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Mechanical properties of polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymers crosslinked in the disordered state

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Abstract

The mechanical properties of crosslinked polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer films were examined by dynamic viscoelastic measurements and tensile stress–strain tests. The lamellar forming SBS sample was used in this study. The sample was chemically crosslinked in the disordered state in the presence of solvent and then was subjected to microphase separation by extracting the solvent. It was found that the degree of completion of the microphase separation is suppressed due to the chemical crosslinks. It was also revealed that crosslinking in the disordered state is a useful method to improve mechanical properties of the SBS thermoplastic elastomers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crosslinked triblocked copolymer films; SBS; Crosslinking

1. Introduction

Block copolymers comprising glassy and rubbery microdomains are used as thermoplastic elastomers [1]. A polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer is one of the examples. We have reported that chemically crosslinking the polybutadiene (PB) block chains in the disordered state is a useful method to control a morphology of the microphase-separated structures in SBS copolymers [2]. In this study, we examine structure–property relationships using dynamic viscoelastic measurements and tensile stress–strain tests. A lamellar forming SBS copolymer was chemically crosslinked in the disordered state in the presence of solvent and then was subjected to microphase separation by extracting the solvent.

It is also interesting to examine the possibility of strain-induced morphological transition which has been suggested by a theoretical study by Panyukov and Rubinstein [3]. In order to apply such an external field as stretching, it is required that the block copolymers can be stretched mechanically at temperatures above the glass-transition temperature of polystyrene (PS) blocks. The method of crosslinking SBS samples is a candidate to satisfy the above requirement. It is expected that important results are obtained from this work for fundamental studies of the morphological control in the block copolymers [4].

2. Experimental

2.1. Sample preparation

The characteristics of the SBS sample (code name: TR2400 supplied by Japan Synthetic Rubber Company) are as follows. The number-average molecular weight, M_n, was measured by the membrane osmometry and was determined to be 6.31×10^4. The ratio M_w/M_n as determined by the gel permeation chromatography was 1.15, where M_w denotes the weight-average molecular weight. The composition was evaluated by a ^{1}H-n.m.r. measurement and it was found that the volume fraction of PS is 0.53. This sample forms a lamellar microdomain structure at the equilibrium state, for instance when cast from a toluene solution [5].

The SBS sample, dioctyl phthalate (DOP) as a low volatile solvent, and 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane as a crosslinking agent (peroxide) were dissolved in methylene chloride with the concentration of SBS + DOP being ca. 5 wt%. The methylene chloride solution was poured into a Petri dish and then the methylene chloride is allowed to freely evaporate. Thus, the homogeneous mixture of SBS + DOP obtained with the crosslinker after complete evaporation of the methylene chloride was annealed at 150°C for 100 min in order to activate the crosslinker. The volume fraction of SBS in the SBS + DOP mixture was 0.41. Note that the order–disorder transition temperature determined by small-angle X-ray scattering is

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located around 105°C for this mixture [2]. The crosslinked material was then immersed in toluene for 1 day to extract DOP and uncrosslinked polymers. Toluene was refreshed at least seven times for complete extraction. Finally, the crosslinked SBS sample was obtained by evaporating toluene thoroughly from the swollen material. The concentration of the crosslinker (c_x) was in the range 1.0–2.0 wt% of the SBS sample. It was reported previously [2] that the volume fraction of the crosslinked polymer is in the range 0.68–0.96 for c_x from 1.0 to 2.0 wt%. For comparison, uncrosslinked samples were cast from heptane and toluene solutions with an initial polymer concentration of ca. 5 wt%. Note that a bicontinuous microdomain structure was formed in the as-cast sample from the heptane solution [5] as well as in the crosslinked SBS samples [2].

2.2. Dynamic mechanical measurement

DVE-V4FT Rheospectoler (Rheology Co., Ltd.) was operated under an oscillatory tensile deformation with a dynamic amplitude of 10 μm (0.1% dynamic strain). The thickness of the sample was in the range 0.5–1.0 mm. A 3-mm width film was squeezed by chucks with a 10-mm interchuck distance.

2.3. Tensile stress–strain test

TENSILON/UTM-II-5H (Orientec Co., Ltd.) was used with a 50-mm min^{-1} stretching rate. The thickness of the sample was in the range 0.1–0.4 mm. Approximately 3-mm width film was squeezed by chucks with a 15-mm interchuck distance. Since the as-crosslinked material is too thick to conduct the measurement, the crosslinked material was thin-sliced and was subjected to the measurement.

3. Results and discussion

Fig. 1 shows the temperature dependence of the dynamic loss tangent, tan δ, for an as-cast film of SBS from its heptane solution and crosslinked SBS samples. The concentrations of the crosslinker were 1.0, 1.5, 1.75, and 2.0 wt%. The frequency of the oscillatory tensile deformation was 128 s^{-1}. To avoid overlaps, the curves were shifted vertically with 0.5 steps. Values labeled on the tan δ axis are for the curve of the crosslinked SBS sample with $c_X = 2.0$ wt%. For all samples, two distinct peaks were observed. The peaks in lower and higher temperature regions are due to mechanical dispersions of PB- and PS-rich phases, respectively. Therefore, it can be confirmed from these results that the microphase separation took place in all samples. In order to discuss an effect of crosslinks on the degree of completion of the microphase separation, the peak temperatures were extracted from the temperature dependence of tan δ (Fig. 1). We practically refer to the peak temperature as the glass transition temperature, T_g. The dependence of glass transition temperatures on the concentration of crosslinker for PS- and PB-rich phases are shown in Fig. 2. Monotonous increase and decrease in T_g with an increase of the concentration of the crosslinker were detected for PB- and PS-rich phases, respectively. These results suggest partial mixing of PS and PB block chains in the PB- and PS-rich phases, respectively. Namely, a moiety of PS segments mixed in the PB phase increases $T_{g,PB}$ and, similarly, a moiety of PB segments mixed in the PS phase decreases $T_{g,PS}$. Therefore, it is concluded that the degree of completion of the microphase separation decreases due to the crosslinks. Note that these samples were crosslinked in the disordered state in the presence of solvent (DOP) and then were subjected to the microphase separation by extracting the solvent. In the latter process, the chemical crosslinks prevent the samples from achieving a perfect microphase separation.

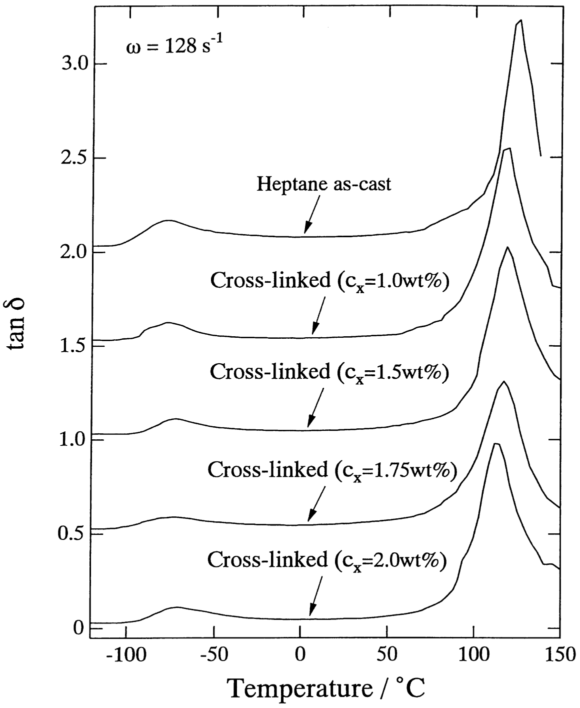

Fig. 1. Temperature dependence of the dynamic loss tangent, tan δ, for an as-cast film of SBS from a heptane solution and crosslinked SBS samples. The concentrations of the crosslinker were 1.0, 1.5, 1.75, and 2.0 wt%. The frequency of the oscillatory tensile deformation was 128 s^{-1}. To avoid overlaps, the curves were shifted vertically with 0.5 steps. Values labeled on the tan δ axis are for the curve of the crosslinked SBS sample with $c_X = 2.0$ wt%.

Fig. 3 shows the temperature dependence of the dynamic storage modulus, E', in a high temperature range (higher than $T_{g,PS}$) for an as-cast film of SBS from its heptane solution and crosslinked SBS samples. As is clearly seen, crosslinks prevent the samples from the melt flow at temperatures above $T_{g,PS}$. At crosslinker concentrations of 1.75 and 2.0 wt%, constant values of E' with 1.3 and 12.5 MPa, respectively, were attained for $T > 150$°C. Thus, when the crosslinking condition is appropriate, the crosslinked SBS samples behave as a normal crosslinked rubber, as expected,

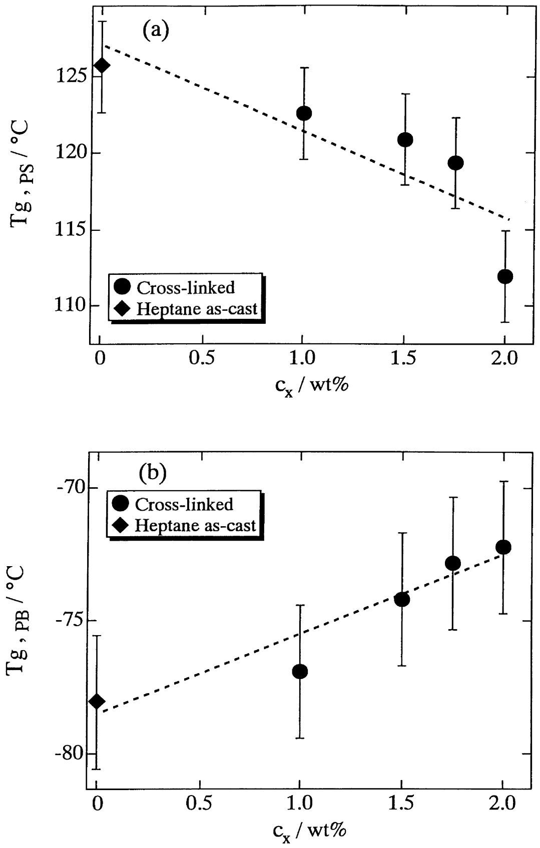

Fig. 2. Dependence of the glass transition temperatures on the concentration of crosslinker for: (a) polystyrene; and (b) polybutadiene-rich phases.

even when the PS microdomains no longer act as physical crosslinks. In order to discuss this point further, we examine frequency (ω) dependence of the storage modulus E' and the loss modulus E'' in Fig. 4. For all samples, master curves were obtained. Although at the highest temperature range ($T > 115°\mathrm{C}$) E' exhibits inflection, the following scaling relationship with the exponent $\alpha \approx 0.5$ is confirmed as a limiting frequency dependence:

$$E' \sim E'' \sim \omega^{\alpha} \tag{1}$$

This power-law dependence is ascribed to a ‘self-similar’ relaxation which is associated with self-similar structures on the molecular to super-molecular level [6]. This kind of power-law behavior is widely observed in many systems such as microgels [7], polymer blends, and block copolymers [8–13]. In particular, for a melt of microphase-separated block copolymers [8] a similar relationship is observed for the frequency dependence of the shear modulus, G' and G''. Values of $\alpha = 0.5$, 0.4, and 0.6 are found experimentally for block copolymers having lamellar [9–11], cylindrical [12], and spherical microdomains [13], respectively. On the other hand, theoretically $\alpha = 0.5$ and 0.25 are obtained for lamellar and cylindrical morphologies, respectively [14]. One of the reasons for the power-law behavior is the random crosslinking, as pointed out in Ref. [6]. Another reason is microphase-separated structures in block copolymers. Although it is unknown whether or not the value of α depends on the shape of microdomains, the relationship as expressed by Eq. (1) with $\alpha \approx 0.5$ may be ascribed, at least partly, to microdomain structures in our crosslinked SBS samples. Note that the morphology of the crosslinked SBS observed with a transmission electron microscopy is not an ordered lamella but a bicontinuous type [2]. Nevertheless, it is considered that the chemical crosslinks in the PB matrix enabled us to conduct the dynamic tensile measurements (E' and E'') and the samples exhibit a mechanical response similar to that of microphase-separated block copolymers under an oscillatory shear (G' and G'').

Fig. 5 shows the results of tensile stress–strain tests for an as-cast film of SBS from a heptane or toluene solution and

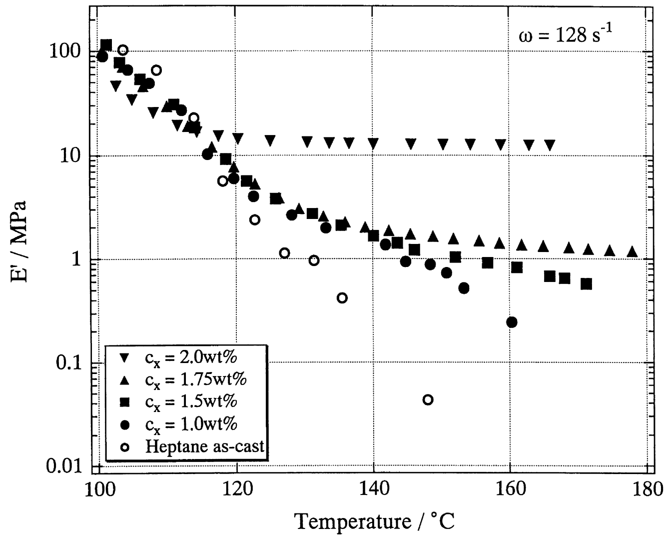

Fig. 3. Temperature dependence of the dynamic storage modulus, E', in a high temperature range (higher than $T_{\mathrm{g,PS}}$) for an as-cast film of SBS from a heptane solution and crosslinked SBS samples. The concentrations of the crosslinker were 1.0, 1.5, 1.75, and 2.0 wt%. The frequency of the oscillatory tensile deformation was $128\ \mathrm{s}^{-1}$.

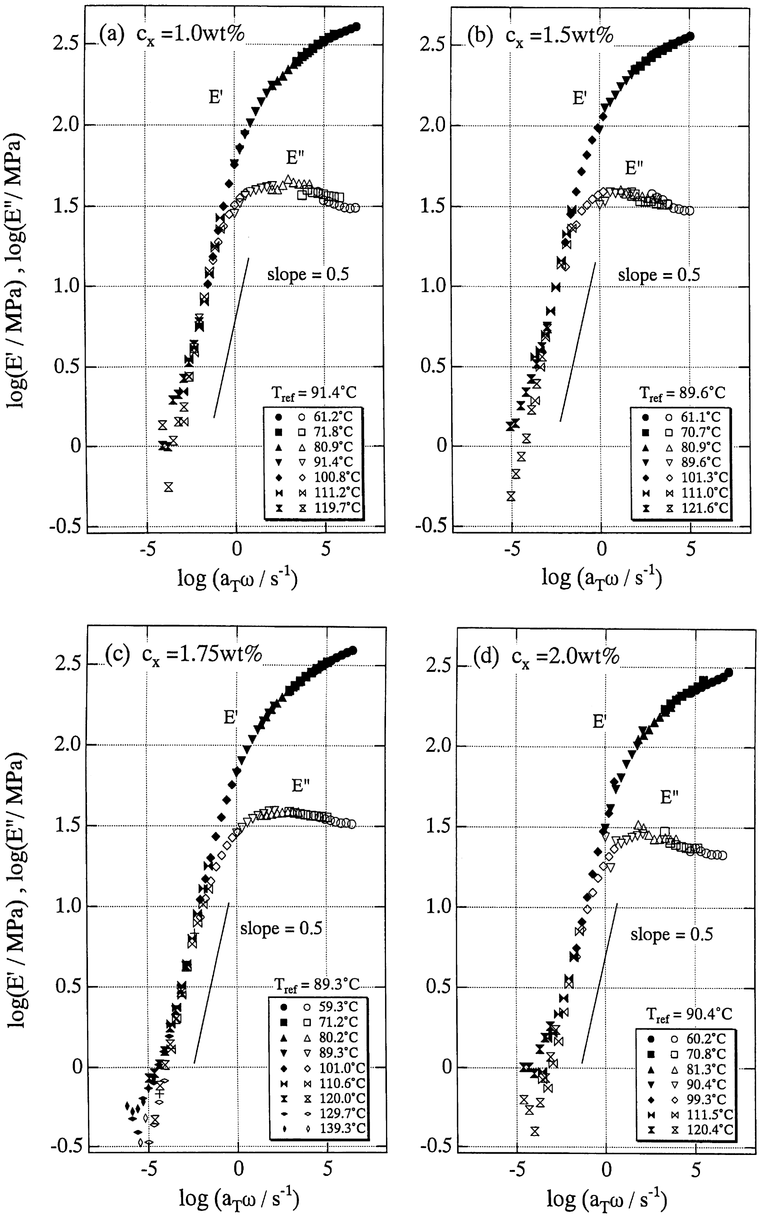

Fig. 4. Frequency dependence of the storage modulus E' and the loss modulus E'' for crosslinked SBS samples with (a) $c_X = 1.0$ wt%, (b) $c_X = 1.5$ wt%; (c) $c_X = 1.75$ wt%; and (d) $c_X = 2.0$ wt%. a_T is the shift factor with respect to the data obtained at approx. 90°C (T_{ref}).

crosslinked SBS samples. For all samples it was found that after a steep increase in the stress, an almost constant level is maintained for a while and then the stress increases linearly with strain [5]. The abrupt increase in the stress is attributed to deformation of the glassy PS microdomains. It is suggested from the observation of the constant level in the stress that fracture and segmentation of the glassy PS microdomains take place during the successive strain. Owing to the segmented PS microdomains acting as a physical crosslink in the rubbery PB matrix, after completion of the segmentation, the sample starts to exhibit a typical elastomeric behavior, i.e., the stress increases with an increase of strain. This is the well-known strain-induced plastic-to-rubber transition [15–17]. In addition to the segmented PS domains, effects of the chemical crosslinks in the SBS samples are examined here. Note that a lamellar microdomain structure is formed in the as-cast sample from a toluene solution. The difference in the behaviors for the as-cast samples from toluene and heptane solutions are therefore ascribed to the different type of morphology, as reported in our previous study [5]. On the other hand, a similar microdomain structure can be considered for the heptane as-cast and crosslinked samples. It is a bicontinuous morphology as previously reported [2], [5]. Therefore, the different stress–strain behaviors suggest effects of network formation in the PB matrix, as well as trivial change in the microdomain structures. Although many features can be focused on in the

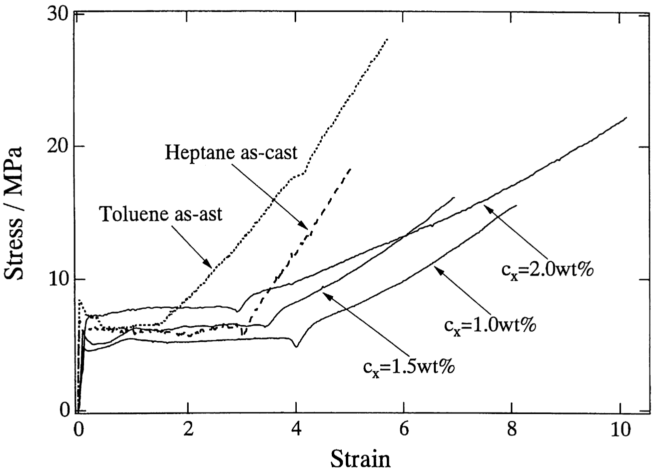

Fig. 5. Tensile stress–strain behaviors for an as-cast film of SBS from a heptane or toluene solution and crosslinked SBS samples. The concentrations of the crosslinker were 1.0, 1.5, and 2.0 wt%.

stress–strain behavior, we discuss mainly the stress and strain at break.

Fig. 6 shows the dependence of strain and stress at break on the concentration of crosslinker. Both strain and stress at break increase gradually with the concentration of the crosslinker. Therefore, it can be stated that the chemical crosslinks in the PB block chains improve elongation and strength of the material. However, it is found that none of the crosslinked SBS samples show higher values of the stress at break than the as-cast samples. To examine this point further, the true stress at break is estimated. Although the samples exhibited necking in the course of the stress–strain measurement, after the necking thoroughly propagating over the sample film, the thickness seems to be uniform. By assuming that the volume of the sample film remains unchanged, the true stress at break (σ) can be estimated from the nominal stress (σ_{obs}) with the strain at break (ε_{b}).

$$\sigma = \sigma_{\mathrm{obs}}(\varepsilon_b + 1) \qquad (2)$$

Fig. 7 displays dependence of the true stress at break on the concentration of crosslinker. Although the crosslinked samples with the concentration of the crosslinker below 2.0 wt% are weaker as compared with the as-cast samples, the sample crosslinked with 2.0 wt% crosslinker shows the highest value of σ. For comparison, Fig. 7 also shows the true stress at the break (σ) obtained for the SBS samples that were cast from toluene and heptane solutions without the presence of DOP and then crosslinked, in the *ordered* state, at $c_{\mathrm{X}} = 4.0$ wt (shown by dotted and broken lines, respectively). The value of σ for the sample crosslinked in the disordered state at $c_{\mathrm{X}} = 2.0$ wt% is comparable with the values of σ for those samples two times heavier crosslinked in the ordered state. From this result, it is concluded that crosslinking in the disordered state is a useful method to improve mechanical properties of the SBS thermoplastic elastomers.

4. Conclusions

The mechanical properties of crosslinked SBS films were examined by dynamic viscoelastic measurements and tensile stress–strain tests. It was found that the degree of

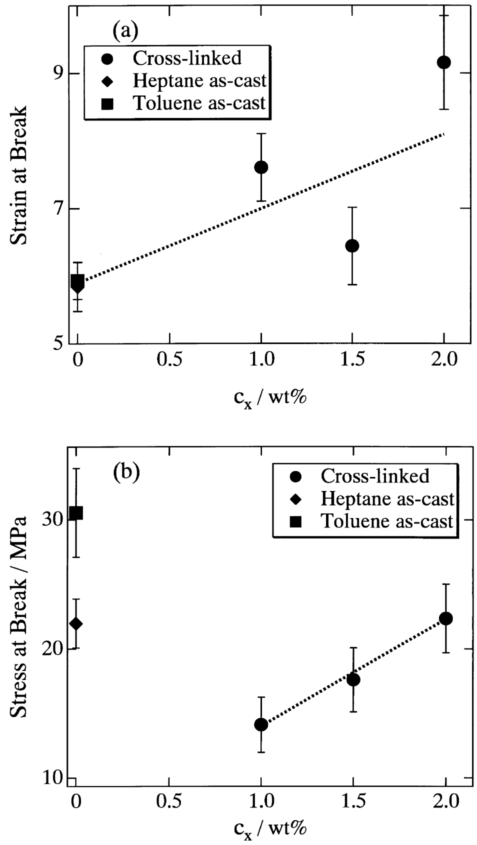

Fig. 6. Dependence of (a) strain; and (b) stress at break on the concentration of crosslinker. Circles, diamonds, and squares are for the crosslinked, heptane as-cast, and toluene as-cast samples, respectively.

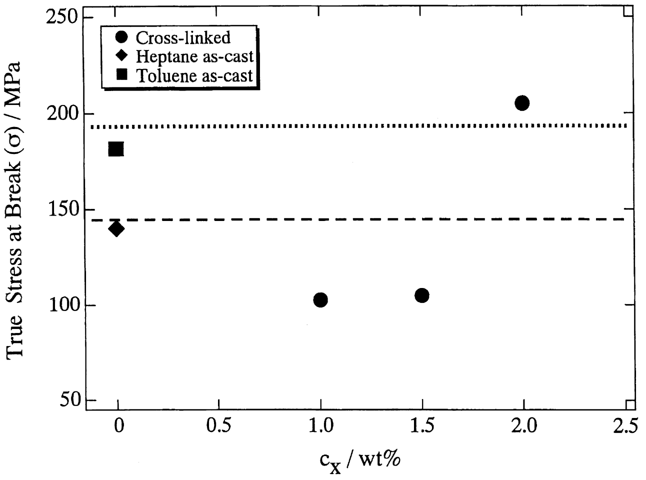

Fig. 7. Dependence of the true stress at the break, σ, on the concentration of crosslinker. Symbols as in the legend of Fig. 6. Dotted and broken lines indicate values obtained for crosslinked samples in the ordered state after casting from toluene and heptane solutions, respectively ($c_X = 4.0$ wt%).

completion of the microphase separation is suppressed due to the chemical crosslinks. It was also revealed that crosslinking in the disordered state is a useful method of improving the mechanical properties of the SBS thermoplastic elastomers. Finally, we mention the possibility of controlling the microdomain structures or morphology with stretching at higher temperature by applying this technique [18], since it is found to be possible to stretch the crosslinked samples even at temperatures higher than $T_{g,PS}$ owing to the presence of the chemical crosslinks.

Acknowledgements

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