the thickness and the value of  $E$  for the PS layer near to the free surface was evaluated as 10 nm and 52 MPa, respectively, in the case of PS with low molecular weight ( $M_n = 2300$ ). Note here that the other layer on the side of bulk has the value of  $E$  for PS bulk. On the other hand, Kajiyama et. al. demonstrated that storage modulus ( $E'$ ) at a region near to the free surface of PS bulk corresponds to that for PS bulk when  $M_n$  is higher than  $5 \times 10^4$ . Below the characteristic molecular weight,  $E'$  becomes strongly dependent on  $M_n$  and reaches 300 MPa when  $M_n$  is 1700. They attributed the  $M_n$  dependency of  $E'$  at the surface region for PS with low  $M_n$  to the surface localization of chain end groups. In case of low  $M_n$ , the effect of the localization of chain end groups becomes more significant because the density of the chain end groups is higher as compared with the case of high  $M_n$ . As mentioned above, the effect of thinning and lowering of molecular weight was found to decrease the value of  $E$  or  $E'$  by a factor of 10 at most. On the basis

of the fact, it can be expected that  $E$  or  $E'$  for PS block chains constrained to a microscopic region with a several nano-meters scale significantly decreases. Therefore, I consider that the deformation of PS microdomains, which was experimentally observed for the SEBS-16 specimen under stretched state, is sufficiently understandable.

Inoue et. al. are the first to mention a possibility that the deformation of PS microdomains occurs during stretching of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock and polystyrene-*block*-polyisoprene (SI) diblock copolymer films, and blended samples of SIS and SI. They studied on the deformation behavior of these specimens during stretching via small-angle light scattering and SAXS techniques. During the stretching, a specific streak-like pattern parallel to the stretching direction was observed in the  $V_V$  light scattering pattern measured for the SIS specimen. As a first step to interpret the specific pattern, they attempted to take into consideration of the uniaxial deformation of PS microdomains toward the stretching direction. But, the possibility was denied because any shifts in the particle scattering peaks could not be observed in the stretching direction. In 1988, the deformation phenomenon was firstly observed by Seguela et. al., in which the shifts in the particle scattering peaks were clearly seen in the 2d-SAXS patterns measured for an SBS triblock copolymer specimen. However, they did not mention the shifts, and moreover stated that the particle scattering peak remained circular even under the stretched state. After that, Prasman et. al. reported and clearly mentioned a subtle deformation of the PS microdomains in SIS triblock copolymer specimens, which was published in 1998. But, the deformation behavior was not fully discussed by them.

Another technique having been used to observe the deformation behavior was FT-IR measurement with polarized light. In FT-IR spectra, PS provides an adsorption band at  $1493\text{ cm}^{-1}$ , which can be assigned to C-H in plane stretching mode. In the unstretched state, the adsorption band can be observed irrespective of the polarization of infrared light because of ensemble average of the random orientation of PS block chains. When the deformation of PS microdomains occurs upon stretching, the PS block chains must be elongated to an extent toward the stretching direction, which leads to orientation of the planes of benzene rings inclined to the stretching direction with a certain polar angle. Since the vibration mode on the plane of benzene rings is only sensitive to infrared light polarized parallel to the plane, FT-IR measurement with polarized infrared light is able to detect the degree of the deformation of PS microdomains. Duan et. al.

showed experimental results of SAXS and FT-IR measurements conducted during the stretching of PS-g-PI multi-graft copolymer films with spherical microdomains. They concluded that the deformation of the glassy spheres took place because orientation factor of PS block chains increased with strain, even though any shifts of the particle scattering peaks could not be observed in the 2d-SAXS images. Furthermore, the extent of the orientation of PS block chains was found to be comparable with that of PI block chains, which is not acceptable. The extremely high extent of the orientation of PS block chains might be a measure of fracture or fragmentation of PS microdomains. Between the fractured domains highly extended PS chains might exist, while PS block chains in undamaged spheres did not undergo any elongation. Ensemble average of that situation leads to overestimation of the degree of the orientation of PS block chains.

To understand deeply the deformation behavior of the PS microdomains upon stretching, I conducted 2d-SAXS measurements for several kinds of triblock copolymers, namely SEBS and polystyrene-*block*-polyisobutylene-*block*-polystyrene (SIBS) triblock copolymers, which have PS block chains with different molecular weights. For all the specimens, the stretch-induced deformation of PS microdomains was definitely observed as the shifts of the particle scattering peaks. The extent of the deformation was clearly dependent on both the strain of specimens and molecular weight of PS block chains.

The longest-relaxation time ( $\tau$ ) of polymer chains is one of important parameters which determine the viscoelastic property of the polymer. In dynamic viscoelastic measurement, number-average relaxation time ( $\langle\tau\rangle_n$ ) or weight-average relaxation time ( $\langle\tau\rangle_w$ ) can be estimated from storage and loss moduli logarithmically plotted against frequency. In past, many researchers were devoted into investigation of the viscoelastic properties of PS homopolymers with various molecular weights and temperatures. But, almost all the studies concerning the estimation of the relaxation times are conducted at temperatures sufficiently high above  $T_g$  of the PS or comparable to the  $T_g$ . This is because the relaxation time becomes extremely high as experimentally inaccessible at temperatures below the  $T_g$ . In case of my experiments using SEBS-16, since  $T_g$  of PS was determined as 49.5°C, the relaxation time is expected to be extremely high at room temperature, which means that the deformation of PS microdomains must not proceed with time when the specimen was under stretched state. However, the deformation of the PS microdomains was found to proceed with time for all the specimens under stretched state, which is a quite surprising finding. Furthermore, the characteristic

times related to the deformation were in the order of  $10^3 \sim 10^4$  s, which is extremely short as compared with that predicted from experiments for PS homopolymers with the comparable molecular weight. Actually, the proceeding of the deformation of PS microdomains with time was analyzed by time-resolved 2d-SAXS measurements for the specimens under stretched state. The details of the 2d-SAXS measurements will be discussed in Chapter 4.

In Chapter 1, cylinder orientation resulted from applying an uniaxial and compressional flow to the SEBS-16 as-cast film which had contained non-equilibrium PS spheres was examined. After applying the flow, the SEBS specimen was further thermally annealed in the absence of an applied load. The resulting orientation of the cylindrical phase was analyzed by 2d-SAXS. The cylinder orientation parallel to the FD was clearly seen to improve with an increase in the preannealing temperature and time. With subsequent thermal annealing, the cylinder orientation was found to rapidly improve within 10 minutes of the annealing. When further annealed for a long time above 10 minutes, the fraction of grains in which the  $\{10\bar{1}0\}$  planes were parallel to the substrate surface gradually increased. The application of flow directly to a cylindrical morphology resulted in a lesser degree of cylinder orientation than by transitioning from spheres to cylinders. This indicates the superiority of utilizing the coalescence of spheres for achieving cylindrical orientation via application of flow.

Chapter 2 presented experimental results of an attempt to control the orientation of cylinders by using the directional coalescence of the non-equilibrium spheres along SD of the SEBS-16 as-cast film. Here, the SEBS-16 specimen was subjected to a thermal annealing under stretched state, which was maintained by sandwiching the specimen with a couple of glass plates. The orientational state of BCC lattice composed of spheres and hexagonal lattice of cylinders were analyzed via AFM and in-situ 2d-SAXS measurements. It was found that the uniaxial stretching caused not only the deformation of BCC lattice but also the orientation of the  $\langle 111 \rangle$  direction to SD. Upon the thermal annealing of the specimens under the stretched state, such a preferential orientation was found to proceed. Eventually, the cylinder orientation parallel to SD could not be achieved by the present method. However, the 2d-SAXS pattern for the specimen under the uniaxially stretched state showed four-streak pattern which quickly became more evident one upon the thermal annealing and finally changed into four-spots just before the transformation of spheres into cylinders. By a close examination, the

specific change in the 2d-SAXS patterns was successfully attributed to commensuration (or a kind of epitaxy) in the transformation from the deformed BCC lattice to the undeformed one without large-scaled rearrangement of spheres.

In Chapter 3, I discussed experimental results of simultaneous measurements of SS curves and 2d-SAXS for the SEBS specimens, which indicated that PS spherical microdomains deformed upon stretching. Actually, the deformation of the PS microdomains was detected as shifts of the peak position of the particle scattering toward lower and higher  $q$ -regions in  $q$  directions parallel and perpendicular to SD, respectively. By assuming that spheres simply deformed into prolate spheroids with its major axis parallel to SD, 1d-SAXS profiles measured at several strains were successfully reproduced with model calculation of the 1d-SAXS profiles. Since the extent of the deformation of microdomains was found to increase as the initial size of microdomains decreased, it was concluded that the deformation of glassy microdomains might be due to a high extent of the stress concentration at microdomains.

Chapter 4 presented experimental results of time-resolved 2d-SAXS measurements for the triblock copolymer specimens under stretched state at strain of 4.0. The strain-induced deformation of glassy microdomains was observed clearly. In addition, the deformation of glassy microdomains was found to proceed as time elapsed. To examine the effect of the deformation behavior of PS microdomains on the stress relaxation, stress relaxation curves were separately measured for the specimens under the stretched state. The stress was found to decrease abruptly with time. At a glance, this profound stress relaxation was caused by the deformation of PS microdomains. However, since the extent of the deformation of PS microdomains was trivial ( $\sim 5\%$ ), the deformation of PS microdomains failed to explain such a rapid relaxation in stress. Therefore, I assumed that the profound stress relaxation was due to fracture of PS microdomains in the specimens under the stretched state. To examine the relationship between the deformation and fracture of PS microdomains, characteristic times related to the deformation and fracture were evaluated from the change in strain of the glassy microdomain and from the stress relaxation curves, respectively. Good agreements of the characteristic times were found, and therefore it was concluded that the deformation of the glassy microdomains has a strong correlation with the stress relation and therefore with the fracture of the elastomeric film specimen.