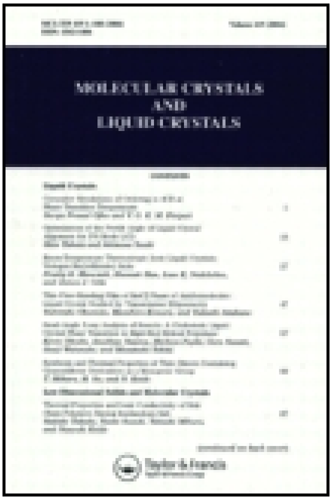

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Study on an Electrorheological Effect of Side-Chain Polysiloxanes Including Fluorine Atoms by the Preshearing Method

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Study on an Electrorheological Effect of Side-Chain Polysiloxanes Including Fluorine Atoms by the Preshearing Method

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Side-chain liquid-crystalline polysiloxane derivatives possessing fluorinated mesogens that have positive dielectric-anisotropy parallel to the long axis of mesogen were synthesized to study phase-transition behavior and electrorheological (ER) effect of the polymers with a preshearing method. About 2000 Pa increments in shear stress could be obtained after preshearing as an ER effect. In addition, shear rate dependence on shear stress as a function of temperature was investigated. As a result, it was shown that the preshearing treatment with high shear rate was important to generate a larger ER effect.

Keywords: electrorheological (ER) effect; polysiloxane; preshearing

INTRODUCTION

Electrorheological (ER) fluids are materials whose rheological properties can be controlled by an external electric field. This phenomenon is called the electrorheological (ER) effect. When the viscosity of an ER fluid increases with applied electric field, this is termed the positive ER effect. On the other hand, if the viscosity decreases with applied electric field, this is called the negative ER effect. Some liquid-crystalline materials show a positive ER effect. In particular, a large ER effect has been observed in side-chain liquid-crystalline polymers [1–3].

The effect of the liquid-crystalline materials arises from a change of an orientation of the dielectrically anisotropic mesogens under the

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applied field. This effect is more remarkable when the materials have a large positive dielectric anisotropy ($\Delta\varepsilon$), *i.e.*, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are values of the dielectric constant measured parallel and perpendicular to the long axis of mesogen, respectively [4]. Therefore, to obtain a larger ER effect, it is necessary to introduce a mesogenic group where dielectric anisotropy is positive and large. For example, the mesogens including halogen atoms in a terminal part parallel to the long axis have a positive and large $\Delta\varepsilon$ [5].

A main disadvantage of the ER effect of the liquid-crystalline polymers is high inherent viscosity, which disturbs the orientation of the mesogens under an electric field. Recently, we proposed a new method for the measurement of the ER effect of liquid-crystalline polymers to cause a large increment of shear stress under the electric field. This new method was named *preshearing* [6]. To arrange the terminal mesogens to a shearing direction, a shear strain with high shear rate ($350\,\mathrm{s}^{-1}$) was applied to the material before conventional measurements of the ER effect. This caused a reduction in the inherent viscosity when compared to that without preshearing.

In this research, side-chain liquid-crystalline polysiloxane derivatives possessing fluorinated mesogens were synthesized, and phase-transition behavior and the ER effect of the polymers with preshearing were studied. Moreover, we investigated shear rate dependence on the shear stress as a function of temperature.

EXPERIMENTAL

Synthesis

The synthetic procedure used in this research has been described in our previous paper [6] and others [7]. Therefore, only the procedure for new mesogens is described in detail here. Polysiloxane derivatives were prepared by a typical hydrosilylation of allyl-bearing substituted compound with 50–55% methylhydrosiloxane–dimethylsiloxane copolymer containing Si-H groups under a platinum catalyst. Figure 1 shows a synthetic route of the polysiloxane derivatives. As is shown later, the mesogens and the polysiloxane derivatives obtained here are denoted by MF-*n* and PF-*n* ($n = 1,2,3$), respectively, where *n* represents a number of fluorine atoms introduced in the mesogen.

4-Fluorophenyl-4′-allyloxybenzoate (MF-1)

4-Allyloxybenzoic acid (4.45 g; 0.025 mol), 4-fluorophenol (2.80 g; 0.025 mol), and an excess amount of polyphosphate ester (PPE) (17 g)

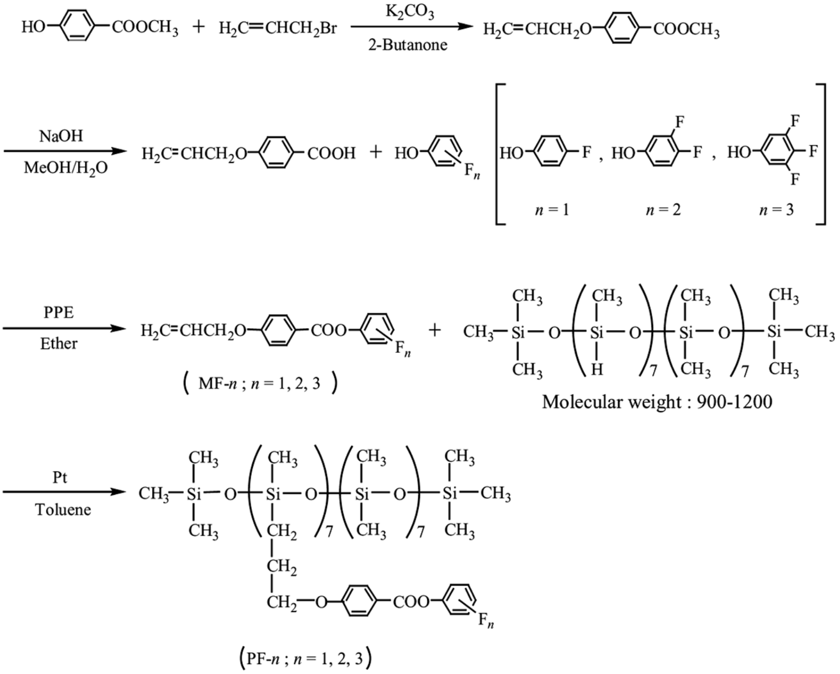


FIGURE 1 Synthetic route of the polysiloxane derivatives.

were dissolved in 150 ml of ether under an argon atmosphere, and the mixture was refluxed for 24 h. Then, 200 ml of water were added, and the mixture was extracted with CH_2Cl_2. After the solvent was distilled off, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. As a result, 2.30 g of 4-fluorophenyl-4′-allyloxybenzoate were obtained as a white solid. Yield 35%. ^{1}H NMR ($CDCl_3$) δ: 8.14 (dt, 2H, $J = 9.4$, 2.4 Hz), 7.19–7.07 (m, 4H), 7.00 (dt, 2H, $J = 9.6$, 2.2 Hz), 6.12–6.02 (m, 1H), 5.45 (dd, 1H, $J = 17.6$, 1.5 Hz), 5.34 (dd, 1H, $J = 10.2$, 1.5 Hz), 4.63 (d, 2H, $J = 5.4$ Hz).

3,4-Difluorophenyl-4′-allyloxybenzoate (MF-2) and 3,4,5-Trifluorophenyl-4′-allyloxybenzoate (MF-3)

3,4-Difluorophenyl-4′-allyloxybenzoate (MF-2) and 3,4,5-Trifluorophenyl-4′-Allyloxybenzoate (MF-3) were synthesized using 3,4-difluorophenol and 3,4,5-trifluorophenol instead of 4-fluorophenol in the same manner as mentioned previously. Data of ^{1}H NMR of MF-2 and MF-3 are shown next.

MF-2

^{1}H NMR (CDCl$_3$) δ: 8.12 (dt, 2H, $J = 9.6$, 2.2 Hz), 7.21 (q, 1H, $J = 9.3$ Hz), 7.12–7.07 (m, 1H), 7.02–6.93 (m, 3H), 6.07 (dq, 1H, $J = 22.4$, 5.4 Hz), 5.45 (dd, 1H, $J = 17.1$, 1.5 Hz), 5.35 (dd, 1H, $J = 10.5$, 1.2 Hz), 4.64 (d, 2H, $J = 5.4$ Hz).

MF-3

^{1}H NMR (CDCl$_3$) δ: 8.10 (dt, 2H, $J = 9.4$, 2.2 Hz), 7.00 (dt, 2H, $J = 9.4$, 2.2 Hz), 6.92 (dq, 2H, $J = 16.7$, 4.6 Hz), 6.09–6.05 (m, 1H), 5.45 (dd, 1H, $J = 17.6$, 1.5 Hz), 5.35 (dd, 1H, $J = 10.5$, 1.2 Hz), 4.64 (d, 2H, $J = 5.4$ Hz).

Characterization

^{1}H NMR measurements were made by a Jeol Alpha-400 FT NMR (400 MHz) spectrometer using CDCl$_3$ and DMSO as a solvent. Gel-permeation chromatography (GPC) measurements were carried out by a Tosoh HLC-8020 instrument with tetrahydrofuran as eluent to check the purity of the polymers. Standard polystyrenes were used for calibration.

Transition temperatures of the materials were determined by differential scanning calorimetry (DSC) using a Mettler DSC30 calorimeter at scanning rate of 4, 9, 16, 25°C/min. The transition temperatures were identified by extrapolation with on-set temperatures obtained at each scanning rate. Textures of the liquid-crystalline phase were observed using an Olympus BX51 polarizing optical microscope (POM) equipped with a Linkam THMS 600 hot stage and TMS 94 thermocontrol system.

X-ray difraction measurement was carried out using Laue camera. The Cu Kα radiation was used from a Rigaku generator operating at 30 kV and 15 mA, and an Ni filter was utilized in front of the detector ($\lambda = 0.154$ nm). The distance between sample and imaging plate was 45 mm, and the measurements were performed at 20°C under vaccum to prevent a scattering of the air.

Measurements

The rheological properties were measured by a rotational rheometer (Rheosol-G2000, UBM Ltd.) equipped with an electric field controller (Matsusada Precision Devices high-voltage supply). All measurements were performed using parallel plates with a diameter of 25 mm and a gap of 0.1 mm. Because the fixtures did not provide a uniform shear strain, shear rates reported in this article have been defined as the shear rate at the edge of the plate.

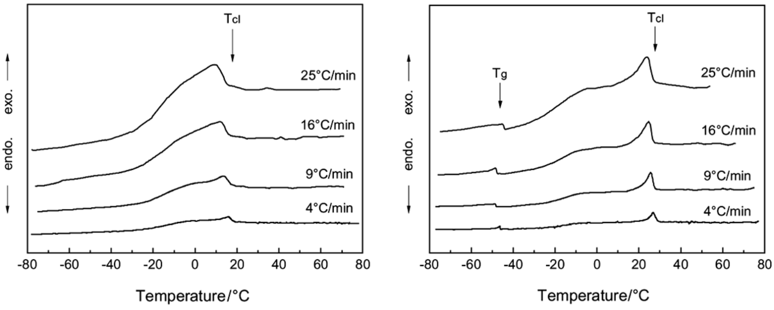
The measurements were carried out as follows. The sample was placed between the parallel plates in the isotropic phase and was held at the temperature in the isotropic phase for about 10 min. Then, the sample was cooled to the desired temperature, and the gap was readjusted to 0.1 mm long. Generated shear stress was defined as the difference between the measured shear stresses with and without applied electric field. Then, the sample was sheared with high shear rate (300–400 s^{-1}) for about 5 min before the measurement in gain a lower viscosity. After the preshearing, rheological properties under an electric field were measured at each temperature. The electric field of 2 kV/mm was applied between upper plate and lower one with shearing at a constant shear rate (50 s^{-1}), when the ER effect was measured.

With regard to the measurement of shear stress as a function of shear rate, shear stress was measured with increasing shear rate at each temperature. Note that shear rate was increased step by step from 0 s^{-1} to 500 s^{-1}.

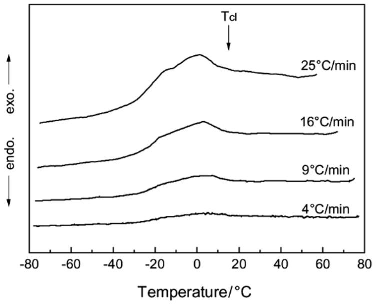
RESULTS AND DISCUSSION

Phase-Transition Behavior

DSC curves of the polymers synthesized here are shown in Fig. 2, and phase-transition temperatures are summarized in Table 1, in which the temperatures are determined by an extrapolation against 0 scanning rate using on-set temperature of the peaks obtained by various scanning rates of DSC measurements. For PF-2 in Fig. 2b, a sharp exothermic peak was observed at around 28°C. This peak was identified as a transition point from an isotropic liquid to a liquid-crystalline phase, because a sand texture was observed by polarizing optical microscope just below the peak. This sand texture changed into a bâtonnet one by annealing. These results suggested that this phase has a possibility of being smectic A. These textures are shown in Figs. 3 and 4, respectively. In addition, the typical smectic A diffraction pattern was obtained by X-ray diffraction. The diffraction pattern is shown in Fig. 5. Sharp spots are observed in the horizontal direction, and broad peaks exist in vertical ones, respectively. Under this clearing point, the side chains containing mesogenic groups were arranged in a director. Thermal molecular motion of backbones was slowing down from the clearing point with decreasing temperature, and finally it became difficult at around -17°C, accompanying shoulder of the peak in the DSC curve. Under the temperature, the motion of the side chains was still possible, but the motion began



(a) PF-1 (b) PF-2



(c) PF-3

FIGURE 2 DSC curves of (a) PF-1, (b) PF-2, and (c) PF-3 on the cooling process.

slowing gradually with decreasing temperature, and subsequently it stopped. The motion was frozen at around −48°C. Therefore, it was identified as the glass transition point.

On the other hand, PF-1 had a broad peak corresponding to its clearing temperature. The broadening of the peak is attributed to an existence of a shoulder very close to the peak. The clearing point was observed at 18.0°C, and no glass transition point was observed

TABLE 1 Phase-Transition Behavior Observed by DSC on Cooling Process

Sample		Tg (°C)		Tcl (°C)	
PF-1	G	—	SmA	18.0	IL
PF-2	G	−48.0	SmA	27.8	IL
PF-3	G	—	SmA	15.6	IL

Note. G: glass state; S_mA: smetic A; IL: isotropic liquid. The transition temperatures were determined with on-set value.

FIGURE 3 Sand texture of PF-2 taken at 25°C.

in the temperature range of the DSC measurements. Phase-transition behavior of PF-3 was fairly similar to that of PF-1. Molecular motions of the siloxane backbone and side chains are considered to exhibit basically similar behavior.

The characteristic point of PF-1 and PF-3 is that these two compounds showed a broader peak at around the clearing point compared with that of PF-2. In general, the shape of the phase-transition peak of liquid-crystalline polymers could be influenced by molecular-weight distribution. Values of molecular-weight distribution determined by GPC were 1.34 for PF-1, 1.33 for PF-2, and 1.35 for PF-3, respectively.

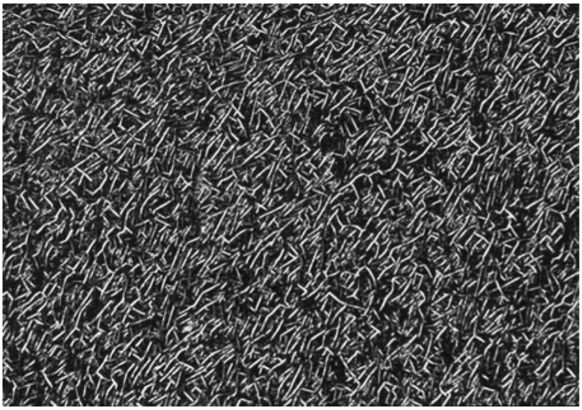


FIGURE 4 Bâtonnet texture of PF-2 after annealing.

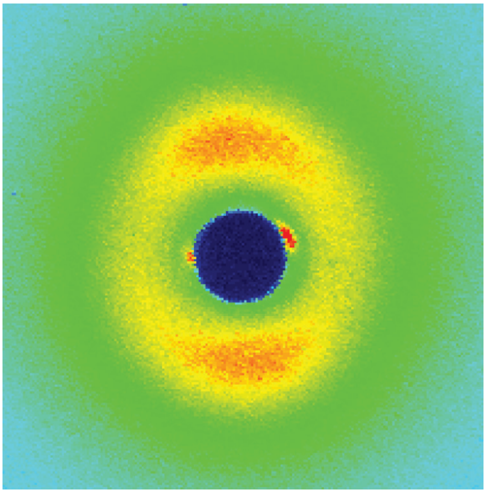


FIGURE 5 X-ray diffraction pattern for PF-2 at 20°C.

This suggests that the influence of the molecular-weight distribution on the broadness of the peaks of PF-1 and PF-3 was ruled out because these three values are regarded as almost the same.

ER Effect

Figures 6a and b shows the ER effect results of PF-1 without and with pre-shearing, respectively. These measurements were performed with $50\,s^{-1}$ of shear rate. In both cases, shear stress apparently increased with lowering temperature. As shown in Fig. 6a, the ER effect was not observed at all at each temperature. Figure 6b showed that shear stresses with the preshearing became lower than those obtained without preshearing, especially at a lower temperature range. Then, ER effect could be observed at low temperature, though an increment of shear stress was not observed in the higher temperature range.

Shear stress at 50°C and 60°C in Figs. 6a and b could not be increased by the applied electric field. This was not due to the high inherent viscosity of the sample. This was attributed to a relatively active thermal motion of the polymer backbones and flexible spacers under such temperature. It may be possible to arrange the terminal mesogens parallel to the applied electric field in this state. However, the orientation was unable to be detected well as flow resistance. In other words, the sample itself may move to the shearing direction. Consequently, the increment in shear stress became too small.

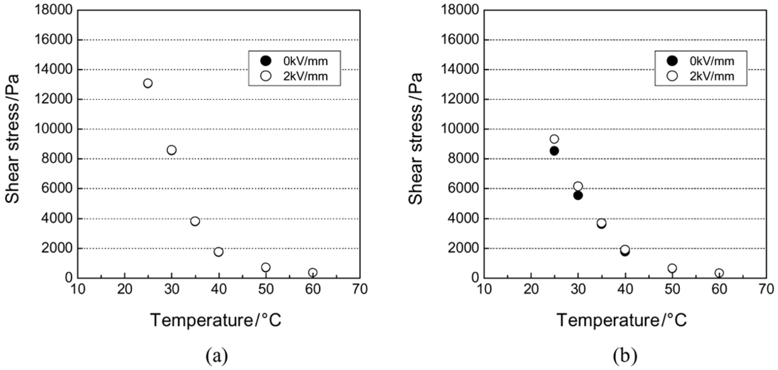


FIGURE 6 Shear stress of PF-1 under an applied electric field (2 kV/mm) with (a) no preshearing and (b) preshearing.

At temperatures colder than 40°C, the ER effect was observed at each temperature by means of preshearing.

Results of the ER effect of PF-2 and PF-3 are shown in Figs. 7 and 8, respectively. Both compounds showed the ER effect after preshearing. For PF-2, shear stress at about 30°C could not be measured because of an overloaded torque at low temperature. This was caused by the formation of the liquid-crystalline phase. It is assumed that microscopic molecular motion forming a liquid-crystalline phase began at around 30°C.

PF-3 showed the largest increase in shear stress as the ER effect in a wider temperature range. As shown in Fig. 8b, increase in shear

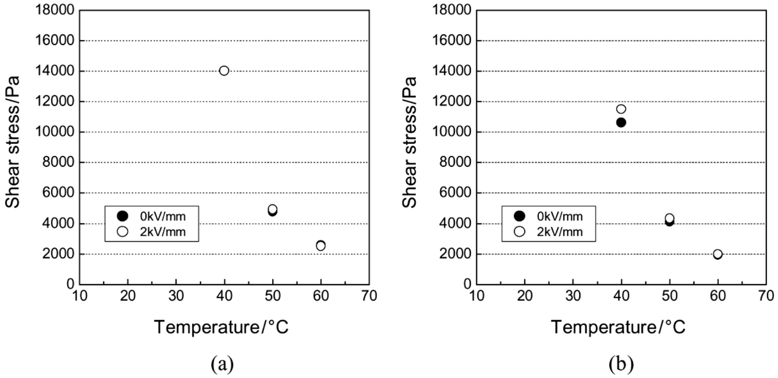


FIGURE 7 Shear stress of PF-2 under an applied electric field (2 kV/mm) with (a) no preshearing and (b) preshearing.

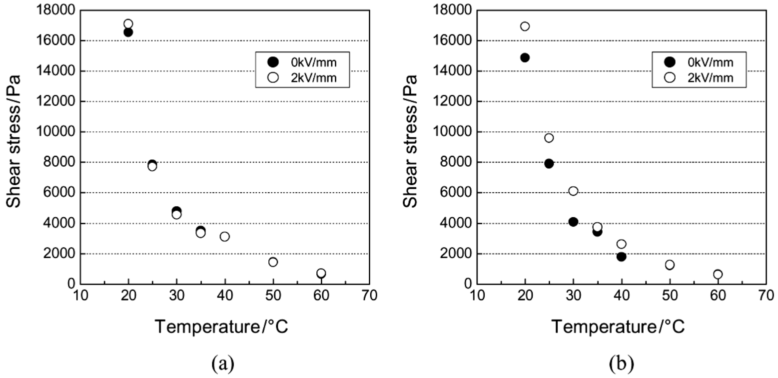


FIGURE 8 Shear stress of PF-3 under an applied electric field (2 kV/mm) with (a) no preshearing and (b) preshearing.

stress by an applied electric field was estimated to be about 2000 Pa at 20°C, 25°C, and 30°C. In the case of ER fluids composed of low-molecular-weight liquid-crystalline materials, the increase in shear stress is relatively smaller than that of liquid-crystalline polymers, though the response time is fast. For example, the enhanced shear stress of liquid-crystalline oligomers remained up to about 1000 Pa and was reported as the ER effect [8]. A few thousand generated shear stress is better taken into account for mechanical application. Therefore, it is considered that the generated shear stress observed in this study is large enough for commercial use.

A clearing point of PF-3 was observed at 15.6°C, and the ER effect was observed above the clearing point. Similar behavior was already observed by Inoue *et al.* [6]. It is likely that molecular arrangement begins gradually just above the clearing point when the measuring temperature approaches the clearing point in the cooling process. This state may be suitable for appearance of the ER effect because the polymer probably possesses middle viscosity between an isotropic liquid and liquid-crystalline phase. In addition, preshearing could be more useful in the region just above the clearing point because of easy arrangement of the mesogens to a shearing direction.

The fluorine atom is one of the strongest electronegative elements. Introduction of plural fluorine atoms into terminal part of mesogen results in a larger positive dielectric-anisotropy parallel to the long axis of mesogen. Therefore, it is correct that PF-3 showed a larger ER effect in the wider temperature range. It can be said that a large positive dielectric anisotropy led to the larger ER effect and played an important role in giving rise to orientation of the mesogens under an applied electric field.

Rheological Behavior

Shear rate dependence on shear stress of PF-3 is shown in Fig. 9. Applied shear rate was from 0 s^{-1} to 500 s^{-1}. At 60°C and 50°C, shear stress was in proportion to the shear rate, which is known as a behavior of Newtonian fluid. At 40°C, a similar behavior was also observed until 200 s^{-1}, and then the shear stress deviated from the Newtonian behavior. This may indicate that structural change in the sample will occur, for example, separation of entanglement among polymer backbones, an orientation of terminal mesogens toward a shearing direction, and so on. This deviation from the Newtonian behavior was also observed on 100 s^{-1} at 30°C and 50 s^{-1} at 25°C, respectively. At 20°C, shear stress could not be measured at more than 70 s^{-1} because of its high viscosity, which was greater than the detection limit of the instrument. It is clear that a deviation from the Newton behavior occurred earlier upon decreasing the temperature. Results of shear rate dependence on shear stress of PF-1 and PF-2 were almost similar to that of PF-3.

By means of the data obtained here, it was found out that a shearing with high shear rate apparently caused some changes in the samples, such as an arrangement of terminal mesogens toward a shearing

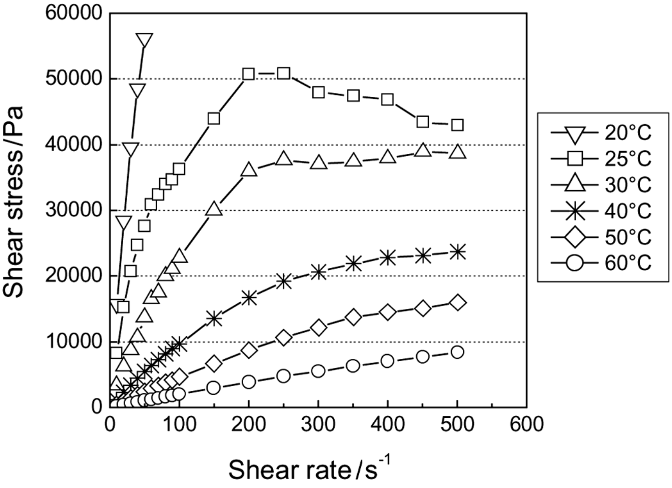


FIGURE 9 Shear rate dependence on shear stress of PF-3.

direction. In addition, a larger ER effect could be observed after preshearing, as shown in the previous section. In Newtonian behavior observed in the low-shear-rate range, response of shear stress was proportional to shear rate, suggesting that the internal change of the sample did not occur. Therefore, preshearing with high shear rate evidently caused the terminal mesogens to arrange to a shearing direction. It can be strongly concluded that preshearing is one of the most useful methods for the ER effect measurements in side-chain liquid-crystalline polymers.

CONCLUSIONS

In this study, side-chain liquid-crystalline polysiloxanes with fluorine atoms in mesogenic groups were synthesized and their rheological properties were investigated. In the measurement of the ER effect, PF-3 (of which the dielectric anisotropy in the mesogenic group was largest within the samples studied here) showed the largest increment of viscosity. A large positive dielectric anisotropy led to a larger increment of the shear stress, and the orientation of the mesogens under an applied electric field was one of the main factors showing the ER effect.

We could show the importance of preshearing with high shear rate, which generated a larger ER effect. In this case, we should apply preshearing with a higher shear rate at which shear stress completely deviated from Newtonian behavior.

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