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Conformational Changes of Linear Polymers in the Glassy State

Mitsuru Nagasawa* and **Akio Koizuka**[†]

Toyota Technological Institute, Hisakata, Tempaku-ku, Nagoya, Japan 468

Kohki Matsuura and Motoshi Horita

Department of Electrical and Computer Engineering, Faculty of Technology, Kanazawa University, Kanazawa, Ishikawa-ken, Japan 920

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ABSTRACT: Internal stresses in glassy polymer materials arise from two different sources; deviation of polymer conformation from its equilibrium state and change of intersegment distances. These stress components may be separately observed by carrying out simultaneous measurements of tensile stress and birefringence relaxations of polymer films, assuming that they are additive. It is pointed out that the change of intersegment distances occurs first, and conformational deformation is gradually induced if a glassy polymer film is elongated.

1. Introduction

If temperature is above the glass transition temperature, T_g, in amorphous linear polymer materials, stresses and, hence, optical anisotropy caused by various strains, are due to deviation of polymer conformations from their equilibrium states, i.e., due to decrease in entropy of molecular conformation. The molecular theory for the phenomena is now well established. If the temperature is far below T_g, on the other hand, the change in molecular conformation can hardly occur, but the stresses and optical anisotropy caused by external forces may be due to changes of intersegment distances, just as in crystal, i.e., due to increase in enthalpy of the system. In the intermediate temperatures or even in the glassy state, it may be assumed that the stresses and optical anisotropy may arise from combination of the two kinds of deformations. In this paper, the former stress originating in polymer conformation change is denoted as the rubberlike stress, σ_r, while the latter originating in change of intersegment distances, as the glasslike stress, σ_g. The same subscripts are used for the stress-optical coefficients, too, such as C_r and C_g. The two kinds of stresses are clearly distinguished in stress-optical phenomena. The stress-optical coefficient in the rubber and molten states as well as in solution is entirely different from the coefficient in the glassy state.

Two kinds of deformations in amorphous linear polymer materials in the glassy state may be experimentally separated if we carry out simultaneous measurements of stress and birefringence in tensile stress relaxation experiments of polymer films and also if we assume that two kinds of stresses, σ_r and σ_g, are additive such as

$$\sigma(t) = \sigma_r(t) + \sigma_g(t) \qquad (1)$$

Then, the birefringence Δn would also be additive, such as

$$\Delta n(t) = C_r\sigma_r(t) + C_g\sigma_g(t) \qquad (2)$$

since the extinction angle should agree with the direction of elongation in tensile stress relaxation. Considering the molecular mechanisms for the two stresses, it is reasonable to assume that each stress-optical coefficient does not depend on temperature. Since contributions of the two kinds of deformations to birefringence are different with temperature, the apparent stress-optical coefficient at a temperature, which is defined as the ratio of observed birefringence and stress at that temperature, changes with temperature, as was sometimes reported in literature. It can be, moreover, predicted that the apparent stress-optical coefficient would vary with time at a constant temperature if there is difference between relaxation behaviors of the two different sources of stresses.

On the basis of this idea, the separation of σ_r and σ_g in stress relaxation of butadiene–acrylonitrile vulcanizate films in the transition region was reported by Priss et al.[1] Also, a similar analysis using a dynamic birefringence method was reported for some amorphous polymers by Read.[2] The purpose of this paper is to show that, by use of a polystyrene sample, the two kinds of stresses can be separately observed even in the glassy state by simultaneously observing the stress and birefringence relaxations and also that the change of intersegment distances first occurs immediately after an elongational strain is given to a polymer film in the glassy state and the conformational deformation is gradually induced. Polystyrene has a feature that C_r and C_g have different signs, so the above conclusions may be obtained without serious assumptions.

2. Experimental Section

2.1. Ellipsometer. Since a conformational deformation of polymers may be very small in the glassy state, we need an ellipsometer with high precision. Although the extinction angle is kept constant in the present elongational experiments, it is useful for more general applications if one can determine not only the birefringence but also the extinction angle at high speed. A block diagram of the ellipsometer constructed for these purposes is given in Figure 1. The instrument is a rotating-analyzer ellipsometer, and the data processing is carried out by Fourier analysis of the photodetector's output signal.[3] A light beam from a He–Ne laser (λ = 632.8 nm) is converted to an elliptically polarized beam by a polarizer and wave plate. The elliptically polarized light beam is transmitted through a birefringent sample and eventually converted to another elliptically polarized beam. The elliptically polarized beam is brought into a rotating analyzer in which a Glan–Thompson polarizing prism is rotating at 75 rpm. The intensity of the beam passed through the prism is measured with a photodiode at every 0.04° rotating angle of the analyzer, using a hollow shaft rotary encoder of Heidenhain Japan K K (RON255, 9000 pulse/turn) together with pulse-shaping electronics (EXE60211-F). The data are sent to a personal computer (NEC PC-9801VX21) through an A/D converter (Model 121 autodigitizer of Autnics Co., Ltd.; 12 bits). An example of beam intensities at various rotating angles observed on the computer display, which consisted of 9000 data points per 360°, is shown in Figure 2. The beam intensities and rotating angles

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[†] Corporate Research & Development, Ube Industries, Ltd., 3-10, Nakamiya Kita-machi, Hirakata, Japan 573.

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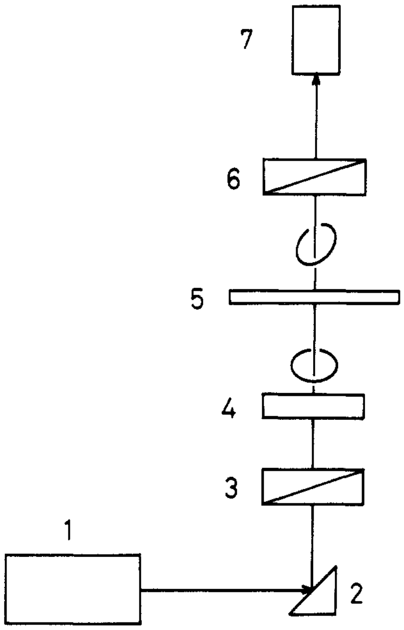

Figure 1. Optical alignment in the ellipsometer: 1, He–Ne laser; 2, prism; 3, polarizer; 4, wave plate; 5, sample film; 6, rotating analyzer; 7, photodiode.

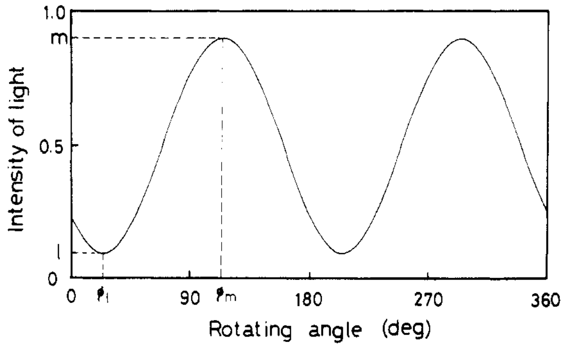

Figure 2. Intensity of light measured at the detector. The curve consists of 9000 points per 360°.

at the maximum and minimum in observed sinusoidal waves are determined by a curve-fitting method, and the optical retardation angle between two principal axes (δ) and the azimuth of the principal axis (extinction angle χ) are computed.[3] The optical retardation angle, δ, is related to birefringence, Δn, by

$$\Delta n = (\lambda/2\pi L)\delta \tag{3}$$

where L is the optical path length and λ is the wavelength in the medium. The sensitivity in retardation is about 0.01° and the reproducibility was found to be 0.04° for an optical glass. It takes 5 s for computer calculation at present.

2.2. Stress Relaxation Measurements and Samples. The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, of the polystyrene sample used, which was prepared by an anionic polymerization method, were estimated to be $M_w = 2.2 \times 10^5$ and $M_w/M_n \approx 1.1$ by gel permeation chromatography. Films of polystyrene with 0.2–0.3-mm thickness were cast from 20% toluene solution on mercury surface. The sample films used for the present experiments contained 3.1% of the solvent, and the glass transition temperature of the sample was about 80 °C, as estimated from the change in heat capacity obtained by a Perkin-Elmer DSC-2C. Loss of the solvent from the sample films is negligible in the present experimental temperature range. The contamination of the sample films by solvent is not important for the present purpose. With polystyrene, the stress-optical coefficient is positive for change of intersegment distances (i.e., for σ_g) and negative for deformation in molecular conformation (i.e., for σ_r). Their values in the literature are $C_g = +8.3 \times 10^{-13}$ and $C_r = -5.0 \times 10^{-10}$ cm^2/dyn.[4-6]

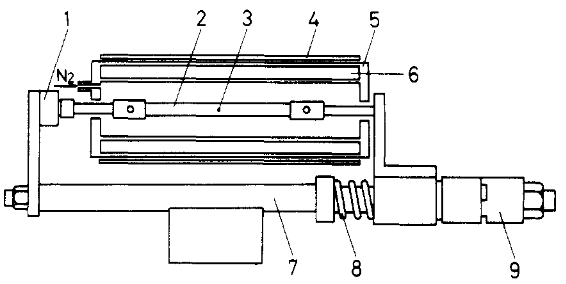

Figure 3. Apparatus for simultaneous measurements of stress and birefringence relaxations: 1, load cell; 2, sample film; 3, laser beam (the laser beam is passed from the back of paper); 4, heater; 5, chamber; 6, heat-insulating materials; 7, supporting rod; 8, spring; 9, release collar.

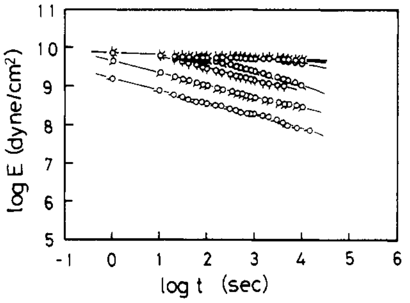

Figure 4. Double-logarithmic plots of relaxation modulus vs time at various temperatures: ȯ, 43.5; ó, 51.0; o-, 55.0; ọ, 65.0; o̧, 69.0; ϕ, 76.5; -o, 80.5 °C.

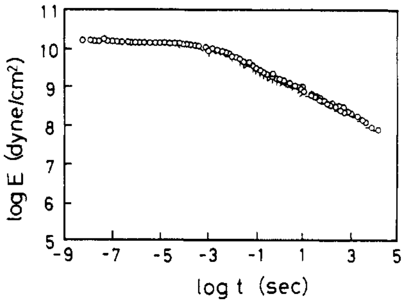

Figure 5. Master curve obtained by shifting the data in Figure 4 according to the time–temperature superposition principle (T_0 = 80.5 °C).

A film was elongated to a strain by releasing a strong spring, using the apparatus shown in Figure 3. Strains given to the films were about 1% at lower temperatures and slightly higher at higher temperatures. Tensile stresses were measured with time by using a load cell, and the birefringence at the center of the film was simultaneously measured by the ellipsometer. The temperature was maintained within ±0.5° by circulating a constant-temperature nitrogen gas.

3. Results and Discussion

Relaxation moduli calculated from observed tensile stresses are double-logarithmically plotted against time at various temperatures in Figure 4. Figure 5 shows a master curve obtained by shifting the data at various temperatures on the curve at a reference temperature, 80.5 °C, according to the time–temperature superposition principle. The correction for change in density with temperature was given to the data, following the method of Ferry.[7] However, the correction was in any case within the present experimental uncertainty. Additional slight vertical adjustments were given to the data at 43.5 and 51.0 °C in constructing a smooth master curve. The shift factors assumed are shown in Figure 6. The shift factors were in practice determined in connection with the superposition of E_r in Figure 9, as will be explained later.

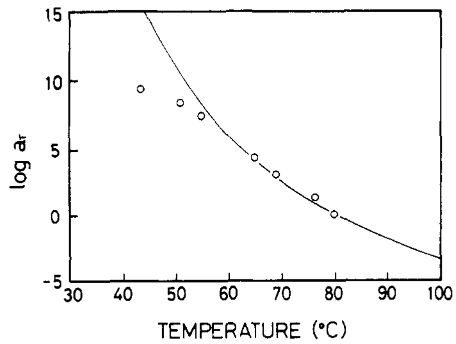

Figure 6. Temperature dependence of shift factor a_T. The solid line shows a WLF equation $\log a_T = -16.4(T - T_g)/[74.3 + T - T_g]$, where $T_g = 80.5$ °C is assumed. See the text concerning the determination of a_T.

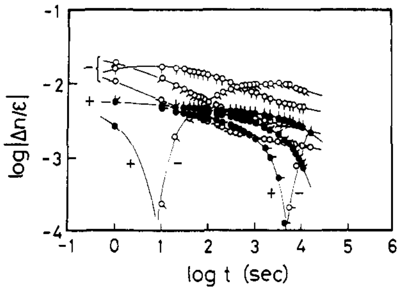

Figure 7. Double-logarithmic plots of the ratio of birefringence to strain ($\Delta n/\epsilon$) at various temperatures. Symbols are the same as in Figure 4, except that the symbols with positive sign are filled. The data below 51.0 °C are positive, those above 69.0 °C are negative, and the data at 55.0 and 63.0 °C change their signs from positive to negative with time, as shown in the figure.

The master curve and shift factors obtained here may be different from those for pure polystyrenes since the present sample contains 3.1% of toluene. The relaxation moduli thus observed may arise from two kinds of deformations in molecular conformation and intersegment distance.

The ratio of birefringence, Δn, to strain, ϵ, observed together with tensile stress are plotted against time in a double-logarithmic way in Figure 7. The birefringence due to change of intersegment distances is predominant at low temperatures so that $\Delta n/\epsilon$ is positive. At high temperatures the contribution of conformational deformation on birefringence becomes significant, so that the birefringence is negative at temperatures higher than ca. 70 °C. In the vicinity of 55–65 °C, the birefringence changes its sign from positive to negative with time. This means that the intersegment distances are first changed immediately after a strain is given on the film and then the conformational deformation is induced gradually. Naturally, the apparent stress-optical coefficient, C, which is defined by the ratio between birefringence and stress observed at the same time, shows behavior similar to that shown in Figure 8. At low temperatures C is positive, whereas at high temperatures it is negative. In the intermediate region, it changes its sign from positive to negative with time. If we estimate the limiting value of C at the infinitely short time and also at the infinitely low temperature from these data, the limiting value of C is found to be in good agreement with the literature value of C_g.[6]

By inserting the data in Figures 4 and 7 into eqs 1 and 2 and assuming the literature values for C_r and C_g, we can obtain two components, σ_r and σ_g. The calculated values of both stresses at different temperatures are plotted against time in the form of the relaxation modulus in Figure 9. Although σ_r in polymer films in the glassy state is only slight, the observation of the stress is possible since the absolute magnitude of C_r is much higher than C_g.

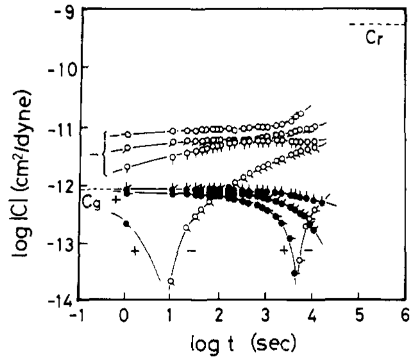

Figure 8. Temperature and time dependences of the apparent stress-optical coefficient $C(t)$. The data correspond to those in Figure 7.

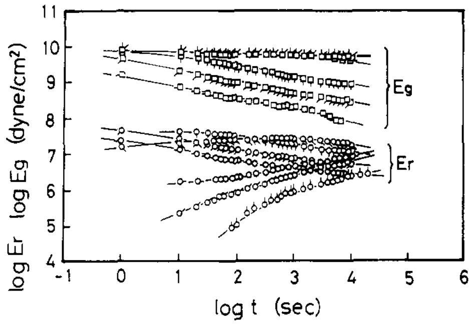

Figure 9. Separation of rubberlike stress (E_r) and glasslike stress (E_g) in observed relaxation modulus $E(t)$. Circles denote E_r, while squares denote E_g. Symbols correspond to those in Figure 4.

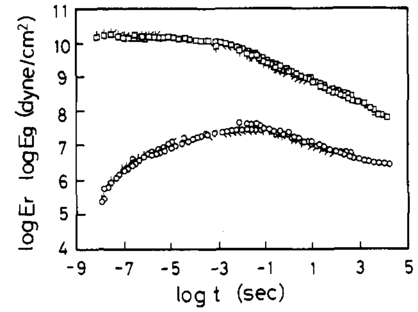

Figure 10. Master curves of $E_r(t)$ and $E_g(t)$ obtained by shifting the data in Figure 9, assuming the same shift factors as in Figure 6. The standard temperature is 80.5 °C.

The plots of $\log E_g$ vs $\log t$ in Figure 9 as well as those of $\log E$ vs $\log t$ in Figure 4 are so flat that it is difficult to determine the shift factors to construct their master curves. The shift factors were in practice determined by shifting the data of $\log E_r$ vs $\log t$ in Figure 9 to form a master curve. Then, the master curves for E_g and E were constructed, assuming the same shift factors as those for E_r. The shift factors thus determined are shown in Figure 6, in comparison with a WLF equation.[7,8] Although it is well-known that the WLF equation is not applicable in the glassy state, it may be worthwhile to compare it with the data determined from E_r.

The master curves thus obtained for E_g and E_r are compared with each other in Figure 10. It is observed that the conformational deformation of macromolecules does not occur immediately when a strain is given to the film if the sample is in the glassy state. The change of intersegment distances occurs first and the conformational deformation is gradually induced. The additivity of σ_r and σ_g and also the use of the same shift factors for both σ_r and σ_g are merely assumptions to be carefully studied in the future. However, the above conclusion may be at least qualitatively accurate, since the apparent stress-optical coefficient changes its sign from positive to negative with time in the optically transient region, as is discussed in Figures 7 and 8.

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References and Notes

(1) Priss, L. S.; Vishnyakov, I. I.; Pavlova, I. P. *Int. J. Polym. Mater.* **1980**, *8*, 85.

(2) Read, B. E. *Polym. Eng. Sci.* **1983**, *23*, 835.

(3) Aspnes, D. E.; Studna, A. A. *Appl. Opt.* **1975**, *14*, 220.

(4) Janeschitz-Kriegl, H. *Adv. Polym. Sci.* **1969**, *6*, 170.

(5) Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer-Verlag: Berlin, 1983.

(6) Rudd, J. F.; Andrews, R. D. *J. Appl. Phys.* **1960**, *31*, 818.

(7) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.

(8) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.