Birefringence of Amorphous Polymers. 4. Large Deformation of Polystyrene near Its Glass Transition Temperature

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ABSTRACT: The stress, f, and the birefringence, Δn, were measured for polystyrene at 98 °C under large deformations; after an instantaneous elongation (0.6–2%) and during an elongation at constant speed (initial rate of elongation = 5.5×10^{-4}–2×10^{-3} s^{-1}). The stress-optical rule was not valid. The data were analyzed in terms of the modified stress-optical rule, in which each of f and Δn was assumed to be a sum of two terms and the stress-optical rule was assumed valid separately for each set of components: $f = f_R + f_G$ and $\Delta n = C_R f_R + C_G f_G$, where C_R and C_G are material constants. The slowly relaxing component of Young's relaxation modulus, $E_R = f_R/e$, was independent of the strain, e, while the rapidly relaxing component, $E_G = f_G/e$, decreased with strain. At a constant speed of elongation, one component of stress, f_R, increased with time and was close to that evaluated from E_R with linear viscoelasticity theory. The other component, f_G, exhibited a marked overshoot and then decreased with time. This component was much smaller than that derived from E_G through a linear viscoelasticity relation. The yield phenomenon at a constant speed of elongation is due to the behavior of the G component, and the slow increase of stress at long times is due to the increase of the R component, presumably associated with the deformation of polymer segments.

Introduction

The strain-induced birefringence of polymer melts and rubbers is related to the stress through the stress-optical rule.[1] The rule does not hold valid for polymers in the glassy or the glass-to-rubber transition zones. Read proposed the use of the birefringence data to study the conformational change of polymer chains in the transition zone based on his modified stress-optical rule.[2] The present authors have proposed another version of the modification and claimed its usefulness in the studies of glassy polymers.[3-6] The new version is formally the same as that of Read and reads

$$E(t) = E_G(t) + E_R(t) \qquad (1)$$

$$O(t) = C_G E_G(t) + C_R E_R(t) \qquad (2)$$

where E is Young's relaxation modulus and O is the strain-optical ratio, the ratio of the birefringence, Δn, to the strain, e, following a small instantaneous elongation of the polymer; E_G and E_R are components of Young's modulus, and C_G and C_R are material constants. One of the constants, C_R, is assigned the stress-optical coefficient obtained in the rubbery plateau zone. The other, C_G, is given by

$$C_G = O''(\omega)/E''(\omega) \text{ (at high frequencies)} \qquad (3)$$

where E'' and O'' are respectively the imaginary parts of the complex Young's modulus and the complex strain-optical ratio in oscillatory measurements. The ratio on the right-hand side was found to be constant over a wide range of high frequencies for polystyrene[3] and some other polymers.[6] Read chose the short-time limit of the ratio $O(t)/E(t)$ or the high-frequency limit of the ratio of the real parts of dynamic complex quantities, $O'(\omega)/E'(\omega)$, as the value of C_G.[2] Given the values of C_R and C_G, eqs 1 and 2 can be regarded as a simultaneous equation and solved for two unknowns, E_R and E_G, at each time, t.

For a few polymers studied so far, the component functions derived with the new version of the modified stress-optical rule exhibited some remarkable features.[3-6]

(1) The reduced variables method with respect to time and temperature is applicable to each of the component functions, $E_G(t)$ and $E_R(t)$, and the failure of the method for viscoelastic functions as discussed by Plazek[7] may be accounted for as due to the difference in the temperature dependence of the two components.[4,5]

(2) The component function E_G represents a large part of the glass-to-rubber relaxation. The functions for various polymers are reduced to an almost unique function independent of the polymer species if the scales for time and modulus are suitably chosen. The variety of behavior of the birefringence for various polymers is evidently due to the variety of values of C_G and C_R.[6]

(3) The component function E_R, representing the relaxation at long times of the glass-to-rubber transition zone, may be compared to the function derived from a spring–bead model theory.[8] The size of a segment obtained from comparison of theory and experiment is in reasonable agreement with that obtained for dilute polymer solutions.[3,6,9]

These features may be useful in elucidating the relaxation mechanism of glassy polymers. For example, the third feature suggests a possibility that the relaxation of the entropic elasticity of flexible polymers is separated out as E_R from the rest of the glass modulus.

The purpose of the present study is to apply the modified stress-optical rule to the large deformation of polystyrene near the glass transition temperature. First, we apply eqs 1 and 2 to the stress and birefringence following an instantaneous elongation of up to 2% and see what the component functions, E_G and E_R, look like at large deformations. Second, we apply the same method to the stress and birefringence in an elongation at constant speed to examine if the birefringence measurement could be useful in investigating the large deformation behavior including the yield phenomenon.

Experimental Section

The specimen of 0.7 mm thickness was made by melt-pressing the pellet of polystyrene (Toporex GP550-51, Mitsuitoatsu Chemicals, Inc.) at 150 °C followed by slow cooling down to room temperature in the press. The tensile stress and the birefringence in uniaxial elongation were measured at 98 °C with a tensile tester equipped with a simple optical system, of which details were described previously.[4,10] At 98 °C, the modulus varied from about 10^9 to 10^6 Pa in the time range of measurement and the glass-to-rubber transition zone was covered in each relaxation

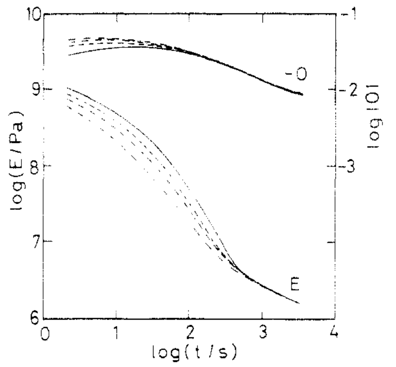

Figure 1. Young's relaxation modulus, E, and the strain-optical ratio, O, for polystyrene at 98 °C. Magnitudes of strain, e, are 0.006–0.009 (solid line), 0.012 (dashed line), 0.017 (dash-dotted line), and 0.02 (dash-two-dotted line).

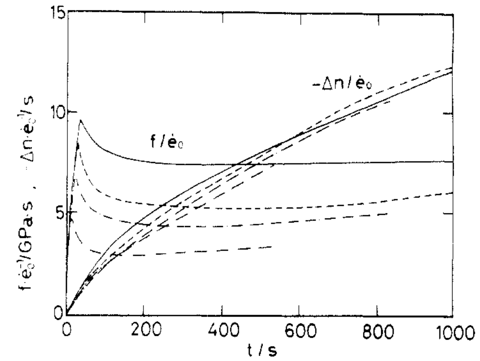

Figure 2. Ratios $f/\dot{e}_0$ and $\Delta n/\dot{e}_0$ at various speeds of elongation. Various types of lines represent the initial rates of elongation, $\dot{e}_0$; $\dot{e}_0/10^{-3}$ s^{-1} = 0.55 (solid line), 1.1 (dashed line), 1.4 (dash-dotted line), and 2.0 (dash-two-dotted line).

measurement. The specimen was attached to the clamp of the apparatus with one end free and kept at 120 °C for 15 min to remove the remaining birefringence. The temperature was lowered to 100 °C at a rate of 1 °C/3 min, and the free end of the specimen was tightened. The temperature was lowered at a rate of 1 °C/h to 98 °C, at which the specimen was kept for 1 h before the measurement.

The tensile stress, f, and the birefringence, Δn, were measured after an instantaneous elongation of 0.6–2%. The strain was applied within 0.5 s. The sample was broken at a higher elongation. Measurements were also performed in an elongation at a constant speed corresponding to the initial elongation rate, $\dot{e}_0$, of 0.055–0.2%/s. Since the elongation ratio, $\lambda = 1 + \dot{e}_0 t$, was large (up to about 2 for each measurement), the rate of elongation was not constant during the experiment. The elongation rate at time t is given by

$$\dot{e}(t) = \dot{e}_0/\lambda(t) \tag{4}$$

In evaluating the stress and the birefringence from the directly detected quantities, the tensile force and the retardation, respectively, one needs the exact thickness of the specimen. We estimated the thickness from the initial thickness assuming that the material is incompressible or that the Poisson ratio is equal to 0.5. The Poisson ratio for glassy polystyrene is reported to be 0.33.[11] If this value is good for our sample, the estimated error for the stress due to our assumption is 13% at $e = 0.5$. The error for the birefringence is smaller. We expect that the Poisson ratio at 98 °C is larger than 0.33 and hope that the error due to the assumption of incompressibility is not too serious.

Results

The results for instantaneous deformation are shown in Figure 1. The strain-optical ratio, O, was negative over the whole range of measurements. The relaxation Young's modulus, E, varied from about 10^9 to 10^6 Pa in the range of measurement. The E as well as the O was independent of strain when the elongation was less than 0.9%. At higher elongations, E decreased and $|O|$ increased with increasing strain. The effect of varying strain was weak at long times. For the modulus, the effect became weak at the level of about 3×10^6 Pa where the curves show a tendency of leveling off. This result may indicate that the nonlinear behavior is a characteristic property in the glass-to-rubber transition zone and disappears in the rubbery plateau zone.

The results for the elongation at a constant speed are shown in Figure 2 as the ratios $f/\dot{e}_0$ and $\Delta n/\dot{e}_0$ plotted against t. These ratios decreased with increasing $\dot{e}_0$ except for some deviation in $\Delta n/\dot{e}_0$ at long times, which is probably due to the uncertainty of the data. The birefringence was always negative, and its absolute value increased with time. The stress exhibited a marked overshoot (yield) at a short time, decreased over a certain time, and finally turned to increase slowly with time. At very short times, each of $f/\dot{e}_0$ and $\Delta n/\dot{e}_0$ was independent of the strain; the behavior in this range may represent the linear viscoelastic behavior.

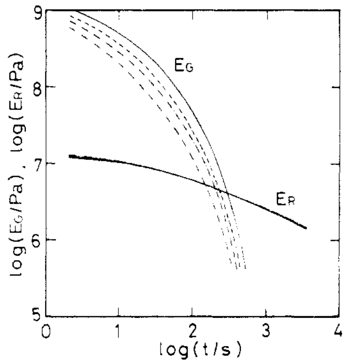

Figure 3. Two components of Young's relaxation modulus, E_G and E_R, evaluated from the data of Figure 1. Various types of lines represent magnitudes of strain as in Figure 1.

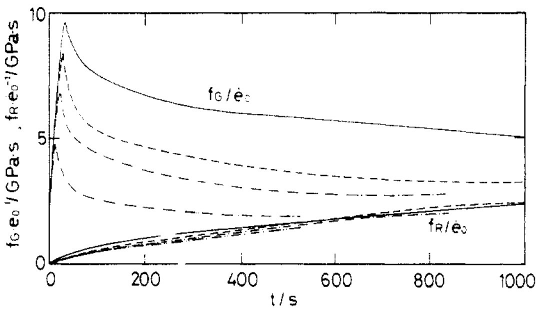

Figure 4. Two components of stress, f_G and f_R, at various speeds of elongation evaluated from the data of Figure 2. The ratios $f_G/\dot{e}_0$ and $f_R/\dot{e}_0$ are plotted against time. Various types of lines have the same meaning as in Figure 2.

Discussion

Modified Stress-Optical Rule. The modified stress-optical rule, eqs 1–3, was applied to the data of Figure 1. The coefficients were taken from a previous study; $C_R = -5.0 \times 10^{-9}$ Pa^{-1} and $C_G = 3.0 \times 10^{-11}$ Pa^{-1}. The component functions, E_G and E_R, are shown in Figure 3. E_G was a rapidly decreasing function of time, while E_R decreased more slowly over a wider range of time. This result is in accord with the previous result obtained at small strains.[4] The function E_G decreased with increasing strain, but E_R remained independent of the strain over the range of measurement. The nonlinearity of E and O seen in Figure 1 can be attributed to the nonlinear nature of E_G.

The modified stress-optical rule to be applied to the data of Figure 2 may be given by eqs 1–3 with all the letters E in eqs 1 and 2 replaced by f. The equations are

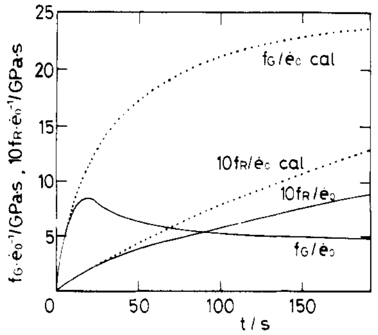

Figure 5. Comparison of the experimental values (solid line) and the calculated values from eq 5 (dotted lines) for the stress components f_G and f_R at a constant speed of elongation; $\dot{e}_0 = 1.1 \times 10^{-3}$ s^{-1}.

to be solved for two quantities, f_R and f_G, with measured quantities, f and Δn, placed on the left-hand side. The result of the analysis is shown in Figure 4. The G component of stress, f_G, is very close to the total stress, f, especially at short times. The difference is that the former keeps decreasing or levels off at long times while the latter increases. The ratio $f_G/\dot{e}_0$ decreases much with increasing $\dot{e}_0$; f_G exhibits a marked feature of nonlinear viscoelasticity. The R component, f_R, is an increasing function of t over the range of measurements and obviously the increase of f at long times is attributable to the increase of f_R. It is to be noted that the ratio $f_R/\dot{e}_0$ decreases with increasing $\dot{e}_0$ but only very slightly.

Comparison of Two Strain Histories. In Figure 5 the observed f_G and f_R are compared with those derived from E_G and E_R, respectively, with the linear viscoelasticity relation:[12]

$$f_X(t) = \int_0^t E_X(t-t')\, \dot{e}(t')\, dt' \quad (X = \mathrm{G\ or\ R}) \qquad (5)$$

As expected, the observed values of f_G are close to the calculated ones only over a limited range of very short times where the strain is small. On the other hand, the observed values of f_R are in good agreement with the calculated ones up to about 3% elongation. The agreement is not very bad even at quite a large elongation, 20%, corresponding to the longest time shown in Figure 5. This result is consistent with the result shown in Figure 3 that the component E_R was independent of the strain at least up to 2% elongation. The R component of stress may exhibit nonlinear behavior at strains higher than a few percent, but the degree of nonlinearity may not be as large as that of the G component.

In order to take account of the three-dimensional nature of the simple elongation, one may prefer to replace $\dot{e}(t')$ of eq 5 with

$$\frac{d}{dt'}\frac{(\lambda^2 - \lambda^{-1})}{3} \qquad (6)$$

However, the difference between this expression and that of eq 4 is small and does not cause a significant difference in the calculation for the range of strain shown in Figure 5. The deviation between the observed and the calculated values is not due to such a geometrical factor but to a real nonlinear characteristic of each component of stress.

Considering the fact that the stress–strain relation in the rubbery zone is linear, one may note that the deviation between the observed and the calculated values of f_R is rather large. As a possible origin of the deviation, one may speculate that the strain-induced change of the matrix, as represented by the marked nonlinearity of f_G, affects the effective deformation of the segment. It may be interesting to investigate theoretically the dynamics of a polymer chain immersed in a nonlinear matrix. One may also imagine that an additional relaxation mode appears at large deformations, and the present method of analysis becomes invalid. We have no idea how to prove or deny such a possibility.

On the Origin of the Two Components of Stress. In previous studies, we have conjectured that the G component of stress is due to some kind of interatomic potential and the R component to the entropic elasticity of polymer segments originating from the thermal motion of flexible polymer chains.[3,4] The approximately linear property of the R component observed over a wide range of strain may be consistent with the suggested entropic origin; a typical model based on the concept of the segment[8] is well-known for its linearity of viscoelasticity at large deformations apart from that caused by the geometrical factor, such as the difference between eqs 4 and 6.[14]

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References and Notes

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