Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Wu, Chang-Cheng(2007) 'Synthesis and liquid crystalline properties of a series of cholesterol-based dimesogenic compounds', Liquid Crystals, 34: 3, 283 — 288
To link to this Article: DOI: 10.1080/02678290601111390
URL: http://dx.doi.org/10.1080/02678290601111390

Liquid Crystals, Vol. 34, No. 3, March 2007, 283–288

Synthesis and liquid crystalline properties of a series of cholesterol-based dimesogenic compounds

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(*Received 14 April 2006; in final form 21 August 2006; accepted 13 September 2006*)

The synthesis and mesomorphic properties of a series of novel dimesogenic compounds containing the cholesteryl ester unit and a phenyl benzoate group are reported. The two mesogenic units of these compounds are linked through dicarboxylic ester bonds, with alkylene spacer lengths of 2, 4, 6 and 8 methylene units. The chemical structures and liquid crystalline properties of this series of compounds were characterized by FTIR, ^{1}H NMR, hot stage-coupled polarizing microscopy and DSC. The results show that this series of compounds are cholesteric liquid crystals over a wide range, both during heating and cooling, and they exhibit iridescent colours in the liquid crystalline state.

1. Introduction

During the past two decades, the dimesogenic compounds (dimers) composed of either two structurally identical (symmetrical) or non-identical (unsymmetric) mesogenic units, linked through a flexible central spacer such as a polymethylene group, have attracted much attention. These compounds can not only be regarded as model compounds for liquid crystal polymers, but they also have many interesting liquid crystalline (LC) properties [1–4]. In particular, unsymmetric dimers with one substituted aromatic groups and one cholesteryl moiety are especially interesting because they are chiral and strongly asymmetric. Many unsymmetric dimers that possess a cholesteryl ester unit joined to an aromatic mesogenic moiety such as a benzoate ester, Schiff's base, azobenzene or biphenyl have been synthesized [5–13]. These cholesterol-based dimers exhibit a strong odd–even effect in the phase transitional properties depending on the parities of the spacer and terminal group attached to the aromatic rings; and some show unique phase transitions because of the possible formation of a wide variety of mesomorphic phases. However, the correlation between the structure of unsymmetric dimers and their LC properties is far from established.

The LC properties of unsymmetric cholesterol-based dimers may be affected by spacer length and parity, the type of bridging group between the two aromatic rings of the non-cholesteryl moiety, the length of the terminal group attached to the aromatic rings, as well as the type of linking group between the spacer and mesogenic units, such as ethers and esters. In the dimers described above, a cholesteryl ester unit and an aromatic moiety were usually linked through an ester bond on the cholesterol side and an ether bond on the aromatic mesogenic side, with a polymethylene spacer or two ether bonds between the spacer and mesogenic units. Very recently, Tamaoki *et al.* synthesized seven cholesterol-based azobenzene dimers in which the two mesogenic units are linked through 10,12-docosadiynedioic or docosanedioic carboxylic ester bonds. Most of these compounds exhibited only one liquid crystalline phase (smectic or cholesteric) during both heating and cooling. Their LC properties are quite different from those of cholesterol-based dimers in which the two mesogenic units are linked through one ester bond and one ether bond, or two ether bonds with a polymethylene spacer [14].

Moreover, cholesterol-based compounds have many unique optical properties, such as selective reflection, circular dichroism, electro-optical and magneto-optical effects; they could be applied to optical storage, optical switching, nonlinear optics and liquid crystal display devices [15–17].

In the present work, a series of novel dimesogenic compounds containing cholesteryl and phenyl benzoate groups were synthesized. The two mesogenic units were linked through dicarboxylic ester bonds, and the alkylene spacer lengths were 2, 4, 6 and 8 methylene units. The LC properties of these compounds were also characterized. The results show that this series of compounds are cholesteric liquid crystals over a wide range of temperature during heating and cooling, and that they exhibit iridescent colours in the LC states.

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601111390

2. Experimental

2.1. *Characterization*

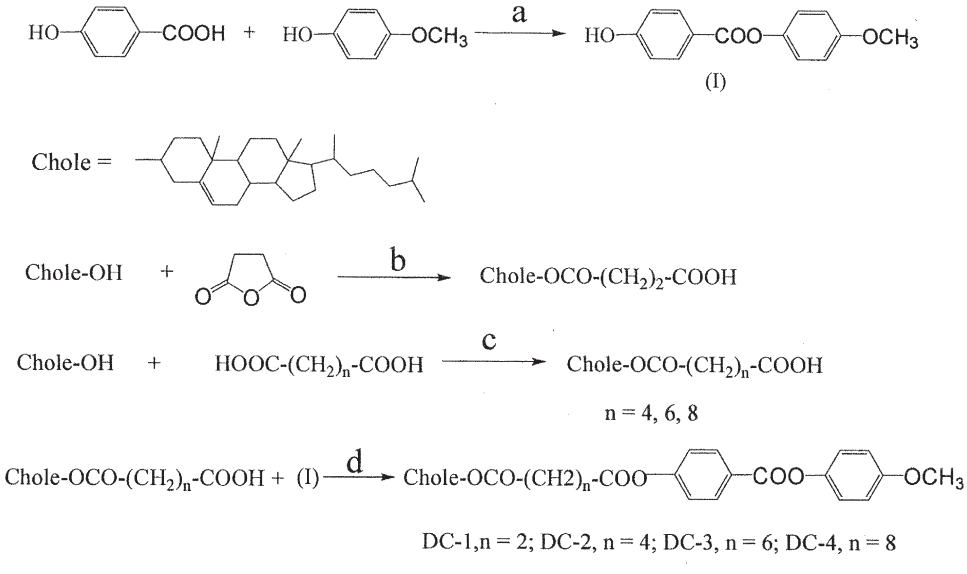
Chemical structures of the intermediates and dimesogenic compounds were characterized with FTIR using a Bruker Tensor 307 spectrometer and ^{1}H NMR spectroscopy using a Bruker 300 MHz instrument with tetramethylsilane as internal standard. The melting point and phase transitions of the intermediates and dimesogenic compounds were determined by means of an Olympus BX51 polarizing optical microscope (POM) equipped with a Linkam THMS600 hot stage. A differential scanning calorimeter (Perkin Elmer DSC-7) was used to measure the transformation temperature and transformation enthalpy at heating and cooling rates of 10°C min^{-1}.

2.2. *Synthesis*

Cholesterol, as a biochemical reagent, was obtained from Tianjin Yingbo Biochemical Reagent Company (Tianjin, PR, China); *N*, *N*-dicylcohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were used as received (Arcos). Tetrahydrofuran (THF) was distilled from sodium–benzophenone; other solvents and reagents were AR or CP grade and used without further purification. The synthetic route used to prepare this series of dimesogenic compounds containing cholesteryl and phenyl benzoate groups is shown in scheme 1.

2.2.1. 4-methoxyphenyl 4-hydroxybenzoate (I) [18]. To a suspension of 4-methoxyphenol (18.6 g, 0.15 mol) and 4-hydroxybenzoic acid (13.8 g, 0.10 mol) in toluene (500 ml), concentrated sulphuric acid (1.5 g) and boric acid (0.31 g) were added. The reaction mixture was heated under reflux for 21 h under a Dean-Stark trap. The solvent was then removed under reduced pressure, and the product washed twice with diethyl ether/petroleum ether (30–60°C) (1/1). The resulting 4-methoxyphenyl 4-hydroxybenzoate was recrystallized from acetonitrile to give 18.3 g of pure product, yield 75%, m.p. 191–192°C. FTIR (KBr, cm^{-1}): 3388, 1708, 1509, 1186, 858. ^{1}H NMR (CD_3COCD_3, ppm): 3.80 (s, 3H), 6.95 (2d, 4H), 7.25 (2d, 2H), 8.05 (2d, 2H).

2.2.2. Cholesterol-based carboxylic acids. Succinic acid monocholesteryl ester was synthesized using equal molecular quantities of cholesterol and succinic anhydride as raw materials in a heptane reaction medium with a trace of pyridine as catalyst. The reaction mixture was heated under reflux for 21 h and cooled to room temperature. The precipitated product was recrystallized from acetone; yield 73%, m.p.179–181°C. FTIR(KBr, cm^{-1}): 2942, 1730, 1710, 1378, 1317, 1180, 1001. ^{1}H NMR ($CDCl_3$, ppm): 5.39 (m, 1H), 4.66 (m,



Scheme 1. Synthesis route for the series dimesogenic compounds DC-1 to DC-4.

1H), 2.62–2.70 (2t, 4H), 2.34 (d, 2H), 1.8–0.69 (broad, 41H).

In the synthesis of adipic acid monocholesteryl ester, DCC (5 mmol, 0.5 equiv) was added to a solution of adipic acid (10 mmol, 1 equiv) in 40 ml dry THF. The mixture was stirred at room temperature for 12 h; cholesterol (5 mmol, 0.5 equiv) and DMAP (1 mmol, 0.1 equiv) were then added, and stirring continued for a further 12 h. The dicyclohexylurea formed was removed by filtration, and the filtrate was poured into a large amount of distilled water. The resulting precipitate was filtered and washed with hot water three times, dried in air and recrystallized twice from heptane; yield 62%. Cr124Ch150.5I. FTIR (KBr, cm^{-1}): 2939, 1723, 1697, 1378, 1261, 1173, 1008. ^1H NMR ($CDCl_3$, ppm): 5.37 (m, 1H), 4.62 (m, 1H), 2.31–2.37 (d, 6H), 0.67–2.1 (broad, 45H).

The synthesis procedures for suberic acid monocholesteryl ester and sebacic acid monocholesteryl ester were similar to the procedure described for adipic acid monocholesteryl ester. *Suberic acid monocholesteryl ester*: Yield 58%. Cr118Ch134I. FTIR (KBr, cm^{-1}): 2938, 1737, 1705, 1378, 1326, 1170, 1005. ^1H NMR ($CDCl_3$, ppm): 5.39 (m, 1H), 4.64 (m, 1H), 2.28–2.36(m, 6H), 1.8–0.69(broad, 49H). *Sebacic acid monocholesteryl ester*: Yield 56%. Cr112Ch121I. FTIR (KBr, cm^{-1}): 2936, 1734, 1708, 1377, 1325, 1168, 1005. ^1H NMR ($CDCl_3$, ppm): 5.39 (m, 1H), 4.66 (m, 1H), 2.20–2.41 (m, 6H), 0.69–2.00 (broad, 53H).

2.2.3. Cholesterol-based dimesogenic compounds (DC-1, DC-2, DC-3 and DC-4). The series of cholesterol-based dimesogenic compounds were synthesized using a common general synthetic procedure. Thus, equal molecular quantities of cholesterol-based carboxylic acid and 4-methoxyphenyl 4-hydroxybenzoate were dissolved in dry THF; an equal molecular quantity of DCC and a 10% quantity of DMAP were added, and the reaction mixture was heated under reflux for 12 h. The dicyclohexylurea formed was removed by filtration. The product obtained on evaporation of the filtrate was purified by column chromatography on silica gel (100–200 mesh) using a mixture of petroleum ether (60–90°C) and ethyl acetate (4/1) as eluant, yielding a white solid. The products of 4-methoxyphenyl 4-hydroxybenzoate reacted with succinic acid monocholesteryl ester, adipic acid monocholesteryl ester, suberic acid monocholesteryl ester and sebacic acid monocholesteryl ester are denoted as DC-1, DC-2, DC-3 and DC-4, respectively.

DC-1: Yield 65%. FTIR (KBr, cm^{-1}): 2939, 1732, 1602, 1510, 1313, 1194, 869, 832. ^1H NMR ($CDCl_3$, ppm): 8.24(d, 2H), 7.28 (d, 2H), 7.15 (d, 2H), 6.97 (d, 2H), 5.40 (m, 1H), 4.73 (m, 1H), 3.83 (s, 3H), 2.92 (t, 2H), 2.78(t, 2H), 0.70–2.4 (broad, 43H). DC-2: Yield 63%. FTIR (KBr, cm^{-1}): 2947, 1732, 1606, 1509, 1378, 1167, 857, 826. ^1H NMR ($CDCl_3$, ppm): 8.25(d, 2H), 7.27 (d, 2H), 7.15 (d, 2H), 6.97 (d, 2H), 5.40 (m, 1H), 4.70 (m, 1H), 3.84 (s, 3H), 2.64 (t, 2H), 2.38(2d, 4H), 0.70–2.10 (broad, 45H). DC-3: Yield 62%. FTIR (KBr, cm^{-1}): 2936, 1733, 1606, 1510, 1331, 1196, 870, 820. ^1H NMR ($CDCl_3$, ppm): 8.25(d, 2H), 7.28 (d, 2H), 7.15 (d, 2H), 6.97 (d, 2H), 5.40 (m, 1H), 4.65 (m, 1H), 3.84 (s, 3H), 2.61 (t, 2H), 2.34 (t, 4H), 0.69–2.10 (broad, 49H). DC-4: Yield 60%. FTIR (KBr, cm^{-1}): 2937, 1738, 1603, 1507, 1374, 1199, 872, 802. ^1H NMR ($CDCl_3$, ppm): 8.24(d, 2H), 7.28 (d, 2H), 7.15 (d, 2H), 6.97 (d, 2H), 5.40 (m, 1H), 4.73 (m, 1H), 3.83 (s, 3H), 2.60 (t, 2H), 2.42 (2d, 4H), 0.70–2.10 (broad, 53H).

3. Results and discussion

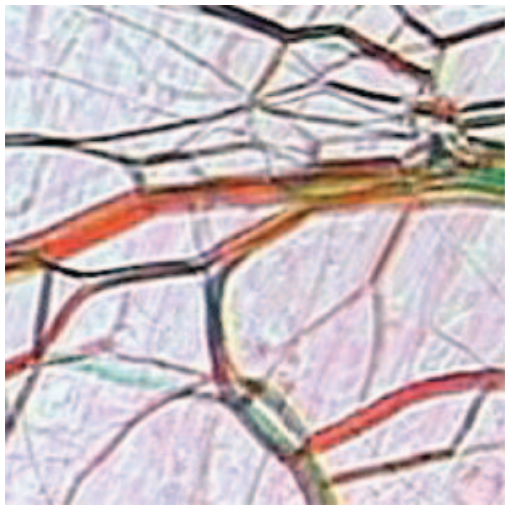
3.1. *Synthesis*

This series of dimesogenic compounds were synthesized according to scheme 1. Four cholesterol-based carboxylic acids were obtained from the reaction of cholesterol with the corresponding anhydride or dicarboxylic acid. The dimesogenic compounds were then prepared by the reaction of the cholesterol-based carboxylic acids with 4-methoxyphenyl 4-hydroxybenzoate in the presence of DCC/DMAP catalysts. The chemical structures and purities of all these dimesogenic compounds and intermediates were confirmed by FTIR, ^1H NMR and thin layer chromatography (TCL).

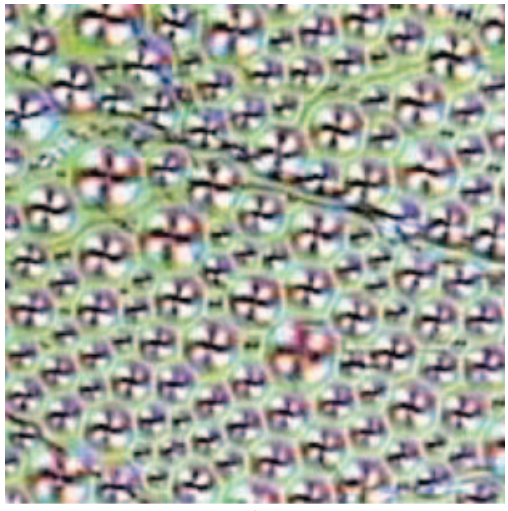
3.2. *Thermotropic behaviour*

The liquid crystalline properties of the dimesogenic compounds were characterized by hot stage coupled polarizing microscopy and DSC. In the POM observation of DC-1, when it was heated at 171°C, a typical cholesteric oily-streak texture appeared, as can be seen from figure 1 (*a*). By further heating to 231°C, the LC texture was turned to a droplet texture, figure 1 (*b*), and the birefringence disappeared at 233.1°C. When the isotropic phase was cooled to 225.8°C a focal-conic texture appeared, figure 1 (*c*), and the LC phase began to crystallize at 88°C; the focal-conic texture was easily transformed to an oily-steak texture on shearing, confirming that the LC phase was cholesteric.

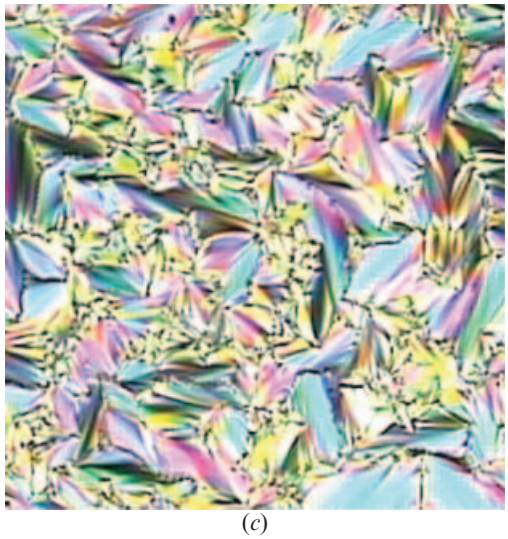
During heating of DC-2, DC-3 and DC-4 in POM observation, oil-streak textures appeared at 84, 106 and 87°C, respectively, and their droplet textures appeared at 215, 186 and 175, respectively. On further heating, they isotropized at 216.5, 191.8 and 176.2°C,



(*a*)



(*b*)



(*c*)

Figure 1. POM micrographs of compound DC-1 (200 ×): (*a*) oily-streak texture at 177°C on heating; (*b*) droplet texture at 231°C on heating; (*c*) focal-conic texture at 200°C on cooling.

respectively. During cooling of DC-2, DC-3 and DC-4 in POM observation, focal-conic textures appeared at 204.5, 188 and 168.2°C, respectively. Coexistent liquid crystal structures of DC-2 and DC-4 appeared at 49 and 48°C, respectively, and were retained at room temperature. In DC-3, the transition of cholesteric phase to crystal phase occurred at 80.5°C.

During both heating and cooling of these dimesogenic compounds, iridescent colours appeared in the cholesteric LC states. This property of the cholesteric phase is due to the presence of a helical super-structure. Variation in temperature results in the change of the pitch of the helical structure, leading to the colour changes at different temperature at different observation angles. For example, when DC-4 is heated into the LC phase, it appears red in the vertical direction and green in the oblique direction; as the temperature increases, the red colour changes to yellow and green in the vertical direction, and the green colour changes to blue and purple in the oblique direction. The colour changes are reversed during cooling. With this interesting optical property of the cholesteric phase, these dimesogenic compounds are potential candidates for applications in optical exhibitors and other devices.

The DSC analysis results show a slight difference from the observations by POM, because some of the DSC transition peaks are somewhat broad. The DSC traces for DC-1, DC-1, DC-3 and DC-4 during heating and cooling are shown in figures 2 and 3, respectively. During heating two peaks appeared in the DSC curves of DC-1, DC-2 and DC-3; one is the melting transition

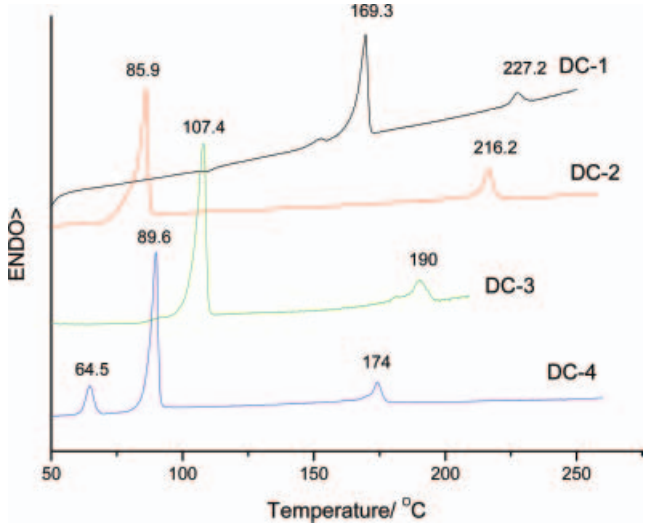


Figure 2. DSC traces for the dimesogenic compounds during heating.

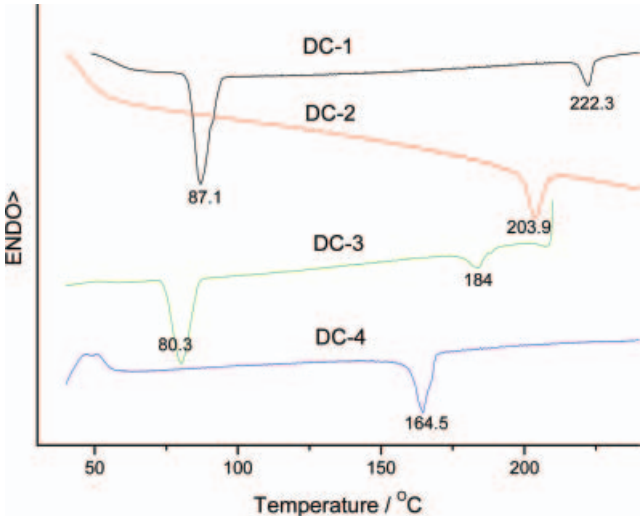


Figure 3. DSC traces for the dimesogenic compounds during cooling.

at lower temperature, the other is the LC to isotropic (I) phase transition at higher temperature. In the DSC curve of DC-4, three peaks appeared at peak values of 64.5, 89.6 and 174°C; accompanying POM observations showed that they represented crystal to crystal transition, melting transition and LC to I phase transition, respectively. During cooling two peaks appeared on the DSC curves of DC-1 and DC-3, revealing an I to LC phase transition at higher temperature and LC to crystal transition at lower temperature. In the DSC curves of DC-2 and DC-4, only one peak was seen, corresponding to the I to LC phase transition; the absence of a LC to crystal transition was due to the formation of the coexistent LC/crystal structures at low temperatures. The phase transition temperature peak values and enthalpies of these dimesogenic compounds are listed in table 1.

From the results shown in table 1, we see that, with increase in alkylene spacer length, the LC to I and I to LC transition temperatures fell steadily. The crystal to LC transition temperatures also fell, except on going from DC-2 to DC-3. These observations indicate that the longer the alkylene spacer length, the more flexible is the dimesogenic compound, so that the liquid crystalline phase appears at a lower temperature.

In the earlier studies, chiral dimers possessing a cholesteryl ester unit as the chiral entity joined to an aromatic moiety such as, a Schiff's base, azobenzene, stilbene, or biphenyl through a polymethylene spacer, usually exhibited a rich polymorphic squence including an incommensurate smectic A mesophase. In most of these compounds, the two mesogenic groups were linked through an ester (or ether) bond on the cholesteryl ester unit side, and an ether bond on the aromatic mesogenic unit side with a polymethylene spacer [5–13]. In this report, all the dimesogenic compounds, in which the cholesteryl ester unit and aromatic moiety are linked by a polymethylene spacer with two ester bonds, exhibit only one cholesteric phase. The formation of LC phases of cholesterol-based dimesogenic compounds may be effected by many factors, such as the length and parity of spacer, the type of bridging group between the two aromatic rings of the non-cholesteryl moiety, the length of terminal group attached to the aromatic rings, the type of linking groups between the spacer and mesogenic units, etc. This result prompted us to study the relationship between the chemical structure and physical properties of chiral unsymmetric dimers in more detail.

4. Conclusions

A series of novel dimesogenic compounds containing cholesteryl and phenyl benzoate groups were synthesized. All these compounds were cholesteric liquid crystals over a wide range of temperature during both heating and cooling, and they exhibited iridescent colours in the liquid crystalline states. With increasing length of alkylene spacer, the temperatures of liquid crystalline to isotropic, and isotropic to liquid

Table 1. Phase transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of the dimesogenic compounds DC1–DC4. Ch=cholesteric, I=isotropic, Cr=crystal.

Compound	Heating	Cooling
DC-1	Cr 169.3(39.17) Ch 227.2(4.05) I	I 222.3(4.21) Ch 87.1(26.35) Cr
DC-2	Cr 85.9(22.65) Ch 216.2(4.31) I	I 203.9(5.88) Ch 49[a]
DC-3	Cr 107.4(30.73) Ch 190(5.31) I	I 184(4.78) Ch 80.3(23.44) Cr
DC-4	Cr_1 54.5(7.08) Cr_2 89.6(36.22) Ch 174(6.93) I	I 164.5(6.09) Ch 48[a]

[a]The liquid crystalline phase and crystal coexist at room temperature, as observed by POM.

crystalline, phase transitions decreased; the crystal to liquid crystalline phase transition temperatures decreased as the alkylene spacer lengths increased, except on going from DC-2 to DC-3.

Acknowledgements

The author is grateful to the Tianjin Municipal Education Commission for financial support (20040102).

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