

Electric-Field-Induced Transitions of Liquid Crystalline Comb-Shaped Polymers

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The orientational behavior of liquid crystalline comb-shaped polymers (LCPs) with a chiral tartrate unit was examined. The electric-field-induced cholesteric-nematic phase transitions were observed for LCPs. The LCP with a mesogenic side chain in the repeating unit showed two steps of the planar alignment-finger print texture and finger print texture-perpendicular alignment transitions.

Key words: liquid crystalline polymer, cholesteric, electric-field-induced, cholesteric-nematic phase transition

1. INTRODUCTION

The orientational transition of liquid crystalline comb-shaped polymers upon application of alternating current (AC) electric fields has been studied from the theoretical and technological viewpoints [1-3]. In particular, the orientational control of the liquid crystalline comb-shaped polymers is a very important and an interesting subject in order to intend their technological application. We synthesized the liquid crystalline chiral polymers with mesogenic side-groups (Fig.1) [4]. Their thermal properties were examined. The liquid crystalline chiral polymers, which have two mesogenic

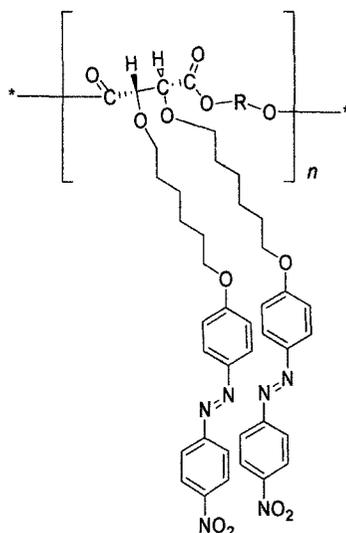


Fig.1. Structures of liquid crystalline chiral polymers (P1-P4) with two mesogenic side-groups.

Table I. Structures of liquid crystalline comb-shaped polymers

Sample	Mn	R
P1	6,000	(CH ₂) ₄
P2	10,000	(CH ₂) ₆
P3	8,000	(CH ₂) ₁₀
P4	5,000	(CH ₂ CH ₂ O) ₂ CH ₂ CH ₂
P5	7,000	—

side-groups in the repeating unit, showed a chiral smectic C phase (Tables I and II). P1 and P4 formed a cholesteric (Ch) phase as well as the chiral smectic C phase. P2, P3, and P4 exhibited high viscosity and a much lower response when compared to P1. The electro-optical properties for the chiral smectic C phase of P1 were previously reported [4,5]. We investigated electric-field-induced transitions for the cholesteric phases for P1 and P5 (Fig.2), which have a chiral tartrate skeleton. This paper describes the orientational behavior of the cholesteric phases for P1 and P5 upon application of electric fields.

2. EXPERIMENTAL

Measurements

Molecular weights of polymers were determined by a Toso HLC-802UR GPC in THF, and calibrated against polystyrene standards. Phase transitions were measured with a Mettler thermosystem and a polarizing microscope equipped a Mettler FP82 hot stage with a Mettler FP900 controller.

Table II. Phase transition temperatures of liquid crystalline comb-shaped polymers

Sample	Phase transition temp./°C					
P1	K	54.0	SmC*	94.0	Ch	114.5 I
P2		g	45.0	SmC*	145.0	I
P3		g	18.0	SmC*	147.0	I
P4	K	42.2	SmC*	95.0	Ch	112.0 I
P5		K	60.0	Ch	130.0	I

Synthesis

The liquid crystalline chiral polymer (P3) with a decamethylene chain was synthesized by polycondensation using 4-nitroazobenzene mesogenic compound and 1,10-decanediol. A mixed solution of tetraisopropyl orthotitanate and diethylene glycol dimethyl ether was used as the polymerization catalyst. The reaction mixture was heated to melt (120°C) under dry nitrogen atmosphere. Then a few drops of above catalyst were added, and the reaction mixture was heated for 6 h. Subsequently, the reaction temperature was raised at 150 °C, and atmospheric pressure was controlled at low vacuum. Finally, the reaction mixture was heated at 160 °C under high vacuum. After the reaction, the cooled reaction mixture was dissolved in THF, and the polymer was reprecipitated by adding methanol to its THF solution. Other polymers (P1, P2, P4, and P5) except P3 were also obtained by the same method.

3. RESULTS AND DISCUSSION

The liquid crystalline comb-shaped polymers (P1-P4), having two mesogenic side-groups in the repeating unit, showed a chiral smectic C (SmC*) phase. P1 and P4 also formed a cholesteric phase as well as the SmC* phase. P5, which has one mesogenic side-group, exhibited only a cholesteric phase. P5 formed finger print and fan textures, and easily showed a photo-induced cholesteric-isotropic phase transition by the light source (30 mW) of the polarizing microscope (Fig.5). In the cholesteric phase of P1, the finger print texture was also observed. In the cell-a (Fig.3), the electro-optical properties were examined for P1 and P5 upon application of electric fields. The homogeneous alignment of P1 was obtained upon application of electric fields in the cell-b (Fig.4).

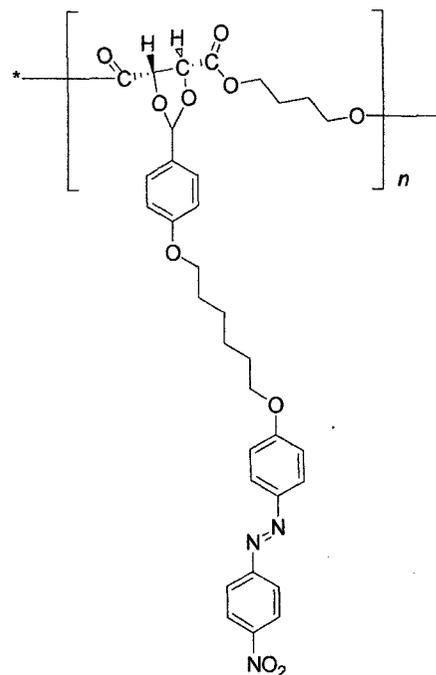


Fig.2. Liquid crystalline polymer (P5) exhibiting a cholesteric phase.

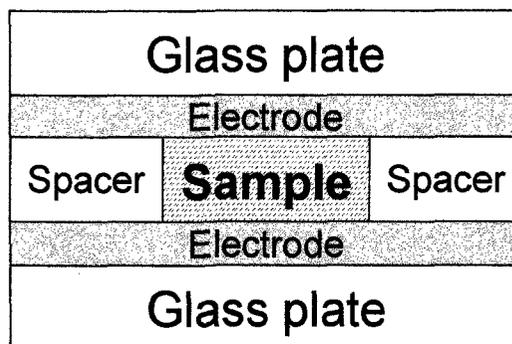


Fig.3. Sandwich cell (cell-a) with ITO glass plates. Cell thickness = 25µm. The electric-field direction is perpendicular to the glass plates.

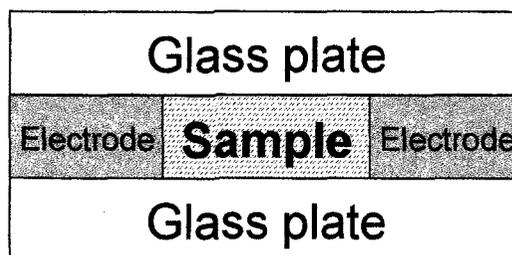


Fig.4. Sandwich cell (cell-b) to obtain homogeneous alignment. Distance between electrodes = 0.5 mm.

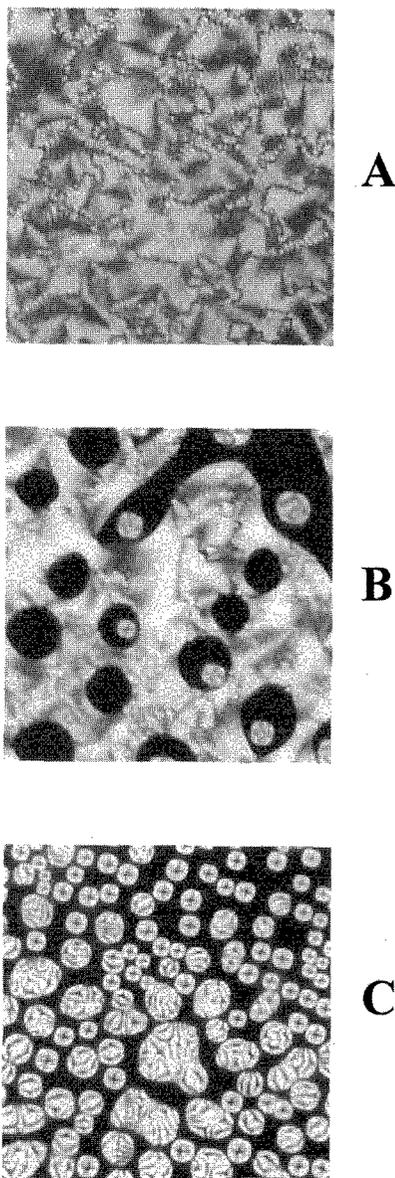


Fig.5. Photo-induced cholesteric-isotropic phase transition (120°C). Irradiation time of halogen light: A;0 s, B;30 s, C;90 s.

P1 and P5 showed an induced cholesteric-nematic phase transition upon application of the electric fields in the cell-a. P1 and P5 formed a perpendicular alignment upon application of the electric field. The perpendicular alignment obtained for P1 also maintained unaltered without the electric field. P5 showed a reversible transition as shown in Figure 6.

Figure 7 shows the electric-field-induced phase transition of P5 observed in the cell-a under parallel Nichols. The photographs a-e in Figure 7 correspond to

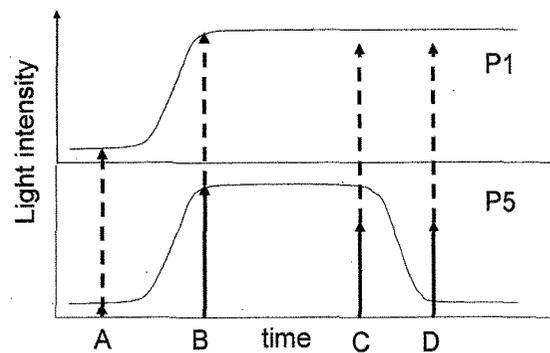


Fig.6. Schematic representation of change of light intensity for electric-field-induced phase transitions of P1 and P5 under parallel Nichols in cholesteric temperatures. A: electric field on; C: electric field off; A-B (upon application of electric field): phase transition from cholesteric to nematic phase; B-C (under electric field): nematic phase with perpendicular alignment; C-D (without electric field): The phase transition from nematic to cholesteric phase was observed in P5. In the case of P1, the nematic phase with the perpendicular alignment also maintained unaltered.

the range A-B in Figure 6. In P5, a planar alignment (initial state, Fig.7a) changed to a finger print texture (Figs. 7b and 7c) upon application of the electric field (2 kHz, 25 μ m). Figure 7d exhibits the change from the finger print texture to a perpendicular alignment upon application of 25 V. The formation of the perpendicular alignment was obtained as shown in Figure 7e. The cholesteric-nematic phase transition in P5 consists of two reorientational behaviors, which are the reorientation of the units with the helical structures and the transition from the finger print texture to the perpendicular alignment. In the case of P1, the phase transition from the finger print texture to the perpendicular alignment was examined because the planar alignment was not homogeneously obtained. Figure 8 shows the relationship between the electric field and the phase states for P1 in the cell-a. The finger print texture-perpendicular alignment and perpendicular alignment-dynamic scattering state transitions were observed. The homogeneous alignment of P1 was obtained by using the cell-b. Diagonal and extinction positions were observed under crossed Nichols as shown in Figure 9. The homogeneous alignment was formed upon application of DC and AC (50, 1k and 20k Hz) electric fields.

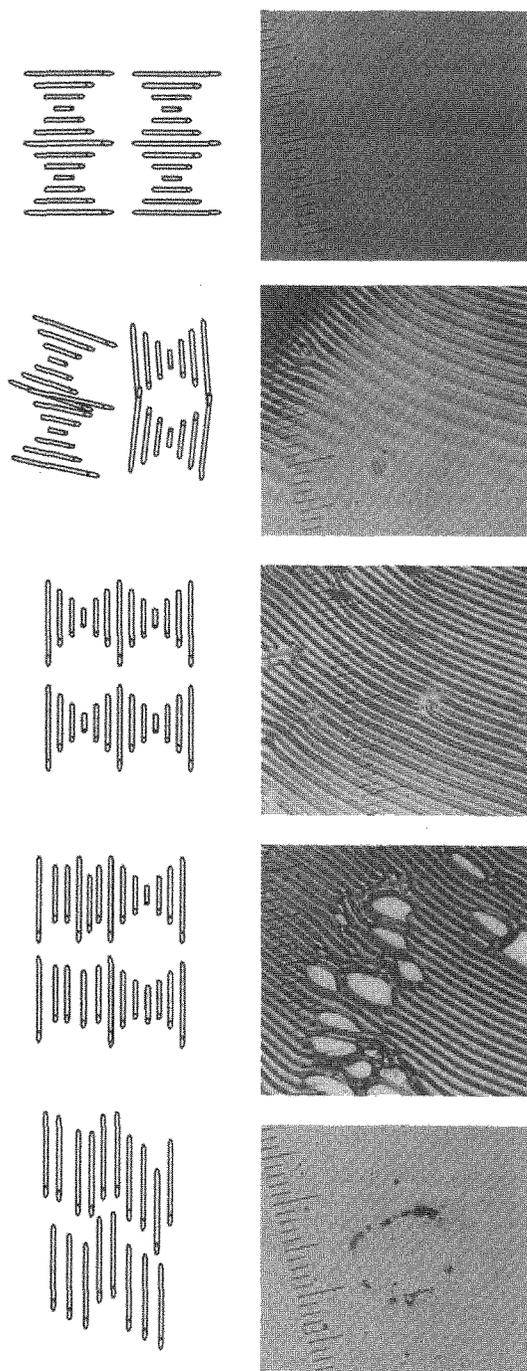


Fig.7. Electric-field-induced cholesteric-nematic phase transition of P5 in cell-a under parallel Nichols ($25 \mu\text{m}$, 2 kHz). a:0 V; b:16 V; c:20 V; d:25 V, e: 55 V.

4. CONCLUSION

P1 and P5 showed the electric-field induced cholesteric-nematic phase transitions. In the nematic phase, the perpendicular alignment was formed. In the case of P1 with two mesogenic groups in the repeating

unit, this perpendicular alignment maintained unaltered without the electric field. This behavior of P1 corresponds to the property that P1 shows the spontaneous formation of the perpendicular alignment. In the case of P5, the electric-field-induced cholesteric-nematic phase transition consists of two steps of the planar alignment-finger print texture and finger print texture-perpendicular alignment transitions.

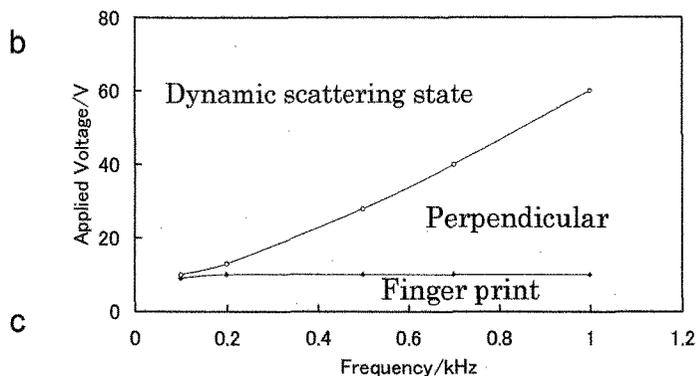


Fig.8. Relationship between electric field and phase states for P1 in cell-a.

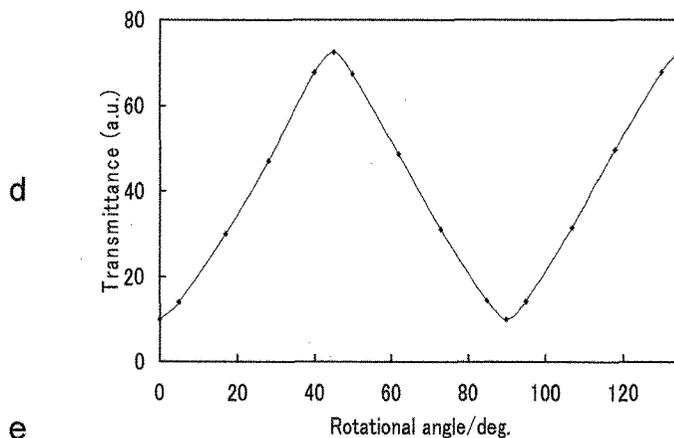


Fig.9. Rotational angle dependence of transmittance obtained for homogeneous alignment formed upon application of 10 V (50 Hz, cell-b). 0° , 90° :extinction position; 45° , 135° :diagonal position.

5. REFERENCES

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(Received December 10, 2005; Accepted March 13, 2006)