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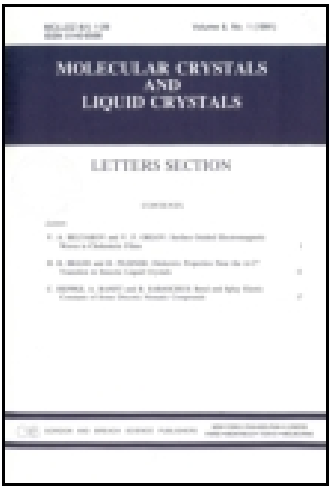

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Thermotropic Liquid Crystalline Dimers with Varying Alkoxy Terminal Chain Length

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Published online: 17 Nov 2014.

To cite this article: Joo-Hoon Park, Ok-Byung Choi, Hwan Myung Lee, Jin-Young Lee, Sung-Jo Kim, Eun-Hee Cha, Seon-Nam Park, Bong-Keun So, Ran-Hee Kim, Tae-Wha Sohn, Chang Sin Lee, Soo-Min Lee & Kuk-Ro Yoon (2014) Thermotropic Liquid Crystalline Dimers with Varying Alkoxy Terminal Chain Length, Molecular Crystals and Liquid Crystals, 599:1, 96-104, DOI: 10.1080/15421406.2014.935970

To link to this article: http://dx.doi.org/10.1080/15421406.2014.935970

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Mol. Cryst. Liq. Cryst., Vol. 599: pp. 96–104, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.935970

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We have design and synthesized of homologous Series I dimers and to study the effect of molecular structure variation and change in alkoxy terminal chain length (n = 6, 7, 8) on mesomorphic properties of liquid crystals. Explore further understanding of the structure-property relationship of liquid crystal homologous Seriesl dimers having varying alkoxy terminal chain length. It was found that the decrease in crystalline phase, smectic C and nematic phase transition temperatures with increasing terminal alkoxy chain length. The molecular structures of the Seriesl dimer were characterized by Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Their mesomorphic properties were investigated by differential scannning calorimetry (DSC) and on the hot-stage of a polarizing microscope (POM).

Keywords: Theromotropic liquid crystal dimers; differential scanning; calorimetry (DSC); dimesogenic compounds

Introduction

Research on liquid crystals exploded from the 1970s to 2010. Scientifically, liquid crystals are an important phase for the investigation of cooperative phenomena, and liquid crystal synthesis a field in its own right, especially in investigating structure-property relationships. Technologically, liquid crystals have become a part of our daily lives, first showing up in wristwatches and pocket calculators, but now being used for displays in all sorts of instrumentation, including portable computers, flat panel televisions, electronic newspapers and high intensity projection systems. Their advantage was first their low power consumption and small size; now liquid crystal displays compete with other technologies for attractiveness, ease of viewing, cost, and durability [1]. Mesomorphic behaviour of an organic compound is basically dependent on its molecular architecture in which a slight

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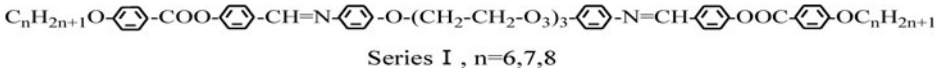
change in the molecular geometry brings about considerable change in its mesomorphic properties. These types of compounds are important not only as a new class of liquid crystalline compositions but also as models for the corresponding main chain liquid crystalline polymers containing flexible spacers. In typical dimers where two individual mesogenic entities are attached to each other via flexible polymethylene spacer units, the structure of the mesophases can be modified through the change in spacer length and terminal chain length [2–5]. Terminal groups (other than hydrogen) are virtually always employed in liquid crystal systems. Terminal units are many and varied but the most successful, and hence important materials employ either a small polar substituted (the most significant is the cyano group) or a fairly long, straight hydrocarbon chain (usually alkyl or alkoxy). The role of the terminal units in the generation of liquid crystal phases is still not yet fully understood. However, the long alkyl/alkoxy chains add flexibility to the rigid core structure that tends to reduce melting points and allow liquid crystal phases to be exhibited. Additionally the alkyl/alkoxy chains are believed to be responsible for stabilising the molecular orientations necessary for liquid crystal phase generation. The choice of terminal moieties is crucial in the generation of a specific type of liquid crystal phase. Physical properties are also strongly dependent upon the choice of terminal unit [1,6–14].

In the present work, in order to explore further understanding of the structure-property relationship of liquid crystal dimers having varying alkoxy terminal chain length, we synthesized homologous Series I dimers shown in Scheme 1. The molecular structures of the Seriesl dimer were characterized by Fourier transform infrared spectroscopy (FT-IR) and NMR techniques. Their mesomorphic properties were investigated by Differential scanning calorimetry (DSC) and on the hot-stage of a polarizing microscope.

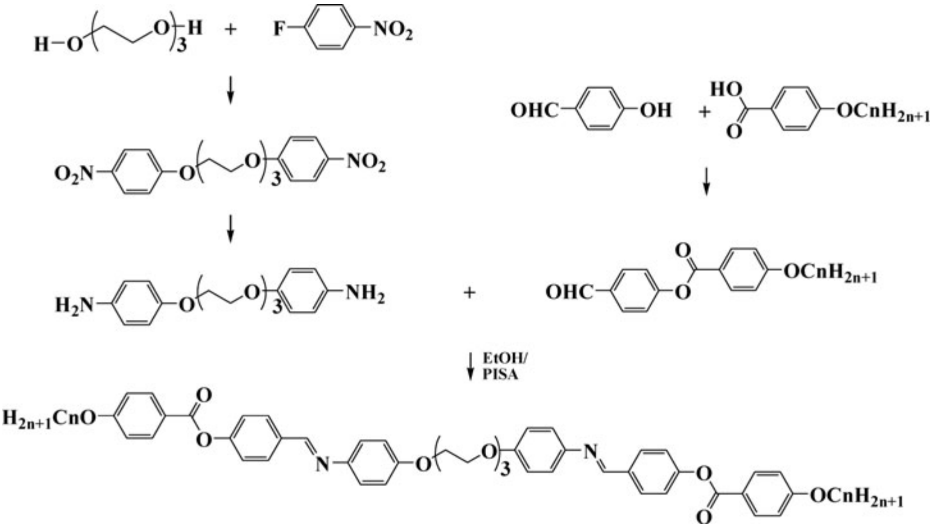
Experimental

Chemicals and Characterizations

Triethylene glycol, 1-fluoro-4-nitrobenzene, 1-bromohexane, 1-bromoheptane, 1-bromooc tane, 4-hydroxybenzoic acid, hydrazine monohydrate, palladium on activated carbon (Pd/C, 10%), 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane(APPE), 4-hydroxybenzaldehyde, 1,3-dicyclohexylcarbodiimide (DCC), tetrahydrofuran (THF), 4-(4-hexyloxybenzoyloxy) benzaldehyde (BOB), *p*-toluenesulfonic acid (PTSA), anhydrous EtOH were purchased from Aldrich Chemical Co. and used as received, with the exception of several solvents which were purified before use by the literature methods [15]. The FT-IR and H-NMR spectra of the intermediates and final dimers were obtained on a Perkin-Elmer FT-IR spectrophotometer (Spectrum 1000) on KBr pellets and on a Varian Unity 300 NMR spectrometer, respectively. Thermal history of the dimers was studied under a N_2 atmosphere on a Dupont DSC 2100 Model 910S (differential scanning calorimetry: DSC, TA instruments) with a heating or cooling rate of 10°C/min. Indium was used as a reference for temperature calibration and estimation of thermodynamic parameter for the phase transitions. The optical textures of the melts was carried out using a Nikon Labophot-2 polarizing microscope fitted with a RTC-1 temperature controller (Instec Inc., Broomfield, CO) and a mettler FP-82HT hot stage. Magnification was 100X.



Scheme 1. The structures of the Series I.



Scheme 2. Synthetic routes for Series I dimers.

Synthesis of Series I

The Series I dimers were synthesized as illustrated in Scheme 2. The synthetic pathway used in the synthesis of Series I dimers involved several steps [11]:

Synthesis of Final Dimer BPEE-6

1,2-bis(2-(4-(4-(4-hexyloxybenzoyloxy)benzlideneamino)phenoxy)ethoxy)ethane(BPEE-6): the reaction of 4-(4-hexyloxybenzoyloxy)benzaldehyde (22 mmol) in anhydrous EtOH(50 ml) with 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane (11mmol) in presence of PTSA [11,16,17]. The reaction mixture was stirred for 16 h at the room temperature. The crude precipitate was separate by filteration and purified by the recrystallization of both chloroform and ethyl acetate solvents. The syntheses of final dimer (BPEE-6) were confirmed by FT-IR and ^{1}H-NMR (off-white powder, 75%). FT-IR (KBr pellet, cm^{-1}): 3071(aromatic C—H), 2936, 2865(aliphatic C—H), 1740(C=O), 1615, 1525(—C=C—). ^{1}H-NMR($CDCl_3$, ppm): 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—).

Synthesis of Final Dimer BPEE-7

1,2-bis(2-(4-(4-(4-heptyloxybenzoyloxy)benzlideneamino)phenoxy)ethoxy)ethane(BPE-E-7): BPEE-7 was synthesized following the similar method described in the BPEE-6. Off-white powder(30%). FT-IR(KBr pellet, cm^{-1}): 3070(aromatic C—H), 2930, 2860(aliphatic C—H), 1742(C=O), 1610, 1510(—C=C—). ^{1}H-NMR($CDCl_3$, ppm): 0.92–0.84(t, 6H, —CH_3), 1.51–1.24(m, 16H, —$(CH_2)_4$—), 1.86–1.77(m, 4H, $\underline{—CH_2}CH_2O—$), 3.76(s, 4H, $—CH_2\underline{CH_2}O—$), 3.88–3.84(t, 4H, —OCH_2—), 4.03–3.99(t, 4H, —OCH_2), 4.14–4.11(t, 4H,

Table 1. Thermodynamic data of Series I dimers[a)]

	Transition temperatures (°C) and associated enthalpy change (△H, J/g)			Heating cooling
Designation	C_r	S_A	S_c	N
BPEE-6	143.5(95.6)		269.4(1.50)	274.0(2.93)
	107.6(50.1)		263.1(1.21)	266.3(2.20)
BPEE-7	142.9(90.9)		266.1(2.50)	268.2(1.12)
	111.8(505)		249.0(1.21)	251.2(0.83)
BPEE-8	140.6(46.6)		255.4(2.33)	257.2(1.53)
	117.0(39.3)	136.1(1.64)	251.9(2.08)	253.3(9.92)

a) C_r = crystalline state, S_A = smectic A, S_C = smectic C, N = nematic state.

$-OCH_2-$), 6.96–6.91(t, 8H, Ar–H), 7.28–7.21(d, 8H, Ar–H), 7.97–7.92(d, 4H, Ar–H), 8.15–8.11(d, 4H, Ar–H), 8.45(s, 2H, $-CH{=}N-$).

Synthesis of Final Dimer BPEE-8

1,2-bis(2-(4-(4-(4-octyloxybenzoyloxy)benzlideneamino)phenoxy)ethoxy)ethane(BPEE-8): BPEE-8 was synthesized following the similar method described in the BPEE-6 (Off-white powder, 75%). FT-IR(KBr pellet, cm^{-1}): 3074(aromatic $C-H$), 2920, 2858(aliphatic $C-H$), 1738($C{=}O$), 1611, 1512($-C{=}C-$). ^{1}H-NMR($CDCl_3$, ppm): 0.91–0.86(t, 6H, $-CH_3$), 1.56–1.24(m, 20H, $-(CH_2)_5-$), 1.85–1.78(m, 4H, $\underline{-CH_2}CH_2O-$), 3.78(s, 4H, $-CH_2\underline{CH_2}O-$), 3.90–3.87(t, 4H, $-OCH_2-$), 4.05–4.01(t, 4H, $-OCH_2$), 4.16–4.12(t, 4H, $-OCH_2-$), 6.97–6.92(t, 8H, Ar–H), 7.32–7.19(d, 8H, Ar–H), 7.96–7.93(d, 4H, Ar–H), 8.14–8.12(d, 4H, Ar–H), 8.46(s, 2H, $-CH{=}N-$).

Results and Discussion

These new Series I dimers, 1,2-bis(2-(4-(4-(4-alkyloxybenzoyloxy)benzylideneamino) pheno-xy)ethoxy)ethane(BPEE-6,7,8) were synthesized starting from diamine derivative(APEE). The dimers, BPEE-n, were then obtained by the condensation reaction between aldehydes and diamine(see Scheme 1). The molecular structures of all intermediates and final dimers were characterized by the FT-IR and ^{1}H-NMR spectroscopy. The liquid crystalline properties exhibited by these symmetrical dimers were confirmed by means of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). All dimers synthesized in the Series I found to exhibit mesomorphic properties. The thermodynamic data and liquid crystal textures for Series I dimers were summarized in Table 1. The thermodiagrams in Figs. 1–3 represent all DSC first (heating and cooling curves) traces of the Series I dimers. In the first heating curve of BPEE-6, it shows a crystal to smectic C phase transition at 143.5°C, a smectic C to a nematic phase transition at 269.4°C and a nematic to isotropic liquid phase transition at 274.0°C, In the first cooling curve of BPEE-6, it shows an isotropic liquid phase to nematic phase transition at 266.3°C, a nematic to smectic C phase transition at 263.1°C and a smectic C to crystal phase transition at 107.6°C. Supercooling effect is more pronounced with the crystallization than other phase transitions. The thermal history of BPEE-7 on the mesomorphic behaviour of this Series I

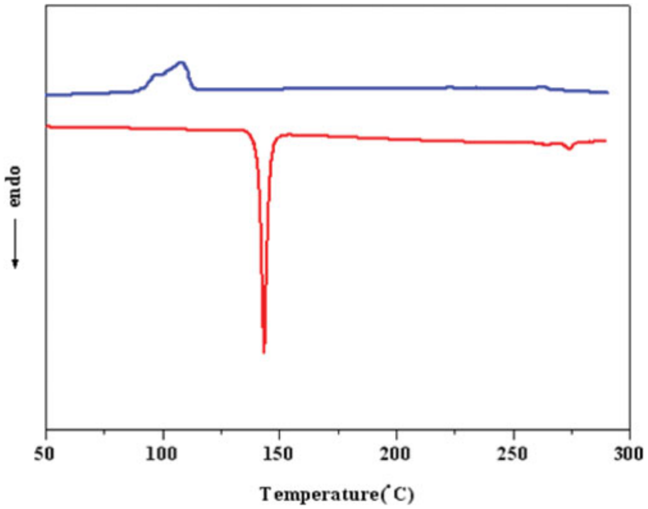


Figure 1. Differential scanning calorimetry curves for BPEE-6 in the heating and cooling scans (10°C/min).

dimer was similar to that seen in BPEE-6. In the first heating curve of BPEE-8, it shows a crystal to smectic C phase transition at 140.6°C, a smectic C to a nematic phase transition at 255.4°C and a nematic to isotropic liquid phase transition at 257.2°C. In the first cooling curve of BPEE-8, it show an isotropic liquid phase to nematic phase transition at 253.3°C, a nematic to smectic C phase transition at 251.9°C, a smectic C to smectic A phase transition at 136.1°C and a smectic A to crystal phase transition at 117.0°C. With increase in terminal alkoxy chain length from 6 to 8, smectic to nematic phase transition appears. The optical textures of BPEE-8 of Series I in the observed mesophase window are shown

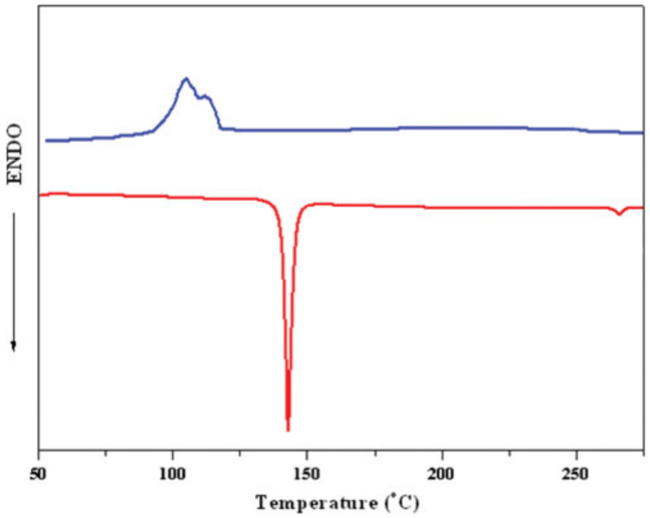


Figure 2. Differential scanning calorimetry curves for BPEE-7 in the heating and cooling scans (10°C/min).

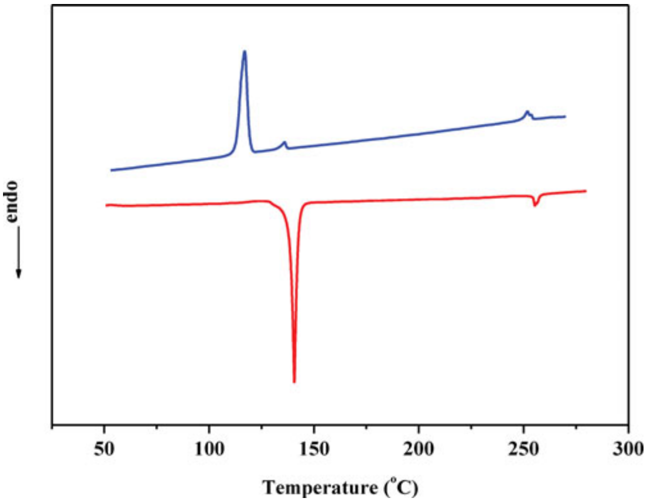


Figure 3. Differential scanning calorimetry curves for BPEE-8 in the heating and cooling scans (10°C/min).

Fig. 4 [18,19]. Optical properties of mesophases were studied using POM with a hot stage. Optical micrographs of BPEE-8 obtained during the heating and cooling cycle at different temperatures are shown in Fig. 4 [18,19]. The existence of smectic C to nematic phase transition was characterized by the observation of marbled textures in optical microscopy when dimers were heated from smectic C phase (See Fig. 4(3)). In heating cycle, Cr phase of BPEE-8 at 100°C show in Fig. 4(1), smectic C phase of BPEE-8 at 246°C show in Fig. 4(2) and nematic (N) phase of BPEE-8 at 257°C show in Fig. 4(3) respectively. In cooling cycle, smectic C phase of BPEE-8 at 220°C show in Fig. 4(4), smectic A phase of BPEE-8 at 130°C show in Fig. 4(5) and Cr phase of BPEE-8 at 105°C show in Fig. 4(6), respectively [18,19]. It can be seen from Table 1, the crystal to smectic C phase transition at 143.5°C(BPEE-6) decreased to 140.6(BPEE-8) with increase in terminal alkoxy chain length indicating the reduction in crystallinity and increase in flexibility of the dimers. With increase in terminal alkoxy chain length ($n = 6$–8), the smectic C phase transition decreased from 269.4 to 255.4°C and also the nematic phase transition decreased from 274.0 to 257.2°C. Table 1 represents the dependence of the transition temperature on the terminal alkoxy chain length. Table 1 clearly illustrates the decrease in crystalline, smectic C and nematic phase transition temperatures with increasing terminal alkoxy chain length. Similar observations were previously reported by us for dimers having azo type mesogenic groups [10] attached terminal alkoxy chain length. But another observation in smectic phase was reported by us for dimers having Shiff base [10] and ester-Schiff base mesogenic groups attached terminal alkoxy chain length [11]. In our early paper [10,11], the increasing terminal alkoxy chain length is anticipated to increase significantly the length-to-breadth ratio in resulting in mesomorphic phases, and particularly smectic phases, being stabilized at higher temperatures for higher homologues. These results demonstrate that the tendency toward smectic mesomorphism and the thermal stability of smectic phase increases with increasing terminal alkoxy chain length. But in this paper, our results shows the decrease in crystalline phase, smectic C and nematic phase transition temperatures with increasing terminal alkoxy chain length. With increase in terminal alkoxy chain length, the decrease

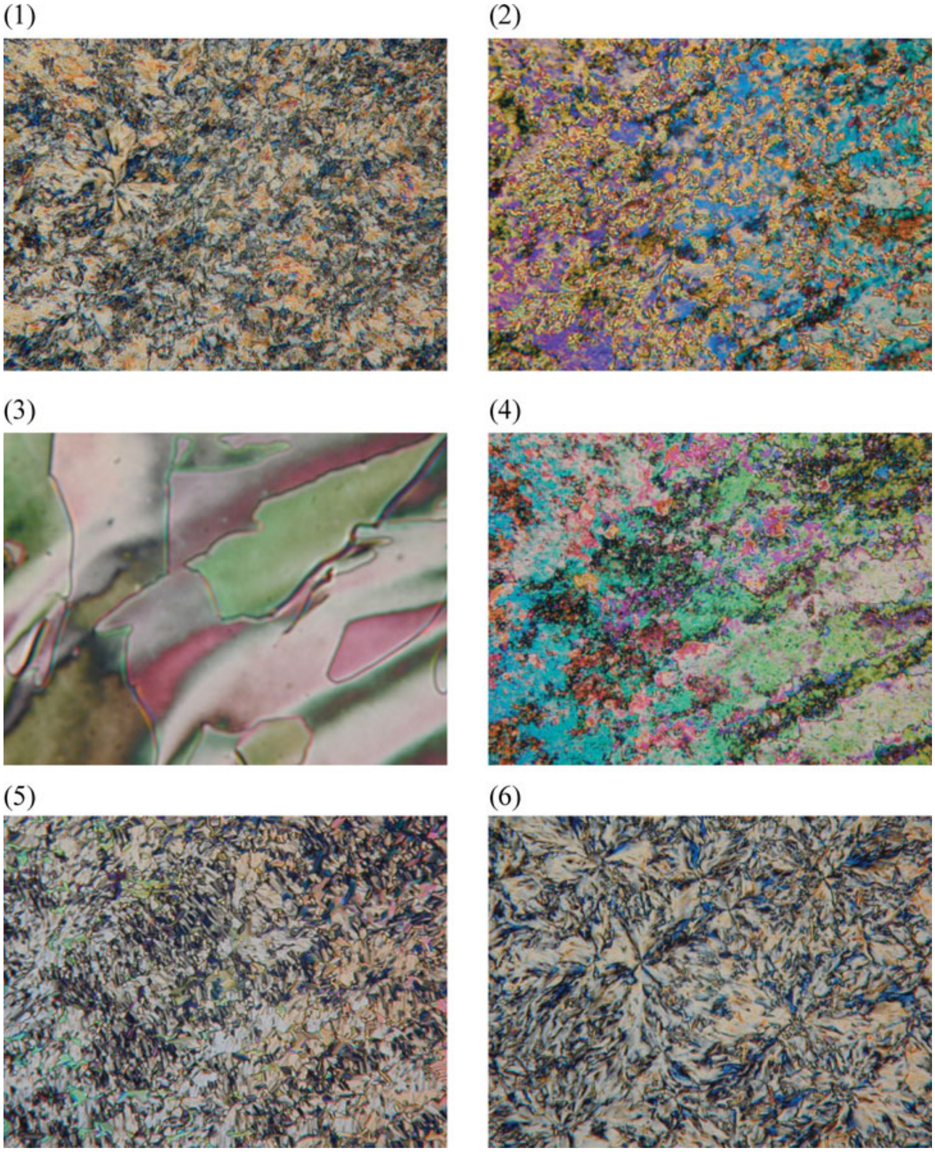


Figure 4. Optical textures of (1) Cr(100°C, H); (2) Sc(216°C, H); (3) N(257°C, H); (4) Sc(140°C, C); (5) S_A(130°C, C); (6) Cr(105°C, C) of BPEE-8.

of the transition temperatures of crystalline and nematic phase observed in this series are in accordance with those observed for our early reports [10,11] but the smectic C phase is not. Unfortunately, It was unclear the reason of unidentified smectic phase for such difference. But the observed diminished smectic C temperature with the increasing terminal alkoxy chain length may be due to the central flexible spacer. Early reports [10,11] used ethylene glycol as a central flexible spacer but this report used triethylene glycal. Therefore, when triethylene glycol was applied as a central flexible spacer, the length of terminal alkoxy chain become extended because of alkyl group in central flexible spacer can engulf more oxygen molecules.

Conclusions

We have synthesized of homologous Series I dimers and to study the effect of molecular structure variation and change in alkoxy terminal chain length ($n = 6, 7, 8$) on mesomorphic properties of liquid crystals. The chemical structures of the final products were investigated by FT-IR and 1H NMR spectroscopy. The mesomorphic properties and optical textures of the resultant dimers were characterized by DSC and OM. The existence of central flexible spacer may have an oxygen flexibility effect rather than thermal stabilization of smectic phase, which leads to transition temperature decrement of smectic C phase. It was found that the molecular structure of central flexible spacer affect crystalline, smectic, and nematic phase transition temperature as well as terminal alkoxy chain length.

Funding

This research was supported by the Academic Research Fund of Hoseo University in 2012 (2012-0299).

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