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# Photoactive liquid crystalline polyesters based on bisbenzylidene and pyridine moieties

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### ABSTRACT

Photoactive main chain liquid crystalline polyesters containing bis(benzylidene)acetone and aromatic heterocyclic pyridine were synthesized by solution polycondensation. Chemical structure of monomers and polymers were confirmed by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Thermal property was investigated by TGA and DSC. Optical property of polyesters was studied in chloroform solution and in thin film under UV irradiation and exhibited *cis-trans*-photoisomerization. This behavior was witnessed by solubility, carbonyl group absorption band in FT-IR, optical microscopy as well as DSC analysis through existence of liquid crystallinity after irradiation of polymers.

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### 1. Introduction

Liquid–crystalline polymers (LCPs) are of interest ascribable their ability to combine the properties of simple molecular liquid crystals with those of polymers [1,2]. LC moieties can be designed to exhibit a conformational change on the molecular level in response to thermal [3], pH [4], electrical [5,6] or optical [7–10] stimulation. The increasing attention in synthesis, characterization and application of photoactive liquid crystalline polymer systems provide fascinating advantage in molecular, supramolecular design and in photo controlled changes of optical property.

The thermotropic main chain liquid crystalline polymers extend opportunity for development of high performance materials with improved processability, thermal stability and mechanical property over the past decades [11–18]. Furthermore, aromatic polyesters composed of entirely rigid, linear aromatic ester units possess high melting temperature [19–21]. They are not only demonstrating thermotropic liquid crystalline (TLC) mesophases but also good physical properties. Incorporation of methylene spacer plays a significant role in determining the relationship between thermo-mechanical history, structural and morphological organization of polymers [22–25]. Nature of heterocyclic unit has high potential in TLC formation owing to permanent dipole moment arising from polarity of hetero atoms in the molecules. Thus, LCPs has been extensively studied; several review articles described progress on this domain [26-28]. Conjugated organic dye molecules are promising materials for electronic and photonic application suitable for technological innovation [29]. Historically, azo dye containing polymers were studied with interest for their specific photo induced effects [30,31]. When illuminated with a polarized light of appropriate wavelength, azobenzene moiety undergoes a reversible trans-cis-trans isomerization process. The present investigation dealt with a similar photo induced effect noticed with bis(benzylidene)acetone moietv is hitherto unreported in the literature which comprises synthesis of photoactive main chain liquid crystalline polymers containing bis(benzylidene)acetone with aromatic pyridine heterocyclic units. They exhibited photoisomerization behavior under UV irradiation. This phenomenon was demonstrated by various supporting evidences and discussed.

### 2. Experimental

### 2.1. Materials and methods

*p*-Methylacetophenone, benzaldehyde, ammonium acetate, thionyl chloride, and *p*-hydroxybenzaldehyde were used as received. 2-chloroethanol, 4-bromobutanol (Merck) 1-bromohexanol, 1-bromooctanol, 1-bromodecanol and anhydrous potassium carbonate were used as received. Solvents such as acetone, glacial acetic acid, pyridine, ethanol, methanol, benzene, tetrahydrofuran, triethylamine (Spectrochem, India) were purified and dried using reported procedures [32,33].





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#### 2.2. Synthesis of precursors

### 2.2.1. Synthesis of (4-phenyl)-2,6-bis(4-methylphenyl)pyridine (PBMPP)

Mixture of *p*-methylacetophenone (10.51 ml, 0.078 mol), benzaldehyde (4 ml, 0.039 mol), ammonium acetate (30 g; 0.0389 mol) and glacial acetic acid (75 ml, 0.131 mol) were taken and refluxed for 5 h with constant stirring. Then the reaction mixture cooled to ambient, an oily layer thrown out and crystallized slowly. The crystals thus obtained was filtered, washed with acetic acid (50%), cold ethanol and dried at 60 °C under vacuum (yield 63%; m. p. 154–156 °C) [34].

IR(KBr): Absence of peak at 1680 cm<sup>-1</sup> for carbonyl group confirms the formation of product. <sup>1</sup>H NMR (CDCl<sub>3</sub>)–δ: 2.42(s, 6H, C<u>H</u><sub>3</sub>), 7.2–8.2 (m, 13H, aromatic protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>)–δ: 21.32(Ar–<u>C</u>H<sub>3</sub>), 127–129.41(aromatic carbons), 157.41(<u>C</u>=N in heterocyclic ring), 116.57(β-<u>C</u>arbon in pyridine ring), 150.09( $\gamma$ -<u>C</u> in pyridine ring).

### 2.2.2. Synthesis of (4-phenyl)-2,6-bis(4-carboxyphenyl)pyridine (PBCPP)

PBMPP (4.5 g, 0.013 mol) was dissolved in pyridine-water mixture (each 150 ml) and heated to 50 °C. KMnO<sub>4</sub> (5 equivalents; 10.61 g; 0.0671 mol) was added in one portion with vigorous stirring. Then the temperature was elevated to 100 °C and stirred for 2 h. An additional portion of KMnO<sub>4</sub> (10.61 g, 0.067 mol) was added and stirring continued for another 1 h. Excess KMnO<sub>4</sub> was quenched with ethanol; solid filtered and washed with hot water. Colorless filtrate thus collected was concentrated and acidified with HCl. White precipitate thus obtained was collected by filtration, washed with water, and dried in vacuum (yield 75%; m. p. 320 °C) [35].

IR (KBr): 1680 cm<sup>-1</sup>( $\nu_{c=0}$ ), and 3449 cm<sup>-1</sup>(spacer-OH) <sup>1</sup>H NMR- $\delta$ : 7.3–8.0 (m, aromatic-<u>H</u>), 11–12 (for COOH).<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 127–130(aromatic carbons), 156.2 (<u>C</u>=N–).169.4 (COOH).

### 2.2.3. 1,3-Bis(4- hydroxybenzylidene) acetone (BHBA)

*p*-Hydroxybenzaldehyde (12.2 g, 0.1 mol) and acetone (3.7 ml, 0.05 mol) were dissolved in methanol (160 ml), then dry HCl gas purged and stirred at room temperature until content of flask turned to dark pink color. Precipitate thus obtained was filtered and dried in vacuum at 30 °C. It was recrystallized from methanol (yield 90%, m. p. 222–224 °C) [36].

IR (KBr): 1682 cm<sup>-1</sup> ( $v_{c=0}$ ), and 1564 cm<sup>-1</sup> ( $v_{c=c}$  exocyclic) for aromatic OH; <sup>1</sup>H NMR- $\delta$ : 9.2(s, 2H, O<u>H</u>), 7.7 (s, 2H, C<u>H</u>=), 6.8–7.4(m, 6H, aromatic-<u>H</u>), 2.1–2.5(m, 8H, C<u>H</u><sub>2</sub> spacer). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 125–128(aromatic carbons).

### 2.3. Synthesis of monomers

## 2.3.1. Synthesis of (4-phenyl)-2, 6-bis(4-chlorocarbonylphenyl) pyridine(a)

PBCPP (4 g; 0.01 mol) was dissolved in dry benzene (25 ml). Thionyl chloride (2.2 ml; 0.03 mol) was added drop-wise to the mixture with vigorous stirring. At the end of addition, one drop of DMF was added and bath temperature slowly brought up to 70 °C. As the reaction proceeds, dispersed diacid was slowly dissolved in benzene and then refluxed for 4 h. At the end of reaction, benzene and excess of thionyl chloride were removed by vacuum distillation; a yellow colored powder was obtained and used *in situ* for subsequent reaction (yield 81%; m. p. 160–162 °C) [37].

IR (KBr): 2920 cm<sup>-1</sup> ( $\nu$ CH<sub>3</sub>) and 1600 cm<sup>-1</sup> (C=C and C=N). <sup>1</sup>H NMR- $\delta$ : 7.3–8.0 (m, aromatic-<u>H</u>), 2.4(s, 6H, C<u>H<sub>3</sub></u>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 25–28(<u>C</u>H<sub>3</sub>), 127–130(aromatic carbons), 156.2 (<u>C</u>=N–).

## 2.3.2. Synthesis of 1,3-bis[4-(m-hydroxyalkyloxy)benzylidene)] acetone (m = 2, 4, 6, 8 and 10) (i-v)

The monomers (i-v) were prepared by Williamson aryl-alkylether synthesis. A typical procedure followed for the synthesis of 1,3-bis/4-(2-hydroxyethyloxy) benzylidene) acetone (i) is as follows: 1,3-bis(4-hydroxybenzylidene) acetone (3 g; 0.011 mol) was dissolved in dry dimethylformamide (20 ml). Potassium carbonate (7.8 g; 0.056 mol) was then added to it; instantly change in color from yellow to red was observed as an indication for formation of anion. The temperature was kept at 90 °C for 1 h. This was followed by addition of 2-chloroethanol (2.3 ml; 0.033 mol) dropwise to reaction mixture with constant stirring for 24 h at 90 °C. At the end of reaction, the mixture was cooled to room temperature and poured over crushed ice to precipitate product. The product was filtered, washed with excess of distilled water and dried in vacuum. The crude precipitate thus obtained was recrystallized from ethanol-water mixture (50:50: vield 81%; m. p. 149-151 °C) [38].

IR (KBr): 1682 cm<sup>-1</sup> ( $v_{C=O}$ ), 3359 cm<sup>-1</sup> (spacer-OH) and 1564 cm<sup>-1</sup> ( $v_{C=C}$  exocyclic); <sup>1</sup>H NMR- $\delta$ : 9.2(s, 2H, O<u>H</u>), 7.7 (s, 2H, C<u>H</u>=), 6.8–7.4(m, 6H, aromatic-<u>H</u>), 2.1–2.5(m, 8H, C<u>H</u><sub>2</sub> spacer), 3.8(t, 8H, -OC<u>H</u><sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 26–28(Ar–O–CH<sub>2</sub>–C<u>H</u><sub>2</sub>–), 64–67 (Ar–O–C<u>H</u><sub>2</sub>–), 125–128 (aromatic carbons).

The remaining monomers (**ii-v**) were synthesized by an analogous procedure using respective bromoalkanols instead of 2-chloroethanol, with 1,3-bis(4-hydroxbenzylidene)acetone respectively.

## 2.3.3. Synthesis of 1,3-bis[4-(4-hydroxybutyloxy)benzylidene]acetone (**ii**)

Yield 77%; m. p. 145–147 °C IR (KBr): 1680 cm<sup>-1</sup> ( $v_{c}=_{O}$ ), 3346 cm<sup>-1</sup> (spacer-OH) and 1571 cm<sup>-1</sup> ( $v_{c}=_{C}$  exocyclic); <sup>1</sup>H NMR- $\delta$ : 8.8 (s, 2H, O<u>H</u>), 7.4(s, 2H, C<u>H</u>=), 6.9–7.3(m, 6H, aromatic-<u>H</u>), 3.2(s, 4H,  $\beta$ C<u>H</u><sub>2</sub>), 1.8 (s, 2H,  $\gamma$ C<u>H</u><sub>2</sub>), 2.1–2.5(m, 8H, C<u>H</u><sub>2</sub> spacer), 3.8(t, 8H, -OC<u>H</u><sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 25–28(Ar–O–CH<sub>2</sub>–C<u>H</u><sub>2</sub>–), 64–67 (Ar–O–C<u>H</u><sub>2</sub>–), 126–129(aromatic carbons).

### 2.3.4. 1,3-bis[4-(6-hydroxyhexyloxy) benzylidene]acetone (iii)

Yield 79%; m. p. 140–142 °C. IR (KBr): 1684 cm<sup>-1</sup> ( $\nu_{C=0}$ ), 3376 cm<sup>-1</sup> (spacer-OH) and 1569 cm<sup>-1</sup> ( $\nu_{C=C}$  exocyclic); <sup>1</sup>H NMR- $\delta$ : 9.0(s, 2H, O<u>H</u>), 7.5(s, 2H, C<u>H</u>=), 6.9–7.3(m, 6H, aromatic-<u>H</u>), 3.0(s, 4H,  $\beta$ C<u>H</u><sub>2</sub>), 1.6(s, 2H,  $\gamma$ C<u>H</u><sub>2</sub>), 2.2–2.6(m, 16H, C<u>H</u><sub>2</sub> spacer), 3.7(t, 8H,  $-OC\underline{H}_2$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 25–29(Ar–O–CH<sub>2</sub>–C<u>H</u><sub>2</sub>–), 63–68 (Ar–O–C<u>H</u><sub>2</sub>–), 126–130(aromatic carbons). Elem. Anal. Calcd. for C<sub>29</sub>H<sub>38</sub>O<sub>5</sub> (466.2): C, 74.63; H, 8.26. Found: C, 74.42; H, 8.12.

### 2.3.5. 1,3-bis[4-(8-hydroxyoctyloxy) benzylidene]acetone (iv)

Yield 78%; m. p. 135–137 °C. IR (KBr): 1679 cm<sup>-1</sup>( $\nu_{c}=_{0}$ ), 3396 cm<sup>-1</sup>(spacer-OH) and 1590 cm<sup>-1</sup> ( $\nu_{C}=_{C}$  exocyclic). <sup>1</sup>H NMR– $\delta$ : 8.5(s, 2H, O<u>H</u>), 7.8 (s, 2H, C<u>H</u>=), 7.0–7.4(m, 6H, aromatic-<u>H</u>), 2.6(s, 4H,  $\beta_{C}$ (<u>h</u>2), 1.9(s, 2H,  $\gamma_{C}$ (<u>h</u>2), 2.4–2.7(m, 24H, C<u>H</u>2) spacer), 3.9(t, 4H, -OC(<u>H</u>2). <sup>13</sup>C NMR (CDCl<sub>3</sub>) $\delta$ : 26–29(Ar–O–CH<sub>2</sub>–C<u>H</u>2–), 69 (Ar–O–C<u>H</u>2–), 130–137 (aromatic carbons). Elem. Anal. Calcd. for C<sub>33</sub>H<sub>46</sub>O<sub>5</sub> (522.26): C, 75.71; H, 8.68. Found: C, 75.79; H, 8.93.

### 2.3.6. 1,3-bis[4-(10-hydroxydecyloxy)benzylidene]acetone (v)

Yield 82%; m. p. 131–133 °C. IR (KBr): 1683 cm<sup>-1</sup> ( $\nu_{c=0}$ ), 3395 cm<sup>-1</sup> (spacer-OH) and 1592 cm<sup>-1</sup> ( $\nu_{c=c}$  exocyclic) <sup>1</sup>H NMR- $\delta$ : 9.0(s, 2H, O<u>H</u>), 7.4 (s, 2H, C<u>H</u>=), 6.8–7.4(m, 6H, aromatic-<u>H</u>), 3.0(s, 4H,  $\beta$ C<u>H</u><sub>2</sub>), 1.8(s, 2H,  $\gamma$ C<u>H</u><sub>2</sub>), 1.8–2.5(m, 32H, C<u>H</u><sub>2</sub> spacer), 3.6 (t, 8H,  $-OCH_2$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>) $\delta$ : 26–30(Ar– $O-CH_2$ – $CH_2$ –), 68 (Ar– $O-CH_2$ –), 129 (aromatic carbons). Elem. Anal. Calcd. for C<sub>37</sub>H<sub>54</sub>O<sub>5</sub> (578.76): C, 76.71; H, 9.38. Found: C, 76.83; H, 9.48.

#### 2.4. Polymerization

2.4.1 Synthesis of poly{1,3-bis[4-(m-alkyloxy)benzylideneacetone]-(4-phenyl)-2,6-bis(4-phenyl) pyridine dicarboxylate}s (m = 2, 4, 6, 8 and 10) (I-V)

The polymers were prepared by solution polycondensation technique at room temperature using triethylamine (TEA) as an acid acceptor. Typical procedure for synthesis of poly{1,3-bis [4-(2-ethyloxy)benzylideneacetone]-(4-phenyl)-2,6-bis(4-phenyl) pyridine dicarboxylate} (I) is as follows: 1,3-*bis*[4-(2-*hydroxyethyloxy)benzylidene)]acetone* (i) (1 g; 0.0028 mol) was dissolved in THF(20 ml). To this TEA (0.39 ml, 0.0028 mol) was added with constant stirring. Then (4-phenyl)-2,6-bis(4-chlorocarbonylphenyl)pyridine (1.217 g, 0.0028 mol) dissolved in THF (20 ml) was added drop-wise to reaction mixture at ambient temperature and reaction continued for 24 h. Then, it was refluxed, cooled and poured into excess of methanol. A yellow colored precipitate thus formed was purified by re-precipitation using THF-methanol, filtered and dried in vacuum (yield 82%, m. p. 164–166 °C) [39].

### 2.5. Characterization

The intrinsic viscosity of polymers was determined in an Ubbelohde viscometer using chloroform at 30 °C. Infrared spectra were obtained on a Thermomattson satellite model FT-IR spectrometer using KBr pellets. High-resolution <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker spectrometer at 500 MHz in CDCl<sub>3</sub>. Tetramethvlsilane (TMS) was used as an internal standard. TGA thermograms were recorded on a NETZSCH-Gerâtebau Gmbh thermal analysis system. DSC measurements were performed at a heating rate of 10 °C/min up to 500 °C on sample taken in an aluminium pan with a pierced lid, in dry nitrogen atmosphere with an empty pan as reference. Polarized optical microscopy (POM) study was performed on a Euromex polarizing microscope equipped with a Linkem HFS 91 heating stage and a TP-93 temperature programmer. Small quantity of sample was placed between two thin glass cover slips, heated and cooled at the rate of 5 °C min<sup>-1</sup> and mesophases observed. Photographs were taken on a Nikon FM10 camera and exposed on Kodak 200 film. Elemental analyses were performed using Perkin Elmer 2400 elemental analyzer. Photoisomerization behavior was investigated by observing absorptions between 320 and 420 nm on a Shimadzu UV-160A UV-visible recording spectrophotometer in thin film as well as chloroform solution ( $10^{-2}$  M). Typical procedure adopted is as follows: Polymer film was formed on a guartz plate and subjected to UV irradiation emanating from a 125 W medium pressure mercury lamp kept at a distance of 10 cm from sample at various intervals of time followed by UV absorption measured on the spectrophotometer respectively. This procedure was repeated until reduction in absorption was completed.



Scheme 1. Synthesis of monomers and polymers.

### 3. Results and discussion

### 3.1. Synthesis and characterization

Pyridine based diacid chloride monomer was prepared by modified Chichibabin reaction. 1,3-Bis-(4-hydroxybenzylidene)acetone was prepared by reacting acetone and p-hydroxybenzaldehyde in the presence of dry HCl gas. It was subsequently converted to 1,3-bis[4-(m-hydroxyalkyloxy)benzylidene)]acetone (m = 2, 4, 6, 8and 10) by Williamson aryl-alkyl-ether synthesis. Solution polycondensation method was carried out at 60 °C in THF solvent in the presence of triethylamine as an acid acceptor to produce polyesters with good yield (77-84%; Scheme 1). The solubility behavior of polyesters was examined in different solvents and soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF and THF and insoluble in methanol, ethanol, 2-propanol, benzene and toluene attributed to flexible methylene chain and polarity of ester linkage. Intrinsic viscosity of polymers obtained in chloroform solution as a measure of molecular weight, values are in the range of  $0.73-0.99 \text{ dl g}^{-1}$  and increases with increasing length of aliphatic chains. The solution polycondensation provided moderate molecular weight polymers.

The polymers were characterized by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The spectral values are in accordance with assigned structures. The FT-IR spectrum of **IV** is shown in Fig. 1. The stretching vibration at 1599  $\text{cm}^{-1}$  is due to CH=CH and C=O stretching vibration of ester appeared around 1719 cm<sup>-1</sup>. Aryl alkyl ethers give rise to strong bands an asymmetric C-O-C stretching near 1257 cm<sup>-1</sup> and a symmetric stretching near 1043 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of III in CDCl<sub>3</sub> is illustrated in Fig. 2. The benzylidene aromatic protons are resonated around 6.79-7.32 ppm, alkyl group connected with ether linkage resonated at 3.85 ppm and olefinic protons appeared as a singlet around 7.02 ppm. The <sup>13</sup>C NMR spectrum of **IV** in CDCl<sub>3</sub> is shown in Fig. 3, the C=O signal of ester group resonated at 165.94 ppm, together with carbon signals for aromatic rings resonated around 128.76–130.62 ppm. The carbon in aliphatic chains  $(CH_2)_{m-2}$  resonated around 22–25 ppm and OCH<sub>2</sub>- next to ester group appeared at 68.91 ppm. The other polymers displayed similar <sup>13</sup>C NMR spectra.

#### 3.2. Mesomorphic studies

DSC measurements and POM observations were performed to confirm the existence of mesomorphic behavior of monomers and polymers. Table 1 shows variation in transition temperatures with spacer length (m). Fig. 4 displays representative DSC thermograms of monomers and polymers and indicated three endothermic transitions correspond to glass transition temperature  $(T_g)$ , crystalline–liquid crystalline (T<sub>m</sub>), and liquid crystalline–isotropic transitions  $(T_i)$ , respectively. The DSC analysis revealed  $T_m$  and  $T_i$ of polymers I-V were decreased with an increase in flexible methylene chain [40]. The transition temperatures ( $T_m$  and  $\Delta T$ ) of representative monomers and polymers are shown in Fig. 5. T<sub>m</sub> and T<sub>i</sub> of polymers were in the range of 94-154 °C and 123-166 °C, respectively. The identification of mesophases and transition temperatures were conducted by examining textures of polymer melt sandwiched between glass substrate in polarized optical microscope. The POM microphotographs of mesomorphic textures of monomers and polymers are shown in Fig. 6 and data listed in Table 1. The pyridine based monomer and **v** displayed liquid crystalline state at 160 °C, and 127 °C, and become isotropic at 165 °C and133 °C respectively. The optical texture suggests the liquid crystalline phase is nematic [41,42]. Polymer I exhibited a transition at 166 °C on DSC heating scan, ascribed to isotropic transition temperature  $(T_i)$ . The lower methylene chain containing polymer did not show mesophase transitions in DSC and thermal decomposition of polymer occurs after melting instead of isotropic transition temperature attributed to high rigidity of the polymer system owing to the presence of shorter spacers caused broadening of molecular geometry and prevented liquid crystallinity.

Polymer II appears as grainy in the temperature range of 163–156 °C during cooling cycle. The observation from POM for III and IV indicates enantiotropic nature of mesophases, where polymers showed similar feature and assigned nematic phase of Schlieren texture, IV at 121 °C and V also exhibits nematic phase from its isotropic state at 123 °C. Mesophase is stable in a temperature range ( $\Delta T$ ) over 30 °C and finally solidifies at 90C. Consequently  $T_i$  and  $T_m$  were decreased monotonically at the length of



Fig. 1. The FT-IR spectrum of polymer IV, (a) before and (b) after irradiation.



Fig. 2. <sup>1</sup>H NMR spectrum of polymer III.



Fig. 3. <sup>13</sup>C NMR spectrum of polymer IV.

Table 1	
DSC and POM data of polymer I–V.	

Monomer/ polymer	DSC (°C)			POM (°C)				
polymer	$T_{\rm g}$	T <sub>m</sub>	Ti	$\Delta T$	T <sub>m</sub>	Ti	$\Delta T$	Mesophase
a		160	165	5	161	167	6	Nematic
v	-	127	133	6	126	133	7	Nematic
I	-	-	166	-	-	-	-	No mesophase
II	-	154	160	6	156	163	7	Grainy
III	71	143	158	15	144	160	16	Nematic
IV	66	104	129	25	107	131	24	Schlieren
v	-	94	123	29	95	125	30	Nematic Smectic

increased spacers. This is ascribed to decrease in polarity and rigidity of the system as increased with spacer lengths.

Except I, the remaining polymers showed enantiotropic nematic phases. The ester linkages bridging the spacer and rod-like core had an essential effect on stability of mesophases. It is well known that characteristic liquid crystal behavior has an essential relationship with molecular interaction between mesogenic moieties of main chain liquid crystalline polymers.

### 3.3. Thermal property

The thermal behavior of polymers was evaluated by TGA in nitrogen atmosphere at a heating rate of 10 °C/min, their traces shown in Fig. 7, and data presented in Table 2. Thermal stability was evaluated by 5% and 50% weight loss at minimum temperature. The results disclosed that they are stable up to 326 °C and start degrading thereafter in nitrogen. The thermal stability increases with decreasing spacer lengths [I > III > III > IV > V] [43]. It



Fig. 5. Transition temperatures of representative monomers and polymers.

is attributed to the presence of ether linkage in the spacers were expected to introduce significant flexibility and consequently brought down thermal stability. Degradation occurred in two-step manner; first step between 435 and 460 °C corresponds to cleavage of ester linkage and second step between 580 and 640 °C may be the outcome of cleavage of aryl–alkyl–ether linkage present in the polymer chain. Char yield was calculated by measuring the amount of residual substance at 800 °C. The data revealed that char yield increased with decreasing spacer lengths as follows:

Dimethylene > tetramethylene > hexamethylene > octamethylene > decamethylene.



Fig. 4. Representative DSC thermograms of monomers and polymers.



Fig. 6. Representative HOPM photographs of monomers and polymers at  $20 \times$  magnification.



Fig. 7. TGA thermograms of polymers I-V.

### 3.4. Optical property

The optical property was studied in chloroform solution and in thin film; by irradiating under UV light, the structural changes were monitored using UV spectrophotometer. Fig. 8 shows the change of UV–visible spectra of **III** both in chloroform solution and in thin film as a typical example of photochemical behavior upon irradiation at  $\lambda > 300$  nm. As shown in Fig. 8, during irradiation, a continuous decrease in absorption at 367 nm, ascribable to  $\pi - \pi^*$  transition of bisbenzylidene chromophore and increase of absorption band at 285 nm were noted with an isobestic point at 302 nm. The isobestic point indicates photoisomerization process takes place upon irradiation (Fig. 9). The similar trend was de-

Table 2Thermal decomposition data of polymer I–V.

Polymer	TGA	TGA							
	5%	50%	% Char yield at 800 °C						
I	403	534	19.45						
II	380	503	18.14						
III	363	477	14.53						
IV	340	473	12.09						
V	326	469	11.33						



**Fig. 8.** Changes in UV spectral characteristics during photolysis of polymer **III** in both solution and thin film at various time intervals.

tected for remaining polymers. It was observed in the initial 15 s irradiation that an increase in intensity as well as small blue shift at 367 nm for poly[bis(benzylidene)]acetone esters. This increase in intensity reverses on further irradiation and decreases regularly thereafter may be assigned to disorganization caused by randomly oriented bisbenzylidene-acetone chromophore as polymer changes to isotropic state. Such disordered structure could be introduced by *trans*-to-*cis* photoisomerization of bisbenzylidene chromophore on irradiation. This kind of isomerization is reported in similar low molecular weight compounds [44] which disrupt parallel stacking of chromophore in aggregate attributed to nonlinear conformation of *cis*-isomer (Fig. 9). Similar results were observed and reported by Gangadhara and Kishore [45].

To support this photoisomerization phenomenon, polymer samples were subjected to irradiation under UV light for long time and then examined by solubility test, FT-IR, DSC and POM. The photo-irradiated polymers were found to be soluble in organic solvents and confirmed photoisomerization process. The peak at  $1719 \text{ cm}^{-1}$  assigned to C=O carbonyl group conjugated with peak at  $1635 \text{ cm}^{-1}$  assigned to C=C double bond of chalcone moiety was unaltered to higher wave number (Fig. 1b), in FT-IR spectroscopy, indicates the unaffected nature of conjugated system in chalcone.

The liquid crystalline texture unchanged for **III**, when irradiated for more than 4 h and testify photoisomerization process. There is an identical mesophase region between Tm and Ti noticed before and after irradiated samples in DSC analysis. During initial stages of photo-irradiation of nematic LC sample containing *trans*-form, dark spots were unobserved in the POM. It suggests the isotropic domains were unorganized at irradiated sites where sufficient amount of *cis*-form produced upon photoirradiation and nematic-isotropic phase transition did not take place in local domain. This is attributed to *trans*-and-*cis* isomers show a rod-like molecular structure, and *trans*-cis isomerization produces little change in molecular shape [46]. All these evidences clearly confirmed the *cis*-*trans*-photoisomerization phenomenon prevailed in the molecular system as that of azobenzene polymers.



Fig. 9. Photochemical reactions of bis(benzylidene)acetone.

### 4. Conclusion

New class of thermotropic main chain liquid crystalline polyesters containing bisbenzylidene and pyridine units has been synthesized, where the effect of mesogenic chain extender, with various spacer lengths, their properties investigated and reported. The presence of heterocyclic ring and bulky pendant group in polyester backbone are resistant to high temperature and modify the properties of polymers. The intrinsic viscosity data disclosed the polymers are of moderate molecular weights. The bisbenzylidene containing photoreactive functionality undergo photoisomerization under the influence of UV irradiation and further supported by FT-IR, POM and DSC analysis. The performance of irradiation sensitive polymers depends not only on inherent photo reactivity of their functional groups but also on spatial arrangements. The thermal stability displayed good thermal stability characteristics. Liquid crystalline property of monomers and polymers demonstrated development of mesophase depends on length of flexible spacers.

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