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Measurement of Transient Behavior of the Thermal Diffusivity of Flowing Polymer Melt[1]

H. Miyamoto[2] and A. Nagashima[2,3]

Molecular orientation of polymer molecules created by shear force due to the flow of the polymer melt in a duct rapidly relaxes after the change in the shear rate. This relaxation causes the changes in anisotropic behavior of mechanical, thermal, and optical properties which have strong effect in precision forming of casted polymer products. Among these properties, thermal diffusivity is one of the most difficult properties to measure by the conventional techniques. The present paper describes and discusses the subsecond measurement of relaxation characteristics in thermal diffusivity anisotropy of flowing polymer melt in conjunction with measurements of some typical flow characteristics. The method used was the forced Rayleigh scattering method, an optical method which was developed and modified by the authors' group for applying to oriented polymer materials. The measuring time of 1 ms can trace the relaxation occurred in the order of several seconds. Measured results of thermal diffusivity anisotropy were compared with transient characteristics of the flow and quantitatively showed a good agreement with estimated behavior of oriented polymer molecules.

KEY WORDS: anisotropy; forced Rayleigh scattering method; polymer melt; thermal diffusivity; transient behavior.

1. INTRODUCTION

When steady shear force is applied to a polymer-melt layer, molecular orientation takes place and this causes anisotropy of mechanical, optical, as well as thermophysical properties of the melt. Quantitatively precise information on the anisotropy especially in thermal properties is strongly needed for industrial processing of advanced polymer products because

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[2] Department of Mechanical Engineering, Keio University, Hiyoshi, Yokohama 223, Japan.

[3] To whom correspondence should be addressed.

flow behavior and solidification of the process are affected by the anisotropy of the thermal conduction in the polymer layer.

The present paper reports the subsecond determination of the anisotropy of the thermal diffusivity in a flowing polymer-melt layer with the aid of the so-called forced Rayleigh scattering method. In this case, the molecular orientation and the anisotropy were created by the shear force in the flowing melt layer, and the main interest of the study lies in transient responses of fluid dynamic and thermal behavior of the melt.

Using an experimental system with a two-dimensional flow Channel, measurements were carried out for determinations of (1) anisotropic flow characteristics of melt, (2) transient response of anisotropy in the thermal diffusivity at the start of flow, and (3) relaxation of the anisotropy of the thermal diffusivity due to sudden stop of the steady flow. Described here are the outline of the method, the experimental arrangement, and a conclusion of results, which have been partly reported before.

2. PRINCIPLE OF THE METHOD AND ESTIMATION OF TIME CONSTANT

The principle of the present experimental method, the forced Rayleigh scattering (FRS) method, details of the method, and of reliability tests were reported in previous publications on various substances including high-temperature molten salts, polymer films, and microscopic samples [1–3]. Here we present only an outline of the principle.

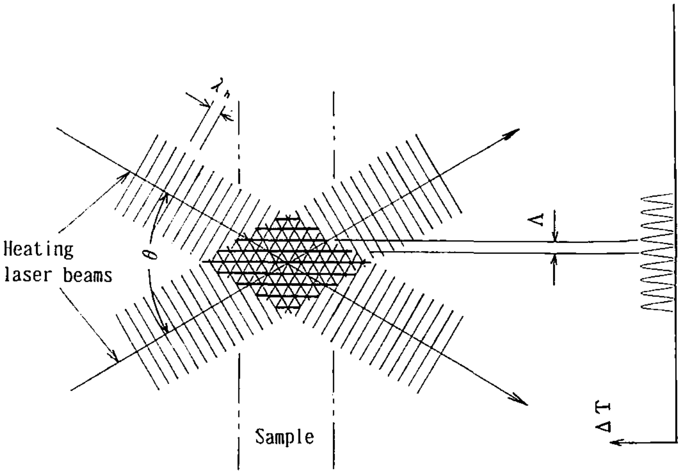


Fig. 1. Distribution of refractive index.

As shown in Fig. 1, two heating laser beams of wavelength λ with crossing angle θ coincide on the layer of a thin sample and create a periodic distribution of temperature ΔT, which corresponds to a periodic distribution of the refractive index. The periodic distance Λ is determined from the wavelength and the crossing angle. If the heating is terminated in a short time (for example, less than 1 ms in the case of the present study), the periodic temperature distribution decays with time due to heat conduction in the sample layer. Thermal diffusivity is determined by solving the heat conduction equation considering the time constant of this decay. Various factors affecting the measurement, such as three-dimensional conduction, depth dependence of absorption of the laser beam, and Gaussian distribution of heating power on the surface, were studied experimentally and analytically in earlier publications [1–3].

Since heat conduction takes place in the direction perpendicular to the fringe pattern, the directionally selective measurement can be made. Figure 2 shows a typical example of heating and decaying processes in one experiment. From the time constant of the decay τ, thermal diffusivity a is calculated. The decay is measured by recording the strength of the first-order diffraction of a probing laser beam through the heated spot.

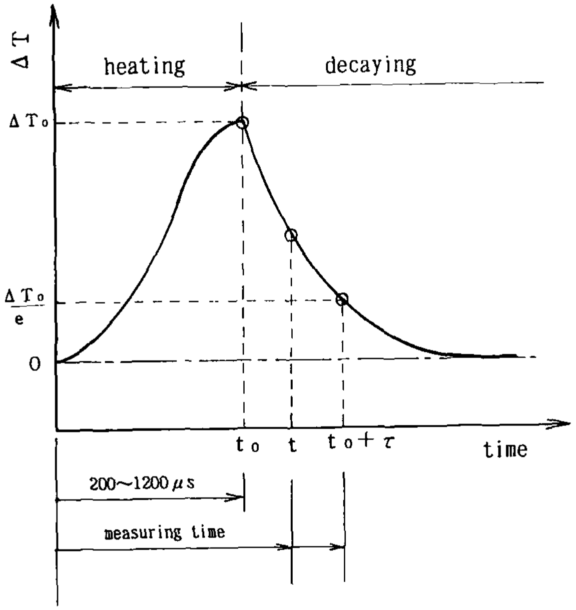


Fig. 2. Temperature distribution in the sample during heating and decaying periods.

In the present study, our main interest is on the transient response of the thermal diffusivity anisotropy after sudden changes of flow. Therefore, it is important to estimate the order of measurement time or time constants of heating–cooling and detecting processes. From our earlier check measurement [3], the time needed for heating by a laser beam for our purpose is 400 μs and the appropriate magnitude of the grating is about 40 μm. As explained later, the thermal diffusivity of molten polystyrene (PS) is about $6 \times 10^{-8}\,m^2 \cdot s^{-1}$. Therefore, τ is of the order of 0.7 ms and it is possible to complete one run of measurement in 1 ms even with the heating period included. Since the cooling curve shown in Fig. 2 is exactly exponential, it is possible to extrapolate the time t to τ, the time constant. The time constant τ can also be calculated from the decay of refracted beam-intensity. These facts indicate that the submicrosecond measurement is performed with the forced Rayleigh scattering method.

An additional feature of the forced Rayleigh scattering method is that the method is capable of direction-selective measurement of the thermal diffusivity for its easy adjustability of grating direction.

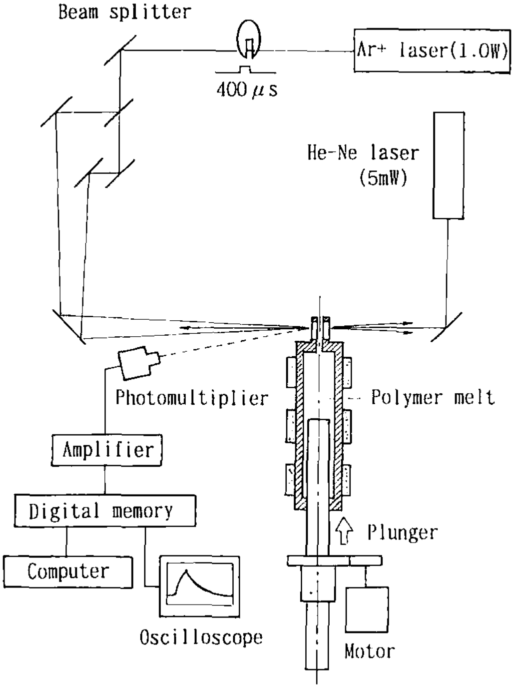


Fig. 3. Schematic diagram of the experimental apparatus.

Figure 3 shows the schematic diagram of an apparatus based on the forced Rayleigh scattering method. After the sample attains the stable molten state at the aimed temperature, transient flow field was created by changing the driving speed of the plunger by adjusting the rotational speed of a variable-speed motor. A part of the flow channel is formed by two parallel plates made of Pyrex glass (15 mm in height and 55 mm in length) which is used as an observation window. Through the window, a heating beam (argon laser) and a detecting beam (He–Ne laser) were applied to a flowing sample, namely, polymer melt. The melt, transparent polystyrene resin in the present study, was faintly colored by dye in order to absorb argon laser radiation.

3. CONSIDERATIONS AT STEADY STATE

Before starting the transient measurements, the flow parameters and the molecular orientation due to shear force under steady state were checked.

For testing flow parameters for polymer melt, the LDV system shown in Fig. 4 was used. Poiseuille flow of polymer melt was created in a circular

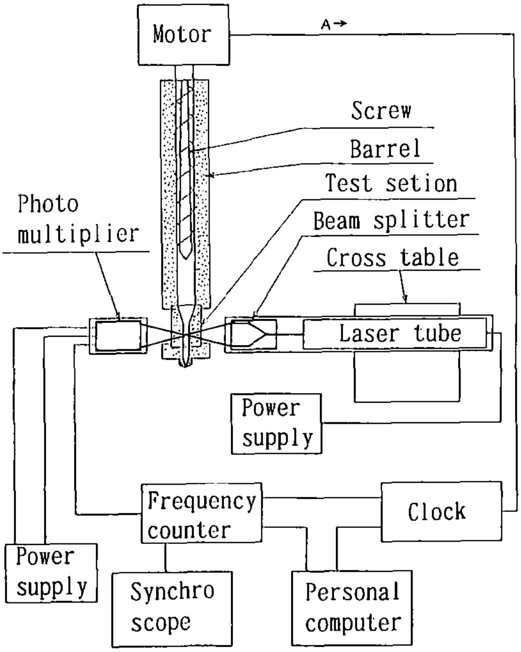


Fig. 4. Inner velocity measuring system in the extruder.

extension part made of glass (inner diameter, 8 mm) and the velocity distribution was measured by LDV. Time signal A is sent to the LDV system. Figure 5 shows the velocity distribution of polystyrene melt at different temperatures. Measured data (circles) are compared with the calculation (solid curve) based on the assumption of the power-law model, for which the shear rate versus viscosity curve was obtained by fitting data of polystyrene melt measured by capillary method at various temperatures.

The results show a good agreement and it is appropriate to assume that the exponential model is suitable for polystyrene melt. When discussing the thermal diffusivity, we need to select parameters representing the flow characteristics, such as mean velocity, velocity gradient, pressure gradient, shear force, shear force gradient, and Reynolds number. However, in the case of the present experimental method, the laser-induced grating is clear at the glass surface due to absorption in the melt. This means that the distribution of molecular orientation is affected by local flow characteristics. The velocity distribution in the vicinity of the wall surface is important. We have taken this consideration into account using the results reported in an earlier publication [4].

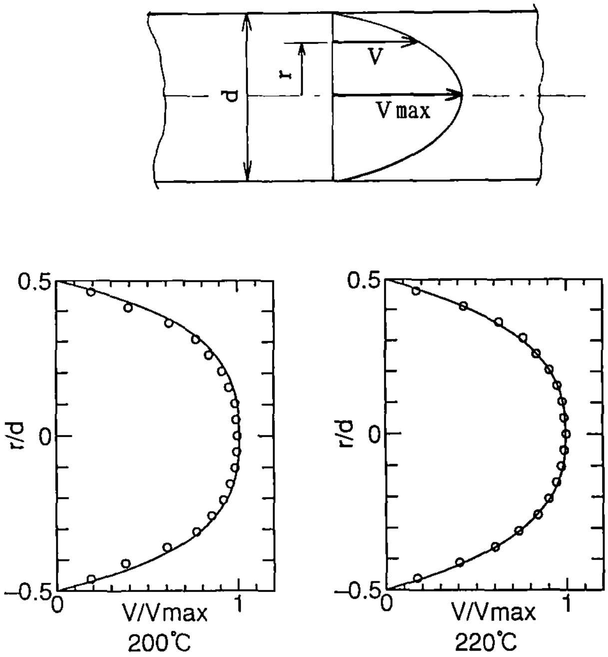


Fig. 5. Tube flow velocity profiles for a power-law fluid (numerical calculation and experimental values).

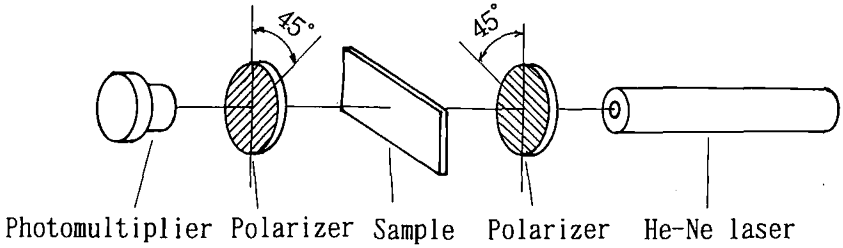


Fig. 6. System to measure birefringence.

The ratio $a_{\parallel}/a_{\perp}$ is a parameter which shows the magnitude of anisotropy in thermal diffusivity in conjunction with the flow direction, where $a_{\parallel}$ is the thermal diffusivity parallel to and $a_{\perp}$ is that perpendicular to the flow. Molecular orientation is often checked with the aid of birefringence. Using the principle shown in Fig. 6, birefringence was

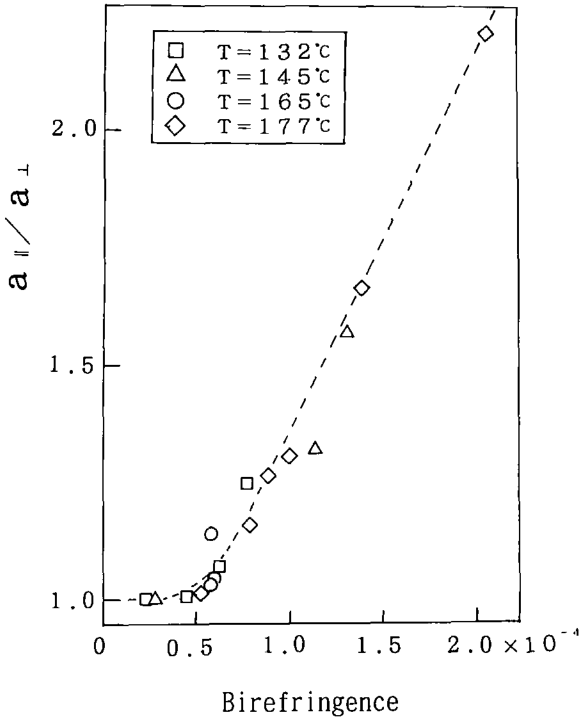


Fig. 7. Comparison of the anisotropy in thermal diffusivity with results on birefringence.

measured and compared with the ratio $a_{\perp}/a_{\perp}$. Figure 7 shows the relation between the thermal diffffusivity ratio and the birefringence for a mean flow velocity of 16.7 to 217 mm $\cdot$ s^{-1} at various temperatures. A linear relation is confirmed at a higher velocity of melt flow. At a lower velocity, some deviation from linearity is observed since birefringence represents the total anisotropy across the flow layer, while the ratio $a_{\parallel}/a_{\perp}$ gives anisotropy near the solid wall.

4. TRANSIENT BEHAVIOR OF THERMAL DIFFUSIVITY ANISOTROPY

In the molten state molecular movement is easier and therefore the transient behavior of molecular orientation in response to the change of flow conditions is interesting. The melt flow was controlled by adjusting the movement of a plunger. Figure 8 shows the transient response of the measured thermal diffusivity as a function of time after the sudden start of melt flow at different temperatures. Numerical figures show calculated values of the shear rate at the wall surface assuming the exponential fluid model. A very interesting feature is the "overshoot phenomenon" of the thermal diffusivity 0–10 s after the start of flow. The overshoot is more significant at a higher shear velocity. This fact means that the molecular

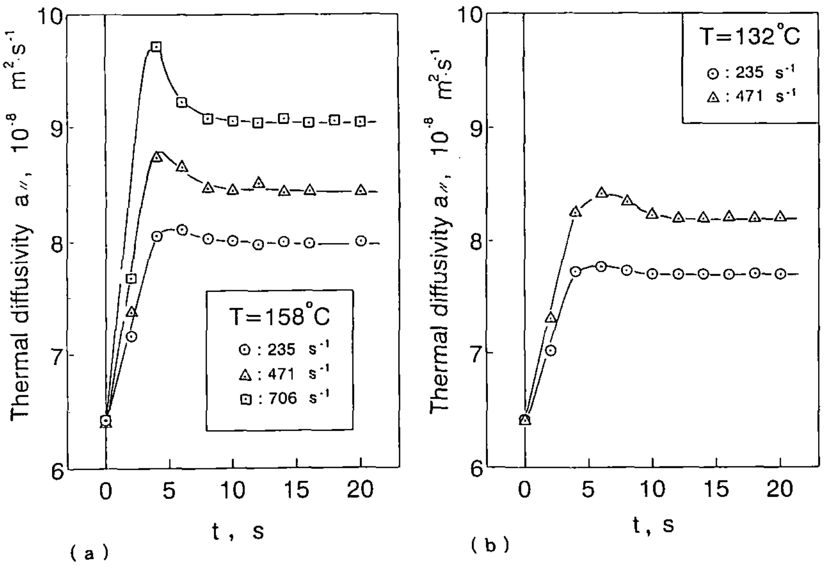


Fig. 8. Startup response of the thermal diffusivity parallel to the flow.

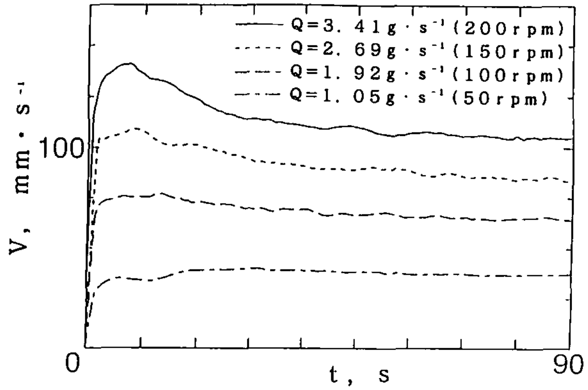


Fig. 9. Flow velocity in the extension part of an extruder after a sudden start of the shear flow, which changes the screw revolution of the extruder.

orientation gradually returns to that at steady state of the flow after the quick response of the molecular orientation.

Figure 9 shows the response of the flow velocity after the sudden start of the flow at the center of the circular tube (8 mm in diameter) measured by LDV. The curves show mean values for polystyrene at 220°C. *Q* is the

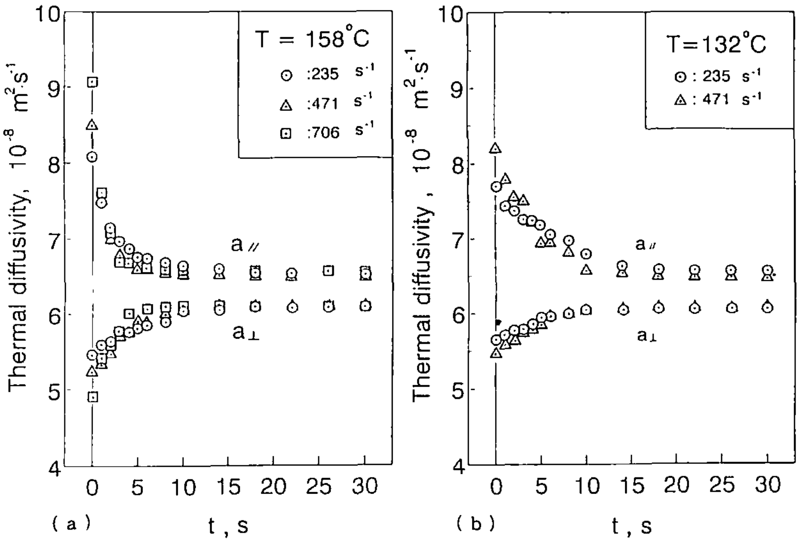


Fig. 10. Relaxation of thermal diffusivity parallel and perpendicular to the flow after sudden stop of the flow.

mass flow rate calculated from the rotational speed (RPM means revolutions per minutes) of a driving motor. At higher flow rates the shear rate at the wall surface is larger. This behavior is similar to that in Fig. 8.

The overshoot phenomenon of thermal conductivity has been experimentally confirmed for a polymer melt for the first time. The result corresponds to the already known overshoot phenomenon of the stress–strain relation in viscoelastic fluids.

If steady flow of polymer melt is stopped suddenly, relaxation of molecular orientation takes place. Figure 10 shows quantitative results of measurement of thermal diffusivity $a_{||}$ and $a_{\perp}$ as a function of time after the sudden stop. The relaxation of anisotropy, namely, the ratio $a_{||}/a_{\perp}$, is given in Fig. 11. Figure 12 shows relaxation of birefringence. We can see a very good correspondence between the exponential relaxation behavior of thermal and optical properties, although there is a small difference due to the difference in observation path in the fluid layer as mentioned before.

In order to generalize these considerations, the nondimentionalized ratio shown below is compared with the nondimentionalized time, namely, the product of time t and shear rate γ.

$$\frac{(a_{||}/a_{\perp})-(a_{||}/a_{\perp})_b}{(a_{||}/a_{\perp})_{\max}-(a_{||}/a_{\perp})_b}$$

where $(a_{||}/a_{\perp})_{\max}$ is the ratio of the thermal diffusivities at $t=0$ and $(a_{||}/a_{\perp})_b$ is the ratio of thermal diffusivities at $t \to \infty$. The results are shown

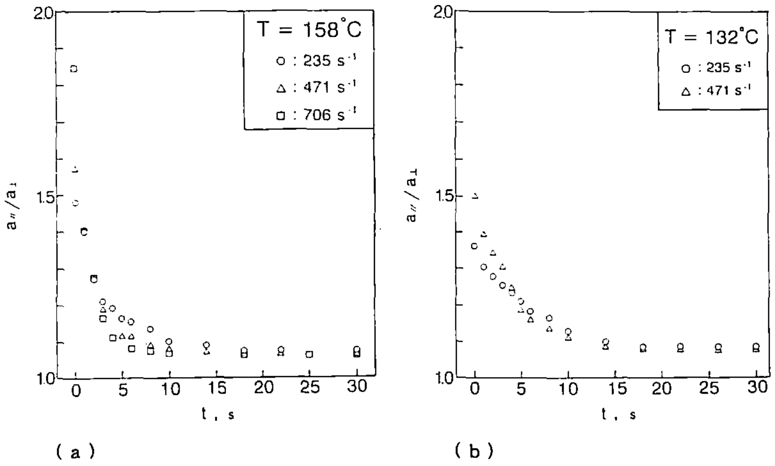
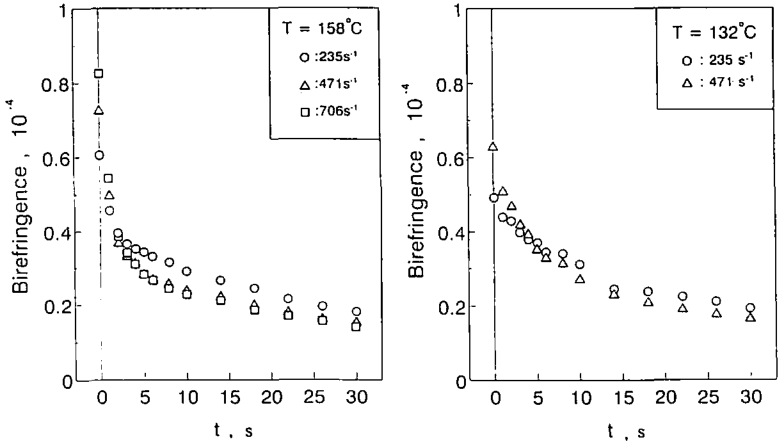


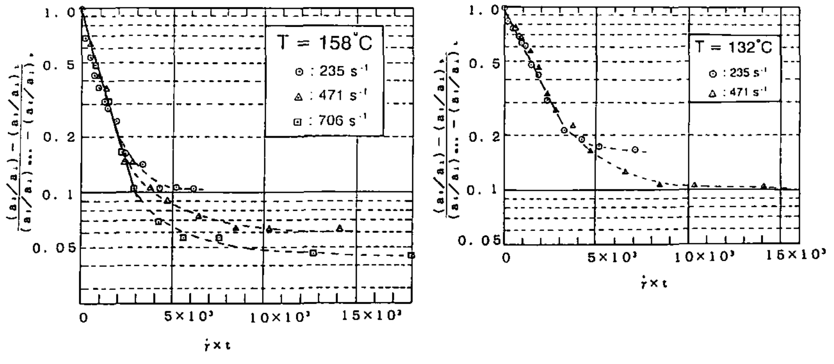
Fig. 11. Relaxation of anisotropy in thermal diffusivity.



(a) (b)

Fig. 12. Relaxation of birefringence.

in Fig. 13. In the range of smaller nondimensionalized times (0 to about 3000), all the data show exponential decay and can be represented by a single curve in spite of the different shear rate. The effect of different shear rate is represented by the time of departure from the curve, and this time is shorter for a smaller shear rate. The effect of different temperatures is represented by the gradient of the curve at the earlier part of the nondimensionalized time. As seen from Fig. 13, relaxation of thermal diffusivity anisotropy is more rapid at higher temperatures.



(a) (b)

Fig. 13. Relaxation of anisotropy in thermal diffusivity expressed in a dimensionless form.

5. CONCLUSIONS

The transient response of molecular orientation in a flow of polymer melt was experimentally and quantitatively studied by measuring thermal diffusivity anisotropy with the aid of the forced Rayleigh scattering method. When a high shear force is suddenly applied to a molten polymer layer in an initially stationary condition, an overshoot phenomenon takes place not only for the mechanical but also for thermal and optical properties. When a steady flow of molten polymer is suddenly stopped, relaxation of thermal diffusivity appears due to the relaxation of molecular orientation. This relaxation is exponential, and the relaxation time is short at higher temperatures and for higher shear rates in the initial shear flow.

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