Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006

To cite this article: Takahiro Uedaira & Naoyuki Koide (2001): Thermal Properties of Pentaerythritol Derivatives with Chiral Moiety, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 23-32

To link to this article: http://dx.doi.org/10.1080/10587250108025278

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 23-32
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Thermal Properties of Pentaerythritol Derivatives with Chiral Moiety

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Pentaerythritol derivatives containing four mesogenic groups with chiral moieties were synthesized. Cholesterol and 2-methyl-1-butanol were used as a chiral moiety. All compounds which derivate from pentaerythritol and mesogenic group showed a glass transition temperature above room temperature. Crystallization from melt of these compounds was strongly suppressed. The compound that the mesogenic group has one benzene ring linked by ester bonding between mesogenic and cholesteryl group exhibited the smectic A_1 phase. While the compounds that the mesogenic group has two benzene rings linked by ester bonding with cholesteryl group exhibited the cholesteric phase. The compounds that the mesogenic group has three benzene rings linked by one ester bonding with 2-methlbutyl group also exhibited the smectic A_2 phase and the cholesteric phase.

Keywords: pentaerythritol derivative; cholesteric phase; low molar mass liquid crystalline vitrifying material

INTRODUCTION

Glassy liquid crystals are generally realized the liquid crystalline polymer(LCP)s. LCPs also easily fix their orientation of the liquid crystalline phase below a glass transition temperature. In particular, the investigations to be fixed selective reflection film in the cholesteric

mesophase at room temperature have been studied by many research groups.[1],[2]

In this study, we investigated a new type of low molar mass liquid crystalline vitrifying materials with a chiral moiety to be fixed the orientation of cholesteric mesophase. As a role, most low molar mass liquid crystalline materials will crystallize on cooling from the liquid crystalline state. But certain compounds were reported as an exception. Those compounds usually have oligomeric structure and have molecular weight not less than 2000 from roughly 1000 at least. Pentaerythritol derivatives,[3],[4] cyclohexane derivatives[5],[6] and cyclic siloxane compounds are generally used as a flexible group in the center part of the oligomeric molecules. We selected pentaerythritol derivatives (Figure 1). We synthesized pentaerythritol derivatives that have four mesogens containing a chiral moiety. Cholesterol and 2-methyl-1-butanol were used as a chiral moiety (Figure 2).

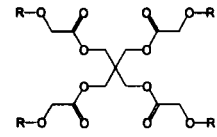
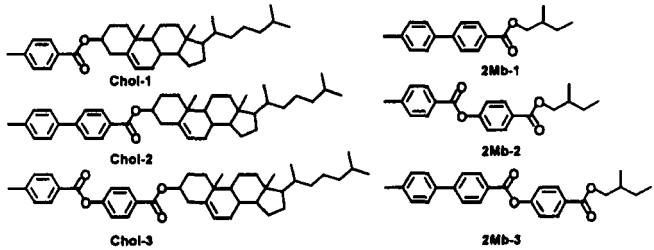


FIGURE 1 Center part of vitrifying materials



EXPERIMENTAL

Characterization

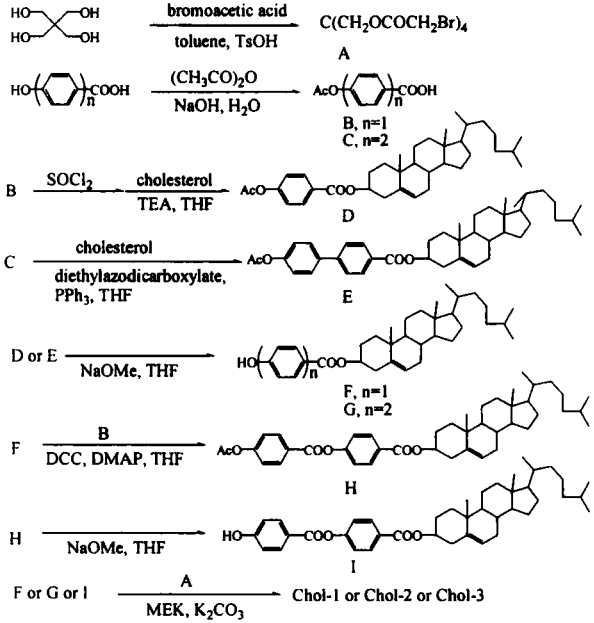
All pentaerythritol derivatives and their precursors were characterized by ^{1}H NMR (JNM-LA400 and JNM-LA500) using solution in $CDCl_3$ or DMSO (tetramethylsilane as internal standard), and by FT-IR spectrometry (JEOL JIR7000). A NIKON UFX-II A polarizing optical

FIGURE 2 Mesogenic groups with chiral moiety

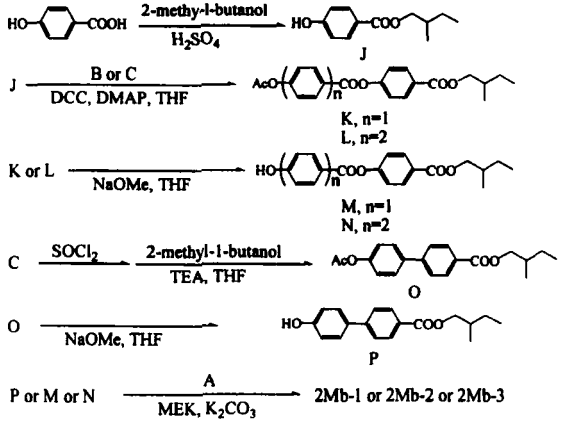
microscope (POM) equipped with a Mettler FP80 HT Central Processor and a Mettler FP82 HT hot stage was used to study the mesophase texture and to determine the phase transition temperatures. The phase transition temperature and heats of phase transition were measured with a Mettler DSC821^e thermosystem differential scanning calorimeter (DSC). The scan rate was varied in the range of 5-10℃min^{-1}. The phase transition temperatures were taken at the endo-thermic maxima of the heating curves at a scan rate of 10 ℃ min^{-1}. Glass transition temperatures were taken from the inflexion points. X-ray diffraction measurements on a liquid crystalline phase of the compounds were recorded with a RIGAKU RINT 2500 series. The samples, in glass capillaries, were held in a temperature-controlled cell

Synthesis

The total syntheses of vitrifying compounds are shown in Scheme 1 and 2, respectively.



SCHEME 1 Syntheses of vitrifying compounds with cholesteryl group as a chiral moiety



SCHEME 2 Syntheses of vitrifying compounds with 2-methylbutyl group as a chiral moiety

Pentaerythrityl tetrabromoacetate (A)

The mixture of pentaerythritol (4.9g), bromoacetic acid (25g), 4-toluenesulphonic acid (3.1g) and 200ml of toluene was heated at reflux for 2 hour with constant removal water (Dean and Stark apparatus). The hot mixture was poured into the mixture of 200g of ice and 200ml of a 10% aqueous sodium hydroxide solution. After separation, the toluene layer was washed with 200ml of water, dried over anhydrous magnesium sulfate and evaporated. The product was crystallized slowly and was dried under vacuum. The yield of (A) was 19.3g(86.5%), m.p. 44℃.

^{1}H NMR ($CDCl_3$, δppm) : 4.45(s, 4H), 4.70(s, 4H)

IR (nujol, cm^{-1}) : 1733

4-Acetoxybenzoic acid (B) and 4,4'-acetoxybiphenylcarboxyric acid (C)

The hydroxyl group of 4-hydrobenzoic acid (PHB) or 4,4'-hydroxybiphenylcarboxylic acid (HBCA) was protected by an acetyl group. To a solution of PHB (125g) and 1.5M aqueous sodium hydroxide, acetic anhydride (209g) was added dropwise at 0℃. The reaction mixture was stirred at room temperature for 1 hour, and

hydrochloric acid was added, and the mixture was stirred for 1 hour. The mixture was washed with water for three times and recrystallized from the methanol solution. The product was dried under vacuum at 60℃. The yield of (B) was 129.3g(70%).
IR (nujol, cm^{-1}) : 1602, 1687, 1753
The acetyl protection of HBCA was carried out with a similar method to the acetyl protection of PHB. The yield of (C) was 7g(59%).
IR (nujol, cm^{-1}) : 1529, 1565, 1608, 1683, 1747

Cholesteryl 4-acetoxybenzoate (D)
The mixture of 4-acetoxybenzoic acid (B, 13g), thionyl chloride (150ml), and a small amount of N,N-dimethylformamide was stirred at 50℃ for 5 hour. Thionyl chloride was removed under reduced pressure, and then the residue was dissolved in dry tetrahydrofuran. The product was added dropwise into a solution of cholesterol (17.1g), triethylamine (14.6g), and dry tetrahydrofuran (200ml). The mixture was stirred under nitrogen at room temperature for 24 hour. Upon evaporating the solvent in vacuum, the residue was washed with dilute aqueous sodium hydroxide solution and water for several times, and finally washed with methanol. The product was recrystallized from acetone to yield 11.7g (48.2%)
^{1}H NMR ($CDCl_3$, δppm) : 0.70(s, 3H), 0.80-2.10(m, 40H), 2.40(s, 3H), 2.50(d, 2H), 4.85(m, 1H), 5.45(s, 1H), 7.15(d, 2H), 8.05(d, 2H)
IR (nujol, cm^{-1}) : 1602, 1720, 1753, 1764,

4-Cholesteryl 4'-acetoxybiphenyl carboxylate (E)[7]
The mixture of 4,4'-acetoxybiphenylcarboxylic acid (C, 7g), cholesterol (10.6g), triphenyl phosphine (14.3g) and dry tetrahydrofuran (300ml) were cooled at −15 ℃ , and diethylazodicarboxylate (8.1g) were dropwized into the mixture. After stirring at 48 hour, the solvent was evaporated. The crude mixture was poured into methanol and was washed with methanol at 3 times. The product was dried under vacuum at 60℃. The yield of (E) was 5.9g(34%).
^{1}H NMR ($CDCl_3$, δppm) : 0.70(s, 3H), 0.80-2.10(m, 40H), 2.40(s, 3H), 5.25(m, 1H), 5.30(s, 1H), 7.20(d, 2H), 7.60(dd, 4H), 8.05(d, 2H)
IR (nujol, cm^{-1}) : 1608, 1710, 1749

Deprotecting reaction of (D) and (E)
Cholesteryl 4-hydroxybenzoate (F) and 4-cholesteryl

4'-hydroxybiphenylcarboxylate (G) were synthesized by deprotecting reaction of (D) or (E). Acetyl protected compound (D, 8.9g) were dissolved a minimum amount of tetrahydrofuran. Sodium methylate (1.0g) diluted with methanol was dropwized into the solution, and after three minutes later, the crude product was poured into 10% of aqueous solution of hydrochloric acid. After washing with water and methanol at three times, the crude product was recrystallized with chloroform. The product was dried under vacuum at 60℃. The yield of (F) was 7.7g(93%).

IR (nujol, cm^{-1}) : 1608, 1672, 3309

The acetyl deprotection of (E) was carried out with a similar method of (D). The yield of (G) was 1.3g(93%).

IR (nujol, cm^{-1}) : 1602, 1687, 3423

Cholesteryl 4-(4-acetoxybenzoyloxy)-benzoate (H) and cholesteryl 4-(4-hydroxybenzoyloxy)-benzoate (I)

The mixture of cholesteryl 4-hydroxybenzoate (F, 5.0g), 4,4'-acetoxybiphenylcarboxyric acid (C, 2.3g) and dimethylaminopyridine (0.2g) was dissolved in 200ml of dry tetrahydrofuran. Tetrahydrofuran solution of dicyclohexylcarbodiimide (2.6g) was dropwized into the mixture. The reaction mixture was stirred at room temperature for 24 hour. After the by-product was removed by filtration, the solvent was evaporated. The crude mixture was dissolved in chloroform and the chloroform layer was washed with water at three times, and then dried over magnesium sulphate. After the solvent was evaporated, the residue was washed with methanol at three times. The product was dried under vacuum at 60℃. The yield of (H) was 1.1g(17%).

^{1}H NMR ($CDCl_3$, δppm) : 0.70(s, 3H), 0.80-2.10(m, 40H), 2.40(s, 3H), 2.50(d, 2H), 4.40(m, 1H), 5.45(s, 1H), 7.25(m, 4H), 8.10-8.20(dd, 4H)

IR (nujol, cm^{-1}) : 1606, 1706, 1726, 1758

The acetyl deprotection of (H) was carried out with a similar method of (D). The yield of (G) was 0.2g(33%).

^{1}H NMR ($CDCl_3$, δppm) : 0.70(s, 3H), 0.80-2.10(m, 40H), 2.50(d, 2H), 4.80(m. 1H), 5.45(s. 1H), 6.25(s, 1H), 6.95(d, 2H), 7.30(d, 2H), 8.10(dd, 4H)

IR (nujol, cm^{-1}) : 1606, 1706, 1742, 3390

Pentaerythrityl tetra-(4-cholesteryloxycarbonylphenoxy)acetate

The mixture of cholesteryl benzoate (F, 2.0g), potassium carbonate

(1.6g), 2-butanone and small amount of potassium iodine was refluxed at 90℃ for 2 hour. The 2-butanone solution of pentaerythrityl tetrabromoacetate (A, 0.49g) was dropwized into the mixture, and refluxed at 90℃ for 6 hours. After 2-butanone was evaporated, the mixture was poured into dilute aqueous sodium hydroxide solution and washed with water. The raw material was extracted in acetone with a Soxhlet extractor, and main product was recovered with chloroform. The product was dried under vacuum at 60℃.

^{1}H NMR ($CDCl_3$, δppm) : 0.6-2.1(m, 172H), 2.45(d, 8H), 4.00(s, 8H), 4.60(s, 8H), 4.80(m, 4H), 5.40(s, 4H), 6.85(d, 8H), 7.95(d, 8H)

IR (nujol, cm^{-1}) : 1510, 1606, 1712, 1766

RESULT AND DISCUSSION

Phase transition

Table 1 shows the phase transition temperatures of vitrifying materials. Chol-1 showed a glass transition temperature at 85.4℃ by a DSC measurement. The compounds showed a fan-shaped texture on cooling from the isotropic phase by a POM measurement. The X-ray diffraction

TABLE 1 Phase transition temperatures of vitrifying compounds

compounds	phase transition temperatures	specific rotation	molecular weight
Chol-1	$g \underset{82.3}{\overset{85.4}{\rightleftharpoons}} SmA_1 \underset{243.9}{\overset{248.6}{\rightleftharpoons}} I$	-11.7	2323.03
Chol-2	$g \underset{99.3}{\overset{101.7}{\rightleftharpoons}} I$	-17.7	2627.67
Chol-3	$g \underset{90.6}{\overset{95.9}{\rightleftharpoons}} Ch \xrightarrow{249.3} Decomp.$	-1.36	2803.71
2Mb-1	$g \underset{32.9}{\overset{36.3}{\rightleftharpoons}} I$	-1.36	1385.61
2Mb-2	$g \underset{40.4}{\overset{40.7}{\rightleftharpoons}} I$	+21.9	1561.65
2Mb-3	$g \underset{36.3}{\overset{39.8}{\rightleftharpoons}} SmA_2 \underset{160.6}{\overset{164.4}{\rightleftharpoons}} Ch \xrightarrow{212.8} Decomp.$	+12.1	1866.04

g : glassy state, I : isotropic phase, M : mesophase , SmA : smectic A phase, Ch : cholesteric phase, Decomp : thermal decomposition

pattern of Chol-1 at 180℃ showed a strong first- and weak second-order reflection in the small angle region and a broad reflection in the wide angle region, respectively. The first strong peak at 1.70° corresponded to the molecular length of the compounds. The calculated value for Chol-1 is 51.9Å. Therefore, Chol-1 showed a smectic A_1 phase. Chol-2 showed a glass transition temperature at 101.7℃. This compound did not show any birefringence at the measured temperature region. Chol-3 showed a glass transition temperature at 95.9℃. This compound exhibited a schlieren and fingerprint texture on cooling from the isotropic phase. Only Chol-3 containing of the cholesteryl group for chiral moiety showed a cholesteric mesophase.

2Mb-1 and 2Mb-2 showed a glass transition temperature at 36.3℃ and 40.7℃, respectively. These compounds did not show any birefringence at the measured temperature region. However, 2Mb-3 showed a glass transition temperature at 39.8℃, and exhibited a fingerprint texture between 164.4℃ and 212.8℃, and the pitch of a fingerprint texture changed with temperature. Therefore 2Mb-3 showed a cholesteric phase at this temperature region. Figure 3 shows the X-ray diffraction patterns of 2Mb-3 at 140 ℃ and 200 ℃, respectively. The broad peak at 4.00 ° corresponded to the half of a molecular length. The calculated value for 2Mb-3 is 22.1 Å. Therefore, 2Mb-3 showed a smectic A_2 phase between 39.8 ℃ and 164.4℃.

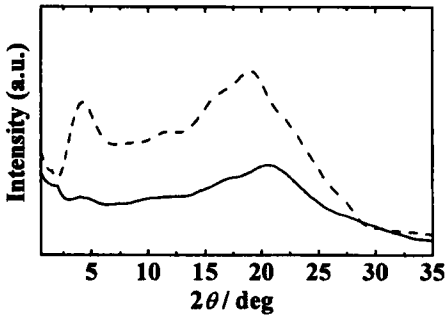


FIGURE 3. X-ray diffraction patterns of 2Mb-3 at 200℃ (solid line) and 140℃ (dashed line)

Vitrifying properties

All vitrifying compounds we synthesized showed a grass transition temperature (Table 1). The compounds containing cholesteryl group showed glass transition temperature in the vicinity of 80 and 100℃, and the one containing 2-methylbutyl group showed a glass transition

temperature between 35℃ and 45 ℃. The grass transition temperatures of the compounds containing cholesteryl group were higher than those of the compounds containing of 2-methylbutyl group.

Figure 4 shows the X-ray diffraction patterns of Chol-1 at 180℃ and room temperature, respectively. The first order peak of this diffraction pattern at room temperature was a same position as that of 180℃. And in the POM measurement of Chol-1, a fan shaped texture was observed at 180℃ (Figure 5(a)), and the texture was frozen at room temperature (Figure 5(b)). As results of X-ray diffraction and POM measurements, the smectic layer structure was fixed at room temperature.

2Mb-3 showed two kinds of mesophase, one is a smectic A_2 phase between 39.8 ℃ and 164.4℃, and the other is a cholesteric phase between 164.4℃ and 212.8℃. In the POM measurement, a fingerprint texture was observed in a temperature range of a cholesteric phase. On the other hand, an optical texture in the

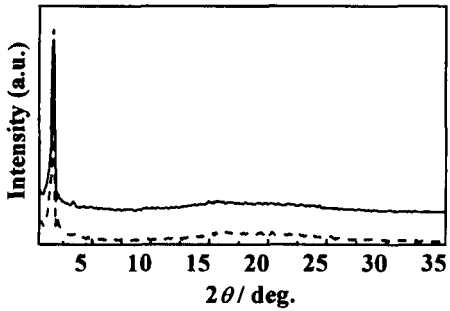
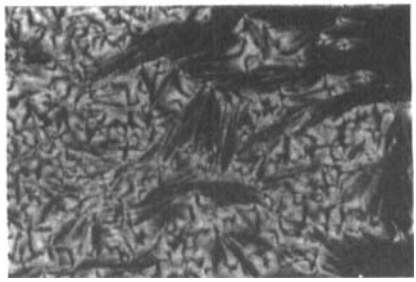


FIGURE 4. X-ray diffraction patterns of Chol-1 at 180℃ (dashed line) and room temperature (solid line)

(a)



(b)

FIGURE 5. (a) Fan-shaped texture of SmA phase of Chol-1 at 180℃. (b) Frozen texture of Chol-1 at room temperature.

smectic A_2 phase was observed upon cooling to 140℃ at the scanning rate of 10℃min^{-1}. Furthermore, with cooling to room temperature, this texture was frozen at temperature below a glass transition temperature. On the other hand, the finger print texture was frozen at room temperature by suddenly cooled from 200℃ with liquid nitrogen. The structure of cholesteric phase was fixed at room temperature by rapidly quenching with liquid nitrogen.

CONCLUSION

A new type of low molar mass liquid crystalline vitrifying materials has been prepared by the use of pentaerythritol derivatives. Chol-1 showed a smectic A_1 phase and the layer structure of a smectic A_1 phase was fixed at room temperature. Chol-3 and 2Mb-3 displayed a cholesteric phase and the layer structure of a cholesteric phase for 2Mb-3 was fixed at room temperature by rapidly quenching with liquid nitrogen.

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