

Thermoelastic Properties of Block Copolymers of the Polystyrene-Polybutadiene-Polystyrene Type

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Synopsis

The thermoelastic properties of block copolymers of the type polystyrene-polybutadiene-polystyrene were studied. It was found that the f_U values depend on the content of styrene and the strain history as well. These relationships are discussed from the point of view of polymer structure.

INTRODUCTION

Thermoelastic properties have been studied of nearly all known elastomers.^{1,2} Main attention has been paid to the energetic portion of the equilibrium stress $f_U = (\partial U / \partial L)_{T,V}$ which can be obtained from the dependence of equilibrium stress on temperature. This expression calculated for small elongations corresponds to the change in conformation energy and is related to the temperature coefficient of unperturbed chain dimensions.³

By suitable modification of the polymer network (e.g., by chlorination), a change in the values of thermodynamic properties can occur.⁴ A special case of modification is represented by the block copolymer of structure ABA, where A and B denote a thermoplastic and elastic block, respectively. These copolymers may form a two-phase system. Under suitable conditions of composition and molecular length, block B forms a continuous phase, while the dispersed phase of end blocks A acts as a system of multifunctional junction points in this network. Though the system is not vulcanized, it shows the properties of crosslinked elastomers up to the approximate glass transition temperature T_g of the A component.⁵

The aim of this study was to investigate the thermoelastic properties of block copolymers of the type polystyrene-polybutadiene-polystyrene.

EXPERIMENTAL

Copolymers of the Type Polystyrene-Polybutadiene-Polystyrene Used

The block copolymers (Table I) were prepared by consecutive polymerization of butadiene and styrene in toluene at 50°C. As starter 1,4-dithiobutane in the form of 0.27 molar solution in diethyl ether was used.

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TABLE I
Characterization of Block Copolymers of Polystyrene-Polybutadiene-Polystyrene

Sample	$M_n \times 10^{-4}$	Polystyrene content, wt-%
1	7.5	25.3
2	—	30.0
3	7.0	33.4
4	7.9	37.6
5	7.1	45.5

The content of polystyrene component was determined from densities assuming that the volumes were additive.

The proportions of the configurations in polybutadiene component were: *cis*-1,4-, 27%; *trans*-1,4-, 33%; 1,2-, 40%.

Methods

The samples were prepared in the shape of bands by pressing them at 140°C. Their dimensions were 0.3 mm × 5.0 mm × 38.0 mm.

A Cambridge Textile Extensometer adapted for the temperature control of samples was used to obtain the thermoelastic curves. The samples containing more than 30 wt-% of styrene were prestretched to about 350%. The relaxed dimensions of samples after release of the prestress were taken as starting dimensions.

The relative extension varied within the range of 1.0 to 2.0. The relationships between equilibrium stress and temperature were obtained in the temperature region of 25°–55°C. The equilibrium stress at 55°C was reached after 15 hr of relaxation, approximately. The values of the coefficient of longitudinal thermal expansion λ were determined in the temperature range of 25° to 55°C by means of the cathetometer KM-6; they varied from 1.2×10^{-4} to 1.5×10^{-4} deg⁻¹. The calculation of thermodynamic quantities was based on the well-known equation⁶

$$f = (\partial U / \partial L)_{T,V} - T(\partial S / \partial L)_{T,V} = f_U + f_S \quad (1)$$

where

$$-(\partial S / \partial L)_{T,V} = (\partial f / \partial T)_{V,L}, \quad (2)$$

and f , U , S , L , V , and T denote equilibrium stress, internal energy, entropy, length of sample, volume of sample, and temperature in degrees Kelvin, respectively. The coefficients $(\partial f / \partial T)_{P,\alpha}$ found experimentally were adapted by using the correction factor calculated from the coefficient of longitudinal thermal expansion of the sample,⁷

$$(\partial f / \partial T)_{P,\alpha} = (\partial f / \partial T)_{V,L} + f\lambda \quad (3)$$

where $\lambda = L^{-1}(\partial L / \partial T)_P$ and $\alpha = L / L_0$, i.e., relative elongation.

RESULTS AND DISCUSSION

The morphology of the block copolymers considered were mainly dependent on styrene content. At low styrene contents (<25 wt-%), the polystyrene domains are spheroid-like, not affecting each other significantly. In the course of stretching of the samples, the polystyrene domains become ellipsoid-like.⁸ At higher styrene contents, mutual contacts of polystyrene domains, i.e., formation of reticular structure occurs.^{8,9} During stretching, the connection between the polystyrene domains, oriented in the stretching direction, break. The destruction of reticular structure of polystyrene domain becomes manifest by the yielding and drawing processes.¹⁰ At relatively higher styrene contents (~40–50 wt-%), when the structure of polystyrene domains becomes rod-like until lamellar,¹¹ the yielding and drawing processes in stretching are still more significant, which is due to the destruction of these structures. In the samples shown in Table I, the yielding and drawing processes become manifest, except for sample 1. The dependencies of the stress on temperature for this sample are shown in Figure 1a. The curves obtained for temperature decrease and increase are identical, indicating the thermodynamic reversibility of the process. The dependence of the quantities f_s and f_v on α (Fig. 2) is not the same as was observed with crosslinked elastomers,^{6,12} including polybutadiene.¹ For small elongations ($\alpha = 1.1$ – 1.2), relatively high positive values of f_v have been found which decrease with increasing

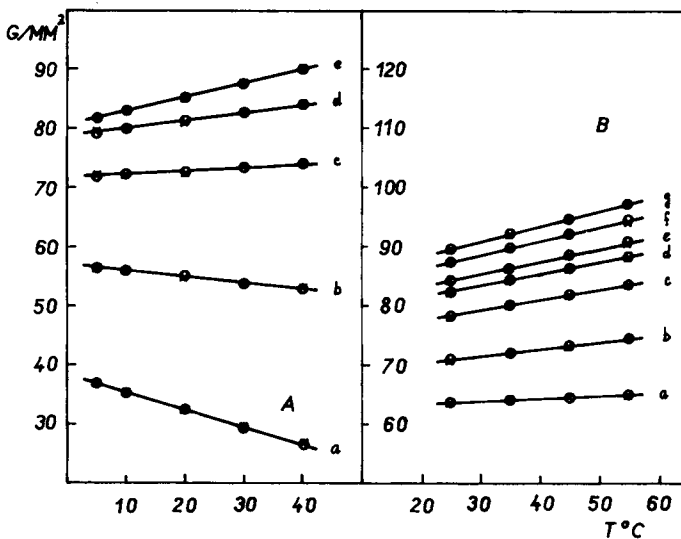


Fig. 1. Dependence of equilibrium stress on temperature for the block copolymer polystyrene-polybutadiene-polystyrene at different elongations: (A) styrene content 25.3 wt-%; elongations: a = 1.054; b = 1.108; c = 1.162; d = 1.216; e = 1.324; (B) styrene content 37.6 wt-% (after prestretching); elongations: a = 1.107; b = 1.221; c = 1.321; d = 1.428; e = 1.535; f = 1.642; g = 1.749; (O) decreasing temperature; (X) increasing temperature.

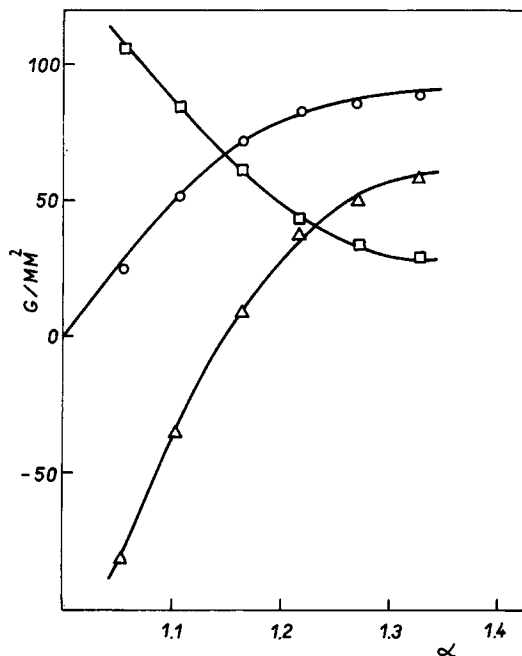


Fig. 2. Dependence of equilibrium stress f , energetic contribution f_v , and entropic contribution f_s on elongation. Styrene content 25.3 wt-%: (O) f ; (Δ) f_s ; (\square) f_v .

α . This phenomenon is most likely due to the strain of polystyrene domains which occurs as early as during the first stage of sample elongation.⁸ It agrees with the observation that the uniaxial strain of polystyrene involves endothermic effects.¹³

Since samples 2-5 were subject to yielding and drawing processes, the thermoelasticity measurements were carried out after prestretching. For the sake of comparison, sample 1 was also treated in the same way. The dependence of equilibrium stress on temperature is linear in the investigated range of elongation and temperature under conservation of reversibility. A typical course of this dependence is presented in Figure 1b for sample 4 containing 37.6 wt-% of styrene. The dependences of f , f_s , and f_v on α are given in Figure 3. In the case of sample 1, a distinct decrease in the values of f , f_s , and f_v , in contrast to the data presented in Figure 2, is evident while the values of f_v approximate those obtained for polybutadiene.¹ With increasing content of styrene in the samples, an increase in the value of f_v may be observed, especially for small α . This is most likely due to further strain of polystyrene domains. On the other hand, greater elongations evoke a smaller change in internal energy f_v for which a relatively steady strain of polystyrene domains and prevailing strain of polybutadiene blocks may be responsible. To test the effect of strain of the polystyrene domains on the thermoelastic properties of the copolymers, some measurements were made with samples that were prestretched and

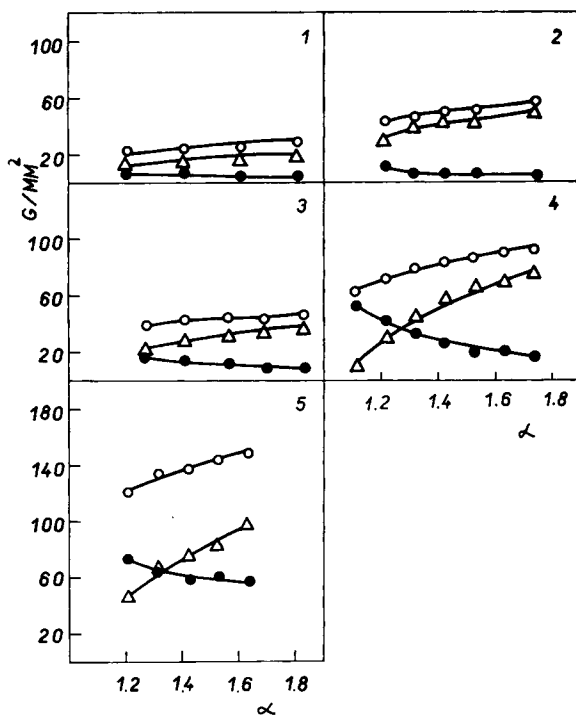


Fig. 3. Dependence of equilibrium stress f , energetic contribution f_U , and entropic contribution f_S on elongation after prestretching. Styrene contents in wt-%: (1) 25.3; (2) 30.0; (3) 33.4; (4) 37.6; (5) 45.5; (O) f ; (●) f_U ; (Δ) f_S .

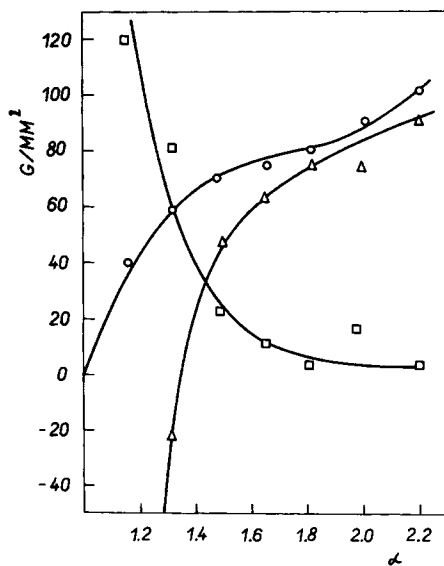


Fig. 4. Dependence of equilibrium stress f , energetic contribution f_U , and entropic contribution f_S on elongation. The sample with 45.5 wt-% styrene content was pre-stretched and after the release of stress, relaxed for 16 hr. (O) f ; (\square) f_U ; (Δ) f_S .

subsequently relaxed for 16 hr. The typical dependence of f , f_s , and f_U on α is presented in Figure 4; the values of f_s and f_U are considerably higher, especially at small elongations. That may be explained by the assumption that a relatively fast decrease takes place in the strain of the polystyrene domains after the release of stress, even at room temperature, which produces a partial regeneration of the thixotropic reticular structure. The change in internal energy measured at small elongations indicates an additional strain of polystyrene domains or decay of the thixotropic reticular structure.

As expected, the influence of crystallization is negligible in the whole range of elongations. The presence of both the configurations in the polybutadiene blocks gives very little opportunity for the nucleation of crystallites.

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Received August 11, 1972