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Synthesis and Characterization of Novel Combined Type Ferroelectric Liquid Crystalline Polymers Having Polyester Main Chains

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ABSTRACT: A novel synthetic route for the preparation of a new class of side chain liquid crystal (LC) polymers with an aromatic polyester main chain utilizing a diacid chloride/diol solution polycodensation is detailed in this report. Mesogenic α,β-diols, (S)-(−)-4-(((methylbutyl)oxy)carbonyl)phenyl 4′-(((bis(6-hydroxyhexyl)methylsilyl)alkyl)oxy)biphenyl-4-carboxylate, which are composed of a long methylene spacer with a carbon−silicon−carbon linkage at the center and a side chain mesogen connected via the silicon atom, exhibited smectic A (S_A) and chiral smectic C ($S^{-}{}_{C}$) mesophases. Molecular weights of the LC polymers of the above diols with terephthaloyl chloride and biphenyl-4,4′-dicarbonyl chloride were found to be in the range 7000−20 000. The polymer having a terephthalic ester moiety and a hexyl spacer was found to be isotropic at room temperature. When the side chain hexyl spacer was replaced by an octyl spacer, the polymer exhibited an enantiotropic room-temperature $S^*{}_C$ phase. When a biphenyl moiety was introduced to the main chain, instead of a phenyl group, the polymer isotropization temperature increased, suggesting a strong LC character. In this series, when the side chain spacer was hexyl and octyl, the polymers exhibited LC phases with a fine grain texture, while the polymer with a decyl spacer exhibiting a fan textured $S^*{}_C$ phase. The latter polymer was switchable by an external electric field.

Introduction

In addition to the conventional main chain and side chain liquid crystalline polymers (LCPs), recent developments in LCP synthesis have produced novel materials which will provide the basis for fundamental and applied research. Combined type liquid crystals, in which the mesogenic side groups with flexible spacers are attached to the mesogenic main chains, are a new design for the LCPs. Over the past few years, several combined LCPs with different combinations ahve been reported.[1−7]

It has been found that many of these polymers exhibit very broad smectic mesophases,[1,4,5] occasionally including room-temperature chiral smectic C ($S^*{}_C$) phases. As for the molecular arrangement in these mesophases, it was proposed that the main chains and the side chains align parallel to each other to form layered structures.[2] Recently, X-ray investigations of some of these polymers led to the proposal of anti-ferroelectric and ferroelectric ordering in the $S^*{}_C$ phases.[8]

Let us now consider the synthetic pathways for some of the above-mentioned combined LCPs. In most cases, the melt transesterification method has been employed for the synthesis of the polyester main chains. Here, at first, a precursor polymer consisting of a polyester main chain and a part of the side chain having a hydroxy function has been prepared. Then, the terminal part of the side chain mesogen was connected to the hydroxy function via an ester linkage.[4−6] Some major disadvantages of this procedure include the following: (1) High-temperature conditions have to be used; thus, undesired side reactions can occur during preparation of the precursor polymers. (2) If there are ester or acid functions in the side group, this method cannot be applied due to main chain side chain transesterification reactions or, in other words, cross-linking reactions. Therefore, we have concentrated on developing an alternative method for the synthesis of combined LCPs avoiding the melt transesterification polymerization.

Our particular work explains a new synthetic route for the preparation of combined LC polymers with aromatic polyester main chains utilizing an aromatic diacid chloride/diol solution polycondensation reaction. The symmetrical diols prepared in this study consisted of a long methylene spacer having a carbosilane linkage (C−Si−C) in the center of the spacer, and the side chain mesogen was connected to the diol spacer via the central silicon atom.

Experimental Section

Measurements. ^{1}H-NMR spectra were recorded on a JEOL FX90Q instrument. Obvious multiplicities and routine coupling constants were usually not listed here. IR spectra were recorded on a Shimadzu FT/IR 8000 spectrophotometer. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) at room temperature with a Shodex KF 802.5 column equipped with a Shimadzu RID-60A refractive index detector using tetrahydrofuran (THF) as the eluent. The GPC column was calibrated using polystyrene standards ranging from 5.8×10^2 to 6.8×10^4. Preparative GPC was run with a Shodex H 20025 column using chloroform as the solvent. Differential scanning calorimetry (DSC) was carried out with a Rigaku DSC-8240D instrument at a heating rate of 1.0 °C/min under nitrogen on both heating and cooling processes.

The optical polarizing microscope (OPM) studies were made at a heating rate of 0.1 °C/min using a Olympus BH2 polarizing instrument fitted with a Metler FP-82 hot stage. The general procedures for the electro-optical measurements are as follows: cells (3.0 μm thick), aligned by rubbing after coating the indium tin oxide (ITO) deposited glass plates with polyimide films, were filled with the liquid crystalline compounds in their isotropic states. The resulting cell was slowly cooled at a rate of 0.1 °C/min to orient the liquid crystalline molecules. While cooling, a triangular wave voltage of ±80 V at 0.5 Hz was applied. The cell was set between a pair of cross polarizers, in such a manner that the direction of the longer

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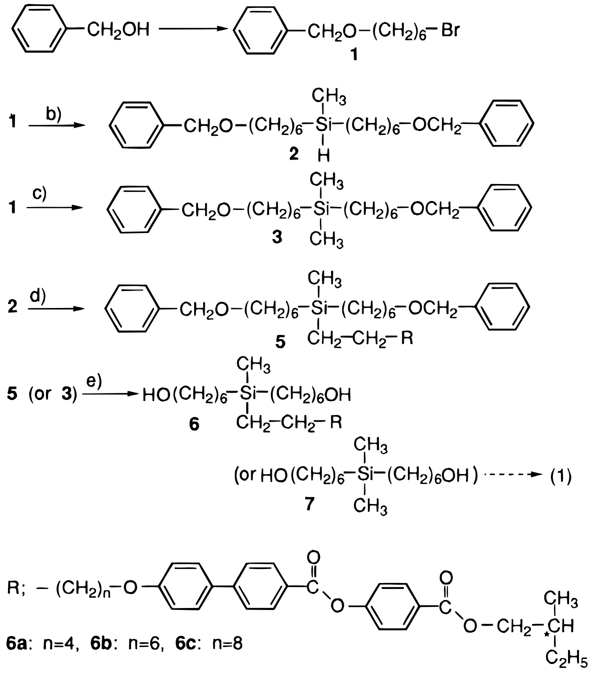
Scheme 1



Reaction conditions
a) i. THF / NaH at 0°C ii. Tetrabutylammonium bromide / $Br(CH_2)_6Br$ b) i. Mg / THF ii. CH_3SiCl_2 / THF at r. t. c) i. Mg / THF ii. $(CH_3)_2SiCl_2$ at r. t d) CH_2=CH-R (**4**) / toluene / PDTD catalyst e)10% Pd-C / H_2 in EtOAc with few drops of acetic acid.

axis of the molecule was parallel to the one of the polarizer when there is no applied voltage, and changes of transmittance were monitored by oscilloscope. X-ray diffraction studies were carried out using a Rigaku RU 200 (60 kV, 200 mA) instrument equipped with a temperature control unit. Diffraction patterns were recorded on flat films using Ni-filtered Cu Kα radiation. The samples were in the form of (a) a melt drawn fiber scaled in a glass capillary or (b) a melt spread on a very thin glass substrate plate. They were mounted in an electrically heated stage.

Synthesis (see Scheme 1). 6-(Benzyloxy)-1-bromohexane (1). A suspension of 55% sodium hydride (0.44 g, 0.1 mol) in 200 mL of dried THF, under nitrogen atmosphere, was cooled to 0 °C in an ice water bath; to this was added benzyl alcohol (10.8 g, 0.1 mol) dropwise over a 30 min period. After the addition was completed, the mixture was stirred at room temperature for 1 h. Then, tetrabutylammonium bromide (3.2 g, 0.01 mol) in 50 mL of THF, and 1,6-dibromohexane (24.4 g, 0.1 mol) were added. The reaction mixture was stirred at room temperature overnight, and then a few milliliters of methanol were added. After that, 200 mL of water were added and the reaction product was extracted three times with diethyl ether. The combined ether solution was washed successively with dilute HCl and water, and the ether layer was dried over anhydrous magnesium sulfate. The solvent was removed in a rotatory evaporator, and the pale yellow liquid obtained was then purified by column chromatography (silica gel, hexane/ethyl acetate = 10:1) to yield 7.6 g (30%) of the product as a colorless liquid. ^{1}H-NMR ($CDCl_3$, δ, ppm) 7.30 (5H, s, Ar-H), 4.50 (2H, s, Ar-CH_2O), 3.55−3.30 (4H, m, CH_2Br and CH_2O), 2.00−1.30 (8H, m, CH_2).

Bis(6-(benzyloxy)hexyl)methylsilane (2). Magnesium turnings (0.42 g, 18 mmol) were placed in a 100 mL three-necked round bottom flask, equipped with a magnetic stirring bar, a refluxing condenser, and a rubber septa. The system was heated under vacuum conditions. After cooling it to room temperature, 30 mL of THF (distilled over sodium/benzophenone and then over lithium aluminum hydride) was transferred to the reaction flask under vacuum. Then a few drops of methyl iodide were added as a catalyst for the reaction, and 6-(benzyloxy)-1-bromohexane (**1**) (5.4 g, 20 mmol) was added dropwise. The reaction mixture was stirred under an argon atmosphere until all the magnesium was dissolved. After that, dichloromethylsilane (0.74 g, 5 mmol) in 5 mL of THF was added dropwise during a 30 min period, and the mixture was stirred at room temperature for 8 h. The white precipitate of magnesium salt was filtered under nitrogen, and then the solvent was evaporated. The unreacted bromide and the other low-boiling components were removed by distillation. The remaining pale yellow liquid was used for the next step without any further purification. ^{1}H NMR ($CDCl_3$, δ, ppm) 7.30 (10H, s, Ar-H), 4.50 (4H, s, Ar-CH_2O), 3.55−3.80 (1H, m, SiH), 3.40 (4H, t, OCH_2), 1.80−1.10 (16H, m, CH_2), 0.70−0.40 (4H, b, $SiCH_2$), −0.05 (3H, d, $SiCH_3$).

Table 1. Phase Transition Temperatures of the Vinyl Mesogens (4)

		phase transition temperature (°C)	
compound	*n*	cooling	heating
4a	4	I 190 S_A 120 S^*_C 77 S_X 45 C	C 90 S^*_C 122 S_A 193 I
4b	6	I 182 S_A 116 S^*_C 58 S_X 24 C	C 61 S^*_C 118 S_A 182 I
4c	8	I 162 S_A 113 S^*_C 42 S_X 9 C	C 18 S_X 46 S^*_C 115 S_A 174 I

Bis(6-(benzyloxy)hexyl)dimethylsilane (3) was also prepared by the same procedure using dimethyldichlorosilane.

Vinyl Mesogen (4). Detailed procedures for the preparation of precursor vinyl mesogens (*n* = 4, 6, 8) are given elsewhere.[9]

(*S*)-(−)-4-(((2-methylbutyl)oxy)carbonyl)phenyl 4′-((n-(Bis(6-(benzyloxy)hexyl)methylsilyl)alkyl)oxy)biphenyl-4-carboxylate (5). In order to get compound **5**, the hydrosilylation between compound **2** and compound **4** was carried out in the presence of platinum divinyltetramethyldisiloxane (PDTD) catalyst. The crude product was purified by column chromatography on silica gel using hexane and ethyl acetate (10:1) as the eluent and yielded a white waxy product of **5** in 20% yield. ^{1}H NMR of compound **5c** ($CDCl_3$, δ ppm) 8.25−8.00 (4H, m, Ar-H), 7.75−7.45 (4H, m, Ar-H), 7.35−7.15 (12H, m, Ar-H), 7.05−6.85 (2H, d, Ar-H), 4.45 (4H, s, OCH_2), 4.25−4.10 (2H, dd, $COOCH_2$), 4.05−3.85 (2H, t, $ArOCH_2$), 3.60−3.30 (4H, t, benzyl-OCH_2), 2.10−1.10 (33H, m, 16(CH_2) + CH), 1.10−0.90 (6H, m, 2(CH_3)), 0.70−0.30 (6H, b, $SiCH_2$), −0.10 (3H, s, $SiCH_3$).

(*S*)-(−)-4-(((2-Methylbutyl)oxy)carbonyl)phenyl 4′-((*n*-(Bis(6-hydroxy)hexyl)methylsilyl)alkyl)oxy)biphenyl-4-carboxylate (6). A mixture of compound **5c** (0.40 g) and 10% palladium−carbon (0.04 g) in ethyl acetate (20 mL) with a few drops of acetic acid was stirred under a hydrogen atmosphere at 30 °C for 24 h. After the filtration and the solvent evaporation, the resultant white waxy product was purifed by column chromatography on silica gel using a mixture of hexane and ethyl acetate (first 10:2 and then 10:4) in 80% yield. ^{1}H NMR of the product **6c** ($CDCl_3$, δ, ppm) 8.40−8.10 (4H, m, ArH), 7.80−7.50 (4H, m, ArH), 7.45−7.25 (2H, d, ArH), 7.10−6.90 (2H, d, ArH), 4.30−4.10 (2H, dd, $COOCH_2$), 4.00 (2H, t, $ArOCH_2$), 3.60 (4H, t, CH_2OH), 2.00−0.80 (39H, m, 2(CH_3) + 16(CH_2) + CH), 0.50 (6H, b, $SiCH_2$), −0.10 (3H, s, $SiCH_3$). The DSC patterns of **6c** is illustrated in Figure 3. Phase transition temperatures of these compounds are shown in Table 1.

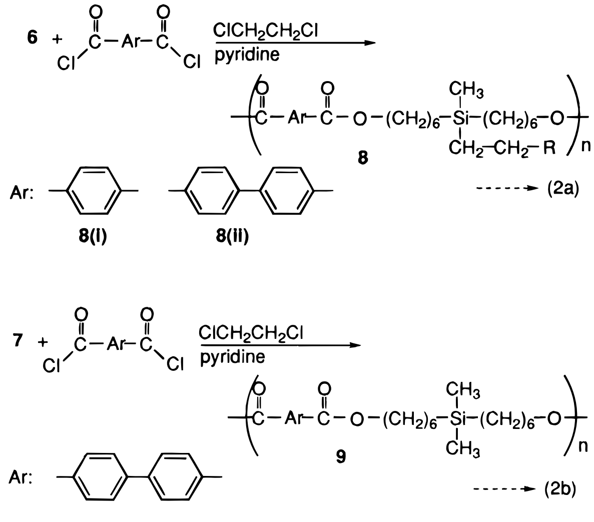
Bis(6-hydroxyhexyl)dimethylsilane (7) was also prepared from **3** by the same procedure.

Biphenyl-4,4′-dicarbonyl Chloride. A mixture of biphenyl-4,4′-dicarboxylic acid (5.0 g, 20 mmol), excess thionyl chloride, and a catalytic amount of DMF was refluxed for 2 h. Then, excess thionyl chloride was removed by evaporation. The diacid chloride was purified by sublimation under vacuum (0.3 mmHg) at 165 °C.

Polymerization (see Scheme 2). A typical method of polymerization is given below.

In a flask equipped with a refluxing condenser and an argon inlet−outlet purge system was placed biphenyl-4,4′-dicarbonyl chloride (140 mg, 0.50 mmol) in 5 mL of 1,2-dichloroethane. To this mixture was added 0.1 mL of pyridine and **6c** (400 mg, 0.5 mmol) in 2 mL of dichloroethane. The mixture was refluxed for 24 h. The polymer purification was carried out by the preparative GPC method.

Scheme 2



Results and Discussion

The most important part of this work was the synthesis of the symmetric diols bearing a side chain mesogen. This was achieved as described in eq 1. In the first step of this synthesis, 6-(benzyloxy)-1-bromohexane (**1**) was prepared by the partial etherification of 1,6-dibromohexane with sodium benzyl alkoxide. The product was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (10:1) as the eluent. A Grignard reagent prepared from compound **1** and magnesium in THF was coupled with dichloromethylsilane. In this step, as all the Si−Cl bonds had to be converted into Si−C linkages, excess Grignard reagent was employed. After the completion of the reaction, filtration followed by solvent evaporation yielded a yellow oily product. Since there is a Si−H group in the required compound **2** which is in some extent sensitive to water and to air, further purification of compound **2** was avoided. However, a strong peak at 2108 cm^{-1} for the Si−H bond in the IR spectrum together with the proton intensity ratios in the ^{1}H NMR spectrum revealed that the above-mentioned crude product contained mostly compound **2**.

Because of the use of crude **2**, the yield of the next step, which includes the hydrosilylation of compound **2** with the vinyl mesogen **4** followed by column chromatography separation, was found to be low (20%).

Benzyl deprotection of compound **5** was readily achieved by the hydrogenation with 10% palladium−carbon in ethyl acetate. Finally, compound **6** was purified by column chromatography on silica gel using hexane and ethyl acetate (10:4) as the eluent. By using the same procedure, three mesogenic diols, **6a**−**c**, were prepared.

The solution polycondensation of mesogenic diols **6** with biphenyl-4,4′-dicarbonyl chloride and terephthaloyl dichloride was carried out in 1,2-dichloroethane in the presence of pyridine for 24 h, as shown in eq 2. The polymer purification was done by preparative gel permeation chromatography using chloroform as the eluent. Polymer yields were around 50%. Molecular weights of the polymers were estimated by GPC with THF as the eluent. The IR and the ^{1}H NMR spectra (Figure 1) exhibited the expected signals of both reacted monomeric units to substantiate the formation of aryl alkyl polyesters.

As explained in our earlier report,[9] vinyl mesogens **4**, (S)−(−)-4-(((2-methylbutyl)oxy)carbonyl)phenyl 4′-(alkyloxy)biphenyl-4-carboxylate, used in this study exhibited three smectic phases: S_A, S^*_C, and an unidentified smectic phase (S_X). The phase transition temperatures of these vinyl mesogens are given in Table 1.

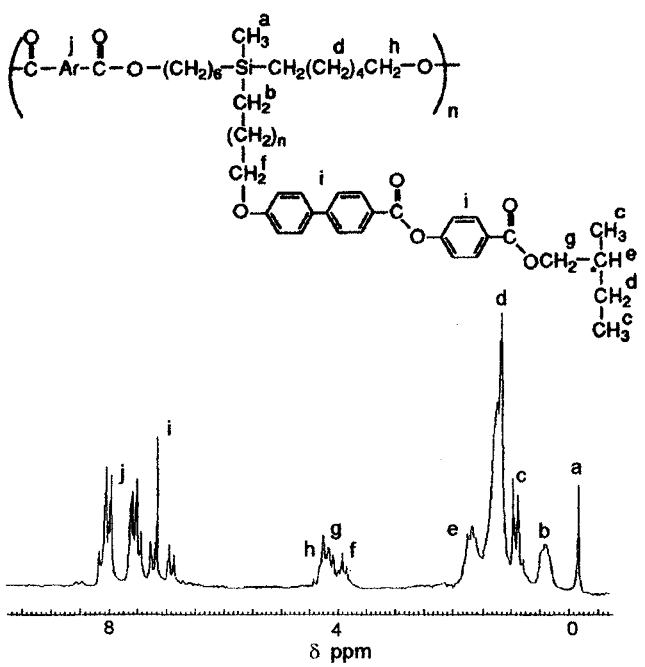


Figure 1. ^{1}H-NMR spectrum of polymer **8(ii)c**.

Table 2. Phase Transition Temperatures of Precursor Diols (6)

		phase transition temperature (°C)	
compound	*n*	cooling	heating[a]
6a	4	I 81.0 S^*_C <rt	C * S^*_C 87 I
6b	6	I 102.6 S^*_C <rt	C * S^*_C 111 I
6c	8	I 117.9 S_A 114.0 S^*_C <rt	C 20 S^*_C 120 I

[a] * stands for not detected.

Benzyl-protected diols (**5**) were found to be transparent liquid at room temperature. Hence, the LC properties of these compounds were not investigated.

The liquid crystal (LC) properties of mesogenic diols (**6**) were assigned on the basis of their optical textures, DSC patterns, and in some cases electro-optical measurements. All three compounds (**6a**−**c**) show enantiotropic mesomorphic behaviors. Their transition temperatures are given in Table 2. A typical polarized optical micrograph of the unaligned sample **6c** is presented in Figure 2a. When the sample was cooled from the isotropic state, a Schlieren texture for S^*_C appeared; in homogeneous areas, a clear focal conic fan texture with equidistant lines characteristic of the S^*_C phase was observed (Figure 2a). This texture persisted below room temperature. In homogeneously aligned samples, upon cooling, a narrow temperature range S_A phase appeared.

The second heating and cooling DSC scans of **6c** are presented in Figure 3, and these data are consistent with the results of the optical polarized microscopic studies.

Comparison of Tables 1 and 2 clearly shows that when the vinyl mesogens are converted to the corresponding diols, the clearing temperatures were depressed drastically and the S^*_C phase becomes very broad. For the vinyl mesogens, the phase transition temperatures decreased as the spacer length was increased. In

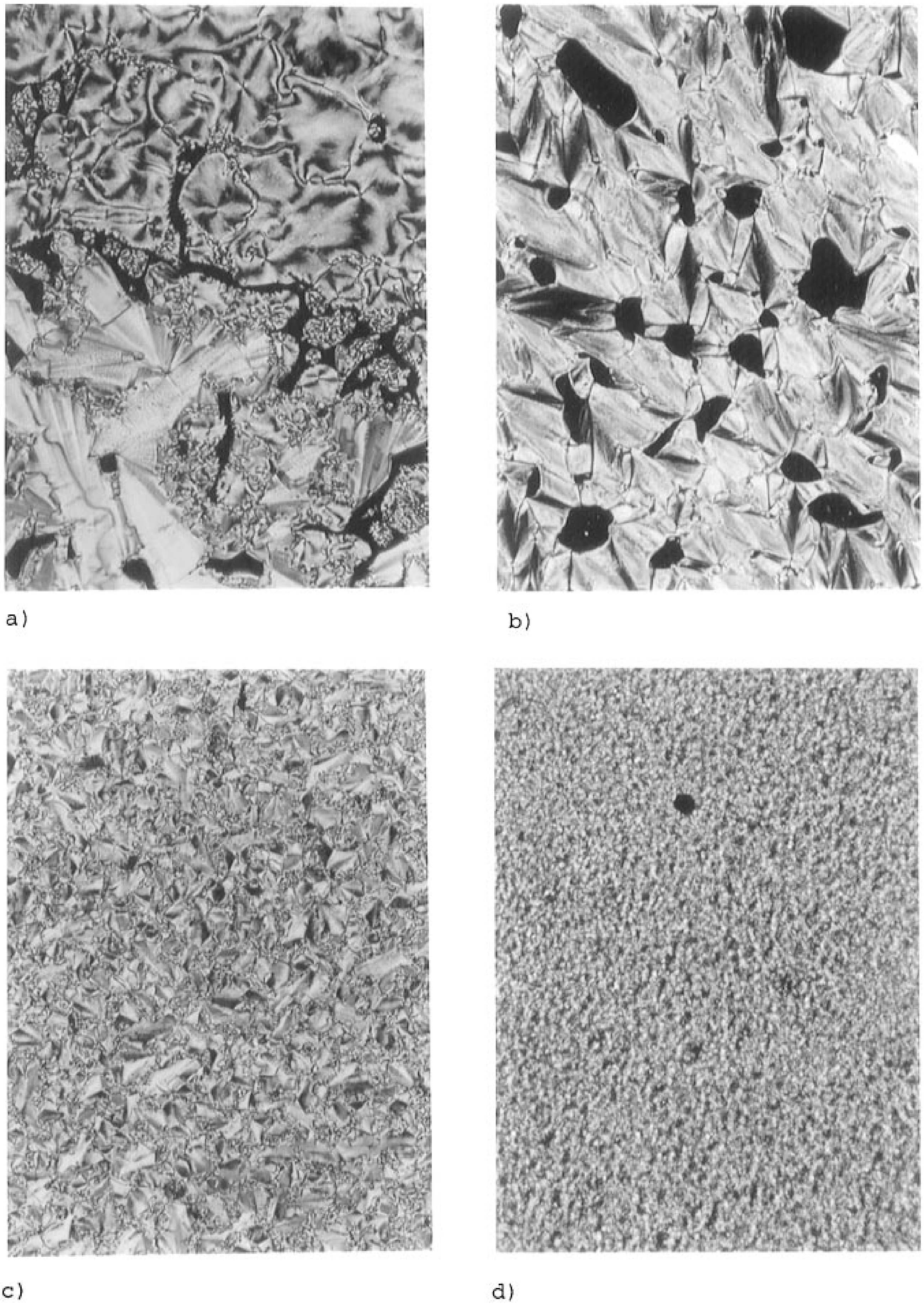


Figure 2. Optical polarized micrographs of (a) diol **6c** at 100 °C, (b) polymer **8(i)b** at 25 °C, (c) polymer **8(ii)c** at 100 °C, and (d) polymer **8(ii)a** at 70 °C.

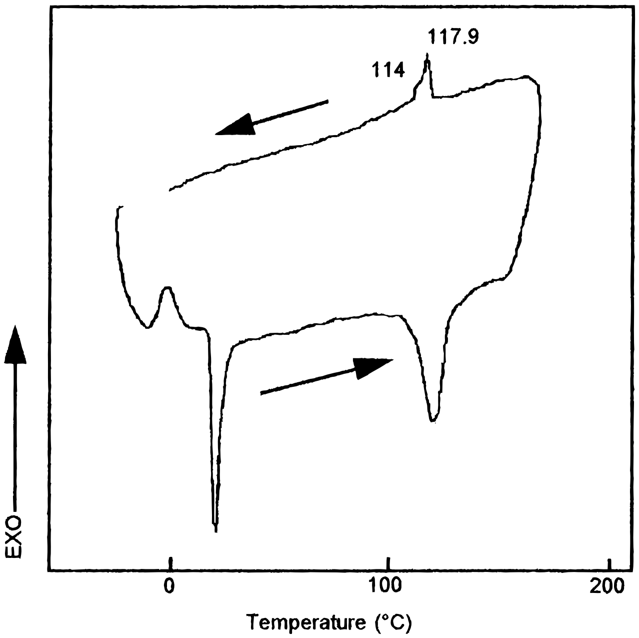


Figure 3. DSC scan of compound **6c**.

Table 3. Phase Transition Temperatures of LC Polymers (8)

polymer	n	Ar[b]	M_n	M_w/M_n	phase transition temperature[a] (°C) cooling	phase transition temperature[a] (°C) heating
8(i)a	4	Ar_1	11 000	1.2		
8(i)b	6	Ar_1	10 000	1.5	I 40 S^*_C * g	g * S^*_C 60 I
8(ii)a	4	Ar_2	21 000	1.3	I 95 LC * g	g * LC 110 I
8(ii)b	6	Ar_2	7 000	1.3	I 83 c * g	g * LC 89 I
8(ii)c	10	Ar_2	11 000	1.2	I 129 LC 124 S^*_C * g	g 0 S^*_C 128 I

[a] * stands for not detected. [b] Ar_1, phenyl; Ar_2, biphenyl.

contrast, for mesogenic diols, transition temperatures increased when the spacer length was increased. This behavior is rare for low molecular weight liquid crystals. It may be attributed to the presence of hydroxy groups at either end of the molecule, which led to the formation of intermolecular hydrogen bonds; thus, they behave to some extent like side chain LC polymers. For side chain LC polymers, when the spacer becomes longer, the side chain mesogens tend to be well aligned, thus exhibiting a strong mesogenic character.

Polymer mesogenic behaviors were investigated by DSC and optical polarizing microscopy as well as through X-ray diffraction studies. The phase transition temperatures of the LC polymers are given in Table 3.

Polymer **8(i)a**, which is composed of a terephthalic acid polyester main chain with a hexyl spacer in the side chain, was found to be isotropic at room temperature. When the side chain hexyl spacer was replaced by an octyl spacer, polymer **8(i)b** exhibited an enantiotropic mesophase. For this polymer, at room temperature a focal conic fan texture was observed, as shown in Figure 2b. Upon heating, around 50 °C, it started to clear, and at around 60 °C it became a viscous liquid. During the subsequent cooling process, around 40 °C, the LC phase started to appear, but in order to get the well-developed fan texture, it required several hours at room temperature. The DSC heating scan of the polymer **8(i)b** exhibited a broad peak for the smectic–isotropic transition. Consistent with the OPM studies, as the phase transitions were very slow upon cooling, no distinct peak was observed from the cooling scan.

The nature of this mesophase was also investigated by X-ray diffraction studies. In this experiment, the sample in its isotropic state was spread on a very thin glass substrate plate, and the X-ray scattering was measured at varying temperatures. A peak around the small angle region appeared, confirming the smectic nature of the polymer. Layer thickness variation with temperature is depicted in Figure 4. At first the layer thickness did not vary with the temperature, and then it increased with the temperature. This is strong evidence which shows the presence of a tilted smectic mesophase. The observed layer spacing (46.7 Å) was found to be 1.3 times longer than the length of the side group (34.7 Å), thus suggesting a interdigitated bilayer structure for this mesophase.

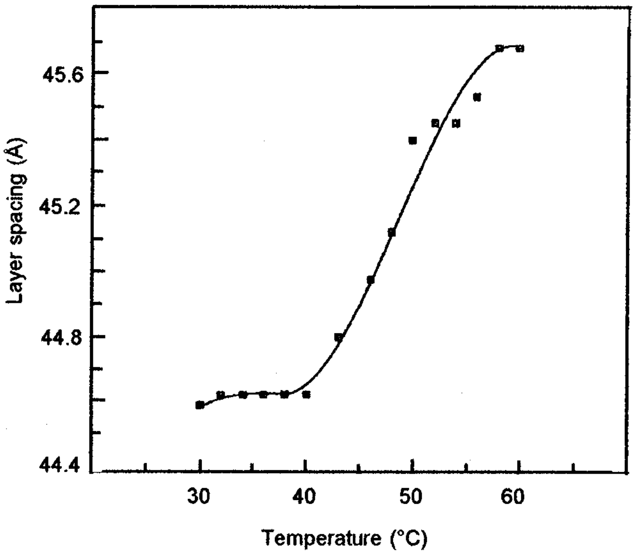


Figure 4. Effect of temperature on the layer thickness of polymer **8(i)b**.

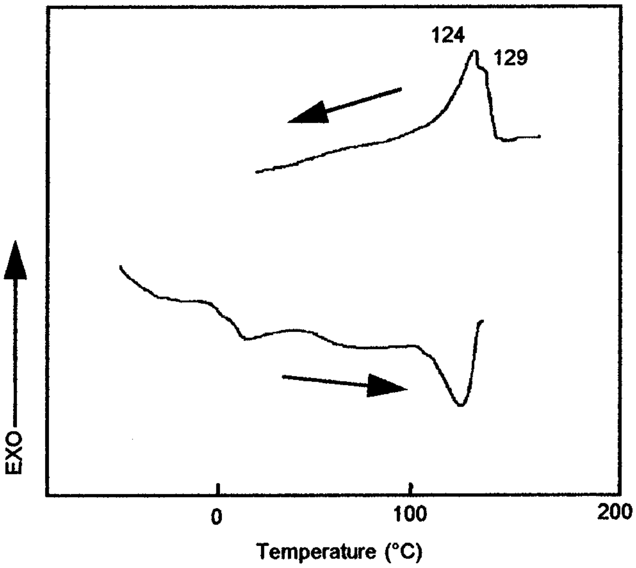


Figure 5. DSC pattern of polymer **8(ii)c**.

Figure 5 shows the DSC thermogram of polymer **8(ii)c**. On heating, it showed a step due to the T_g and then another endotherm for isotropization. Upon cooling, two overlapped peaks appeared at the isotropic–liquid crystal transition region and after that no significant changes occurred. When observed under polarized light microscopy, the narrow temperature range mesophase exhibited a fine grain texture, which could not be identified. Upon further cooling it displayed batonnets, confirming the smectic nature of this

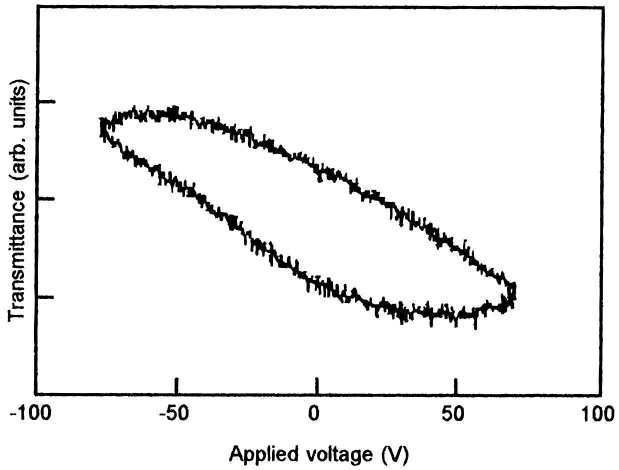


Figure 6. Optical response of polymer **8(ii)c** to a triangular voltage wave.

mesophase. A well-developed fan texture of this mesophase is shown in Figure 2c.

The electro-optical studies of this polymer (±80 V, 0.5 Hz) yielded a single hysteresis loop, as presented in Figure 6, revealing the bistable nature of this polymer. Due to the poor molecular alignment in the cell, the contrast ratio of the hysteresis loop was found to be low.

In order to understand the molecular orientational structure of the mesophase of this polymer, the analogous polymer (**9**) without the side chain mesogen was prepared. From the OPM and X-ray diffraction studies it was understood that this polymer shows no mesophase. However, Watanabe et al.[10] reported that similar main chain polyesters without a Si−C linkage show S_A and S_{CA} mesophases when the number of methylene units in the spacer is smaller than 11. Further chain extension resulted in the disappearance of LC phases. Therefore, we believe that in our main chain polymer the spacer is too long ($n = 13$) for the mesogenic group to form a mesophase.

The small angle X-ray diffraction pattern obtained using an oriented fiber of polymer **8(ii)c** shows two sharp reflections, a very intense ring at 27.3 Å (d_1) and a weak ring at 54.5 Å (d_2). These reflections indicated a negligible temperature dependence. As $d_1/d_2 = 2$, we assume that the polymer has a bilayered structure. Since the analogous main chain does not form a smectic mesophase, we consider that only the side chains take part in mesophase formation. It seems reasonable to assume that the polymer backbone is located in the center of the smectic layer, first-order reflection of the X-ray pattern being much larger than the length of the mesogenic side group in its most extended conformation ($l = 34.7$ Å, calculated by molecular simulation, Polygraf version 3.1). This implies some form of bilayer arrangement with interdigitated side chains in the smectic phase.

Figure 2d gives the photograph of the fine grained texture displayed by polymers **8(ii)a** and **8(ii)b**. Even though the polymers were annealed at a temperature 10 °C below the isotropization point for a long period, this texture remained unchanged. This kind of fine grain texture is characteristic for smectic or nematic liquid crystal polymers.[11,12]

In conclusion, this study presented a new synthetic pathway for the preparation of side chain liquid crystalline polymers consisting of a polymer backbone. This synthetic method is free of side reactions, which occur in usual transesterification polymerization—a common method applied for the synthesis of combined liquid crystalline polymers having polyester main chains. The mesogenic diols, which are composed of long methylene spacers with a C−Si−C linkage at the center and the side chain mesogen connected to the silicon atom, exhibited S_A and S^*_C mesophases. The liquid crystal polymers prepared with this new design exhibited room-temperature ferroelectric mesophases. Polymer **8(ii)c** was found to be the first reported switchable combined liquid crystalline polymer ever.

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