Viscoelastic Properties of Homogeneous Diblock Copolymers of Styrene and α -Methylstyrene

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ABSTRACT: The molecular theory of viscoelasticity of Rouse–Bueche–Zimm has been modified to apply to block copolymers. The new model consists of strings of beads and springs whose values correspond to the type of blocks in the polymer. Maximum relaxation times were predicted by this model, which can be compared with experimental data obtained from homogeneous block copolymers. Viscoelastic data for poly(styrene–b- α -methylstyrene) were determined by stress relaxation methods. The results compare favorably with those predicted by the theory.

There has recently been considerable interest in the studies of the extension of the Rouse–Bueche–Zimm molecular theory of polymer viscoelasticity to block copolymers. $^{1-5}$ These theories were able to predict the relaxation time spectra of block copolymers for a number of different block configurations, such as diblock, triblock, and multiblock copolymers. In a recent publication from this laboratory, 6 we compared the calculated maximum relaxation times of one system, namely the triblock copolymers, with the experimental data on the homogeneous poly(styrene–b- α -methylstyrene–b-styrene). Satisfactory agreement was obtained between theory and experiment. In order to test the theory for another block configuration, we now report on the experimental data for two diblock copolymers of styrene and α -methylstyrene (SA).

Two samples of equimolar poly(styrene–b- α -methylstyrene) were obtained from Union Carbide Corp. The characteristics of these samples are given in Table I. They were prepared for mechanical testing by hydraulically pressing them at 165 °C and subsequently annealing in vacuo at 150 °C for 24 h to release any locked-in stresses.

Samples were cut into strips and sanded to attain uniform dimensions. The typical dimensions were $5\times1\times0.2~\mathrm{cm^3}$. The dimensions were measured with a micrometer to $\pm0.0005~\mathrm{cm}$. Stress relaxation experiments were performed on an Instron Universal Testing Machine. The temperature was controlled to $\pm0.2~\mathrm{^{\circ}C}$ with a Missimer Model PITC Temperature Conditioner. Flexural mode experiments were used for moduli above $10^9~\mathrm{dyn/cm^2}$. Below this value, the tensile mode was used.

Stress relaxation isotherms for the samples are shown in Figure 1. These isotherms were shifted into smooth viscoelastic master curves (Figure 2) by the Time Temperature Superposition Principle. 8.9 Only part of the master curve was constructed for BP-II because the quantity of the sample was not sufficient to render tests over the entire temperature range possible. The more important rubbery and flow regions were determined. Shift factor data used in effecting the superposition are given in Figure 3. The curve in the figure was computed from the Williams-Ferry-Landel (WLF) equation using the values $C_1=13.7$ and $C_2=50.0$ characteristic of polystyrene. 9 The same constants were also found to fit the shift data of triblock copolymers of styrene and α -methylstyrene. Reference temperatures (Table I) were chosen by obtaining a best fit between the WLF equation and the experimental

data. The close agreement of WLF equation with the experiment shift factors is another evidence of the thermorheological simplicity of these block copolymers.

Isochronal modulus-temperature curve can be obtained from the isotherms by crossplotting moduli at 100 s as a function of temperature. The temperature at which the modulus reaches $10^9 \, {\rm cyn/cm^2}$ is taken as the inflection temperature, $^8 \, T_{\rm i}. \, T_{\rm i}$ for BP-II was estimated by assuming the difference between $T_{\rm i}$ and $T_{\rm ref}$ for the WLF equation to be the same for the two samples. The viscoelastic parameters are summarized in Table I.

The RBZ model represents the polymer molecule by a collection of beads held together with entropy springs. For block copolymers, the equation of motion can be written as²

$$\dot{\mathbf{x}} = -\sigma_{\mathbf{s}} \mathbf{D}^{-1} \mathbf{Z} \mathbf{x} \tag{1}$$

In this equation, \mathbf{x} and $\dot{\mathbf{x}}$ are column vectors of bead positions and velocities, respectively, \mathbf{Z} is the nearest neighbor Zimm matrix, and $\sigma_s = 3kT/b_s^2f_s$, where k is Boltzmann's constant, T is the absolute temperature, b_s^2 is the mean-square end-to-end distance of a polystyrene submolecule, and f_s is the friction coefficient of a polystyrene submolecule. For the diblock copolymer, \mathbf{D}^{-1} is the inverse of the following matrix where $\sigma_A = f_A/f_s$, f_A is the friction coefficient of a poly(α -methylstyrene) submolecule. Further development of the theory has been shown previously by Hansen and Shen.² Their

$$\mathbf{D} = \begin{bmatrix} \mathbf{1}_{1} & & & \\ & \mathbf{1}_{\sigma_{A}} & & \\ & & \mathbf{0}_{A} & \\ & & & \mathbf{0}_{A} \end{bmatrix}$$
 (2)

predicted value of log $(\tau_{\rm m}/\tau_{\rm m}^{0})$ is 1.75 for equimolar SA, where $\tau_{\rm m}$ is the maximum relaxation time of the block copolymer and $\tau_{\rm m}^{0}$ is the maximum relaxation time of pure polystyrene.

The experimental maximum relaxation times of the block copolymers were determined from the master curves (Figure 2) by procedure X of Tobolsky and Murakami. Since the maximum relaxation times are sensitive functions of temperature and molecular weight, these effects were compensated for to ensure a meaningful comparison. We used $T_{\rm i}$ + 29 °C as the reference temperature. The relationship d ln $\tau_{\rm m}/{\rm d}$ ln $M_{\rm w}=3.4$ was assumed to extrapolate the maximum relaxation times to the reference molecular weight of 1.2×10^5 . An average of literature values for polystyrene, $\log\tau_{\rm m}^0=2.36$

Table I
Characteristics and Viscoelastic Parameters of Diblock Copolymers

Sample	Composition wt % styrene	H.I.				$T_{ m ref}$, °C	$-\log (\tau_{\rm m}/\tau_{\rm m}{}^0)$	
		$M_{ m w} imes 10^{-5}$	$(M_{\rm w}/M_{\rm n})$	T _g , °C⁴	T _i , °C	(WLF)	Exptl	Theor
BP-I BP-II	50 50	0.8 1.5	1.08 1.01	134 132	115 (116)*	113 114	1.76 1.48	1.75 1.75

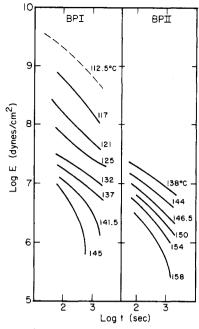


Figure 1. Stress relaxation isotherms for samples BP-I and BP-II of poly(styrene–b- α -methylstyrene). Solid curves: tensile data; broken curve: flexural data.

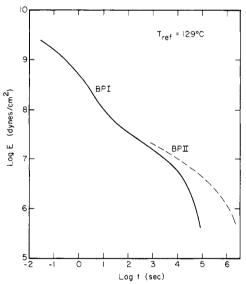


Figure 2. Viscoelastic master curves of poly(styrene–b- α -methylstyrene). Solid curve: sample BP-II; broken curve: sample BP-III.

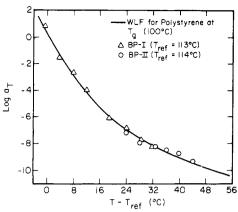


Figure 3. Viscoelastic shift factor data for samples BP-I (triangles) and BP-II (circles) of poly(styrene-b- α -methylstyrene). The solid curve was calculated from the WLF equation with C_1 = 13.7 and C_2 = 50.0

s, was adopted for our calculation.⁶ Experimental log $(\tau_{\rm m}/\tau_{\rm m}^0)$ values for BP-I (1.76) and BP-II (1.48) are seen to compare favorably with the calculated value of 1.75 (Table I). Thus, the present work seems to provide further indication of the validity of the molecular theory of viscoelasticity for homogeneous block copolymers.

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