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# Birefringence of a Block Copolymer Solution in the Stress-Relaxation Process

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ABSTRACT: The shear stress, $\sigma$, the birefringence, $\Delta n$, and the extinction angle, $\chi$, were measured after an instantaneous shear deformation for an 11% solution of a triblock copolymer, poly(methyl methacrylate)-*block*-polystyrene-*block*-poly(methyl methacrylate), in polychlorinated biphenyl. The quantity $\chi$ was independent of time and satisfied a relation $2 \cot 2\chi = \gamma$, where $\gamma$ is the magnitude of shear. All the data, throughout the stress-relaxation process at various $\gamma$, satisfied a relation, $\Delta n \sin 2\chi = 2C\sigma$, derived from the stress-optical law where $C = -1.8 \times 10^{-9}$ Pa$^{-1}$. This result is inconsistent with the tube model theory or the Rouse model theory, from which the birefringence is expected to decrease more slowly than the shear stress for the present polymer. The present result may imply that the decay rate of the segment orientation should not depend on the location of the segment on the polymer chain.

## 1. Introduction

When a polymeric material is deformed, the refractive index as well as the stress becomes anisotropic. A simple relation, called the stress-optical law, holds valid for melts and concentrated solutions of homopolymers.[1] This law states that the principal directions of the refractive index tensor are the same as those of the stress and that the deviations from average of refractive index in various directions are proportional to the corresponding deviations of stress. Thus, one may write

$$\Delta \mathbf{n} = C\sigma \tag{1}$$

where $\Delta \mathbf{n}$ and $\sigma$ are deviatoric components of refractive index tensor and stress tensor, respectively. The proportionality constant, $C$, is called the stress-optical coefficient and is determined by the anisotropy of polarizability of the polymer segment. The stress-optical law may be easily derived for polymer models composed of Gaussian segments.[1,2]

Following the same type of calculation, we showed that the stress-optical law would fail to be valid for a block copolymer of an ABA type.[3,4] In place of eq 1, one obtains

$$\Delta \mathbf{n} = C_A\sigma_A + C_B\sigma_B \tag{2a}$$

$$\sigma = \sigma_A + \sigma_B \tag{2b}$$

where $C_A$ and $C_B$ are constants, approximately equal to the stress-optical coefficients of homopolymers consisting of A and B components, respectively. Quantities $\sigma_A$ and $\sigma_B$ are the portions of stress attributable to the A block and B block, respectively. Due to the different locations of A and B blocks along the chain, $\sigma_A$ would decrease more rapidly than $\sigma_B$ in a stress-relaxation process.[3] The ratio $\sigma_B/\sigma$ would decrease more largely with increasing $\dot{\gamma}$ than does $\sigma_A/\sigma$ in steady shear flow where $\sigma$, $\sigma_A$, and $\sigma_B$ represent the shear components of the respective tensors and $\dot{\gamma}$ is the rate of shear.[4] Calculations based on the Rouse model[5] and the tube model[6,7] exhibited that the deviation from the stress-optical law is of measurable magnitude. The purpose of the present study is to experimentally examine the prediction in the case of stress-relaxation processes.

## 2. Method

**Principle.** We consider a shear deformation field shown in Figure 1. The components of the deformation vector in a Cartesian coordinate system $xyz$ are given by

$$u_x = \gamma y, \qquad u_y = u_z = 0 \tag{3}$$

The $xy$ component of eq 1 is written as

$$\Delta n \sin 2\chi = 2C\sigma \tag{4}$$

Here, $\sigma$ is the shear stress, $\Delta n$ is the amount of birefringence with respect to the principal axes, $X$ and $Y$, in the $xy$ plane, and $\chi$ is the extinction angle; i.e., the angle between the $x$ axis and one of the principal axes in the $xy$ plane.

A stepwise shear is applied to the material for measurement of stress-relaxation; a shear of magnitude $\gamma$ is applied at time $t = 0$ and the shape is kept constant for $t > 0$. For homopolymer systems, the extinction angle, $\chi$, was constant throughout the process of stress-relaxation and filled a simple relation[8-10]

$$2 \cot 2\chi = \gamma \tag{5}$$

The $xy$ components of eq 2 for a block copolymer can be written as

$$\Delta n \sin 2\chi = 2C_A\sigma_A + 2C_B\sigma_B \tag{6a}$$

$$\sigma = \sigma_A + \sigma_B \tag{6b}$$

where $\sigma_A$ and $\sigma_B$ are $xy$ components of tensors $\sigma_A$ and $\sigma_B$, respectively. The tube model calculation[3] for a block copolymer of ABA type exhibited that the extinction angle, $\chi$, is constant and given by eq 5 and that the contribution to shear stress from the central block, $\sigma_B$, is given by

$$\frac{\sigma_B}{\sigma} = \sum_{p:\mathrm{odd}} \left[ \frac{8}{(p\pi)^2} \exp\left(-\frac{tp^2}{\tau_1}\right) \cos\left(\frac{p\pi(1-\xi)}{2}\right) \right] \Bigg/ \sum_{p:\mathrm{odd}} \left[ \frac{8}{(p\pi)^2} \exp\left(-\frac{tp^2}{\tau_1}\right) \right] \tag{7}$$

where $\tau_1$ is the reptation time and $\xi$ is the content of the B component. Here, the two A blocks are assumed to be of the same length. The quantity $\sigma_B/\sigma$ is an increasing function of time. The limiting values are

$$\frac{\sigma_B}{\sigma} = \xi \qquad (t \to 0) \tag{8a}$$

$$\frac{\sigma_B}{\sigma} = \sin\left(\frac{\pi\xi}{2}\right) \qquad (t \to \infty) \tag{8b}$$

Thus, the increase of $\sigma_B/\sigma$ may be of considerable magnitude when $\xi$ is not very close to 1. Qualitatively, the same results were obtained for the Rouse model.[3]

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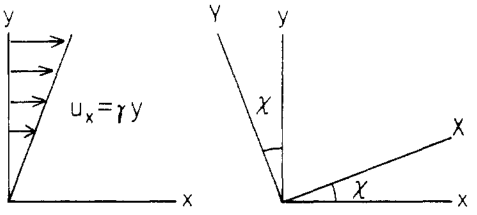

**Figure 1.** Simple shear deformation (left) and principal axes of a refractive index, $X$ and $Y$, on $xy$ plane (right). Another principal axis, $Z$, coincides with the $z$ axis.

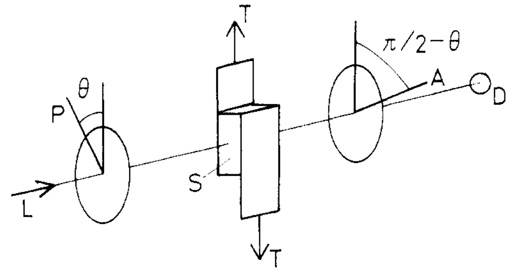

**Figure 2.** System for birefringence measurement: S, sample; P and A, polarizing films; T, clamps of tensile tester; L, light beam; D, optical detector.

**Materials.** The measurements were performed for an 11.0% solution of a poly(methyl methacrylate)-*block*-polystyrene-*block*-poly(methyl methacrylate) in polychlorinated biphenyl. The synthesis and characterization of the block copolymer (denoted PMSM hereafter; code 27B of ref 11) are reported elsewhere.[11] The number average molecular weight, $M_n$, of the styrene block was $5.14 \times 10^5$, and that of the copolymer was $1.24 \times 10^6$. The ratio of the weight average molecular weight $M_w$ to $M_n$ of PMSM was 1.19. The content of styrene, $\xi$, is about 0.4 irrespective of whether it is defined as the weight fraction or the mole fraction of monomer.

The solvent was Aroclor 1248 supplied from Monsanto Chemical Co. The refractive index of the solvent,[10] 1.60, is not much different from those of homopolymer corresponding to the component of PMSM: 1.60 for polystyrene and 1.55 for poly(methyl methacrylate). Thus, the form birefringence would be rather small even at relatively low concentrations. For the present solution, the concentration of the polymer as well as that of each component is quite high. Thus, the form birefringence may not be of importance[12] unless the solution has a structure of high order such as a microdomain structure.

The stress-optical coefficient of polystyrene solution in chlorinated biphenyl is $-6.0 \times 10^{-9}$ Pa$^{-1}$, and that of poly(methyl methacrylate) solution is about $8 \times 10^{-10}$ Pa$^{-1}$. The optical anisotropy of the segment of central block is much larger than that of the end blocks. Thus, we expect that the contribution to the birefringence from the central block is amplified and that the birefringence relaxes more slowly than the shear stress.

**Apparatus.** The amount of birefringence, $\Delta n$, and the extinction angle, $\chi$, were measured with a tensile tester equipped with a special sample holder and an optical system (Figure 2).[9] The deformed sample is placed in between a crossed pair of polarizing films, P and A, and a light beam, L, is passed along the $z$ axis defined in Figure 1. The intensity of light that passed through the set of polarizing films and the deformed polymer is measured. The quantities $\Delta n$ and $\chi$ can be evaluated by combining two sets of data of light intensity obtained for different angles, $\sigma$, between the shear direction and the polarization direction of incident light.

The shear stress in stress-relaxation was measured also with an apparatus of cone-and-plate type.[13] The dynamic complex modulus was measured with a cone-and-plate rheometer (Rheopexy Analyzer, Iwamoto Seisakusho Co., Ltd.).

## 3. Results and Discussion

**Complex Modulus.** The 20% solution of the block copolymer exhibited a strong light scattering of a blue color, possibly due to a microdomain structure. The scattering weakened with decreasing concentration. The 15% solution exhibited a slight milky scattering. Solutions of 12% and lower concentrations were completely transparent and colorless to naked eyes.

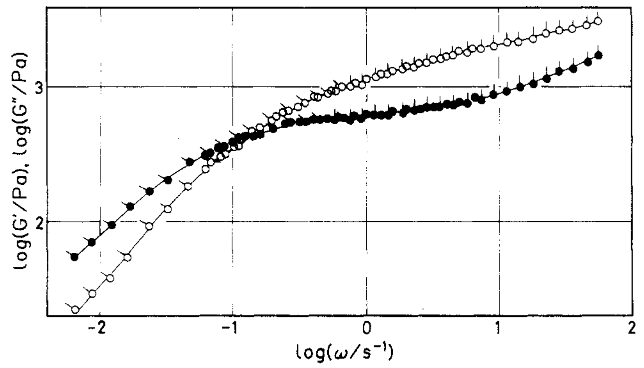

**Figure 3.** Storage modulus, $G'(\omega)$ (unfilled circles), and loss modulus, $G''(\omega)$ (filled circles), measured at 17 °C (pip up), 30 °C (no pips), and 52 °C (pip slant), reduced to 30 °C with method of reduced variables.

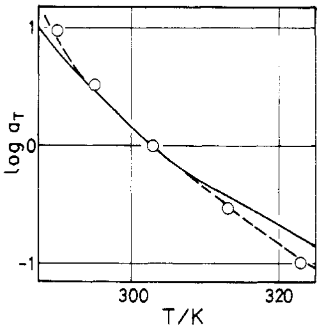

**Figure 4.** Shift factor, $a_T$, for solutions of block copolymer (circles), polystyrene (solid line), and poly(methyl methacrylate) (dashed line).

The storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, were measured for solutions of 11% and 15% over a range of angular frequency, $\omega$, from 0.0628 to 6.28 s$^{-1}$ at several temperatures. The result was reduced to a reference temperature, 30 °C, by plotting $G'$ and $G''$ against a reduced angular frequency, $\omega a_T$. The reduced plot for the 11% solution is shown in Figure 3, where the data points for 22 and 40 °C are omitted to avoid overlapping. One sees that data points obtained at various temperatures superimpose on one another with appropriate choices of the shift factor, $a_T$, and compose master curves for $G'$ and $G''$. The shape of the master curves is similar to that for a solution of polystyrene or poly(methyl methacrylate) with approximately the same molecular weight and concentration.[14]

The shift factor, $a_T$, is plotted against the temperature, $T$, in Figure 4. The results for 10% solutions of polystyrene and poly(methyl methacrylate) are also shown. The shift factor for the solution of the block copolymer is approximately equal to that for the solution of poly(methyl methacrylate).

The results shown in Figures 3 and 4 may indicate that the viscoelastic behavior of the solution of the block copolymer is similar to that of the solution of polystyrene or poly(methyl methacrylate) with about the same molecular weight and concentration. Qualitatively, the same result was obtained for the 15% solution. High-order structures like the microdomain structure may give rise to some of the various characteristic features such as the change of the shape of the viscoelastic function, a very strong concentration dependence of the maximum relaxation time, and the failure of the thermorheological sim-

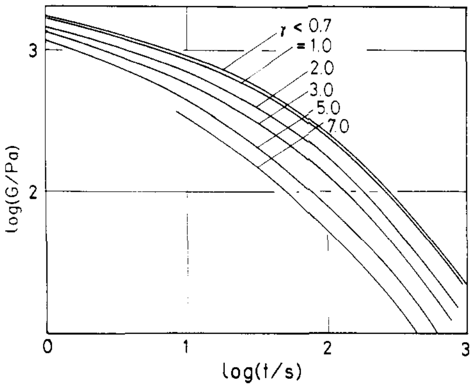

**Figure 5.** Relaxation modulus, $G(t, \gamma)$, at 18 °C. Number of each curve indicates magnitude of shear, $\gamma$.

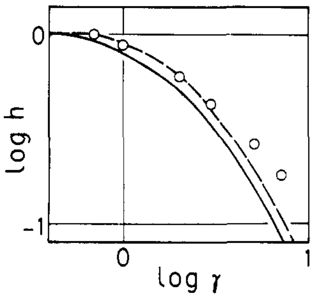

**Figure 6.** Function $h(\gamma)$ of eq 9 taken from data of Figure 5: solid line, prediction of tube model theory by Doi and Edwards; dashed line, typical result for solution of polystyrene with sharp molecular weight distribution.

plicity; even when the thermorheological simplicity holds good, the shift factor may vary in a different manner from that of the component polymer. Our solution of the block copolymer did not exhibit any of such features. This may not be a sufficient proof, but it is likely that the solution does not include any microdomain structure.

**Relaxation Modulus.** The relaxation modulus, $G(t, \gamma)$, was measured at various magnitudes of shear, $\gamma$, at 18 °C. The result is shown in Figure 5. The data obtained with the tensile tester with a special sample holder were in good agreement with those obtained with the cone-and-plate apparatus. The relaxation modulus at small magnitudes of shear, $\gamma \leq 0.7$, was consistent with the data of complex modulus in view of the phenomenological theory of linear viscoelasticity. As seen in Figure 5, the relaxation modulus decreases with increasing magnitude of shear. The strain dependence becomes stronger with increasing time until about 150 s.

The effect of varying $\gamma$ at longer times is shown in Figure 6 in terms of a function

$$h(\gamma) = \frac{G(t, \gamma)}{G(t, 0)} \qquad (t > 150 \text{ s}) \qquad (9)$$

The solid line indicates the prediction of the tube model theory[7] and the dashed line a typical result for polystyrene solution.[15] The strain dependence of the block copolymer solution is a little weaker than that for a solution of polystyrene with sharp molecular weight distribution.

**Birefringence in the Stress–Relaxation Process.** Measurements were performed at 18 °C at three magnitudes of shear, $\gamma$ = 0.65, 1.3, and 2.2. The extinction angle, $\chi$, was independent of time and satisfied the relation of eq 5 at each magnitude of shear. The result for the birefringence, $\Delta n$, is shown in Figure 7. The quantity $-(\Delta n \sin 2\chi)/2$ is plotted against the time, $t$. The graph essentially represents the time variation of $\Delta n$ since the other factors are time-independent.

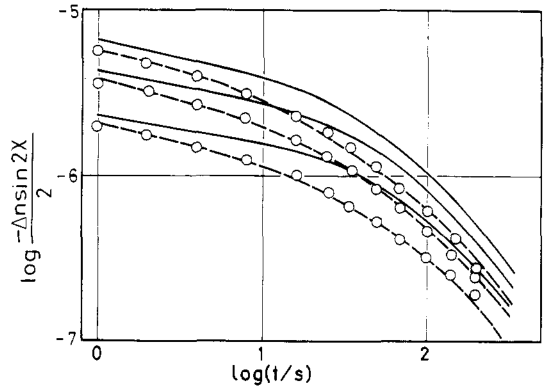

**Figure 7.** Quantity $(\Delta n \sin 2\chi)/2$ in a stress-relaxation process at 18 °C; $\gamma$ = 2.2, 1.3, and 0.65 from top to bottom: circles, measured values; dashed lines, estimated from $\sigma$ with the stress–optical law where $C = -1.8 \times 10^{-9}$ Pa$^{-1}$ was used as the stress–optical coefficient; solid lines, estimated from assuming nonuniform relaxation of segment orientation along a polymer chain as predicted by the tube model theory.

The dashed lines are drawn not just to connect the data points but to test the stress–optical law; they were composed from the measured values of shear stress, $\sigma$, by assuming eq 4 and by choosing an arbitrary value, $-1.8 \times 10^{-9}$ Pa$^{-1}$, for the coefficient $C$. One value of $C$ was sufficient to fit the optical data with eq 4 throughout the stress–relaxation process at various magnitudes of shear. Thus, the stress–optical law held valid as far as the shear component of eq 1 was concerned. It may be remarked that the best fit value, $-1.8 \times 10^{-9}$ Pa$^{-1}$, for $C$ is very close to the average value of the stress–optical coefficient, $-1.9 \times 10^{-9}$ Pa$^{-1}$, estimated by using $-6.0 \times 10^{-9}$ Pa$^{-1}$ for a polystyrene solution, $8.0 \times 10^{-10}$ Pa$^{-1}$ for a poly(methyl methacrylate) solution, and the mole fraction of the components of the block copolymer.

The solid lines of Figure 7 were drawn according to eq 6 and 7, derived from the tube model theory; a measured value of shear stress, $\sigma$, was used to evaluate $\sigma_A$ and $\sigma_B$ from eq 6b and 7, and other parameters were $C_A = 8.0 \times 10^{-10}$ Pa$^{-1}$, $C_B = -6.0 \times 10^{-9}$ Pa$^{-1}$, and $\xi = 0.4$. The choice may not be the best but may be sufficient to examine the general trend of the theoretical result in comparison with the observed. The theoretical values are fairly close to the observed at short times but becomes far larger than the observed at long times.

**Discussion.** One may safely say that, in Figure 7, the dashed lines fit with the data points much better than the solid lines do. The measurement is not easy but the experimental errors cannot be so large as to reverse the conclusion. One problem still to be examined experimentally is a possibility of a higher order structure in the test fluid. This may give rise to a form birefringence, which was not taken into account in deriving eq 6 and 7. On the other hand, the stress–optical law fails to be valid when the contribution of form birefringence is large.[16] Thus, the present result is not likely to be disturbed by the form birefringence. A high-order structure may cause a structural change on deformation, and this may add complication to the observed birefringence. In fact the decay of birefringence of block copolymer systems with evident microdomain structures is rather complicated, and the stress–optical law would not hold good.[17] As far as one can guess from these evidences, a high-order structure may not be an important factor to explain the present result.

Provided that the solution was homogeneous and could be regarded as an ordinary entangled system, the present result would raise an important question to the theories of polymer dynamics. A straightforward interpretation of the result may be that the rate of decay of segment orientation does not depend on the location of the segment on the polymer chain. This statement is inconsistent with the tube model for entangled polymers or with the Rouse model. Either of the theories tells that the rate of decay should be higher at the chain ends than at the central part of chain. If the theoretical results for the Rouse model[3] are used in place of eq 7, the deviation between the observed and theoretical values of $(\Delta n \sin 2\chi)/2$ becomes slightly larger than that shown in Figure 7.

The present polymer solution may not be a very well-entangled system to be quantitatively compared with entanglement theories. However, comments on earlier studies of entangled systems may be of some interest. The tube model theory has been successful in describing the nonlinear viscoelasticity of polymers.[18] Especially, the complicated data for the relaxation of shear stress and birefringence following double-step shear deformations were well explained in terms of the tube model theory.[19] The results were consistent with the assumption that the decay rate of anisotropic orientation of segments is larger at the chain ends than at the center of chain.[20] Lee and Wool observed that the orientation of the central block of a centrally deuterated triblock polystyrene in a matrix of polystyrene with a high molecular weight decayed more rapidly than the orientation of a fully deuterated polystyrene did.[21] Thus, we now have two inconsistent observations concerning the decay rate of segment orientation.

One possibility of compromise may be to find a defect of the calculation method of birefringence based on the addition of the segment polarizability. On the other hand, the method seems to give consistent descriptions of a variety of data for birefringence and segment polarizability.[1,2,16] The method was effective even in deriving the form birefringence in dilute polymer solutions provided that the effect of anisotropic distribution of segments was taken into account.[22] Thus, it may not be easy to find the defect of the theory for the origin of birefringence. It has been pointed out that a nematiclike interaction,[23,24] such as attractive coupling between neighboring segments, may lead to the results different from above-mentioned theoretical treatments.

In any case, the implication of the present observation seems important. Better understanding may be attained by additional experiments on block copolymers with a reversed structure, polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene, or with components of cosoluble polymers like polystyrene and poly(vinyl methyl ether).

**Registry No.** (Styrene)(methyl methacrylate) (block copolymer), 106911-77-7.

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# Segmental Dynamics in Block Copolymers

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ABSTRACT: We have studied the segmental dynamics of a styrene/isoprene diblock copolymer in a melt of deuterated polyisoprene using quasi-elastic neutron scattering. The static structure factor of the block copolymer in the homogeneous melt state was measured by small-angle X-ray (SAXS) scattering. Static and dynamic data were interpreted in the RPA theory. The result is a good description of the observed SAXS profiles and their temperature dependence. The $q$ dependence of the initial slope in the intermediate scattering law is also accounted for by the same theory. The segmental dynamics of the block copolymer are thus described on the basis of a Rouse model.

## I. Introduction

Block copolymers are a class of materials of particular interest because of the specific interaction between their constituents. The interactions, in general, lead to special incompatibility effects, which in turn cause block copolymers to produce a variety of interesting morphologies. The dependence of morphology on molecular architecture and thermal history has been a subject of intensive study in recent years mainly because of the valuable technological applications.[1]

More recently, theoretical[2-4] and experimental[5,6] work has attempted to provide a microscopic understanding of

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