

Orientation Relaxation of Triblock Copolymer with Cylindrical Microdomain by *in situ* Stress-Birefringence Measurements

By Kenichi SHIMIZU^{1,*} and Hiromu SAITO²

The orientation relaxation behavior of polystyrene-*block*-hydrogenated polyisoprene-*block*-polystyrene (SEPS) with cylindrical microdomains of polystyrene (PS) dispersed in the rubbery segments was investigated by simultaneous measurements of stress and birefringence, and small angle X-ray scattering (SAXS) measurements. At short relaxation time, the stress σ and the birefringence Δn decreased at almost constant rate with time and temperature. At long relaxation time, however, the σ and Δn decreased steeply with time, and the decrease became larger with increasing time and temperature. The decrease of the Δn stopped and large Δn remained at high temperature, while the σ was close to zero. Such characteristic relaxation behavior is ascribed to the form birefringence induced by the orientation of the parallel arranged cylindrical microdomains and the conformational change of the phenyl ring side group associating with the orientation relaxation of PS. The analysis of these results suggest that the orientation relaxation of the rubbery segments occurs at short relaxation time during the stress relaxation after the uniaxial stretching, and then the orientation relaxation of the PS segments in the cylindrical PS microdomains occurs associating with the conformational change of the phenyl side group at long relaxation time at high temperature while the orientation of the cylindrical domain is not changed.

KEY WORDS: Triblock Copolymer / Cylindrical Microdomain / Birefringence / Stress / Orientation Relaxation /

Triblock copolymers consisting of glassy end blocks and rubbery midblock such as polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) are typical thermoplastic elastomers.^{1,2} Since the elastomeric deformation properties are directly related to the molecular and phase structures, the deformation properties such as stress-strain^{3–21} and stress relaxation behavior^{22–35} have been widely studied. Especially, the stress relaxation behavior is closely related to the practical important properties for elastomers, such as tension and compression permanent set.

The birefringence method is often used in combination of the deformation studies.^{8,15,19–21,29–32,36,37} It has shown a great advantage to estimate the physical property and molecular structure because 1) birefringence is sensitive to the change of orientation at small deformation, 2) *in situ* measurement of high-speed deformation processes is possible by fast measurement, and 3) the orientations of microdomain segments and matrix ones can be evaluated separately by using the additive rule for each segment.

Recently, we found that the birefringence of polystyrene-*block*-hydrogenated polyisoprene-*block*-polystyrene (SEPS) with cylindrical microdomains of glassy polystyrene (PS) dispersed in the rubbery ethylene-propylene matrix changed little below a yield strain, increased sharply with strain above a yield strain up to a strain of 0.5, and then increased gradually during uniaxial stretching, while the stress increased sharply with strain below the yield strain and then it gradually increased.²¹ The grain boundaries are broken at the yield strain

and the cylindrical microdomain can rotate above the yield strain. Then, the cylindrical microdomains, which are arranged parallel each other in the grains, start to orient obliquely in the stretching direction by associating with the orientation of the rubbery segments.¹³ The characteristic birefringence behavior is attributed to the form birefringence induced by the orientation of the cylindrical microdomains. An analysis of the birefringence revealed that the orientation of the cylindrical microdomains occurs above the yield strain up to a strain of 0.5 and the orientation does not increase above a strain of 0.5 in spite of the continuous orientation of the rubbery ethylene-propylene segments, as shown in Figure 1.²¹ The birefringence in the second run was almost same to that in the first run above the strain of 1.0, suggesting that the intrinsic form birefringence is not changed due to the absence of the fragmentation of the cylindrical PS segments.

In this study, our interest is the orientation relaxation of each segment and cylindrical microdomains in block copolymers during the stress relaxation after the uniaxial stretching. To understand the orientation relaxation of the segments and cylindrical microdomains, we simultaneously measured stress and birefringence during the stress relaxation after the uniaxial stretching of SEPS with cylindrical microdomains of PS dispersed in the rubbery ethylene-propylene matrix. The results of SEPS with spherical microdomains dispersed in the rubbery ethylene-propylene matrix are also presented for comparison. The characteristic orientation relaxation behavior of the segments and the cylindrical microdomains are discussed by

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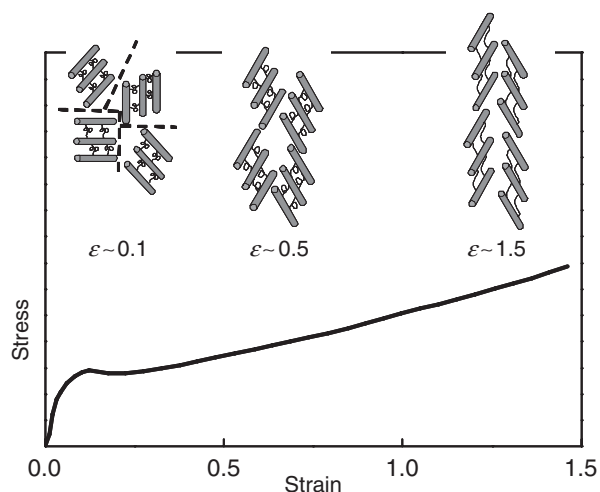


Figure 1. Schematic drawings of stress-strain curve and orientation process of rubbery ethylene-propylene segments and cylindrical PS microdomains of SEPS-30 during the uniaxial stretching.

taking into account the orientation of the cylindrical microdomains estimated by the small angle X-ray scattering (SAXS) and the form birefringence induced by the orientation of the cylindrical microdomains.

EXPERIMENTAL

The SEPS used in this study were commercial products SEPTON2043 (SEPS-13) and SEPTON2002 (SEPS-30) manufactured by Kuraray Co., Ltd. SEPS-13 and SEPS-30 are triblock copolymers with nominal compositions of 13 wt % and 30 wt % of PS, respectively. The weight average molecular weights of SEPS-13 and SEPS-30, determined by size exclusion chromatography calibrated by standard polystyrene, are 10.7×10^4 g/mol and 5.5×10^4 g/mol, respectively.

Films with *ca.* 0.1 mm thick and *ca.* 1 mm thick were prepared by casting from a 10 wt % toluene solution and annealing at 100 °C for 3 h. The films were cut into rectangular shaped specimens with a width of 5 mm. The film specimens with *ca.* 0.1 mm thick were used for the simultaneous measurements of stress and birefringence, and the specimens with *ca.* 1 mm thick were used for the SAXS measurement.

Simultaneous measurements of stress and birefringence during the orientation relaxation after the uniaxial stretching were carried out by the apparatus mentioned in our previous paper.³⁶ In the tensile testing system (Far-East Manufacturing Inc.), two crossheads moved up and down at same speed so that the light beam for birefringence measurements irradiated the midpoint of the film specimen throughout the stretching and relaxation processes. The specimen was clamped with clamps 30 mm apart and was stretched quickly (90 mm/s) up to a strain $\varepsilon = 0.5$. The measurements were carried out at various temperatures in the range from 30 to 70 °C. The nominal stress was obtained by dividing the force by the cross-sectional area of the unstretched film specimen. By assuming that the specimens were deformed without the change of the volume, a

nominal stress σ_n was converted by a true stress $\sigma = \sigma_n(1 + \varepsilon)$. For the birefringence measurement, a He-Ne laser beam with a wavelength of $\lambda_0 = 633$ nm was passed through a Gran-Thomson polarizer, a photoelastic modulator, a film specimen, a Gran-Thomson analyzer, and a photo diode detector. It is noted that the light scattering of the SEPS in the Hv geometry was so little as to be negligible. The force and the retardation Δ measured by the load cell and the photodiode, respectively, were processed by a personal computer through an A/D converter. The nominal birefringence Δn_n is given by $\Delta n_n = \Delta \cdot \lambda_0 d / 2\pi$, where d is the thickness of the unstretched film specimen. By assuming that the specimens were deformed without the change of the volume, a nominal birefringence Δn_n was converted by a true birefringence $\Delta n = \Delta n_n(1 + \varepsilon)^{0.5}$.

For SAXS measurement, the film specimen was stretched up to a strain $\varepsilon = 0.5$ by a film stretching device at room temperature and was annealed at desired temperature for 1800 s in a stretched state to induce the orientation relaxation, and then was rapidly cooled to room temperature to freeze the structure obtained by the orientation relaxation. SAXS measurements for the orientation relaxation specimen thus obtained were performed with RINT2400 (Rigaku Corporation) equipped with a graphite crystal monochromator, a two-pinhole collimator system, and a 2-dimensional imaging plate detector. The monochromated $\text{CuK}\alpha$ X-ray was generated at 50 kV and 200 mA. Pinhole collimation was obtained with two 0.2-mm pinholes separated 110 mm apart. The distance from the sample to the imaging plate was 550 mm. The imaging plate was exposed by X-ray for 1 h.

RESULTS AND DISCUSSION

Figure 2 shows the time dependence of the relaxation stress σ , birefringence Δn and stress-optical coefficient $\Delta n/\sigma$ of SEPS-13 with spherical polystyrene (PS) microdomains dispersed in rubbery matrix at various temperatures obtained after uniaxial stretching at strain of 0.5. Both σ and Δn decrease linearly with time in the double-logarithmic plots, indicating that the σ and Δn decrease with time by power law (Figure 2a and 2b). The decrease becomes larger at a constant rate with increasing temperature. These relaxation behaviors are same to those of rubbery polymers, indicating that the SEPS-13 with spherical PS microdomains behaves like rubbery polymers during the orientation relaxation. Though the birefringence of the PS segments changes its sign from positive to negative with time^{8,29,36,37} and the photo-elastic coefficient $\Delta n/\sigma$ should change during the stress relaxation at the temperature above 60 °C when the oriented PS segments relax (see Figures 5 and 7), the $\Delta n/\sigma$ are almost constant with time at the observed temperatures, *i.e.*, the relaxation behavior follows a photo-elastic law of rubbery polymers (Figure 2c). These results suggest that the orientation relaxation of the PS segments does not occur. Thus the relaxation behaviors of σ and Δn are originated from the rubbery ethylene-propylene segments. This might be attributed to the efficient crosslink points of the spherical PS segments in the SEPS-13.

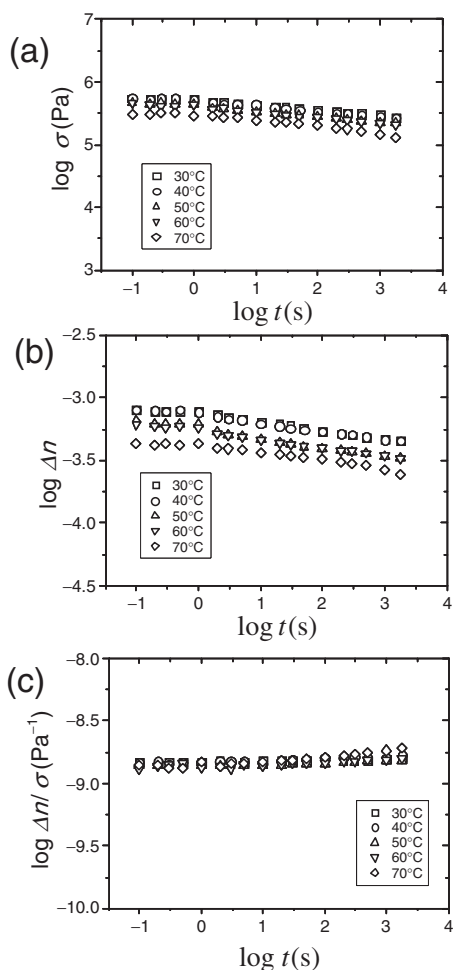


Figure 2. Time dependence of relaxation of SEPS-13 at various temperatures obtained after uniaxial stretching at the strain of 0.5: (a) stress, (b) birefringence, (c) stress-optical coefficient.

As shown in Figure 1, the cylindrical microdomains are oriented above the yield strain up to a strain of 0.5 in SEPS-30 with cylindrical PS microdomains. Figure 3 shows the time dependence of the relaxation stress σ of SEPS-30 at various temperatures obtained after uniaxial stretching at strain of 0.5. The σ decreases almost linearly with time in the double-logarithmic plot at short relaxation time and the decrease becomes larger at a constant rate with increasing temperature. This result suggests that the cylindrical PS microdomains act as efficient crosslink points and the orientation relaxation is originated from that of rubbery ethylene-propylene segments at short relaxation time, as observed in the SEPS-13. However, the σ decreases steeply with time and the decrease is nonlinear with time in the double-logarithmic plots at long relaxation time. The σ does not decrease at a constant rate with temperature, but the decrease becomes larger with increasing time and temperature, *e.g.*, the σ is close to zero at long time at 70 °C. These results are quite different from those of SEPS-13 in which the orientation relaxation of the PS segments does not occur. The difference might be attributed to the orientation of the cylindrical microdomains and the orientation relaxation of the PS segments, as discussed in the following.

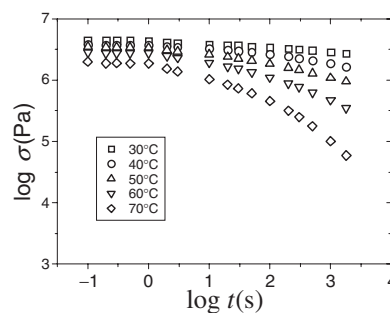


Figure 3. Time dependence of relaxation stress of SEPS-30 at various temperatures obtained after uniaxial stretching at the strain of 0.5.

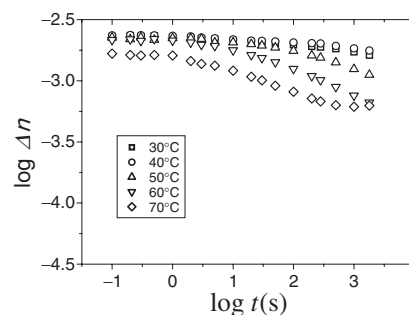


Figure 4. Time dependence of relaxation birefringence of SEPS-30 at various temperatures obtained after uniaxial stretching at the strain of 0.5.

Figure 4 shows the time dependence of the relaxation birefringence Δn of SEPS-30 at various temperatures obtained after uniaxial stretching at strain of 0.5. The Δn decreases at a constant rate with time and temperature in the double-logarithmic plots at short relaxation time as in the case of the σ . The Δn decreases steeply with time, and the decrease becomes larger with increasing time and temperature as in the case of the σ at long relaxation time. The interesting result here is that the decrease of the Δn is much smaller than that of the σ . The decrease of the Δn stops and large Δn remains at long relaxation time above the time of 10^2 s at 70 °C, while the σ is close to zero. That is, large residual Δn is observed in spite of large stress relaxation at long relaxation time at 70 °C. Since the decrease of the σ and Δn with time are different, the relaxation behavior does not follow a photo-elastic law, as shown in Figure 5. The $\Delta n/\sigma$ is almost constant with time at short relaxation time, but it increases with time at long relaxation time. The increase of the $\Delta n/\sigma$ becomes larger with increasing temperature. Such characteristic photo-elastic behavior might be attributed to the orientation of the cylindrical PS microdomains.

To understand the orientation of the cylindrical PS domains, we carried out the SAXS measurements. Figure 6a and 6b show the 2-dimensional SAXS patterns of SEPS-30 observed for the specimen stretched at the strain of 0.5 and then relaxed by annealing for 1800 s at 30 °C and 70 °C, respectively. Here, the stretching direction is vertical. The SAXS patterns correspond to the cylindrical domain morphologies at long

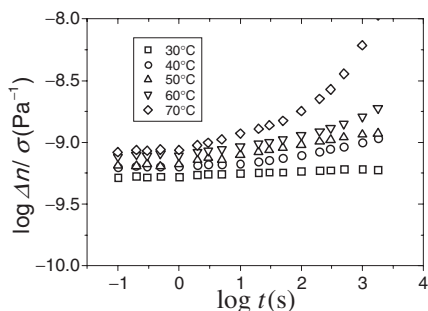


Figure 5. Time dependence of stress-optical coefficient of SEPS-30 at various temperatures obtained after uniaxial stretching at the strain of 0.5.

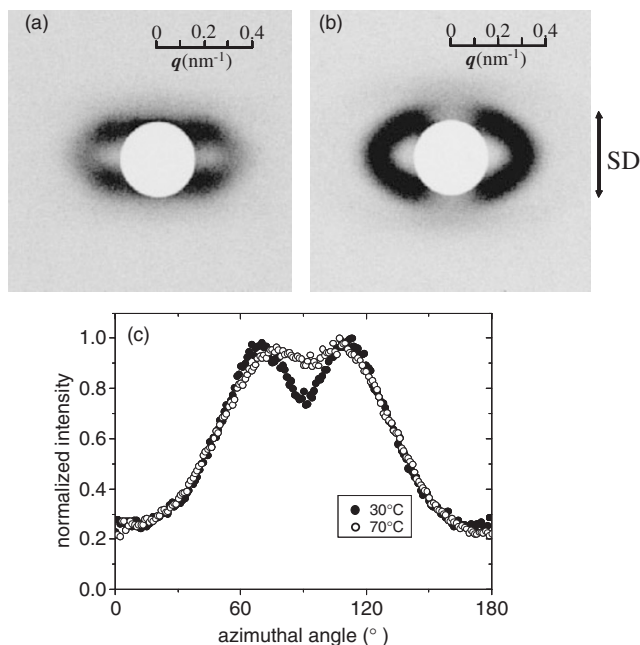


Figure 6. SAXS results of SEPS-30 stretched at the strain of 0.5 and then relaxed by annealing for 1800 s: (a) 2-dimensional SAXS pattern at 30 °C, (b) 2-dimensional SAXS pattern at 70 °C, (c) azimuthal distributions of the first scattering maximum for relaxation specimen at 30 °C and 70 °C.

relaxation time of 1800 s during the orientation relaxation for the birefringence relaxation measurements, in which the relaxation of stress and birefringence is little at 30 °C while large residual birefringence is observed in spite of large stress relaxation at 70 °C. Four points pattern is seen in both relaxation specimens, suggesting that cylindrical domains which arranged parallel each other within the grains are oriented to the stretching direction as schematically shown in Figure 1. Though the shapes of the SAXS patterns are different for the relaxation specimen at 30 °C and 70 °C, the azimuthal intensity distributions of the first scattering maximum are almost same, as shown in Figure 6c. These results suggest that the orientation of the cylindrical domain induced by the uniaxial stretching is not changed during the relaxation of σ and Δn . That is, the orientation relaxation of the cylindrical domains does not occur in spite of the orientation relaxation of

PS and rubbery segments. Thus, the residual birefringence demonstrated in Figures 4 and 5 might be attributed to the form birefringence induced by the orientation of the cylindrical PS domains, and the orientation relaxation of σ and Δn are ascribed to those of PS segments and rubbery ones.

Form birefringence is induced by the parallel arrangement of cylindrical microdomains,^{14–16} caused by the difference in refractive index between the cylindrical domain and the matrix. The intrinsic form birefringence Δn_F^0 , which is the form birefringence of perfectly parallel cylinders consisting of component A dispersed in the matrix of component B, is given by Wiener's equation:³⁸

$$\Delta n_F^0 = \frac{\phi_A \phi_B (n_A^2 - n_B^2)^2}{2(\phi_A n_A^2 + \phi_B n_B^2)^{1/2} [(\phi_A + 1)n_B^2 + \phi_B n_A^2]} \quad (1)$$

where ϕ_i is the volume fraction and n_i is the average refractive index of each component i . The n is not changed when the specimens are deformed without the change of the volume.

The average distance between the cylindrical microdomains estimated by SAXS of the unstretched SEPS is about 20 nm. Apparent Hv light scattering was not detectable in the SEPS, suggesting that the size of grain is smaller than 100 nm. Since the form birefringence becomes larger with an increasing the orientation of such short cylindrical microdomains, we assume that the Δn_F is described by the orientation function of cylindrical microdomains f :³⁹

$$\Delta n_F = \Delta n_F^0 \times f \quad (2)$$

$$f = \frac{3(\cos^2 \alpha) - 1}{2} \quad (3)$$

where α is the angle between the cylinder axis and the stretching direction.

As demonstrated in our previous paper,²¹ the Δn_F^0 was calculated to be 1.87×10^{-3} . The f can be obtained from a SAXS pattern. It is well known that cylindrical microdomains form a hexagonal lattice within a grain. The first scattering maximum indicates the reflection of (100) cylinder planes. The orientation function of the (100) cylinder planes f_a is estimated from the azimuthal distribution of the first scattering maximum $I(\alpha)$, where $\langle \cos^2 \alpha \rangle$ is calculated by the following equation.

$$\langle \cos^2 \alpha \rangle = \frac{\int_0^\pi I(\alpha) \cos^2 \alpha \sin \alpha d\alpha}{\int_0^\pi I(\alpha) \sin \alpha d\alpha} \quad (4)$$

The orientation function of the cylindrical microdomain is obtained by $f = -2f_a$ in case of a hexagonal lattice in which the normal of (100) cylinder planes are perpendicular to the cylindrical microdomains. The f was obtained for the azimuthal intensity distribution of first scattering maximum in the region of the scattering vector $q = 4\pi \sin \theta / \lambda$ from 0.21 to 0.41 nm^{-1} , where 2θ is the scattering angle in Figure 6. The f of the stretched specimen at 30 °C after stretching and relaxing for 1800 s is almost same to that at 70 °C, *i.e.*, the f at 30 °C is 0.48 and f at 70 °C is 0.49. Thus, the value of Δn_F at 70 °C estimated by eq. 3 was 0.92×10^{-3} . The form birefrin-

gence Δn_F thus obtained is significantly larger than the $\Delta n = 0.63 \times 10^{-3}$ observed at long relaxation time at 70 °C shown in Figure 4. The small observed Δn might be ascribed to the change in the sign of the Δn in the PS segments during the orientation relaxation at around the glass transition temperature as demonstrated in the following.

The birefringence of SEPS-30 with cylindrical morphology is formulated by

$$\Delta n = (\Delta n_{PS} + \Delta n_{EP}) + \Delta n_F = \Delta n_{seg} + \Delta n_F \quad (5)$$

where Δn_F is the form birefringence, Δn_{PS} and Δn_{EP} are the birefringence induced in PS domain segments and ethylene-propylene matrix ones, respectively. It is assumed that the Δn_F is almost constant with time during the stress relaxation, since the orientation function of the cylindrical domain f is not changed during the orientation relaxation as suggested by the SAXS results and specimens are deformed without the change of the volume. Hence, the birefringence of the segments Δn_{seg} ($= \Delta n_{PS} + \Delta n_{EP}$) is obtained by subtracting $\Delta n_F = 0.92 \times 10^{-3}$ estimated by SAXS results from the observed Δn during the stress relaxation process. The time dependence of the Δn_{seg} at various temperatures thus obtained are shown in Figure 7. The Δn_{seg} decreases gradually with time at short relaxation time, and then it decreases steeply at long relaxation time. The steep decrease of the Δn_{seg} is observed at shorter relaxation

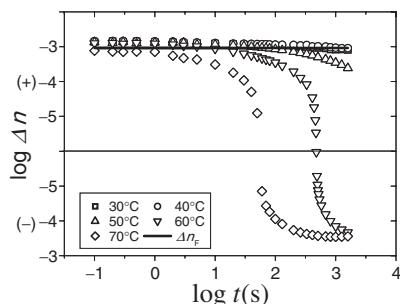


Figure 7. Time dependence of the orientation birefringence of segments Δn_{seg} of SEPS-30 at various temperatures obtained after uniaxial stretching at the strain of 0.5.

time as the temperature is higher. At 60 °C and 70 °C, the Δn_{seg} is initially positive, decreases to attain zero, changes its sign from positive to negative, and then decreases with time. This is characteristic to the birefringence relaxation behavior of PS and it is ascribed to the conformational change of the phenyl ring side group associating with the orientation relaxation of PS.^{8,29,36,37}

The results suggest that the PS segments in the cylindrical domains of SEPS-30 are oriented by uniaxial stretching and they are relaxed during the stress relaxation, while the orientation relaxation of the PS segments in the spherical domains of SEPS-13 is not observed. Owing to the different orientation, the initial stress of SEPS-30 is larger than those of SEPS-13, *i.e.*, the initial stress of SEPS-30 is about 10 times as large as that of SEPS-13, as shown in Figures 2a and 3. Since the large strain is applied to the PS segments in SEPS-30 due to the large stress, the PS segments are oriented and the orientation relaxation of the PS segments is remarkably detectable.

Thus the orientation relaxation of the PS segments in the cylindrical domains occurs associating with the conformational change of the phenyl ring side group while the orientation of the cylindrical PS domains is not changed. When the Δn_{PS} changes the sign from positive to negative due to the orientation relaxation of the PS segments and the Δn_{seg} becomes small comparing with the Δn_F , the change in the Δn becomes small during the stress relaxation as observed at high temperature in Figure 4.

CONCLUSION

We found characteristic orientation relaxation behavior of the SEPS with cylindrical PS microdomains by simultaneous measurements of stress and birefringence, and SAXS measurements. The orientation relaxation of the rubbery segments occurs at short relaxation time during the stress relaxation after the uniaxial stretching (Figure 8a and 8b). Then the orientation relaxation of the PS segments in the cylindrical PS microdomains occurs associating with the conformational change of the phenyl ring side group at long relaxation time at high

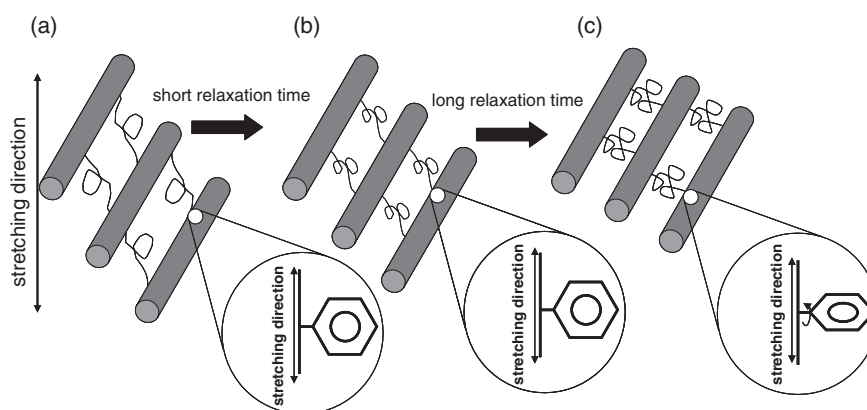


Figure 8. Schematic drawing of orientation relaxation process of cylindrical glassy microdomains and segments of SEPS-30 during the stress relaxation revealed by birefringence and SAXS measurements.

temperature, while the orientation of the cylindrical domain is not changed (Figure 8c). Owing to the characteristic relaxation behavior, the photo-elastic coefficient $\Delta n/\sigma$ was almost constant at short relaxation time and then it increased gradually with time, and the increase became larger with increasing temperature at long relaxation time.

Received: November 21, 2008

Accepted: April 7, 2009

Published: May 27, 2009

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