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New Polymeric Ferroelectric Liquid Crystal with Two Chiral Groups

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New Polymeric Ferroelectric Liquid Crystal with Two Chiral Groups

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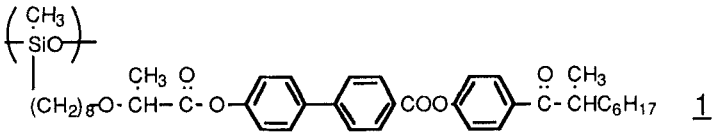
A new polymeric ferroelectric liquid crystal (PFLC) with an optically active alkanoyl group and a chiral group derived from lactic acid has been synthesized. The PFLC shows the smectic A phase, chiral smectic C phase and higher-order smectic phase, and exhibits large spontaneous polarization.

Keywords: polymeric liquid crystal, ferroelectricity, preparation, liquid crystal phase, spontaneous polarization

INTRODUCTION

Ferroelectric liquid crystals (FLCs) have attracted much attention because of their fast switching rate and bistability. Polymeric ferroelectric liquid crystals (PFLCs) have also been prepared to improve the processability of FLCs,[1–5] but their switching rates are low because of their high viscosity.

To increase the switching rate of PFLCs, we have been trying to increase their spontaneous polarization, and we have already reported a PFLC with a spontaneous polarization of 50 nC/cm^2. The main chain of this PFLC is polysiloxane and its side chain mesogen has an alkanoyl group.[6] On the other hand, low molecular weight dichiral FLC, having a chiral group derived from lactic acid on one side and an optically active alkanoyl group on the other side of the core, has recently been shown to exhibit very large spontaneous polarization.[7] We have extended this study and synthesized a new PFLC 1 with this FLC as its side chain.



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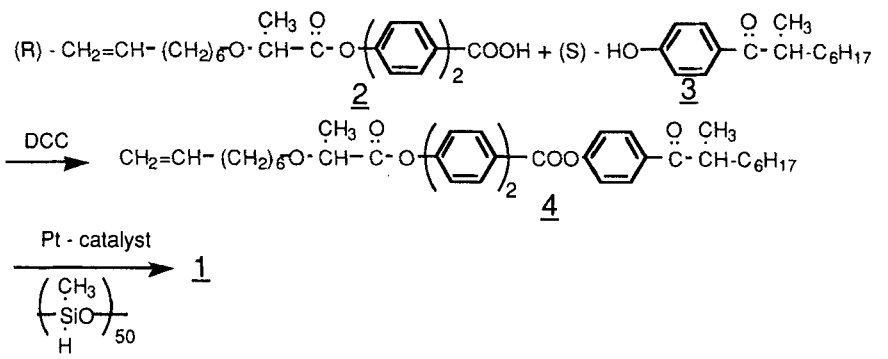


SCHEME 1 The preparation of PFLC 1.

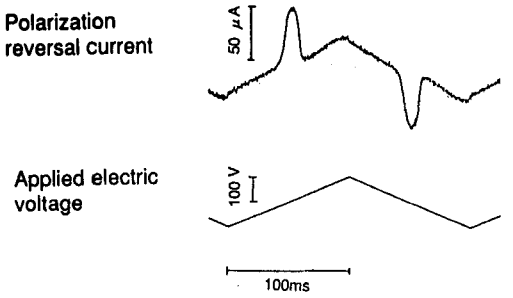


FIGURE 1 Applied voltage (lower) and polarization reversal current (upper) (10-μm cell, 5 Hz, 110 V, at 112°C).

EXPERIMENTAL

The polymer was prepared according to Scheme 1. Compound 2 reacted with phenol 3 in the presence of dicyclohexylcarbodiimide to give the olefinic derivative 4. Compound 4 was purified by chromatography, and then recrystallized from ethanol. The target polymer 1 was obtained from a hydrosilylation reaction[8] between Compound 4 and poly(methylhydrosiloxane) in the presence of a Pt-catalyst. Polymer 1 was purified by several precipitations from methanol and by gel filtration. The molecular structure was confirmed by IR and ^{1}H-NMR.

Liquid crystalline phases were identified by polarized microscopy (Nikon XTP-11) with a Mettler FP82 hot stage. Phase transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC-7). The spontaneous polarization was measured by the triangular wave method. A 110-V triangular wave was applied across a 10-μm-thick polymer. A current-to-voltage converter transformed the polarization reversal current into a voltage signal, that was recorded on a digitizing oscilloscope. As shown in Figure 1, the polarization reversal current peak was separated from an ionic current peak by optimizing the measuring conditions.

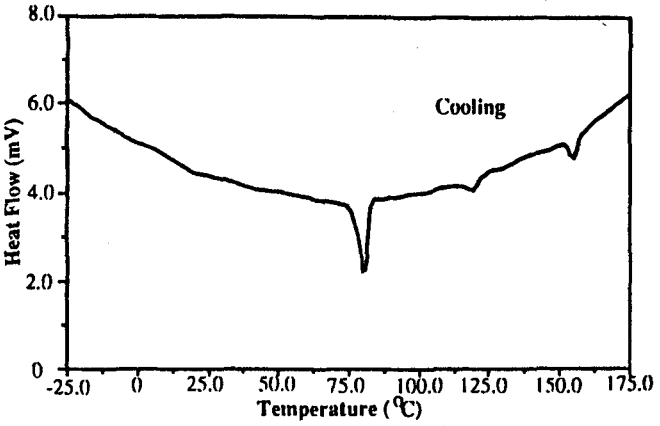
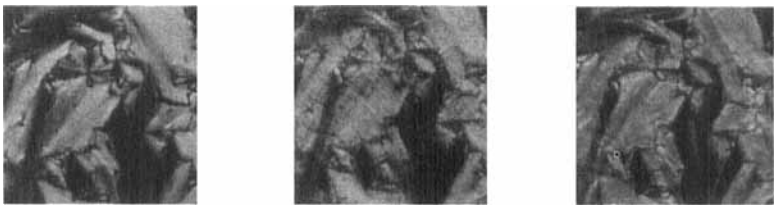


FIGURE 2 DSC curve of PFLC 1.



(a) 125 °C (b) 110 °C (c) 70 °C

FIGURE 3 Polarized micrographs of PFLC 1. See Color Plate XXI.

RESULTS AND DISCUSSION

The DSC curve of PFLC 1 in the cooling process is shown in Figure 2. The isotropic to SmA transition appears around 160°C, and the transition temperature from the SmA to SmC* phase is around 120°C. The peak at 80°C is due to a phase transition from SmC* to a higher-order smectic phase. A glass transition is not clear.

Figure 3 is the polarized micrographs of PFLC 1. At 125°C a typical fan-shaped texture is observed, suggesting the SmA phase. At 110°C dechiralization lines appear in the fan-shaped texture. It is identified as the SmC* phase. At 70°C the texture somewhat resembles that in the SmC* phase, and the response to an electric field was observed at this temperature. The switching rate was very low. No polarization reversal current peak was confirmed. This response revealed that this is a higher-order tilted smectic phase.

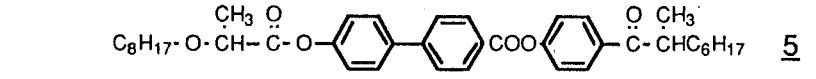
The transition temperatures of PFLC 1 and corresponding FLC 5 are listed in Table I. The thermal stabilities of liquid crystal phases are increased by polymerization. PFLC 1 has enantiotropic liquid crystalline phases, while those of the corresponding FLC 5 are monotropic. The ranges of liquid crystalline phases, especially for the SmA phase, spread and a higher-order smectic phase appeared for PFLC 1.

The temperature dependences of the spontaneous polarization for PFLC 1 and

TABLE I

Phase transition temperatures

Compound	temperature (°C)
PFLC 1	G -20 Sx 82 Sc* 117 SA 158 Iso
FLC 5	Cr 80 (Sc* 73 SA 75) Iso



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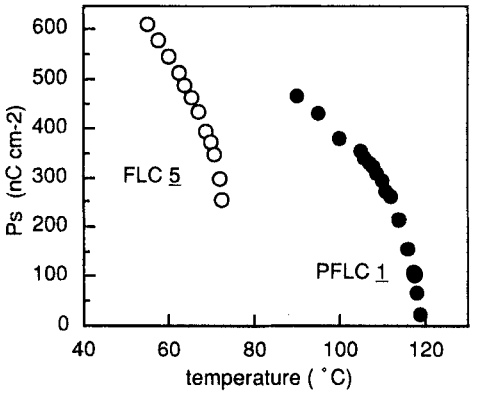

FIGURE 4 Temperature dependences of spontaneous polarization for PFLC 1 and FLC 5.

the corresponding FLC 5 are shown in Figure 4. The highest spontaneous polarization for PFLC 1 was 465 nC/cm^2 at 90°C. At 10°C below the SmC*-SmA transition temperature the spontaneous polarization for PFLC 1 is smaller than that for FLC 5. The reason for this is the difference in their temperature dependences. Upon heating, the spontaneous polarization for PFLC 1 decreases to zero continuously toward the SmC*-SmA transition, indicating the second-order transition. The spontaneous polarization of FLC 5, on the other hand, falls abruptly to zero at the transition, which suggests that the transition is first-order.

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