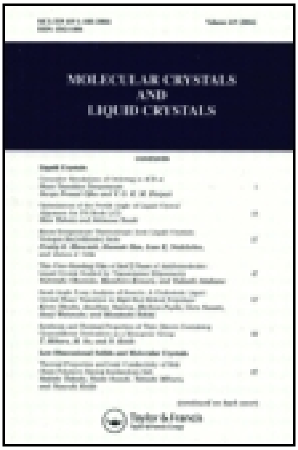

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Synthesis of Some Smectic Liquid Crystalline Polymers and Their Ferroelectricity

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SYNTHESIS OF SOME SMECTIC LIQUID CRYSTALLINE POLYMERS AND THEIR FERROELECTRICITY

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Abstract Ferroelectric smectic liquid crystalline polymers were synthesized. They are acrylate polymers whose side chains contain a flexible spacer unit, a mesogen unit and an optically active substratate. Their liquid crystalline properties were determined by DSC analysis, optical microscopy, X-ray diffraction and the observation of spontaneous polarization. The response time was as small as milliseconds.

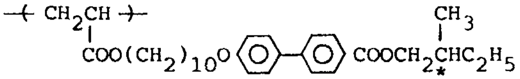
INTRODUCTION

Studies on liquid crystalline polymers (LCPs) have evoked much interest in recent years, especially in ferroelectric LCPs. The use of some optically active substituents in the side chains of LCPs has been tried by analogy with low molecular weight ferroelectric liquid crystals[1-4]. Shibaev et al.[5] and Dubois et al.[6-7] have reported the possibilities for the synthesis of ferroelectric LCPs.

We have succeeded in a synthesis of ferroelectric LCPs of the polyacrylate type. This paper reports on the synthesisandthecharacterization oftheferroelectric LCPs.

EXPERIMENTAL

The polymer



$-(CH_2CH)-$ with $COO(CH_2)_{10}O-C_6H_4-C_6H_4-COOCH_2\overset{*}{C}H(CH_3)C_2H_5$

was synthesized as follows. 4'-hydroxybiphenyl-4-carboxylic acid[8] was quantitatively esterified with (S)-(-)-2-methylbutanol in the presence of acid catalyst. The product was quantitatively etherified with an excess of 1,10-dibromodecane in the presence of potassium carbonate. The product was esterified with acrylic acid in the presence of an equivalent amount of tetramethylammonium hydroxide pentahydrate at room temperature. Finally the monomer, (S)-(+)-2-methyl butyl 4'-(10-acryloyloxydecyloxy)biphenyl-4-carboxylate was obtained in more than 60% overall yield.

Various molecular weight polymers were obtained under the conditions which are listed in Table 1. AIBN and V-70 (2,2'-azobis(4-methoxy-2,4-dimethylvaleronitorile), Wako Junyaku Co., Ltd.) were used as initiators. The molecular weights $\overline{M}n$ were from 1.9×10^3 to 4.2×10^4.

A differential scanning calorimeter (Perkin Elmer model VII) was used for phase transition measurements. Before DSC

TABLE 1. Polymerization data and results for various molecular weight LCPs.

Initiator [Conc. (mmole/l)]	Solvent	Monomer conc. (mole/l)	Temperature(°C)	Conv. (%)	$\overline{M}n$ [Pn]$^{1)}$
AIBN [8]	THF	0.05	80	97	1,900 [4]
AIBN [4]	THF	0.1	60	95	3,300 [7]
AIBN [2]	THF	0.2	60	89	7,500 [15]
AIBN [8]	DMF	0.2	60	73	14,800 [30]
AIBN [4]	DMF	0.4	60	76	26,000 [53]
V-70$^{2)}$[4]	DMF	0.2	r.t.	52	37,300 [76]
V-70$^{2)}$[2]	DMF	0.2	r.t.	56	42,300 [86]

1) Measured by GPC.
2) V-70 : 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile).

measurements were done, each sample was preheated in the cell to a certain temperature where the sample was isotropic. The preheated samples were cooled down at a cooling rate of 1 °C/min. and thermograms were obtained under a nitrogen atmosphere.

An optical microscope equipped with a hot stage (Mettler FP-82) was used for the texture studies of the LCPs. The samples were 10 µm thick.

X-ray diffraction measurements were made with a rotaflex (Geigerflex RAD rA, Rigaku Corp.) with a power of 50 kV, 150 mA.

Spontaneous polarization was evaluated by the current signal which was generated by applying a voltage with a triangular shaped wave form. The voltage (60 V and 0.02 Hz) was applied to the 4 µm thick samples which were put between two sheets of glass slides coated with conducting In_2O_3/SnO_2.

Response time was measured by applying 200 V to a 10 µm thick cell. The time measured was that required to change the light transmission from 0 to 90%.

RESULTS AND DISCUSSION

THERMAL ANALYSIS

The DSC curve for the polymer (Pn76, $\overline{M}n = 3.7 \times 10^4$) is shown in Fig. 1. The thermogram between 20 °C and 60 °C is magnified in the inset. The figure shows two tiny exotherm at peaks between the clearing temperature at 116 °C and the glass transition temperature at 11 °C. It is deduced that the transition at 57 °C is SmA to SmC^*, since the transition enthalpy was as small as 200 mJ/g and furthermore, the thermogram shows this exotherm while the base line shifts,

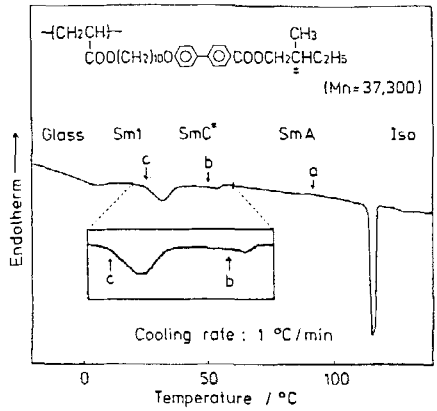


FIG. 1. DSC curve of LCP.

which is a characteristic feature of the transition of SmA to SmC* in low molecular weight ferroelectric liquid crystals[9-10].

OPTICAL MICROSCOPY

The texture of Pn76 is represented in Fig. 2 at the temperatures (a), (b) and (c) indicated in Fig. 1. The fan-shaped texture suggests that the phase at the highest temperature (a) is SmA. The appearance of equidistant lines in the fan-shaped texture at temperatures (b) and (c) proves

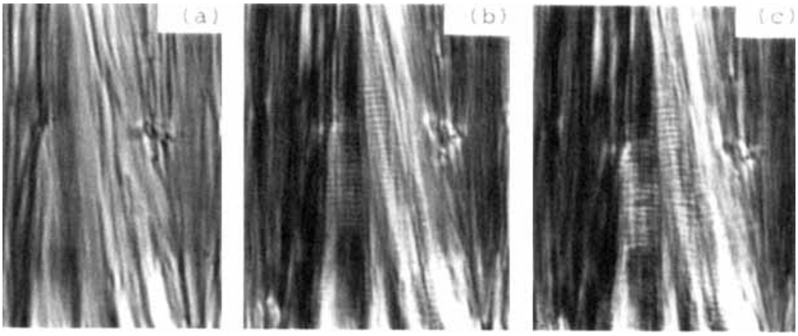


FIG. 2. Micrographs of the textures of Pn76 at various temperatures; (a) at 90 °C, (b) at 52 °C, (c) at 25°C.
See Color Plate I.

the existence of the spiral structure in the SmC* and/or higher ordered state.

X-RAY DIFFRACTION

In Fig. 3, the layer spacing of Pn76 determined by small angle X-ray scattering is plotted against the temperature. The layer spacing between 57 °C and 116 °C was 33 Å, which agrees with the calculated length of the side chain part in Pn76. The layer spacing linearly decreased with decreasing the temperature below 57 °C. This shows that the side chains in the layer begin to incline around 57 °C and the tilt angle increases with decreasing the temperature.

Fig. 4 shows the wide angle X-ray diffraction curves at three temperatures. At temperatures (a) and (b), only broad curves were observed. This proves that there is no intralayer order in the liquid crystalline phase. At the temperature (c), on the other hand, one single peak is observed at 19.3°, which suggests the existence of hexagonal order. We have not yet decided whether this phase is SmF* or SmI*.

We have therefore been able to identify the phases of

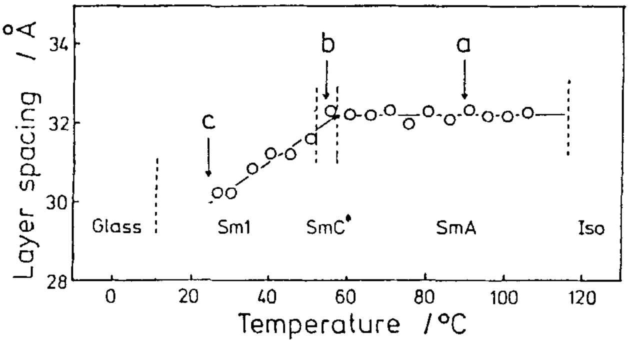


FIG. 3. Temperature dependence of layer spacing of LCP

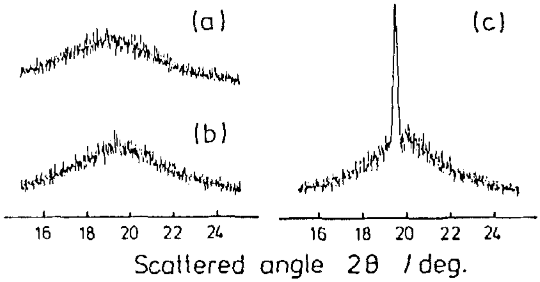


FIG. 4 Wide angle X-ray diffraction curves of LCP at different temperature; (a) at 90 °C, (b) at 55 °C, (c) at 25 °C.

Pn76 at each temperature, SmA between 116 °C and 57 °C, SmC* between 57 °C and 52 °C , and SmF* or SmI* between 52 °C and 11 °C.

OBSERVATION OF SPONTANEOUS POLARIZATION

Fig. 5 shows the dependence of the spontaneous polarization of the LCP ($\overline{M}n$ = 1.5 x 10^4) on temperature. The spontaneous polarization was not observed until the temperature was at 59 °C. It increased steeply with decreasing temperature, and became around 3 nC/cm^2, which is approximately equivalent to the value for a corresponding low molecular weight compound. Below 45 °C it rapidly decreased. It should of course have increased with decreasing temperature, since the phase formed is considered to be SmF* or SmI*, i.e., a higher ordered state than SmC*. However, the lower the temperature became, more rigid did the LCP become. Thus the molecular response goes down. In some cases however, the spontaneous polarization was actually observed to increase with decreasingfrequency of the applied triangular voltage.

As a result of the above, it was proved that our LCPs

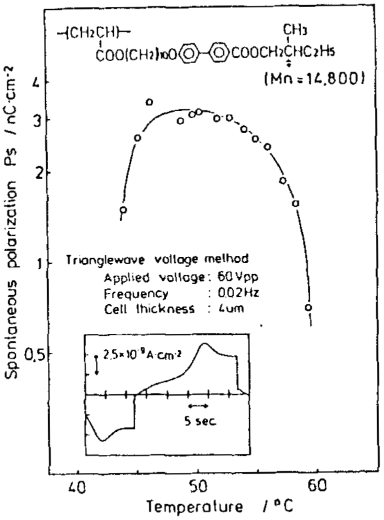


FIG. 5. Temperature dependence of spontaneous polarization in the SmC* phase.

are the first confirmed ferroelectric LCPs.

MOLECULAR WEIGHT DEPENDENCE OF PHASE TRANSITION BEHAVIOR

Phase transition behaviors for various molecular weight LCP are listed in table 2. Each LCP has a similar phase variation, and has a SmC* phase only on cooling.

The molecular weight dependence of phase transition temperature on cooling is shown in Fig. 6. The corresponding low molecular weight LC is shown also. As shown in Fig. 6, the liquid cryatalline region of the LCPs are much broader than that of the low molecular weight LC. This is due to a polymer effect that the main chains of the LCPs contribute to the formation of liquid crystalline state through condensing the chains. The liquid cryatalline state broadened out and the transition temperatures increased with increasing molecular weight. The enantiotropic phase transition temperatures no longer increased as significantly when molecular weight was over 1.5 x 10^4.

TABLE 2. Phase transition temperatures of LCPs.

$\overline{M}n$ [Pn] 1)	Transition temperature 2) (°C)
3,300 [7]	$\mathrm{Glass} \underset{-10}{\overset{-7}{\longleftrightarrow}} \mathrm{Sm1}^{3)} \xrightarrow{42} \mathrm{SmA} \underset{87}{\overset{98}{\longleftrightarrow}} \mathrm{Iso}$; $\mathrm{SmA} \xrightarrow{40} \mathrm{SmC}^{*} \xrightarrow{26} \mathrm{Sm1}$
7,500 [15]	$\mathrm{Glass} \underset{3}{\overset{9}{\longleftrightarrow}} \mathrm{Sm1}^{3)} \xrightarrow{52} \mathrm{SmA} \underset{105}{\overset{112}{\longleftrightarrow}} \mathrm{Iso}$; $\mathrm{SmA} \xrightarrow{50} \mathrm{SmC}^{*} \xrightarrow{38} \mathrm{Sm1}$
14,800 [30]	$\mathrm{Glass} \underset{8}{\overset{11}{\longleftrightarrow}} \mathrm{Sm1}^{3)} \xrightarrow{58} \mathrm{SmA} \underset{115}{\overset{119}{\longleftrightarrow}} \mathrm{Iso}$; $\mathrm{SmA} \xrightarrow{53} \mathrm{SmC}^{*} \xrightarrow{46} \mathrm{Sm1}$
37,300 [76]	$\mathrm{Glass} \underset{11}{\overset{15}{\longleftrightarrow}} \mathrm{Sm1}^{3)} \xrightarrow{60} \mathrm{SmA} \underset{116}{\overset{120}{\longleftrightarrow}} \mathrm{Iso}$; $\mathrm{SmA} \xrightarrow{57} \mathrm{SmC}^{*} \xrightarrow{52} \mathrm{Sm1}$
low molecular weight LC 424	$\mathrm{Cryst} \xrightarrow{48} \mathrm{SmA} \underset{64}{\overset{64}{\longleftrightarrow}} \mathrm{Iso}$; $\mathrm{SmA} \xrightarrow{42} \mathrm{SmC}^{*} \xrightarrow{38} \mathrm{Cryst}$

1) Measured by GPC.
2) Transition temperature was determined by optical microscopic observation, except for Tg, measured by DSC analysis.
3) Sm1 is SmF* or SmI*.

RESPONSE TIME

The temperature dependence of the response time of the SmC* phase of the LCPs is shown in Fig. 7. The response time increased with increasing molecular weight of the LCPs, and became constant above 1.5 x 10^4. It decreased with increasing temperature, and became constant above a certain temperature, which was 5 °C lower than the transition temperature, SmA to SmC*. We have not yet recognized whether this temperature difference is significant or

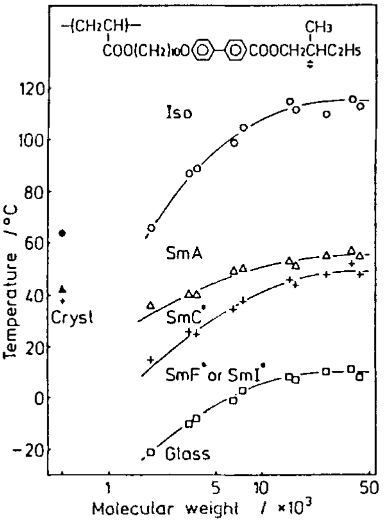


FIG. 6. Molecular weight dependence of phase transition temperatures of the LCP.

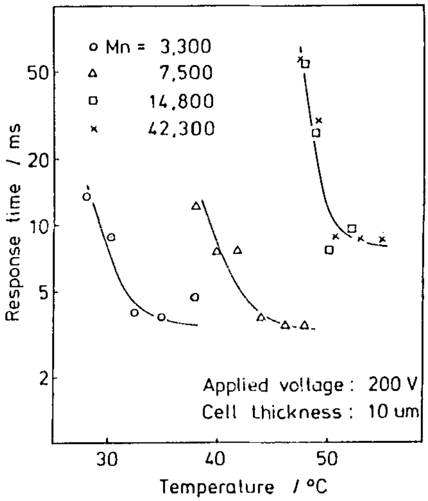


FIG. 7. Temperature dependence of response times of the SmC* phase.

or incidental. The optimum response time is around 4 ms, which was measured above 32 °C for $\overline{M}n = 3.3 \times 10^3$. The response time is around 8 ms even for the highest molecular weight sample, $\overline{M}n = 4.2 \times 10^4$. These response times of the ferroelectric LCPs are much smaller than those of nematic LCPs.

CONCLUSION

Ferroelectric liquid crystalline polymers were obtained. They were confirmed by DSC analysis, optical microscopy, X-ray diffraction, and the observation of spontaneous polarization. The response time was as small as milliseconds, which is a thousand times smaller than for nematic LCPs.

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