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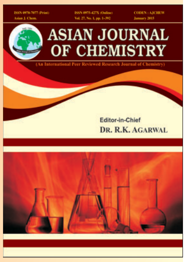

Synthesis and Liquid Crystalline Behavior of Photoreactive Side Chain Liquid Crystalline Polyoxetanes Containing Cinnamoyl Biphenyl Mesogen

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A new series of photo-cross-linkable side chain liquid crystalline polymers based on the oxetane backbone containing 4-cinnamoyl biphenyl groups as the mesogenic and photo reactive group in side chain were prepared by ring-opening polymerization and characterized. The thermal transition and mesomorphic nature of the resulting polymers and monomers were determined by differential scanning caloriametry, polarized optical microscope and X-ray technique. All the synthesized polymers showed enantiotropic liquid crystal behaviour. It was found that the length of the flexible spacer had a great influence on both the thermal transitions and mesomorphic nature for the resulting polymers and monomers.

Keywords: Liquid crystal, Ring-opening polymerization, Photo-cross-linkable.

INTRODUCTION

In the past decade, photo-cross-linkable side chain liquid crystalline polymers have drawn a considerable attention to the aspect of fundamental and applied research on the combination of special physical and chemical properties of both mesogenic units and photoactive group in their structure[1-13]. Because the anisotropic structure of photo-cross-linked side chain liquid crystalline polymers can be locked-in by a photoreaction through photoactive groups[2-14], they would appear to be good candidates for the potential materials that could be applied to electro-optic display, information storage device and nonlinear optical devices. In terms of the research's theoretical view point, photo reaction and photochemical behaviour of such kind of polymers in the mesophase medium have also given rise to an interest in photochemical aspects[1,2].

Much effort has been devoted to design and prepare novel photo-cross-linkable liquid crystalline polymers containing photosensitive group in the side chain position[6-8]. Several photo-cross-linkable side chain liquid crystalline polymers containing cinnamate ester or their analogues as photoactive group have been synthesized to investigate how to lock-in the liquid crystal mesomorphic phase[5-13]. As a whole, most of the photo-cross-linkable side chain liquid polymers reported in the literature contain cinnamate ester group as a photoactive group which leads to the photo-cross-linking through [2 + 2] cycloaddition reaction. Moreover, most of photo-cross-linkable side chain liquid crystalline polymers were prepared based on the polyacrylate and polymethacrylate backbone. Chien *et al.*[5] reported synthesis and liquid crystalline behaviour of photo-cross-linkable side chain liquid crystalline polymers based on polysiloxanes containing cinnamate ester group as photoactive group.

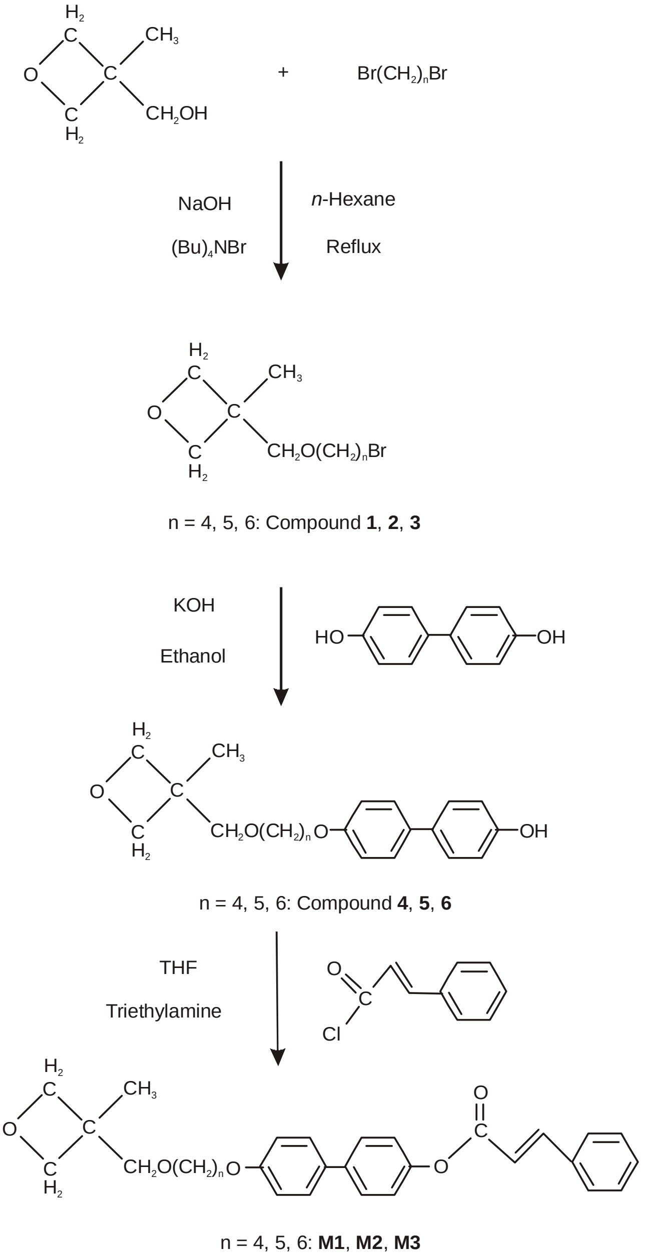
In this study, an approach to design and synthesis of novel photo-cross-linkable side chain liquid crystalline polyoxetanes containing cinnamoyl biphenyl mesogen and various flexible spacer lengths attached to the backbone has been achieved extensively. The extra flexibility of polyoxetane backbone has been proved to facilitate the formation of a stable mesophase with broader temperature range and also lead to a lower glass transition temperature compared to the polyacrylate and polymethacrylate counterparts[15-17]. Herein, the synthesis, thermal behaviour and mesomorphic nature of a series of photo-cross-linkable monomers, 3-{[ω-(4-cinnamoylbiphenyloxy)-alkyloxy]-methyl}-3-methyl oxetane (ω = 4,5,6) and their polymers synthesized by ring-opening polymerization were depicted, respectively. The structure and liquid crystal behaviour of the synthesized polymers and their monomers were characterized using ^{1}H NMR, FT-IR, differential scanning calorimeter (DSC), polarized optical microscope (POM) and X-ray technique, *etc*.

EXPERIMENTAL

Boron trifluoride ether complex was purchased from TCI and was distilled before use. 3-(Hydroxymethyl)-3-methyloxetane, 4,4'-biphenol and dibromoalkanes as well as all other reagents were obtained from Aldrich Chem. Inc. and were used as received. Dichloromethane used in the ring-opening polymerization was refluxed over calcium hydride and then distilled under nitrogen and stored in an inert gas atmosphere.

Apparatus and equipment: ^{1}H NMR spectra (300 MHz) were recorded on a varian VXR-300 spectrometer. FT-IR spectrometer was used to check the structure of the synthesized polymers and monomers. Thermal transitions and thermodynamic parameters were determined by a SeikoSSC/5200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were 10 °C/ min. A Carl-Ziess Axiphot polarized optical microscope equipped with a Mettler FP82 hot stage and a FP 80 central processor was utilized to observe the thermal transitions and to analyze the anisotropic textures. Gel permeation chromatography (GPC) was run on an applied biosystems 400 LC instrument equipped with a differential refracometer, a UV detector and a set of PL gel columns of 10^2, 5×10^2, 10^3 and 10^4 Å. The oven temperature was set at 40 °C. Tetrahydrofuran (THF) was used as eluent and the flow rate was 1 mL/min. The molecular weight calibration curve was obtained using standard polystyrenes. X-ray diffraction measurements were performed with nickel-filtered CuK$_\alpha$ radiation with a Rigaku powder diffractometer.

Synthesis of monomers: The synthesis of the monomers and their precursors is outlined in **Scheme-I**. Chemical structures of all the three compounds were checked with ^{1}H NMR and FT-IR spectrum.



Scheme-I: Synthesis of compounds **M1-M3**

3-{[(3-Bromobutyl)oxy]-methyl}-3-methyloxetane (1); 3-{[(3-bromopentyl)oxy]methyl}-3-methyloxetane (2); 3-{[(3-bromohexyl)oxy]methyl}-3 methyloxetane (3): Compounds **1-3** were prepared by the same method. The synthesis of compound **2** was described below.

A two-phase system composed of dibromopentane (70 g, 0.304 mol) in hexane (100 mL) and 3-(hydroxymethyl)-3-methyloxetane (10 g, 0.098 mol), sodium hydroxide (65 g, 1.625 mol) and tetrabutylammonium bromide (0.50 g) in water (100 mL) was stirred for 24 h at room temperature and heated to reflux under stirring for 2 h. After the reaction system was cooled to room temperature, water (100 mL) was added and the organic layer was extracted three times with hexane. The product was isolated by evaporating the solvent after drying the solution with anhydrous magnesium sulfate. The crude product was purified by distillation (b.p.: 80-85 °C at 0.15 mm Hg) to yield 18.4 g of colourless liquid. Chemical structure of the compounds was checked with ^{1}H NMR spectrum.

3-{[3-(4'-Hydroxybiphenyloxy)butyloxy]methyl}-3-methyloxetane (4); 3-{[3-(4'-hydroxybiphenyloxy)pentyloxy]methyl}-3-methyloxetane (5); 3-{[3-(4'-hydroxybiphenyloxy)hexyloxy]methyl}-3-methyloxetane (6): Compounds **4-6** were prepared by the same method. The synthesis of compound **4** was described below.

To a solution of 4,4'-biphenol (8.38 g, 45 mmol), KOH (5.05 g, 90 mmol) and a trace of KI in 90 % ethanol (450 mL), the compound **1** (5.05 g, 21.5 mmol) was added dropwise within 0.5 h after the solution mentioned above was refluxed for 1 h. The solution continued to be refluxed for 24 h and then cooled to room temperature. After the reaction was completed, the solvent was removed to reduce pressure distillation. The solid residues was boiled with 500 mL of water for 1 h to remove reactants and inorganic salt and then cooled to room temperature. The crude product was filtered out and washed with water several times and consequently dissolved in 200 mL of ethyl acetate. The solution of the product in ethyl acetate was washed twice with a 10 % aqueous solution of K_2CO_3 in separation funnel and acidified with dilute hydrochloric acid. The solution was dried with $MgSO_4$ and then filtered to remove $MgSO_4$. Finally, the solvent was removed by reducing pressure distillation to give 7.2 g of a white solid product.

Compound 4: ^{1}H NMR ($CDC1_3$, 300 MHz, TMS, ppm): 1.32 (s, 3H, $-C\underline{H}_3$); 1.78-1.90 (m, 4H, $-C\underline{H}_2C\underline{H}_2-$); 3.48(s, 2H,

-C$\underline{H}_2$O-); 3.57(t, 2H, -C$\underline{H}_2$O-); 3.98(t, 2H, -C$\underline{H}_2$O-); 4.40(d, 2H, -C$\underline{H}_2$O-, cycle); 4.57 (d, 2H, -C$\underline{H}_2$O-, cycle); 6.13(s, 1H, -O$\underline{H}$); 6.84-6.93 (m, 4H, $\underline{Ph}$); 7.25-7.46 (m, 4H, $\underline{Ph}$). FT-IR (KBr, ν_{max}, cm^{-1}): 3171 (-OH), 2950, 2866, 1612, 1500, 1252.

Compound 5: ^{1}H NMR (CDC1$_3$, 300 MHz, TMS, ppm): 1.30 (s, 3H, -C$\underline{H}_3$); 1.53-1.83 (m, 6H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.48 (m, 4H, -C$\underline{H}_2$O-); 3.97 (t, 2H, -C$\underline{H}_2$O-); 4.36(d, 2H, -C$\underline{H}_2$O-, cycle); 4.53(d, 2H, -C$\underline{H}_2$O-, cycle); 5.65(s, 1H, -O$\underline{H}$); 6.83-6.92 (m, 4H, $\underline{Ph}$); 7.24-7.43 (m, 4H, $\underline{Ph}$). FT-IR (KBr, ν_{max}, cm^{-1}): 3210 (-OH), 2947, 2860, 1613, 1503, 1256.

Compound 6: ^{1}H NMR (CDC1$_3$, 300 MHz, TMS, ppm): 1.31 (s, 3H, -C$\underline{H}_3$); 1.44-1.85 (m, 8H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.46 (m, 4H, -C$\underline{H}_2$O-); 3.98 (t, 2H, -C$\underline{H}_2$O-); 4.35 (d, 2H, -C$\underline{H}_2$O-, cycle); 4.51 (d, 2H, -C$\underline{H}_2$O-, cycle); 5.66 (s, 1H, -O$\underline{H}$); 6.81-6.93 (m, 4H, $\underline{Ph}$); 7.25-7.41 (m, 4H, $\underline{Ph}$). FT-IR (KBr, ν_{max}, cm^{-1}): 3183(-OH), 2948, 2862, 1613, 1501, 1255.

3-{[4-(4'-cinnamyloxybiphenyloxy)butyloxy]methyl}-3-methyloxetane (M1); 3-{[4-(4'-cinnamyloxybiphenyloxy)-pentyloxy]methyl}-3-methyloxetane (M2); 3-{[4-(4'-cinnamyloxybiphenyloxy)hexyloxy]methyl}-3-methyloxetane (M3): The synthesis of monomers **M1-M3** were described below with an example of 3-{[4-(4'-cinnamyloxybiphenyloxy)-butyloxy]methyl}-3-methyloxetane (**M1**).

A solution of the compound **4** (1 g, 2.92 mmol) and triethylamine (0.79 g, 6 mmol) in 30 mL of tetrahydrofuran (THF) was cooled to 0 °C with stirring. A solution of cinnamoyl chloride (1 g, 6 mmol) in THF (5 mL) was added dropwise to the mixture solution mentioned above within 2 h at 0 °C. The resulting solution was kept stirring for 10 h and poured into 200 mL of water. The precipitate was filtered out and then recrystallized twice from ethanol to yield 0.70 g of a white product.

Compound M1: ^{1}H NMR (CDC1$_3$, 300 MHz, TMS, ppm): 1.32 (s, 3H,-C$\underline{H}_3$); 1.56-1.93 (m, 4H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.56 (m, 4H, -C$\underline{H}_2$O-); 4.04 (t, 2H, -C$\underline{H}_2$O-); 4.36 (d, 2H, -C$\underline{H}_2$O-, cycle); 4.52 (d, 2H, -C$\underline{H}_2$O-, cycle); 6.66(d, 1H, -C$\underline{H}$=CH-$\underline{Ph}$); 6.94-6.97 (m, 2H, $\underline{Ph}$); 7.19-7.25 (m, 2H, $\underline{Ph}$); 7.44-7.92 (m, 9H, $\underline{Ph}$); 7.88 (d, 1H, -CH=C$\underline{H}$-Ph). FT-IR (KBr, ν_{max}, cm^{-1}): 2934, 2859, 1730, 1635, 1606, 1494, 1246, 761, 691.

Compound M2: ^{1}H NMR (CDC1$_3$, 300 MHz, TMS, ppm): 1.30 (s, 3H, -C$\underline{H}_3$); 1.56-1.85 (m, 6H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.48 (m, 4H, -OC$\underline{H}_2$-); 3.99 (t, 2H, -C$\underline{H}_2$O-); 4.35 (d, 2H, -C$\underline{H}_2$O-, cycle); 4.51 (d, 2H, -C$\underline{H}_2$O-, cycle); 6.65 (d, 1H, -C$\underline{H}$=CH-$\underline{Ph}$); 6.95-6.98 (m, 2H, $\underline{Ph}$); 7.21-7.43 (m, 2H, $\underline{Ph}$); 7.42-7.62 (m, 9H, $\underline{Ph}$); 7.85(d, 1H, -CH=$\underline{CH}$-Ph). FT-IR (KBr, ν_{max}, cm^{-1}): 2934, 2859, 1730, 1635, 1606, 1494, 1246, 761, 691.

Compound M3: ^{1}H NMR (CDC1$_3$, 300 MHz, TMS, ppm): 1.31(s, 3H, -C$\underline{H}_3$); 1.44-1.85 (m, 8H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.46 (m, 4H, -OC$\underline{H}_2$-); 4.00 (t, 2H, -C$\underline{H}_2$O-); 4.34 (d, 2H, -C$\underline{H}_2$O-, cycle); 4.50 (d, 2H, -C$\underline{H}_2$O-, cycle); 6.63 (d, 1H, -C$\underline{H}$=CH-Ph); 6.93-6.96 (m, 2H, $\underline{Ph}$); 7.20-7.23 (m, 2H, $\underline{Ph}$); 7.42-7.56 (m, 9H, $\underline{Ph}$); 7.87 (d, 1H, -CH=C$\underline{H}$-Ph). FT-IR (KBr, ν_{max}, cm^{-1}): 2933, 2857, 1730, 1635, 1606, 1494, 1246, 761, 691.

Synthesis of polymers: Polymers **P1-P3** in this study were synthesized by cationic ring-opening polymerization with monomers (**M1**, **M2**, **M3**)[15].

Monomers used boron trifluoride ether complex as initiator in dichloromethane under Ar atmosphere. The polymerization carried out at room temperature for 24 h. The resulting polymers were precipitated in methanol and purified further by dissolving in dichloromethane and then precipitating in methanol repeatedly. Yield: 60-85 %. The structure of the synthesized polymers was identified by ^{1}H NMR and FT-IR, respectively.

Polymer P1: ^{1}H NMR (CDC1$_3$, 300 MHz, TMS, ppm): 0.95 (s, 3H, -C$\underline{H}_3$); 1.71-1.85 (m, 4H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.24-3.56 (m, 8H, -OC$\underline{H}_2$-); 3.96 (t, 2H, -C$\underline{H}_2$O-Ph); 6.62 (d, 1H, -C$\underline{H}$=CH-Ph); 6.90 (m, 2H, $\underline{Ph}$); 7.16-7.24 (m, 2H, $\underline{Ph}$); 7.40-7.53 (m, 9H, $\underline{Ph}$); 7.86 (d, 1H, -CH=$\underline{CH}$-Ph). M_n:47700, M_w:131200.

Polymer P2: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS, ppm): 0.94 (s, 3H, -C$\underline{H}_3$); 1.52-1.80 (m, 6H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.23-3.56 (m, 8H, -OC$\underline{H}_2$-); 3.95 (t, 2H, -C$\underline{H}_2$O-Ph); 6.59 (d, 1H, -C$\underline{H}$=CH-Ph); 6.91 (m, 2H, $\underline{Ph}$); 7.18-7.24 (m, 2H, $\underline{Ph}$); 7.40-7.56 (m, 9H, $\underline{Ph}$); 7.86 (d, 1H, -CH=C$\underline{H}$-Ph). M_n:23500, M_w:56800.

Polymer P3: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS, ppm): 0.95 (s, 3H, -C$\underline{H}_3$); 1.45-1.80 (m, 8H, -C$\underline{H}_2$C$\underline{H}_2$-); 3.24-3.56 (m, 8H, -OC$\underline{H}_2$-); 3.96 (t, 2H, -C$\underline{H}_2$O-Ph); 6.63(d, 1H, -C$\underline{H}$=CH-Ph); 6.94 (m, 2H, $\underline{Ph}$); 7.16-7.24 (m, 2H, $\underline{Ph}$); 7.40-7.56 (m, 9H, $\underline{Ph}$); 7.88 (d, 1H, -CH=C$\underline{H}$-Ph). M_n:14200, M_w:41800.

RESULTS AND DISCUSSION

The molecular structure and the general synthetic procedures of these compounds are shown in **Scheme-I** and all the final products are examined by the NMR spectrometer and FT-IR in order to verify the correction of the molecular structure.

FT-IR spectra of these monomers (**M1-M3**) showed a strong absorption at 1730 cm^{-1} that was attributed to the stretching of C=O group in the ester. The 1635 cm^{-1} was associated with the stretching of double bond (-C=C-) in cinnamoyl group. In this regard, the vibration out of plane of H-C in cinnamoyl group appeared at 761 cm^{-1}. ^{1}H NMR spectra of Fig. 1(a) revealed a doublet resonance peak at 6.63 and 7.87 ppm that was assigned to the proton of double bond of cinnamoyl group. These evidence the successful synthesis of the resulting monomers.

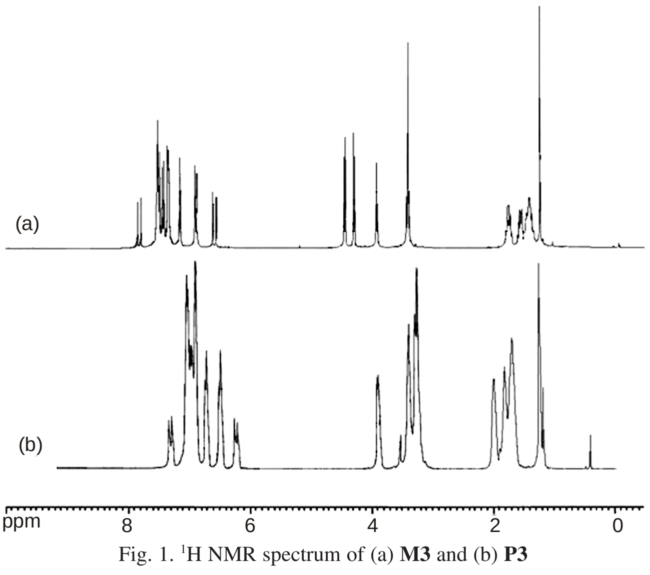


Fig. 1. ^{1}H NMR spectrum of (a) **M3** and (b) **P3**

According to the results obtained from FT-IR spectra of the polymer, **P1-P3** (n = 4, 5, 6) exhibit that the characteristic absorption of carbon-carbon double bond of cinnamoyl group still appears at 1635 cm^{-1} and the characteristic absorption of the vibration out of plane of hydrogen-carbon (H-C) of cinnamoyl group presents at 762 cm^{-1} after cationic ring-opening polymerization of oxetane monomer. ^{1}H NMR spectrum of **P3** shown in Fig. 1(b) revealed that the proton resonance peaks of methylene in oxetane cycle disappeared after cationic ring-opening polymerization. This indicates that the polymer was synthesized successfully and none of the monomer remained in the polymer. The doublet resonance peaks related to the proton of carbon-carbon double bond in cinnamate group were still present at 6.63 and 7.88 ppm or so. This reveals that the cinnamate photo reactive group still existed after the polymerization, that is, cross-linked reaction doesn't occur to this series of the synthesized polymers during polymerization. Additionally, all the synthesized polymers were easily dissolved in many common polar organic solvents such as chloroform, N-methyl pyrrolidone, tetrahydrofuran and dichloromethane. Therefore, we readily obtained uniform thin films of the polymers for further study.

The thermal and mesomorphic properties of compounds **M1-M3** and **P1-P3** were measured by DSC, polarized optical microscopy and X-ray. All the synthesized monomers in this study showed liquid crystalline behaviour. The thermal transition temperature and thermodynamic parameter of the monomers were summarized in Table-1. Due to the bulky oxetane group, the monomer with longer spacer length showed a higher ordered texture. Monomer **M1** containing a shorter spacer length (four methylene units) showed an enantiotropic mesophase nematic phase and crystal phase; monomer **M2** exhibited an enantiotropic nematic phase, monotropic mesophase smectic A phase and crystal phase. Following the transition and texture of **M3**, two endothermal transitions presented at 67 and 117.6 °C during the heating process, respectively. As to the cooling process, two exothermal transitions appeared at 112.1 and 56.6 °C with respect to the endothermal transition temperature on the cooling scan. The results obtained from the observation based on polarized optical microscopy and X-ray diffraction measurement showed that two transitions were corresponding to a transition of smectic B-nematic phase and nematic-isotropic state, respectively. Surprisingly, no crystal phase for **M3** was detected by polarized optical microscopy and X-ray diffraction measurement. Fig. 2 presented the polarized optical microphotograph of **M3**. Fig. 2(a) showed schlieren texture of N while Fig. 2(b) displayed the mosaic texture of S_B.

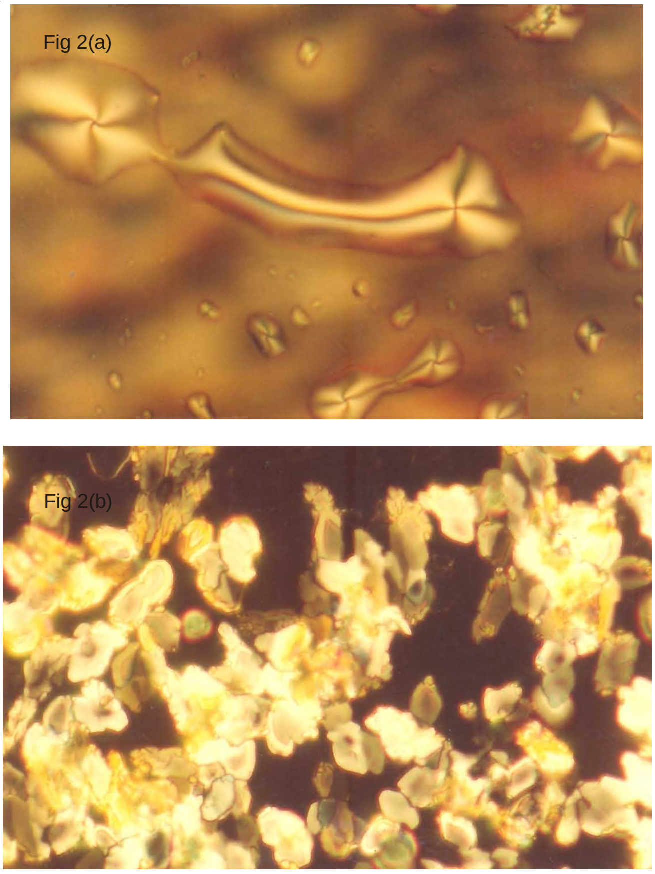


Fig. 2. Polarized optical microscope photograph of **M3** at (a) 89.9 °C; (b) 50.1 °C on cooling from isotropic state (×320)

The thermal transition temperature and thermodynamic parameter of the polymers were summarized in Table-2. According to Table-2, we could find all the synthesized polymers showed enantiotropic liquid crystalline behaviour and have a stable mesophase with a broader temperature range comparing to their corresponding monomers. Polymer **P1** with a shorter spacer length (n = 4) displayed only an enantiotropic nematic phase. With the increase of spacer length, the polymer owning a longer spacer length (n = 5, 6) showed multiphase transition temperature and formed polymorphic mesophase (Table-2). Polymer **P2** showed enantiotropic nematic and smectic A phase; however, polymer **P3** exhibited enantiotropic nematic phase, smectic A phase and smectic C phase. Fig. 3 illustrates

TABLE-1
PHASE TRANSITION TEMPERATURE AND THERMODYNAMIC PARAMETERS OF MONOMER **M1-M3**

Compound	n	Phase transitions, °C (corresponding enthalpy changes, mJ/mg) $\frac{\text{heating}}{\text{cooling}}$
M1	4	$\frac{\text{K } 134.0(79.2)\text{N}140.2(-)^{a}\text{ I}}{\text{I } 115.0(-1.3)\text{ N}57.8(-50.7)\text{K}}$
M2	5	$\frac{\text{K}_1\ 62.4(-17.9)\text{K}_2 103.2(55.5)\text{ N } 118.7(0.9)(-)\text{ I}}{\text{I } 106.3(-1.0)\text{ N}66.9(-9.4)\text{S}_A\ 50.8(-13.4)\text{ K}}$
M3	6	$\frac{\text{S}_B 67.0(8.1)\text{ N } 117.6(1.4)\text{ I}}{\text{I } 112.1(-1.7)\text{ N } 56.6(-7.4)\text{ S}_B}$

K = Crystal, N = Nematic, S_A = Smectic A, S_B = Smectic B, I = Isotropic; a = Overlapped transition

TABLE-2
PHASE TRANSITION TEMPERATURE AND THERMODYNAMIC PARAMETERS OF POLYMER **P1-P3**

Compound	n	Phase transitions,°C (corresponding enthalpy changes, mJ/mg) $\frac{\text{heating}}{\text{cooling}}$
P1	4	$\frac{g\ 132.30(22.0)N190.0(2.0)\ I}{I\ 185.5(-2.1)\ N122.8(-18.2)g}$
P2	5	$\frac{g\ 62.8(-)S_A 111.7(9.4)\ N\ 176.2(1.4)\ I}{I\ 173.0(-1.7)\ N113.4(-9.5)S_A\ 48.2(-)\ g}$
P3	6	$\frac{g36.4(-)S_C 107.0(4.8)S_A 123.1(6.1)\ N\ 180.4(2.8)\ I}{I\ 177.6(-2.2)\ N\ 117.6(-8.4)\ S_A 97.9(-3.7)S_C 35.9(-)g}$

g = Glass, N = Nematic, S_A = Smectic A, S_C = Smectic C, I = Isotropic

the optical polarized micrograph of polymer **P3**. Upon cooling from isotropic state, the thread texture (nematic phase) appeared at the temperature range from 177.6 to 117.6 °C, followed a smectic A phase with a broader temperature range from 117.6 to 97.9 °C and a smectic C phase below 97.9 °C. As the X-ray diffraction measurement of **P3** shown in Fig. 4, a diffuse diffraction appears at 2θ = 18.5° at 170 °C [Fig. 4(a)] upon cooling from isotropic state which indicated the formation of nematic phase. When the sample was cooled to 125 °C [Fig. 4(b)], a small sharp diffraction (d = 29.80Å) that was corresponded to the first order diffraction appeared at 2θ = 2.96°. The diffuse diffraction displayed at 2θ = 19°. As usual, the first diffraction at small angle is related to the layer spacer of smectic liquid crystals. In this case, the result was indicative of the formation of smectic phase for the measurement temperature was close to the nematic-smectic transition. On cooling to 100 °C [Fig. 4(c)], a strong diffraction (d = 28.50 Å) that corresponds to the layer of smectic phase appeared at 2θ = 3.10°. Meanwhile, the diffraction (d = 4.69 Å) at 2θ = 20° became much sharper, which is related to the diffraction of the space distance between the mesogens in side chain. The results obtained from X-ray identify that **P3** formed a nematic, smectic A and smectic C phase.

Moreover, the clearing temperature of the synthesized polymers showed an even-odd effect with the different flexible spacer lengths. The length of the flexible spacer influences not only the thermal transitions, but also the mesomorphic nature of the synthesized polymer in this study. The results demonstrate that the thermal stability temperature range of mesogenic phase (n = 4, ΔT = 62.7 °C; n = 5, ΔT = 124.8 °C; n = 6, ΔT = 141.7 °C) and multmesogenic phase (n = 4, N phase; n = 5, N and S_A phase; n = 6, N, S_A and S_C phase) increase as the spacer length increased.

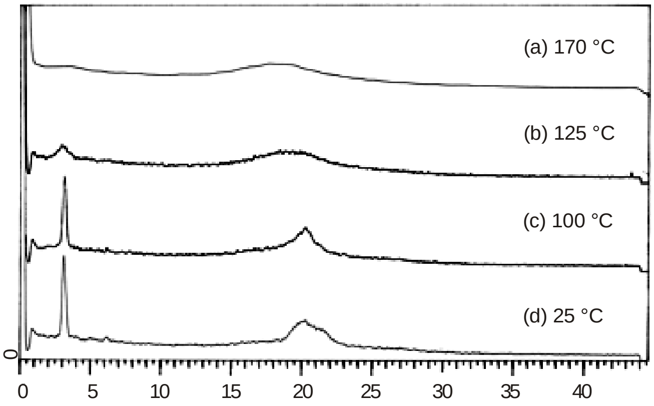


Fig. 4. X-ray diffraction curve of **P3** at (a) 170 (b) 125 (c) 100 and (d) 25 °C on cooling from isotropic state

Conclusion

A new series of photo-cross-linkable side chain liquid crystalline polyoxetanes containing cinnamoyl biphenyl mesogen with various spacer lengths were synthesized by cationic ring-opening polymerization using boron trifluoride ether as initiator. The results obtained in this study showed that all the synthesized monomers and polymers formed mesophase. The monomer, **M1**, formed a monotropic nematic phase due to the shorter spacer length, performing an unstable mesophase. The monomers containing longer spacer length (n = 5, 6) showed an enantiotropic liquid-crystalline behaviour with polymorphic mesophase. This implies that increasing spacer length would be in favor of forming a stable mesophase for this series of monomers. All the resulting polymers (**P1-P3**, n = 4, 5, 6) exhibited the enantiotropic liquid crystalline properties. Contrary to the monomer **M1**, the polymer **P1** showed an enantiotropic nematic phase with a broader temperature range.

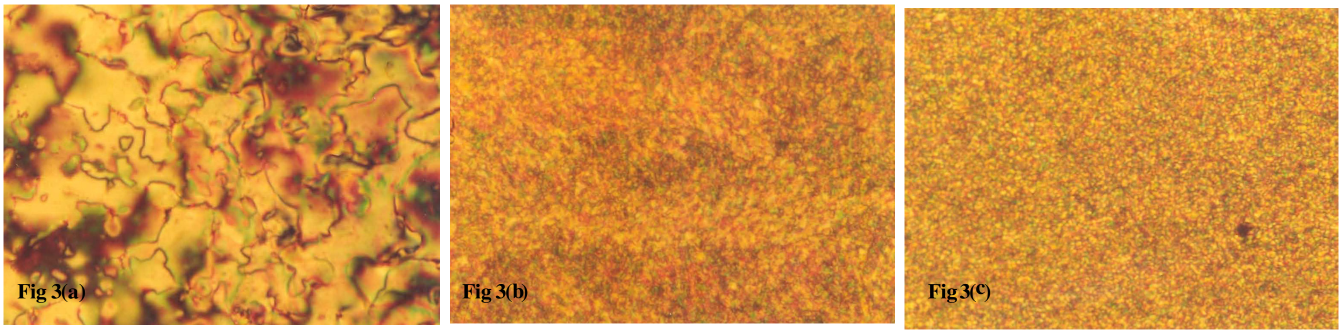


Fig. 3. Polarized optical microscope photograph of the polymer **P3** at (a)175.9 (b)110.6 and (c) 89.90 °C on cooling from isotropic state (×320)

Similar to their corresponding monomers, however, polymers **P2** and **P3** exhibited multiphase transition and polymorphic mesophase with a nematic and smectic characteristics. According to the literature[18], this case demonstrates that the flexible spacer length have a great influence on both the thermal transition temperature and mesomorphic nature of the resulting polymers.

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