Measurement of Orientation Relaxation Process as a Method to Study Polymer Chain Dynamics

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ABSTRACT: Time evolutions of orientation function $f(t)$ of uniaxially stretched polystyrene films were measured in temperature region higher than the glass transition temperature T_g by polarized Fourier transform infrared spectroscopy (FTIR). Time temperature superposition principle was valid for the data of $f(t)$ obtained at $T = 108$—$130°C$. From the observation of the master curve of $f(t)$, it was found that the relaxation in time region from glass transition to the biginning of terminal flow can be observed. Further, from a comparison between $f(t)$ and stress relaxation elastic modulus $E(t)$, it was shown that the same information obtained by rheological measurement in non-linear region can be obtained by observation of $f(t)$.
    KEY WORDS   Orientation Relaxation / Infrared Spectroscopy / Polystyrene
    / Stress Relaxation /

Dynamics of a single polymer chain in melts and concentrated solutions are closely related to the mechanical properties of polymeric materials. Hence, the study of polymer chain dynamics is important at both academic and industrial points of view. Recently, Lee et al.[1,2] measured time evolutions of orientation function f of uniaxially stretched polystyrene films by Fourier transform infrared (FT-IR) spectroscopy at a temperature higher than the glass transition temperature T_g. They concluded that the orientation function $f(t)$ divided by that at time $t = 0$ (or that as stretched) corresponded to the fraction of monomer remained in the original tube formed at $t = 0$, and was described by Doi–Edwards theory[3] yielding the relaxation time T_r having the molecular weight, M_w, dependence of $T_r \propto M_w^{2.9}$. However the relaxation times they

obtained seem to be smaller than those usually obtained by rheological measurement

On the other hand, Monnerie et al.[4,5] measured the orientation function f as a function of strentching rate $\dot{\varepsilon}$. The orientation function f obtained for films with a constant stretching ratio λ was superposed well into the single composite master curve by regarding the inverse of $\dot{\varepsilon}$, $\dot{\varepsilon}^{-1}$, as time and using the WLF equation. Further, the time evolution of the master curve thus obtained was the same as that of the stress relaxation modulus $E(t)$. From the comparison between $f(\dot{\varepsilon}^{-1})$ and $E(t)$, they proved that the time period of observation coressponded to that in the rubbrery plateau region. The temperature at which the orientation relaxation was measured by Lee et al. was comparable to the temperature region where the measurement of $f(\dot{\varepsilon}^{-1})$ was carried out by

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Monnerie et al. Therefore, we think that those relaxation modes observed by Lee et al. and Monnerie et al. cannot be largely different.

In this investigation, we measured time evolution of the orientation function of polymer chain by polarized FTIR and stress relaxation in temperature region higher than T_g. First, we examined the validity of the results of Lee et al. Then, we tried to superpose the relaxation data of $f(t)$ by using WLF equation. From the molecular weight dependece of the muster curve thus obtained, we discuss the molecular motion of polymer chain that can be observed by the measurement of $f(t)$. Further, we measured $\dot{\varepsilon}$-dependence of f according to the method of Monnerie et al., and discuss differences between two methods and the possibility of applying the observation of the orientation relaxation to study polymer chain dynamics.

EXPERIMENTAL

Samples and Sample Preparation

Eight monodisperse polystyrene (PS) samples supplied from Toyo Soda Co. and Pressure Chemical Co. and a polydisperse sample (PS666) were used. Their weight-average molecular weight $\bar{M}_w$ and molecular weight distribution $\bar{M}_w/\bar{M}_n$ are listed in Table I. The PS films were casted from benzene solutions of concentrations $C = 5$—15 wt%. Namely, the benzene solution was at first casted on murculy at atmospheric pressure and room temperature. After that, the obtained film was dried in vacuum at temperature higher than T_g in one day. The thickness of film thus finally obtained was about $80 \mu m$.

Uniaxial Stretching

The film thus obtained was uniaxially stretched in an oben controlled at the required temperature within the experimental error of $\pm 0.5°C$. After stretching a film up to the required stretching ratio λ at the required stretching rate $\dot{\varepsilon}$, the stretched sample was taken

Table I. Molecular weight and molecular weight distribution of polystyrene samples

Sample	$\bar{M}_w$	M_w/M_n	Supplier
F-20	1.9×10^5	1.04	TOHSO
F-36	3.55×10^5	1.02	TOHSO
F-40	3.9×10^5	1.10	Pressure Chemical
F-80	7.1×10^5	1.05	TOHSO
F-126	1.26×10^6	1.05	TOHSO
F-186	1.86×10^6	1.12	Pressure Chemical
F-288	2.89×10^6	1.09	TOHSO
F-334	3.34×10^6	1.04	TOHSO
PS666	6.6×10^5	5.19	

out immediately in order to freeze the residual orientation.

Measurement of Orientation Function

The infrared dichroism $R (= A_{\parallel}/A_{\perp})$ defined as the ratio of the absorbance in the direction pararell to the molecular axis, $A_{\parallel}$, to that perpendicular to the molecular axis, $A_{\perp}$, was measured by FTIR (FTIR 4000, Shimadzu Seisakusho) with grid polarizer at $2 \, cm^{-1}$ resolution and 200 accumulation. The orientation function f was calculated by

$$f = (R-1)(R_0+2)/(R+2)(R_0-1) \qquad (1)$$

where $R_0 = 2 \cot^2 \alpha$ with α being the angle between the dipole moment vector of vibration and the chain axis. The absorption band measured here was $(906 \, cm^{-1})$ and the correspondent value of α was 33 deg[6].

Measurement of Time Evolution of the Orientation Function

The PS films stretched at $T = 114°C$ according to the method described in foregoing paragraph was fixed at the sample cell by using an adhesive. The values of $\dot{\varepsilon}$ and λ are $0.1 \, s^{-1}$ and 3.8, respectively. The sample was inserted in a thermostat controled at required temperature, which is higher than T_g, within $\pm 0.2°C$. The time to attain thermal equilibrium was about 20 s. The sample annealed for 5 min was quickly taken out from the thermostat once to measure the change in infrared dichroism $R(t)$

in every 5 min, and then returned to the thermostat. From the change in $R(t)$ in every 5 min thus determined, the orientation function $f(t)$ was calculated as a function of the annealing time t according to the method described above. For the data of $f(t)$ obtained at temperature $T = 108$—$130°C$, we tried to superpose into a single composite master curve by assuming the applicability of the WLF equation. The standard temperature was 120°C, and the WLF equation in this case was[4]

$$\text{lof } a_T = -9.06(T - 120)/(69.8 + T - 120) \quad (2)$$

Measurement of Dependence of f on the Rate of Strain $\dot{\varepsilon}$

In order to compare our $f(t)$ and $f(\dot{\varepsilon}^{-1})$ of Monnerie *et al.*,[4,5] we measured f at a constant λ as a function of the stretching rate $\dot{\varepsilon}$. Details of the experiment are given in ref 4. In this investigation, data of f ranging in λ from 2 to 5 were measured for films stretched at a constant $\dot{\varepsilon}$. From the λ-dependence thus determined, f at $\lambda = 4$ was read off. The master curve of $f(\dot{\varepsilon}^{-1})$ was obtained by regarding $\dot{\varepsilon}^{-1}$ as time t and assuming the applicability of the WLF equation of eq 2. Values of $\dot{\varepsilon}$ ranged from 0.03 to $0.12\,s^{-1}$.

Stress Relaxation Measurement

Measurement of stress relaxation was carried out by thermo mechanical analyzer (TMA/SS 100, Seiko Instruments Co.). Time evolution of the stress arised in the film immediately after the stretching up to $\Delta L = 50\,\mu M$ at the rate of $100\,\mu m\,min^{-1}$ was recorded. The length, width, and thickness of the film used were $L = 10\,mm$, $W = 2\,mm$, and $T \sim 10\,\mu m$, respectively.

RESULTS

Relaxation of Orientation at a Constant Temperature

Figure 1 shows time evolutions of $f(t)$ obtained at $T = 114.1°C$ for various molecular weight. The relaxation of $f(t)$ for $\bar{M}_w = 1.9 \times$
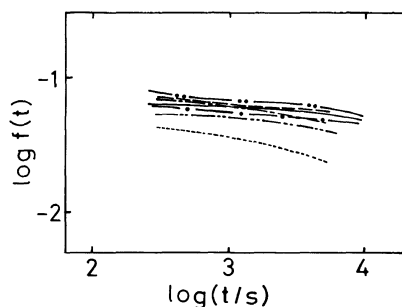

Figure 1. Time evolutions of $f(t)$ at $T = 114.1°C$ for $\bar{M}_w = 1.9 \times 10^5$ (------), 3.55×10^5 (— - - —), 3.9×10^5 (— - —), 7.1×10^5 (——), 1.26×10^6 (-●●-), 2.89×10^5 (—●—), and 3.34×10^5 (——).

10^5 was slightly faster than that for other molecular weights. Further, except for $\bar{M}_w = 1.9 \times 10^5$, the time evolution of $f(t)$ was molecular weight independent. Lee *et al.*[1] observed $f(t)$ at $T = 114.5°C$ for polystyrenes with $\bar{M}_w = 1.7 \times 10^5$—$9.0 \times 10^5$, and reported that $f(t)$ for $\bar{M}_w = 1.7 \times 10^5$—$3.9 \times 10^5$ depended strongly on molecular weight. Since the molecular weight dependence of the relaxation time τ_r was $\tau_r \propto \bar{M}_w^{2.9}$, they concluded that the relaxation of $f(t)$ for $\bar{M}_w = 1.7 \times 10^5$—$3.9 \times 10^5$ corresponded to the reptation process. Although the temperature measured here is almost the same as that of Lee *et al.*, the data obtained here are molecular weight independent except for $\bar{M}_w = 1.9 \times 10^5$. In addition, as described later, the molecular weight dependence at $\bar{M}_w \sim 1.9 \times 10^5$ in Figure 1 is not as strong as that reported by Lee *et al.* Therefore, we think that the relaxation process observed by Lee *et al.* was not the reptation process. Actually, the values of the relaxation time derived by Lee *et al.* are extremely smaller than those for reptation process which are usually obtained from rheological measurement[7-9]. Further, as shown in Figure 2, the time evolution of $f(t)$ for $\bar{M}_w = 3.9 \times 10^5$ agrees fairly well with that of the relaxation modulas $E(t)$ measured at same temperature. The data of $E(t)$ show that the time region where the orientation relaxation was measured corresponds to that of rubbery plateau region.
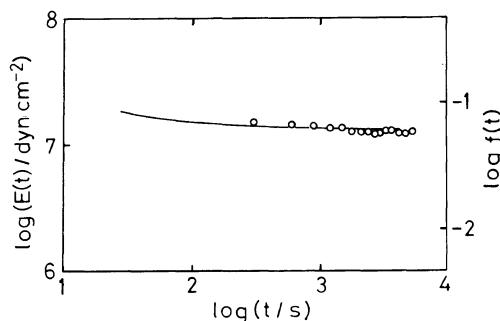
Figure 2. Time evolutions of $f(t)$ ($\bigcirc$) and $E(t)$ (———) at $T=114.1°C$ for $\bar{M}_w=7.1\times10^5$.
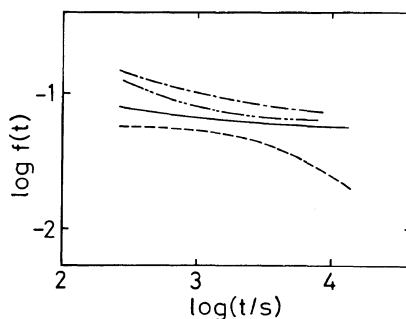

Figure 3. Time evolutions of $f(t)$ for $\bar{M}_w=1.86\times10^5$ measured at $T=108°C$ (— · —), $110°C$ (— · · —), $120°C$ (———), and $130°C$ (— — —).

Test of the Time–Temperature Superposition Principle

Figure 3 shows $f(t)$ for $\bar{M}_w=1.86\times10^6$ measured at temperature T from 108 to 130°C. $f(t)$ gently decreased at $T<110°C$, but was almost independent of t at $T=120°C$, and then largely decreased again at $T=130°C$. In spite of the complexity of the temperature dependence, the superposition of $f(t)$ by shifting the data along the abscissa seems possible. Then we calculated the shift factor a_T by the WLF equation of eq 2, and tried to superpose the data of Figure 3. The standard temperature was 120°C. The composite master curve thus obtained is shown in Figure 4. The superposition is faily good. In order to examine the correspondence between $f(t)$ and $E(t)$, the master curves of $f(t)$ and $E(t)$ measured under same conditions for $\bar{M}_w=7.1\times10^5$ are shown in Figure 5. Until time $t\sim10^3$ s, the time evolutions of $f(t)$ and $E(t)$ are the same showing the relaxation typical in the rubbery plateau region. However, the orientation relaxation function $f(t)$ appears to decrease faster than $E(t)$ in a time region larger than $t\sim10^3$. In order to compare $f(t)$ with $E(t)$ measured in lower $E(t)$ region, we made comparison of $f(t)$ with $E(t)$ measured by Tobolsky *et al.*[8] in Figure 6. The molecular weight used in the comparison is $\bar{M}_w=1.9\times10^5$. The decrease of $f(t)$ is obviously faster than that of $E(t)$. It is known that the stress relaxation elastic modulas after large deforma-
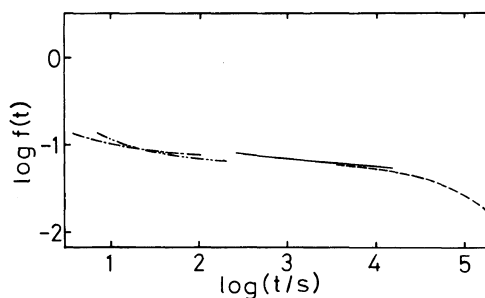

Figure 4. Composite master curve of $f(t)$ at standard temperature $T_s=120°C$. Symbols are the same as those used in Figure 3.
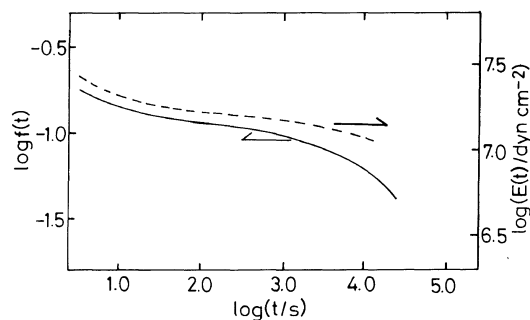

Figure 5. Composite master curves of $f(t)$ (———) and $E(t)$ (— — —) at $T_s=120°C$ for $\bar{M}_w=7.1\times10^5$.

tion starts to decrease faster than $E(t)$ in linear viscoelasticity as a result of the non-linear effect.[10–13] $f(t)$ in this experiment was the data obtained for the PS film deformed up to $\lambda\sim4$. Therefore, the earlier decrease of $f(t)$ observed here may be due to the non-linear effect in
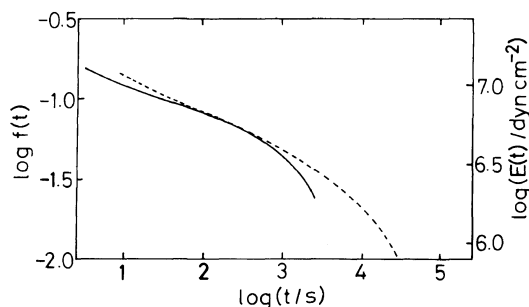
Figure 6. Composite master curves of $f(t)$ (——) and $E(t)$ (———) measured by Tobolsky *et al.*[8] at $T_s = 120°C$ for $\bar{M}_w = 1.9 \times 10^5$.
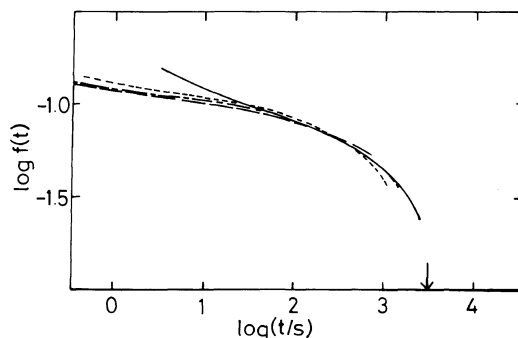

Figure 8. Superposition of $f(t)$ by shifting the data along the abscissa. Symbols are the same as those used in Figure 7.
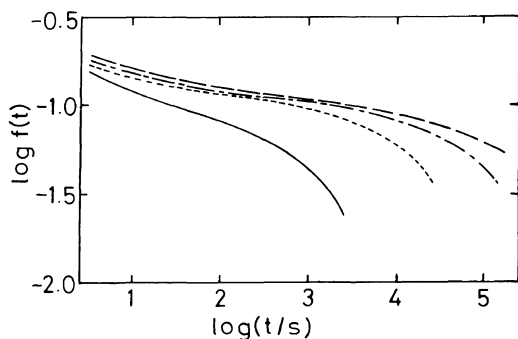

Figure 7. Composite master curves of $f(t)$ at $T_s = 120°C$ for $\bar{M}_w = 1.9 \times 10^5$ (——), 7.1×10^5 (······), 1.86×10^6 (—·—), and 2.89×10^6 (———).
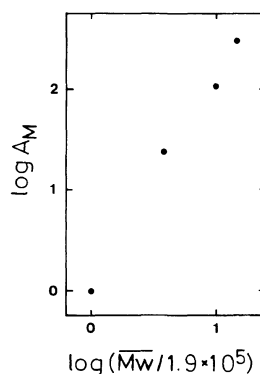

Figure 9. Molecular weight dependence of the shift factor A_M in the superposition of $f(t)$ in Figure 8.

viscoelasticity. Masteer curves of $f(t)$ obtained for $\bar{M}_w = 1.9 \times 10^5 \sim 2.89 \times 10^5$ are shown in Figure 7. $f(t)$ for $\bar{M}_w = 1.9 \times 10^5$ went on decreasing from the biginning of the relaxation, but those for other molecular weights exhibited the evident plateau before decreasing. The time period showing the plateau changed depending on the molecular weight and increases with increasing $\bar{M}_w$. In order to investigate the molecular weight dependence of the relaxation time which characterizes the decrease in longer time region, we tried to superpose the relaxation curve in longer time region to that for $\bar{M}_w = 1.9 \times 10^5$ by shifting the data along the abscissa. The resultant composite curve is shown in Figure 8. The superposition was fairly good. The molecular weight dependence of the shift factor A_M is shown in Figure 9 in a double

logarithmic scale. The slope of the figure is about 2, and hence the shift factor A_M, or the relaxation time τ_1, depends on $\bar{M}_w$ as $A_M \propto M^2$, or $\tau_1 \propto M^2$. According to the Doi–Edwards theory,[3] a polymer chain immediately after the large deformation shrinks along the tube formed by surrounding polymers, in order to recover its equilibrium chain length, and then slips out of the tube and into a new one. The shrinking process obeys the Rouse relaxation mechanism yielding the molecular weight dependence of the relaxation time $\tau_R \propto M^2$. The process of escape from the tube is based on the reptation mechanism, and its characterization time τ_r depends on $\bar{M}_w$ as $\tau_r \propto M^3$. The value of 2 for the slope in Figure 9 suggests that the relaxation in longer time region observed here corresponds to the Rouse relaxation of a

polymer chain in the shrinking process. The Rouse relaxation time was evaluated from linear viscoelastic data for non entangled PS[14] by using the relations of $\tau_R = 6\eta_0 M/\pi^2 \rho T$ and $\eta_0(M) = \eta_0(M_c)M/M_c$, where η_0 is the steady-flow viscosity, ρ the density of the polymer, M_c the critical molecular weight and R the gas constant. τ_R for $\bar{M}_w = 1.9 \times 10^5$ and at $T = 120°C$ is evaluated as $\tau_R \sim 3000\,s$ and is shown in Figure 8 as the arrow. $f(t)$ in Figure 8 shows rapid decrease in the time region from $t \sim 10^3$ to $t \sim 10^4$. This fact is not in conflict with the value of the Rouse relaxation time $\tau_R \sim 3000\,s$. Here, we want to emphasize again that the relaxation in a longer time region is not the reptation process as Lee et al. reported.[1]

Orientation Function $f(\dot{\varepsilon}^{-1})$ as a Function of $\dot{\varepsilon}$

As described above, Monnerie et al.[4,5] showed that the polymer chain dynamics can be investigated by observation of f obtained at a constant stretching ratio as a function of $\dot{\varepsilon}$ and regarding $\dot{\varepsilon}^{-1}$ as time t. Are data obtained by our method and Monnerie's method same? For example, the region and the interval of relaxation times observed by these two method may be different. Therefore, we measured $\dot{\varepsilon}$-dependence of f at $\lambda = 4$, and investigated the period of relaxation time of $f(\dot{\varepsilon}^{-1})$, and compared it with that of $f(t)$. λ-Dependence of $f(\dot{\varepsilon}^{-1})$ obtained at $\dot{\varepsilon} = 0.1\,s^{-1}$ and $T = 110$ and $114°C$ is shown in Figure 10. $f(\dot{\varepsilon}^{-1})$ obtained at $\dot{\varepsilon} = 0.03$—$0.12\,s^{-1}$ changed linearly with λ at intervals of $\lambda = 2$—5. Since there is large experimental error in the data of f, we approximated the λ-dependence of f in Figure 10 by linear function and read off f at $\lambda = 4$ in order to use in following data analysis. According to the method of Monnerie et al., we tried to superpose $f(\dot{\varepsilon}^{-1})$ measured at various temperature and $\dot{\varepsilon}$ by regarding $\dot{\varepsilon}^{-1}$ as time t and applying the WLF equation of eq 3. Along with the master curve of $E(t)$, the obtained curve of $f(\dot{\varepsilon}^{-1})$ is shown in Figure 11. The standard temperature T_s is 120°C. As described by Monnerie et al., time evolutions
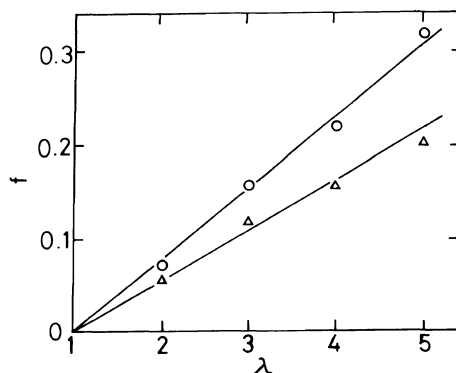

Figure 10. λ-Dependence of f at $\dot{\varepsilon} = 0.1\,s^{-1}$ and $T = 110°C$ (○) and 114°C (△).
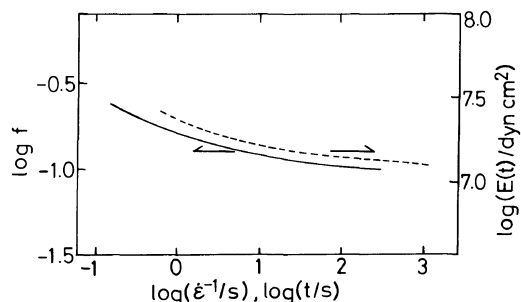

Figure 11. Composite master curves of $f(\dot{\varepsilon}^{-1})$ (———) and $E(t)$ (– – –) for PS666.

of both of $f(\dot{\varepsilon}^{-1})$ and $E(t)$ are the same within the experimental error of these two measurements. The time region of observation of $f(\dot{\varepsilon}^{-1})$ is $t = 0.1$—100 s. By considering the time evolution of $E(t)$, it is understood that the time period of observation which we can study by measuring $f(\dot{\varepsilon}^{-1})$ corresponds to that from the end of glass transition to the rubbery plateau as already shown by Monnerie et al. On the other hand, the time period of the relaxation of $f(t)$ is from $t \sim 1$ to $t \sim 10^5\,s$ as shown in Figure 7 and extends from the end of glass transition to the biginning of the terminal flow.

DISCUSSION

In this study, it was found that the same information which can be obtained by rheological measurement in non-linear region

can be obtained by observation of $f(t)$. The time period of observation ranges six orders of $t = 1$—10^5 s which extends from the end of glass transition to the bignining of the terminal flow. On the other hand, the time period of relaxation observed by measurement of $f(\dot{\varepsilon}^{-1})$ ranges four orders of $t = 0.1$—100 s. Although the temperature ranges of measurements for both of $f(t)$ and $f(\dot{\varepsilon}^{-1})$ are the same, the time regions of both measurements are somewhat different. The data of $f(\dot{\varepsilon}^{-1})$ was measured for the film obtained at $\dot{\varepsilon}$ around $0.1\ \mathrm{s}^{-1}$ and hence the corresponding time scale is around 10 s. On the other hand in measurement of $f(t)$, we measured the time evolutions of the orientation function by annealing the samples. Therefore, the time period of observation for one sample ranges from minute to hour. This makes a difference of the time period of measurement between $f(\dot{\varepsilon}^{-1})$ and $f(t)$. Another difference is that the total amounts of samples to obtain one master curve are very small for measurement of $f(t)$. Namely, the data of λ-dependence of f obtained at a stretching rate $\dot{\varepsilon}$ and a temperature T, i.e., Figure 10, are needed to obtain one data point at $t = \dot{\varepsilon}^{-1}$ and T in Figure 11. Howeveer, the time evolution of $f(t)$ at some temperature can be obtained by the measurement for one sample. On combining the two measurements, the relaxation data in time region from glass transition to terminal flow can be obtained. Moreover, measurement difficult for usual rheological measurement will be possible. For example, it is very difficult to observe individually the molecular motion of a component polymer in polymer blends by usual rheological measurement. However, the orientation relaxation measurement described here is very effective for such observation.

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