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Thermal and Ferroelectric Properties of Chiral Liquid-Crystalline Polytartrate

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Chiral liquid-crystalline polytartrate (LCPTT) with 2R,3R-(+)-tartrate moiety in the skeletal main chain and two mesogenic pendant groups in the repeating unit was prepared. Thermal and ferroelectric properties of LCPTT were dependent on those of the chiral structure. LCPTT exhibited cholesteric and smectic C* phases. The mode value of the spontaneous polarization was 5 mC/m^2.

Cholesteric and smectic C* phases of liquid-crystalline polymers have been studied by several research groups. Side-chain liquid-crystalline polymers (side-chain LCP) with cholesteric and smectic C* phases have been prepared by introducing a chiral moiety into the mesogenic group or the terminal group of the mesogenic side-chain.[1-6] However, there have been few reports on the side-chain LCP with a chiral moiety in the skeletal main chain.

We have synthesized the monomeric liquid-crystalline tartrate (LCTT) which can be applied to prepare of side-chain LCP with the chiral moiety in the skeletal main chain, and have studied on its thermal and ferroelectric properties.[7] In this papar, we report on thermal and ferroelectric properties of the resultant side-chain liquid-crystalline polytartrate (LCPTT).

LCPTT was prepared by the polycondensation of LCTT having 2R,3R-(+)-tartrate moiety with 1,4-butanediol as shown in Fig. 1. A mixed solution of tetra-iso-propyl titanate and diethylene glycol dimetyl ether was used as a polymerization catalyst. The reaction mixture of 2R,3R-(+)-tartrate and 1,4-butanediol was heated to melt (110-120 °C) under dry nitrogen atmosphere. Then a few drops of above catalyst were added, and the reaction mixture was heated for 7 h. Subsequently, the reaction temperature was raised at 140 °C, and atmospheric pressure was controled at low vacuum (0.026 atm) for 3 h. Finally, the reaction mixture was heated at 160 °C

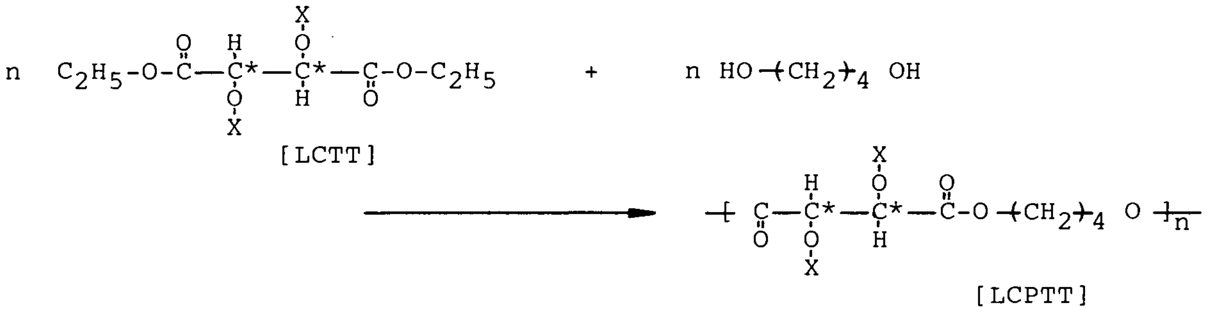

Fig. 1. Synthetic route of LCPTT [2R,3R-(+)]: C* ; chiral center: X ; $-(CH_2)_6-O-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-NO_2$.

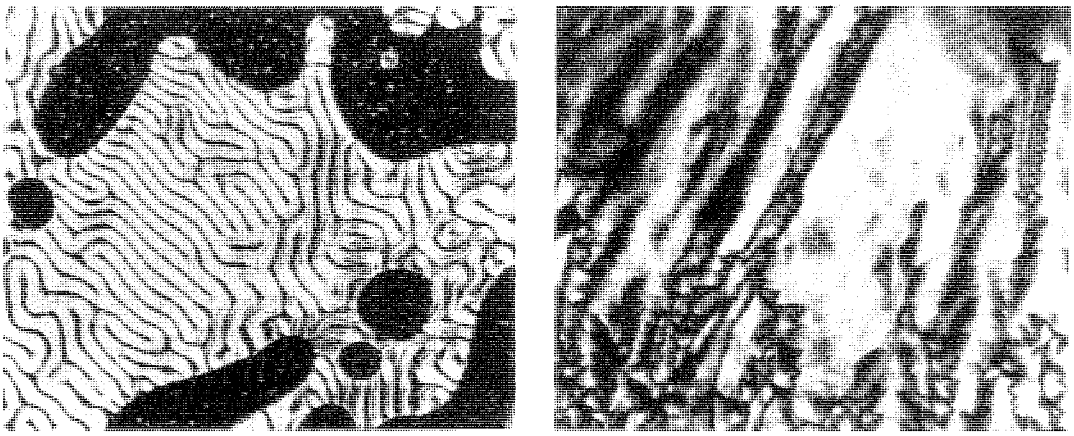
(a) (b)

Fig. 2. Optical textures of LCPTT: (a) ; finger-print texture (cholesteric phase): (b) ; fan texture with striped pattern (smectic C* phase).

Table 1. Phase transition temperatures of LCPTT

$\overline{Mn}$[a)]	Phase transition temperatures[b)] / °C							MR[c)] / °C
6000	K	48.5	SmC*	95.5	Ch	114.5	I	66
9000	K	42.0	SmC*	108.0	Ch	121.0	I	79

a) $\overline{Mn}$:number average of molecular weight determined by GPC in THF, calibrated against polystyrene standards.
b) K:solid phase, SmC*:smectic C* phase, Ch:cholesteric phase, I:isotropic phase.
c) Mesomorphic temperature range.

under high vacuum (0.0026 atm) for 2 h. After the reaction, the cooled reaction mixture was dissolved in tetrahydrofran (THF), and LCPTT was reprecipitated with methanol. Reprecipitations of LCPTT were repeated until no monomers were found.

LCPTT exhibited cholesteric (Ch) and smectic C* (SmC*) phases as same as LCTT. Finger-print and fan textures were observed in Ch and SmC*

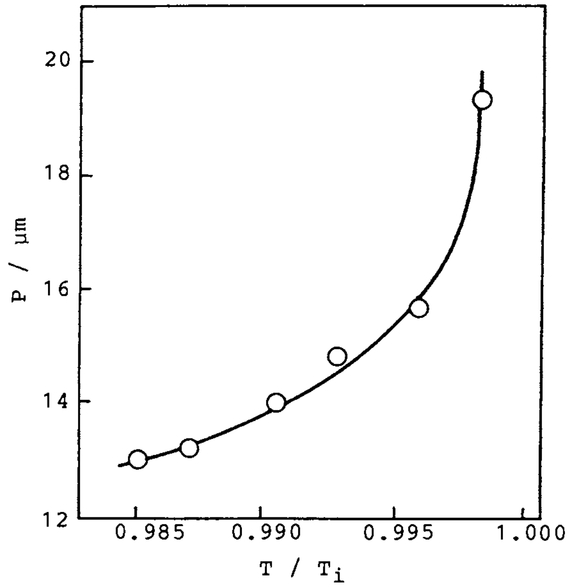

Fig. 3. Temperature dependence of cholesteric pitch (P) for LCPTT ($\overline{Mn}$=6000): Ti ; isotropization temperature: T; measuring temperature.

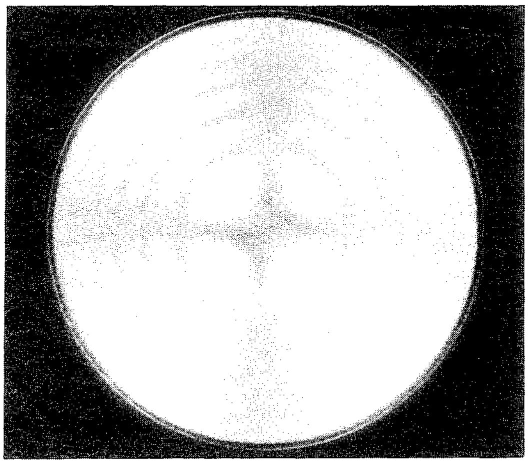

Fig. 4. Conoscopic figure of sample aligned on application of AC electric field.

phases, respectively (Fig. 2). Phase transition temperatures of LCPTT are listed in Table 1. With increasing molecular weight, the Ch-isotropic phase transition temperature increased and the mesomorphic temperature range (MR) became broader. This corresponds with the general fact that the increase of the molecular weight enhances the formation of the liquid-crystalline state.8,9)

A helical pitch (P) in the Ch phase increased with raising temperature as shown in Fig. 3. The minimum value of the P for LCPTT was about 12-13 µm which is the same value as LCTT.

LCPTT was homeotropically aligned by annealing at 90 °C. The homeotoropically aligned state remained unaltered in the solid phase on cooling. The value of the optical rotatory angle for the homeotropically aligned sample was +45 degree/mm. This indicates the existence of the helical structure in the SmC* phase. A conoscopic figure characteristic of an optically biaxial state as shown in Fig. 4 was observed for a sample aligned on application of the AC electric field (6 MV_{rms}/m/5 kHz).

The homeotropically aligned sample exhibited three scattering peaks (2θ / degree = 3.0, 6.3, 9.6) in the X-ray small angle region. The SmC* layer spacing (d) calculated from the first order diffraction angle is 29.4 Å, and the length of the mesogenic side-chain long axis is 21 Å. So, in the SmC* layer structure of LCPTT, the neighboring mesogenic groups overlap about 11.4 Å (tilted angle : 16 degree).

A hysteresis loop observed in the SmC* phase (80 °C) of LCPTT is shown in Fig. 5. The mode value of the spontaneous polarization (Ps) for every

LCPTTs was 5 mC/m^2, and it was the same large value as monomeric LCTT.

The Ps value of ferroelectric liquid-crystalline polymethacrylates and polyacrylates with chiral center in the mesogenic terminal group have been reported by several research groups. The Ps value of LCPTT studied in this work is 150 to 500 times as large as their Ps value.$^{1,6)}$ The Ps value is well-known to become small when a chiral center is located in a nonpolar group, and is far apart from a mesogenic group. The chiral centers in the tartrate moiety are separated with the hexamethylene spacer from the mesogenic group. However, ether oxygens and carbonyl groups, which are polar groups, are directly attached to two chiral centers. In this case, the Ps value of LCPTT is independent of the position of chiral center, whereas a stereopolar coupling takes place.$^{10)}$ Therefore, LCPTT exhibites the large Ps value.

The response time requiring for the realignment of Ps was 50 ms under a electric field of 100 V_{rms} / 2 Hz at 80 °C.

A field-induced realignment of Ps was observed in the Ch phase of LCPTT. This phenomenon of a pseudo-ferroelectric property was the same as that found in the monomeric LCTT.

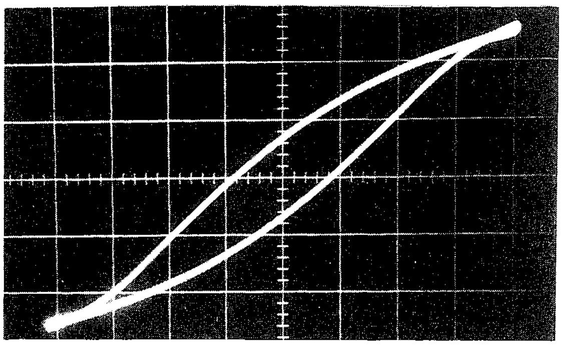

Fig. 5. Hysteresis loop measured in SmC* phase (80 °C, $\overline{Mn}$=6000):
X-axis ; 500 kV_{rms}/m/div:
Y-axis ; 4.6 mC/m^2/div.

References

1) V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov, and N. A. Plate, Polym. Bull., 12, 299 (1984).
2) J. M. Guglielminetti, G. Decobert, and J. C. Dubois, Polym. Bull., 16, 411 (1986).
3) J. C. Dubois, G. Decobert, P. L. Barny, S. Esselin, C. Friedrich, and C. Noel, Mol. Cryst. Liq. Cryst., 137, 349 (1986).
4) H. Finkelmann and H. Ringsdorf, Makromol. Chem., 179, 827 (1978).
5) H. Finkelmann, J. Kaldehoff, and H. Ringsdorf, Angew. Chem., 90, 992 (1978).
6) S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto, and K. Kawasaki, Mol. Cryst. Liq. Cryst., 155, 93 (1988)
7) S. Ujiie and K. Iimura, Chem. Lett., 1989, 2217.
8) S. G. Kostromin, R. V. Talroze, V. P. Shibaev, and N. A. Plate, Makromol. Chem., Rapid Commun., 3, 803 (1982).
9) H. Stevens, G. Rehage, and H. Finkelmann, Macromolecules, 17, 851 (1984).
10) B. Otterholm, M. Nilsson, S. Lagerwall and K. Skarp, Liq. Cryst., 2, 757 (1987).

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