

## Stress-Birefringence Study of Styrene-Butadiene Multiblock Copolymer

A. NISHIOKA,\* J. FURUKAWA, S. YAMASHITA, and T. KOTANI,\*  
*Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan*

### Synopsis

The styrene-butadiene block copolymers of SB, SBS, and SBSBS types were investigated by means of the stress-birefringence technique to elucidate the effects of the block multiplicity on the mechanical properties of copolymers. The SBS-type and the SBSBS-type block copolymers exhibit nonlinear stress-birefringence relations, which were classified into three regions. They are a low stress-optical coefficient region (optical creep), an increasing coefficient region, and a region of retarded increase in coefficient, as pointed out by Henderson et al.<sup>8</sup> It was found that optical creep is associated with the polystyrene continuum. The third region, however, originates not only from the phenyl groups of the polystyrene block but also from a form-birefringence due to the orientation of the polystyrene domain. The multiblock copolymer of SBSBS type was found to be rheo-optically similar to the SBS type, both being affected solely by the details of the terminal styrene block.

Pure gum vulcanizates of the SB-type and SBS-type block copolymers also exhibit optical creep. In a vulcanized block copolymer having both chemical and physical crosslinks, the latter seemed to disappear at elevated temperatures. At decreasing temperatures, the vulcanizates of block copolymers showed higher modulus of elasticity and lower stress-optical coefficients.

### INTRODUCTION

A number of reports<sup>1-7</sup> recently published on SBS-type styrene-butadiene block copolymers have shown that there coexist two types of domain in a system, the polystyrene and the polybutadiene domains, and the former acts as crosslinks for the latter. A block copolymer of SBS type is also known to exhibit a nonlinear behavior in the stress-birefringence measurements.<sup>8,9</sup> Pronounced effects of the size of styrene block were found to exist on the mechanical properties of a copolymer. On the multiblock copolymer SBSBS type, for example, still little information is available. In our previous paper,<sup>7</sup> we found that the mechanical properties of SBSBS-type block copolymer depend more on the length of the terminal block and less on that of the internal block. In other words, the values of modulus, tensile strength, dynamic moduli, and mechanical damping were kept almost unchanged irrespective of the length of the internal blocks, provided that the

\* Present address: Japan Synthetic Rubber Co., Research Center, Ikuta, Kawasaki, Japan.

lengths of the terminal polystyrene blocks were the same. In this connection, the stress–birefringence study of the multiblock copolymers seems to be effective in elucidating the mechanism of the deformation process in a block copolymer sample. This paper presents a study of the block copolymers of SB, SBS, and SBSBS types with various sizes of styrene blocks.

## EXPERIMENTAL

### Materials

Solprene 1205 was employed as SB-type block copolymer; it contains 25% styrene by weight.

SBS-type and SBSBS-type block copolymers were prepared according to the method of living anionic polymerization, using dilithiobutane as initiator.<sup>7</sup> Gel permeation chromatography showed narrow molecular weight distributions. The number-average molecular weights of these block copolymers were all controlled to be about 120,000. In SBS-type block copolymers, both the lengths of S and B were varied. In  $S_1BS_2BS_1$ -type block copolymers, where  $S_1$  and  $S_2$  denote terminal and central blocks, respectively, the lengths of B were kept constant, while the lengths of  $S_1$  and  $S_2$  were varied.

### Simultaneous Measurement of Stress, Strain, and Birefringence

Film specimens were prepared from toluene or cyclohexane solution by casting on glass plate. Some specimens were vulcanized using dicumyl peroxide as crosslinking agent.

Stress, strain, and birefringence were measured simultaneously, using an autograph combined with the optical apparatus. Specimens were approximately 1.0 cm wide, 5.0 cm long, and 0.1 cm thick. They were elongated at a rate of 20 mm/min in a box in which the temperature was controlled from 30° to 140°C.

## RESULTS AND DISCUSSION

### SBS-Type Block Copolymer

In the experiments on SBS-type block copolymer samples with various polystyrene block sizes, a nonlinear relation between stress and birefringence was observed in each case, similar to that reported by Henderson et al.<sup>8,9</sup> Figure 1 indicates an optical creep, i.e., stress not accompanied by birefringence. The copolymer with small styrene blocks generally possessed lower tensile strength. The value of the ultimate strength increased with increasing in the length of styrene blocks, as shown in Figure 2, while the coefficient of stress–birefringence  $\Delta n/\sigma$  seemed to decrease with increasing the length of polystyrene blocks. These types of behavior may also be interpreted with the concept proposed by Henderson et al., who assumed the existence of three different regions for the deformation behavior in sty-

rene-isoprene block copolymers. The first of the three regions has a high value in Young's modulus and a low value in the stress-optical coefficients, which may be due to the disruption of the polystyrene continuum to smaller dispersion. The second region, of rapid increase in the stress-optical coefficient, may be ascribed to the disruption of polystyrene continuum to smaller domains and the uncoiling of the polyisoprene chains. It is

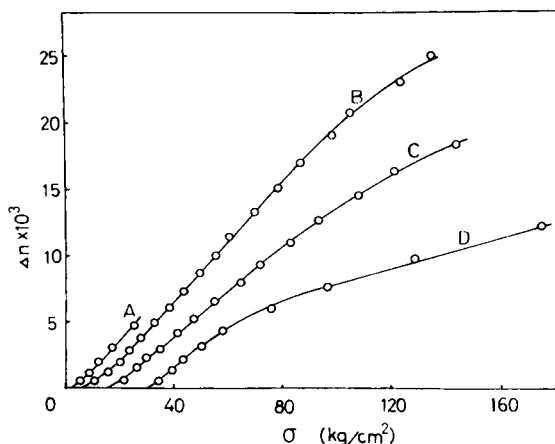


Fig. 1. Relation of  $\Delta n$  to  $\sigma$  for SBS-type block copolymers. S/B/S ratios, in wt. %: (A) 8.0/84.0/8.0; (B) 11.9/76.2/11.9; (C) 15.0/70.0/15.0; (D) 17.0/66.0/17.0.

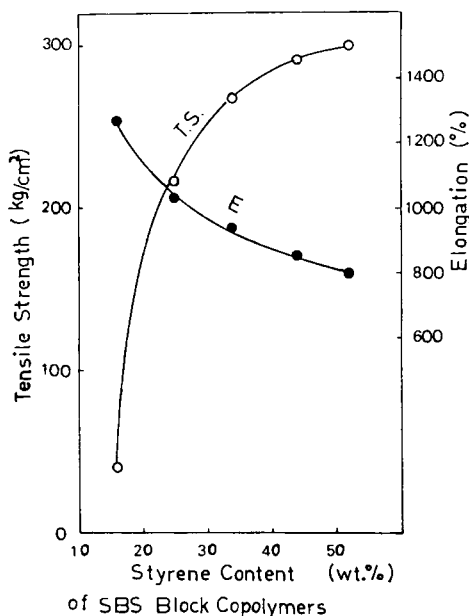


Fig. 2. Relation between styrene content and tensile strength for SBS-type block copolymers.

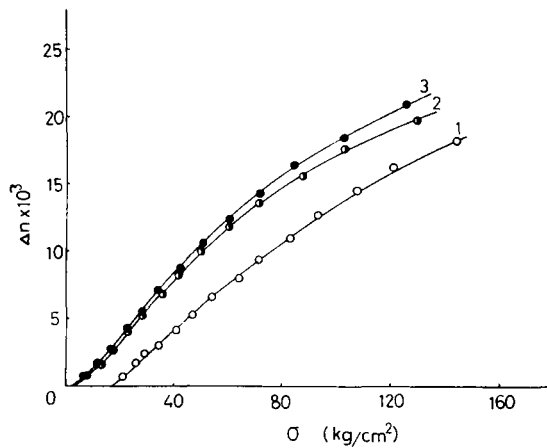


Fig. 3. Relation of  $\Delta n$  to  $\sigma$  at repeated elongation.

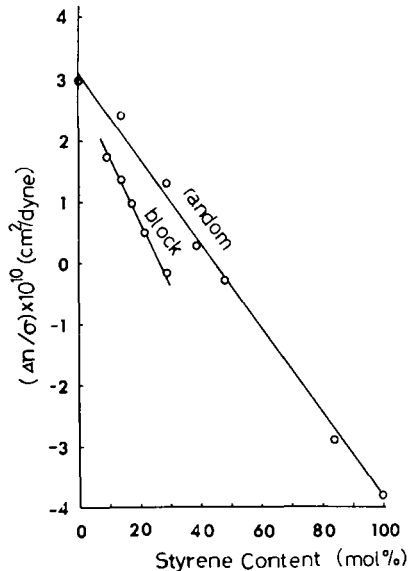


Fig. 4. Relation between styrene content and stress-optical coefficient.

followed by a third region, with retarded increase in birefringence. The existence of the first region, or optical creep, seems to be characteristic of a block copolymer. In fact, in the repeated extension experiments, the successive extension exhibits the same behavior as the initial one in the second and the third regions, as shown in Figure 3, which is similar to that pointed out by Henderson et al.<sup>8</sup> Those authors interpreted the retarded stress-birefringence in the third region in terms of the negative effect of the orientation of the phenyl group in the styrene unit. The phenyl groups along the chain will be perpendicular to the direction of the applied stress, which

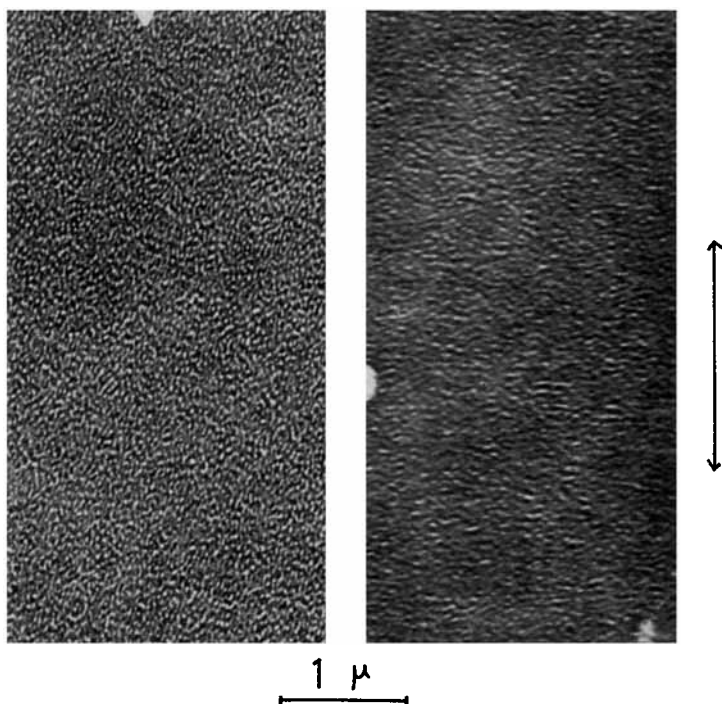


Fig. 5. Electron micrographs of SBS-type block copolymer at unstretched (left) and stretched state (right).

results in a negative contribution to the birefringence.<sup>8,10</sup> However, a block copolymer generally exhibits a lesser stress-optical coefficient in the third region than a random copolymer, as illustrated in Figure 4, and consequently some other effect such as form-birefringence may be considered. In fact, the electron micrograph taken at a stretched state indicates that the polystyrene domain is distinctly aligned perpendicular to the direction extension, as shown in Figure 5, which is similar to that previously reported,<sup>2,4</sup> and this suggests that form-birefringence takes place at high extensions.

#### SBSBS-Type Block Copolymer

The SBSBS-type block copolymers were prepared with terminal polystyrene blocks of various sizes, while total content of styrene unit was kept constant. As seen in Figure 6, little optical creep was observed for these samples, except one specimen which consisted of a large terminal block and was prepared by film casting from toluene solution. A similar solvent effect on the properties of a specimen can be found in the literatures<sup>4,8</sup> for SBS-type block copolymers. Thus an SBSBS-type block copolymer has essentially the same optical and mechanical properties as an SBS type, and both are mainly influenced by the details of the terminal blocks.

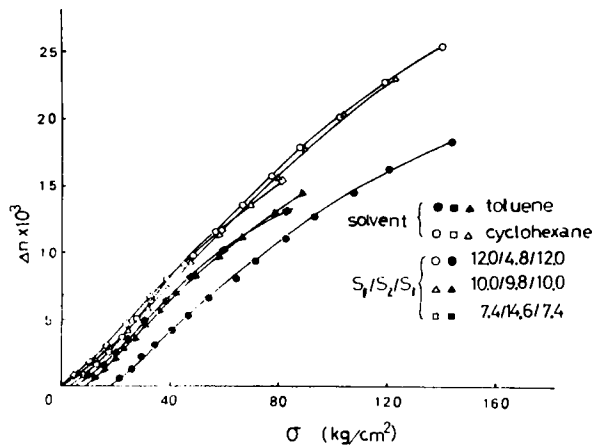


Fig. 6. Relation of  $\Delta n$  to  $\sigma$  for SBSBS-type block copolymers.

### SB-Type Block Copolymer

The SB-type block copolymer sample was not sufficiently elastic, so that its vulcanizate was used for the measurement. Figure 7 indicates that optical creep is observed in the stress-birefringence similar to that for the SBS-type block copolymer. The optical creep might be arising from the

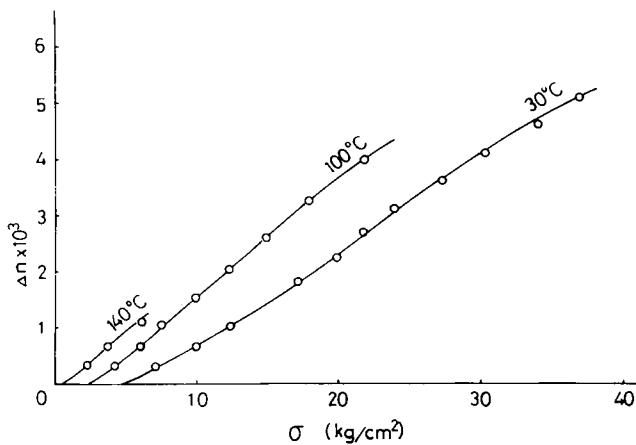


Fig. 7. Relation of  $\Delta n$  to  $\sigma$  for vulcanized SBS-type block copolymers.

polystyrene domain since it decreases with increasing temperature. The fact that the optical creep behavior of SB-type block copolymer vulcanizate is similar to that of the SBS-type block copolymer is not so surprising because the structural difference between SB-type and SBS-type block copolymers are masked in a sense when they are vulcanized.

**Vulcanized Block Copolymer**

We have seen that block copolymers show optical creep even when vulcanized. Then it may be of value to know how a copolymer having both chemical and physical crosslinks behaves at different temperatures ranges. The pure gum vulcanizates of polybutadiene (BR), the styrene-butadiene copolymer (SBR), natural rubber (NR), and polyisoprene (IR) kept their values of stress-optical coefficient unchanged in the temperature range tested, as illustrated in Figure 8. On the other hand, a block copolymer vulcanizate showed significant temperature dependence of its stress-optical coefficient, as shown in Figure 9, namely, birefringence increased with increasing temperature and tended to level off toward a value close to that of the polybutadiene vulcanizate. Thus, stress-birefringence at an

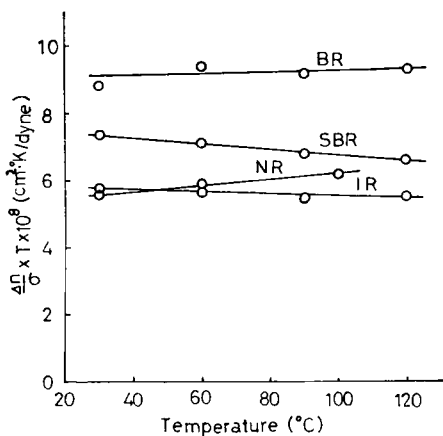


Fig. 8. Relation between  $(\Delta n.T)/\sigma$  and temperature for pure gum vulcanized rubbers.

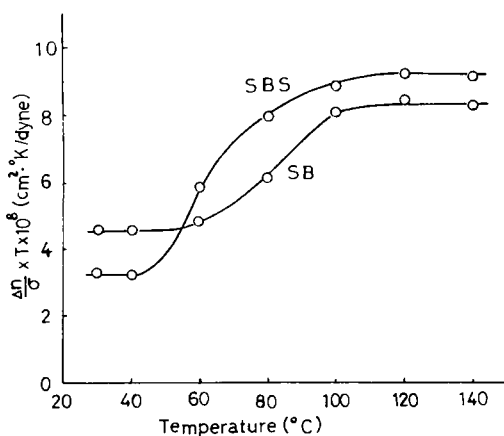


Fig. 9. Relation between  $(\Delta n.T)/\sigma$  and temperature for pure gum vulcanized block copolymers.

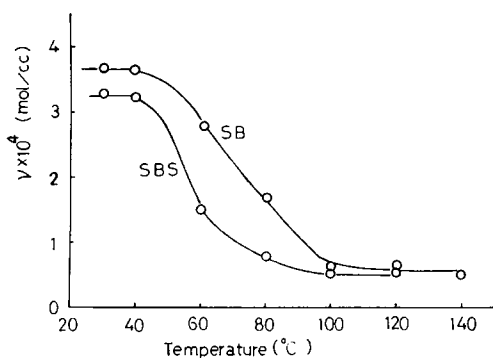


Fig. 10. Relation between  $\nu$  and temperature for pure gum vulcanized block copolymers.

elevated temperature seems to be arising from the chemical crosslinks, whereas at a lower temperature it would be associated with the block structure. In fact, the modulus of elasticity of block vulcanizates is generally much influenced by the change in temperature. In Figure 10, the concentration of the crosslinks,  $\nu$ , both chemical and physical, estimated from the value of the modulus of elasticity, is demonstrated as a function of temperature. The shape of the curve is very similar to that of a thermoplastic resin such as plasticized poly(vinyl chloride). Accordingly, the low value of stress-optical coefficient of a block copolymer at low temperatures may be attributed mainly to the orientation of the polystyrene domain.

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