

Anisotropy of Styrene-Butadiene Rubber

JUNJI FURUKAWA,* TEIZO KOTANI,† and SHINZO YAMASHITA,* *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan*

Synopsis

Anisotropy of styrene-butadiene rubber (SBR) was investigated. The anisotropy of the copolymer varies linearly with the styrene content and the ultimate value coincides with that of polystyrene at elevated temperature. From these facts, the transverse configuration of the pendant phenyl group is estimated irrespective of the styrene content of SBR.

INTRODUCTION

In the previous paper¹ the anisotropic polarizabilities of several kinds of rubbers were investigated by stress birefringential measurements and compared with the calculated values for polymeric units in order to evaluate the length or the molecular weight of statistical equivalent link as stiffness.

On the other hand, anisotropic polarizabilities of polystyrene and derivatives were measured by several authors.²⁻¹¹ The anisotropic polarizability of polymeric units of styrene was calculated by Stein and Tobolsky¹² to be -62.8 , -4.9 and -6.2 in 10^{-25} cm³ units for transverse, parallel, and freely rotating configurations; i.e., the phenyl groups are located in the transverse or parallel planes in relation to the main chain axis or freely rotate around the carbon-carbon bond that connects them to the main chain. Kawata¹³ found that stress birefringence varies with temperature. In practice, it shows positive values in plastic states but negative ones in rubbery states. This phenomenon suggests a configurational change of phenyl groups on heating.

In the case of styrene-butadiene rubber, the rubber exhibits rubbery behavior at the ordinary temperature and consequently the transverse configuration with respect to the backbone chain is expected. This paper deals with the anisotropic polarizability of styrene-butadiene rubber of various styrene contents in order to determine the configurational structure of pendant phenyl groups and its change, if any, caused by elongation and due to neighboring styrene.

* Present address: Kyoto University, Sakyo-Ku, Yoshida, Kyoto, Japan.

† Present address: Japan Synthetic Rubber Co., 7569 Mochizaka, Ikuta, Kawasaki, Japan.

EXPERIMENTAL

Styrene-butadiene rubber (SBR), emulsion polybutadiene (BR), and polystyrene (St) were prepared in a 67-liter vessel at 5°C according to the recipe as shown in Table I. The polymerization was stopped at 50% conversion by addition of sodium dithiocarbonate as stopper; the remaining styrene and butadiene monomers were eliminated by steam distillation. The rubbery products were purified by coagulation of latex with methanol and acetone followed by washing with methanol and acetone to extract soap to be removed. The styrene content in SBR thus obtained was estimated from the refractive index and the density of the polymer. The microstructure was determined by infrared analysis adopting Hampton's method. Styrene content and microstructure are listed in Table II.

The stress-birefringence relation was investigated in a similar way as in the preceding paper.¹ For this purpose, test pieces having dimensions of 10 mm in width, 50 mm in length, and about 2 mm in thickness were cut

TABLE I
Recipe for Polymerization of SBR^a

Monomer		
butadiene	variable	} total 100
styrene	variable	
Soap		
water		148
potassium-degenerated resinate		3.29
sodium ethylene-1,2-dinaphthalene sulfonate		0.105
Initiator		
cumen hydroperoxide		0.045
ferrous sulfonate		0.0045
Activator		
ethylenediaminetetracetic acid		0.035
potassium phosphate		0.35
sodium aldehyde sulfoxylate		0.063
Chain transfer agent: <i>t</i> -dodecyl mercaptan		0.13
Terminator: sodium dimethyldithiocarbamate		0.25

^a Polymerization at 5°C. Values, weight part.

TABLE II
Styrene Content of SBR and Microstructure of the Butadiene Component^a

No.	Refractive index	Styrene content	<i>cis</i> -	<i>trans</i> -	vinyl
1	1.5175	0	9.4	71.2	19.3
2	1.5245	6.4	9.0	67.3	18.3
3	1.5350	13.2	8.7	61.6	16.5
4	1.5630	38.8	5.7	43.6	11.8
5	1.5703	48.0	—	—	—
6	1.5917	84.0	—	—	—
7	1.5950	100.	0	0	0

^a Values, except for refractive index, are mole-%.

out from the vulcanized sheet of rubber. The sheet was prepared by heating with 0.4 to 1.5 weight parts of dicumyl peroxide per 100 parts rubber as a vulcanizing agent at 160°C for 40 min. The stress birefringence measurements were carried out with elongation rates of 0.5/min at from 25° to 140°C.

RESULTS AND DISCUSSION

From the linear relationship between the true stress, S , and the birefringence, Δn , proposed by Kuhn and Grün,¹⁴ the optical coefficient, C , was evaluated from the following equation:

$$C = \Delta n/S$$

$$S = VRT[\lambda^2 - (1/\lambda)] \quad (1)$$

where V , R , T , and λ are the number of chains per unit volume, gas constant, absolute temperature, and elongation ratio, respectively. In practice, stress is a more complicated function of the strain ratio λ , as follows:

$$S = 2C_1[\lambda^2 - (1/\lambda)] + 2C_2[\lambda - (1/\lambda^2)] \quad (2)$$

where C_1 and C_2 are constants depending on the test conditions. By changing the temperature of the measurement and the crosslinking density of SBR, values ranging from about 0.3 to 0.8 were obtained for $C_2/(C_1 + C_2)$. To eliminate the C_2 term, the magnitude of the birefringence was plotted against $C_2/(C_1 + C_2)$ and extrapolated to zero. The relation between stress and strain of SBR of 38.8% bound styrene is shown in Figure 1.

From the coefficient C , or $\Delta n/S$, the anisotropic polarizability of SBR was estimated and demonstrated as a function of the styrene content in the copolymer. Here, the photoelastic constant C , or $\Delta n/S$, of high-styrene SBR is reduced to 30°C using Kuhn and Grün's equation:

$$\frac{\Delta n}{S} = \frac{2\pi}{45kT} \frac{(n_0^2 + 2)^2}{n_0} (\alpha_{11} - \alpha_{22})_{\text{seg}}$$

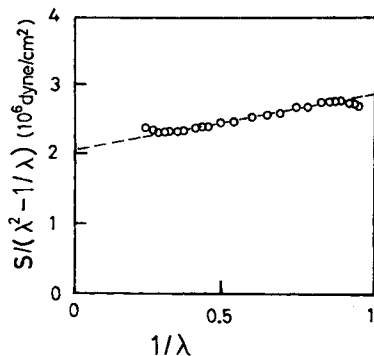


Fig. 1. Relation between $S/(\lambda^2 - 1/\lambda)$ and $1/\lambda$ of SBR at 80°C: bound styrene, 38.8%.

where n_0 , k , T , and $(\alpha_{11} - \alpha_{22})_{\text{seg}}$ respectively are the average refractive index, Boltzmann constant, absolute temperature, and anisotropic polarizability of a segment. Figure 2 indicates that there is a linear relationship between them, and suggests that the mode of contribution of styrene unit to stress birefringence is not varied with styrene contents, or in other words, the orientation of styrene unit is not affected by the neighboring styrene unit even at high styrene content at elevated temperature.

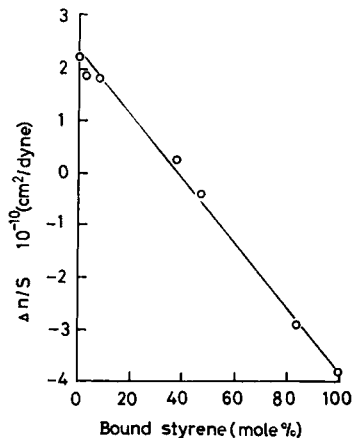


Fig. 2. Stress birefringence coefficient, $\Delta n/S$, and bound styrene of SBR.

The following experimental equation was derived for the polarizability of SBR of styrene content St :

$$(\alpha_{11} - \alpha_{22})_{\text{SBR}} = (\alpha_{11} - \alpha_{22})_{\text{BR}}(1 - St) + (\alpha_{11} - \alpha_{22})_{\text{St}} \times St \quad (3)$$

where $(\alpha_{11} - \alpha_{22})_{\text{SBR}}$ is the anisotropic polarizability of SBR, $(\alpha_{11} - \alpha_{22})_{\text{BR}}$ and $(\alpha_{11} - \alpha_{22})_{\text{St}}$ are the extreme values corresponding to both homopolymers. The anisotropic polarizabilities of emulsion polybutadiene and polystyrene at 30°C are as follows:

$$\begin{aligned} (\alpha_{11} - \alpha_{22})_{\text{BR}} &= 52.8 \times 10^{-25} \text{ cm}^3 \\ (\alpha_{11} - \alpha_{22})_{\text{S}} &= -170 \times 10^{-25} \text{ cm}^3 \end{aligned} \quad (4)$$

These values coincide with those of the respective homopolymers. Consequently, the performance of the styrene unit in the copolymer is that of polystyrene in the amorphous state.

The anisotropic polarizabilities of the polystyrene units are calculated for three cases with respect to the configurations of phenyl groups, i.e., transverse, parallel, and freely rotating configurations, as shown in Figure 3. The values are, respectively, -52.5 , 22.8 , and -4.9 in 10^{-25} cm^3 units. The first figure seems to be more close to the experimental value for the statistical link of polystyrene in the rubbery state, having a photoelastic constant of -4.2 to $-3.8 \times 10^{-10} \text{ cm}^2/\text{dyne}$.

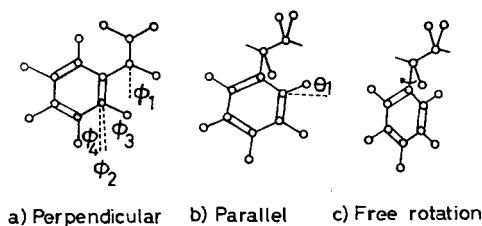


Fig. 3. Configurational structure of polystyrene, where phenyl group is transverse, parallel, or freely rotating to the main chain: (a) $\theta = 90^\circ$, $\phi_1 = 54^\circ 45'$, $\phi_2 = 5^\circ 15'$, $\phi_3 = 65^\circ 15'$, $\phi_4 = 54^\circ 45'$; (b) $\theta = 30^\circ$, $\phi_1 = 54^\circ 45'$.

A transverse configuration of phenyl groups in polystyrene is quite compatible with a similar transverse configuration of cumene. This means that a transverse configuration is ascribed to the interactions both between neighboring phenyl groups in polystyrene and between methylene on the main chain and pendant phenyl groups.

As an expression of stiffness of the copolymer chain, the length of the mean statistical link may be denoted as follows:

$$l = l_1M + l_2(1 - M) \quad (5)$$

TABLE III
Photoelastic Constant of SBR

No.	Styrene content, mole-%	Temp., °C	Photoelastic constant, 10^{-10} cm ² /dyne
1	0	30	2.22
2	6.4	30	1.87
3	13.2	30	1.86
4	38.8	80	0.28*
5	48.0	80	-0.28*
6	84.0	120	-2.9*
7	100	140	-3.8 to -4.2*

* These values were obtained reducing the temperature to 30°C.

TABLE IV
Observed and Calculated Anisotropic Polarizabilities of Mean Monomeric Unit of SBR

No.	Styrene content, mole-%	$(\alpha_{11} - \alpha_{22})_{\text{SBR}}, 10^{-26}$ cm ³		
		observed	calculated	ratio
1	0	52.6	27.4	1.92
2	6.4	45.3	22.3	2.03
3	13.2	45.0	16.9	2.66
4	38.8	6.3	-4.7	—
5	48.0	-6.3	-12.0	—
6	84.0	-119.	-40.0	2.97
7	100	-176.	-52.3	3.24

where l_1 and l_2 are the lengths of statistical links of component 1 and 2 whose mole fractions in the copolymer are M and $(1 - M)$, respectively. In this case, the observed anisotropy of the copolymer, $(\alpha_{11} - \alpha_{22})_{\text{SBR}}$, is the mean anisotropy of the link composed of the two components whose anisotropies are $(\alpha_{11} - \alpha_{22})_{\text{BR}}$ and $(\alpha_{11} - \alpha_{22})_{\text{St}}$, respectively.

In conclusion, the configuration of the pendant phenyl group was estimated to be affected neither by the stretching nor by the neighboring group of SBR. The plane of the benzene ring is always transverse in the copolymer in the rubbery state.

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