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Liquid crystal dimers having vary oxyethylene flexible spacers

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ABSTRACT

In this article, we are prepared that the liquid crystal dimers have aromatic-ester type mesogenic units or aromatic-Schiff base type mesogonic units and confirmed by ^{1}H-NMR spectrometry. The mesomorphic and optical properties of the resultant dimers were studied by differential scanning calorimetry and polarizing optical microscopy.

KEYWORDS
Aromatic-Schiff base type mesogonic unitsl; liquid crystal dimers; aromatic-ester typemesogenic units

1. Introduction

The overwhelming majority of dimers reported in the literature consists of molecules comprising two rod-like mesogenic units linked via a flexible alkyl or alkoxy chain normally containing between 1 and 12 methylene groups [1–14]. Liquid crystalline properties of an organic compound are basically dependent on its molecular structure in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. These types of compounds are important not only as a new class of liquid crystalline compositions, but also as models for the corresponding main chain liquid crystalline polymers containing flexible spacers [1–19]. Recently, we studied the preparation and liquid crystalline properties of various liquid crystal dimers [3–14, 16–19]. These liquid crystal dimers have aromatic-ester-type mesogenic units or aromatic-Schiff base type mesogonic units bracketing a central polymethylene spacer. The liquid crystal-line properties of the dimers were strongly dependent on the nature of the length of the spacer and the terminal substituents. In the present study, in order to obtain further understanding of the structure–property relationship of liquid crystalline dimers having aromatic-ester type and aromatic-schiff base-type mesogenic units, we have prepared homologous HBPE-*n* series liquid crystal dimers shown in Scheme 1.

2. Experimental

2.1. Materials

Ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1-fluoro-4-nitrobenzene, 1-bromohexane, 4-hydroxybenzoic acid, hydrazine monohydrate, palladium on activated carbon (Pd/C, 10%), 4-hydroxybenzaldehyde, 1,3- dicyclohexylcarbodiimide

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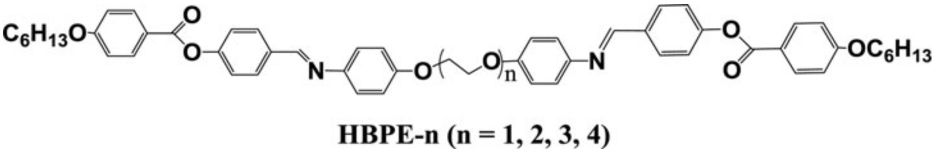
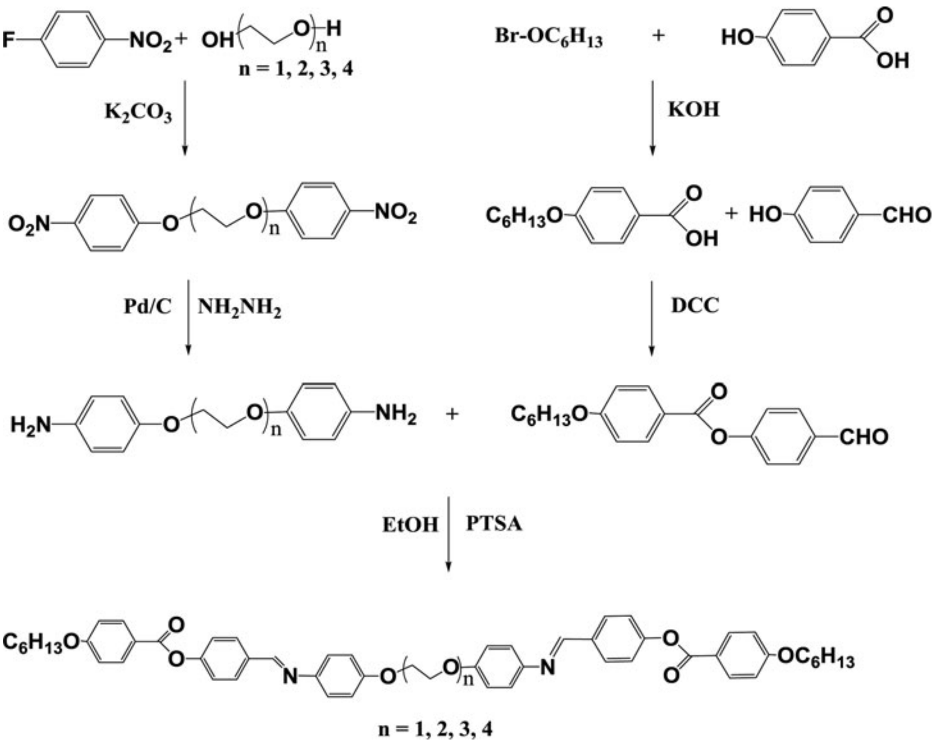


Scheme 1. The molecular structure of the HBPE-*n* series.

(DCC), tetrahydrofuran (THF), *p*-toluenesulfonic acid (PTSA), anhydrous EtOH were purchased from Aldrich Chemical Co. and used as received without further purification.

Preparation of HBPE-n (n = 1,2,3,4) series

1,2-Bis(4-(4-(4-hexyloxybenzoyloxy)benzylideneamino)phenoxy)ethane (HBPE-1), Bis(2-(4-(4-(4-hexyloxybenzoyloxy)benzylideneamino)phenoxy)ethyl)ether (HBPE-2), 1,2-Bis(2-(4-(4-(4-hexyloxybenzoyloxy)benzylideneamino)phenoxy)ethoxy)ethane (HBPE-3) and Bis (2-(2-(4-(4-(4-hexyloxybenzoyloxy)benzylideneamino)phenoxy)ethoxy)ethyl)ether (HBPE-4), a series of dimers were prepared and the preparation process for the designed molecules of HBPE-*n* series dimers involved in several steps and described in Scheme 2.



Scheme 2. Preparation method of HBPE-*n* series of dimers.

Preparation of HBPE-1

The reatcion of 4-(4-hexyloxybenzoyloxy) benzaldehyde (22 mmol) in anhydrous EtOH (50 mL) with [1,2-bis(4-aminophenoxy)ethane (11 mmol) in the presence of PTSA [3, 21, 22]. The reaction mixture was stirred for 16 hr at the room temperature. The crude precipitate was collected by filtration and purified by the recrystallization of both chloroform and ethyl acetate solvents. The prepared HBPE-1 was confirmed by ^{1}H-NMR.

^{1}H-NMR ($CDCl_3$, ppm): δ 0.94-0.85 (t, 6H, $-CH_3$), 1.50-1.24 (m, 12H, $-(CH_2)_3-$), 1.84-1.79 (m, 4H, $-\underline{CH_2}CH_2O-$), 4.07-4.02 (t, 4H, $-CH_2\underline{CH_2}O-$), 4.37 (s, 4H, $-OCH_2-$), 7.02-6.96 (t, 8H, Ar-H), 7.33-7.24 (d, 8H, Ar-H), 7.97-7.94 (d, 4H, Ar-H), 8.16-8.13 (d, 4H, Ar-H), 8.49 (s, 2H, $-CH = N$).

Preparation of HBPE-2

The HBPE-2 was prepared by the similar method described in the HBPE-1 and confirmed by ^{1}H-NMR. ^{1}H-NMR($CDCl_3$, ppm): δ 0.94-0.90 (t, 6H, $-CH_3$), 1.57-1.25 (m, 12H, $-(CH_2)_3-$), 1.90-1.77 (m, 4H, $-\underline{CH_2}CH_2O-$), 3.98-3.95 (t, 4H, $-CH_2\underline{CH_2}O-$), 4.06-4.01 (t, 4H, $-OCH_2-$), 4.21-4.18 (t, 4H, $-OCH_2-$), 6.99-6.94 (t, 8H, Ar-H), 7.32-7.29 (d, 8H, Ar-H), 7.96-7.93 (d, 4H, Ar-H), 8.15-8.12 (d, 4H, Ar-H), 8.47 (s, 2H, $-CH = N$).

Preparation of HBPE-3

The HBPE-3 was prepared by similar method described in the HBPE-1 and confirmed by ^{1}H-NMR. ^{1}H-NMR($CDCl_3$, ppm): δ 0.94-0.91 (t, 6H, $-CH_3$), 1.57-1.24 (m, 12H, $-(CH_2)_3-$), 1.88-1.78 (m, 4H, $-\underline{CH_2}CH_2O-$), 3.75 (s, 4H, $-CH_2\underline{CH_2}O-$), 3.88-3.86 (t, 4H, $-OCH_2-$), 4.06-4.01 (t, 4H, $-OCH_2-$), 4.17-4.14 (t, 4H, $-OCH_2-$), 6.98-6.93 (t, 8H, Ar-H), 7.31-7.20 (d, 8H, Ar-H), 7.95-7.92 (d, 4H, Ar-H), 8.16-8.12 (d, 4H, Ar-H), 8.46 (s, 2H, $-CH = N-$).

Preparation of HBPE-4

The HBPE-4 was prepared by similar method described in the HBPE-1 and confirmed by ^{1}H-NMR. ^{1}H-NMR ($CDCl_3$, ppm): δ 0.93-0.89 (t, 6H, $-CH_3$), 1.58-1.26 (m, 12H, $-(CH_2)_3-$), 1.84-1.77 (m, 4H, $-\underline{CH_2}CH_2O-$), 3.74-3.71 (m, 8H, $-CH_2\underline{CH_2}O-$), 3.89-3.85 (t, 4H, $-OCH_2-$), 4.59-4.00 (t, 4H, $-OCH_2-$), 4.16-4.12 (t, 4H, $-OCH_2-$), 6.97-6.92 (t, 8H, Ar-H), 7.29-7.19 (d, 8H, Ar-H), 7.95-7.90 (d, 4H, Ar-H), 8.14-8.11 (d, 4H, Ar-H), 8.45 (s, 2H, $-CH = N$).

Characterization

^{1}H-NMR spectra of the prepared intermediates and final dimers were recorded with a Varian 300 MHz NMR spectrometer. Thermal history of the dimers was obtained under a N_2 atmosphere on a Dupont 2100 thermal analyzer having a 910S-DSC module (differential scanning calorimetry) with a heating/cooling rate of 10°C/min and indium was used as a reference for

Table 1. Thermal transition behaviors and thermodynamic data for the phase transition of HBPE-*n* series.

	Thermal transition, °C [ΔH, J/g]		Heating Cooling
n	Cr	N	I
1	186.6 [26.6]	351.4 [4.5]	354.0 [1.30]
	—	—	–[b]
2	167.2 [91.1]	286.6 [2.80]	291.4 [1.40]
	136.8 [56.7]	275.4 [1.90]	281.4 [1.30]
3	143.5 [95.6]	269.4 [1.50]	274.0 [2.93]
	107.6 [50.1]	263.1 [1.21]	266.3 [2.20]
4	114.7 [67.2]	251.6 [2.50]	254.2 [1.20]
	73.3 [29.0]	239.4 [2.20]	241.5 [1.10]

[a] Cr = crystalline, I = isotropic states, N = nematic phases, all data were obtained from first heating and cooling scans at 10°C/min.

[b] Reliable peaks were not obtained on cooling scans because the material was decomposed at isotropic state.

[c] Values from Ref. [3].

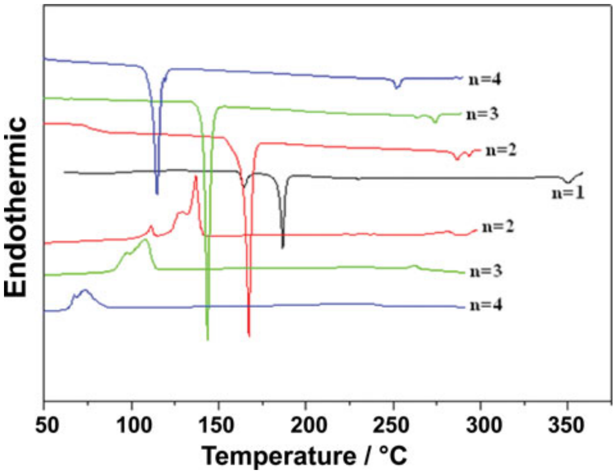


Figure 1. DSC thermograms of HBPE-*n* series ($n = 1, 2, 3, 4$) of dimers.

temperature calibration and estimation of thermodynamic parameter for the phase transitions. The optical textures of the melts were carried out using a Nikon Labophot-2 polarizing microscope.

3. Results and discussion

All the prepared HBPE-*n* ($n = 1$–4) series dimers found to be exhibit liquid crystalline properties. The thermal transition behaviors and thermodynamic data of HBPE-*n* series dimers are summarized in Table 1. Figure 1 represents the DSC thermograms of HBPE-*n* series obtained for both heating and cooling curves. All of the prepared HBPE-*n* series dimers are enantiotropic. Optical properties of prepared materials were studied using optical microscope at hot stage. Optical micrographs of HBPE-4 obtained during the cooling cycle at different temperatures are shown in Fig. 3. The dimers HBPE-4 show an enantiotropic nematic state (Fig. 3(a)) brush Schlieren texture) and smectic C state (Fig. 3(b)) [24, 25].

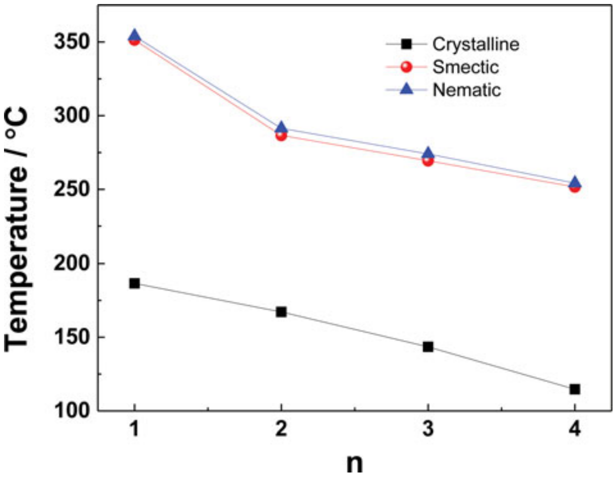


Figure 2. Dependence of transition temperatures of HBPE-*n* on the length (*n*) of central flexible spacer on heating run.

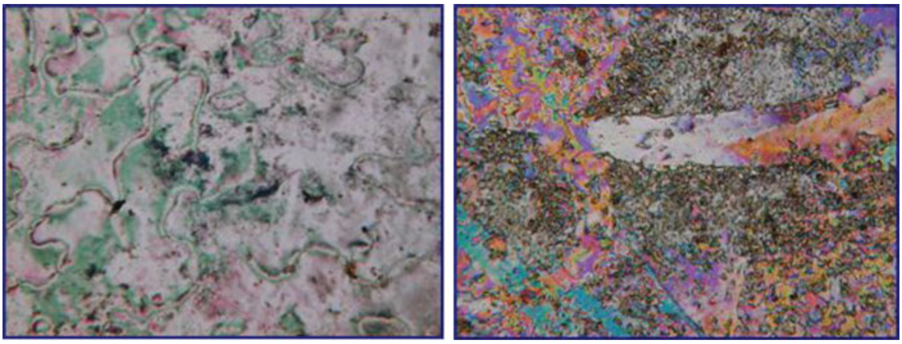


Figure 3. Optical photomicrographs of HBPE-4 on cooling (10°C/min, ×100): (a) nematic (240°C) and (b) smectic C (95°C).

DSC of HBPE-*n* series of materials are analyzed and illustrated in Fig. 1. DSC thermograms show a three-step transition of crystalline → smectic C → nematic → isotropic state, but reliable peaks are not obtained in case of HBPE-1 material on cooling scan because the dimmer was decomposed at isotropic state. In the first heating scan of HBPE-2, it represents a crystalline to smectic C state at 167.2°C, a smectic C to a nematic state at 286.6°C and a nematic to isotropic liquid state at 291.4°C. In the first cooling scan of HBPE-2, it represents an isotropic liquid state to a nematic state at 281.4°C, a nematic to a smectic C state at 275.4°C, and a smectic C to a crystalline state at 136.8°C.

Figure 2 presents the dependence of the phase transition temperature on the central flexible spacer chain length (*n*). This figure clearly shows the decrease in phase window of crystalline, smectic C, and nematic with increasing the central flexible spacer chain length ($n = 1$–4). The thermal behaviors of HBPE-1, 3, and 4 series of dimers and its liquid crystal properties are similar to that seen in HBPE-2.

From Table 1, the crystalline to smectic C state change at 186.6°C (HBPE-1) decreased to 114.7°C (HBPE-4), the smectic C state to nematic state change at 351.4°C (HBPE-1) decreased to 251.6°C (HBPE-4) and the nematic state to the isotropic liquid state change at 354.0°C (HBPE-1) decreased to 254.2°C (HBPE-4) with increase in central flexible spacer chain length indicating the reduction in crystallinity and an increase in flexibility of the dimers. Similar phenomena were previously reported by us for dimesogenic compounds having azo type [23] and schiff base type mesogenic groups [6, 7] attached terminal alkoxy chain. With increase in central flexible spacer chain length, the decrease of the transition temperature of the crystalline, smectic C, and nematic phase observed in this series are in accordance with those observed in our early reports [6, 7, 23]. However, the odd–even effect observed for similar compounds and not observed in HBPE-*n* series of dimers [15–19].

4. Conclusions

We have prepared a new series of aromatic-ester type mesogenic units or aromatic-Schiff base type mesogonic units. The chemical structures of the final products were investigated by ^{1}H NMR spectroscopy. The mesomorphic and optical properties of the prepared dimers were characterized by DSC and OM. The presence of smectic A phase transition was confirmed by the observation in optical microscopy, when the prepared materials were heated from the crystalline phase.

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