



Synthesis and Electroluminescence of Side-chain Liquid Crystalline Polyacrylates and Polyoxiranes Containing Bistolane Side Groups

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Abstract

The synthesis and characterization of side-chain liquid crystalline (LC) polyacrylates and polyoxiranes containing bistolane side-groups are presented. The phase behavior of the prepared monomers and polymers was characterized by differential scanning calorimetry and optical polarizing microscopy. All of the obtained monomers and polymers reveal an enantiotropic nematic phase. The birefringences of the LC monomers are in the range from 0.35–0.6 depending on the measuring wavelength. The photoluminescence (PL) and electroluminescence (EL) properties of the obtained monomers and polymers are also reported.

Introduction

Side-chain liquid crystalline polymers (side-chain LCPs) are of both theoretical and practical interest because they combine the anisotropy of liquid crystals (LCs) with properties of the polymeric backbone. Some new applications based on these materials have been reported [1–3]. Recently, we synthesized some high birefringent side-chain LCPs containing tolane and diphenyldiacetylene side groups [4, 5]. These side-chain LCPs have potential applications in non-linear optics and reflective polarizers [6].

Progress in the field of polymer light emitting diodes (PLED) has been developing rapidly since 1990 [7]. Conjugated polymers can be used for both single layer and multi-layer PLEDs [8] by a spin coating process [9]. Recently, some main-chain LCPs were also used for the application of PLED [10–14]. These LCPs produced linearly polarized electroluminescence based on the self organization of polymer chains. In 2000, we synthesized several series of bistolane LC compounds [15] which possess an extraordinarily high birefringence and low melting points. These LCs are particularly useful for polymer dispersed LC displays [16], cholesteric displays [17] and infrared special light modulators for nondestructive missile seeker simulations [18]. This bistolane LCs with an extended long conjugation length are also useful for light emitting diodes.

The goal of this study is to present the synthesis and characterization of side-chain LC polyacrylates and polyoxiranes containing bistolane side groups. Both the monomers and polymers were characterized by differential scanning calorimetry and optical polarizing microscopy. The wavelength-dependent birefringences of the obtained monomers are reported. The photoluminescence

(PL) and electroluminescence (EL) properties of the obtained monomers and polymers are also discussed.

Experimental

Materials

Tetrahydrofuran (THF) was distilled over sodium. Dichloromethane was distilled over calcium hydride. Ethyl acetate and hexane was distilled before use. Initiator 2,2'-azobisisobutyronitrile (AIBN) was recrystallized by methanol. Bis(triphenylphosphine)palladium (II) chloride, triphenylphosphine, 2-methyl-3-butyn-2-ol, copper (I) iodide, m-chloroperoxybenzoic acid (MCPBA) and all other reagents were purchased from Aldrich and used as received. 1-[4-(6-Hydroxyhexan-1-yloxy)phenyl]acetylene was prepared according to a study [5] reported by our lab.

Characterization Techniques

NMR spectra (300 MHz) were recorded on a Bruker-300 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid nitrogen-cooling accessory. Heating and cooling rates were 10 °C min⁻¹. Transition temperatures reported here were collected during the first cooling and second heating scans. A Carl-Zeiss Axiphot optical polarizing microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and analyze the anisotropic textures. The molecular weights of the obtained polymers were determined by GPC using a

Viscotek T50A differential viscometer and LR125 laser refractometer with THF as eluent solvent and with polystyrene standards.

Synthesis of Monomers and Polymers

The synthetic procedures of monomers **1M** ~ **4M** and polymers **1P** ~ **4P** are outlined in Schemes 1 and 2.

4-[[4-(6-Hydroxyhexan-1-yloxy)phenyl]ethynyl]-3-ethyl-4'-n-propyltolane (1)

1-[4-(6-Hydroxyhexan-1-yloxy)phenyl]acetylene (6.20 g, 28.0 mmol), 3-ethyl-4-iodo-4'-n-propyltolane (12.10 g, 32.3 mmol), bis(triphenylphosphine) palladium (II) chloride (0.21 g, 0.3 mmol), triphenylphosphine (0.55 g, 2.1 mmol), copper (I) iodide (0.29 g, 1.5 mmol) were dissolved in 450 mL of triethylamine. The solution was heated to 50 °C for 24 h, then cooled to room temperature. The solvent was then removed in a rotatory evaporator and the crude product was treated with saturated ammonium chloride solution. The product was extracted into diethyl ether. The ether solution was washed with water, saturated NaCl solution and dried over anhydrous MgSO₄. After ether was removed, the crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/3 as eluent) to yield: 8.01 g (61.9%) of yellow crystals. mp = 61.0 °C.

¹H NMR (CDCl₃, TMS) δ = 0.94 [t, 3H, Ph-(CH₂)₂-CH₃], 1.31 (t, 3H, Ph-CH₂-CH₃), 1.43–1.79 [m, 10H, Ph-O-CH₂-(CH₂)₄- and Ph-CH₂-CH₂-CH₃], 2.59 (t, 2H, Ph-CH₂-CH₂-CH₃), 2.87 (q, 2H, Ph-CH₂-CH₃), 3.64 (t, 2H, -CH₂-OH), 3.95 (t, 2H, Ph-O-CH₂-), 6.85–7.46 (m, 11 aromatic protons).

Synthesis of Monomer 1M

4-[[4-(6-Hydroxyhexan-1-yloxy)phenyl]ethynyl]-3-ethyl-4'-n-propyltolane (8.10 g, 17.0 mmol) was dissolved in a mixture of dried dichloromethane (200 mL) and triethylamine (10 mL, 70.0 mmol). After the solution was cooled in an ice-water bath to 0 °C, acryloyl chloride (3.20 g, 35.0 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The product was isolated by pouring the solution into water and filtering it. The crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/3 as eluent) to yield 7.43 g (84.1%) of yellow crystals. M⁺ = 518, elemental analysis: calculated: C: 83.4%, H: 7.4%, found: C: 83.1%, H: 7.4%.

¹H NMR (CDCl₃, TMS) δ = 0.92 (t, 3H, Ph-(CH₂)₂-CH₃), 1.30 (t, 3H, Ph-CH₂-CH₃), 1.41–1.77 (m, 10H, Ph-O-CH₂-(CH₂)₄- and Ph-CH₂-CH₂-CH₃), 2.56 (t, 2H, Ph-CH₂-CH₂-CH₃), 2.80 (q, 2H, Ph-CH₂-CH₃), 3.89 (t, 2H, Ph-O-CH₂-), 4.14 (t, 2H, -COO-CH₂-), 5.79 (d, 1H, H-CH=CH-COO-), 6.11 (m, 1H, CH₂=CH-), 6.36 (d, 1H, H-CH=CH-COO-), 6.84–7.45 (m, 11 aromatic protons).

4-(6-Hydroxyhexan-1-yloxy)-3'-ethyl-4'-aminotolane (2)

Compound **2** was prepared by Cadiot-ChodKiewicz coupling [17] of 4-(6-hydroxyhexan-1-yloxy)phenylacetylene with 4-iodo-2-ethylaniline according to similar synthetic procedures used for compound **1**. Yield: 61.4%, mp = 84.7 °C.

¹H NMR (CDCl₃, TMS) δ = 1.24 (t, 3H, Ph-CH₂-CH₃), 1.30–1.85 [m, 8H, Ph-O-CH₂-(CH₂)₄-], 2.46 (q, 2H, Ph-CH₂-CH₃), 3.61 (t, 2H, -CH₂OH), 3.92 (t, 2H, Ph-O-CH₂-), 6.58–7.42 (m, 7 aromatic protons).

4-(6-Hydroxyhexan-1-yloxy)-3'-ethyl-4'-iodotolane (3)

Compound **2** (3.50 g, 10.0 mmol) was dissolved in a mixture of THF (10 mL) and hydrochloric acid (4.1 mL, 50.0 mmol), which was kept below 5 °C. The aqueous solution (6.0 mL) of sodium nitrite (2.10 g, 31.0 mmol) was added dropwise. The resulting mixture was cooled to 0 °C and stirred for 10 min. An aqueous solution (20 mL) of sodium iodide (14.50 g, 100.0 mmol) was then added dropwise. The reaction mixture was stirred at 0 °C for 3 h. The product was extracted into ethyl acetate. The collected ethyl acetate solution was washed with 10% sodium thiosulfate aqueous solution, water, and dried over anhydrous MgSO₄. After the ethyl acetate was removed, the crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/5 as eluent) to yield 2.90 g (65.2%) of brown crystals. mp = 49.0 °C.

¹H NMR (CDCl₃, TMS) δ = 1.23 (t, 3H, Ph-CH₂-CH₃), 1.42–1.79 [m, 8H, Ph-O-CH₂-(CH₂)₄-], 2.69 (q, 2H, Ph-CH₂-CH₃), 3.65 (t, 2H, -CH₂-OH), 3.96 (t, 2H, Ph-O-CH₂-), 6.85–7.75 (m, 7 aromatic protons).

4-[[4-(6-Hydroxyhexan-1-yloxy)phenyl]ethynyl]-2-ethyl-4'-n-propyltolane (4)

Compound **4** was prepared by Cadiot-ChodKiewicz coupling of 1-(1-ethynyl)-4-propylbenzene with compound **3** according to similar synthetic procedures used with compound **1**. Yield: 84.7%, mp = 66.8 °C.

¹H NMR (CDCl₃, TMS): δ (ppm) = 0.95 (t, 3H, Ph-CH₂-CH₂-CH₃), 1.32 (t, 3H, Ph-CH₂-CH₃), 1.45–1.81 (m, 10H, Ph-O-CH₂-(CH₂)₄- and Ph-CH₂-CH₂-CH₃), 2.61 (t, 2H, Ph-CH₂-CH₂-CH₃), 2.89 (q, 2H, Ph-CH₂-CH₃), 3.66 (t, 2H, -CH₂-OH), 3.97 (t, 2H, Ph-O-CH₂-), 6.88–7.48 (m, 11 aromatic protons).

Synthesis of Monomer 2M

Monomer **2M** was prepared by the esterification of acryloyl chloride with compound **4** according to similar synthetic procedures used with compound **1M**. Yield: 97.1%, M⁺ = 518, elemental analysis: calculated: C: 83.4%, H: 7.4%, found: C: 83.4%, H: 7.5%.

¹H NMR (CDCl₃, TMS): δ (ppm) = 0.94 (t, 3H, Ph-CH₂-CH₂-CH₃), 1.31 (t, 3H, Ph-CH₂-CH₃), 1.45–1.81 (m, 10H, Ph-O-CH₂-(CH₂)₄- and Ph-CH₂-CH₂-CH₃), 2.60 (t, 2H, Ph-CH₂-CH₂-CH₃), 2.87 (q, 2H, Ph-CH₂-CH₃), 3.96 (t, 2H, Ph-O-CH₂-), 4.17 (t, 2H, (O)CO-CH₂-), 5.80 (d, 1H, H-CH=CH-COO-), 6.15 (m, 1H, CH₂=CH-), 6.40

(d, 1H, H- $\underline{\text{C}}\text{H}=\text{CH}-\text{COO}-$), 6.86–7.48 (m, 11H, aromatic proton).

4-[[4-(4-Penten-1-yloxy)phenyl]ethynyl]-3-ethyl-4'-n-propyltolane (5)

Compound **5** was prepared by Cadiot-ChodKiewicz coupling of 1-[4-(4-penten-1-yloxy)phenyl]acetylene with 4-iodo-3-ethyl-4'-n-propyltolane according to similar synthetic procedures used for compound **1**. Yield: 98.0%, mp = 57.9 °C.

^1H NMR (CDCl_3 , TMS): δ (ppm) = 0.94 (t, 3H, Ph- $\text{CH}_2-\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.29 (t, 3H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.66 (m, 2H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{CH}_3$), 1.88 (m, 2H, Ph-O- $\text{CH}_2-\underline{\text{C}}\text{H}_2-$), 2.23 [m, 2H, Ph-O-(CH_2) $_2$ - $\underline{\text{C}}\text{H}_2-$], 2.59 (t, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{CH}_3$), 2.86 (q, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_3$), 3.98 (t, 2H, Ph-O- $\underline{\text{C}}\text{H}_2-$), 5.03 (m, 2H, $\underline{\text{C}}\text{H}_2=\text{CH}-$), 5.85 (m, 1H, $\text{CH}_2=\underline{\text{C}}\text{H}-$), 6.85–7.45 (m, 11 aromatic protons).

Synthesis of Monomer **3M**

4-[[4-(4-Penten-1-yloxy)phenyl]ethynyl]-3-ethyl-4'-n-propyltolane (0.15 g, 0.35 mmol) was dissolved in the dried dichloromethane (10 ml). m-Chloroperoxybenzoic acid (MCPBA) (0.18 g, 1.0 mmol, 50%) was added slowly at room temperature. The mixture was stirred for 24 hours. After solvent was removed, the crude product was purified using column chromatography (silica gel; hexane/ethyl acetate = 2 : 1) to yield 0.75 g (48.1%) of yellow crystals. $M^+ = 448$, elemental analysis: calculated: C: 85.7%, H: 7.2%, found: C: 85.6%, H: 7.4%.

^1H NMR (CDCl_3 , TMS): δ (ppm) = 0.84 (t, 3H, Ph-(CH_2) $_2$ - $\underline{\text{C}}\text{H}_3$), 1.22 (t, 3H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.50–1.90 (m, 6H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{CH}_3$ and Ph-O- $\text{CH}_2-(\text{CH}_2)_2-$), 2.41 (m, 1H, epoxide proton), 2.49 (t, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_2-$), 2.67 (m, 1H, epoxide proton), 2.76 (q, 2H, Ph- $\underline{\text{C}}\text{H}_2-\underline{\text{C}}\text{H}_3$), 2.89 (m, 1H, epoxide proton), 3.91 (t, 2H, Ph-O- $\underline{\text{C}}\text{H}_2-$), 6.77–7.37 (m, 11 aromatic protons).

4-(4-Penten-1-yloxy)-3'-ethyl-4'-aminotolane (6)

Compound **6** was prepared by Cadiot-ChodKiewicz coupling of 1-[4-(4-penten-1-yloxy)phenyl]acetylene with 4-iodo-2-ethylaniline according to similar synthetic procedures used for compound **1** to yield 3.21 g (90.9%) of brown oil.

^1H NMR (CDCl_3 , TMS): δ (ppm) = 1.25 (t, 3H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.85–1.91 (m, 2H, Ph-O- $\text{CH}_2-\underline{\text{C}}\text{H}_2-$), 2.21–2.25 (m, 2H, Ph-O- $\text{CH}_2-\text{CH}_2-\underline{\text{C}}\text{H}_2-$), 2.48 (q, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_3$), 3.75 (s, broad, 2H, NH_2), 3.96 (t, 2H, Ph-O- $\underline{\text{C}}\text{H}_2-$), 4.89–5.10 (m, 2H, $\text{H}_2\text{C}=\text{CH}-$), 5.75–5.95 (m, 1H, $\text{H}_2\text{C}=\underline{\text{C}}\text{H}-$), 6.60–7.43 (m, 7H, aromatic protons).

4-(4-Penten-1-yloxy)-3'-ethyl-4'-iodotolane (7)

Compound **7** was prepared by iodination of compound **6** with sodium iodide according to similar synthetic procedures used for compound **3** to yield 2.93 g (70.1%) of yellow oil. ^1H NMR (CDCl_3 , TMS): δ (ppm) = 1.24 (t, 3H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.87 (m, 2H, Ph-O- $\text{CH}_2-\underline{\text{C}}\text{H}_2-$), 2.54 [m, 2H, Ph-O-(CH_2) $_2$ - $\underline{\text{C}}\text{H}_2-$], 2.71 (q, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_3$), 3.96 (t, 2H, Ph-O- $\underline{\text{C}}\text{H}_2-$), 5.00–5.11 (m, 2H,

$\text{H}_2\text{C}=\text{CH}-$), 5.78–5.92 (m, 1H, $\text{H}_2\text{C}=\underline{\text{C}}\text{H}-$), 6.86–7.76 (m, 7H, aromatic protons).

4-[[4-(4-Penten-1-yloxy)phenyl]ethynyl]-2-ethyl-4'-n-propyltolane (8)

Compound **8** was prepared by Cadiot-ChodKiewicz coupling of 1-(4-n-propylphenyl)acetylene with compound **7** according to similar synthetic procedures used for compound **1**. Yield: 88.0%, mp = 105.0 °C.

^1H NMR (CDCl_3 , TMS): δ (ppm) = 0.93 (t, 3H, Ph- $\text{CH}_2-\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.29 (t, 3H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.63 (m, 2H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{CH}_3$), 1.88 (m, 2H, Ph-O- $\text{CH}_2-\underline{\text{C}}\text{H}_2-$), 2.22 [m, 2H, Ph-O-(CH_2) $_2$ - $\underline{\text{C}}\text{H}_2-$], 2.59 (t, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{CH}_3$), 2.87 (q, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_3$), 3.97 (t, 2H, Ph-O- $\underline{\text{C}}\text{H}_2-$), 4.95–5.10 (m, 2H, $\underline{\text{C}}\text{H}_2=\text{CH}-$), 5.75–5.92 (m, 1H, $\text{CH}_2=\underline{\text{C}}\text{H}-$), 6.85–7.46 (m, 11 aromatic protons).

Synthesis of Monomer **4M**

Monomer **4M** was prepared by epoxidation of compound **8** with MCPBA according to similar synthetic procedures used for compound **3M**. Yield: 30.4%, $M^+ = 448$, elemental analysis: calculated: C: 85.7%, H: 7.2%, found: C: 85.5%, H: 7.2%.

^1H NMR (CDCl_3 , TMS): δ (ppm) = 0.93 (t, 3H, Ph- $\text{CH}_2-\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.30 (t, 3H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_3$), 1.59–1.95 (m, 6H, Ph- $\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{CH}_3$, Ph-O- $\text{CH}_2-(\text{CH}_2)_2-$), 2.50 (m, 1H, epoxide proton), 2.59 (t, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_2-$), 2.77 (m, 1H, epoxide proton), 2.85 (q, 2H, Ph- $\underline{\text{C}}\text{H}_2-\text{CH}_3$), 2.98 (m, 1H, epoxide proton), 4.00 (t, 2H, Ph-O- $\underline{\text{C}}\text{H}_2-$), 6.85–7.47 (m, 11 aromatic protons).

Synthesis of Polymers **1P** and **2P**

Both polymer **1P** and **2P** were prepared by free radical polymerization of monomers **1M** and **2M** using AIBN as an initiator. The synthesis of **1P** is described below.

Monomer **1M** (1.00 g) and initiator AIBN (0.01 g) were dissolved in THF (1 ml). The reaction bottle was sealed under vacuum, and the reaction proceeded at 60 °C for 24 hours. The product was precipitated in methanol three times.

1P: yield: 82.0%, elemental analysis: calculated: C: 83.4%, H: 7.4%, found: C: 83.1%, H: 7.5%.

2P: yield: 70.0%, elemental analysis: calculated: C: 83.4%, H: 7.4%, found: C: 83.1%, H: 7.4%.

Synthesis of Polymers **3P** and **4P**

Both polymers **3P** and **4P** were prepared by cationic polymerization of monomers **3M** and **4M** using borontrifluoro etherate as an initiator. The synthesis of **3P** is described below.

Compound **3M** (0.50 g) was dissolved in dichloromethane (0.5 ml) under a nitrogen atmosphere at 0 °C. Borontrifluoro etherate (2.0 μml) was added into the solution, and the solution was stirred at room temperature for 24 hours. The product was precipitated in hexane three times. ^1H NMR and GPC were used to check for the absence of monomer **3M**. The results of the polymerization

Table 1. Phase transition temperatures and corresponding enthalpy changes of monomers **1M** ~ **4M** and compounds **5** and **8**

Compound	Phase transition temperatures (°C) and enthalpies ^a (Kcal mol ⁻¹)
1M	K 43.8 (8.14) N 92.3 (0.14) I I 89.5 (0.18) N < 50°C ^b K
2M	K 50.9 (8.05) N 93.8 (0.27) I I 90.8 (0.31) N < 50°C ^b K
3M	K 82.1 (3.86) N 158.1 (0.29) I I 144.9 (0.10) N 40.6 (2.12) K
4M	K 93.8 (11.22) N 162.3 (0.40) I I 157.4 (0.47) N -1.6 (4.88) K
5	K 88.9 (8.37) N 150.1 (0.37) I I 144.9 (0.34) N 87.6 (7.23) K
8	K 105.3 (8.71) N 156.9 (0.36) I I 153.5 (0.35) N 40.9 (6.15) K

^a K: crystalline, N: nematic, I: isotropic.

^b The sample was cooled to -50°C and the crystallization peak did not appear.

Table 2. Polymerization results of monomer **1M** ~ **M4**

Polymers	Yield (%)	\overline{M}_n ($\times 10^{-3}$)	\overline{M}_w ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$
1P	82.0	38.3	41.3	1.18
2P	70.6	33.7	44.1	1.31
3P	72.7	9.8	21.0	2.15
4P	68.3	8.6	16.4	1.91

of all monomers are summarized in Table 2. As shown in Table 2, all of the polymers gave reasonable yields in the polymerization. The molecular weight distributions were less than 2.15.

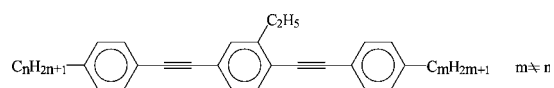
3P: yield: 72.0%, elemental analysis: calculated: C: 85.7%, H: 7.2%, found: C: 85.6%, H: 7.2%.

4P: yield: 68.0%, elemental analysis: calculated: C: 85.7%, H: 7.2%, found: C: 85.6%, H: 7.2%.

Results and Discussion

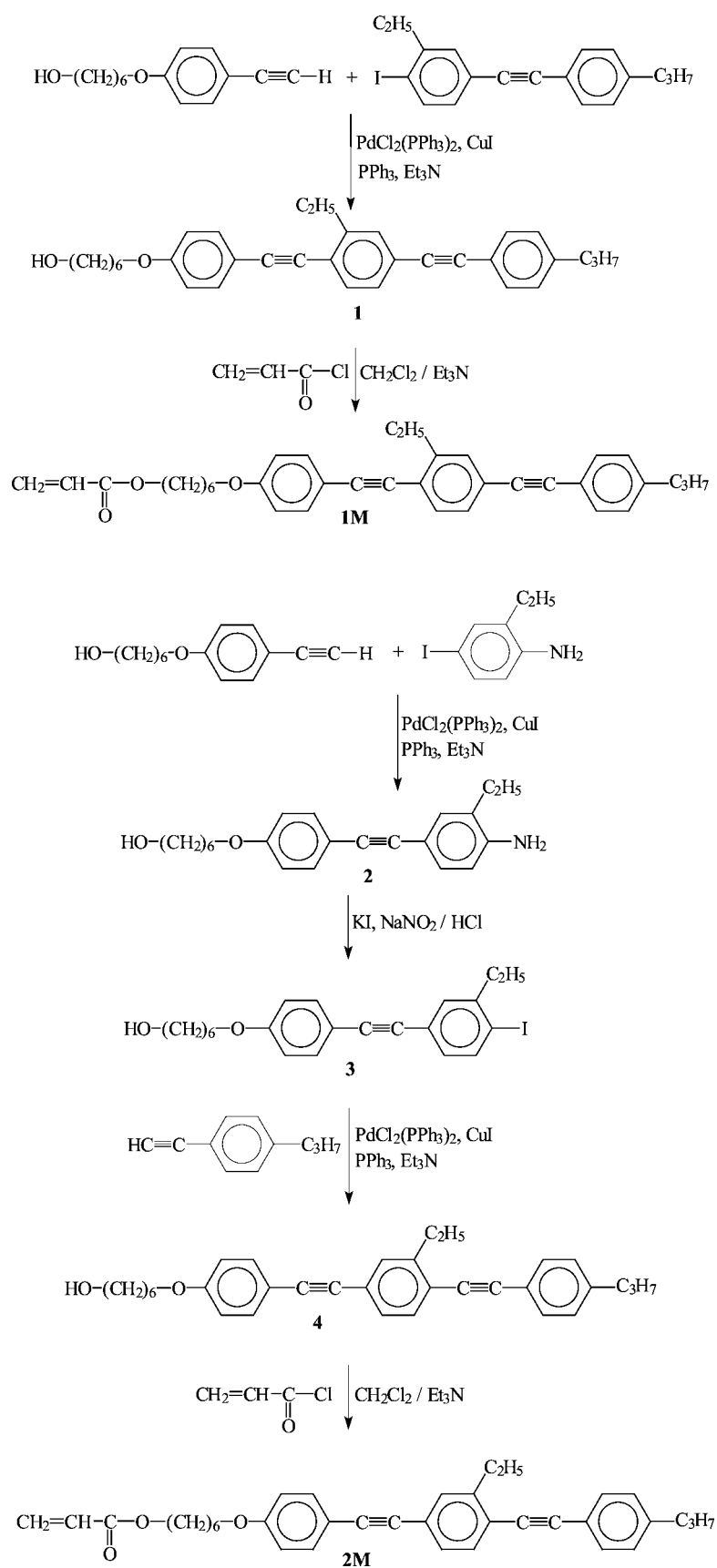
The synthesis of acrylate monomers **1M** and **2M** and epoxide monomers **3M** and **4M** is outlined in Schemes 1 and 2. All monomers gave reasonably high yields. The purity of the obtained monomers was determined via chromatography to be high after purification. Figure 1 shows the representative DSC thermalgrams of monomer **2M**. The heating scan revealed a melting point at 50.9°C and a nematic to isotropic phase transition at 93.8°C. On the cooling scan, only an isotropic to nematic transition was present at 90.8°C. The sample did not crystallize even if it was cooled to -50°C at a cooling rate of 1°C/min. The crystallization of acrylate monomers **1M** and **2M** is a kinetic controlled process. Both monomers were crystallized after they were stored in a

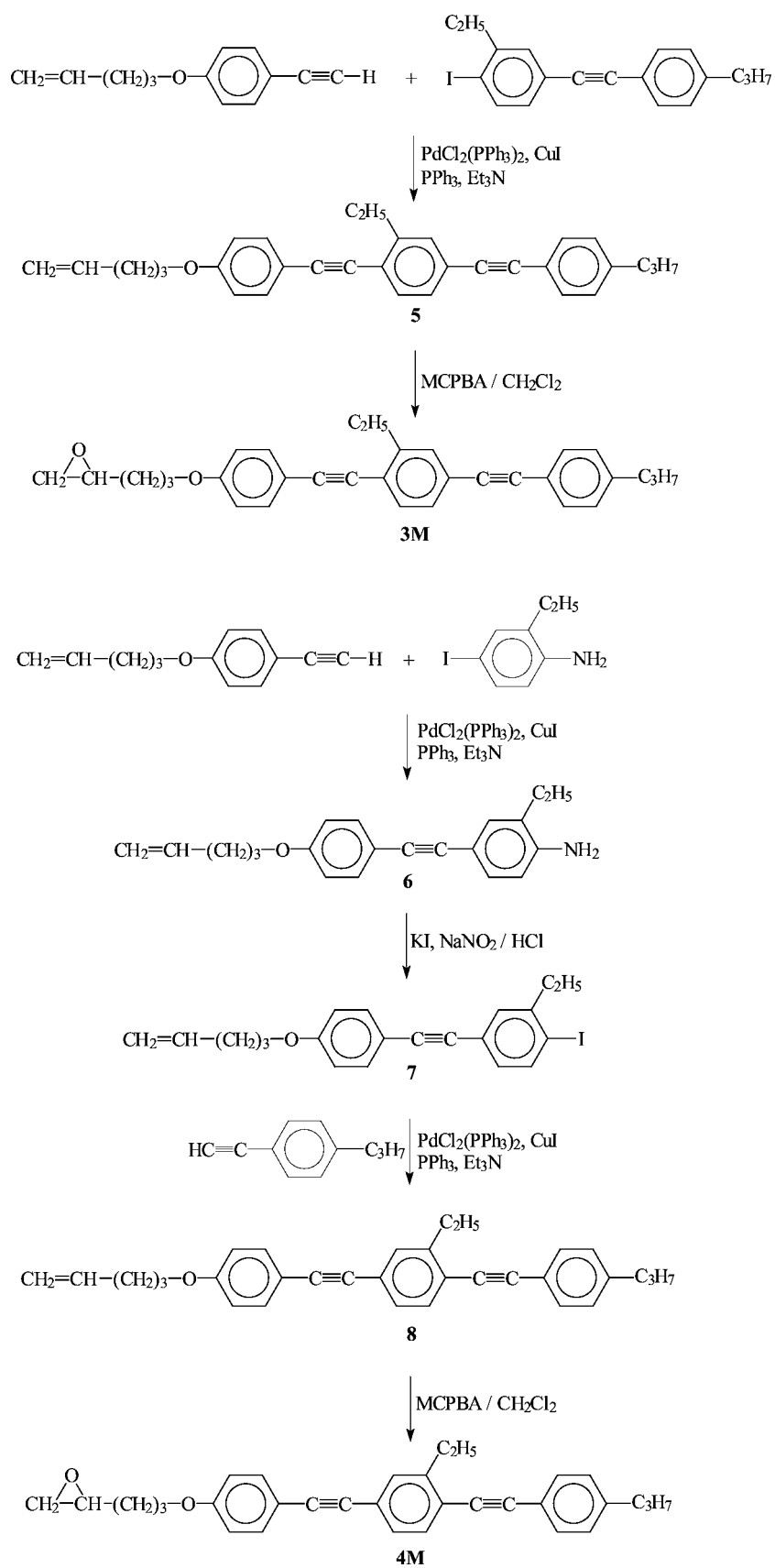
refrigerator (0°C) for several days. The reason for this crystallization could be due to the lateral ethyl side group and acrylate head group that obstruct the crystallization of the liquid crystals. Table 1 summarizes the phase transitions of monomers **1M** ~ **4M** and intermediate compounds **5** and **8**. Comparing the chemical structures of monomer **1M** and **2M**, the only difference that can be noticed is in the position of lateral ethyl group. The ethyl group in monomer **1M** is close to the acrylate head, while the ethyl group in monomer **2M** is close to the terminal propyl group. In general, this lateral ethyl group is introduced to increase the lateral width of the mesogenic core. Its presence decreases the packing density of liquid crystal and results in a lowering decrease of the phase transition temperatures. In our previous report [7], we reported the synthesis of a series of asymmetric bistolane liquid crystals with different alkyl chain length on both ends. Their chemical structures were as follows:

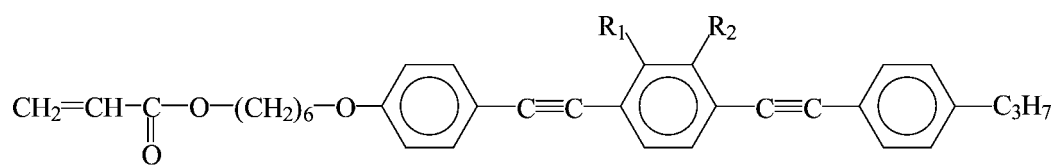


We found that when the lateral ethyl group was close to a longer alkyl chain end, it resulted in a dramatical decrease in the phase transition temperatures. Monomers **1M** and **2M** contain a propyl group on the right-hand side and a hexyloxy group together with an acrylate head on the left-hand side. The alkyl chain length on the left-hand side is longer than that on the right-hand side; therefore, monomer **1M** reveals lower phase transition temperatures. Similar results can be observed for monomers **3M** and **4M** and compounds **5** and **8**. Furthermore, if we compare three kinds of LC compounds, their melting points show the following tendencies: **1M**, **2M** < **3M**, **4M** < compound **5**, **8**. Again this can be explained by the molecular packing of the LC compounds. Compounds **5** and **8** have perfect linear rigid rod structures and higher melting points. On the other hand, monomers **1M** and **2M** contain a relatively bulky acrylate head and exhibit lower melting points. All six compounds reveal very wide temperature ranges in the nematic phase. Figure 2 shows the birefringence dispersion of monomer **1M** at 25°C. The birefringence of monomer **1M** decreases as the wavelength increases. Its birefringence is about 0.4 when the measuring wavelength is 550 nm.

Scheme 3 outlines the polymerization of monomers **1M** ~ **4M**. Both monomers **1M** and **2M** were polymerized by a free radical polymerization mechanism while monomers **3M** and **4M** were polymerized by a cationic ring-opening polymerization process. Table 2 reports the polymerization results. Both polymers **1P** and **2P** were achieved with number average molecular weights higher than 3.3×10^4 . However **3P** and **4P** were obtained with much lower number average molecular weights ($> 8 \times 10^3$). Table 3 summarizes the thermal transitions of polymers **1P** ~ **4P**. To our surprise, all polymers exhibit an enantiotropic nematic phase. Since the polymers contain six methylene units as spacers and a long rigid rod-like bistolane mesogen, they should reveal smectic phases. We believe that the reason why all polymers show a nematic phase is

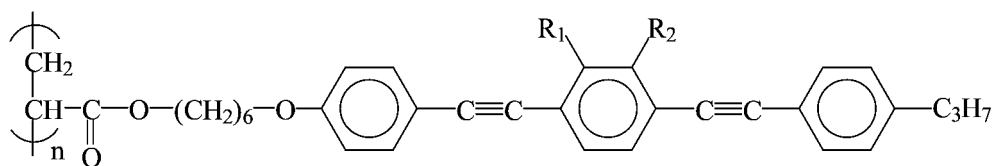

 Scheme 1. Synthesis of acrylate monomers **1M** and **2M**.

Scheme 2. Synthesis of epoxide monomers **3M** and **4M**.



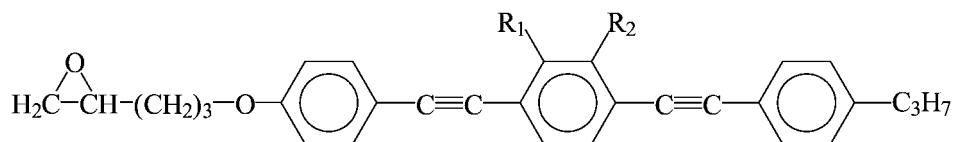
1M: R₁ = C₂H₅, R₂ = H

2M: R₁ = H, R₂ = C₂H₅



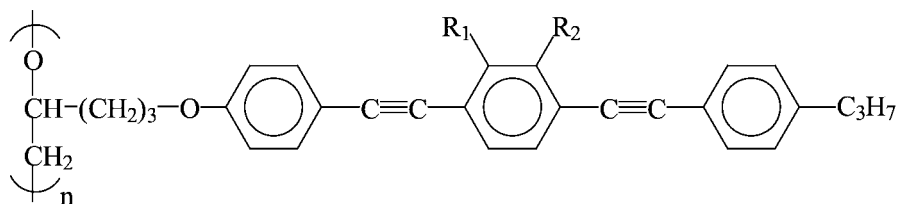
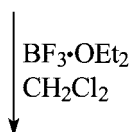
1P: R₁ = C₂H₅, R₂ = H

2P: R₁ = H, R₂ = C₂H₅



3M: R₁ = C₂H₅, R₂ = H

4M: R₁ = H, R₂ = C₂H₅



3P: R₁ = C₂H₅, R₂ = H

4P: R₁ = H, R₂ = C₂H₅

Scheme 3. Polymerization of 1M ~ 4M.

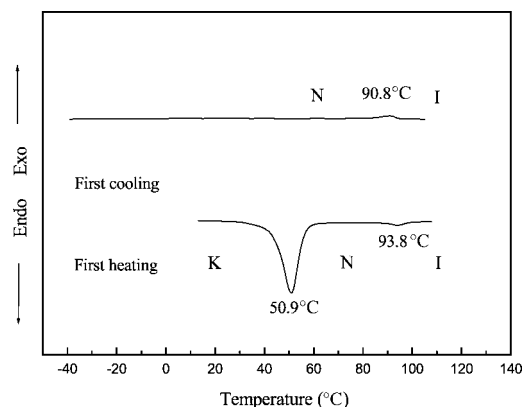


Figure 1. DSC thermalgrams of monomer **2M**.

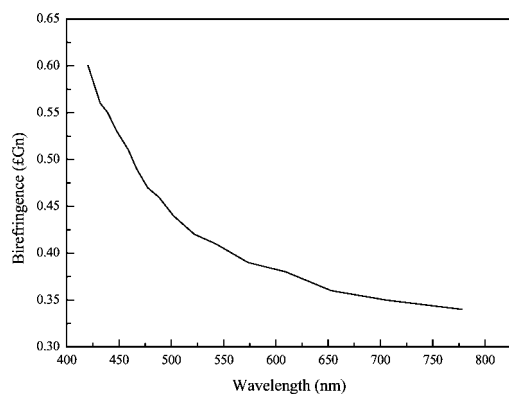


Figure 2. The wavelength-dependent birefringence of monomer **1M** at 25 °C.

because the introduction of the lateral ethyl group. Introducing the lateral ethyl group into the bistolane core decreases the length to width ratio of the mesogen and prevents from forming layer smectic structures. A comparison of the thermal transition of both series of polymers shows their glass transition temperatures to be very close. However the LC temperature ranges of polymers **3P** and **4P** are wider than those of polymers **1P** and **2P**. This could be due to the more flexible polyoxirane backbone. According to the literature [2], a more flexible polymer backbone allows its mesogenic side chains to form a more stable mesophase and hence it exhibits a wider mesomorphic temperature range.

Figure 3 shows the optical spectra of monomer **1M** measured in THF and in its solid state. The UV-vis absorption peak of monomer **1M** are about 330 nm, and both solution and film samples show very similar absorption spectra. The PL emissions of monomer **1M** in THF and in solid state are 378.8 and 427.4 nm, respectively. A bathochromic is observed in the neat film when the solution spectra are compared. This might due to the aggregation of the liquid crystal molecules in the neat film. Table 4 summarizes the optical data of monomers **1M** ~ **4M**. All monomers present almost the same UV absorption and PL emission data. The results demonstrate that the absorption and emission peaks of all monomers are attributed to the $\pi - \pi^*$ transition of the bistolane core. Figure 4 presents the optical spectra of polymer **1P** measured in THF and in the solid state. Basically, the spectra are similar to those of monomer **1M**. This

Table 3. Phase transition temperatures and corresponding enthalpy changes of polymers **1P** ~ **4P**

	Phase transition temperatures (°C) and enthalpies (Kcal mol ⁻¹)	
1P	G 10.7 N 96.7 (0.32) I	
	I 85.9 (0.30) N 5.3 G	
2P	G 5.4 N 70.2 (0.32) I	
	I 68.8 (0.31) N -0.3 G	
3P	G 2.6 N 145.0 (0.42) I	
	I 110.0 (0.21) N -6.9 G	
4P	G 5.4 N 141.5 (0.52) I	
	I 116.5 (0.17) N -3.0 G	

N: nematic, I: isotropic, G: glassy.

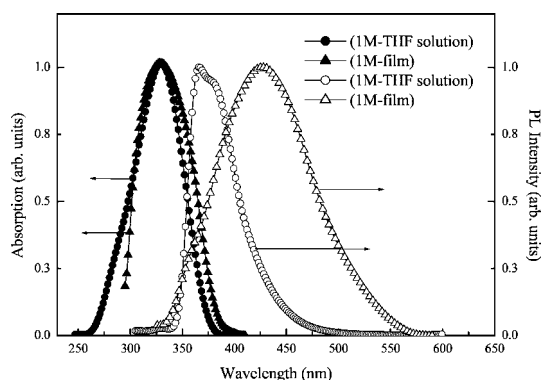


Figure 3. UV-vis absorption and photoluminescence spectra of monomer **1M** in THF and in films.

is reasonable because the absorption and emission of polymer **1P** are attributed to the mesogenic core only. Figure 5 shows the EL spectrum of polymer **1P** that was made as a single layer device (ITO/**1P**/Al). This EL spectrum is very similar to its PL spectrum. The current-voltage (J-V) and the luminance-voltage (L-V) curves are shown in Figure 6. The threshold voltage is 3.0 V. The power efficiency of the device is 1.0×10^{-2} lm/W at 9.0 V.

Table 4. UV-vis absorption and photoluminescence spectra of monomers **1M** ~ **4M** and polymers **1P** ~ **4P** in THF and in films

	UV absorption (λ_{\max} , nm)		PL emission (λ_{\max} , nm)	
	Solution	Film	Solution	Film
1M	330.0	332.0	378.8	427.4
2M	330.0	334.0	378.2	426.8
3M	331.0	333.6	378.6	427.2
4M	331.0	333.9	378.6	425.2
1P	326.8	327.0	378.8	426.8
2P	328.4	332.0	378.8	426.8
3P	331.5	342.5	378.8	427.1
4P	331.5	334.4	378.8	427.6

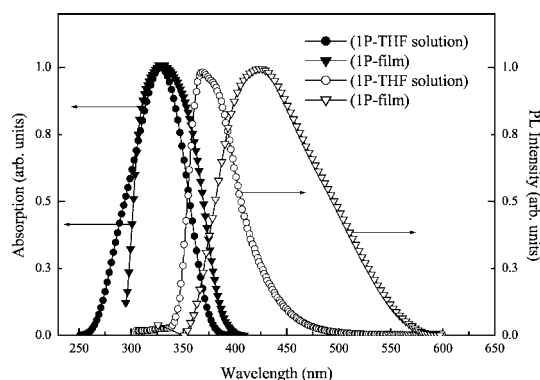


Figure 4. UV-vis absorption and photoluminescence spectra of polymer **1P** in THF and in films.

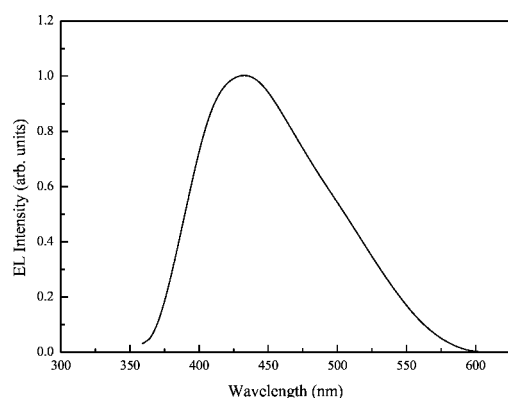


Figure 5. EL emission spectrum of an ITO/**1P**/Al device.

Conclusion

Two kinds of side-chain LC polyacrylates and polyoxiranes were synthesized. All monomers and polymers exhibit an enantiotropic nematic phase. Both polyoxiranes exhibit wider temperature ranges in the nematic phase than polyacrylates because a polyoxirane backbone is more flexible than a polyacrylate backbone. The polymers emit blue light at 427 nm.

Acknowledgement

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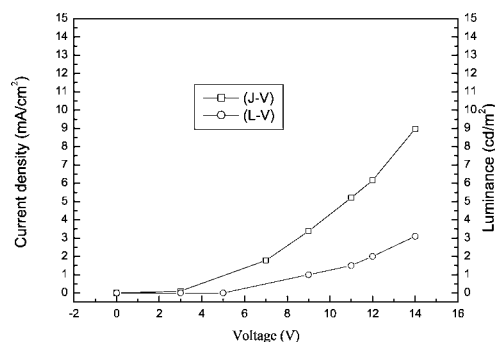


Figure 6. The J-V (□) and L-V (○) curves of an ITO/PEDOT/**1P**/Al device.

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