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## Liquid Crystals

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## Rotational viscosity of ferroelectric liquid-crystalline polysiloxanes

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Some physical parameters of comb-shaped ferroelectric liquid-crystalline polymers were measured. Their rotational viscosities are two or three orders of magnitude larger than that of low molecular weight ferroelectric liquid crystals. Furthermore, they are found generally to be proportional to the second power of the weight-average molecular weight. Spontaneous polarization of the ferroelectric liquid-crystalline polymers has little dependence on molecular weight.

### 1. Introduction

A number of liquid-crystalline polymers exhibiting the chiral smectic C(S<sub>C</sub><sup>\*</sup>) phase have recently been synthesized and studied [1-10]. These materials are promising for use in electro-optical display devices characterized by fast switching speeds and memory effect [11]. Several physical parameters in these materials can be defined in the same way as low molecular weight ferroelectric liquid crystals. We have already presented the smectic layer spacing, the spontaneous polarization, the response time [12] and the helical pitch [13] of the synthesized ferroelectric liquid-crystalline polymers.

Here, we evaluate the rotational viscosity of the materials. Thus far there has been no report on the rotational viscosity of ferroelectric liquid-crystalline polymers. For application purposes the rotational viscosity is one of the most important parameters of these polymers since it greatly influences the response time. The response time  $\tau$  is approximately given by the formula

$$\tau = \frac{\eta}{P_s E}, \quad (1)$$

where  $\eta$  is the rotational viscosity,  $P_s$  is the spontaneous polarization and  $E$  is the applied electric field. We estimated the rotational viscosity of the polymers by measuring the spontaneous polarization and the optical response time. The optical response time depends on a tilt angle, and is not precisely equal to  $\tau$  defined by equation (1). Therefore, we revised the optical response time taking the tilt angle into consideration. In this way we systematically evaluated the rotational viscosity of the polymers of several molecular weights. We investigated the correlation between rotational viscosity and the weight-average molecular weight.

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## 2. Experimental

### 2.1. Materials

The polymer used in our experiments was synthesized as follows (see figure 1). 4-Hydroxy-4'-biphenylcarboxylic acid (0.047 mol; 10.0 g), (*S*)-2-methylbutanol (0.233 mol; 20.5 g) and sulphuric acid (cat.) were added to 100 ml of benzene. The mixture was refluxed with a Dean–Stark apparatus. The reaction mixture was washed with water, dried over magnesium sulphate, and the solvent removed by reduced pressure. The crude ester was recrystallized from hexane/toluene. 13.0 g of **1** was obtained.

8-Bromo-1-octene (0.042 mol; 8.1 g), **1** (0.046 mol; 13.0 g) and potassium carbonate (0.046 mol; 6.4 g) were added to 150 ml of 2-butanone. The mixture was refluxed. The reaction mixture was washed with water and dried over magnesium sulphate and the solvent removed by reduced pressure. The crude product was recrystallized from ethanol. 14.2 g of **2** was obtained.

**2** (0.02 mol; 8.0 g) and poly(hydrogen methyl siloxane) (1.0 g, Aldrich) were resolved in 50 ml of toluene and  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  as catalyst was added. The polymerization reaction was carried out under an argon atmosphere until no remaining Si–H was detected by IR. The crude polymer was purified by silica gel column chromatography.

In order to investigate the dependence of some of the parameters on molecular weight we fractionated the polymer using gel permeation chromatography (GPC). The weight-average molecular weight ( $\bar{M}_w$ ) and the number-average molecular weight ( $\bar{M}_n$ ) of these fractionated polymers were determined by using GPC with chloroform solvent calibrated with polystyrene standards. We determined the transition temperatures using both differential scanning calorimetry (DSC) and polarized optical microscopy. The transition temperatures and the average molecular weights of these polymers are listed in the table.

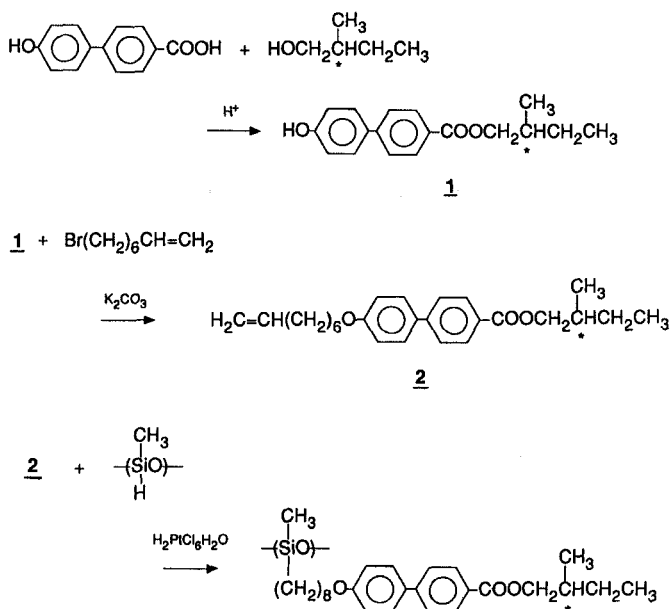


Figure 1. The synthetic route and molecular structure of the ferroelectric liquid-crystalline polymers.

Weight average molecular weight ( $\bar{M}_w$ ), polydispersity ( $\bar{M}_w/\bar{M}_n$ ) and transition temperatures on cooling the ferroelectric liquid-crystalline polymers.

Polymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Transition temperature						
			g	S <sub>C</sub> *	S <sub>A</sub>	I			
s1	5600	1.08	●	315 K†	●	363 K	●	383 K	●
s2	8000	1.16	●	303 K	●	362 K	●	393 K	●
s3	12700	1.19	●	303 K	●	359 K	●	395 K	●
s4	49300	1.82	●	323 K	●	361 K	●	405 K	●

† S<sub>X</sub>-S<sub>C</sub>\* transition temperature. S<sub>X</sub>: high order smectic phase.

## 2.2. Measurements

### 2.2.1. Principle of measurements

There is no appropriate method to measure directly the rotational viscosity of ferroelectric liquid crystals and in consequence several methods have been proposed [14–19]. All of them are based on equation (1). Kimura *et al.* [16] examined the equation of motion of the director on the cone, and proposed a helpful method. They calculated the transmitted light intensity under crossed polarizers and the polarization current after field reversal as a function of time. According to Kimura *et al.* [16] the azimuthal angle of the director  $\phi$  as a function of time  $t$  is expressed by

$$\phi = 2 \tan^{-1} \left[ \tan \left( \frac{\phi_0}{2} \right) \exp \left( \frac{t}{\tau} \right) \right], \quad (2)$$

where  $\phi_0 \equiv \phi (t=0)$  and  $\tau \equiv \eta/P_s E$ . In this equation we neglected the effect due to dielectric anisotropy of the molecule. The polarization current  $i$  and the transmitted light intensity under crossed polarizers  $T$  are expressed by

$$i = \frac{P_s}{\tau} \sin^2 \phi \quad (3)$$

and

$$T = \sin^2 2\Theta \sin^2 \left( \frac{\pi d \Delta n}{\lambda} \right), \quad (4)$$

where  $\Theta$  is the angle between the projection of the director on to the glass surface and the polarizer direction,  $d$  is the cell thickness,  $\Delta n$  is the effective optical anisotropy and  $\lambda$  is the wavelength of the transmitted light.  $\Theta$  is given by

$$\Theta = \Omega - \tan^{-1} (\tan \theta \cos \phi), \quad (5)$$

where  $\Omega$  is the angle between the polarizer and the layer normal and  $\theta$  is the tilt angle. The effective optical anisotropy  $\Delta n$  is given by

$$\Delta n = \frac{n_1 n_2}{(n_1^2 \cos^2 \theta' + n_2^2 \sin^2 \theta')^{1/2}} - n_1, \quad (6)$$

where  $n_1$  and  $n_2$  are principal values for the refractive indices perpendicular and parallel to the director, respectively, and  $\theta'$  is defined as  $\sin \theta' = \sin \theta \sin \phi$ . Kimura *et al.* [16] found that  $t_{10-90}$  and  $t_w$  must be used in order to determine the rotational viscosity of ferroelectric liquid crystals. Here,  $t_{10-90}$  is the time for the transmitted light intensity

by 10–90 per cent to rise on applying the voltage and  $t_w$  is the full width at half-maximum of the peak of polarization current. They simultaneously measured  $t_w$  and the spontaneous polarization from a polarization current and evaluated the rotational viscosity according to the relation,

$$t_w = 1.76 \frac{\eta}{P_s E} \quad (7)$$

When we tried to evaluate the rotational viscosity of ferroelectric liquid-crystalline polymers we also measured  $t_{10-90}$  and  $P_s$ . In our experiments we could not clearly separate the polarization current peak from the contribution due to the charge accumulation after field reversal. Therefore we decided to measure  $t_{10-90}$  instead of  $t_w$ . We found that the relation between  $t_{10-90}$  and  $\eta/P_s E$  was altered when the tilt angle  $\theta$  was changed whereas the relation between  $t_w$  and  $\eta/P_s E$  was not altered (see equation (7)). By using equation (4) we calculated the transmitted light intensity under crossed polarizers as a function of time where  $\phi_0 = 1^\circ$ ,  $\pi d/\lambda = 5$ ,  $n_1 = 1.5$ ,  $n_2 = 1.7$ . Figure 2 shows the optical responses when  $\theta = 20^\circ$  and  $\theta = 30^\circ$ . In this figure, it is obvious that the correlation between  $t_{10-90}$  and  $\eta/P_s E$  changes according to  $\theta$ . For example, in our calculation,

$$t_{10-90} = 1.75\eta/P_s E \quad (\theta = 20^\circ)$$

and

$$t_{10-90} = 1.29\eta/P_s E \quad (\theta = 30^\circ).$$

In this way we evaluated the rotational viscosity of our polymers by using the optical response time, the tilt angle and the spontaneous polarization.

### 2.2.2. Spontaneous polarization

The ferroelectric liquid crystalline polymers were laminated with two ITO-coated glass plates, the gap of which was controlled by inserting silicon oxide spacers. The area of the ITO electrode was  $20 \text{ mm}^2$ . We used  $7 \mu\text{m}$  thick cells for the spontaneous polarization measurements and a Mettler FP 82 hot stage for temperature control. Measurements of spontaneous polarization were achieved by the triangular wave method [20] ( $150 \text{ V}_{\text{p-p}}$ ,  $0.1\text{--}5 \text{ Hz}$ ). The polarization reversal current was amplified by a current-to-voltage amplifier and stored in a transient memory. The spontaneous polarization was evaluated by calculating the area of the polarization reversal current peak. We then obtained the temperature dependence of the spontaneous polarization.

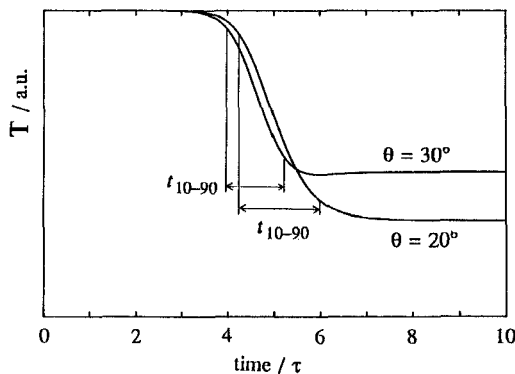


Figure 2. The calculated transmittance change with time after field reversal.

### 2.2.3. Optical response time and tilt angle

1.2  $\mu\text{m}$  thick cells were used for measurements of optical response time and tilt angle. In these measurements we used the shearing method for polymer side chains to align for one direction. We did not have to use the rubbed polymer layer on the ITO surface for alignment by this method. These cells were first heated into the isotropic phase and then slowly cooled. At the same time the alignment was achieved by the shearing method in the smectic A phase. We measured the optical response time on an applied voltage step ( $\pm 20$  V). This voltage was in the range where response time was in inverse proportion to an applied voltage. We measured the optical response time for a 10–90 per cent transmission change under crossed polarizers using a photo diode and a transient memory. We determined the tilt angle by measuring the angle between the two stable directions of the director obtained by applying positive and negative electric field, respectively. Then we obtained the temperature dependences of the optical response time and the tilt angle.

## 3. Results and discussion

### 3.1. Spontaneous polarization

Figure 3 shows the temperature versus the spontaneous polarizations of the polymers. In this figure  $\bar{M}_w$  is the weight-average molecular weight of each polymer. The spontaneous polarizations of the polymers increases with decreasing temperature below the  $S_C^* - S_A$  transition temperature. The maximum spontaneous polarization of polymer s4 ( $\bar{M}_w = 49300$ ) was about  $0.2 \text{ mC m}^{-2}$  at 333 K. However those of polymers s2 ( $\bar{M}_w = 8000$ ) and s3 ( $\bar{M}_w = 12700$ ) exceeded  $0.3 \text{ mC m}^{-2}$ . The maximum spontaneous polarizations of these samples were different. In the ferroelectric phase the free rotation of the side chains, especially their dipole units, around their long axes is hindered by the existence of the chiral centres. As a result of this effect the spontaneous polarization appears. The rotation around their long axes is gradually frozen and the spontaneous polarization increases with decreasing temperature. On the other hand, ferroelectric switching of the side chains is also gradually frozen with decreasing temperature. Finally the side chains are not able to respond to an applied field at lower temperature. Polymer s4, which has a high degree of polymerization, was glassy and could not respond to an applied voltage under 323 K. On the other hand polymers s2 and s3 were in the  $S_C^*$  phase (not the glassy phase) and could respond to an applied voltage up to

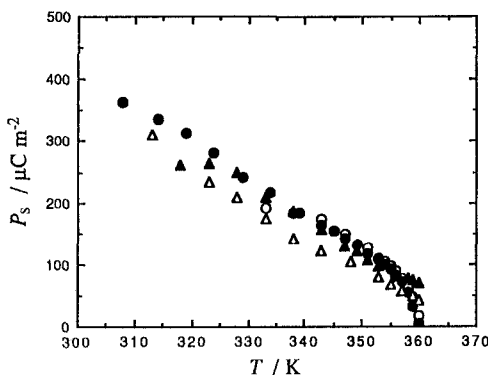


Figure 3. The temperature dependences of the spontaneous polarization  $P_s$ .  $\bar{M}_w = 49300$ ;  $\bullet \bar{M}_w = 12700$ ;  $\triangle \bar{M}_w = 8000$ ;  $\blacktriangle \bar{M}_w = 5600$ .

303 K. In polymer s4 the spontaneous polarization did not manifest itself fully and, therefore, could not be measured when it became glassy. In consequence the maximum spontaneous polarization measured for polymer s4 was smaller than those of polymers s2 and s3. In the case of polymer s1 ( $\bar{M}_w = 5600$ ) a different phase sequence was observed. Beneath the  $S_C^*$  phase we observed a phase at 315 K which did not respond to an applied voltage. Therefore the spontaneous polarization could not be measured in this phase. From DSC measurements we observed a small peak at this temperature for this sample. Therefore this phase was considered to be a high order smectic phase [12]. Due to the existence of this phase the spontaneous polarization of polymer s1 was not large, hence the maximum spontaneous polarization of this polymer was smaller than those of polymers s2 and s3.

On the whole, by comparing these polymers at the same temperature the spontaneous polarization was mostly the same. The spontaneous polarization of ferroelectric liquid-crystalline polymers scarcely depends on the average molecular weight.

### 3.2. Rotational viscosity

Figure 4 shows the temperature dependence of the response time  $t_{10-90}$ .  $t_{10-90}$  shows little variation as the  $\bar{M}_w$  decreases. As previously mentioned the response time is dependent on both the spontaneous polarization and the rotational viscosity, this is obvious from equation (1). The spontaneous polarization of these samples was independent of the average molecular weight, so the difference in the response time comes from the difference in the rotational viscosity.

Figure 5 shows the temperature dependence of the tilt angle  $\theta$ . The tilt angle of these samples increases with decreasing temperature reaching saturation at still lower temperature. The tilt angle of polymer s1 ( $\bar{M}_w = 5600$ ) shows an anomalous temperature dependence near 350 K. However, we could not observe any phase transition at this temperature from DSC and polarized optical microscopy observations. We supposed this came from the experimental error.

We estimated the rotational viscosity of our polymer using equation (1) as described in Experimental. Figure 6 shows the Arrhenius plots of the rotational viscosity of our polymers. Except in the vicinity of the transition temperature  $T_{S_C^*-S_A}$ , a linear relation between  $1/T$  and  $\log \eta$  was obtained. The activation energies for the rotational viscosity

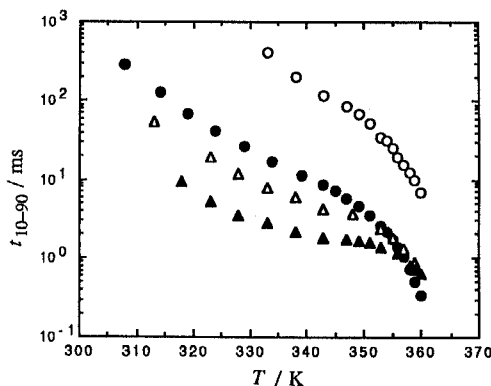


Figure 4. The temperature dependences of the optical response time  $t_{10-90}$ .  $\circ$   $\bar{M}_w = 49300$ ;  $\bullet$   $\bar{M}_w = 12700$ ;  $\triangle$   $\bar{M}_w = 8000$ ;  $\blacktriangle$   $\bar{M}_w = 5600$ .

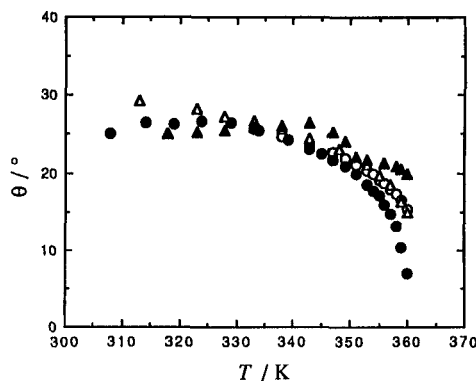


Figure 5. Temperature dependences of the tilt angle  $\theta$ .  $\circ \bar{M}_w = 49300$ ;  $\bullet \bar{M}_w = 12700$ ;  $\triangle \bar{M}_w = 8000$ ;  $\blacktriangle \bar{M}_w = 5600$ .

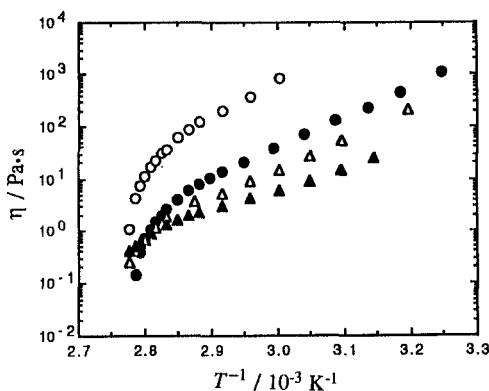


Figure 6. The Arrhenius plots for the rotational viscosity  $\eta$  of the ferroelectric liquid-crystalline polymers.

were estimated to be  $7.7 \times 10^4 \text{ J mol}^{-1}$  for polymer s1,  $1.1 \times 10^5 \text{ J mol}^{-1}$  for polymers s2 and s3, and  $1.4 \times 10^5 \text{ J mol}^{-1}$  for polymer s4. The activation energy for the rotational viscosity has been estimated to be about  $5 \times 10^4 \text{ J mol}^{-1}$  for low molecular weight ferroelectric liquid crystals [17], in comparison the ferroelectric liquid-crystalline polymers had higher activation energies. On the whole the rotational viscosity of ferroelectric liquid-crystalline polymers having a large  $\bar{M}_w$  strongly depends on the temperature.

Figure 6 shows that the rotational viscosity of ferroelectric liquid-crystalline polymers increases with increase in  $\bar{M}_w$  except in the vicinity of  $T_{S_C-S_A}$ . Near  $T_{S_C-S_A}$  variations in the rotational viscosity were large and the transition temperatures of these samples were a little different from one another. Therefore, the relation of the magnitude of the rotational viscosities of these samples near  $T_{S_C-S_A}$  do not necessarily coincide with the relation of the magnitude of  $\bar{M}_w$ . It was reported that the rotational viscosity of low molecular weight ferroelectric liquid crystals was less than  $1 \text{ Pa}\cdot\text{s}$  [16, 17], therefore the rotational viscosity of the ferroelectric liquid-crystalline polymers was two or more orders of magnitude greater. In the case of the polymers the main chains retard the motions of their side chains. On applying an electrical field the side chains consisting of



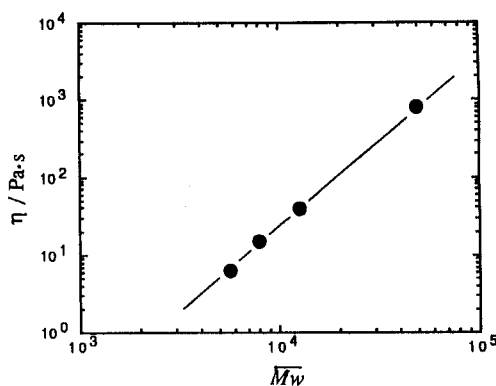


Figure 7. The dependence of the rotational viscosity on molecular weight ( $\bar{M}_w$ ). The values were measured at 333 K.

mesogenic units switch. However, they are hard to move since they are bound to each other through the main chain. Therefore, the motion becomes slower. Thus the rotational viscosity defined by equation (1) becomes larger in ferroelectric liquid-crystalline polymers.

We plotted  $\eta$  against the weight-average molecular weight  $\bar{M}_w$  in order to investigate the dependence of the rotational viscosity on the average molecular weight. Ferroelectric liquid-crystalline polymers have a polydisperse molecular weight. Their viscosity, it seems, comes from the components having a large molecular weight which has a large effect on their rotational viscosity. However, we could not obtain the so-called viscosity-average molecular weight  $\bar{M}_v$  of these polymers. In order to investigate the dependence on the average molecular weight we do not adopt the number average molecular weight  $\bar{M}_n$  but  $\bar{M}_w$ . Since  $\bar{M}_w$  represents more properly the viscosity-average molecular weight  $\bar{M}_v$ , it is possible to compare  $\eta$  with ferroelectric liquid-crystallizing polymers having other structures in the future.

Figure 7 shows the correlation between  $\log \bar{M}_w$  and  $\log \eta$ . We used the values of  $\eta$  which were measured at 333 K. In this figure a linear relation was obtained, so  $\eta$  was represented using  $\bar{M}_w$  by

$$\eta = \eta_0 \bar{M}_w^a \quad (8)$$

In our calculation, the exponent  $a$  defined by this equation was about 2.0. We have not yet determined the means of this exponent  $a$ . Systematic studies of the relation between  $a$  and the molecular structure will be the next assignment.

#### 4. Conclusion

The rotational viscosity of ferroelectric liquid-crystalline polymers was evaluated. It was evaluated from several parameters such as the optical response time, tilt angle and spontaneous polarization. The rotational viscosity was two or more orders of magnitude higher than that of low molecular weight ferroelectric liquid crystals and approximately proportional to the second power of  $\bar{M}_w$ .

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