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Influence of terminal alkyl chain length on helical twisting property of chiral 1,2-propanediol derivatives

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Abstract

In this study, a novel series of chiral 1,2-propanediol derivatives with different terminal alkyl chain length were synthesized and characterized by FT-IR, ^{1}H NMR and DSC. After doped into a nematic liquid crystal host, all the chiral dopants induced chiral nematic liquid crystals exhibiting a helix inversion with temperature variation. The results indicate that terminal alkyl chain length has a prominent influence on helical twisting property of the chiral dopants. With increasing the terminal alkyl chain length, the molecular twisting power increases, the helix inversion temperatures varies slightly while the phase transition temperature decreases. An odd–even effect may exist in the molecular twisting power of the chiral dopants.

Keywords: Chiral dopant; Liquid crystal; Helix inversion; Molecular twisting power

The phenomenon of a helix inversion with temperature variation has been observed in single component thermotropic chiral liquid crystal (LC) [1,2], mixtures of thermotropic chiral LCs [3,4] and mixtures of chiral dopants in a nematic LC host [5–9]. It is well known that a chiral nematic (N*)-LC is formed when a nematic LC host is doped with a chiral dopant, and its helical structure is based on the chiral molecular structure. Due to the chiral nature of the perturbation, either left- or right-handed helix is possible [10]. However, the twisting sense of the helical structure of N*-LC could be changed with temperature variation when a helix inversion occurs, leading to a nematic director configuration at the inversion temperature.

In this communication, we report the synthesis and characterization of a novel series of chiral 1,2-propanediol derivatives with different terminal alkyl chain length. We show that the chiral dopants with different terminal alkyl chain length impart a clearer understanding between molecular structure and helical twisting property of chiral dopants inducing N*-LCs with a helix inversion.

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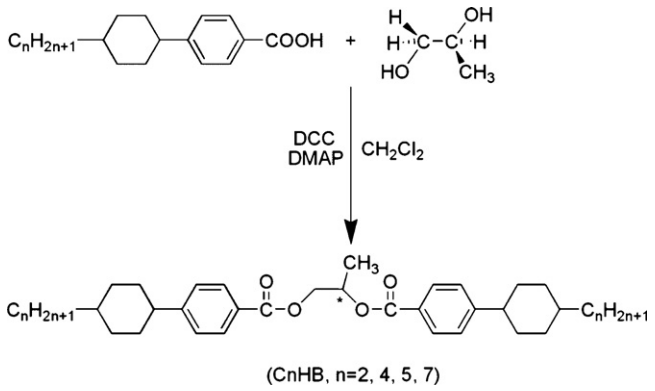

Scheme 1. The synthetic route to chiral 1,2-propanediol derivatives with different terminal alkyl chain length.

1. Experimental

The synthetic route to chiral 1,2-propanediol derivatives is outlined in Scheme 1. The molecular structures of the chiral dopants were ascertained using FT-IR and ^{1}H NMR [11]. The phase transition temperatures were investigated by DSC at a heating rate of 10.0 °C min^{-1} under a dry nitrogen purge.

The desired chiral dopant was doped into the nematic LC host of SLC1717 ($T_{N\text{-}I}$ = 91.8 °C, Shijiazhuang Yongsheng Huatsing Liquid Crystal Material Co., Ltd.) with the concentration C in about 2.0 wt.%. The pitch, P, of the helix corresponding to a 2π molecular rotation was determined by Cano wedge technique [12]. To characterize the twisting power of the chiral dopants, either the product PC or the molecular twisting power $\beta = 1/PNv$ was used (Nv is the number density of the chiral dopant in mol m^{-3}). The values of β were calculated assuming a density of the LC solution of 1 g cm^{-3} [8]. All the N*-LCs induced by the chiral dopants were studied using the contact method [13] and their helical twisting senses were established. As standard for the experiments, the N*-LC induced by R811 (right-handed) was used.

2. Results and discussion

Fig. 1 shows optical textures of contact region between the standard N*-LC induced by R811 and the test N*-LC induced by C5HB with substrates treated for homeotropic orientation. The dark contact region of pseudo-isotropic texture at 25.0 °C shows a homeotropic nematic phase separating the N*-LC induced by R811 and the N*-LC induced by C5HB, while a continuous fingerprint texture at 85.0 °C shows two N*-LCs have the same helical sense. This demonstrates that the helical twisting sense of the N*-LC induced by C5HB changes from left-handed to right-handed with temperature increasing.

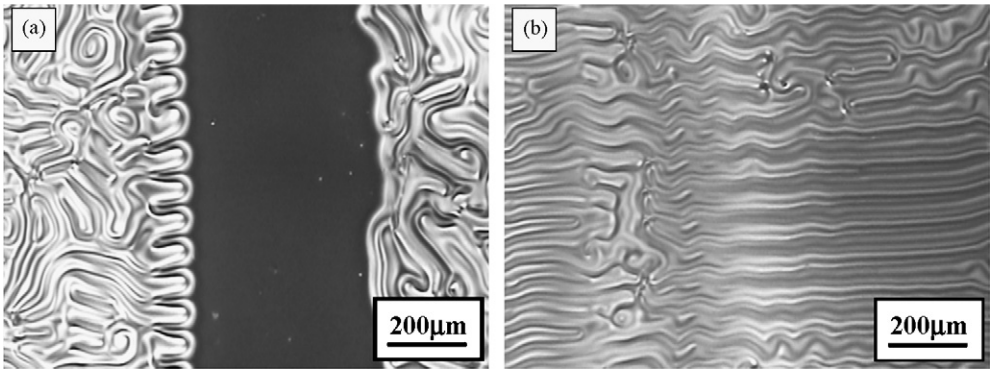

Fig. 1. The optical textures of contact region between the standard N*-LC induced by R811 (left) and the test N*-LC induced by C5HB (right): (a) 25.0 °C, (b) 85.0 °C.

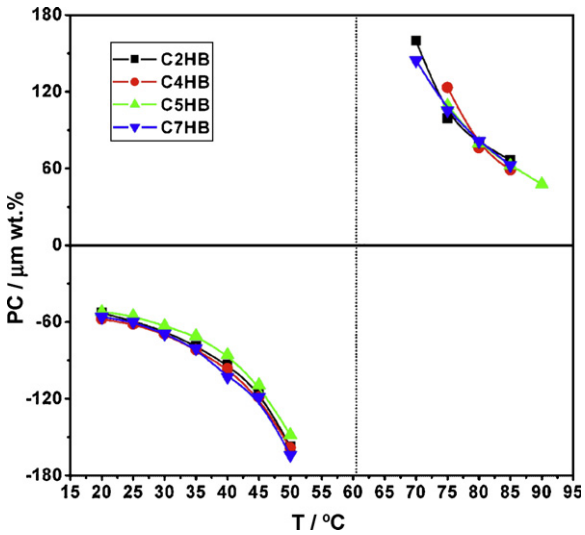

Fig. 2. The temperature dependence of the PC-product of C2HB, C4HB, C5HB and C7HB, respectively.

Table 1
The phase transition temperatures, the PC-products, the molecular twisting power β at 20.0 °C and the helix inversion temperatures of the chiral dopants.

Chiral dopants	Transition temperatures/°C	PC (20.0 °C)/μm wt.%	β (20.0 °C)/m^2 mol^{-1}	T_{HI}/°C
C2HB	Cr 153.4 I	−52.9	−953.4	60.1
C4HB	Cr 109.0 I	−57.7	−971.4	60.8
C5HB	Cr 111.8 I	−52.0	−1131.6	60.6
C7HB	Cr 105.1 I	−56.1	−1149.4	59.5

Fig. 2 shows the temperature dependence of the PC-product of C2HB, C4HB, C5HB and C7HB, respectively. It can be seen that the pitchs of the N*-LCs induced by the chiral dopants mentioned above show a much stronger increase with temperature increasing. The pitchs diverge at about 60.0 °C, which is in agreement with textural observations of the N*-LCs. Above this temperature of a helix inversion, the pitchs of the N*-LCs decrease strongly. Here the signs + and − indicate right-handed and left-handed helices, respectively.

Table 1 lists the phase transition temperatures, the PC-products, the molecular twisting power β at 20.0 °C and the helix inversion temperatures (T_{HI}) of the chiral dopants. It can be seen that with increasing terminal alkyl chain length, the phase transition temperatures of the chiral dopants decrease, the absolute values of β increase while the extrapolated T_{HI} vary slightly.

It was found that the twisting power is weakly dependent on the nature of the aliphatic chiral centre [14,15], the increasing β values from C2HB to C7HB may result from greater anisometry of molecular structure. Besides, the sudden increase of the molecular twisting power of C5HB may derive from the odd–even effect of terminal alkyl chain length. Even-numbered terminal alkyl chain may possess more conformers which allow an essentially parallel arrangement of the mesogenic ring structure and enhance the mutual interactions with nematic LC molecules.

Acknowledgments

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[11] **C2HB**: Yield 78.3%. IR (KBr, cm^{-1}): 2963, 2922, 2850 (–CH_3–, –CH_2–); 1716 (C═O); 1610, 1510 (Ar–). ^{1}H NMR ($CDCl_3$, δ ppm): 7.24–7.97 (8H, Ar–H), 5.50–5.52 (1H, C*H), 4.46–4.47 (2H, C*–CH_2–O–), 2.49–2.52 (2H, cyclohexyl-CH–Ar), 1.21–1.29, 1.44–1.50, 1.87–1.89 (21H, cyclohexyl-H, C*–CH_3), 0.89–0.93, 1.03–1.09 (10H, alkyl-H). **C4HB**: Yield 74.5%. IR (KBr, cm^{-1}): 2956, 2919, 2849 (–CH_3–, –CH_2–); 1713 (C═O); 1609, 1510 (Ar–). ^{1}H NMR ($CDCl_3$, δ ppm): 7.24–7.97 (8H, Ar–H), 5.49–5.53 (1H, C*H), 4.46–4.47 (2H, C*–CH_2–O–), 2.48–2.51 (2H, cyclohexyl-CH–Ar), 1.30–1.31, 1.44–1.49, 1.86–1.89 (29H, cyclohexyl-H, C*–CH_3, alkyl-H), 0.89–0.92, 1.00–1.09 (10H, alkyl-H). **C5HB**: Yield 77.2%. IR (KBr, cm^{-1}): 2953, 2923, 2849 (–CH_3–, –CH_2–); 1716 (C═O); 1610, 1510 (Ar–). ^{1}H NMR ($CDCl_3$, δ ppm): 7.25–7.97 (8H, Ar–H), 5.49–5.53 (1H, C*H), 4.43–4.49 (2H, C*–CH_2–O–), 2.48–2.51 (2H, cyclohexyl-CH–Ar), 1.21–1.34, 1.44–1.55, 1.86–1.89 (33H, cyclohexyl-H, C*–CH_3, alkyl-H), 0.88–0.91, 1.03–1.06 (10H, alkyl-H). **C7HB**: Yield 71.8%. IR (KBr, cm^{-1}): 2951, 2919, 2850 (–CH_3–, –CH_2–); 1716 (C═O); 1611, 1510 (Ar–). ^{1}H NMR ($CDCl_3$, δ ppm): 7.25–7.97 (8H, Ar–H), 5.50–5.51 (1H, C*H), 4.46–4.47 (2H, C*–CH_2–O–), 2.48–2.54 (2H, cyclohexyl-CH–Ar), 1.24–1.28, 1.40–1.54, 1.86–1.89 (37H, cyclohexyl-H, C*–CH_3, alkyl-H), 0.87–0.90, 1.00–1.03, 1.06–1.09 (14H, alkyl-H).
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