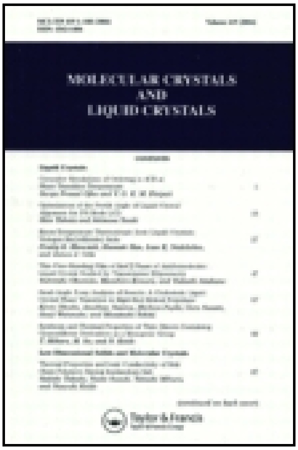

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Electrorheological Properties of Liquid-Crystalline Materials

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ELECTRORHEOLOGICAL PROPERTIES OF LIQUID-CRYSTALLINE MATERIALS

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Abstract Electrorheological properties of binary mixtures of liquid-crystalline polymer and low molecular weight liquid crystal were investigated. The viscosity of the liquid-crystalline mixture increased by application of DC electric field and recovered its original viscosity after the electric field was turned off. The effect appears above a field strength of 1.0 kV/mm, and the viscosity increases with the electric field strength. For shear rate 2 s^{-1} the viscosity was increased by approximately 5 times when 5.0 kV/mm was applied. Above nematic - isotropic transition temperature, electrorheological effect disappeared.

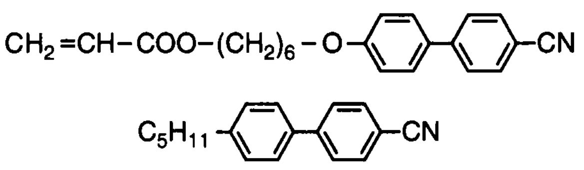
INTRODUCTION

Liquid crystals are materials which show strong anisotropy, but still keep liquid fluidity. Liquid crystals change their orientation reversibly, depending on several external factors, such as electric field, magnetic field, etc. Therefore, the optical and the mechanical anisotropy are changed. Display devices are typical application of liquid crystals, in which the orientation is controlled by the electric field. We already demonstrated electrical - mechanical energy conversion system using thermotropic liquid-crystalline (LC) polymer gel which consists of thermotropic liquid-crystalline elastomer (LCE) and low molecular weight liquid crystal (LLC)[1]. The LC gel in the nematic phase quickly deformed by application of DC electric field and recovered its original shape after the electric field was turned off. Reversible deformation took place rapidly within 300 msec. This electro-mechanical effect suggested that an electrical reorientation of LLC led to the shape change of liquid-crystalline network. If we use uncrosslinked liquid-crystalline polymer (LCP) instead of LCE, other electro-mechanical energy conversion system would be expected. In this work, we studied electrorheological properties of LC materials. The electrorheological effects of LLC were already reported[2-5]. However, the effects of binary mixtures of LCP and LLC have not been investigated.

EXPERIMENTAL

Materials

In this study, we chose to use positive type LC materials. Figure 1 shows the structures of the liquid-crystalline materials used in this study. Poly (6-(4'-cyanobiphenyl-4-yloxy) hexylacrylate) (PCBA6) was prepared by radical polymerization of monomer (I). (I) was synthesized by the method reported by Sibaev et al[6]. The mixture of toluene and dimethyl sulfoxide was used as polymerization solvent to prepare high molecular weight polymer. α,α-azobisisobutyronitrile was used as a radical initiator. Polymerization was undertaken in sealed ampul for 30 h at 60 °C. PCBA6 was purified by repeated precipitation from methylene chloride solution into methanol. Purified polymer was dried in vacuum at room temperature for 48 h to avoid thermal crosslinking of acrylate units. The number-average molecular weight (Mn) of PCBA6 was determined to be 40,000 (Mw/Mn = 2.17) by gel permeation chromatography calibrated with polystyrene standards. 4-cyano-4'-pentylbiphenyl (5CB) (II) was purchased from Merck Inc. PCBA6 was added to 5CB, and stirred at 75 °C until PCBA6 completely dissolved. The concentration of PCBA6 was 10 - 30 mol% with respect to the mesogenic unit.



(I)

(II)

FIGURE 1. Structures of monomer (CBA6) (I) and low molecular weight liquid crystal (5CB) (II).

Measurements

An Olympus BH-2 polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor was used to observe the textures and phase transition of LC materials. Thermotropic properties of LC materials were determined with a SEIKO DSC-120 differential scanning calorimeter at a heating rate of 5 °C/min. Electrorheological properties of LC mixtures (LCM) were measured by a Nihon

Reology NRM-100EM rotational rheometer equipped with parallel plate electrodes (diameter : 50 mm, gap : 100 μm). Temperature of the electrodes was controlled by the silicon oil circulated with a constant temperature bath. DC electric field ranging from 0 to 5.0 kV/mm was applied across the electrodes at a constant or increasing shear rate.

RESULTS AND DISCUSSION

Phase behaviors of LC materials

The sherilene textures characteristic of the nematic liquid-crystalline phase are observed for PCBA6 and 5CB. PCBA6 and 5CB are completely miscible and the mixtures also show the nematic phase at around room temperature. The nematic to isotropic phase transition temperature ($T_{N\text{-}I}$) and the glass transition temperature (T_g) of LC materials were determined by microscopic observation and DSC measurements. The phase transition temperatures of LC materials are summarized in Table 1.

TABLE 1. Phase transition temperature and viscosity of LC materials

	mole fraction of CBA6	mole fraction of 5CB	Phase transition temperature (°C)					Viscosity (Pa·s)
PCBA6	—	—	g	39.1	N	128.1	I	—
5CB	—	—	K	24.1	N	35.4	I	0.025[a]
LCM1	0.1	0.9		—	N	58.0	I	0.365[b]
LCM2	0.2	0.8		—	N	60.3	I	2.64[b]
LCM3	0.3	0.7		—	N	62.7	I	19.3[b]

K:Crystal, g:glass, N:nematic, I:isotropic. a) : data from ref.7. b) : measured by rotational rheometer equipped with parallel plates.

$T_{N\text{-}I}$ of the LCM was increased with increasing amount of the LCP. The T_g of LCM was not detected by DSC measurement. The viscosity of 5CB is very low, about 0.025 Pa·s at room temperature[7]. The addition of PCBA6 brought about the remarkable increase in viscosity (Table 2).

Electric field strength and shear rate effects

LCMs showed electrorheological effect. LCM increased the viscosity by application of DC electric field and recovered its original viscosity after the electric field was turned off. Figure 2 shows the electrorheological properties of LCM3 at 25 °C when an

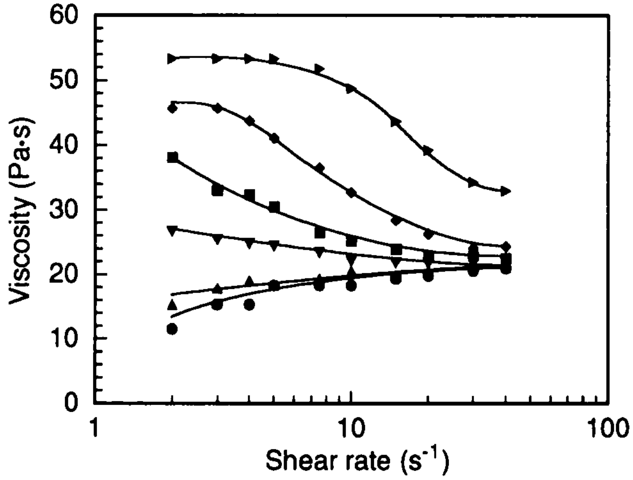


FIGURE 2. Electrorheological effects of LCM3. Electric field, ● : OFF, ▲: 1.0 kV/mm, ▼ : 1.5 kV/mm, ■ : 2.0 kV/mm, ◆ : 3.0 kV/mm, ▶ : 5.0 kV/mm.

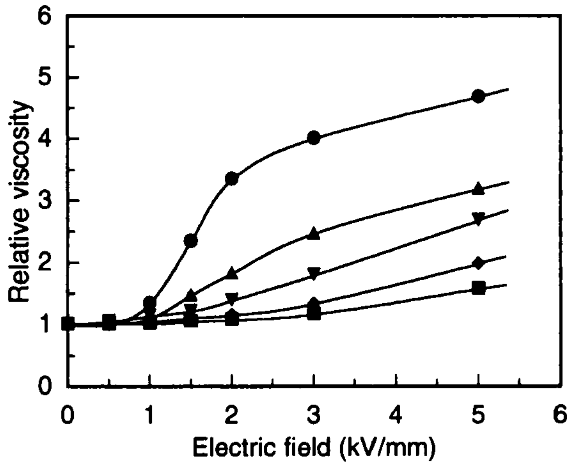


FIGURE 3. The dependence of the relative viscosity on the applied electric field. Material : LCM3, Shear rate, ● : 2 s^{-1}, ▲ : 5 s^{-1}, ▼ : 10 s^{-1}, ◆ : 20 s^{-1}, ■ : 40 s^{-1}.

electric field ranging from 0 to 5.0 kV/mm was applied. The effect appears above a field strength of 1.0 kV/mm, and the viscosity increases with the electric field strength. It was suggested that the electrorheological effect results from the orientation change of mesogenic groups. The dependence of the relative viscosity on the electric field applied at various shear rate is illustrated in Figure 3. The relative viscosity was defined as the ratio between the apparent viscosity with and without electric field. A sharp increase of the relative viscosity is observed at low shear rate. For shear rate 2 s^{-1}, the viscosity was increased by approximately 5 times when 5.0 kV/mm was applied. The relative viscosity decreases with increasing the shear rate. These results suggests that orientation of mesogenic groups was restricted by entanglement of polymer chains.

Temperature effects

The viscosity of LCM3 depends on the temperature, as shown in Figure 4. Below $T_{N\text{-}I}$ (25 - 55 °C) the electrorheological effect was observed by application of DC electric field. The viscosity decreases with increasing the temperature, and electrorheological effect seems to be reduced. However, the values of the relative viscosity at any temperature are almost the same in the low shear rate region. On the other hand, above

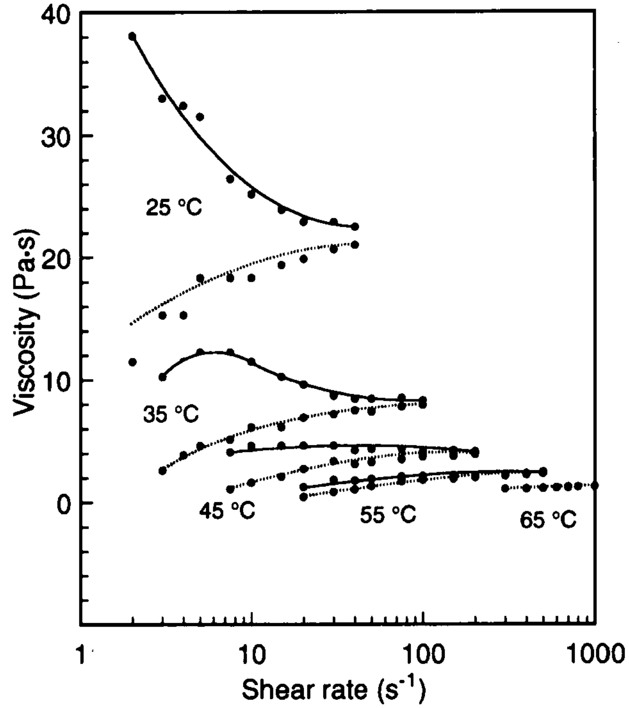


FIGURE 4. Temperature effect on electrorheology of LCM3. Dashed line : OFF, Solid line : 2.0 kV/mm.

TN-I (65 °C) electrorheological effect disappeared. The electric current across LCM3 is shown in Figure 5 as a function of applied electric field strength and temperature. The electric current increased almost linearly with electric field strength, and also increased with the temperature.

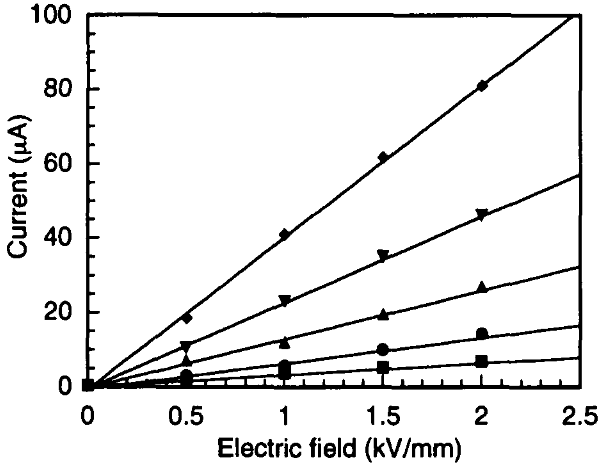


FIGURE 5. Relationship between applied electric field and current. Material : LCM3, Temperature, ■ : 25 °C, ● : 35 °C, ▲ : 45 °C, ▼ : 55 °C, ◆ : 65 °C.

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