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## Liquid Crystals

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# A novel pre-shearing technique for measurement of the electrorheological effect of a side-chain liquid crystalline polysiloxane

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A side-chain liquid crystalline polysiloxane derivative possessing mesogens was synthesized. The mesogens included a large dielectrically-anisotropic moiety. Phase transition behaviour was investigated and the electrorheological (ER) effect of the polymer considered. No ER effect was observed in non-sheared polysiloxane derivative because of its high inherent viscosity. However, a large ER effect was observed after pre-shearing. Pre-shearing, i.e. shearing with a high shear rate before the measurements, arranges the terminal mesogens in the shearing direction. Furthermore, a dilution of the sample led to a larger ER effect exceeding 10 000 Pa. We thus were able to demonstrate a new approach for the appearance of the ER effect.

## 1. Introduction

The electrorheological (ER) effect is a phenomenon via which, in general, the apparent viscosity of a fluid increases with an increase in an applied electric field and then decreases with a decreasing field. Fluids which show the effect are called ER fluids. The ER fluids are divided into two types by the mechanism of the appearance of the effect; some are particle-dispersion ER fluid and other are homogeneous. There are many reports about the former consisting of dielectric particles in insulating oil, but their practical utilization has been limited by their tendencies for the particle sedimentation, aggregation, solidification, etc. [1]. On the other hand, the latter have attracted attention from the viewpoint of mechanical applications because these fluids do not have such problems.

Some kinds of liquid crystalline materials show enhanced viscosity when an electric field is applied. They have been known to be useful as ER fluids, and there have been many reports concerning the effect [2–8]. In particular, it has been found that side-chain liquid crystalline polymers show a large ER effect. The ER effect in liquid crystalline materials arises by an orientation of the dielectrically-anisotropic mesogens under the applied field. The mechanism of the ER effect is shown in figure 1, using a model of side-chain liquid

crystalline polymer. The angle between the direction of the mesogens along shear and that of an applied electric field has been considered to play an important role in the appearance of the ER effect [7]. As a consequence of these orientations, a flow resistance is generated and the viscosity of a fluid increases. This effect is considerable when the materials have a positive dielectric anisotropy ( $\Delta\epsilon$ ), i.e.  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} > 0$ , where  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  are values of the dielectric constant parallel and perpendicular to the director, respectively [9]. Therefore, in order to obtain a large ER effect, a large value of the dielectric anisotropy in the mesogenic group is required. In general, mesogens including halogen atoms in terminal locations along the director have a large  $\Delta\epsilon$  [10].

In this research, a side-chain liquid crystalline polysiloxane derivative, possessing mesogens which included a cyano group and fluorine atom, was synthesized. The phase transition behaviour and ER effect of the polymer were investigated. In addition, we propose a new method for arrangement of the mesogens to the shearing direction in order to make a complete orientation, which plays an important role in the observance of a larger ER effect. Moreover, we tried to dilute the sample for an easy orientation of terminal mesogens under an electric field, using a solvent which makes a homogeneous solution. This may be effective in improving the response time of the ER effect.

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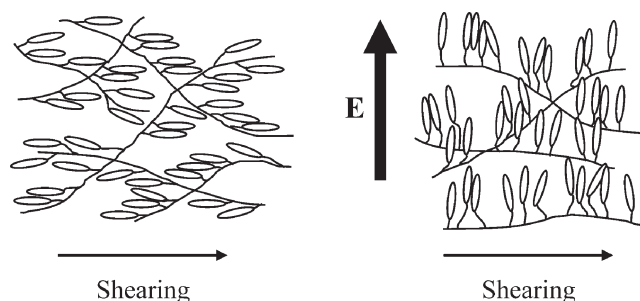


Figure 1. Mechanism of the ER effect using a model of side-chain liquid crystalline polymer.

## 2. Experimental

### 2.1. Materials

Methyl 4-hydroxybenzoate and allyl bromide were purchased from Nacalai tesque. The reagents used here, 2-fluoro-4-hydroxybenzotrile and 50–55% methylhydro-siloxane–dimethylsiloxane copolymer, were obtained from AZmax Co. Ltd. The catalysts, polyphosphoric ester (PPE) was prepared according to literature [11]. Ether and toluene used in this research were dried by sodium wire, and other solvents were used without further purification. The structure of the polymer prepared in this research is shown in figure 2.

### 2.2. Characterization

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

Differential scanning calorimetry (DSC) was conducted by using a DSC Pyris 1 (PERKIN ELMER) at heating and cooling rates of  $5^\circ\text{C min}^{-1}$ . Nikon ECLIPSE E600 optical polarizing microscope equipped with a Mettler FP-82 hot stage and a Mettler FP-90

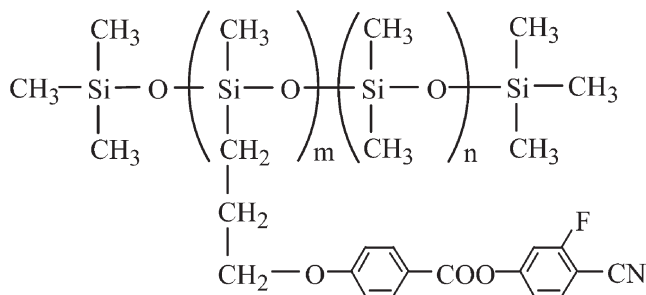


Figure 2. Structure of an objective compound.

central processor were used to observe the phase transition and analyse the anisotropic texture.

### 2.3. Synthesis

**2.3.1. Methyl 4-Allyloxybenzoate.** Methyl 4-hydroxybenzoate (10.7 g; 0.07 mol),  $\text{K}_2\text{CO}_3$  (11.1 g; 0.08 mol) and allyl bromide (16.9 g; 0.14 mol) were dissolved in 100 ml of 2-butanone, and the mixture was refluxed for 18 h. Then, the solution was washed with water and an objective compound was extracted with ethyl acetate. After the solvent was distilled off, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/5 by volume) as eluent. As a result, 12.8 g of Methyl 4-allyloxybenzoate was obtained as a transparent colourless liquid. Yield 95%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.98 (dt, 2H,  $J=9.4$ , 2.4 Hz), 6.92 (dt, 2H,  $J=9.4$ , 2.4 Hz), 6.09–5.99 (m, 1H), 5.42 (dd, 1H,  $J=17.1$ , 1.5 Hz), 5.31 (dd, 1H,  $J=10.5$ , 1.2 Hz), 4.58 (td, 2H,  $J=3.2$ , 1.6 Hz), 3.88 (s, 3H).

**2.3.2. Methyl 4-Allyloxybenzoic acid.** The obtained 4-allyloxybenzoate (11.5 g; 0.06 mol) was dissolved in 100 ml of methanol. This solution was poured into a solution containing NaOH (4.8 g; 0.12 mol) in 70 ml of water and methanol (2:5), and the mixture was refluxed for 1.5 h. After the solvent was distilled off, the residue was dissolved in water, and hydrochloric acid was added until the solution became acidic, where upon a white precipitate formed. The resulting white precipitate was filtered, washed with water. Then, the residue was washed with hexane and dried to obtain 10.1 g of 4-allyloxybenzoic acid as a white solid. Yield 95%.  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$ : 12.66 (s, 1H), 7.89 (t, 2H,  $J=4.1$  Hz), 7.04 (d, 2H,  $J=8.5$  Hz), 6.10–6.01 (m, 1H), 5.42 (dd, 1H,  $J=17.3$ , 1.7 Hz), 5.29 (dd, 1H,  $J=10.6$ , 1.3 Hz), 4.65 (d, 2H,  $J=5.1$  Hz).

**2.3.3. 4-Cyano-3-fluorophenyl 4'-allyloxybenzoate.** 4-Allyloxybenzoic acid (4.43 g; 0.025 mol), 2-fluoro-4-hydroxybenzotrile (3.43 g; 0.025 mol) and an excess amount of PPE (17 g) were dissolved in 150 ml of ether under argon atmosphere, and the mixture was refluxed for 24 h. Then, 200 ml of water was added and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . After the solvent was distilled off, the residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  as eluent. As a result, 5.45 g of 4-cyano-3-fluorophenyl 4'-allyloxybenzoate was obtained as a white solid. Yield 73%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 8.12 (dt, 2H,  $J=9.4$ , 2.4 Hz), 7.69 (t, 1H,  $J=8.1$  Hz), 7.22–7.17 (m, 2H), 7.02 (dt, 2H,  $J=9.4$ , 2.4 Hz), 6.12–6.02 (m, 1H), 5.45 (dd, 1H,  $J=17.1$ , 1.5 Hz), 5.35 (dd, 1H,  $J=10.7$ , 1.5 Hz), 4.65 (td, 2H,  $J=3.4$ , 1.8 Hz).

**2.3.4. Side-chain polysiloxane derivative.** The polysiloxane derivative was prepared (see figure 3) by a typical hydrosilylation of an allyl-bearing substituted compound (4-cyano-3-fluorophenyl 4'-allyloxybenzoate) with a 50–55% methylhydrosiloxane–dimethylsiloxane copolymer having Si–H groups under platinum catalyst. Siloxane copolymer (5.77 g;  $4.8 \times 10^{-3}$  mol) and 4-cyano-3-fluorophenyl 4'-allyloxybenzoate (10.9 g; 0.037 mol) were dissolved in 100 ml of dried toluene. Hydrogen hexachloroplatinat(IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) dissolved in a few millilitres of 2-propanol was poured into the solution, and the mixture was refluxed for 24 h. The reaction mixture then poured into an excess of methanol to precipitate the polymer. The polymer obtained was re-precipitated from its acetone solution into excess of methanol, and dried *in vacuum*. If the purification was not enough, the polymer was re-precipitated again by the same manner as mentioned above. IR (neat,  $\text{cm}^{-1}$ ): 2961 (s), 2238 (s, –CN), 1739 (s, –C=O), 1605 (s, aromatic C=C), 1580, 1511, 1471, 1433, 1245, 1149, 1047, 846, 800, 762, 690, 654, 593, 573, 560, 532, 505.

## 2.4. 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. The

measurements were carried out by following procedure. The sample was placed between the parallel plates in an isotropic phase, and was held at the temperature for about 10 min. Then, the sample was cooled to the desired temperature, and the gap was adjusted. An electric field of  $2 \text{ kV mm}^{-1}$  was applied between the upper plate and the lower one under shearing at a constant shear rate. The generated shear stress was defined as the difference between the measured shear stresses with and without application of the electric field. Because the fixtures did not provide a uniform shear strain, shear rates reported in this paper have been defined as the shear rate at the edge of the plate. Since an inherent viscosity of the sample was very high, the sample was sheared with high shear rate before the measurement in order to gain a lower inherent viscosity. This process was named as ‘pre-shearing’ by the present authors. After the pre-shearing, rheological properties under an electric field were measured at each shear rate.

## 3. Results and discussion

### 3.1. Phase transition behaviour

Figure 4 shows the DSC curves of the polysiloxane derivative. On cooling, a sharp peak appeared at  $18^\circ\text{C}$  (on-set temperature) and a baseline shift was observed at around  $-15^\circ\text{C}$ . Sand texture was observed from ca.  $18^\circ\text{C}$  and no texture changes were observed until  $-40^\circ\text{C}$  by polarized optical microscopy (POM). Owing to the typical shape of glass transition on the DSC curve, it

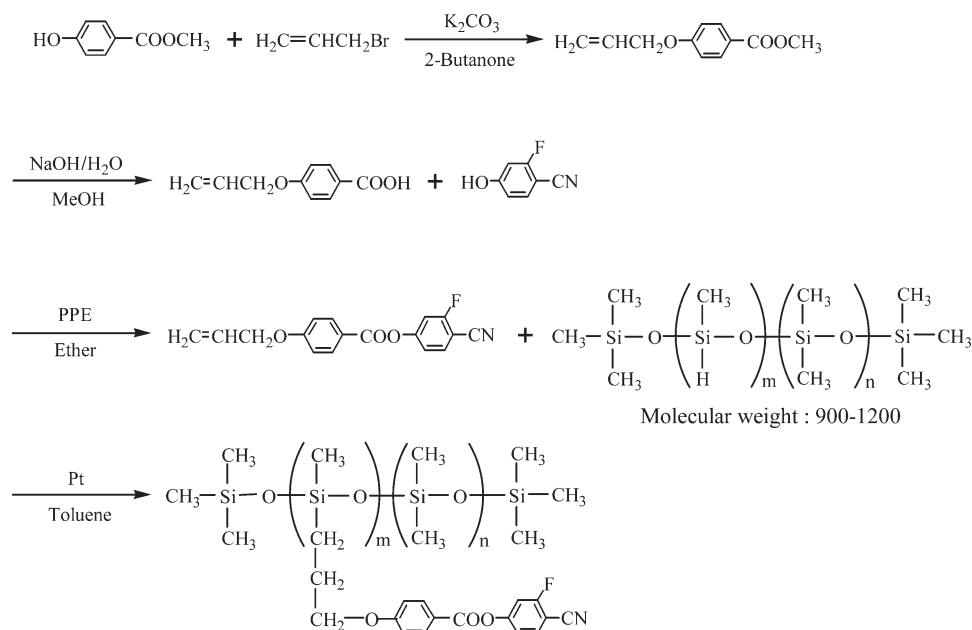


Figure 3. Synthetic route of the polymer.

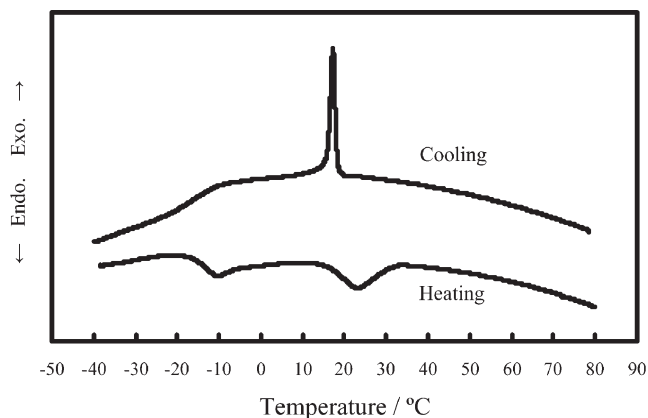


Figure 4. DSC curves of the polysiloxane derivative ( $5^{\circ}\text{Cmin}^{-1}$ ).

was considered that the baseline shift at around  $-15^{\circ}\text{C}$  corresponded to a glass transition point.

On heating, the glass transition was observed at  $-14^{\circ}\text{C}$ , and a broad peak appeared at around  $16^{\circ}\text{C}$  (onset temperature). The sand texture disappeared gradually at about  $20^{\circ}\text{C}$ , i.e. at a clearing point. Above the clearing point, the phase was confirmed as isotropic by POM.

A focal-conic texture taken by POM at  $15^{\circ}\text{C}$  after annealing for 24 h is shown in figure 5. By means of this texture, it is expected that this polymer shows a smectic phase, though it is not identified whether the phase is smectic A or smectic C.

### 3.2. Electrorheological properties

Figure 6 shows the shear rate dependence of the shear stress. It was obvious that the shear stress increased proportionally with increasing shear rate and that the

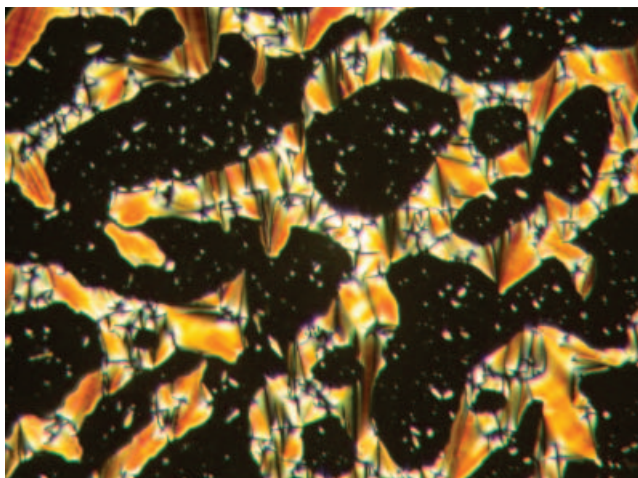


Figure 5. Liquid crystalline texture taken at  $15^{\circ}\text{C}$ .

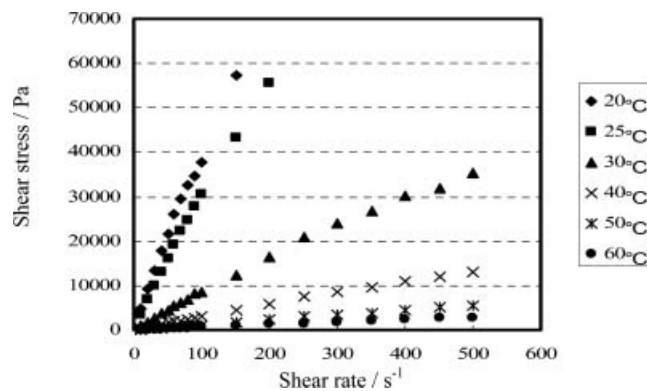


Figure 6. Shear rate dependence of the shear stress (the neat sample).

shear stress became larger with lowering measuring temperature. From the result, it was possible to regard this sample as a Newtonian fluid.

The ER effect obtained under a condition in which the shear rate was  $50\text{ s}^{-1}$  is shown in figure 7. The condition is the normal way to measure the ER effect. These plots are the average shear stresses with and without the electric field for 100 s, respectively. It is clear that no ER effect was observed at the measuring temperatures from  $25^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ . A small ER effect was observed at  $20^{\circ}\text{C}$ , only.

Then, we sheared the sample for 5 min before measurement of the ER effect with a shear rate was  $300\text{ s}^{-1}$ . Figure 8 shows the result for a shear rate of  $50\text{ s}^{-1}$  after the pre-shearing mentioned above at  $20^{\circ}\text{C}$ . After the pre-shearing, the inherent viscosity became lower in the absence of an electric field. When an electric field was applied after 100 s, the shear stress increased up to about 7000–8000 Pa. After removing the electric field at 200 s, the shear stress kept level for about 30 s, and decreased gradually after that.

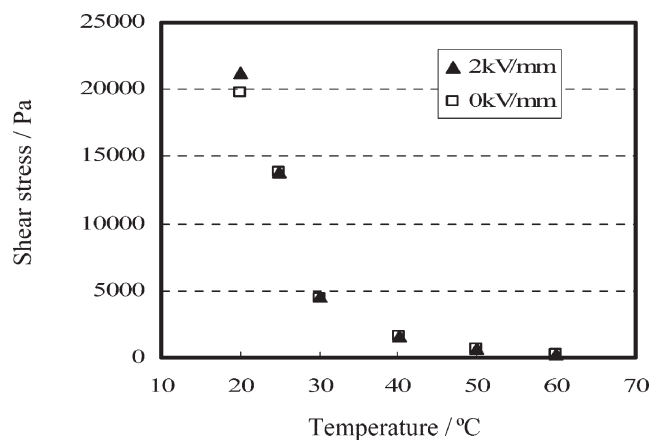


Figure 7. ER effect of the neat sample.

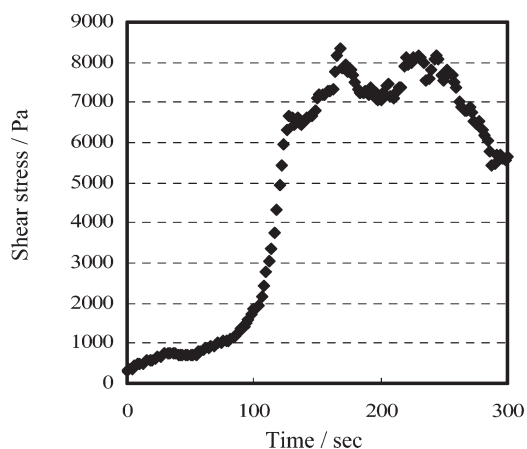


Figure 8. Rheological behaviour of the polymer under shear rate of  $50 \text{ s}^{-1}$  after pre-shearing ( $20^\circ\text{C}$ ).

In order to reduce the inherent viscosity and make an easy arrangement of the terminal mesogens to the direction of an electric field, dilution of the sample was carried out. We prepared the sample diluted by toluene (polymer:toluene=10:1, by weight). No droplets were observed under a microscope in the mixture placed between glass plates. Therefore, it was considered that

no phase separation was caused by the dilution. Figure 9 shows a result obtained for the ER effect after pre-shearing with a  $350 \text{ s}^{-1}$  shear rate. These plots are the average shear stresses with and without an electric field for 100 s, respectively. At  $20^\circ\text{C}$  and  $25^\circ\text{C}$ , a large ER effect was observed, as shown in figures 9a and 9b. Under a shear rate of  $100 \text{ s}^{-1}$ , the shear stress increased to about 12 000 Pa at  $20^\circ\text{C}$  and about 9000 Pa at  $25^\circ\text{C}$ , respectively. The obtained ER effect became smaller with increasing measurement temperature, and a small ER effect was observed at  $30^\circ\text{C}$ , as seen in figure 9c.

There is a possibility that not only the side chains but also the main chain align in the shearing direction. However, it is reasonable to consider that only the alignment of the terminal mesogens plays an important role in observance of the ER effect. As a flow resistance was generated by a change of the mesogen orientation from the shearing direction to that of the electric field, the ER effect tended to increase with an increase in pre-shearing time. However, the influence of the pre-shearing decreased with rising measurement temperature, because a motion of polymer backbones increased and an arrangement of mesogens by the pre-shearing became not so maintainable.

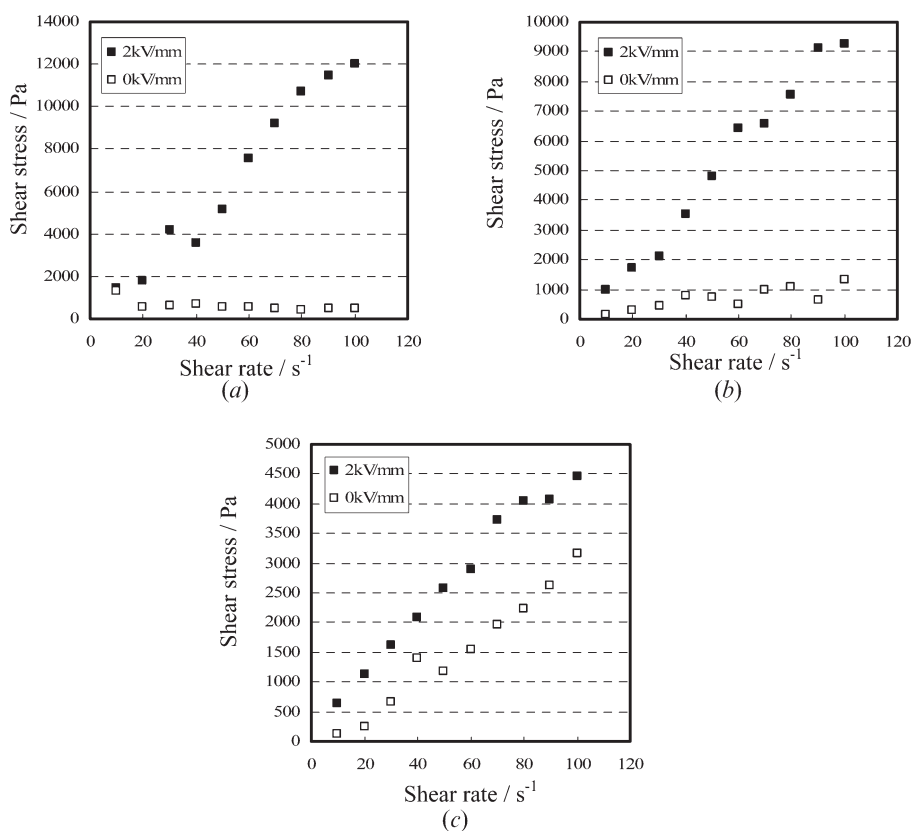


Figure 9. ER effect of the diluted sample at (a)  $20^\circ\text{C}$ , (b)  $25^\circ\text{C}$  and (c)  $30^\circ\text{C}$ .

A small amount of ionic impurities, which are mobile under an applied electric field, may exist in the polymer and cause an increment of the viscosity. However, a large ER effect could not be observed without the pre-shearing in this study. Therefore, we considered that the orientation of the mesogens by the pre-shearing treatment led more influence to the ER effect.

According to the studies reported by other workers [1, 4], the ER effect of the side-chain liquid crystalline polysiloxane derivative was not observable because of its high inherent viscosity. In order to avoid this problem, diluting by silicone oil was carried out in that research [1, 4]. However, there was no complete miscibility between the sample and silicone oil, so that the sample was a binary system. Therefore, the mechanism of the appearance of the ER effect in binary blends has been discussed not only in terms of the orientation of the terminal mesogens but also in terms of droplet size, shape, etc. [2, 3, 12–14]. It was very complicated.

In this research, it was found that a large ER effect was obtained owing to the arrangement of the mesogens to a shearing direction by pre-shearing. In this case, it is obvious that an appearance of the ER effect is influenced by only the arrangement of terminal mesogens because the sample consists of a homogeneous fluid.

In the past studies about the ER effect concerning side-chain liquid crystalline polymers, the viscosity under an electric field was lower than several thousand Pa. An ER effect exceeding 10 000 Pa has not yet been reported. As far as we know, the larger ER effect obtained in this work is the first time that the shear stress has exceeded 10 000 Pa under an applied electric field. As mentioned above, pre-shearing is an effective technique in increasing the ER effect of the samples. Therefore, it may be expected that a considerable ER effect will be observed using this novel pre-shearing method, even if the samples exhibited no ER effect, because of their higher inherent viscosity.

#### 4. Conclusion

A side-chain liquid crystalline polysiloxane derivative was prepared and its ER effect was measured. No ER effect of the non-sheared sample was observed because of its high inherent viscosity. However, it was found out that a large ER effect was measured by the pre-shearing

with high shear rate which makes a desirable arrangement of the terminal mesogens to the shearing direction. In addition, a larger ER effect was observed as a result of dilution by toluene in order to reduce the inherent viscosity. We thus have shown a new approach for the measurements of the ER effect in homogeneous fluids in this study. It may be expected that a new mechanical application is developed via this method involving a homogeneous fluid consisting of liquid crystalline polymers and solvent.

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