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The synthesis of new liquid–crystalline mesogens containing bicyclohexane units

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Abstract—The synthesis and mesomorphism characterization of new thermotropic derivatives of *cis*,*trans* and *trans*,*trans*-4,4′-bicyclohexyl-bis[4-(6-hydroxyhexan-1-oxy)benzoate] are described. This last intermediate produces a liquid crystalline diacrylate, with lower refractive indices than the well-known aromatic analogues, that allows to obtain polymeric network via UV photopolymerization. The acrylate is very useful to optimize the contrast of polymer dispersed liquid crystals (PDLCs). Moreover, the acylation of the intermediates previously mentioned, with alkanoic or perfluoro alkanoic acids give low-molecular liquid crystals that exhibit a broad temperature range of mesophases.
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Liquid crystal monomers with difunctional polymerizable groups are of great interest as starting materials for the production of anisotropic networks.[1–4] These materials, with anisotropic optical and mechanical properties, represent an area of great scientific research and technological potential. In particular, anisotropic networks have lots of possible uses in passive solid state optical devices such as colour filters and polarizer retarders.[5,6] They are highly promising for usage in microelectronics and especially for applications requiring light modulation, as in electro-optics, and non-linear optics.[7–10] Bireactive monomers can be employed for the production of these devices by in situ photopolymerization.[11–14] This technique involves the macroscopic orientation of molecules containing reactive end groups, in liquid crystalline phase, followed by UV irradiation.[15,16] As a result, the molecular orientation within the system is frozen by the formation of a three-dimensional anisotropic network. Broer and co-workers[1,2] initiated the investigation of anisotropic networks obtained in situ by means of photopolymerization of liquid crystal monomers with ultraviolet light. Because of their liquid crystal behaviour, the monomers can be uniaxially oriented by external forces, such as magnetic and electrical fields or surface orientation. One advantage of photopolymerization process, when compared with thermally activated polymerization, is its temperature independence. The temperature of polymerization can be chosen to be in mesomorphic state and, after that the macroscopic orientation has been obtained, the polymerization proceeds with a high degree of conversion. In this way the degree of order and consequently the anisotropic properties of the network can be adjusted as desired. The resulting networks behave anisotropic in a number of properties, such as thermal expansion coefficient and refractive index. In the production of anisotropic networks, various reactive liquid crystal molecules were synthesized.[3] Such molecules, schematically represented in Figure 1, consist of three parts: (1) central mesogenic core, (2) reactive end groups and (3) flexible spacers. Each one of these groups plays an important role in determining the thermal properties, the liquid crystalline phase and the optical properties

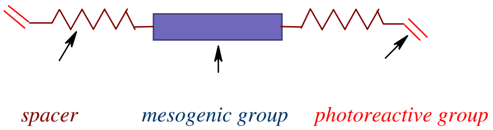

Figure 1.

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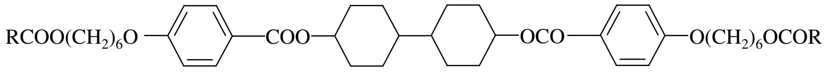
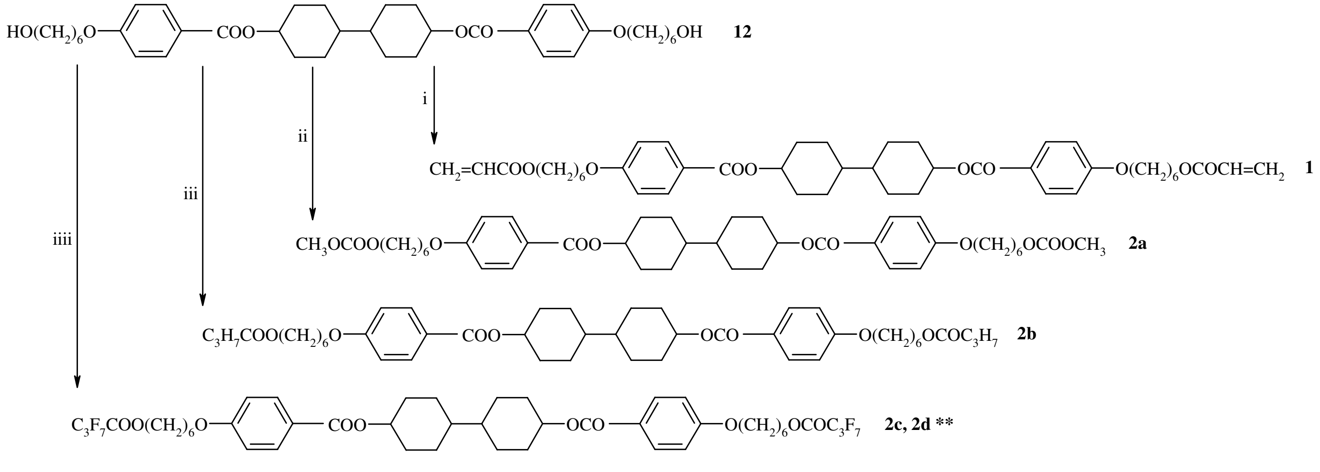
in the monomeric state. They also influence the polymerization behaviour leading to the formation of an anisotropic network. The crosslinked polymer network is formed by the polymerization of each of the photoreactive end groups. In the past years, many scientific groups have developed different synthetic procedures in order to obtain the polymerizable liquid crystalline molecules useful in the realization of composite films (polymer dispersed liquid crystals—PDLCs) that have attracted a lot of interest as electrically controlled light shutters.[17,18] PDLCs can exhibit either a droplet morphology,[19] in which the liquid crystal is separated as distinct micron-sized droplets in a continuous polymer matrix, or a reverse morphology,[20] in which the liquid crystal fills the voids and crevices in a network structure formed by small polymer balls. PDLCs are generally characterized by an opaque OFF state, which can be turned into a transparent ON state by the application of a suitable electric field (normal-mode operation film). On the contrary, reverse-mode PDLCs exhibit a transparent OFF state and an opaque ON state. They have been the subject of a great deal of research. Reverse-mode shutters have been obtained by using dual frequency addressable liquid crystals,[21,22] by polymerizing nematic emulsion,[23] by functionalizing the liquid/polymer matrix interface[24] and by using a larger liquid crystal loading.[25–27] In the present work are shown (Scheme 1) (i) the synthesis of new polymerizable low birefrigence mesogen **1**, useful in the production of PDLC operating in ‘reverse mode’, with a mesogenic bicyclohexyl unit functionalized on each side with an acrylate group connected by a flexible spacer; (ii) the synthesis of analogous mesogens without polymerizable groups **2** and (iii) the characterization of liquid crystalline behaviour of the newly formed compounds **1** and **2**. The polymerization behaviour of compound **1** and the properties of the prepared polymers will be described in the following publications. The synthesis of mesogens **1** and **2** is outlined in Scheme 2 and intermediate **12** in Scheme 3. This preparative procedure was recently adopted[28] for antiferroelectric ester realization.

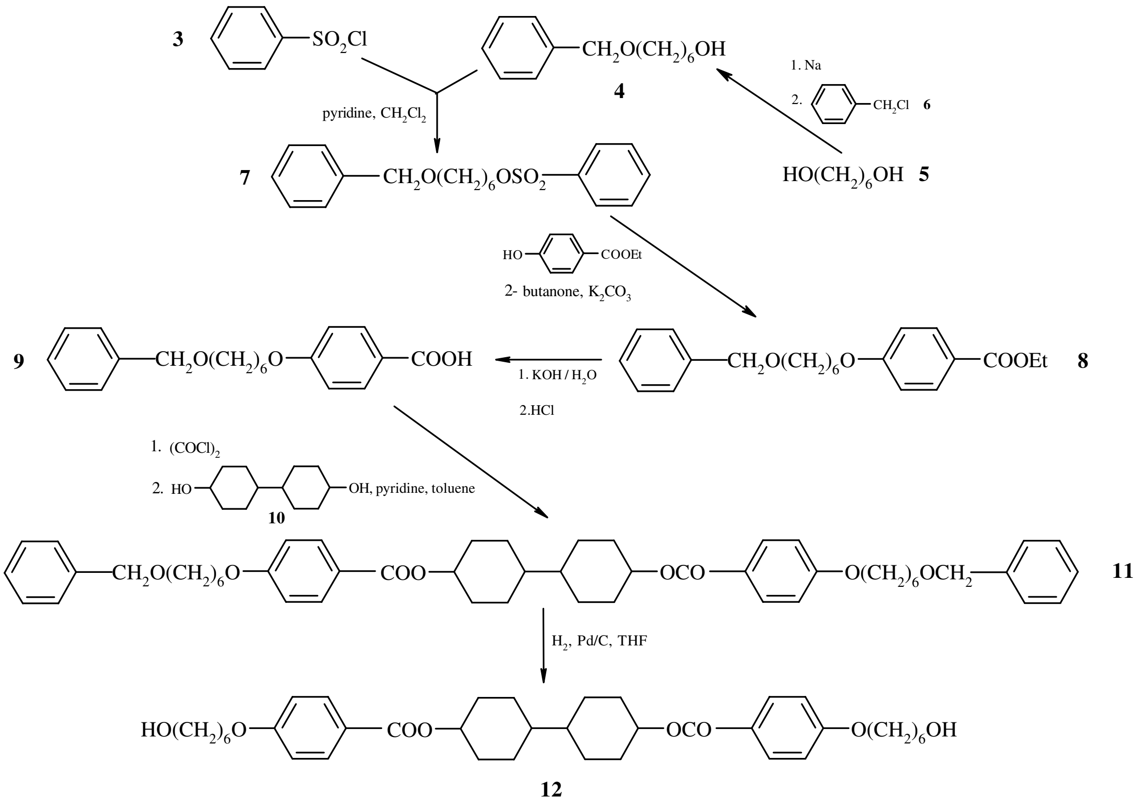
Diol **12** was prepared as follows. The commercial 1,6-hexanediol (**5**) was treated with sodium in equimolar ratio to avoid disubstitution and then with benzyl chloride (**6**). The monosubstituted derivative [6-benzyloxyhexan-1-ol (**4**)] was separated from the raw product by distillation and then coupled with benzenesulfonyl chloride in dichloromethane in the presence of pyridine (Py) to quench HCl. The crude oil product (**7**) was submitted to a reaction with ethyl 4-hydroxybenzoate in 2-butanone as the solvent and potassium carbonate (K_2CO_3) as the base. The ethyl *p*-(6-benzyloxyhexan-1-oxy)benzoate (**8**), a yellow oil sufficiently pure, was obtained. It was hydrolyzed by boiling with potassium hydroxide in ethylene glycol for 7 h. Afterwards, the reaction mixture was acidified and the resulting *p*-(6-benzyloxyhexan-1-oxy)benzoic acid (**9**) was purified by recrystallization from ethanol. It was then treated by boiling with oxalyl chloride using dry toluene as the solvent and a few drops of dry *N*,*N*-dimethylformamide (DMF). Excess of oxalyl chloride and most of the toluene were distilled off and *trans*,*trans*-bicyclohexanediol (**10**) or the commercial isomer mixture of bicyclohexanediol and pyridine as the base were added. Compound **10** was obtained by treating the commercial 4,4′-bicyclohexanediol (*cis*,*trans* isomers mixture with composition 90 wt % of trans producer Valiant, China) with acetyl chloride in the presence of pyridine (Py) and dichloromethane (CH_2Cl_2). The *trans*,*trans* isomer of the acetyl derivative was separated by recrystallization from methanol, purity 99.7 wt %. In the second step it was hydrolyzed, under reflux, with $NaOH/H_2O$. After cooling, the mixture was acidified and the white precipitate was filtered off. The resulting crude product contains the pure *trans*,*trans*-bicyclohexanediol (mp 141–142.5 °C).



Scheme 1. (**1**) R = –CH═CH_2, (**2a**) R = –OCH_3, (**2b**) R = –C_3H_7, (**2c**) R = –C_3F_7, (**2d**) R = –C_3F_7 (mixture cis–trans).



Scheme 2. Reagents: (i) CH_2═CHCOCl, Et_3N, THF; (ii) CH_3OCOCl, Py, CH_2Cl_2; (iii) C_3H_7COCl, Py, CH_2Cl_2; (iv) C_3F_7COOH, THF, DEAD, $P(Ph)_3$ **prepared from cis, trans mixture.



Scheme 3.

Table 1. Phase sequence, transition temperatures (°C) of mesogenic compounds from microscopic observation

Compound	Heating
1	Cr 103.7 SmA polymerizes
2a	Cr 138–140 SmA 224.2–225.6 N 241.8–244.5 I
2b	Cr 94.7–95.4 SmC 131.13 SmA 201.6–203.1 N 210.7–212 I
2c	Cr 96–98 SmC 207–209 SmA 238.7–242.1 I
2d	Cr 79–80 SmC 184 SmA 229 I
11	Cr 76.9–77.2 SmC 139.4 N 198.9 I
12	Cr 154–155 N 275.7 I

Cr = crystal; N = nematic; SmA = smectic A; SmC = smectic C; I = isotropic phase.

trans,*trans*-4,4′-Bicyclohexyl-bis{4-[6-(benzyloxy)hexan-1-oxy]benzoate} **11** or the isomeric mixtures of 4,4′-bicyclohexyl-bis{4-[6-(benzyloxy)hexan-1-oxy]benzoate} **11a** was formed. Hydrogenation of **11**[†] or **11a** led to compounds **12**[‡] or **12a**, respectively. This latter treated with acroyl chloride, in the presence of pyridine, afforded **1**[§] while methylchloroformate, butyryl chloride and heptafluorobutyric acid afforded compounds **2a**–**c**.[¶] The liquid crystalline properties of the target molecules were investigated primarily by optical polarizing microscopy (OPM) and differential scanning calorimetry (DSC). The results are summarized in Table 1. The phases were identified through the comparison of the observed texture with reference textures.[29] Final compounds **1**, **2a**–**d** and intermediates **11** and **12** are mesogenic compounds. Compound **11** shows smectic C and nematic phases (Fig. 2). Acrylate **1** melts into smectic A phase, then rapidly polymerizes on a rigid solid and consequently at higher temperatures no phases were observed. Compounds **2a** and **2b** show nematic and smectic A phases (Fig. 3). Similarly, compounds **2c**

[†] Compound **11**: white powder, yield 17 g (43%). Heating: Cr 98.8 SmC 139.4 N 198.9 I. IR (KBr) ν in cm^{-1}: 3076, 3031, 2941, 2851, 1699, 1275, 1020, 973, 942. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.1 (m, 10H), 1.41 (m, 8H), 1.59–1.72 (m, 16H), 2.1 (m, 2H), 3.42 (t, 4H), 3.93 (t, 4H), 4.8 (m, 2H), 4.44 (s, 4H), 6.82 (m, 4H), 7.23 (m, 10H), 7.9 (m, 4H).

[‡] Compound **12**: white powder, yield 20 g (96%). Cr 151.7 N 273.6 I. IR (KBr) ν in cm^{-1}: 3300, 3040, 3020, 2938, 2860, 1697, 1263. ^{1}H NMR (CD$_6$SO) δ (ppm): 1.1–1.95 (m, 34H), 2.43 (m, 2H), 3.34 (m, 4H, $J_{H,OH} = 5.5$ Hz), 3.96 (m, 4H), 4.14 (m, 2H), 6.93 (m, 4H), 7.8 (m, 4H).

[§] Compound **1**: white powder, yield 3 g (52%). Cr 103.7 SmA decomposes. IR (KBr) ν in cm^{-1}: 3040, 2943, 2852, 1703, 1699, 1604, 1273. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.17–2.17 (m, 36H), 4.01 (t, 4H), 4.18 (t, 4H), 5.82 (dd, 2H), 6.12 (dd, 2H), 6.40 (dd, 2H), 6.89 (m, 4H), 7.98 (m, 4H).

[¶] Compound **2a**: white powder, yield 2.2 g (94%). Cr 138–140 SmA 224.2–225.6 N 241.8–244.5 I. IR (KBr) ν in cm^{-1}: 3030, 2942, 2851, 1745, 1698, 1242, 1047. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.12–2.16 (m, 36H), 3.78 (s, 6H), 4.0 (t, 4H), 4.16 (t, 4H), 6.89 (d, 4H), 7.98 (d, 4H). Compound **2b**: white powder, yield 2.2 g (83%). Cr 94.7–95.4 SmC 131.13 SmA 201.6–203.1 N 210.7–212 I. IR (KBr) ν in cm^{-1}: 3030, 2930, 2849, 1732, 1698, 1186, 1076. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.49–2.29 (m, 50H), 4.0 (t, 4H), 4.07 (t, 4H), 6.88 (d, 4H), 7.96 (d, 4H). Compound **2c**: white powder, yield 2.7 g (83.3%). Cr 96–98 SmC 207–209 SmA 238.7–242.1 I. IR (KBr) ν in cm^{-1}: 3040, 3025, 2938, 2862, 1770, 1699, 1078. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.49–2.12 (m, 36H), 4.12 (m, 4H), 4.4 (m, 4H), 6.88 (m, 4H), 7.98 (m, 4H).

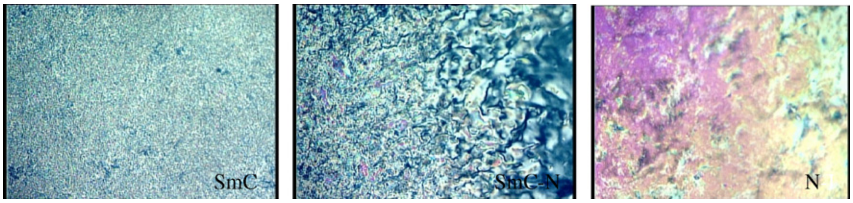


Figure 2. Photos in polarizing light of the SmC and N phases of **11**.

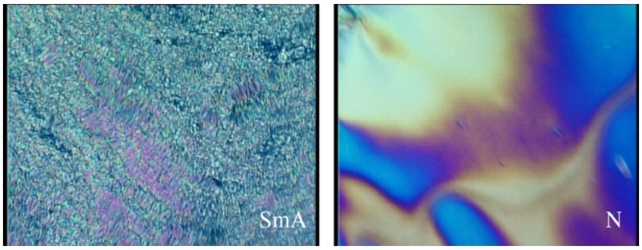


Figure 3. Photos in polarizing of the N, SmA phases of **2a**.

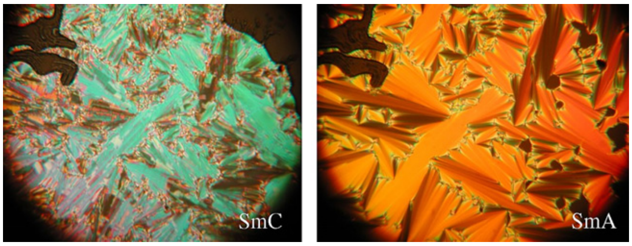


Figure 4. Photos in polarizing of the compound **2c**.

and **2d** display smectic C, smectic A and nematic phases (Fig. 4).

Acknowledgments

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References and notes

1. Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1988**, *189*, 185.
2. Broer, D. J.; Mol, G. N. *Makromol. Chem.* **1989**, *190*, 19.
3. Broer, D. J.; Boven, J.; Mol, G. N. *Makromol. Chem.* **1989**, *190*, 2225; Chain-Shu, H.; Hwai-Len, C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3929.
4. Broer, D. J.; Gossink, R. G.; Hikmet, R. A. M. *Angew. Makromol. Chem.* **1990**, *183*, 3235.
5. Hikmet, R. A. M.; Lub, J.; Broer, D. J. *Adv. Mater.* **1991**, *3*, 392.
6. Broer, D. J.. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier Science: London, 1993; Vol. 3, p 383.
7. Kelly, S. M. *Liq. Cryst.* **1998**, *24*, 71.
8. Geibel, K.; Hammerschmidt, A.; Strohmer, F. *Adv. Mater.* **1993**, *5*, 107.
9. Kurschner, K.; Strohriegl, P. *Liq. Cryst.* **2000**, *27*, 1585.
10. Kelly, S. M. *Helv. Chim. Acta* **1984**, *67*, 1572.
11. Ide, Y.; Chung, T. *J. Macromol. Sci. Phys.* **1984**, *B23*, 497.
12. Broer, D. J.; Mol, G. N. *Integration of Fundamental Polymer Science and Technology*; Elsevier: London, 1986; pp 669.
13. Hikmet, R. A. M.; Broer, D. *Polymer* **1990**, *32*, 1627; Lub, J.; Broer, D. J.; Martinez, M. E.; Mol, G. N. *Liq. Cryst.* **1998**, *24*, 375.
14. Hikmet, R. A. M. *Liq. Cryst.* **1991**, *9*, 405.
15. Lub, J.; Broer, D. J.; Hikmet, R. A. M.; Nierop, K. G. J. *Liq. Cryst.* **1995**, *18*, 319.
16. Kelly, S. M. *Liq. Cryst. Today* **1996**, *6*, 4.
17. Fergason, J. L. U. S. Patent 4,435,047, 1984.
18. Doane, J. W.; Chidichimo, G.; Vaz, N. A. U. S. Patent 4,688,900, 1987.
19. Drzaic, P. S. *Liq. Cryst. Disp*; World Scientific: Singapore, 1995.
20. Yamagishi, F. G.; Miller, L. J.; Van Ast, C. I. *Proc. SPIE* **1989**, 1980.
21. Nolan, P.; Coates, D. *Mol. Cryst. Liq. Cryst. Lett.* **1991**, *8*, 75.
22. Gotoh, T.; Murai, H. *Appl. Phys. Lett.* **1992**, *60*, 392.
23. Nicoletta, F. P.; De Filpo, G.; Lanzo, J.; Chidichimo, G. *Appl. Phys. Lett.* **1999**, *74*, 3945.
24. Ma, Y. D.; Wu, B. G.; Xu, G. *Proc. SPIE* **1990**, *1257*, 46.
25. Hikmet, R. A. M. *J. Appl. Phys.* **1990**, *68*, 1.
26. Hikmet, R. A. M.; Zwerver, B. H. *Liq. Cryst.* **1992**, *12*, 319.
27. Yang, D. K.; Chien, L. C.; Doane, J. W. *Appl. Phys. Lett.* **1992**, *60*, 3102.
28. Drzewiński, W.; Dąbrowski, R.; Czupryński, K. *Pol. J. Chem.* **2002**, *76*, 273–284.
29. Demus, D.; Richter, L. *Textures of Liquid Crystals*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1978; pp 16–26.