Morphology of Poly(styrene-*block*-butadiene-*block*-styrene) Triblock Copolymers Cross-Linked in the Disordered State†

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ABSTRACT: The morphology of poly(styrene-*block*-butadiene-*block*-styrene) (SBS) triblock copolymers, of which the polybutadiene blocks are chemically cross-linked in the disordered state, is investigated by transmission electron microscopy and small-angle X-ray scattering (SAXS). The morphology was "disorder-like" or "strut" according to a cross-link density. The cross-linked specimens were then thermally annealed so as to promote ordering of the structure in the presence of the cross-links. As a result, we could obtain the ordering of the structures and observed "lamellar–catenoid structures" for the weakly cross-linked specimens. It is noteworthy that the competitive effects, i.e., the ordering and the elastic force arising from the deformed cross-linked polymer chains, created an interesting morphology which is hardly formed in ordinary SBS triblock copolymers. Transition from disorder-like to strut was also induced by thermal annealing.

I. Introduction

Block copolymers possess great potentialities in pattern formation from microscopic to macroscopic scale.[1–32] Microscopic patterns as morphologies of microdomain structures[1–4] are exclusively observed in or near thermodynamically equilibrium conditions, whereas macroscopic patterns as observed on an undulating free surface[32] are only observed in dissipative conditions far from equilibrium. Variety in microscopic patterns can be seen in morphologies of microdomain structures.[3] Much attention from the standpoint of technology has been paid to the control of the morphology.[3] This is mainly because the physical properties of the block copolymers strongly depend on the morphology not only in the macroscopic scale, as with polymer blends, but also in the microscopic scale.[14,31] This study concerns the control of the morphology in the microscopic scale.

In general, the morphology can be changed by the volume fraction of one type of repeating unit in a block copolymer chain.[1] In the actual case, however, the morphology can be controlled in various ways. For a pure block copolymer system, designing chemical architectures of the copolymer chain with linear, grafted, star-shaped structures, and so forth has been conducted to create novel morphology from a viewpoint of chemistry.[5–10] Kinetic control by utilizing solvent properties in the solvent-casting process,[11–14] thermodynamic equilibrium control by changing temperature,[15–17] and control by coupling the microphase separation with crystallization[18] have been performed from a physicochemical point of view. Blends of block copolymer/homopolymer[19–26] or block copolymer/block copolymer[27–29] have also been intensively studied experimentally and theoretically.

Cross-linking of polymer chains is widely applied for morphology control in polymer blends. The cross-linking can be formed by photodimerization reaction between anthracene groups that are chemically attached on polymer chains,[33–36] γ-ray irradiation,[37] polymerization of monomers with cross-linkers in the presence of linear polymers,[38–40] thermally induced radical generation using peroxide,[41,42] end-cross-linking of multifunctional prepolymers,[40,43] and so forth. The effects of the cross-linking for the polymer blends are also theoretically considered.[44,45] In the case of block copolymers, the cross-linking of the copolymer chains has not been effectively utilized for the morphology control. In this study, the cross-linking of the block copolymer chains is examined as a novel approach for the control of the morphology from both chemical and physicochemical points of view.

In this work, the morphology of poly(styrene-*block*-butadiene-*block*-styrene) (SBS) triblock copolymers, of which polybutadiene (PB) blocks are chemically cross-linked in the disordered state, is investigated by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). In order to modify the chemical architectures of the block copolymer chains, cross-linking of the block copolymers in the disordered state, where the block copolymer chains are homogeneously mixed without separating into the microphases, is one of the most convenient and effective ways. The block copolymers cross-linked in the disordered state were subjected to microphase separation by increasing effective interactions between polystyrene (PS) and PB block chains. The morphologies were found to be dependent upon the cross-link densities; a structure similar to that observed in a phase-separated polymer mixture was seen for the lower cross-link density, and a vague morphology was obtained at the highest cross-link density of this study. While the former has already been reported for the block copolymers cast using the selective solvent,[3,14] the latter is a novelty showing that the cross-linking could successfully lock the very weakly segregated structure existing even in the disordered state owing to the critical concentration fluctuation.[46] Hence, the latter is referred to as "disorder-like". The cross-linked specimens were then thermally annealed so as to promote ordering of the structure in the presence of the cross-links. As a result, we could obtain the ordering of the structures and observed "lamellar–catenoid structures"[16] for the weakly cross-linked specimens. Although our experimental observation of the lamellar–catenoid is not the first, it is noteworthy that the competitive effects, i.e., the ordering and the elastic force arising from the deformed cross-linked polymer chains, created an interesting morphology which is hardly formed in ordinary SBS triblock copolymers.

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II. Experimental Section

The SBS specimen used was kindly supplied by Japan Synthetic Rubber Co. Ltd. (sample code is TR2400). The number-average molecular weight (M_n) is 6.31×10^4, as characterized by membrane osmometry. M_w/M_n is 1.15 by GPC, where M_w denotes the weight-average molecular weight. The weight fraction of the polystyrene (w_{PS}) is 0.56 by elemental analysis. The microstructure of the PB blocks is characterized by the Morero method[47] to be 33, 55, and 12 mol % cis-1,4-, trans-1,4-, and 1,2-linkages, respectively. The details of the specimen characterization are described elsewhere.[13]

A dioctyl phthalate (DOP) solution of TR2400 was prepared with a volume fraction of polymer (ϕ_P) of 0.41. Since the order–disorder transition temperature (T_{ODT}) for this solution was determined by SAXS to be 105 °C (see section III 1), the chemical cross-linking in the disordered state was performed by maintaining the TR2400/DOP (ϕ_P = 0.41) solution at 150 °C for 100 min with peroxide. The peroxide used is 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane which generates radicals at high temperatures[41,42] and cross-links only PB chains of the SBS molecules. The peroxide was homogeneously mixed into the TR2400/DOP (ϕ_P = 0.41) solution by solvent-casting of a methylene chloride solution containing the peroxide and ca. 3 wt % of the mixture of TR2400/DOP (ϕ_P = 0.41). The concentrations of peroxide were 0.5, 0.8, 1.0, 1.3, and 1.5 wt % to the SBS content. These concentrations correspond to 1.0, 1.5, 2.0, 2.7, and 3.0 molecules of the peroxide per SBS molecule. Finally, the heat treated specimens were washed with methylene chloride to remove un-cross-linked SBS molecules and DOP. These specimens are referred to as "as-prepared" specimens. Samples are then subjected to thermal annealing at 160 °C for ca. 1, 12, 24, or 48 h under vacuum. These are designated as "annealed".

TEM observation was performed on ultrathin sections of the specimens with JEM-100C (JOEL Co. Ltd.) operating at 100 kV. The ultrathin sections were stained with osmium tetraoxide (OsO_4) vapor. The thickness of the ultrathin section was in the range 90–150 nm.

SAXS measurements were performed using synchrotron radiation as an X-ray source at the BL-10C beam line in the Photon Factory of the National Laboratory for High Energy Physics, Tsukuba, Japan. The details of the apparatus were described elsewhere.[48] The incident beam was focused with a bent cylindrical mirror on a detector and monochromatized with a couple of Si(111) crystals. The wavelength λ of the incident beam was 0.1488 nm. The scattered intensity was collected with a one-dimensional position sensitive proportional counter. The sample-to-detector distance was 1.9 m. The measured scattered intensity was further corrected for air-scattering, for absorption due to the specimen, and for thermal diffuse scattering arising from density fluctuations. The film specimens were exposed to the X-ray beam for ca. 300 s at room temperature. Because the flux of the incident X-ray beam was very high, i.e., about 1×10^{12} photons/(cm^2 s), the exposure time should be as short as possible to protect PB against the radiation damage. We could obtain enough statistics in ca. 300 s of exposure.

III. Results and Discussion

III.1. Determination of Order–Disorder Transition Temperature, T_{ODT}. In order to cross-link TR2400 (SBS) in the disordered state, T_{ODT} is required to be located around 100 °C for experimental convenience. Since T_{ODT} of the bulk TR2400 might be very high temperature, DOP was utilized to lower the T_{ODT} by reducing the repulsive interactions between the styrene and butadiene segments. Hence, we prepared the TR2400/DOP (ϕ_p = 0.41) solution and T_{ODT} was quantitatively determined by SAXS for this solution. Figure 1 shows SAXS profiles (the scattered intensity as a function of magnitude of the scattering vector, q, defined by eq 1) for the un-cross-linked TR2400/DOP (ϕ_p = 0.41) solution at various temperatures. These profiles were measured using an ordinary rotating anode type X-ray generator with the apparatus described elsewhere.[49] The logarithm of the scattered intensity $I(q)$ is plotted as a function of the magnitude of the scattering vector q:

$$q = |\mathbf{q}| = (4\pi/\lambda)\sin(\theta/2) \quad (1)$$

where θ is the scattering angle. A single scattering peak was observed for every profile. In Figure 2 plots of I_{max}^{-1} and d are shown as a function of the inverse of the absolute temperature, T^{-1}. I_{max} is the scattered intensity at the peak. d denotes the wavelength of the dominant concentration fluctuation existing in the disordered state or the Bragg spacing of the microdomain structure in the

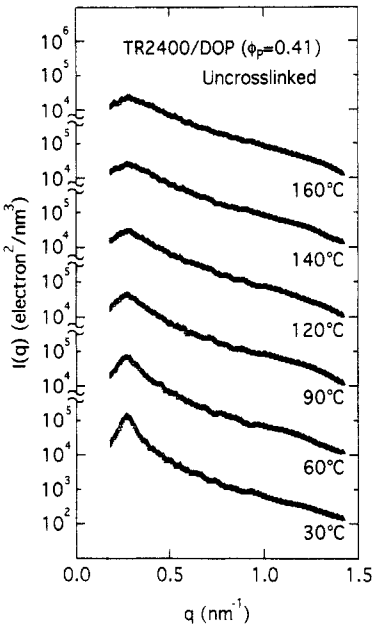

Figure 1. SAXS profiles for an un-cross-linked TR2400/DOP (ϕ_p = 0.41) solution at various temperatures.

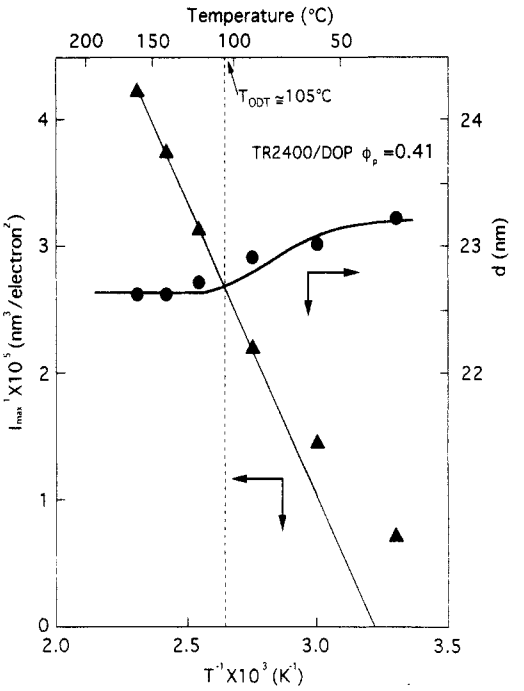

Figure 2. Plots of I_{max}^{-1} and d as a function of the inverse of the absolute temperature, T^{-1}. I_{max} is the scattered intensity at the peak. d denotes the wavelength of the dominant concentration flucutation existing in the disordered state or the Bragg spacing of the microphase-separated structure in the ordered state, given by $2\pi/q_m$ where q_m is the magnitude of the scattering vector at the peak.

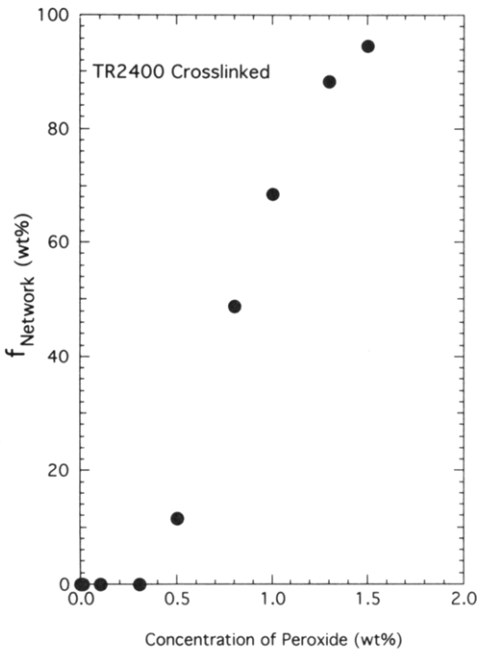

Figure 3. Plot of $f_{Network}$ (wt %) vs concentration of peroxide (wt %). $f_{Network}$ designates the wt % fraction of the macroscopically cross-linked SBS molecules.

ordered state, given by

$$d = 2\pi/q_m \tag{2}$$

where q_m is the magnitude of the scattering vector at the peak. Since the linear relationship of I_{max}^{-1} with respect to T^{-1} and the constant d value with T^{-1} are expected in the disordered state, T_{ODT} can be determined as the deviation temperature from the linear relationship of I_{max}^{-1} with T^{-1} and the temperature at which d starts to increase with decreasing temperature. According to these criteria T_{ODT} was determined to be approximately 105 °C for the un-cross-linked TR2400/DOP (ϕ_p = 0.41) solution. It should be noted here that the linear relationship of I_{max}^{-1} vs T^{-1} in the disordered state is not maintained if the finite size effect (Brazovskii effect) is taken into account.[46,49] Therefore, the determination of T_{ODT} based on the linear relationship of I_{max}^{-1} vs T^{-1} is irrelevant. In Figure 2, the deviation of the d values was also found at ca. 105 °C and hence we determined $T_{ODT} \cong 105$ °C.

III.2. Characterization and Morphologies of Cross-Linked TR2400. If the network structure is required to be quantitatively characterized, the average molecular weight between adjacent cross-linking points should be evaluated by means of, for example, the Flory–Rehner theory.[50] In this evaluation the interaction parameter between the polymer molecule and the swelling solvent is needed. It is difficult to choose the solvent whose interaction parameter for the SBS molecule similar to TR2400 is known. Hence, the qualitative characterization of the cross-linked specimen was done by evaluating the weight fraction of the macroscopically cross-linked SBS molecules, $f_{Network}$. $f_{Network}$ was evaluated with the following equation:

$$f_{Network}\ (\text{wt \%}) = w/w_0 \times 100 \tag{3}$$

where w and w_0 denote, respectively, weights of the cross-linked films without and with un-cross-linked SBS components. As depicted in Figure 3, $f_{Network}$ is zero for the concentration of peroxide below 0.3 wt % and increases with increasing concentration of peroxide. Note that the threshold of the formation of the macroscopic network is roughly located at 0.5 wt % peroxide concentration where the number of peroxides per SBS molecule is equal to unity. It is also noted that $f_{Network}$ reaches 96 wt % at 1.5 wt % peroxide. Thus, the concentrations of peroxide employed in this study covered the wide range of $f_{Network}$ approximately from 0 to 100%.

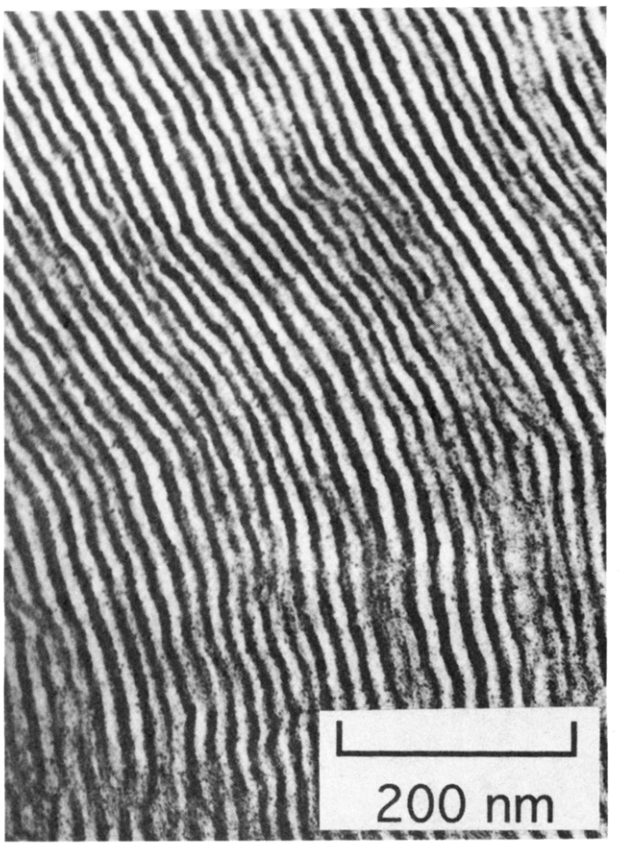

Figure 4. Transmission electron micrograph of an un-cross-linked TR2400 cast from a toluene solution.

Figure 4 is a transmission electron micrograph of an un-cross-linked TR2400 cast from a toluene solution where the black and white parts correspond to OsO_4-stained PB microdomains and unstained PS microdomains, respectively. Since toluene is a neutral solvent for PS and PB,[14] the observed alternating lamellar microdomain structure can be considered as a thermodynamic equilibrium morphology.

On the other hand, as shown in Figure 5 the morphology of a cross-linked TR2400 prepared with the concentration of peroxide at 0.5 wt % turned out to be very much different from the lamellar structure. Here, through and edge views display the images viewed from the directions normal and parallel to the surface of the sample film, respectively. Recall that the specimen contained no un-cross-linked SBS molecule. The morphology is in the category of the so-called "strut structure".[25] This is similar to that seen in phase-separated polymer mixtures,[33–36] but on a different size scale. It is remarkable, however, that recently Russell et al.[40] reported a very small size for the phase-separated domains of the polymer mixtures prepared under high pressure, which was comparable to the size of the microdomain structures of the block copolymers.

Transmission electron micrographs of an annealed specimen (annealed at 160 °C for 12 h) of the cross-linked TR2400 prepared with the concentration of peroxide at 0.5 wt % are presented in Figure 6a for the through view and Figure 6b for the edge view. The cross-linked specimens were thermally annealed so as to promote ordering of the structure in the presence of the cross-links. For the through view the structure is similar to that

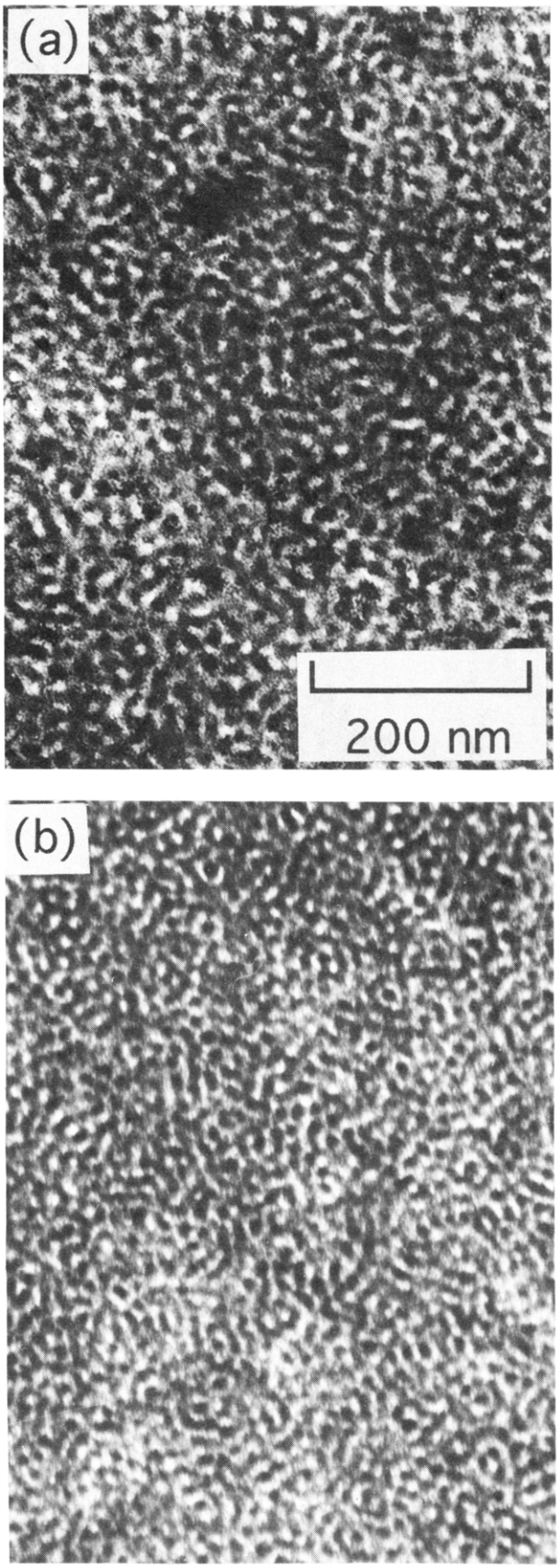

Figure 5. Transmission electron micrographs of a cross-linked TR2400 prepared with the concentration of peroxide at 0.5 wt % (as-prepared specimen) for (a) through and (b) edge views.

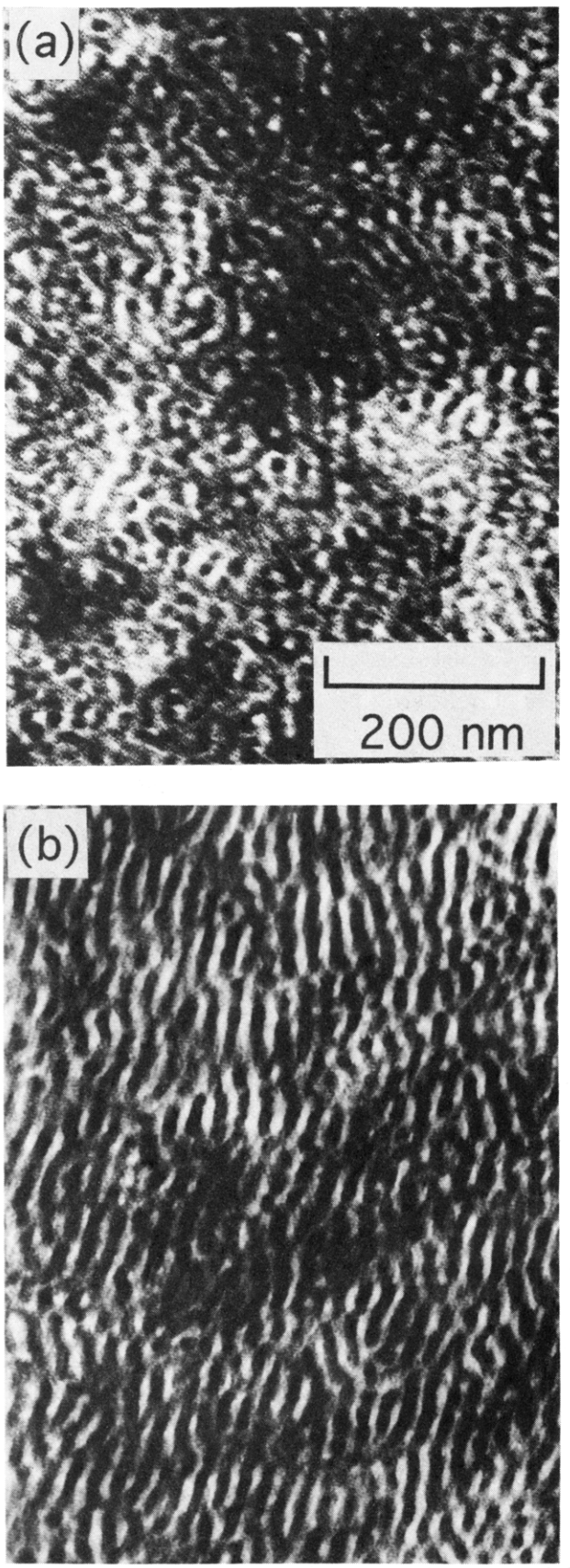

Figure 6. Transmission electron micrographs of annealed specimens (annealed at 160 °C for 12 h) of the cross-linked TR2400 prepared with the concentration of peroxide at 0.5 wt % for (a) through and (b) edge views.

observed in Figure 5. On the other hand, for the edge view, the structure seems to be the alternating lamellae with relatively low regularity and coherency of lamellar stacks. The microdomains are found to be preferentially oriented in a particular direction. Since any special care on the ultrathin sections was not done with respect to the surface of the sample film, the direction of the preferential orientation cannot be identified. However, the ordering

of lamellae may be possibly considered to be stimulated by the film surface during the thermal annealing at 160 °C. Close examination in this photograph of the edge view reveals that there are many grayish regions in the black parts of PB lamellae. The cylindrical channel composed of PS chains going through the PB lamellae is possibly considered for this structure. This is similar to the so-called "lamellar–catenoid structure".[16]

Figure 7 shows transmission electron micrographs of a cross-linked TR2400 prepared with the concentration of peroxide at 1.5 wt % for (a) through and (b) edge views. At the first glance, the structure in the through view looks similar to those in Figures 5a,b and 6a. However, the black parts of the PB microdomains in Figure 7a seem to be smaller than the others in Figures 5a,b and 6a. The TEM photographs of Figure 7 are somewhat grayish. Moreover, the edge view exhibits the characteristic features that contrast between bright and dark regions is ambiguous and there seems to be a broad distribution of the PB domain size. Thus, the structure is likely different from the structures observed in Figures 5 and 6. The dominant effects of the cross-links are the retardation of the mobility and a spatial trapping of the molecules. Since the concentration of peroxide is 1.5 wt % which corresponds to $f_{\text{Network}} = 96$ wt % (see Figure 3), the effect of the cross-links retensioning the nonequilibrium structure may be considerably large. Hence, the cross-linked SBS molecules might not have enough time to develop the microdomain structure during the preparation time for the as-prepared specimen and the structure in the disordered state might be locked in the as-prepared specimen. In other words, the cross-linking might successfully lock the structure in the disordered state. Due to the concentration flucutation existing even in the disordered state,[46] the TEM showed a very weakly segregated structure with a relatively broad distribution of the PB domain size, as observed in Figure 7b, instead of a homogeneous image. Because of this reason, we refer to the structure observed in Figure 7 as "disorder-like", although the structure looks microphase-separated. The disorder-like image was observed in some cases (like Figure 7b), and the microphase-separated structure with a relatively small domain of PB was seen in other cases (like Figure 7a). The observed images differ because the structure formation should be sensitive to the sample preparation for such high peroxide concentration as 1.5 wt %.

III.3. Structure Analyses by SAXS. Figure 8 shows SAXS profiles for (a) a cross-linked TR2400/DOP (ϕ_p = 0.41) solution and (b) a cross-linked TR2400 film ($\phi_p = 1$) (all are through views in part b) at various temperatures. A single scattering maximum is observed for both cases, and the position of the maximum, q_m, turned out to be temperature independent. The value of q_m gives a value of d (=ca. 20.0 nm) slightly smaller than that of the un-cross-linked TR2400/DOP (ϕ_p = 0.41) solution in the disordered state (d = ca. 22.7 nm; see Figure 2). The difference in d is bigger than the experimental error of ±0.5 nm, and it may be stated that the value of d decreased as a consequence of the cross-links. However, the difference is trivial so that more data should be required for the discussion of the effects of the cross-links on the structures. In order to discuss the temperature dependence of the peak intensity, I_{max}^{-1} is plotted against the inverse of the absolute temperature, T^{-1}, for the un-cross-linked TR2400/DOP ($\phi_p = 0.41$) solution, the cross-linked TR2400/DOP (ϕ_p = 0.41) solution, and the cross-linked TR2400 film ($\phi_p = 1$) in Figure 9. For the un-cross-linked TR2400/DOP (ϕ_p = 0.41) solution, the data points and the solid line are the same as those presented before in Figure 2. It is found for the cross-linked solution that the temperature dependence of I_{max}^{-1} crosses the line of the un-cross-linked solution. Without knowing the structure

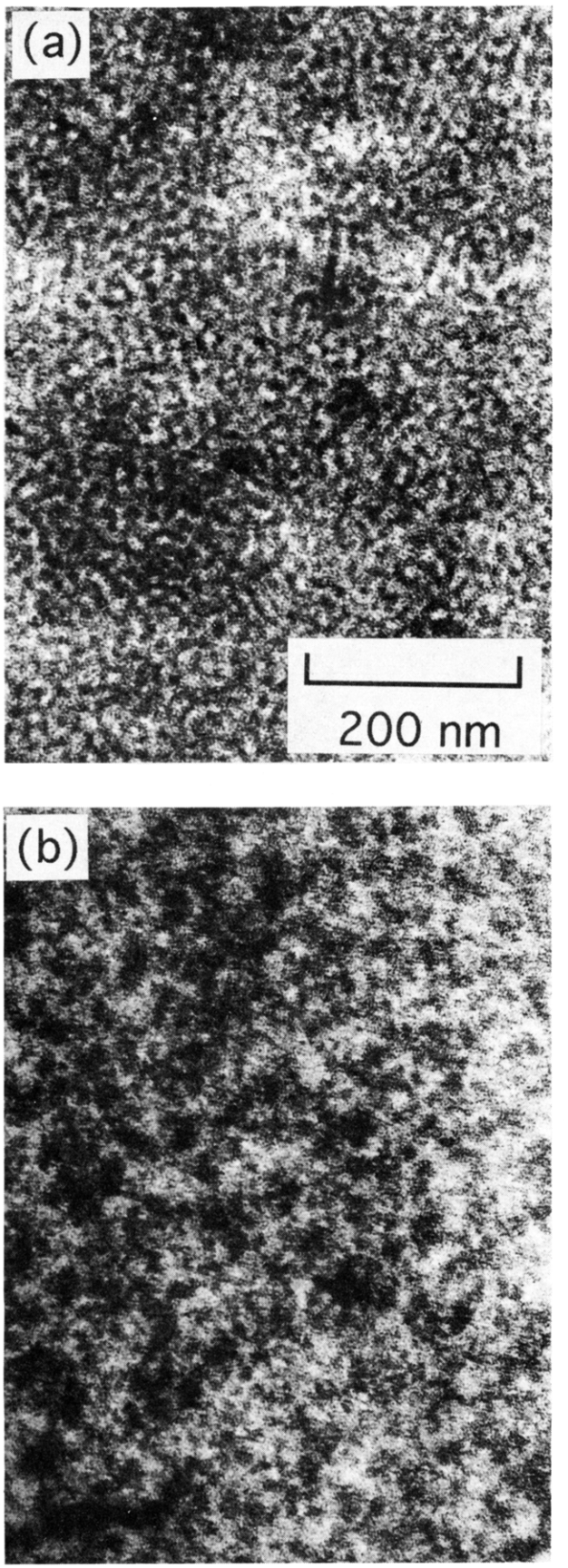

Figure 7. Transmission electron micrographs of a cross-linked TR2400 prepared with the concentration of peroxide at 1.5 wt % (as-prepared specimen) for (a) through and (b) edge views.

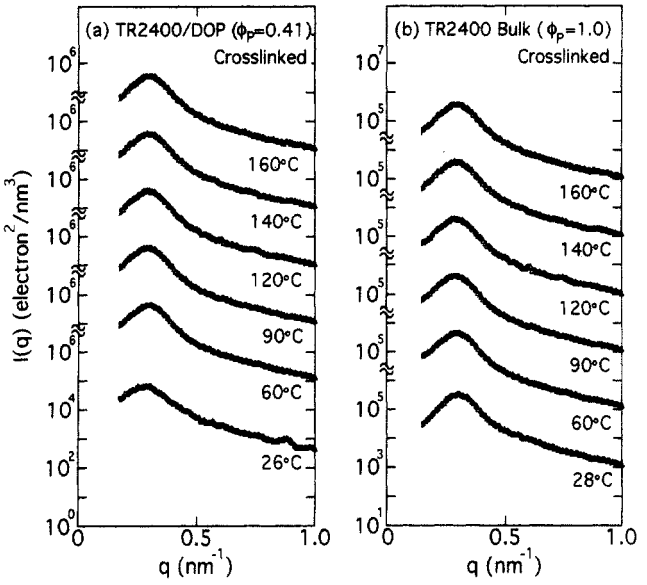

Figure 8. SAXS profiles for (a) a cross-linked TR2400/DOP (ϕ_p = 0.41) solution and (b) a cross-linked TR2400 film (ϕ_p = 1) at various temperatures.

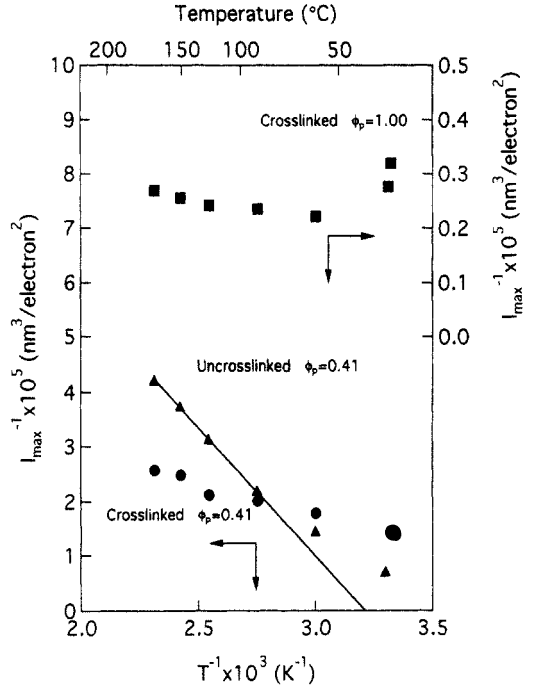

Figure 9. Plots of I_{max}^{-1} vs the inverse of the absolute temperature, T^{-1}, for an un-cross-linked TR2400/DOP (ϕ_p = 0.41) solution, a cross-linked TR2400/DOP (ϕ_p = 0.41), solution and a cross-linked TR2400 film (ϕ_p = 1).

factor of the swollen cross-linked SBS in a homogeneous state, one can only say that I_{max} increased by introducing the chemical cross-links for the temperatures higher than the T_{ODT} of the un-cross-linked solution. On the other hand, the change of I_{max}^{-1} with temperature became smaller, indicating that the peak intensity of the cross-linked TR2400 solution is less sensitive to temperature than that of the solution before cross-linking. As for the cross-linked film (ϕ_p = 1), I_{max} is more intense and less sensitive to temperature than the others shown in this figure. This may indicate the formation of microdomain structures, although only a single scattering maximum was observed in the SAXS profile.

The cross-linked specimens were thermally annealed so as to promote ordering of the structure in the presence of the cross-links. Let us now analyze the microdomain

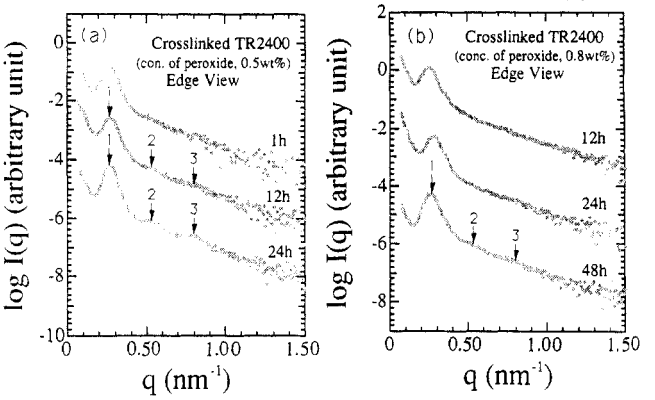

Figure 10. SAXS profiles (edge view) obtained at room temperature for cross-linked TR2400 films with the concentrations of peroxide at (a) 0.5 wt % and (b) 0.8 wt %, as a function of the thermal annealing time at 160 °C. The profiles for 12 and 24 h in part a and those for 24 and 48 h in part b are vertically shifted by -2 and -4, respectively, to avoid overlaps.

structures of the annealed films by SAXS. Figure 10 shows SAXS profiles, which were obtained using synchrotron radiation at room temperature, for the cross-linked films with the concentrations of peroxide at (a) 0.5 wt % and (b) 0.8 wt %, as a function of the thermal annealing time at 160 °C. The film specimens were exposed to the X-ray beam for ca. 300 s in such a way that the film normal is perpendicular to the propagation direction of the incident beam (edge view). For the profiles of 12- and 24-h annealed films shown in part a and for that of the 48-h annealed film in part b, the second and third order scattering maxima can be seen at the positions indicated by the arrows. For part a, the second and third order peaks are found to become distinct with the annealing time. These q values are 2 and 3 times as large as the q values of the first order peak. Therefore, the three-dimensional isotropic microdomains formed in the as-prepared specimens started ordering and became one-dimensionally arrayed with annealing at 160 °C. This tendency has been confirmed by TEM (see Figure 6) for the stained ultrathin section. The results of TEM and SAXS indicate that we could obtain the ordering of the structures in the presence of the cross-links and could observe the lamellar–catenoid structures for the weakly cross-linked specimens. It was also found that longer annealing was required for the ordering in the cross-linked specimen prepared with the higher concentration of peroxide. It is noteworthy that the competitive effects, i.e., the ordering and the elastic force arising from the deformed cross-linked polymer chains, created interesting morphology which is hardly formed in the ordinary SBS triblock copolymers.

Now let us discuss the microdomain structures in terms of the concentration of peroxide and the annealing time. In Figure 11 SAXS profiles, which were obtained using synchrotron radiation at room temperature, for cross-linked TR2400 films with various concentrations of peroxide are shown for (a) as-prepared and (b) annealed specimens (annealed at 160 °C for 48 h). The film specimens were exposed to the X-ray beam for ca. 300 s in such a way that the film normal is parallel to the propagation direction of the incident beam (through view). Although the SAXS profiles for the cross-linked films which were annealed at 160 °C for 1, 12, and 24 h are not included in this figure, a single scattering peak was observed for all cases. It was found that the position of the peak systematically changes with the concentration of peroxide, while there is no obvious change of the peak position with the annealing time. These results indicate

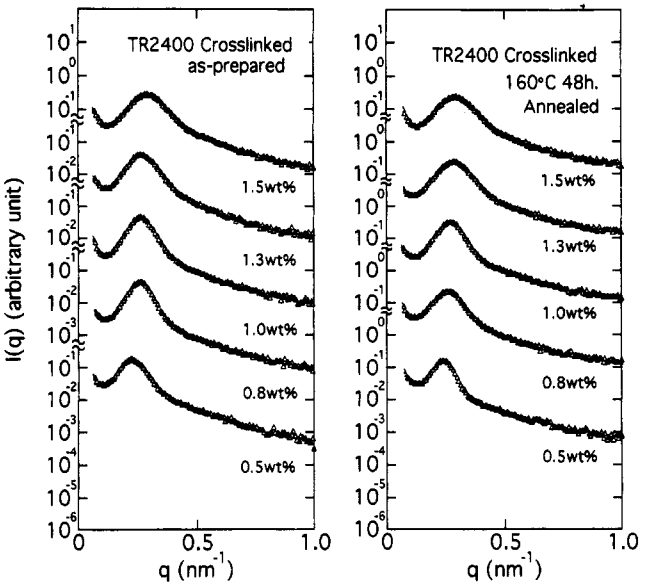

Figure 11. SAXS profiles (through view) obtained at room temperature for cross-linked TR2400 films with various concentrations of peroxide for (a) as-prepared and (b) annealed specimens (annealed at 160 °C for 48 h).

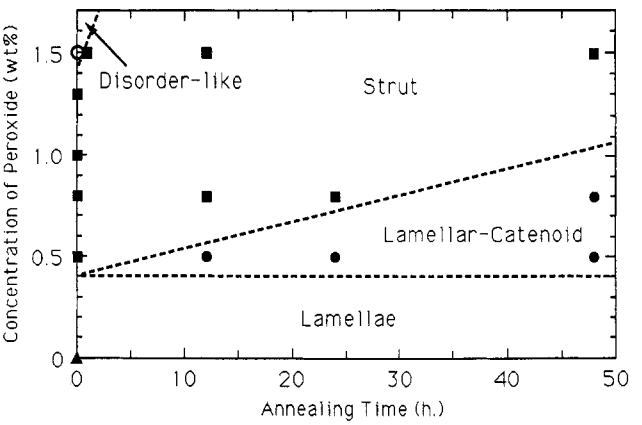

Figure 12. Microdomain morphologies observed for cross-linked TR2400 films shown in a plot of concentration of peroxide vs annealing time at 160 °C. The symbols ○, ■, ●, and ▲ are for disorder-like, strut, lamellar–catenoid, and lamellar structures, respectively.

that the pinning effect of the chemical cross-links on the coarsening of the microdomain structures becomes larger with the concentration of peroxide. Even in the case when the morphological change occurred, as revealed by TEM, the Bragg spacing did not change; i.e., the coarsening of the microdomain structure did not occur by the thermal annealing at 160 °C.

The peak of the SAXS profiles becomes broader with increasing concentration of peroxide. Since regularity of the microdomain structure affects the peak broadness, it can be discussed in terms of the peak broadness, irrespective of the morphology, i.e., disorder-like, strut, or lamellar–catenoid. Hence, it is stated that the pinning effect of the chemical cross-links on the ordering of the microdomains becomes larger with the concentration of peroxide.

One would expect that the amount of the cross-links would dramatically alter the width of the interface between the PS and PB microdomains. In order to examine this, the interfacial thickness was estimated by assuming the sigmoidal concentration profile between the PS and PB microdomains.[51] From the linear relationship of $\ln[I(q)q^4]$ with respect to q^2 for relatively large q, the thickness can be estimated. The estimated values were in the range 1.0–2.7 nm, and there were no systematic changes with the concentration of peroxide and with the thermal annealing time. Due to the very weak scattered intensity for the q range which was used to estimate the thickness, the error encountered in the estimation may be more than 40%.[40] Therefore, it is concluded that the interfacial thickness was not altered by the cross-links and the annealing. Note that these values are consistent with the values for the un-cross-linked TR2400 (2.2–2.5 nm).[52] Although this is against the anticipation, this may be easily expected in fact from the TEM showing that almost all specimens formed sharp interfaces due to microphase separation even at the as-prepared state. However, the thickness of the disorder-like structure (1.5 wt % as-prepared; Figure 7) should be much larger than that for the others. More careful measurements, especially on the thermal diffuse scattering,[51] to accurately estimate the interfacial thickness are desired for the sample which contains the disorder-like structure.

IV. Conclusions

As shown above by TEM and SAXS, the morphology of the cross-linked specimens was disorder-like, strut, or lamellar–catenoid according to the concentration of peroxide and the thermal annealing time at 160 °C. Figure 12 shows microdomain morphologies observed for the cross-linked TR2400 as a function of the concentration of peroxide and the annealing time at 160 °C. The morphology transition from disorder-like to strut occurred at 1.5 wt % peroxide concentration, and that from strut to lamellar–catenoid occurred at 0.5 wt % or 0.8 wt % peroxide concentration by thermal annealing at 160 °C. Although the lamellar–catenoid structure is thought to be transformed to lamellar structures, this transition was not actually observed. It may be due to a pinning effect of the chemical cross-links on the morphology transition. It is noteworthy that the competitive effects, i.e., the ordering and the elastic force arising from the deformed cross-linked polymer chains, created an interesting morphology which is hardly formed in ordinary SBS triblock copolymers.

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