

Calorimetric Study on Plastic-to-Rubber Transition in a Styrene-Butadiene-Styrene Triblock Copolymer

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ABSTRACT: Heat evolution from and mechanical work done on films of a styrene-butadiene-styrene (SBS) triblock copolymer were investigated under tensile strain. The relationship between microphase structure and thermomechanical behavior was examined on SBS films having lamellar, cylindrical, and spherical morphology which were cast from solutions in three mixed solvents. For SBS films having lamellar and cylindrical morphology, the enthalpy changes due to the plastic-to-rubber transition were found to be 0.24 and 0.17 J cm⁻³, respectively. These values correspond to the enthalpy required for irreversible destruction of the polystyrene domains. On the other hand, an SBS film having spherical polystyrene domains exhibited behavior similar to that of a vulcanized rubber.

KEY WORDS Styrene-Butadiene-Styrene Triblock Copolymer / Heat of Deformation / Thermoplastic Elastomer / Enthalpy of Deformation / Microphase Structure / Plastic-to-Rubber Transition / Calorimetry /

Mechanical properties of thermoplastic elastomers such as styrene-butadiene-styrene (SBS) triblock copolymers have been investigated by many authors, and the relationship between their mechanical properties and microphase structure has been well established.^{1,2} An SBS film with spherical polystyrene domains dispersed in the polybutadiene matrix exhibits rubber-like behavior, since the hard polystyrene domains work as crosslinks. In contrast, an SBS film having lamellar morphology shows properties similar to plastics, *i.e.*, its stress-strain curve shows an initial steep rise, followed by a yielding and cold-drawing region. Following this yielding region, the SBS film is transformed irreversibly to a rubber-like soft material, presumably because the continuous polystyrene domains have been destroyed during the initial stretching period. This phenomenon is referred to as strain-induced plastic-to-rubber transition.²

The changes in mechanical property caused by the plastic-to-rubber transition and the

corresponding change in the microphase structure have been investigated by several authors.³⁻¹⁰ For an SBS sample and its blends with polystyrene and with polybutadiene, the structural change due to the transition was studied by electron microscopy (EM).¹³ Kawai *et al.*^{2,4,5} studied the breakdown of the microphase structure of SBS samples by EM and small angle X-ray scattering (SAXS). It was found that the glassy polystyrene phase exhibits considerable plastic flow before the breakdown. A similar study was reported by Aggarwal⁹ for high impact polystyrenes. However, few calorimetric studies have been made on the change in microphase structure due to the plastic-to-rubber transition except measurements of the glass transition temperature by differential scanning calorimetry (DSC).⁸ In this paper, we report the changes in thermodynamic properties of SBS films accompanying the plastic-to-rubber transition caused by tensile deformation.

Regardless of thermodynamic reversibility,

the enthalpy change ΔH in a system is given by

$$\Delta H = W + Q \quad (1)$$

where W and Q denote the work done on and the heat absorbed by the system, respectively. In this study, W and $-Q$ associated with the deformation of SBS films were measured simultaneously and ΔH was calculated from eq 1.

Several authors¹¹⁻¹⁵ studied thermomechanical behavior of vulcanized rubbers. In their studies, the data were analyzed assuming the change caused by deformation to be quasi-static and reversible. In the present systems, irreversible structural changes due to the plastic-to-rubber transition should play an important role. Therefore, the thermomechanical behavior of SBS films should be quite sensitive to morphology, and hence should differ from that of vulcanized rubbers. In order to clarify the influence of morphology on the thermomechanical properties, W and $-Q$ were measured on SBS films with different morphology cast from different solvents.³

EXPERIMENTAL

Materials

A commercial SBS containing 33% styrene (Shell Chemical Co., TR-1101) was used. It was reported³ that the number-average molecular weights of its styrene and butadiene blocks were 1.57×10^4 and 6.37×10^4 , respectively and its content of 1,4-*cis*, 1,4-*trans*, and 1,2-vinyl linkages in the polybutadiene block was 37, 55, and 8%, respectively. Films of about 1 mm thick were prepared by casting 5% solutions of the sample dissolved in the following three mixed solvents: tetrahydrofuran/methylethyl ketone (volume ratio T/M=9/1), cyclohexane/benzene (C/B=1/1), and cyclohexane/*n*-hexane (C/N=3/1). One week after the casting, the films were dried *in vacuo* of about 10^{-1} Pa at room temperature for several days. They were coded as SBS (T/M), SBS (C/B), and SBS (C/N) according to the casting solvents. The films were cut into pieces of $25 \times 3 \times 1$ mm³ by a sharp knife and used for calorimetric measurements.

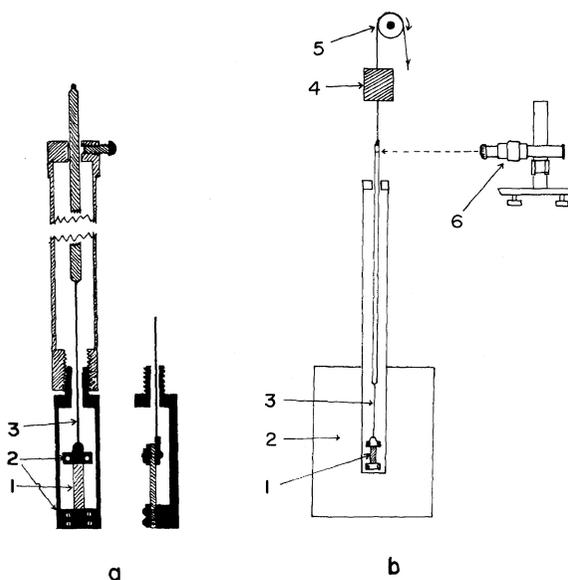


Figure 1. a) Sample holder for the measurement of heat of deformation. 1, sample; 2, clamp; 3, string (steel wire).

b) Schematic view of the calorimeter. 1, sample; 2, microcalorimeter; 3, string; 4, strain gauge; 5, motor; 6, cathetometer.

Methods

The heat of deformation was measured at 313 K with a microcalorimeter (Tokyo Riko, Model SCC-1) described previously.¹⁶ Figure 1a shows the sample holder used, and Figure 1b a schematic view of the instrument. The specimen between the clamps was about 10 mm long. The clamped specimen was stretched at a rate of 0.83 mm min^{-1} until the tensile strain reached about 0.2. The heat evolved during this operation was converted into an electric signal and traced on a pen recorder until it decreased to a detectable lowest limit (*ca.* 10^{-5} J s^{-1}). At the same time, the change in the sample length and the tensile force were measured by a cathetometer and a stress gauge, respectively. It took about 20 min to complete the procedure. The same procedure was repeated until the total extension ratio λ reached about 2.5. The work W was determined by numerical integration of the tensile stress-strain curve.

RESULTS

The dependence of W and $-Q$ on λ for SBS (T/M), SBS (C/B), and SBS (C/N) is shown in Figures 2, 3, and 4, respectively. These figures are for the as-cast films (1st cycle) in both stretching and releasing directions and for the films stretched once (2nd cycle). The arrows indicate the directions of deformation. In the stretching part of the 1st cycle for SBS (T/M) (see Figure 2), the value of W is greater than that of $-Q$, differing from vulcanized rubbers. On the other hand, the magnitudes of W and $-Q$ for SBS (C/N) are about the same, indicating that entropic elasticity is dominant as in vulcanized rubbers. It is seen that SBS (C/B) exhibits behavior intermediate between SBS (T/M) and SBS (C/N). On the other hand, the behavior of the three samples in the 2nd cycle are similar, indicating that the features observed in the 1st cycle were lost in the deformation part of the 1st cycle. Obviously, this is due to a plastic-to-rubber transition.

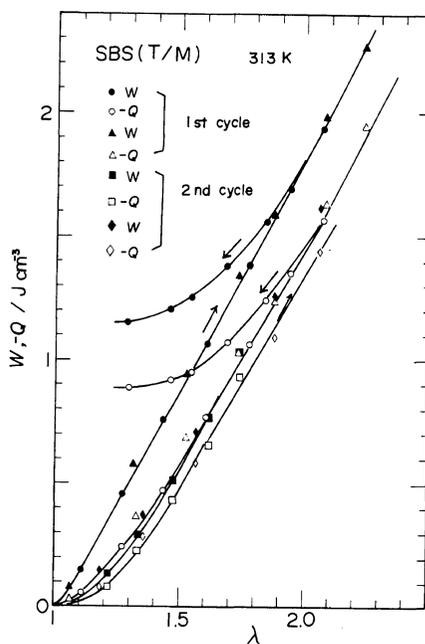


Figure 2. Dependence of W and $-Q$ on extension ratio λ for SBS (T/M) at 313 K. Data represented by ●, ○, ■, and □ were obtained at a rate of extension of 0.83 mm min^{-1} , while ▲, △, ◆, and ◇ at 10 mm min^{-1} .

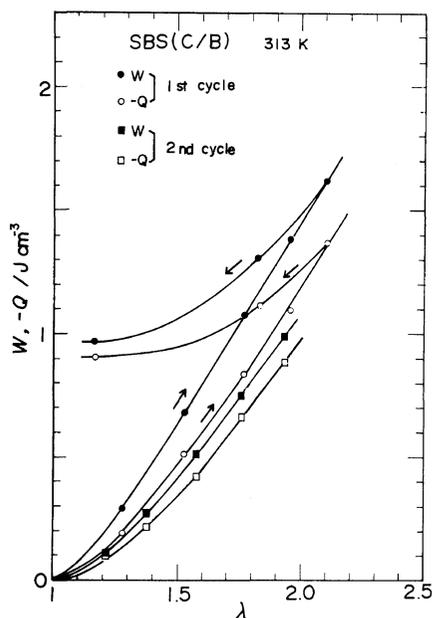


Figure 3. Dependence of W and $-Q$ on extension ratio λ for SBS (C/B).

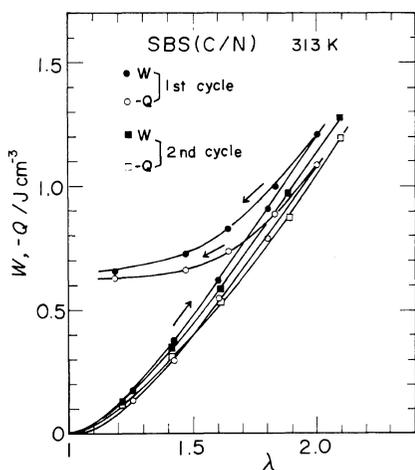


Figure 4. Dependence of W and $-Q$ on extension ratio λ for SBS (C/N).

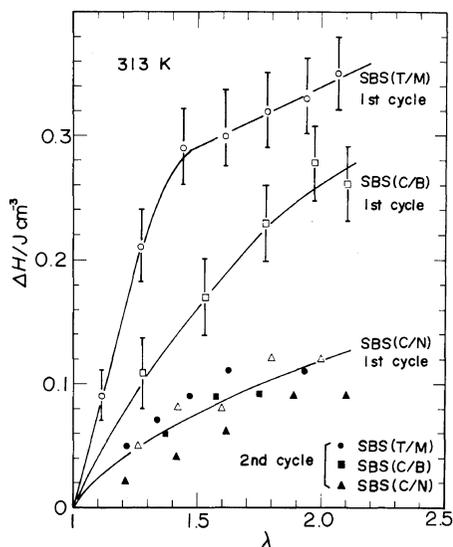


Figure 5. The change in enthalpy ΔH caused by tensile strain.

For all the three samples, stress relaxation was observed during the measurement of heat evolution under a constant strain. Creep was also observed after the 1st cycle, *i.e.*, the length of SBS (T/M), SBS (C/B), and SBS (C/N) films in the stress free state increased by 16, 22, and 15% of the original length, respectively. The value of λ for the releasing part of the 1st cycle

was calculated from the film length relative to the original length. However, before starting the 2nd cycle, the film length at the relaxed state was remeasured to correct for the effect of creep.

Figure 5 shows the enthalpy changes ΔH determined from these data and eq 1. Effects of stretching rate on W and $-Q$ were also examined with SBS (T/M). The results obtained at the rates of 0.83 and 10 mm min⁻¹ are shown in Figure 2. It can be seen that the effect of stretching rate was negligible.

DISCUSSION

Effect of Morphology on the Thermomechanical Behavior

It was reported that the polystyrene domains of SBS (T/M) and SBS (C/B) films are lamella and cylinder-like, respectively.³ Probably, SBS (C/N) has spherical polystyrene domains dispersed in the polybutadiene matrix, since *n*-hexane used for film casting is a nonsolvent for polystyrene. The fact that the tensile modulus of SBS (C/N) was smaller than that of SBS (C/B) also supports this consideration, since SBS films having a discontinuous polystyrene phase have an elastic modulus lower than those having a continuous polystyrene phase.

As shown in Figure 5, ΔH of SBS (T/M) rises steeply in the range of λ between 1 and 1.4. Since yielding was observed around $\lambda = 1.3$, this rise in ΔH may be ascribed to the plastic-to-rubber transition.³ Thus, the measured ΔH should be the enthalpy required for breaking the polystyrene domains.¹⁻¹⁰ For λ below 1.3, it may be considered that the external tensile force is supported by the glassy polystyrene domain. Therefore, the stress should be energetic. In fact, W for the SBS (T/M) film was 2 to 3 times larger than $-Q$ in the range of $\lambda < 1.3$. However, $-Q$ in this range was not negligible. Therefore, the observed heat evolution in the range of small extension ratio must be attributed partly to the

entropy change in the polybutadiene phase and partly to the irreversible heat production due to the destruction of the polystyrene domains.

On the other hand, ΔH of SBS (C/B) exhibited a gradual increase with increasing λ . Thus, the plastic-to-rubber transition or the stress-induced softening in SBS (C/B) occurred more gradually than that in SBS (T/M). This behavior is compatible with the stress-strain behavior of SBS (C/B), which did not exhibit yielding.³

It was found that SBS (C/N) gave smaller W and $-Q$ than SBS (T/M) and SBS (C/B). The ratio of W to $-Q$ was close to unity, indicating that the stress was entropic as in vulcanized rubbers. As shown in Figure 2—4, all the three samples exhibited irreversible W and $-Q$ versus λ curves, i.e., W and $-Q$ in the contraction process did not agree with those in the extension process. This may be due partly to the plastic-to-rubber transition and partly to the creep of the sample.

Thermomechanical Model

The irreversible thermomechanical behavior was analyzed using a thermomechanical model shown in Figure 6; in this model, the elements 1 and 2 represent enthalpic and entropic springs, respectively. The enthalpic spring stores the work (W_H) done on it as a strain energy. Therefore, it absorbs or evolves no heat in stretching and contraction. On the other hand, the work (W_S) done in stretching

the spring 2 causes a decrease in entropy and *vice versa*. Thus, the entropy change ΔS evolves or absorbs heat equal to $T\Delta S$ ($= -W_S$). The element 3 is a dash-pot representing an irreversible energy dissipation due to internal friction. This element evolves heat $-Q_\eta$ which is proportional to the absolute value of $d\lambda/dt$, where t denotes time. However, since the observed W and $-Q$ were almost independent of the rate of stretching as shown in Figure 2, this element does not play a dominant role in the present system. Hence, we assume that $-Q_\eta=0$.

The element 4 consists of an enthalpic spring ($W_{H'}$) and a ratchet or a slider (denoted R in Figure 6), which undergoes a plastic-to-rubber transition. When a stress greater than the yield strength of the ratchet is applied, it is disconnected and never reformed. We assume that when the ratchet is disconnected, part of enthalpy $W_{H'}$ is spent for disconnecting the ratchet and stored as a potential energy ΔH_R , but the rest is dissipated by friction in the process of disconnecting the ratchet to heat $-Q_R$. Thus, W and $-Q$ for the stretching part of the first cycle (W_{1st} and $-Q_{1st}$) in the state where the ratchet is disconnected are given by

$$W \equiv W_{1st} = W_H + W_S + \Delta H_R - Q_R \quad (2)$$

$$Q \equiv -Q_{1st} = W_S - Q_R \quad (3)$$

Since the element 4 does not play a role in the 2nd cycle, W and $-Q$ for the second cycle (W_{2nd} and $-Q_{2nd}$) may be given by

$$W \equiv W_{2nd} = W_H + W_S \quad (4)$$

$$W \equiv -Q_{2nd} = W_S \quad (5)$$

From the data of W and $-Q$ for the SBS samples, we attempted to evaluate the parameters appearing in these equations at $\lambda=2.0$. In this calculation, it was necessary to take the effect of creep into account. Since the original length l_0 of the sample increased to l_0' after the 1st cycle, it was assumed that the values of W_H and W_S in the 1st cycle at $\lambda=2.0$ were equal to

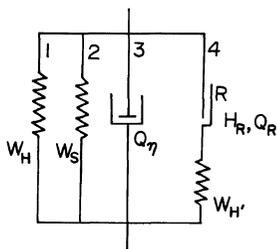


Figure 6. Mechanical model which represents the thermomechanical behavior of the SBS films.

those at $\lambda = 2l_0/l_0'$ in the 2nd cycle. The results of the calculation are summarized in Table I.

Reversible Change

The W and $-Q$ versus λ curves for SBS (C/N) in the 1st cycle and those for SBS (T/M) and SBS (C/B) in the 2nd cycle were similar to those of vulcanized rubbers. Therefore, the thermomechanical properties of these samples may be explained in terms of the theory of rubber elasticity. In a system in which deformation goes reversibly, the tensile force f at constant volume V and temperature T is given by

$$f = (\partial A / \partial l)_{V,T} = (\partial U / \partial l)_{V,T} - T(\partial S / \partial l)_{V,T} \quad (6)$$

where l denotes the length of the specimen, and A , U , and S have the usual meaning. The first term in eq 6 is referred to as the energetic force f_e . To determine the ratio f_e/f from thermomechanical data obtained under a constant pressure, Allen *et al.*¹³ used the relation

$$f_e/f = [\Delta H - VT\beta f'(1 - \alpha^{-1})/(\alpha - \alpha^{-2})]/W \quad (7)$$

where f' is the force per unit cross-sectional area of the unstrained rubber, and V , α , and β denote the volume, the microscopic extension ratio in the polybutadiene phase and the thermal expansion coefficient, respectively. The value of α was estimated from the macroscopic extension ratio λ by the Einstein-Guth-Gold equation¹⁷

$$\alpha = (1 + 2.5c + 14.1c^2)\lambda \quad (8)$$

where c denotes the volume fraction of the filler. In the present system, c refers to the polystyrene phase and is calculated to be 0.27 from the bulk densities of polystyrene and polybutadiene and the polystyrene content of the SBS sample. For polybutadiene¹⁸ having a microstructure similar to the polybutadiene block of the present SBS sample, β is reported to be $7.5 \times 10^{-4} \text{ K}^{-1}$.

With these data, f_e/f for SBS (C/N) was

calculated to be 0.091 and 0.068 at $\lambda = 1.6$ and 2.0, respectively. The f_e/f values for vulcanized polybutadiene were reported to be 0.05 to 0.17 by several authors.^{12,19-22} The present result is close to the data of Gent and Kuan,²¹ who reported f_e/f to be 0.05 to 0.09. However, it should be noted that because of creep during the stretching process, the value of λ included an error of about 15%. The error in f_e/f due to creep was estimated to be 0.03 and 0.01 at $\lambda = 1.6$ and 2.0, respectively.

Enthalpy of Plastic-to-Rubber Transition

ΔH_R in the mechanical model (Figure 6) was estimated to be 0.24 and 0.17 J cm^{-3} for SBS (T/M) and SBS (C/B), respectively. These values correspond to the enthalpies of the plastic-to-rubber transition, and from the microscopic view point, they may be considered the energies for creating fracture surfaces in the polystyrene phase.

Using EM and SAXS, Hashimoto *et al.*² studied the morphological change in the microdomain of a stretched SBS (49% styrene content) specimen having lamellar morphology. They observed orientation, shearing, kinking and destruction of the polystyrene domains at $\lambda = 1.8$, and also fragmentation of the disrupted domains when λ was further increased to 6.0. The electron micrograph reported previously³ for SBS (T/M) also appears to indicate that the polystyrene lamellae possess 10 to 50 crazes per $1 \mu\text{m}$ at $\lambda = 2.5$. Thus, the area (s) of fracture surfaces created in the polystyrene domains as a result of the plastic-to-rubber transition was estimated to range from 3×10^4 to $1.5 \times 10^5 \text{ cm}^2$ per unit volume of the sample.

Berry²³ estimated the fracture surface energy (Γ) of bulk polystyrene to be 0.17 J cm^{-2} , using Griffith's theory. If this value is applied to the disrupted microdomains, the change in enthalpy due to the plastic-to-rubber transition ($= \Gamma s$) ranges from 5×10^3 to $3 \times 10^4 \text{ J cm}^{-3}$. These values are 10^4 to 10^5 times larger than the observed enthalpy of transition ΔH_R .

Table I. The values of W and $-Q$ at $\lambda=2.0$ in the 1st cycle, those in the 2nd cycle,^a and the parameters appearing in eq 2–5 (unit: J cm^{-3})

	W_{1st}	$-Q_{1st}$	W_{2nd}	$-Q_{2nd}=W_s$	W_H	ΔH_R	$-Q_R$
SBS (T/M)	1.80	1.43	0.96	0.86	0.10	0.24	0.57
SBS (C/B)	1.46	1.19	0.62	0.52	0.10	0.17	0.67
SBS (C/N)	1.21	1.08	0.78	0.68	0.10	0.03	0.40

^a The values of W and $-Q$ in the 2nd cycle for SBS (T/M), SBS (C/B), and SBS (C/N) were those at $\lambda=1.72$, 1.64, and 1.74, respectively.

Thus, it can be concluded that the breakdown of styrene domains due to the plastic-to-rubber transition follow a mechanisms very different from the fracture mechanism for bulk polystyrene.

A probable reason for the discrepancy between Γ_s and ΔH_R is as follows. When glassy polystyrene is fractured, scission of the main chains may occur, giving a high fracture surface energy. On the other hand, the fracture of polystyrene domains in SBS proceeds through a plastic flow of the domains.^{2,4,5} This implies that polystyrene chains are somewhat mobile, and therefore, they slip out of entanglements without scission of the chains. Thus, the fracture energy for the polystyrene domains in SBS (T/M) and SBS (C/B) should be much smaller than that for bulk polystyrene. It should be noted that the plastic flow of the polystyrene domains dissipates only the energy by friction (Q_R in Table I). Hence, the flow does not contribute to the change in enthalpy.

We next examine whether the fracture surface energy of the polystyrene domain is equal to the interfacial free energy (interfacial tension γ_i) for the boundary between the polystyrene and polybutadiene phases. Since no experimental data of γ_i are available at present, we estimated γ_i to be 2.0 erg cm^{-2} from the theory of Helfand and Tagami^{24,25} and the available data for the solubility parameter and density.¹⁸ When the entropy term in γ_i was neglected, the enthalpy change ($=\gamma_i s$) due to the change in contact area was found to be 0.002 to 0.03 J cm^{-3} . In contrast to the value

of Γ_s , these values are 10 to 10^2 times smaller than ΔH_R , indicating that ΔH_R originates partly from the contact energy ($\gamma_i s$) and partly from scission of the main chains or from some other mechanisms. Scission of only *ca.* 0.01% of total chains suffices to explain the magnitude of ΔH_R .

Two other mechanisms were considered by Kelterborn and Soong⁶ for the structural breakdown of SBS. In one, polystyrene chains are pulled out of the domains and are mixed with polybutadiene. In the other, voids and crazes are formed in the polystyrene domains.¹⁰ If it is assumed that about 3% of polystyrene chains are transferred into the polybutadiene matrix, the magnitude of ΔH_R can be explained. However, it is difficult to estimate the change in enthalpy due to the second mechanism, since no quantitative data on the sizes of voids and crazes are available at present.

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