Molecular orientation of poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer with cylindrical microdomains of polystyrene

June Sakamoto, Shinichi Sakurai, Kazuhiro Doi and Shunji Nomura*
Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

The molecular orientation of poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer with cylindrical microdomains of glassy polystyrene (PS) is investigated by i.r. spectroscopy and is discussed in relation to the structural changes of the microdomains caused by the uniaxial strain. For evaluation of the molecular orientation, the dichroic orientation factor (F_D) was calculated from the dichroic ratio (D) of the absorption bands at 1493 and 966 cm^{-1} for PS and polybutadiene (PB), respectively. It was found that PB chains exhibit molecular orientation parallel to the stretching direction whereas there was no orientation for PS chains. The results indicated that PB chains are oriented parallel to the stretching direction but did not imply that the glassy PS microdomains are not deformed by the strain. The reason why the PS orientation was not clearly detected may be ascribed to a bad signal-to-noise ratio for the F_D of the PS band used to evaluate PS orientation. It was also found that the orientation of PB chains effectively proceeded in an extremely stretched state, which is in good agreement with the results from wide-angle X-ray scattering.

INTRODUCTION

Poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymers (SBS) in the phase-separated state are utilized as thermoplastic elastomers[1,2]. Since elastomeric properties are governed by their microdomain structure, it is worth studying the structural changes involved in uniaxial strain. Small-angle X-ray scattering (SAXS)[3-19] or small-angle neutron scattering (SANS)[20,21] and transmission electron microscopy (TEM)[6,11,13,14,16,22-30] are generally used to study microdomain structures. Recently, i.r. spectroscopy has been used to study the structure of SBS block copolymers[31-35]. The i.r. technique is a great advantage in the studies of a multicomponent system because it is possible to analyse separately the behaviour of i.r. absorption bands of interest. Although it had been expected that the orientation behaviour of polystyrene (PS) block chains in SBS would be difficult to detect by i.r., we found the orientation of PS blocks in SBS in a previous study[35]. In that work, we studied the effects of the microdomain structures on the molecular orientation of PS and polybutadiene (PB) chains in SBS with PS–PB alternating lamellae, PB cylinders in a PS matrix or PS–PB bicontinuous microdomains. The orientation behaviour was discussed in relation to the change in the microdomain structures induced by the uniaxial strain. In this study, we apply the i.r. technique to the study of molecular orientation of an elastomeric SBS with glassy PS cylinders in a PB matrix.

Figure 1 schematically shows the levels of order in a macroscopically isotropic film of SBS with cylindrical microdomains. A microscopic level, submicroscopic level and molecular level are represented in parts (a), (b) and (c), respectively. Although there is no macroscopically preferred orientation of the cylinders, preferential orientation exists on a submicroscopic level. In the submicroscopic region, the so-called 'grain', the cylindrical microdomains are preferentially oriented but orientation of the cylinder differs from that in a neighbouring grain. The structure in the as-cast film can
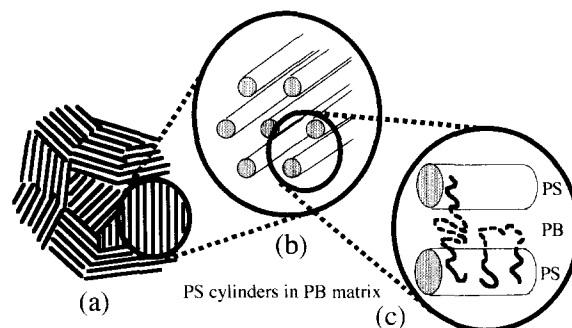

Figure 1 Schematic diagram showing the levels of order in a macroscopically isotropic as-cast film of SBS with cylindrical microdomains of polystyrene. A microscopic level, submicroscopic level and molecular level are represented in (a), (b) and (c), respectively. In the submicroscopic region, the so-called 'grain', the cylindrical microdomains are preferentially oriented but orientation of the cylinders differs from that in a neighbouring grain. The structure in the as-cast film can be therefore taken as an assembly of grains, as represented in (a)

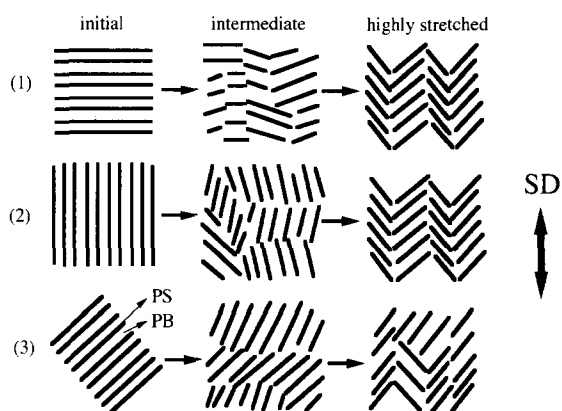* To whom correspondence should be addressed

Figure 2 Schematic diagram of structural changes caused by uniaxial strain applied to a SBS triblock copolymer with cylindrical microdomains of polystyrene. The tensile strain was applied (1) parallel, (2) perpendicular and (3) at 45° to the preferential orientation of the cylinders. SD denotes the stretching direction

be taken as an assembly of grains, as depicted in *Figure 1a*. Pakula *et al.*[10] studied structural changes in SBS with cylindrical PS microdomains caused by uniaxial strain using SAXS. The structural changes for three extreme cases were examined using preferentially oriented PS cylinders. The cases were such that the stretching direction (SD) was parallel, perpendicular or at 45° to the preferential orientation direction of the cylinders. The deformation process is schematically represented in *Figure 2*, where the black regions designate glassy PS microdomains. It should be emphasized that the glassy PS cylinders were eventually fractured into smaller microdomains irrespective of the orientation direction of the cylinder in an undrawn film so that the segmented PS domains act as rigid crosslinks for rubbery PB chains. Although more complicated schemes should be considered for the actual as-cast film rather than the simple mixtures of those presented in *Figure 2*, the scheme is useful for the discussion of the molecular orientation in the current study.

EXPERIMENTAL

The SBS specimen used in this study is a commercial product (Kraton D-1102, Shell) with a number-average molecular weight (M_n) of 5.7×10^4, a polydispersity (M_w/M_n) of 1.2 ± 0.15 (where M_w denotes the weight-average molecular weight) and a weight fraction of PS (w_{PS}) of 0.28. The microstructures of the PB chains are 36.6, 53.6 and 9.8 wt% of *cis*-1,4-, *trans*-1,4- and 1,2-linkages, respectively. More details of the characterization are described elsewhere[36]. The specimen was dissolved into methyl ethyl ketone/toluene (8/1 v/v) mixtures to prepare ~5 wt% polymer solutions. Film samples (~30 μm thick) were obtained by gradually evaporating the solvent mixture at room temperature. SAXS revealed a cylindrical morphology in the as-cast film. The cylindrical morphology was observed by others[10] using TEM for a press-moulded TR-1102 (SBS), which is very similar to the Kraton D-1102 used in the current study.

For tensile stress–strain measurements, CATY-500BH (Yonekura Co.) was used as a rectangular-shaped film (10 mm wide), clamped between a pair of chucks which were 30 mm apart. The drawing speed was 100 mm min⁻¹. The SD is parallel to the surface of the

as-cast films. I.r. spectra were obtained at 25% strain increments between 0% and 725% using a FIRIS 100 Fourier transform i.r. (*FT*i.r.) spectrometer (Fuji Electric Co. Ltd) operated at 64 scans and with a spectral resolution of 4 cm⁻¹. Since the actual *FT*i.r. spectrum is comprised of several individual absorption peaks overlapping each other, the spectrum should be broken down into individual contributions in order to obtain accurate values of the dichroic ratio (D). This was performed using peak resolving software developed in our laboratory[37], where the individual peak is assumed to be represented by a weighted sum of Gaussian and Lorentzian functions. The tensile stress–strain and *FT*i.r. measurements were both conducted at room temperature.

RESULTS AND DISCUSSION

The stress–strain behaviour is shown in *Figure 3*, where the stress is the nominal stress which is the drawing force divided by the cross-sectional area of the undrawn film. Typical elastomeric behaviour is shown and is very similar to that for the SBS with PS cylinders reported by Pakula *et al.*[10]. It is remarkable that a drastic increase in stress was observed within 7% strain. This implies plastic deformation. Two contributions to the plastic deformation can be considered: one is the fracture of glassy PS cylinders, which causes PS fibrils, as considered in a previous study[35]; the other is the plastic deformation occurring at the grain boundary. As mentioned above, the structure in the as-cast film is taken as an assembly of grains. Since it is necessary to minimize the free energy of the system, the cylinders with different orientation directions should be commensurately connected to each other in the grain boundary. Therefore, unusual bicontinuous interpenetrating microdomain structures may be formed locally at the grain boundary. It is reasonable to consider that the stress would be concentrated in the weakly connected glassy microdomains in the grain boundary in the initial stage of the strain.

An i.r. absorption spectrum of an undrawn as-cast film of Kraton D-1102 at room temperature is shown in *Figure 4* for wavenumbers from 500 to 2000 cm⁻¹. In order to discuss the molecular orientation of PS and PB chains, the dichroic orientation factor (F_D) was calculated from D of the absorption bands at 1493 and 966 cm⁻¹ for PS and PB, respectively[35]. D is given by:

$$D = A_{\parallel}/A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ denote the absorbances of light polarized parallel and perpendicular to the SD of the specimen, respectively. The peak area of the
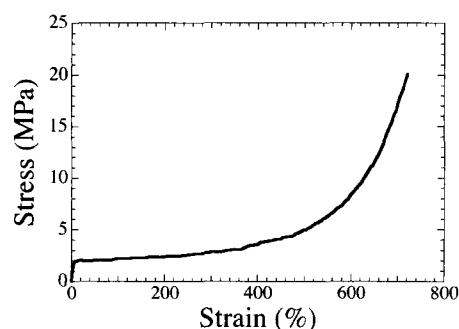

Figure 3 Stress–strain behaviour of a Kraton D-1102 as-cast film at room temperature
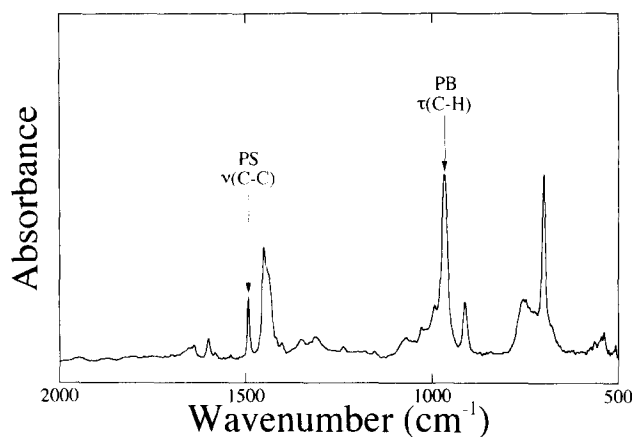
Figure 4 I.r. absorption spectrum of an undrawn as-cast film of Kraton D-1102 at room temperature
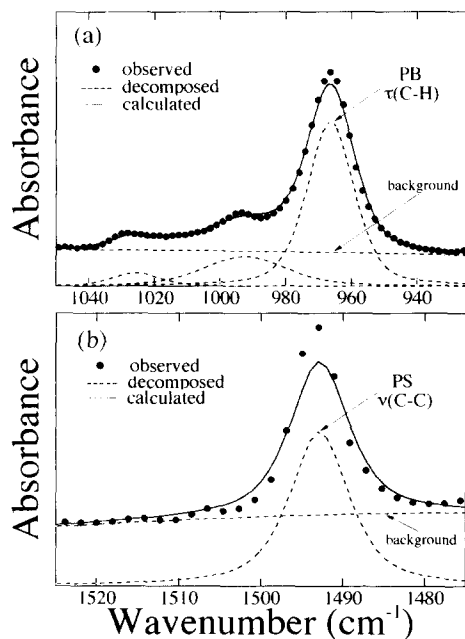

Figure 5 Curve resolving of i.r. spectra of the Kraton D-1102 film (a) for wavenumbers from 925 to 1050 cm^{-1} and (b) for wavenumbers from 1475 to 1525 cm^{-1}

individual contributions for the absorption band was used to calculate the D values. The decomposed spectra are shown in *Figure 5a* with original spectra for wavenumbers from 925 to 1050 cm^{-1} and in *Figure 5b* for wavenumbers from 1475 to 1525 cm^{-1}. The molecular orientation can be discussed qualitatively by means of F_D, which is defined as:

$$F_D = \frac{D-1}{D+2} \qquad (2)$$

As mentioned previously[35], the transition moment directions are roughly perpendicular to the axis of the chain segment for PS and PB absorption bands at 1493 and 966 cm^{-1}, respectively, and hence the negative value of F_D indicates parallel orientation of the PS and PB chains to the SD.

F_D values for PS and PB chains are presented in *Figure 6* as a function of strain. In general, the F_D values for PS chains are approximately zero over the entire range of strain, while the F_D values for PB chains monotonically decrease from zero with strain. These

results indicated that PB chains are oriented parallel to the SD but did not imply that the glassy PS microdomains are not deformed by the strain. Following the deformation scheme of the SBS with PS cylinders, one can expect more or less parallel orientation of the PS chains to the SD in the micronecking regions because PS fibrils should appear, as considered for a different type of SBS triblock copolymer[35]. The reason why the PS orientation was not clearly detected may be ascribed to a bad signal-to-noise ratio for the F_D of the PS band at 1493 cm^{-1}. The PS band at 1493 cm^{-1} is not so sensitive to the orientation as the PB band at 966 cm^{-1}. As a matter of fact, in a previous paper[35], the F_D value of the 1493 cm^{-1} band was found to be only -0.046 even when the homopolystyrene film was stretched by a draw ratio of 5.4. On the other hand, the w_{PS} of the specimen used in this study is not so large and hence the experimental error in evaluation of F_D is relatively large. In fact, the error can be considered to be ± 0.02 from a statistical standpoint. Thus, the microfibrils of PS, which probably exist in the specimen at high strains, are not discernible by this i.r. method. However, if it is acceptable to discuss the significance of the data at 650 and 675% strains, the PS orientation can be implied in the region from 600% strain up to break, as shown by the broken line in *Figure 6*. In this case, the PS orientation strongly correlates with the drastic increase in the PB orientation at 600% strain.

The drastic increase of absolute values of F_D for PB was detected in the region from 600 to 675% strain and the F_D values were roughly constant in the successive strains until break, indicating that the PB chains were extremely stretched. Similar behaviour of a drastic increase in the orientation of PB chains was observed for the different SBS with PS–PB bicontinuous microdomains, which accompanied orientation of PS chains[35]. It was considered for the case of the PS–PB bicontinuous microdomains that fracture and segmentation of the glassy PS struts might occur. By analogy with this, it may be possible to suppose the fracture and segmentation of the PS cylinders in the current study, although it was difficult to detect the orientation of PS chains because of the bad signal-to-noise ratio for the PS band at 1493 cm^{-1} as mentioned above. Since the fractured glassy PS microdomains behave as crosslinks, the PB chains, in turn, can be more effectively stretched.
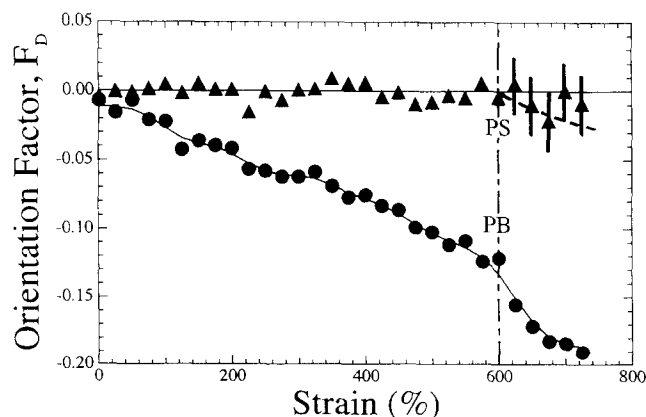

Figure 6 Strain dependence of the dichroic orientation factor F_D for PS and PB block chains. The values of F_D were calculated from the dichroic ratio D of the absorption band at 1493 cm^{-1} for PS and that at 966 cm^{-1} for PB

20° 0° 20°

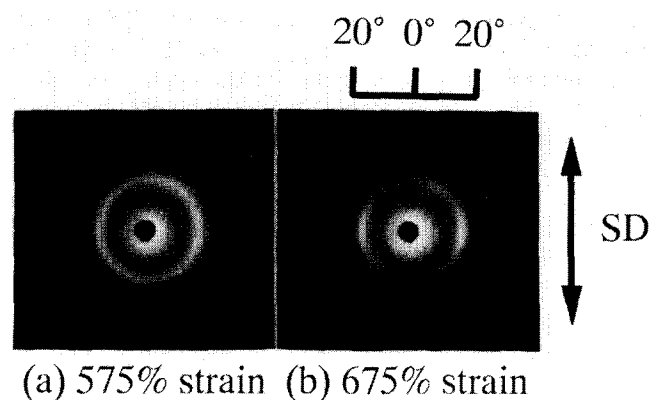(a) 575% strain   (b) 675% strain

Figure 7 Wide-angle X-ray diffraction patterns of the drawn Kraton D-1102 film at room temperature at (a) 575% and (b) 675% strains. SD denotes the stretching direction

Hence, the fracture and segmentation of the PS microdomains can be a possible explanation for the drastic increase of the PB orientation.

The drastic increase of the PB orientation after 600% strain may also imply strain-induced crystallization of the PB chains, because strain-induced crystallization can, in turn, effectively enhance the orientation of amorphous PB chains. Wide-angle X-ray diffraction patterns for drawn films at 575% and 675% strains are presented in *Figure 7*; they were obtained in order to detect the strain-induced crystallization of PB chains. Hashimoto et al.[38] reported two strong diffractions at ~20°, one from the (020) plane on the equator and another from the (110) plane at the off-equatorial position for the strain-induced crystallization of PB having 99% cis-1,4 units. However, in *Figure 7* no obvious diffraction was observed in both drawn films, whereas the amorphous halo of PB chains was seen at a scattering angle of ~20°. It is noted that the amorphous halo seems to be concentrated onto the equator in the drawn film at 675% strain. Therefore, the slightly stronger intensities for the scatterings at ~20° on the equator are considered to be due to the orientation of the amorphous PB chains in the direction parallel to the SD rather than due to the strain-induced crystallization of the PB chains. Thus, the i.r. technique proved to be useful for studying structural changes of elastomeric materials through changes in molecular orientation behaviour.

REFERENCES

1   Gergen, W. P., Lutz, R. G. and Davison, S. in 'Thermoplastic Elastomers' (Eds N. R. Legge, G. Holden and H. E. Schroeder), Hanser, Munich, 1987, Ch. 14
2   Aggarwal, S. L. *Polymer* 1976, **17**, 938
3   Séguéla, R. and Prud'homme, J. *Macromolecules* 1978, **11**, 1007
4   Séguéla, R. and Prud'homme, J. *Macromolecules* 1981, **14**, 197
5   Séguéla, R. and Prud'homme, J. *Macromolecules* 1988, **21**, 635
6   Kawai, H., Hashimoto, T., Miyoshi, K., Uno, H. and Fujimura, M. *J. Macromol. Sci., Phys.* 1980, **B17** (3), 427
7   Hashimoto, T., Suehiro, S., Shibayama, M., Saijo, K. and Kawai, H. *Polym. J. (Tokyo)* 1981, **13**, 501
8   Fujimura, M., Hashimoto, T. and Kawai, H. *Mem. Fac. Eng., Kyoto Univ.* 1981, **43** (2), 224
9   Mori, K., Hasegawa, H. and Hashimoto, T. *Polym. J. (Tokyo)* 1985, **17**, 799
10 Pakula, T., Saijo, K., Kawai, H. and Hashimoto, T. *Macromolecules* 1985, **18**, 1294
11 Shibayama, M. and Hashimoto, T. *Macromolecules* 1986, **19**, 740
12 Mori, K., Hasegawa, H. and Hashimoto, T. *Polymer* 1990, **31**, 2369
13 Tanaka, H., Hasegawa, H. and Hashimoto, T. *Macromolecules* 1991, **24**, 240
14 Hashimoto, T., Kimishima, K. and Hasegawa, H. *Macromolecules* 1991, **24**, 5704
15 Sakurai, S., Okamoto, S., Kawamura, T. and Hashimoto, T. *J. Appl. Cryst.* 1991, **24**, 679
16 Han, C. D., Baek, D. M., Kim, J., Kimishima, K. and Hashimoto, T. *Macromolecules* 1992, **25**, 3052
17 Roe, R.-J., Fishkis, M. and Chang, C. J. *Macromolecules* 1981, **14**, 1091
18 Polizzi, S., Bösecke, P., Stribeck, N., Zachmann, H. G., Zietz, R. and Bordeianu, R. *Polymer* 1990, **31**, 638
19 Sakurai, S., Momii, T., Taie, K., Shibayama, M., Nomura, S. and Hashimoto, T. *Macromolecules* 1993, **26**, 485
20 Bates, F. S., Cohen, R. E. and Berney, C. V. *Macromolecules* 1982, **15**, 589
21 Bates, F. S., Berney, C. V. and Cohen, R. E. *Macromolecules* 1983, **16**, 1101
22 Berney, C. V., Cohen, R. E. and Bates, F. S. *Polymer* 1982, **23**, 1222
23 Hashimoto, T., Tanaka, H. and Hasegawa, H. *Macromolecules* 1990, **23**, 4378
24 Sadron, C. and Gallot, B. *Makromol. Chem.* 1973, **164**, 301
25 Thomas, E. L., Alward, D. B., Kinning, D. J., Martin, D. C., Handlin, D. L. and Fetters, L. J. *Macromolecules* 1986, **19**, 2197
26 Hasegawa, H., Tanaka, H., Yamasaki, K. and Hashimoto, T. *Macromolecules* 1987, **20**, 1651
27 Hashimoto, T., Koizumi, S., Hasegawa, H., Izumitani, T. and Hyde, S. T. *Macromolecules* 1992, **25**, 1433
28 Winey, K. I., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1992, **25**, 422
29 Mogi, Y., Kotsuji, H., Kaneko, Y., Mori, K., Matsushita, Y. and Noda, I. *Macromolecules* 1992, **25**, 5408
30 Mogi, Y., Mori, K., Matsushita, Y. and Noda, I. *Macromolecules* 1992, **25**, 5412
31 Kraus, G. and Rollmann, K. W. *J. Macromol. Sci. Phys.* 1980, **B17** (3), 407
32 Noda, I., Dowrey, A. E. and Marcott, C. in 'Fourier Transform Infrared Characterization of Polymers' (Ed. H. Ishida), Plenum Publishing Corporation, New York, 1987, pp. 33–59
33 Noda, I., Smith, S. D., Dowrey, A. E., Grothaus, J. T. and Marcott, C. *Mater. Res. Soc. Symp. Proc.* 1990, **171**, 117
34 Zhao, Y. *Macromolecules* 1992, **25**, 4705
35 Sakurai, S., Sakamoto, J., Shibayama, M. and Nomura, S. *Macromolecules* 1993, **26**, 3351
36 Sakurai, S., Mori, K., Okawara, A. Kimishima, K. and Hashimoto, T. *Macromolecules* 1992, **25**, 2679
37 Yamamoto, T., Shibayama, M. and Nomura, S. *Polym. J.* 1989, **11**, 895
38 Hashimoto, T., Saijo, K., Kość, M., Kawai, K., Wasiak, A. and Ziabicki, A. *Macromolecules* 1985, **18**, 472