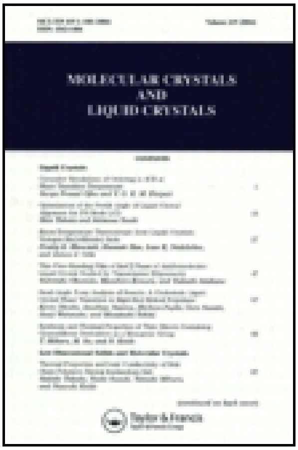

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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DC-Induced Molecular Orientations of Liquid Crystalline Polysiloxanes Mixed with Low Molecular Weight Liquid Crystals

Michiyuki Amano [a] , Yoshiaki Takeuchi [a] & Fumio Yamamoto [a]

[a] NTT Opto-electronics Laboratories, Tokai-Mura, Naka-Gun, Ibaraki-Ken, 319-11, Japan

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DC-Induced Molecular Orientations of Liquid Crystalline Polysiloxanes Mixed with Low Molecular Weight Liquid Crystals

MICHIYUKI AMANO, YOSHIAKI TAKEUCHI and FUMIO YAMAMOTO

NTT Opto-electronics Laboratories, Tokai-Mura, Naka-Gun, Ibaraki-Ken, 319-11 Japan

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Stable DC-induced molecular orientations of side-chain liquid crystalline polymers at room temperature (~25°C) are attained by mixing with low molecular weight liquid crystals (LLC). Polysiloxanes with the spacer carbon number m ($m = 4, 6$) are mixed with LLCs with the alkyl carbon number n ($n = 1, 3, 4, 6$). For all mixtures, their DC-induced molecular orientations are attained over wide mixing ratio ranges at the liquid crystalline temperatures. At room temperature, the molecular orientations are preserved at proper mixing ratios when m is 4, but not preserved at any mixing ratio when m is 6 because of the crystallization. The sample resistances increase with increases in the order parameters, which indicates that oriented samples have the intrinsic anisotropic resistances. The preserved molecular orientations are kept stably at room temperature for more than 4 months when m is 4 and the LLC ($n = 1, 3, 4$) fraction is 10%w/w.

INTRODUCTION

Recently, liquid crystalline polymers (LCPs) with side-chains as mesogenic units have been of interest, because they have great potential as highly functional polymers. These were synthesized first by Finkelmann *et al.*[1] and Shibaev *et al.*[2] in the 1970s, and their physical properties were also studied. It was shown that their molecular orientation is controlled by electric[3] and magnetic fields[4] similarly to those of low molecular weight liquid crystals (LLCs). For LCPs, the molecular orientation is frozen by quenching,[5] but not for LLCs. The orientation preservation of LCPs has been applied to display[6] and recording devices.[7]

For liquid crystalline polysiloxanes, the electro-optic effect has been extensively studied in regard to their applicability in those devices.[8,10] Molecular orientations of liquid crystalline polysiloxanes are induced by an alternative current (AC) electric field, and they are preserved at room temperature.[8] However, it is reported that the orientation is not induced by a direct current (DC) electric field.[8] There has been only few studies on the molecular orientation in a DC electric field, although the DC-induced orientation may be applied to opto-electronic devices.[12,13] On the other hand, the orientation of LLCs is attained by both AC and DC electric fields, and LCPs mixed with LLCs exhibits easy orientation than LCPs in an AC electric field.[9-11] Thus, in LCPs mixed with LLCs, it is thought that the DC-induced molecular orientation is attained.

In this study, in order to obtain stable DC-induced liquid crystalline orientations, mixtures of liquid crystalline polysiloxanes and LLCs are examined.

EXPERIMENTAL

Materials

The molecular structures of the materials used are shown in Figure 1. The LLCs were benzoic acid *p*-cyanophenylesters with *n* alkyl

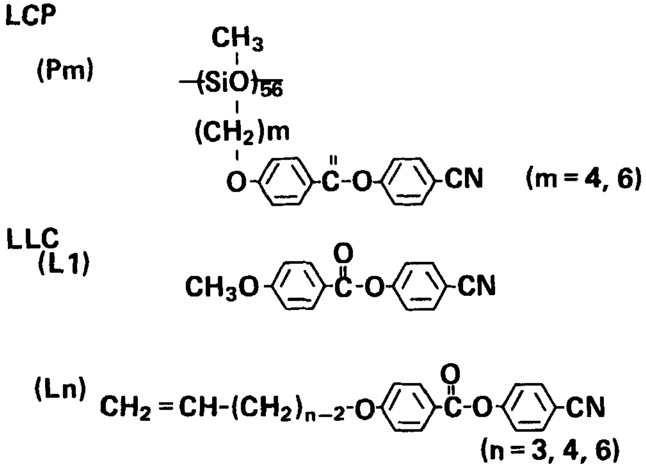


FIGURE 1 Molecular structures of LCPs and LLCs.

carbons, which were synthesized according to well-known procedures. The LCPs were poly(methylsiloxane)s with benzoic acid *p*-cyanophenyl esters as mesogenic side groups via *m* spacer carbons. They were synthesized by an addition reaction with a platinum catalyst[14,15] as shown in Figure 2. Commercially available poly(methylhydrogensiloxane) (TSF486 Toshiba silicone) was used without further purification. The average degree of polymerization was about 56. Synthesized LCPs were purified by reprecipitation with methanol. The precipitate was then dissolved in acetone. Only the soluble part was collected in order to separate the insoluble product made by the crosslinking reaction between cyano groups.[11,16] The LCPs with *m* spacer carbons and the LLCs with the *n* alkyl carbons are abbreviated as P*m* and L*n*, respectively. Structures of all the compounds and synthetic intermediates were identified by ^{1}H NMR. They were shown to be pure by thin layer chromatography. P*m* and L*n* were mixed in various weight ratios and dissolved in acetone which was then evaporated. The mixture (abbreviated as P*m*–L*n*) was dried completely by heating at about 60°C.

Method

Samples were observed with a polarizing microscope (XTP-11, Nikon) equipped with a hot stage system (FP80, Mettler). Clearing and crystalline to liquid crystalline transition temperatures were determined from the change in transmission light intensity between crossed polarizers, which was detected by a photometer (P1, Nikon). The clearing temperatures were determined by cooling from the isotropic phase at a rate of 1.0°C/min. The crystalline to liquid crystal transition temperatures were determined by heating at a rate of 1.0°C/min. Noncrystalline to liquid crystalline temperatures were determined using a differential scanning calorimeter (DSC-20, SEIKO).

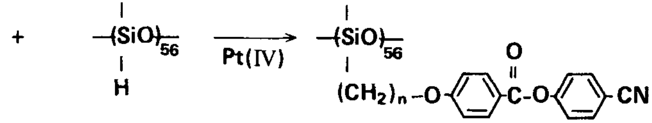


FIGURE 2 Synthetic reaction of LCPs.

DC fields from 10 to 200 V were applied to film samples with monitoring the currents. The sample temperatures were set at their reduced temperatures (*Tm*/*Tc* where *Tm* = measuring temperature, *Tc* = clearing temperature) of 0.98 for all samples. The film thickness was controlled to be 12.5 μm by polyimide (KAPTON, DuPont) films. Mixture samples were melted on glass substrates with interdigital electrodes, and covered with thin glass substrates. The electrodes were 200 μm-wide evaporated chrome, with interdigital spacings of 200 μm. The glass substrates were cleaned ultrasonically in acetone before use. The geometry of the experimental devices are shown in Figure 3.

Liquid crystalline orientations were observed by optical anisotropy between crossed polarizers. 4-(dimethylamino)-4′-nitrostilbene was doped into the mixtures as a probe for the order parameter. The doping concentration was 0.05%w/w. The order parameter (S) was determined from the optical absorption anisotropy at 470 nm from

$$S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp}) \qquad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the electric field direction, respectively.

The stability of liquid crystalline orientations was examined at room temperature (~25°C) by the time dependence of the order parameter.

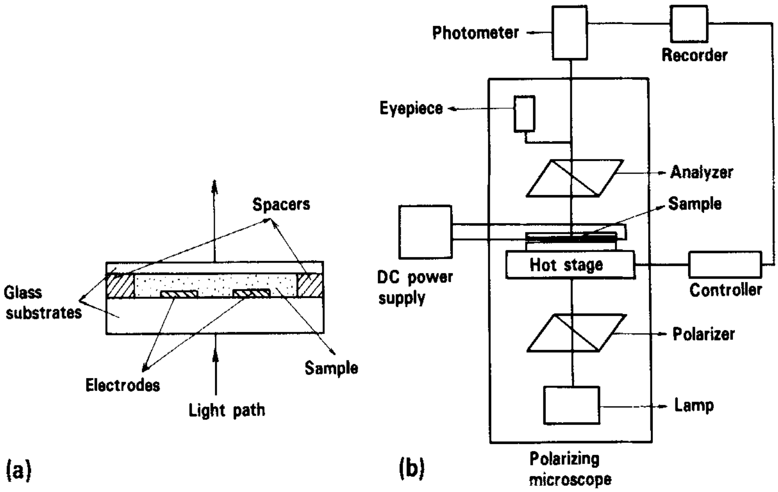


FIGURE 3 (a) A drawing of a typical sample cell and (b) a schematic diagram of the optical system.

RESULTS AND DISCUSSION

Preservation of DC-induced Molecular Orientations

For LCPs mixed with LLCs, molecular orientations were examined by a DC field. Figure 4 shows the relationship between threshold voltage for a molecular orientation of P4-L6 and LLC (L6) fraction when a DC electric field was applied. The sample temperature was at the reduced temperature of 0.98. For a mixture with the LLC

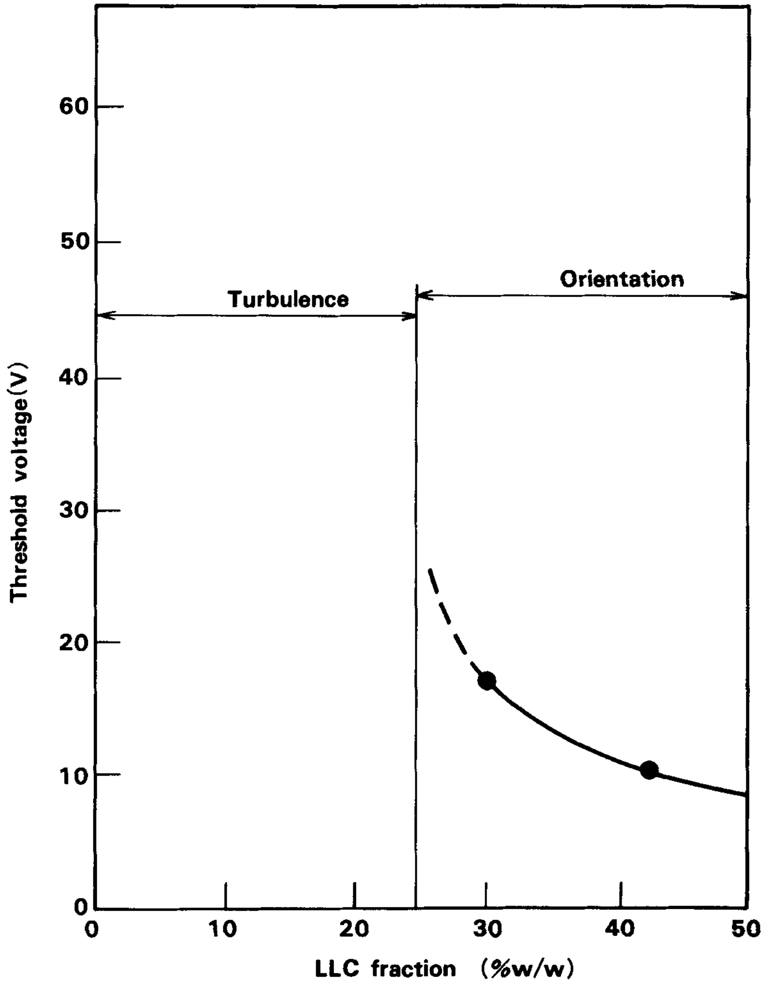
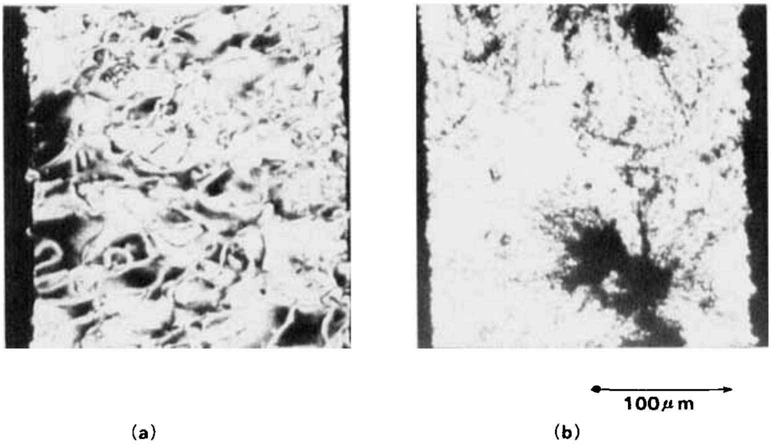


FIGURE 4 Threshold voltage as a function of the LLC fraction for P4-L6.

fraction lower than 30%w/w, no molecular orientation was observed. The mixture showed a turbulence at voltages higher than a certain value.[8] Molecular orientations were attained by a DC electric field at the LLC fraction higher than 30%w/w. The threshold voltage decreased with an increase in LLC fraction.[9-11] Then, the stability of the DC-induced orientation was examined as shown below.

It is known that a molecular orientation of a LCP is preserved by quenching below the liquid crystalline transition temperature.[5] In a mixture of LCP and LLC, however, the molecular orientation is not necessarily preserved because of the crystallization when the LLC fraction is high.[9] Figure 5 (a) and (b) are the microtexture of P6-L6 at the reduced temperature of 0.98 (75°C) and at room temperature, respectively. The mixing ratio of the LLC (L6) was 80%w/w. At 75°C, a schlieren texture (Figure 5 (a)) was observed, which shows that this sample is in a liquid crystalline state. When this sample was cooled to room temperature, a crystalline texture (Figure 5 (b)) appeared. The liquid crystalline state was not preserved at the LLC (L4) fraction of 80%w/w. Thus, the liquid crystalline orientation is not preserved for this sample. In order to determine mixing ratios for preservation of liquid crystalline states at room temperature, phase diagrams were obtained for all mixtures. Figure 6 shows a phase diagram of P4-L6 system. The crystallization occurred above 40%w/w LLC (L6) fraction. Therefore, the LLC (L6) fraction for preser-



(a) (b)

FIGURE 5 Microscopic photographs of the liquid crystalline state at 75°C (a) and the crystalline state at room temperature (25°C) (b) between crossed polarizers for P6-L6 (L6 = 80%w/w).

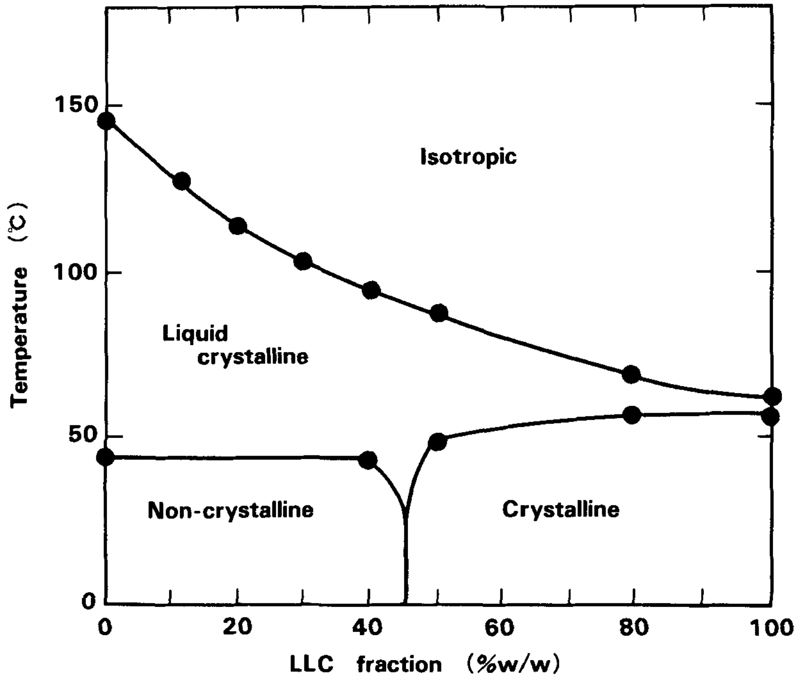


FIGURE 6 Phase diagram of P4-L6.

vation of the molecular orientation at room temperature should be less than 40%w/w.

Mixing regions for preservation of DC-induced orientations at room temperature is determined both from mixing regions for DC-induced molecular orientations at the liquid crystalline temperatures and those for non-crystalline states at room temperature. From Figures 4 and 6, the mixing region of P4-L6 was determined to be from 30%w/w to 40%w/w of the LLC (L6) fraction.

For all mixtures, the mixing regions for preservation of DC-induced orientations were determined. The results are summarized in Figure 7. Figure 7 (a)s show the dependency of mixing regions for preservation of liquid crystalline states (non-crystalline states) at room temperature on alkyl spacer number *n*. These two regions increase with an increase in *n*, and show little difference with each other, which shows that the crystallizability of the mixtures scarcely depends on the species of the LCPs. Figure 7 (b)s show the dependency of mixing regions for the DC-induced orientations on *n* at the liquid crystalline temperatures. These two regions decreases with an increase in *n*. The

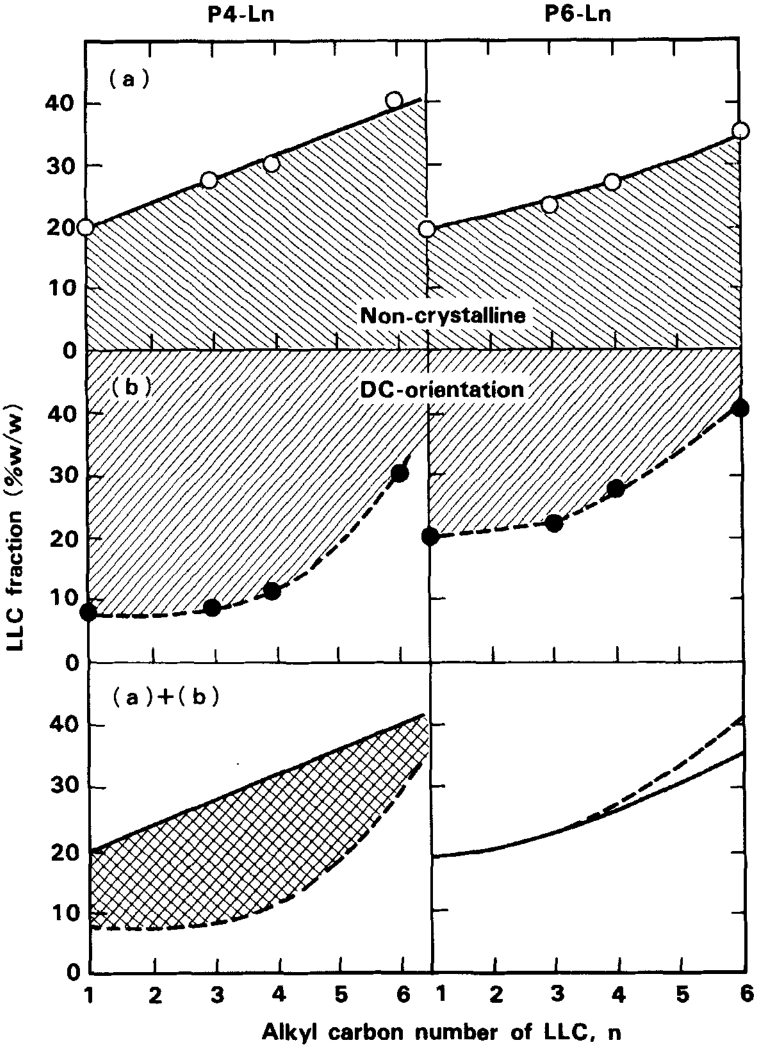


FIGURE 7 LLC fraction for (a) non-crystalline phase, (b) DC-induced orientation and (a) + (b) overlapping of (a) and (b).

region of P4-L*n* is larger than that of P6-L*n* for all *n*. Thus, the mixing region for the DC-induced orientation depends on the species of both the LLCs and the LCPs. The mixing regions for preservation of the DC-induced orientations at room temperature are determined from Figures 7 (a)s and (b)s. Figure 7 (a) + (b)s show the overlapping of these figures. For all P6-L*n*s, there is no overlapping region, which shows that the DC-induced orientations are not preserved at room temperature. For P4-L*n*s, on the other hand, the DC-induced orientations are preserved for all *n*.

Preservation of the DC-induced orientation for P4-L3 is shown photographically in Figure 8. The mixing ratio of the LLC (L3) was

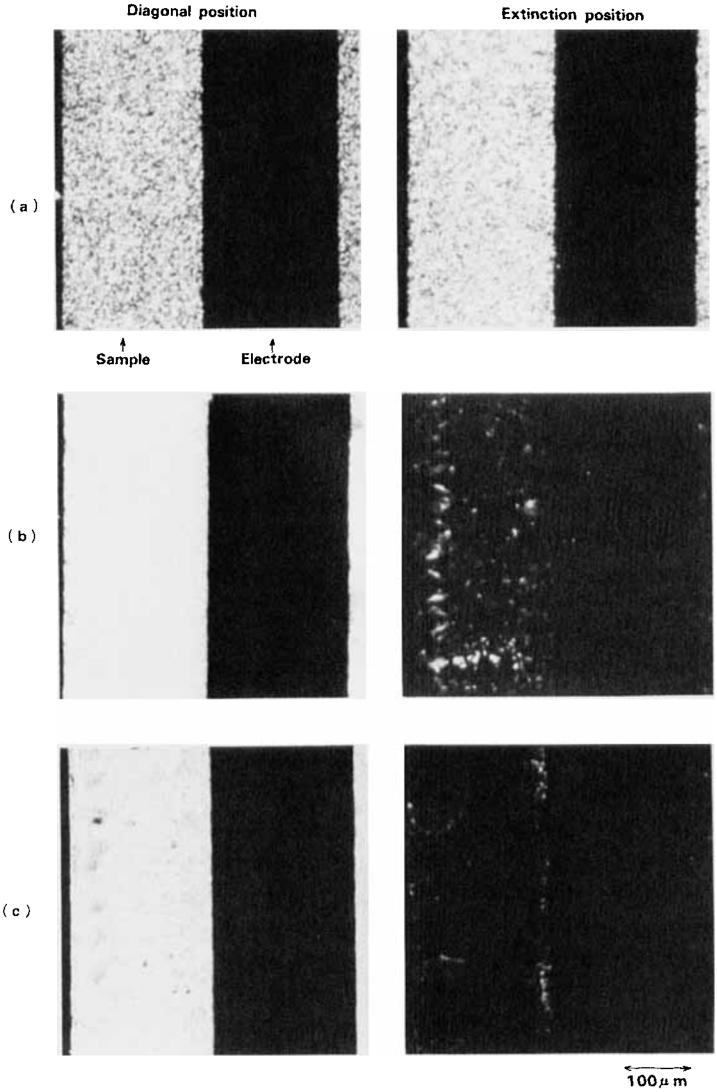


FIGURE 8 Microscopic photographs of P4-L3 under extinction (right) and diagonal position (left) with no electric field at 122°C (a), with 100 V at 122°C (b) and with no electric field at 25°C (c).

9.0%w/w. The electrode and the sample are indicated in this figure. A DC electric field direction was perpendicular to the electrode. Photographs (a)s represent the liquid crystalline state without an electric field, which shows that the sample exhibits no molecular orientation. Photographs (b)s show the DC-induced orientation under 100 V/200 μm, which also shows the orientation direction is parallel to the DC field. Photographs (c)s show that the oriented liquid crystalline state is preserved at room temperature. Thus, for liquid crystalline polysiloxanes mixed with LLCs, transverse molecular orientations are obtained by a DC electric field, which is the first demonstration.

Orientation Behavior

The development of the molecular orientation by a DC electric field at the liquid crystalline temperature was examined by the order parameter and sample resistance measurements.

The dependence of order parameter on applied voltage for P6-L1 are shown in Figures 9 (a). The sample reduced temperature was 0.98. The mixing ratio of LLC was 8.6%w/w. The order parameter detected by the doped dye increased with an increase in the applied voltage above the threshold voltage of 20 V, reached 0.42, and almost saturated at 80 V. Convective instability (flow) of the liquid crystalline texture was observed around the electrodes above 80 V. This instability may be caused by charge injected from electrodes,[17] and inhibit the order parameter increase. Further orientation development may be obtained if the injected charge is depressed.

The dependence of sample resistance on applied DC voltage is shown in Figure 9 (b) for P4-L1 and P6-L1 at their reduced temperature of 0.98 with mixing ratios of 8.6%w/w and 12.0%w/w, respectively. The resistance was determined from the measured current. The resistance of P4-L1 increased with an increase in the applied DC voltage. This resistance change corresponds to the order parameter change in Figure 9 (a). For P6-L1, the resistance did not change, and the liquid crystalline orientation was not observed below 200V. At the voltage above 200V, a turbulence was observed.[8] These results show that the resistance change is caused by the liquid crystalline orientation.

The relationship between the order parameter and the resistance of P4-L1 is obtained from Figure 9. This is shown in Figure 10. The resistance increased with an increase in the order parameter. The same relationship between the order parameter and the resistance

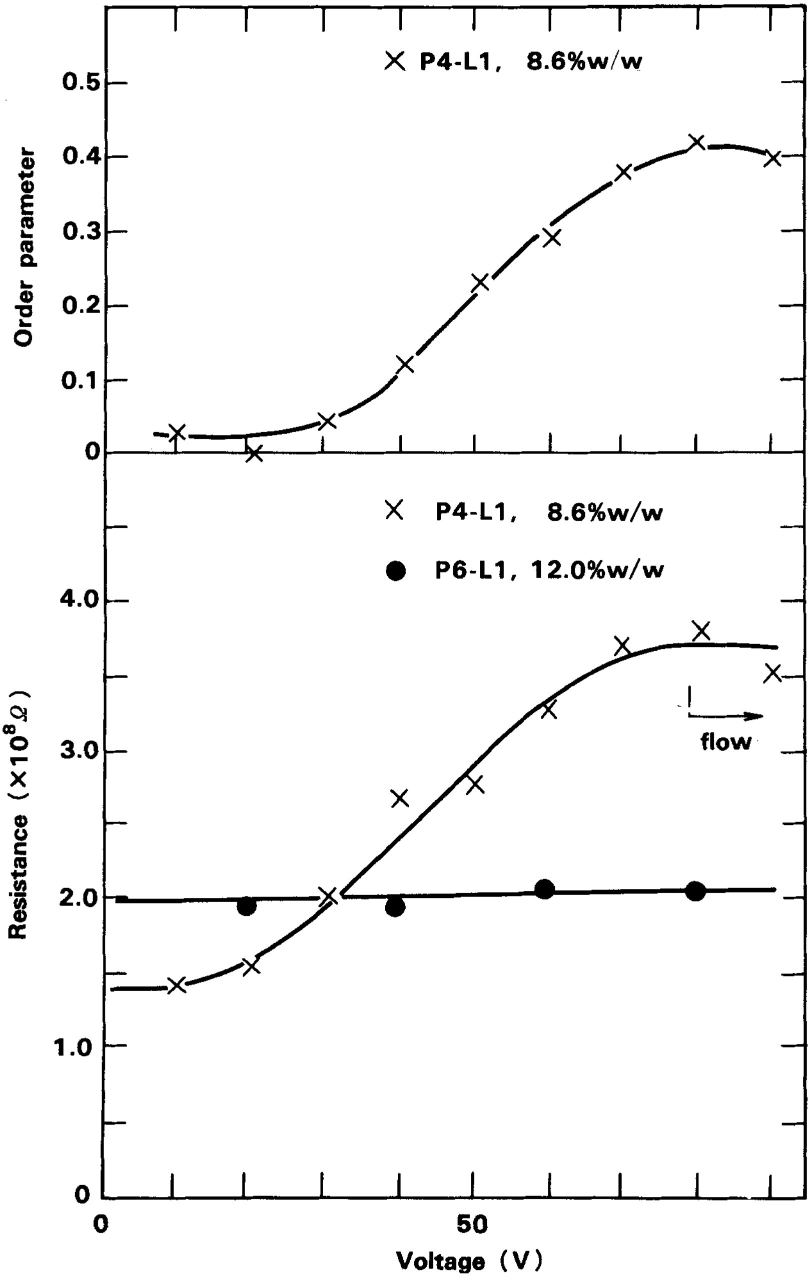


FIGURE 9 Order parameter (a) and resistance (b) as a function of applied voltage for P4-L1.

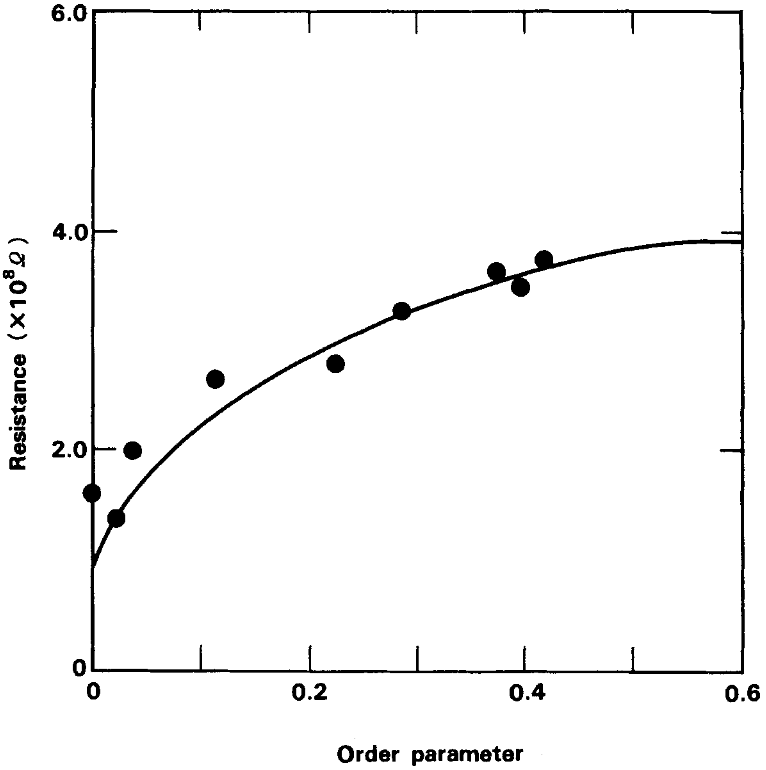


FIGURE 10 Resistance as a function of the order parameter for P4-L1.

was also observed for all mixtures. These indicates that the oriented LCPs have intrinsic anisotropic resistances. Conductive anisotropy is well-known as an electrical property of liquid crystals.[17] In our case, the resistance parallel to the molecular axis direction is thought to be higher than that perpendicular to the axis, because the resistance increases with an increase in the order parameter.

Stability of Preserved Orientation

It is reported that the molecular orientation of polysiloxanes is preserved stably below the liquid crystalline transition temperature.[8] As shown above, the orientations of P4-L*n* are preserved at proper mixing ratios without the crystallization. However, the preserved molecular is not necessarily stable because of the orientation relaxation. Then, the stability of the preserved DC-induced orientation of P4-L*n* was examined by sample aging at room temperature. The aging

TABLE I

Orientation stability

	P4-L1	P4-L3	P4-L4
10%w/w	>1.7 × 10^5 min	>1.7 × 10^5 min	>1.7 × 10^5 min
20%w/w	4.0 × 10^4 min	4.0 × 10^3 min	4.0 × 10^3 min

times until the order parameter was zero are shown in Table I. At LLC (n = 1, 3, 4) fraction of 10%w/w, the order parameters were unchanged for more than 1.7 × 10^5 minutes (4 months), and these preserved orientations were stable. When n = 6, the orientation was not induced by a DC field at L6 fraction lower than 30%w/w, and the preserved orientation relaxed within 4 × 10^3 min (~2.8 days). At LLC fraction of 20%w/w, however, the orientations relaxed within 4 × 10^4 min. These results show that the stability of orientation decreases with an increase in the LLC fractions and that the orientation is very stable at room temperature when LLC (n = 1, 3, 4) fraction is 10%w/w.

CONCLUSION

For mixtures of LCPs with the spacer carbon number m (m = 4, 6) and LLCs with the alkyl carbon number n (n = 1, 3, 4, 6), DC-induced molecular orientations are attained at their liquid crystalline temperatures. The orientations are preserved at room temperature when m is 4, but not preserved when m = 6 because of the crystallization. The preserved molecular orientations of mixtures with 10 %w/w LLC fraction (n = 1, 3, 4) are stable at room temperature for more than 4 months. Thus, DC-induced orientations of proper mixtures with proper mixing ratios are very stable at room temperature.

Acknowledgments

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