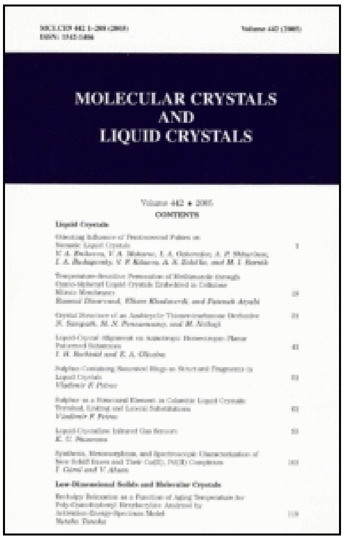

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Synthesis and Characterization of Ethyl Cellulose–Based Liquid Crystals Containing Azobenzene Chromophores

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Two compounds based on the ethyl cellulose having azobenzene side chain mesogenic units were prepared and the structures of the cellulosic liquid crystals were confirmed by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectra. Liquid-crystalline properties were characterized by differential scanning calorimetry and polarizing optical microscopy in which compound ***4a*** *shows a columnar phase and compound* ***4b*** *shows a semectic A phase. The absorption spectra of the azobenzene units display a high-intensity* π–π^* *transition at about 364 and 366 nm for compounds* ***4a*** *and* ***4b****, respectively, and a lower intensity* n–π^* *transition at around 468 nm for both compounds. Hence, photochromism can be achieved by the introduction of the azo linkage to ethyl cellulose containing liquid crystals.*

Keywords Azo chromophores; ethyl cellulose (EC); liquid crystals; photochromism

Introduction

Liquid crystal polymers are of considerable theoretical and practical interest, because they offer a unique combination of desirable properties, such as (1) a self-organizing nature over a certain temperature range with fluidity and long-range order, (2) a cooperative effect, (3) a large optical anisotropy, and (4) an alignment change by an external field at the surface and interface [1]. Several cellulose-based liquid-crystalline materials have been synthesized and characterized [1–7]. Cellulose is the main structural component of green plants, and a most abundant material in the biosphere, and its properties are of interest as a source of biodegradable and renewable materials [8]. However, it has many other uses, such as in paper, film, explosives, plastics, and many other industrial uses. Werbowyi and Gray [9] first reported that hydropropyl cellulose shows liquid-crystalline behavior. Since then,

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the liquid-crystalline properties of cellulose derivatives have been of much interest in the field of liquid-crystalline polymers [5]. The study of composite materials making use of cellulose layers and liquid crystals for electro-optical applications opened new horizons for using cellulose derivatives [10,11]. A large number of cellulose derivatives form lyotropic and thermotropic liquid-crystalline phases under suitable conditions have been reported [12]. A range of cellulose esters such as propionic, *n*-butyric, isobutyric, and phthalic acid esters of hydroxypropyl cellulose were modified structurally and show thermotropic liquid-crystalline behavior [13,14]. Acetoxypropyl cellulose, hydroxyethyl cellulose acetate, and ethyl cellulose with ethoxy content 45 and 42.8 wt% have also been reported to exhibit thermotropic behavior [5,15,16]. Most cellulosic liquid crystals are cholesteric, possessing the exceptionally high optical rotatory power characteristic of the helicoidal supermolecular arrangement [3]. One of the most studied thermotropic cellulose esters is acetoxypropylcellulose, which shows the cholesteric mesophase from below room temperature up to 180°C [17]. Ethyl-cyanoethyl cellulose formed a cholesteric liquid crystal in acrylic acid [18]. Among the many variants of cellulose, phenyl-4′-oxyacetic acid benzoate grafted onto ethyl cellulose (EC) has also been reported and gathered considerable attention because it has been used as a substrate film to act as an alignment layer for liquid crystals [19]. The synthesis and thermotropic behavior of 4-methoxyphenyl-4′-oxyacetic acid benzoate grafted onto ethyl cellulose has also been reported [4].

Recently, there has been much interest in azobenzene containing liquid-crystalline polymers because of their potential use in various optical applications, such as optical information storage, optical switching, reversible optical storage systems, nonlinear optical waveguides, photorefractive switches, and holographic gratings [20–25]. There are few reports describing azobenzene chromophores grafted onto cellulose [5,19,26]. On the other hand, ultraviolet (UV) the absorption spectra of LC compounds depend on the conjugation length, and both the core and the terminal group make a contribution to form the molecular conjugation length [4]. In this work, a new ethyl cellulose derivative containing azobenzene-based mesogenic moieties were synthesized and their mesophase behavior was determined using differential scanning calorimetry and polarizing optical microscopy.

Experimental

Materials

Ethyl 4-aminobenzoate (Fluka), sodium nitrite (BDH), urea (BDH), phenol (Fluka), 1-bromohexane (Aldrich), 1-bromodecane (Aldrich), potassium carbonate (Fluka), potassium iodide (Riedel-de Haen), potassium hydroxide (Merck), ethyl cellulose (EC, degree of substitution 2.25–2.58; ethoxy content 48 wt%; J. T. Baker), 1,3-dicycloxylcarbodiimide (DCC; Merck), and 4-(N,N-dimethylamino) pyridine (DMAP) (Aldrich): were purchased from a local company in Malaysia. Acetone (Lab-Scan, Malaysia) and dichloromethane (Merck, Malaysia) were dried separately over phosphorus pentoxide (Merck) and distilled before use. Other solvents and chemicals were used without further purification.

Ethyl 4-(4-hydroxyphenylazo)benzoate (1). Compound **1** was prepared according to procedure described by Lutfor *et al.* [23]. 4-Amino ethyl benzoate (11.46 g, 0.0698 mol) was dissolved in acetone (200 mL) and concentration hydrochloric acid (22 mL) was added and the mixture was cooled to 2°C. Sodium nitrite (4.913 g, 0.0712 mol) was added drop-wise. Then, phenol (5.52 g, 0.0586 mol) dissolved in an acetone/water mixture (300 mL/100 mL) was added to the diazotated mixture and the reaction mixture was maintained at pH 8–9 by adding sodium hydroxide solution, and stirring was continued for 2 h. The resulting mixture was made slightly acidic ($pH < 5$) with dilute hydrochloric acid and 400 mL of water for precipitation of the product and the precipitate was collected by filtration. The product was recrystallized twice from methanol. Yield: 11.460 g (70.15%) as brown crystals and melting point 160.6°C. FTIR (KBr, υ_{max}, cm^{-1}): 3399 (–OH), 169 3 (–C=O), 1599, 1505 (C=C, Ar), 1403 (–N=N–), 1280, 1135 (C–O), and 840 (=C–H). ^1H NMR (acetone-d_6): δ 8.18 (d, 2H, $J = 8.2$ Hz), 7.92 (d, 2H, $J = 6.9$ Hz), 7.89 (d, 2H, $J = 7.9$ Hz), 7.01 (d, 2H, $J = 8.8$ Hz), 5.54 (s, 1H, OH), 4.41 (q, 2H, $J = 6.8$ Hz, $-CH_2CH_3$), 1.44 (3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.41, 61.40, 116.01, 122.43, 125.50, 130.64, 131.61, 147.16, 155.36, 159.18, 166.39.

*4-(4-Hexyloxyphenylazo)benzoate (**2a**).* A solution of compound **1** (3.087 g, 11.43 mmol) was dissolved in dry acetone (100 mL) and was placed in a round-bottom flask. 1-Bromohexane (2.829 g, 17.0 mmol), potassium carbonate (2.336 g, 17.0 mmol), and a catalytic amount of potassium iodide (20 mg) were added and refluxed for 24 h under argon atmosphere. After 24 h the mixture was poured into ice-cold water and acidified ($pH < 5$) with dilute hydrochloric acid. The precipitate was filtered off and was crystallized from methanol:chloroform (10:2). Yield: 2.88 g (71.14%) as light brown color and melting point 85°C. FTIR (KBr, υ_{max}, cm^{-1}): 2940 (CH_2), 2868 (CH_2), 1713 (–C=O), 1604, 1584 (–C=C, Ar), 1403 (–N=N–), 1271, 1139 (–C–O–), and 866 (=C–H). ^1H NMR (acetone-d_6): δ 8.16 (d, 2H, J = 8.9 Hz), 7.92 (d, 2H, J = 7.5 Hz), 7.88 (d, 2H, J = 9.6 Hz), 7.00 (d, 2H J = 7.5), 4.39 (t, 2H, $-OCH_2$), 4.03 (t, 2H,$-CH_2CH_3$), 1.82 (t, 2H, $-CH_2$), 1.54 (d, 2H, $-CH_2$), 1.42 (d, 2H, $-CH_2$), 1.40 (d, 2H, $-CH_2$), 1.36 (d, 2H, $-CH_2CH_3$), 0.91 (t, 3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.45, 18.23, 62.25, 69.15, 115.13, 120.13, 122.41, 125.22, 129.91, 130.65, 131.67, 135.70, 147.20, 151.43, 155.39, 161.71, 166.23.

*4-(4-Decyloxyphenylazo)benzoate (**2b**).* Compound **2b** was prepared by the same procedure used for synthesis of **2a**. Yield: 2.12 g (71.38%) as light brown color and melting point 106°C. FTIR (KBr, υ_{max}, cm^{-1}): 2920 (CH_2), 2850 (CH_2), 1713 (–C=O), 1604, 1503 (–C=C, Ar), 1407 (–N=N–), 1274, 1258 (–C–O–), and 864 (=C–H). ^1H NMR (acetone-d_6): δ 8.17 (d, 2H, $J = 8.9$ Hz), 7.96 (d, 2H, $J = 8.2$ Hz), 7.88 (d, 2H, $J = 10.3$ Hz), 7.01 (d, 2H $J = 9.62$), 4.40 (t, 2H, $-OCH_2$), 4.04 (t, 2H, $-CH_2CH_3$), 1.83 (t, 2H, $-CH_2$), 1.80 (t, 2H, $-CH_2$), 1.54 (d, 2H, $-CH_2$), 1.52 (d, 2H, $-CH_2$), 1.43 (d, 2H, $-CH_2$), 1.41 (d, 2H, $-CH_2$), 1.37 (d, 2H, $-CH_2$), 0.91 (d, 2H, $-CH_2CH_3$), 0.87 (t, 3H, $-CH_2CH_3$), ^{13}C NMR ($CDCl_3$): δ 14.42, 15.12, 16.78, 18.23, 62.25, 63.28, 69.20, 115.13, 118.20, 120.11, 122.40, 125.20, 126.66, 130.65, 131.70, 132.54, 147.15, 151.22, 155.40, 161.72, 165.95.

*4-(4-Hexyloxyphenylazo)benzoic acid (**3a**).* Compound **3a** (1.013 g, 3.26 mmol) was dissolved in 120 mL of methanol. A solution of potassium hydroxide (0.915 g, 1.63 mmol) in water (10 mL) was added and the solution was refluxed for 4 h. After cooling the mixture was poured into ice water and the precipitate was acidified ($pH < 5$) with dilute hydrochloric acid. The precipitate was filtered off, washed with water, and crystallized from ethanol. Yield: 0.513 g (51.79%) as yellow color and melting point 160.15°C. FTIR (KBr, υ_{max}, cm^{-1}): 2945 (CH_2), 2800 (CH_2), 1682 (C=O acid), 1601 (C=C, vinyl), 1582 (C=C, Ar), 1248, 1139 (C–O), 860, 839 (=C–H). ^1H NMR (acetone-d_6): δ 8.16 (d, 2H, $J = 8.9$ Hz), 7.92 (d, 2H, $J = 7.5$ Hz), 7.88 (d, 2H, $J = 9.6$ Hz), 7.00 (d, 2H $J = 7.5$), 4.39 (t, 2H, $-OCH_2$), 1.82 (t, 2H, $-CH_2$), 1.54 (d, 2H, $-CH_2$), 1.42 (d, 2H, $-CH_2$), 0.91 (t, 3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.45, 18.23, 62.25, 69.15, 115.13, 120.13, 120.25, 125.24, 130.77, 131.66, 132.70, 147.23, 155.38, 161.70, 166.98.

*4-(4-Decyloxyphenylazo)benzoic acid (**3b**).* Compound **3b** was prepared by the same procedure used for synthesis of **3a**. Yield: 1.57 g (62.01%) as yellow color and melting point 112.34°C. FTIR (KBr, υ_{max}, cm^{-1}): 2920 (CH_2), 1685 (C=O acid), 1602 (C=C, vinyl), 1501 (C=C, Ar), 1250, 1145 (C–O), 864, 840 (=C–H). ^1H NMR (acetone-d_6): δ 8.17 (d, 2H, $J = 8.9$ Hz), 7.96 (d, 2H, $J = 8.2$ Hz), 7.88 (d, 2H, $J = 10.3$ Hz), 7.01 (d, 2H $J = 9.62$), 4.40 (t, 2H, $-OCH_2$), 4.04 (t, 2H, $-CH_2$), 1.83 (t, 2H, $-CH_2$), 1.80 (t, 2H, $-CH_2$), 1.54 (d, 2H, $-CH_2$), 1.52 (d, 2H, $-CH_2$), 1.43 (d, 2H, $-CH_2$), 1.41 (d, 2H, $-CH_2$), 1.37 (d, 2H, $-CH_2$), 0.87 (t, 3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.42, 15.12, 16.78, 18.23, 62.25, 63.28, 69.18, 115.22, 118.28, 122.53, 125.32, 130.66, 131.59, 132.72, 147.23, 155.28, 161.66, 165.95, 167.91.

*Ethyl β-D-glucopyranoside [4-(4-hexyloxyphenylazo)benzoate] (**4a**).* Compound **4a** was prepared according to the method described by Wu *et al.* [5]. Yield: 0.65 g. FTIR (KBr, υ_{max}, cm^{-1}): 2921 (CH_2), 2810 (CH_2), 1722 (–C=O, ester), 1641 (C=C, vinyl), 1626, 1599 (–C=C, Ar), 1281, 1255 (C–O), 841 (=C–H). ^1H NMR (acetone-d_6): δ 8.3 (d, 2H, $J = 8.2$ Hz), 7.9 (d, 2H, $J = 7.4$ Hz), 7.9 (d, 2H, $J = 8.9$ Hz), 7.0 (d, 2H, $J = 8.9$ Hz), 6.9–4.05 (m, 6H, $-(OCH_2)_3$), 3.9 (q, 2H, $-CH_2CH_3$), 2.2–1.2 (m, 6H, $-(CH_2)_3$), 1.1–1.0 (m, 9H, $-(CH_3)_3$), and 0.9 (m, 3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.41, 15.82, 23.44, 25.01, 25.69, 26.54, 30.86, 34.02, 49.27, 58.67, 65.01, 67.88, 67.90, 114.56, 115.65, 123.87, 125.00, 128.86, 147.89, 158.67, 165.23.

*Ethyl β-D-glucopyranoside [4-(4-hecyloxyphenylazo)benzoate] (**4b**).* Compound **4b** was prepared by the same procedure used for synthesis of **4a**. Yield: 0.040 g. FTIR: 2921 (CH_2), 1821 (CH_2), 1723 (–C=O, ester), 1644 (C=C, vinyl), 1602, 1501 (–C=C, Ar), 1251, 1139 (C–O), 839 (C–H). ^1H NMR (acetone-d_6): δ δ 8.1 (d, 2H, $J = 8.2$ Hz), 7.92 (d, 2H, $J = 8.9$ Hz), 7.90 (d, 2H, $J = 8.9$ Hz), 7.0 (d, 2H, $J = 8.9$ Hz), 6.90–4.40 (m, 6H, $-(OCH_2)_3$), 3.94 (q, 2H, $-CH_2CH_3$), 2.1–1.2 (m, 6H, $-(CH_2)_3$), 1.1–0.9 (m, 9H, $-(CH_3)_3$), and 0.8 (m, 3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.23, 14.41, 15.82, 23.44, 23.54, 25.01, 25.89, 26.88, 29.88, 32.76, 34.56, 49.65, 49.89, 52.66, 58.76, 67.77, 115.03, 123.89, 125.56, 128.87, 131.06, 138.67, 147.89, 158.67, 165.7.

Characterization

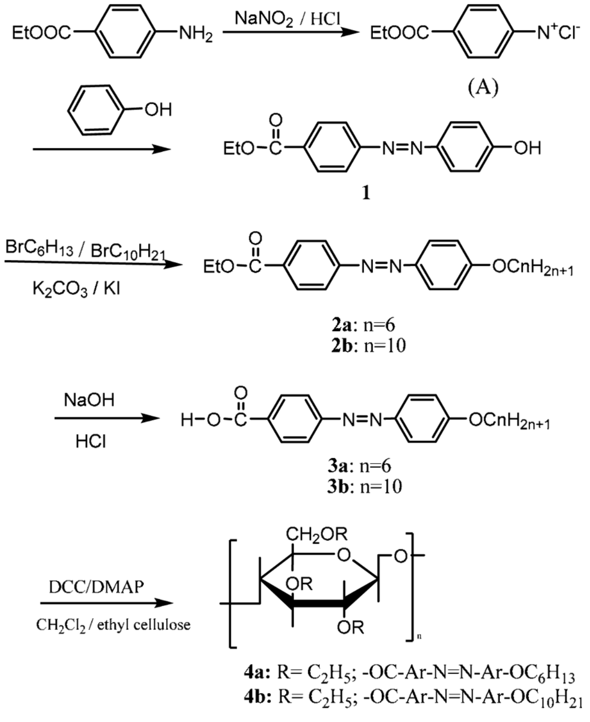
The structures of the intermediates and the final product were confirmed by spectroscopic methods. Fourier transform infrared (FTIR) spectra were measured and recorded with a Perkin Elmer-1000 spectrometer and the peaks were interpreted from 4000 to 600 cm^{-1} in the IR region. ^1H nuclear magnetic resonance (NMR) (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded with a Jeol (ECA

600, JEOL (Malaysia) SDN BHD, 205, Block A, Kelana Business Centre, Petaling Jaya, Selangor, Malaysia) spectrometer using tetramethylsilane $(CH_3)_4Si$ (TMS) as an internal chemical shift standard and chloroform-D ($CDCl_3$) as the solvent. Phase transition temperatures and thermodynamic parameters were determined by using a DSC 6 (Perkin Elmer) under nitrogen atmosphere and the heating and cooling rates were $10°C\,min^{-1}$. Phase transition structures were determined using an Olympus BX 50 Polarizing Optical Microscope (POM, Japan) equipped with a Linkam THMSE-600 (Linkham, Waterfield, Tadworth, Surrey, KT20 5LR, England) hot stage with a liquid nitrogen cooling system and a TMS 92 control unit. The spectra of UV/vis were collected by using Perkin Elmer Lambda 25 at wavelength from 250 to 500 nm.

Results and Discussion

Synthesis

Scheme 1 illustrates the synthetic approach to the ethyl cellulose derivative containing azobenzene-based mesogenic moiety. The azobenzene was prepared by diazotization of 4-aminobenzoate and coupling of the resulting salt with phenol yielding ethyl 4-(4-hydroxyphenylazo) benzoate (**1**). Compound **1** was alkylated with 1-bromohexane or 1-bromodecane in the presence of potassium carbonate to give ester compound **2a** or **2b**. Then the ester compounds of **2a** and **2b** were hydrolyzed under basic conditions to yield the acids **3a** and **3b**, respectively. In the final step, the



Scheme 1. Synthetic route of ethyl cellulose containing azobenzene-based liquid crystals.

acids were esterified with ethyl cellulose by using DCC and DMAP to achieve the target compounds **4a** and **4b**.

Azo compound (**1**) without a flexible chain did not show any liquid-crystalline properties due to its higher rigidity and the insertion of an azo unit into the structure with the phenol moiety increased the polarity of the molecules with the melting point without mesomorphic behavior [27]. The esters of cellulose and its derivatives can be prepared by the acid-catalyzed esterification of cellulose or its derivative with acetic anhydride under relatively mild conditions [16]. The reactivity of this procedure decreased markedly and more drastic conditions were required with increasing the chain length of the carboxylic acid [5]. The esterification can be carried out using acid chloride as the reagent and pyridine or triethylamine as catalyst. Acid chlorides are more sensitive to moisture and thionyl chloride corrodes the equipment when it is removed from the acid chloride under reduced pressure [5]. Esterification can be achieved by activating the carboxylic acids using DCC and DMAP as catalyst [28]. It is more convenient to prepare the ethyl cellulose containing azobenzene mesogenic moiety by reaction with DCC and DMAP. FTIR spectra revel that bands at 2921 and 2826 cm^{-1} are associated with the symmetric and asymmetric vibrations of $-CH_2$ groups on the EC and AZO-EC side chains. The band at 1722 cm^{-1} in the spectrum of AZO-EC indicated the formation of an ester function that was absent in the spectrum of EC. The broad hydroxyl peak at 3485 cm^{-1} in the spectrum of EC was almost absent in AZO-EC. The peaks at 1626 and 1521 cm^{-1} in the AZO-EC spectrum attributed to C=C stretching in aromatic rings. For C−O stretch the spectrum appears at 1251 and 1139 cm^{-1}, and the C−H bending spectrum appears at 839 cm^{-1}.

Mesomorphic Properties

According to the literature ethyl cellulose exhibits thermotropic behavior when its ethoxy content reaches 45wt % [29]. Ethyl cellulose also shows strong birefringence when its ethoxy content is 42.8 wt% in the temperature range 150–180°C [4]. The ethyl cellulose used in this research has been ethoxy content of 48 wt%. Using polarizing optical microscopy, **4a** shows a typical texture for columnar phase and the texture obtained at 100°C (Fig. 1a) and **4b** shows a typical focal conic texture that is captured at 120°C, and it is assigned a smectic A phase (Fig. 1b). There was no further phase structure obtained until crystallization. The formation of

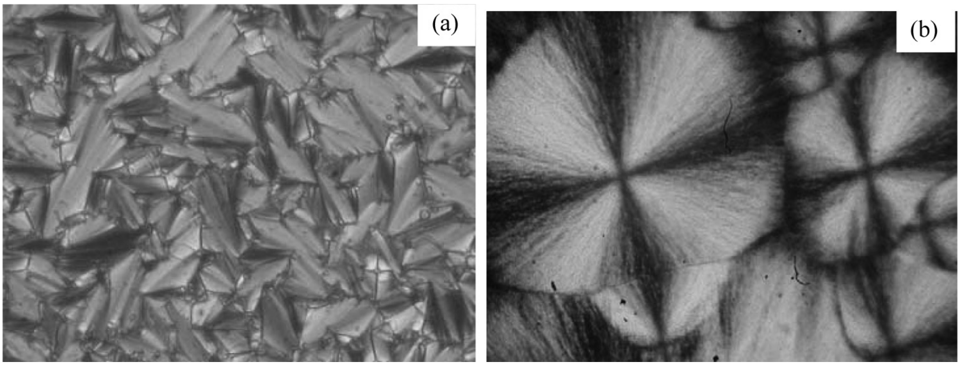


Figure 1. Optical micrographs of compound (a) **4a** at 100°C and (b) **4b** at 120°C.

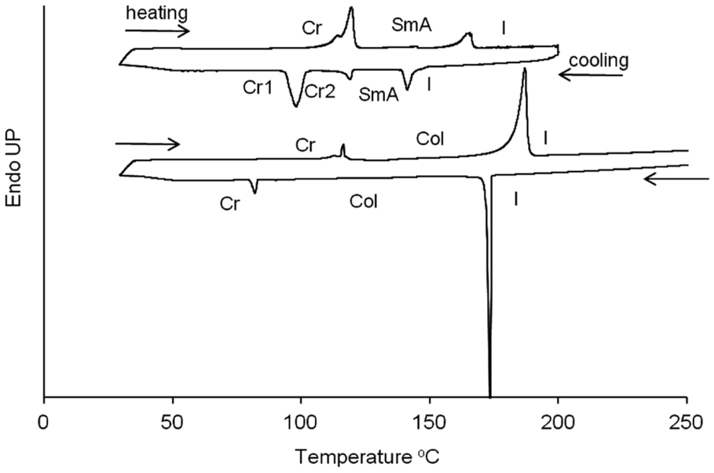


Figure 2. DSC second heating and cooling traces of compounds **4a** and **4b**.

different types of mesophases to the both molecules might be due to the attachment of a long chain on ethyl cellulose.

Compound **4a** shows two endothermic peaks, a small peak at 116.9°C (enthalpy change 4.0 J/g) and a larger peak at 187.1°C (enthalpy 50.1 J/g) in the second heating cycle. On second cooling, two exothermic peaks were also observed at 173.6°C (enthalpy 48.0 J/g) and 89.6°C (enthalpy 4.8 J/g), respectively. The transition temperatures were 116.9°C and 187.1°C, which correspond to Cr-Col and Col–I transitions (Fig. 2a). Compound **4b** shows two endothermic peaks on second heating at 119.53°C (enthalpy 88.1 J/g) and 159.6°C (enthalpy 13.0 J/g), which corresponds to the Cr-SmA and SmA-I transitions. On second cooling, three peaks observed at 141.3°C, 119.1°C, and 98.0°C and the enthalpy changes were 25.3, 8.9, and 84.0 J/g^{-1}, respectively, which corresponds to I-SmA, SmA-Cr_2, and Cr_2-Cr_1 transitions (Fig. 2b). The results of differential scanning calorimetry (DSC) experiments are in good agreement with the observations by POM and the results are presented in Table 1.

Comparison of the transition temperature determined by POM and DSC shows slight discrepancies because the ethyl cellulose containing azo compounds tended to decompose at different rates depending on the rate of heating at an elevated temperature and the nature of the supporting substances [30]. Most of the cellulosic liquid crystals are cholesteric [3,17,18]. Cellulose and its derivatives, being chiral,

Table 1. Phase transition temperatures (°C) and enthalpies (J/g in parentheses) obtained from second heating and cooling DSC scan for compounds **4a** and **4b**

Compound	Scan	Phase transition
4a	Heat	Cr 116.9(4.0) Col 187.1 (50.1) I
	Cool	I 173.6 (48.0) Col 89.6 (4.8) Cr
4b	Heat	Cr 119.5 (88.1) SmA 159.6(13.0) I
	Cool	I 141.3 (25.3) SmA 119.1 (8.9) Cr2 98.0 (84.0) Cr1

Cr = crystal, Col = columnar, SmA = smectic, and I = isotropic phases.

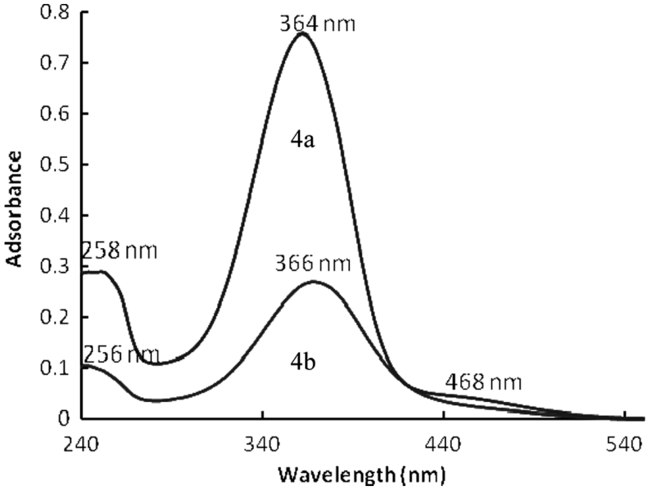


Figure 3. UV/visible absorption spectra of **4a** and **4b** in chloroform at a concentration of 5.0×10^{-5} mol L^{-1}.

tend to have cholesteric supermolecular ordering in solutions [31]. In this research, cellulosic liquid crystals show columnar and smectic A phase, which is confirmed by the DSC and POM result.

Photoisomerization Study

The preliminary studies of the photochemical properties of both compounds **4a** and **4b** were carried out in chloroform solution with concentration of 5.0×10^{-5} mol L^{-1} to obtain the UV/visible absorption spectra. It was found that spectra of **4a** show three absorptions with maximum absorbance at 256, 366 and 480 nm and **4b** also shows three absorptions at 258, 364, and 480 nm, as shown in Fig. 3. This is due to the auxochromes effect for substituted with unshared pair of electrons when attached to π chromophore they generally move the absorption maximum to longer wavelength. The azo containing monomers in the *trans* form show a strong band in the UV region (~365 nm), which is attributed to the $\pi-\pi^*$ transition, and a weak band in the visible region (~450 nm) due to the n–π^* transition. The *trans* form is more stable then the *cis* form, and each isomer can be converted into either *trans* or *cis* form by light irradiation of the appropriate wavelength. Polarized light can induce the reorientation of azobenzene groups through photochemical *trans-cis-trans* isomerization [23].

Cellulose has no chromophore in the visible or near UV region of the spectra [9]. Mainly cellulose exhibits a good stability toward UV light [32]. The azobenzene units are introduced to the cellulose for the possibility of photoisomerization and photochromic behavior [33,34]. Azo-EC exhibited a higher reflection property than EC [35].

Conclusion

A new ethyl cellulose derivative containing azobenzene-based mesogenic moieties was synthesized from 4-(4-hexyloxyphenylazo)benzoic acid and 4-(4-decyloxyphenylazo)benzoic acid using esterification by DCC and DMAP. The thermotropic behavior of the cellulosic azo liquid crystals polymer was determined by POM and DSC. It is clear that EC reacts with 4-(4-hexyloxyphenylazo)benzoic acid, which exhibits a columnar phase, and EC reacts with 4-(4-decyloxyphenylazo)benzoic acid, which shows SmA phase. UV results show that the presence of an azo linkage in these liquid-crystal monomers is suitable for photochromism studies. The photochemical *cis-trans* isomerization study of liquid and solid samples is now in progress and will be reported in due course.

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