Ferroelectric liquid crystalline polyoxetanes bearing chiral dimesogenic pendants

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Two new polyoxetanes bearing dimesogenic pendants were prepared and their liquid crystalline properties were studied by differential scanning calorimetry (DSC), polarizing microscopy, and X-ray diffractometry. The dimesogens consist of cholesterol and biphenyl moieties connected through polymethylene spacers. Their biphenyl ends were attached to the oxetane monomer through a hexamethylene unit and the dimesogenic monomers were subjected to cationic ring-opening polymerization. The molecular weights of the polymers were very low and the degree of polymerization was only about 6. The two polymers were found to be thermotropic and formed only the chiral smectic C (Sc*) phase and, thus, their ferroelectricity was studied. Their spontaneous polarization values at the Sc* phase were about 20 nC cm^{-2} with responsive times of around 0.3 ms at 7 °C below the clearing temperature.

Introduction

In recent years, there has been much interest in the liquid crystallinity (LC) of twin dimeric[1–6] and dimesogenic[7–17] compounds that contain two identical or different mesogenic units. They are not only used as model compounds for the main chain liquid crystalline polymers (LCPs), but are also known to reveal very interesting mesophase behavior that is unexpected on the basis of the behavior of the corresponding monomeric LC compounds. We found that some of them formed incommensurate and twisted grain boundary (TGB) phases.[10,13,15,16]

On the other hand, many side-chain liquid crystalline polymers (SCLCPs) based on poly(meth)acrylate,[18–21] polyoxetane,[22–28] and polysiloxane[29–39] backbones, with and without chiral centers, have been reported. In particular, some of the SCLCPs bearing chiral centers exhibit the chiral smectic C (Sc*) phase and, thus, ferroelectric properties.[21,26,28,29,31,32] Those derived from polysiloxanes appear to show high spontaneous polarization values and fast response times. One of the examples[31] was reported to reveal spontaneous polarization as high as 420 nC cm^{-2}. Polyoxetane SCLCPs also are actively being investigated because of the relative flexibility of their main chain when compared, for example, with poly(meth)acrylates. Hsu *et al.*[26] reported that some of the Sc* SCLCPs based on polyoxetanes showed very fast switching times in the range of microseconds. We have also reported previously the LC properties of the Sc* polyoxetanes.[28] We, however, could not measure the values of spontaneous polarization (P_s), although a weak bistability was observed.

It should be noted that all of the SCLCPs reported up to now bear monomesogenic pendants. As alluded to above, we have been studying the LC properties of dimesogenic compounds and also SCLCPs in order to establish their structure–property relationships.

In this investigation, we prepared two new SCLCPs based on the polyoxetane backbone that bears pendants consisting of two different mesogenic units. For the sake of brevity, we call the two polymers **Pox-4Dm** and **Pox-5Dm**. Pox stands for polyoxetane, 4 and 5 indicate the number of the methylene groups in the spacer between the two mesogenic units and Dm stands for the 'dimesogenic' pendant. The LC properties of the polymers were studied by DSC, polarizing microscopy, X-ray analysis, and also by the measurements of their ferroelectricity.

Experimental

The synthetic route to the polymers is shown in Scheme 1. The numbers given in this section for the intermediates and monomers are the same as given in the scheme.
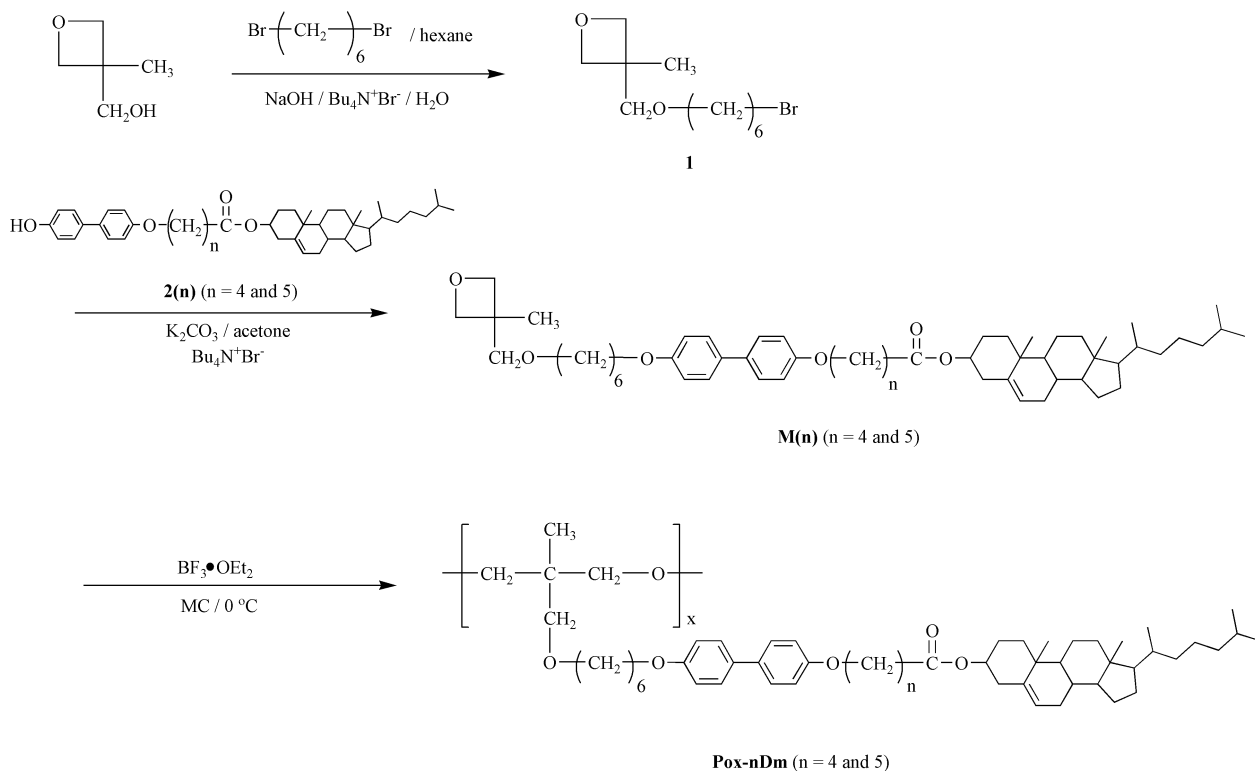
Synthesis of monomers

3-(6-Bromohexyloxymethyl)-3-methyloxetane, 1. This compound was prepared following the literature method.[28]

Cholesteryl 5-(4′-hydroxybiphenyl-4-yloxy)pentanoate, 2(4). Into a 100 mL two-necked round-bottomed flask equipped with a water condenser and an argon gas inlet were placed
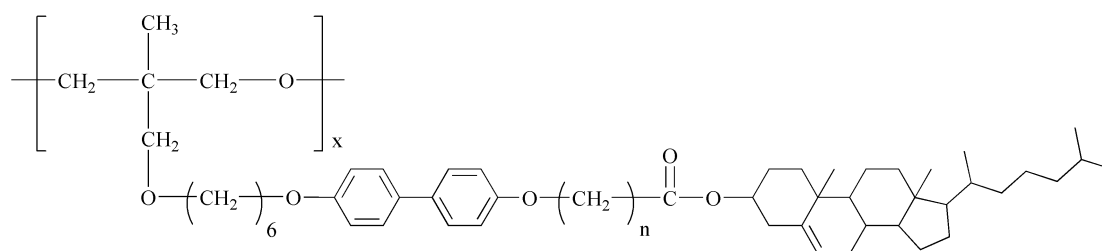
n = 4 (**Pox-4Dm**) and 5 (**Pox-5Dm**)

Scheme 1 Synthetic routes to the monomers and polymers.

N,*N*-dimethylformamide (50 mL), anhyd. potassium carbonate (2.9 g, 21.3 mmol), cholesteryl 5-bromopentanoate (3.9 g, 7.1 mmol) and 4,4′-dihydroxybiphenyl (3.2 g, 17.08 mmol) sequentially through the second neck of the flask and flushed with argon gas. After closing the neck with a septum, the reaction mixture was heated at 85 °C for 12 h. The reaction mixture was cooled to room temperature and poured into ice-cold water (200 mL). The solid formed was collected by filtration and was dissolved in a mixture of ethyl acetate : methylene chloride (1 : 1). The resultant solution was washed twice with brine (100 mL ×2) and dried over anhyd. Na_2SO_4. Evaporation of solvent furnished a white solid that was purified by column chromatography using silica gel (60-120 mesh). Elution with a mixture of ethyl acetate : hexanes (1 : 9) afforded a white solid compound. R_f = 0.43 (ethyl acetate : hexanes = 1 : 4). Phase transition: Cr_1 108.3 °C (ΔH = 3.5 J g^{-1}) Cr_2 157 °C (ΔH = 61.4 J g^{-1}) I; yield: 3.8 g (82%).

IR (KBr, cm^{-1}): 3385 (O–H stretching), 3031 (aromatic C–H stretching), 2949 and 2867 (aliphatic C–H stretchings), 1735 (C=O stretching), 1603 and 1500 (aromatic C=C stretchings), and 1251, 1177, and 979 (C–O stretchings); ^{1}H-NMR (CDCl$_3$, δ): 7.44 (d, 2H, Ar), 7.41 (d, 2H, Ar), 6.93 (d, 2H, Ar), 6.87 (d, 2H, Ar), 5.37 (br d, 1H, olefinic), 4.85 (s, 1H, -OH), 4.61 (m, 1H, -CH-O-CO-), 4.0 (t, 2H, -OCH$_2$-), 2.31 (m, 4H, 2 × allylic methylene), 2.25–1.05 (m, 30H, CH$_2$, CH), 1.02 (s, 3H, CH$_3$), 0.92 (d, 3H, CH$_3$), 0.87 (d, 3H, CH$_3$), 0.86 (d, 3H, CH$_3$), and 0.67 (s, 3H, CH$_3$); elemental analysis: calc. for C$_{44}$H$_{62}$O$_4$: C 80.69, H 9.54; found C 80.44, H 9.61%.

Cholesteryl 6-(4′-hydroxybiphenyl-4-yloxy)hexanoate, 2(5). This compound was prepared following the procedure as described for compound **2(4)**. A white solid compound. R_f = 0.43 (ethyl acetate : hexanes = 1 : 4). Phase transition: Cr_1 133.1 °C (ΔH = 3.67 J g^{-1}) Cr_2 164.3 °C (ΔH = 50.7 J g^{-1}) N* 182.8 °C (ΔH = 8.9 J g^{-1}) I; yield: 3.5 g (74%).

IR (KBr, cm^{-1}): 3379 (O–H stretching), 3036 (aromatic C–H stretching), 2927 and 2867 (aliphatic C–H stretchings), 1735 (C=O stretching), 1603 and 1500 (aromatic C=C stretchings), and 1246, 1169, and 978 (C–O stretchings); ^{1}H-NMR (CDCl$_3$, δ): 7.43 (d, 2H, Ar), 7.41 (d, 2H, Ar), 6.92 (d, 2H, Ar), 6.87 (d,

2H, Ar), 5.37 (br d, 1H, olefinic), 4.95 (s, 1H, OH), 4.61 (m, 1H, CH-O-CO), 3.98 (t, 2H, OCH$_2$), 2.33 (m, 4H, 2 allylic methylene), 2.25–1.05 (m, 32 H, CH$_2$, CH), 1.01 (s, 3H, CH$_3$), 0.91 (d, 3H, CH$_3$), 0.87 (d, 3H, CH$_3$), 0.86 (d, 3H, CH$_3$), and 0.67 (s, 3H, CH$_3$); elemental analysis: calc. for C$_{45}$H$_{64}$O$_4$: C 80.79, H 9.64; found C 80.75, H 9.70%.

3-{6-[4′-(4-Cholesteryloxycarbonylbutyloxy)biphenyl-4-yloxy]-hexyloxymethyl}-3-methyloxetane, M(4). 3-(6-Bromohexyloxy-methyl)-3-methyloxetane, **1** (0.57 g; 2.1 × 10^{-3} mol) and compound **2(4)** (1.4 g; 2.1 × 10^{-3} mol) were dissolved in 150 mL of acetone containing 1.4 g of K$_2$CO$_3$ and 0.01 g of tetra-*n*-butylammonium bromide. The mixture was refluxed overnight under a nitrogen atmosphere. Insoluble precipitates were removed by filtration and acetone was distilled off using a rotary evaporator. The residue was dissolved in methylene chloride and the solution poured into excess hexane. The precipitated solid was collected by filtration and purified by column chromatography using silica gel (60–120 mesh). Elution with a mixture of methylene chloride : hexanes (1 : 3) afforded a white solid compound. R_f = 0.40 (methylene chloride : hexanes = 1 : 3). Phase transition: Cr 96.2 °C (ΔH = 31.0 J g^{-1}) S$_A$ 100.5 °C (ΔH = 4.1 J g^{-1}) I; yield: 1.4 g (78%).

IR (KBr, cm^{-1}): 3037 (aromatic C–H stretching), 2935 and 2866 (aliphatic C–H stretchings), 1733 (C=O stretching), 1606 and 1499 (aromatic C=C stretchings), and 1243, 1174, and 979 (C–O stretchings); ^{1}H-NMR (CDCl$_3$, δ): 7.46 (d, 4H, Ar), 6.94 (d, 4H, Ar), 5.38 (br d, 1H, olefinic), 4.64 (m, 1H, CH-O-CO), 4.52 and 4.36 (d, 4H, oxetane CH$_2$), 4.01 (t, 2H, OCH$_2$), 3.48 (t, 4H, oxetane-CH$_2$-O-CH$_2$), 2.32 (m, 4H, allylic methylene), 2.25–1.05 (m, 43H, CH$_2$ and CH), 1.02 (s, 3H, CH$_3$), 0.92 (d, 3H, CH$_3$), 0.87 (d, 3H, CH$_3$), 0.86 (d, 3H, CH$_3$), and 0.67 (s, 3H, CH$_3$); elemental analysis: calc. for C$_{55}$H$_{82}$O$_6$: C 78.71, H 9.85; found C 78.63, H 9.90%.

3-{6-[4′-(5-Cholesteryloxycarbonylpentyloxy)biphenyl-4-yloxy]-hexyloxymethyl}-3-methyloxetane, M(5). This compound was prepared following the same procedure as described for

compound **M(4)**. A white solid compound. $R_f = 0.40$ (methylene chloride : hexanes = 1 : 3). Phase transition: Cr 88.2 °C ($\Delta H = 23.1$ J g^{-1}) S$_A$ 148.1 °C ($\Delta H = 4.6$ J g^{-1}) N* 152.1 °C ($\Delta H = 4.1$ J g^{-1}) I; yield: 1.1 g (75%).

IR (KBr, cm^{-1}) 3039 (aromatic C–H stretching), 2935 and 2870 (aliphatic C–H stretchings), 1733 (C=O stretching), 1605 and 1500 (aromatic C=C stretchings), and 1242, 1173, and 979 (C–O stretchings); ^{1}H-NMR (CDCl$_3$, δ): 7.46 (d, 4H, Ar), 6.93 (d, 4H, Ar), 5.35 (br d, 1H, olefinic), 4.64 (m, 1H, CH-O-CO), 4.52 and 4.36 (d, 4H, oxetane CH$_2$), 4.01 (t, 2H, -OCH$_2$-), 3.49 (t, 4H, oxetane-CH$_2$-O-CH$_2$), 2.32 (m, 4H, allylic methylene), 2.25–1.05 (m, 45H, CH$_2$ and CH), 1.02 (s, 3H, CH$_3$), 0.92 (d, 3H, CH$_3$), 0.87 (d, 3H, CH$_3$), 0.86 (d, 3H, CH$_3$), and 0.67 (s, 3H, CH$_3$); elemental analysis: calc. for C$_{56}$H$_{84}$O$_6$: C 78.83, H 9.92; found C 78.80, H 9.94%.

Synthesis of polymers Pox-4Dm and Pox-5Dm

Poly(2-{6-[4′-(4-cholesteryloxycarbonylbutyloxy)biphenyl-4-yloxy]hexyloxymethyl}-2-methyltrimethylene oxide), Pox-4Dm. Monomer **M(4)** (1.2 g; 1.4×10^{-3} mol) was dissolved in 10 mL of dichloromethane and to this solution boron trifluoride–diethyl ether (0.005 mL; 2.84×10^{-3} mmol) was added under an argon atmosphere. The solution was stirred for 24 h at 0 °C, and then poured into 200 mL of methanol. The precipitate thus obtained was filtered. The polymer was purified by reprecipitation into n-hexane and methanol. The resulting polymer was subjected to Soxhlet extraction using methanol. The recovered yield was 0.95 g (68%).

IR (KBr, cm^{-1}): 3040 (aromatic C–H stretching), 2933 and 2874 (aliphatic C–H stretchings), 1732 (C=O stretching), 1606 and 1501 (aromatic C=C stretchings), and 1270, 1243, and 1106 (C–O stretchings); ^{1}H-NMR (CDCl$_3$, δ): 7.43 (d, 4H, Ar), 6.93 (d, 4H, Ar), 5.37 (br d, 1H, olefinic), 4.63 (m, 1H, CH-O-CO), 3.20–3.54 (m, 8H, OCH$_2$), 2.32 (m, 4H, allylic methylene), 2.25–0.67 (m, 60H, CH$_2$, CH and CH$_3$); elemental analysis: calc. for C$_{55}$H$_{82}$O$_6$: C 78.71, H 9.85; found C 78.63, H 9.96%.

Poly(2-{6-[4′-(5-cholesteryloxycarbonylpentyloxy)biphenyl-4-yloxy]hexyloxymethyl}-2-methyltrimethylene oxide), Pox-5Dm. The recovered yield was 0.91 g (62%). IR (KBr, cm^{-1}): 3038 (aromatic C–H stretching), 2934 and 2872 (aliphatic C–H stretchings), 1731 (C=O stretching), 1604 and 1499 (aromatic C=C stretchings), and 1270, 1242, and 1103 (C–O stretchings); ^{1}H-NMR (CDCl$_3$, δ): 7.43 (d, 4H, Ar), 6.93 (d, 4H, Ar), 5.37 (br d, 1H, olefinic), 4.63 (m, 1H, CH-O-CO), 3.25–3.56 (m, 8H, OCH$_2$), 2.32 (m, 4H, allylic methylene), 2.21–0.64 (m, 62H, CH$_2$, CH and CH$_3$); elemental analysis: calc. for C$_{56}$H$_{84}$O$_6$: C 78.83, H 9.92; found C 78.77, H 10.01%.

Characterization

The FT-IR and H-NMR spectra of the compounds were recorded respectively on a Bomem MB instrument and on a Varian Gemini 300 spectrometer, respectively. Thermal properties were studied in a nitrogen atmosphere on a differential scanning calorimeter (DSC; Mettler DSC 821^e, Germany) at a heating and cooling rate of 10 °C min^{-1}. Molecular weights were determined using a Waters 150CV PLUS gel permeation chromatograph. The phase transitions and optical textures were examined on a polarizing microscope (Olympus BH-2, Japan) equipped with a hot stage (Mettler FP-82HT, Germany) controlled by an automatic thermal

controller (Mettler FP-90, Germany). The X-ray diffractograms of the compounds were obtained at varying temperatures using synchrotron radiation (1.542 Å) of the 3C2 beam line at the Pohang Synchrotron Laboratory, Korea. Polarization switching of the polymers was studied using ITO electrooptic cells 1.5 µm thick coated with a rubbed polyimide. The measuring instrument consists of a function and arbitrary wave generator (DS345, Stanford Research Inc., USA), a high voltage amplifier (FA20A, FLC Electronics, Sweden), a digital storage oscilloscope (54600B, Agilent, USA), and a transimpedence amplifier with an operation amplifier chip (OPA-627) and a 10 kΩ detection resister. During the measurement the sample cell was placed on a hot stage (FP-82HT, Mettler, Germany), which was controlled by an automatic thermal controller (FP-90, Mettler, Germany).

Results and discussion

Liquid crystallinity of monomers, M(4) and M(5)

Since the two monomers, **M(4)** and **M(5)**, bear mesogenic structures, we have examined their liquid crystallinity by DSC and polarizing microscopy. Both compounds exhibited focal conic optical textures with some parts being homeotropic. We examined their miscibility with **Pox-4Dm** and **Pox-5Dm** and found that they are immiscible with the polymers that, as will be described below, form only the chiral smectic C phase. Although **M(4)** and **M(5)** differ only in the length of the central spacer between the cholesterol and biphenyl moieties, we found that they reveal an interesting difference in the LC phase they form. The **M(4)** monomer melts at 96 °C into the Smectic A phase which became isotropic at 100.5 °C. Therefore, the mesophase temperature range was only 4.5 °C. In contrast, the **M(5)** monomer melted at 88 °C to form the Smectic A phase which was transformed to the cholesteric phase at 148 °C. The cholesteric phase underwent isotropization at 152 °C. We note that the mesophase temperature range (64 °C) of **M(5)** is much greater than that (4.5 °C) of **M(4)**. Moreover, **M(5)** forms the cholesteric phase in addition to the smectic phase. The slightly longer spacer between the two mesogenic units in **M(5)** lowers the melting temperature and stabilizes the thermal stability of the mesophases. It is rather surprising to observe such differences in phase behavior between the two monomers.

General properties of Pox-4Dm and Pox-5Dm

The two polymers considered here, **Pox-4Dm** and **Pox-5Dm**, were prepared at 0 °C by cationic ring-opening polymerization of the corresponding oxetane monomers, **M(4)** and **M(5)**. The cationic initiator utilized in the polymerization was BF$_3$·OEt$_2$, which has been widely used in the ring-opening polymerization of oxetane and its derivatives.[22–24,27,28] Methylene chloride was the reaction medium. Polymerization proceeded homogenously throughout the polymerization. The resulting polymers were subjected to Soxhlet extraction using methanol in order to remove soluble impurities and low molecular weight products. Table 1 summarizes the general properties of the polymers thus obtained. The polymers were soluble in common organic solvents such as tetrahydrofuran (THF), methylene chloride (MC) and chloroform. The number average molecular weights ($\bar{M}_n$) were relatively low: 5200 for **Pox-4Dm** and 4500 for **Pox-5Dm**. These values correspond to a degree of polymerization

Table 1 General properties of **Pox-4Dm** and **Pox-5Dm**

Polymer	$T_g{}^a$/°C	$T_m{}^a$/°C	$T_i{}^a$/°C	$\bar{M}_n{}^b$	$\bar{M}_w{}^b$	PDI^b	DP^b
Pox-4Dm	68.2	105.5	178.6	5160	7930	1.54	6.2
Pox-5Dm	72.5	108.1	214.8	4480	7810	1.63	5.7

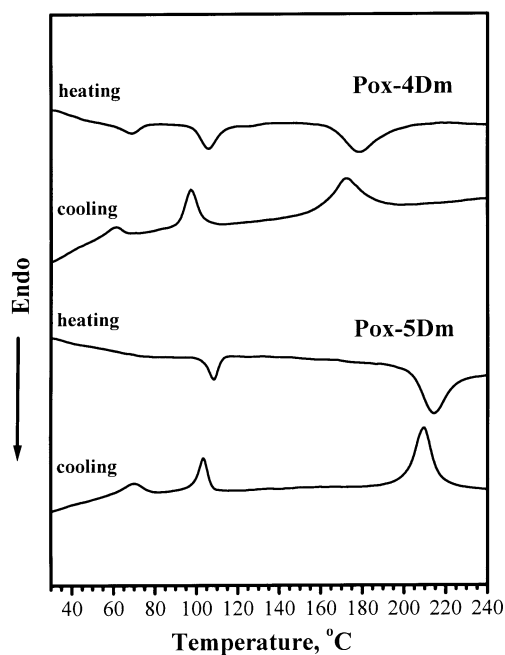^{a}The values were obtained from DSC (heating rate:10 °C min^{-1}). ^{b}The values were obtained from GPC (eluent: THF).

Fig. 1 DSC thermograms of **Pox-4Dm** and **Pox-5Dm** obtained under a nitrogen atmosphere at the heating and cooling rates of 10 °C min^{-1}.

Fig. 2 Wide angle X-ray diffractograms of (a) **Pox-4Dm** and (b) **Pox-5Dm**.

(DP) of only about 6. Their average polydispersity index (PDI) or the ratio of weight average molecular weight ($\bar{M}_w$) to $\bar{M}_n$ is about 1.5.

Usually, cationic ring-opening polymerization of oxetane derivatives bearing small substituents results in high molecular weight (MW) polymers.[22–24] In contrast, monomers having bulky substituents give rise to low MW polymers, most probably due to steric hindrance in the propagation stage.[27] The same phenomenon has been observed by us previously.[28]

The two polymers are semicrystalline, and their glass transition temperatures are 68.2 and 72.5 °C, respectively (see Fig. 1). According to the DSC thermograms shown in Fig. 1, the two polymers exhibit three endothermic peaks in the heating cycle and the transitions were reversible as one can see from the cooling DSC thermograms; three corresponding exothermic peaks appeared in the cooling cycle. The low temperature peaks represent glass transitions, while the second peaks are associated with melting transitions and the high temperature peaks with mesophases, *i.e.*, isotropization. Further discussion on the mesophase transitions will be made in the following subsection.

Liquid crystalline properties

As alluded to above, both **Pox-4Dm** and **Pox-5Dm** exhibit two reversible phase transitions involving mesophases according to their DSC thermograms (Fig. 1). Table 2 summarizes the thermodynamic parameters associated with the transitions. **Pox-5Dm** exhibits higher transition temperatures than **Pox-4Dm**. In particular, the isotropization temperature (T_i) of **Pox-5Dm**, 214.8 °C, is significantly higher than the T_i (178.6 °C) of **Pox-4Dm**. A similar phenomenon was observed for the T_g and T_m values of the two monomers. For both polymers, the

heat of isotropization (ΔH_i) is much higher than the ΔH_m value of the low temperature melting transition. We observed the same phenomenon in the accompanying entropy changes (ΔS_i) for the two transitions but their differences were much smaller. These observations imply the polymers have a very low degree of crystallinity. The wide angle X-ray diffractograms shown in Fig. 2 tell us that the two polymers are only slightly crystalline and in the light of the broad diffractions at $2\theta = 15$–$22°$ (5.9–4.4 Å) they form fluid mesophases that correspond to short spacing or interchain distance.

When we examined the optical textures of the two polymers, they both revealed focal conic textures (Fig. 3 (a)). According to the small angle X-ray analysis shown in Fig. 4, the two polymers commonly show one sharp diffractogram peak in the mesophase temperature range. The spacing estimated from the diffraction angle $2\theta = 2.0°$ and $1.9°$, are 49.0 and 51.6 Å respectively for **Pox-4Dm** and **Pox-5Dm**. Since the molecular breadths of the two polymers are 46.0 and 47.3 Å, when the spacers are assumed to be in the *trans,anti* conformation, the pendant groups must be interdigitated. Combining the microscopic observation with the X-ray analysis and the electro-optic behavior of the polymers, to be described below, leads to the conclusion that the mesophase formed by the two polymers is the chiral smectic C (Sc*) phase.

Fig. 4 also shows that the two polymers did not diffract in the small angle region above their T_is.

Optical switching and electro-optic behavior

The electro-optic response was measured for the polymer samples sandwiched between two indium–tin oxide (ITO) coated glass plates having rubbed polyimide orienting layers.[39] Rectangular alternating electric fields were applied to the samples.[25,30,35,40] Fig. 5 shows the dependence of response times of **Pox-4Dm** and **Pox-5Dm** on the temperature and applied electric field. We used a reduced temperature, $T - T_i$, as well as the temperature in the abscissa of Fig. 5. As expected, higher temperatures and applied electric fields result in faster response times ranging from 0.3 ms to 0.4 ms near T_i. These response times are faster than for common low molecular

Table 2 Thermodynamic data for the phase transitions of **Pox-4Dm** and **Pox-5Dm**[a]

Polymer	ΔH_m		ΔH_i		ΔS_m		ΔS_i	
	J g^{-1}	kJ mol^{-1}	J g^{-1}	kJ mol^{-1}	J g^{-1} K^{-1}	J mol^{-1} K^{-1}	J g^{-1} K^{-1}	J mol^{-1} K^{-1}
Pox-4Dm	3.6	3.0	9.8	6.4	9.5	8.0	21.7	14.2
Pox-5Dm	3.7	3.2	14.2	12.1	9.8	8.3	29.0	24.8

[a]Heating and cooling rate: 10 °C min^{-1}; atmosphere: N$_2$ blow, 15 mL min^{-1}.
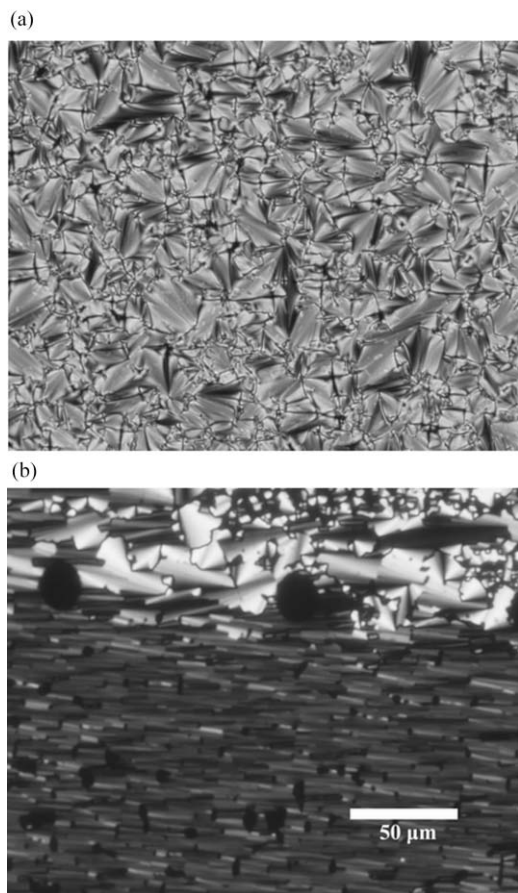
(a)

(b)

Fig. 3 Optical photomicrograph of (a) **Pox-4Dm** taken at 169 °C and (b) oriented **Pox-5Dm** taken at 167 °C (magnification 200 ×).
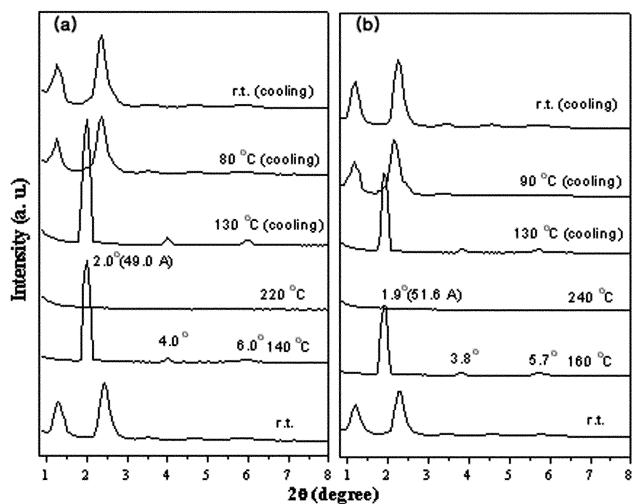

Fig. 4 Small angle X-ray diffractograms of (a) **Pox-4Dm** and (b) **Pox-5Dm**.

weight nematic LCs and even some Sc* FLCPs from polysiloxanes. Part of these fast responses can be ascribed to a high measurement temperature or Sc* phase temperature and a relatively low degree of polymerization of the two polymers. It, of course, is well known that optical switching in ferroelectric LCs (FLCs) requires a much shorter time than the nematic LCs. It is also noted that the response time for **Pox-5Dm** appears to be slightly faster than that for **Pox-4Dm**. Suzuki and Okawa[19] have reported previously the same phenomenon for polysiloxanes FLCs: longer spacers resulted in faster response times probably due to easier polarization of the mesogenic groups.
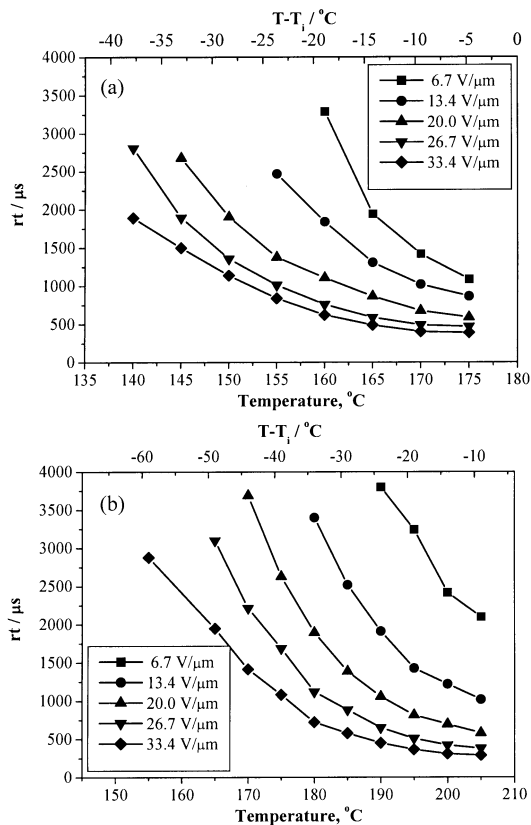

Fig. 5 Response time *versus* temperature and reduced temperature for (a) **Pox-4Dm** and (b) **Pox-5Dm** at various applied electric fields.

The sign of the spontaneous polarization P_s was determined by the field reversal method through the optical observation of the extinction direction by rotating the stage according to Lagerwall and Dahl's convention.[41] The tilt angles (θ) were measured as a function of temperature between crossed polarizers as half the rotation between two extinction positions corresponding to opposite polarization orientations. The P_s signs for the polymers reported here are negative and tilt angles (θ) are found to be relatively small, 2° and 2.5°, respectively.

We measured P_s of the polymers using the triangular wave method and the results are graphically presented in Fig. 6. For both polymers, the P_s values smoothly decrease with increasing temperature as observed by many others for low molar mass as well as polymeric FLCs.[19,20,38] The faster response times and the greater P_s values of the polymers at higher temperatures within the Sc* mesophase temperature ranges must result from diminished melt viscosity leading to easy molecular reorientation.

The P_s values range from 22 to 16 nC cm^{-2} with the values for **Pox-5Dm** being slightly higher than those for **Pox-4Dm**. This parallels the response times of the two polymers. The P_s
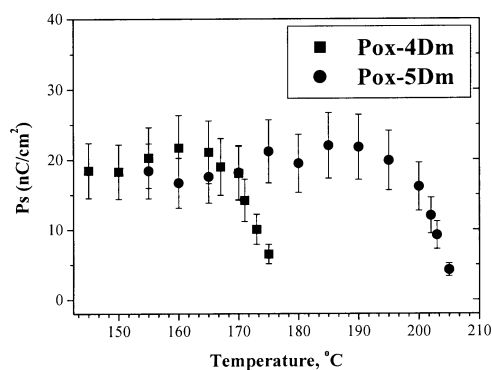

Fig. 6 Temperature dependence of spontaneous polarization.

values for the polymers reported herein are significantly higher than those reported for FLC poly(meth)acrylates, but lower than for polysiloxanes. Poths et al.[31] reported a P_s value as high as 420 nC cm^{-2} for a side-chain FLC polysiloxane.

Conclusion

We have described the synthesis and LC properties of first examples of side-chain FLCPs bearing dimesogenic pendants. The Sc* phase could be induced simply by combining biphenyl and cholesterol moieties through polymethylene spacers and attaching the dimesogenic pendants onto a polyoxetane backbone through a spacer. The two polymers (to be exact, they should be called oligomers) form only the Sc* phase over a rather broad temperature range. Their response times in electro-optic switching are several hundred µs and the P_s values are about 20 nC cm^{-2}. Both values are considered to be fairly significant even for the development of practical applications. Modification of the structure of the dimesogenic pendant to increase the dipole moment and to increase in the degree of polymerization or molecular weight of the polymers are subjects for future research.

Acknowledgement

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