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Miroslav Kašpar [a], Alexej Bubnov [a], Věra Hamplová [a], Vladimíra Novotná [a], Iveta Lhotáková [a], Jaroslav Havlíček [b] & Michal Ilavský [c]

[a] Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

[b] Institute of Chemical Technology, Technicka, Prague, Czech Republic

[c] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic, and Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

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Miroslav Kašpar
Alexej Bubnov
Věra Hamplová
Vladimíra Novotná
Iveta Lhotáková
Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Jaroslav Havlíček
Institute of Chemical Technology, Technicka, Prague, Czech Republic

Michal Ilavský
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic, and Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Two series of new ferroelectric liquid-crystalline diols with 1,3-propandiol group connected by a flexible spacer to the mesogenic part of the molecule have been synthesized. Both series are laterally substituted by methyl, methoxy, or chlorine substituents in the meta position to the carboxylic group of the 4-alkoxybenzoate unit. Phases and phase-transition temperatures were determined by polarizing microscopy and Differential Scanning Calorimetry (DSC). Mesomorphic properties of the studied compounds are compared and the effect of lateral substitution is evaluated. These new series of diols are predestined for preparation of liquid-crystalline polyurethanes by bulk polymerization in the temperature range of the SmC^* phase.

Keywords: chiral diols; DSC studies; ferroelectric liquid crystals; monomers

Address correspondence to Alexej Bubnov, Liquid Crystal Group, Department of Dielectrics, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Prague, Czech Republic. Fax: +420286890527, Phone: +420266052134, E-mail: bubnov@fzu.cz

INTRODUCTION

Crosslinked polyurethanes are one of the major groups of polymer networks and the investigation of the relation between their structure and physical properties is of great importance, both practical and theoretical. Because of a comparatively simple buildup of the structure from hydroxyl and insulation groups, the networks based on polyols and polyisocyanates have often been used as model systems for testing theory of network formation and rubber elasticity theories, viscoelasticity, and so forth (cf. Refs. 1–4).

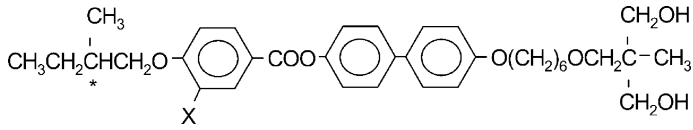
Introduction of the rigid mesogenic groups into the polymer chain (in the backbone or side chain) usually leads to liquid-crystalline polymers (LCP), which show an intermediate state of aggregation between the crystalline and amorphous structures. Generally, Liquid Crystal (LC) mesophase (showing more-ordered smectic or less-ordered nematic structure) greatly affects the physical properties of LCP. LC-ordered networks (LCN) form a recent discipline in the field of LCP; introduction of crosslinks between chains guarantees the dimensional stability of these ordered systems.

Network formation based on well-defined diols leads to controlled chain constitution with well-predicted final network structure. Introduction of the mesogenic groups into diols then allows the preparation of LC-polyurethane networks. If crosslinking proceeds in the isotropic state of the components, one can expect conventional isotropic topology. On the other hand, crosslinking in the LC state of reactants can give not only a locally anisotropic structure but macroscopically uniform as well (microscale-reinforcing effect).

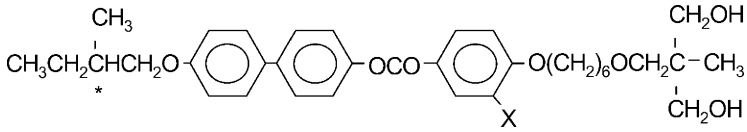
Recently, similar nonchiral liquid-crystalline diols with three phenyl rings were synthesised [5] and used for preparation of bisurethanes and polymers. The main aim of this work is to synthesize LC diols from which liquid-crystalline polyurethane networks and uncrosslinked systems could be prepared by bulk polymerization in the temperature range of the SmC^* phase using commercial diisocyanates of different rigidity.

In the case of LC diols, the introduction of two hydroxy groups at the end of the terminal chain of liquid crystals can lead to unexpected polymorphism [6]. Hydrogen bonding plays a significant role in the arrangement of molecules into layers and in some cases even in bilayers [7]. Our study is focused on the influence of the lateral substitution on the mesomorphic properties of the chiral liquid-crystalline diols. The diols are predestined for preparation of liquid-crystalline polyurethanes [8] by bulk polymerization in the SmC^* phase. The LC state of the initial diols should be located around 100°C because of the condition of polymerization.

Two series of new chiral laterally substituted ferroelectric liquid-crystalline diols with 1,3-propandiol groups connected by flexible spacers to the mesogenic part of the molecules have been synthesized. General formulae of studied compounds are



denoted as **1H** (X = H), **1M** (X = CH_3), **1MO** (X = OCH_3), **1CL** (X = Cl), and



denoted as **2H** (X = H), **2M** (X = CH_3), **2MO** (X = OCH_3), **2CL** (X = Cl).

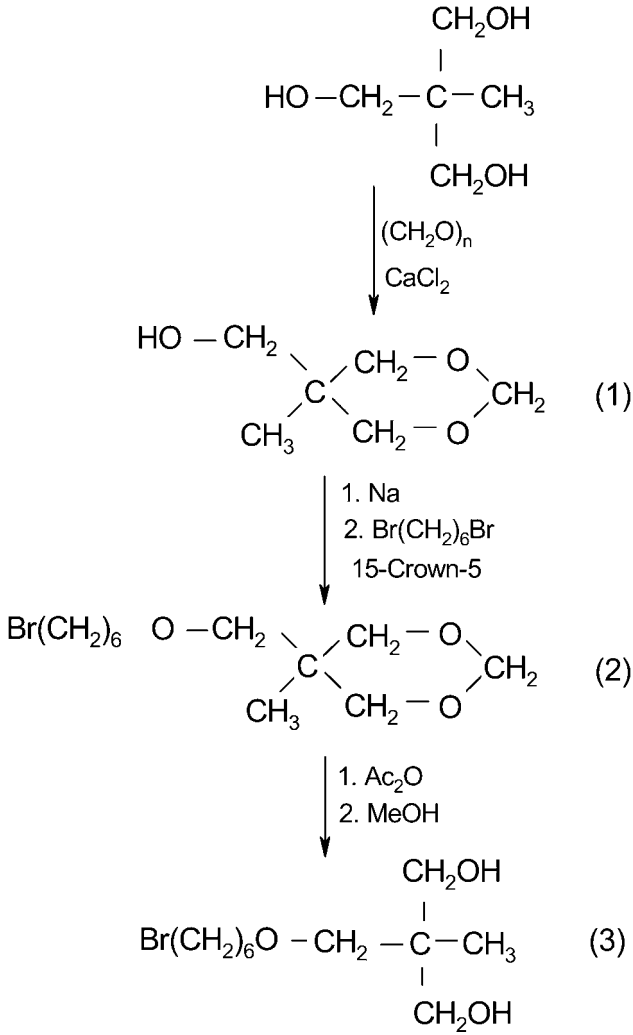
Mesogenic behavior has been studied by texture observations in polarizing microscope and DSC measurements.

SYNTHESIS

Preparation of Bis(2-Hydroxymetyl)-6′-Bromohexyl Propylether

The synthesis of the bis (2-hydroxymetyl)-6′-bromohexyl propylether (3) was carried out according to Scheme 1. Seventy-five g of pentaglycerolformal (1) bp 103/10 torr was heated with 0.3 mol of the metal sodium. After dissolving of all metal, 500 ml of dry dioxane was added and the reaction mixture was cooled down to room temperature. Then 0.5 mol (112 g) of dibromohexane and 3 ml of 15–Crown-5 was added in one step. The mixture was stirred and refluxed for 20 h, then cooled to room temperature; solid natrium bromide was filtered off and washed with a small amount of hot dioxane. The filtrate was evaporated and distilled in vacuum. The yielded acetal (2) is a colorless liquid, bp 138–140°C/1 torr.

Acetal (2) was hydrolyzed in two steps. The excess of acetanhydride was added to acetal with several drops of hydrochloric acid and by



SCHEME 1 Scheme of the synthesis of bis (2-hydroxymetyl)-6′-bromohexyl propylether.

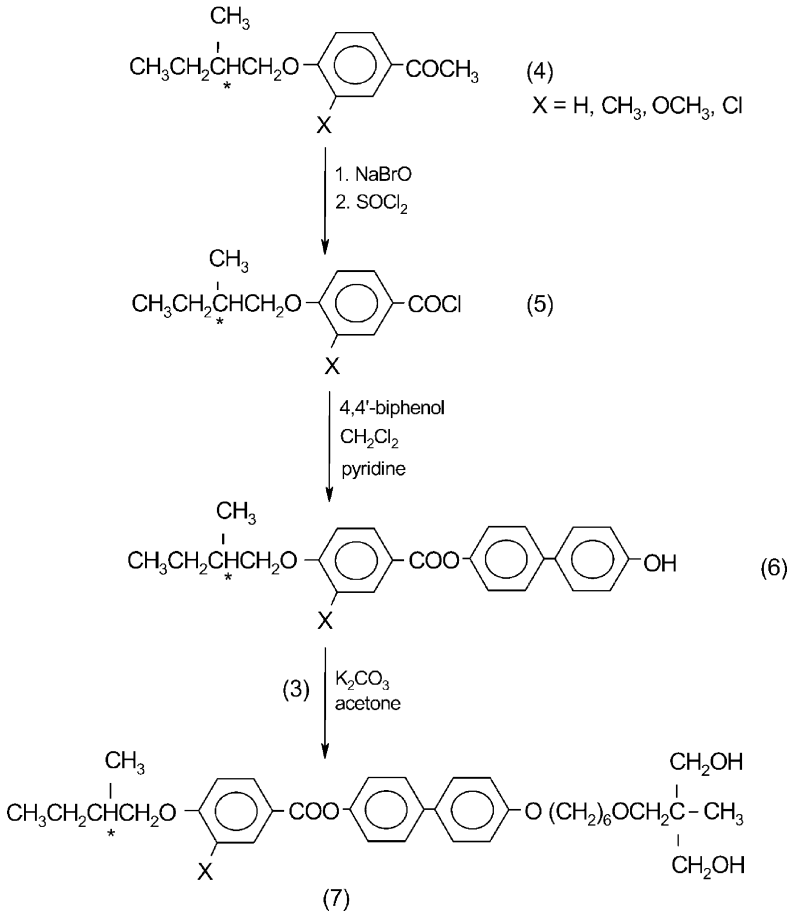
boiling for 2 h the acetal was transfered into diacetate. Redundant acetanhydride was removed on a rotatory evaporator. The residue in the flask was boiled three times with excess of fresh methanol. Arising methylacetate and the rest of methanol were evaporated and the product was dried with potasium carbonate.

[1]*H-NMR spectrum of diol(3) (200 MHz, in* $CDCl_3$*):* 3.50–3.70 dd (4H, CH_2OH); 3.35 m (6H, CH_2OH, and CH_2Br); 3.00 brs (2H, OH); 1.85

quint. (2H, $\underline{CH_2}CH_2Br$); 1.60 quint (2H, $\underline{CH_2}CH_2OH$); 1.40 m (4H,CH_2); 0.80 s (CH_3).

Preparation of Diols 1H, 1M, 1MO, and 1CL

The synthesis of the **1H, 1M, 1MO**, and **1CL** diols was carried out according to Scheme 2. The 3-X-4-(2-methylbutyloxy)acetophenones (4) were obtained by the alkylation of hydroxy compounds by (S)-(-)-1-iodo-2-methylbutane in an ethanol/water solution in the presence of NaOH.



SCHEME 2 Scheme of the synthesis of **1H, 1M, 1MO**, and **1CL** diols.

The preparation of acid chlorides (5) was carried out by the common haloform reaction with NaOBr in a dioxane solution followed by crystallization of the acids from ethanol and by reaction with thionyl chloride.

The acid chlorides were reacted with 4,4′-biphenol by refluxing in a dichlormethane/pyridine mixture for several hours. The yielded mesogenic phenols (6) were crystallized from ethanol and recrystallized from toluene.

The mesogenic phenols (6) were reacted with diol (3) by the standard Claisen etherification technique. The components were boiled in acetone with excess of potassium carbonate and 1 g of KI for 10–12 h. The hot reaction mixture was filtered and the product was crystallized in a refrigerator at –20°C.

The crude product was chromatographed on silica gel (Kieselgel 60, Merck, Darmstadt) using a mixture of chloroform and ethanol (97:3) as an eluent. After repeated crystallization from ethanol, the product purity was determined by High Performance Liquid Chromatography (HPLC), which was carried out with an Ecom high-performance liquid chromatograph using C18 column 3×150, particle diameter 7 μm, with a mixture of methanol and toluene as the eluent. Structure of all compounds was confirmed by ^{1}H-Nuclear Magnetic Resonance (H^1-NMR) spectrometry.

(^{1}H-NMR) Spectra of 3-Substituted-4-(2-Methylbutyloxy)Benzoic Acids (200 MHz, in $CDCl_3$)

For X = H: 8.10 d (2H, ortho to –COOH), 6.95 d (2H, meta to –COOH); 3.75 m (2H, CH_2OAr); 1.80 m (1H, *CH); 1.20 and 1.50 m (2H; $\underline{CH_2}CH_3$); 0.92 d (3H, CH_3-C^*); 0.85 t (3H, CH_3).

For X = CH_3: 7.98 d (1H, para to CH_3–); 7.92 s (1H, ortho to CH_3–); 6.85 d (1H, meta to CH_3–); 3.85 m (2H, CH_2OAr); 2.26 s (3H, CH_3Ar); 1.90 m (1H, CH*); 1.30–1.60 m (2H, $\underline{CH_2}CH_3$); 1.02 d (3H, CH_3–C*); 0.98 t (3H, CH_3).

For X = OCH_3: 7.72 dd (1H, para to OCH_3–); 7.60 d (1H, ortho to OCH_3–); 6.90 d (1H, meta to OCH_3-); 3.92 s (3H, CH_3OAr); 3.90 m (2H, CH_2OAr); 1.95 m (1H, CH*); 1.30–1.60 m (2H, $\underline{CH_2}CH_3$); 1.02 d (3H, CH_3-C*); 0.95 t (3H, CH_3).

For X = Cl: 8.10 s (1H, ortho to –Cl); 7.95 d (1H, para to –Cl); 6.92 d (1H, meta to –Cl); 3.90 m (2H, CH_2OAr); 1.95 m (1H, CH*); 1.30–1.60 m (2H, $\underline{CH_2}CH_3$); 1.04 d (3H, CH_3–C*); 0.95 t (3H, CH_3).

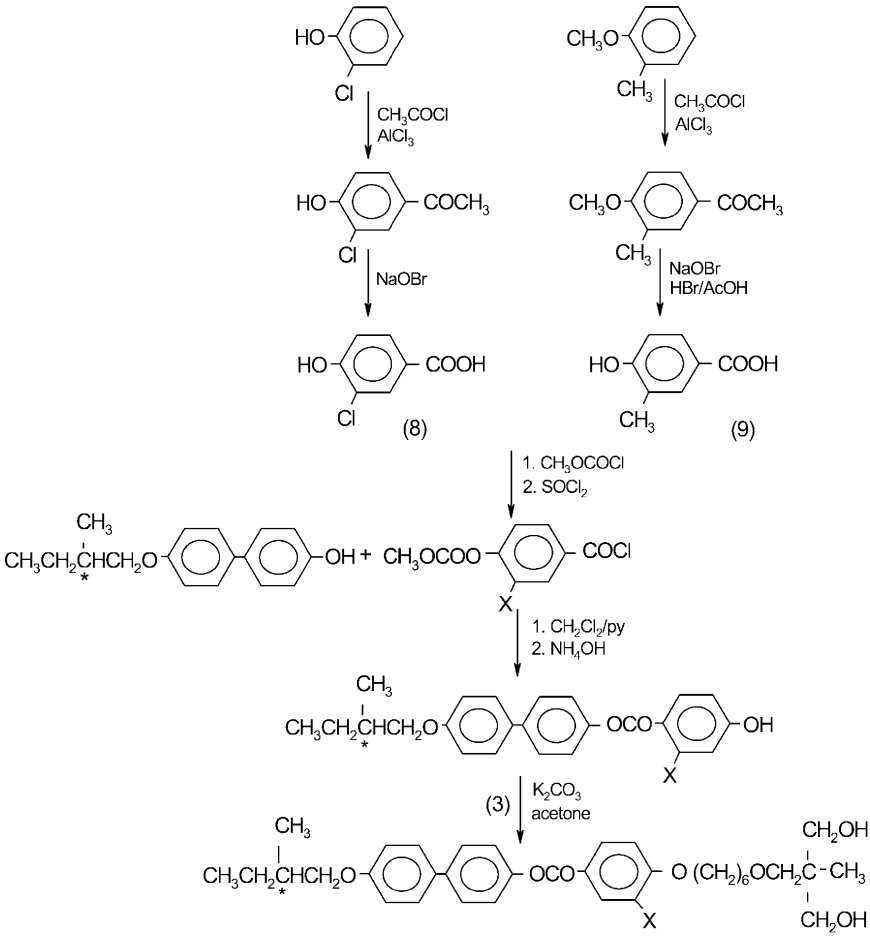
^{1}H-NMR Spectra for 1M (200 MHz, in $CDCl_3$)

8.05 d (1H, para to CH_3); 8.0 s (1H, ortho to CH_3–); 7.50–7.60 dd (4H, ortho to Ar–Ar); 7.25 d (2H, ortho to COO–), 6.98 d (2H, ortho to $-OCH_2CH_2$); 6.90 d (1H, meta to CH_3-); 4.05 t (2H, $ArOCH_2CH_2$);

3.90 m (2H, $ArOCH_2C^*$); 3.60–3.8 dd (4H, CH_2OH); 3.40 m (4H, CH_2OCH_2); 2.30 s (3H, CH_3Ar); 2.50 brs (2H, OH); 1.90 m (1H, CH^*); 1.85 quint. (2H, $ArOCH_2\underline{CH_2}$); 1.30–1.70 m (8H, CH_2); 1.05 d (3H, $\underline{CH_3}C^*$); 1.00 t (3H, CH_3CH_2); 0.80 s (3H, $\underline{CH_3}C$–).

Preparation of Diols 2H, 2M, 2MO, and 2CL

The synthesis of the **2H, 2M, 2MO**, and **2CL** diols was carried out according to Scheme 3. Esterification of 4-(4′-alkoxyphenyl)phenol by



SCHEME 3 Scheme of the synthesis of **2H, 2M, 2MO**, and **2CL** diols.

protected p-hydroxybenzoic acid [9] or vanillic acid [10] and deprotection by amonolysis has been described in previous works.

Synthesis of 3-chloro-4-hydroxybenzoic acid (8) was started with a mixture of 0.5 mol (64 g) of chlorophenol and 1 mol (78 g) of acetyl chloride dissolved in 500 ml of 1,2-dichloroethane. $AlCl_3$ (160 g) was added under cooling by ice during 1 h. Then the mixture was stirred for several hours at room temperature and left to stand 1 week. The reaction mixture was then poured into 500 g of ice; the organic layer was washed twice with water and evaporated. The residue was dissolved in ethanol and slowly added into the solution of 0.6 mol of potassium hydroxide (KOH) in water. The acetyl group was removed in this way. The yellow crystalline product was obtained by filtration and acidification by HCl. After recrystallization from ethanol, 50 g of 4-hydroxy-3-chloroacetophenone was obtained.

^{1}*H-NMR spectra of 4-hydroxy-3-chloroacetophenone (200 MHz, in* $CDCl_3$*)*: 7.97 d (1H, ortho to Cl); 7.8 dd (1H, para to Cl); 7.05 d (1H, meta to Cl); 7.20 brs (1H,OH); 2.55 s (3H,CH_3).

The acid (8) was obtained after reaction with NaOBr in dioxane; the yield was 33 g.

^{1}*H-NMR spectra of 3-chloro-4-hydroxybenzoic acid (8) (200 MHz, in* $CDCl_3$*)*: 8.05 d (1H, ortho to Cl); 7.89 dd (1H, para to Cl); 7.06 d (1H, meta to Cl); 5.98 s (1H, OH).

The 3-methyl-4-hydroxybenzoic acid (9) was prepared from 61 g (0.5 mol) of o-cresylmethylether which was added to a suspension of 90 g $AlCl_3$ in 500 ml of dry 1,2-dichloroethane at 0°C. Then, a solution of 40 g of acetyl chloride in dichloroethane (100 ml) was added dropwise to the mixture under stirring during 1 h. The mixture was stirred for 12 h at room temperature, poured into an ice/HCl mixture, washed with water, and evaporated. The residue was distilled in a vacuum, which yielded 50 g of colorless liquid (bp 112°C/1 torr).

^{1}*H-NMR spectra of 4-metoxy-3-methylacetophenone (200 MHz, in* $CDCl_3$*)*: 7.75 d (1H, para to CH_3); 7.70 s (1H, ortho to CH_3); 6.75 d (1H, meta to CH_3); 3.80 s (3H,CH_3O); 2.48 s (3H, $COCH_3$); 2.20 s (3H, CH_3).

The 3-methyl-4-hydroxybenzoic acid (9) was obtained by the usual reaction with NaBrO in dioxane solution. The product was dissolved in the mixture of concentrated acetic acid/hydrobromic acid (1:1) and refluxed for 10 h. After cooling to room temperature, the mixture was diluted by water and crystallized in a refrigerator at –4°C for 2d. The product was recrystallized from the mixture of ethanol/dioxane; the yield was 30 g of yellow solid.

^{1}*H-NMR spectra of 3-methyl-4-hydroxybenzoic acid (9) (200 MHz, in DMSO)*: 7.65 d (1H, ortho to CH_3); 7.60 d (1H, para to CH_3); 6.82 d (1H, meta to CH_3); 4.00 brs (1H,OH); 2.10 s (3H, CH_3).

The protecting of 3–methyl–4–hydroxybenzoic acid and 3-chloro-4-hydroxybenzoic acid by a reaction with phenol and the deprotecting by ammonolysis were carried out similar to procedures described previously [9,10].

The final products were obtained by the reaction of mesogenic phenols with diol (3), prepared according to Scheme 1.

The crude product was chromatographed on silica gel (Kieselgel 60, Merck, Darmstadt) using a mixture of chloroform and ethanol (97:3) as an eluent. After repeated crystallization from methanol, the product purity was determined by HPLC. The analysis was carried out with an Ecom high-performance liquid chromatograph using C18 column 3×150, particle diameter 7 μm, with a mixture of methanol and toluene as eluent and detection of eluted products at 290 nm. The structure of all compounds was confirmed by ^{1}H-NMR spectrometry.

*^{1}H-NMR spectra of **2M** (200 MHz, in $CDCl_3$)*: 8.18 d (2H, ortho to –COO); 7.40–7.60 m (4H, ortho to –Ar); 7,22 d (2H, ortho to –OCO); 6.98 m (4H, ortho to $-OCH_2$); 4.05 t (2H, $CH_2\underline{CH_2}OAr$); 3.80 m (2H, $C^*\underline{CH_2}OAr$); 3.80 m (2H, $C^*\underline{CH_2}OAr$); 3.60–3.80 dd (4H, CH_2OH); 3.40 m (4H, CH_2O CH_2); 2.50 brs (2H, OH); 1.30–1.80 m (11H, $CH_2 + C^*H$); 1.02 d (3H, CH_3C^*); 0.95 t (3H, $\underline{CH_3}CH_2$); 0.80 s (3H, CH_3C).

METHODS OF STUDY

For all studied materials, sequence of phases and phase-transition temperatures were determined from characteristic textures and their changes observed with a polarizing microscope (NIKON ECLIPSE E600POL) on cooling from the isotropic phase and checked by differential scanning calorimetry (DSC). The DSC measurements (Pyris Diamond Perkin-Elmer 7) were carried out on cooling and heating runs at rate of 5 K min^{-1}. The samples of 3–8 mg were placed in a nitrogen atmosphere and hermetically sealed in aluminium pans.

The texture and physical studies were carried out using the samples filed by means of a capillarity into the glass cells with Indium Tin Oxide (ITO) transparent electrodes (5×5 mm^2) and polyimide layers unidirectionally rubbed, which ensured planar (bookshelf) geometry. The temperature stability was better than 0.1 K. The sample thickness was defined by mylar sheets as 25 μm.

EXPERIMENTAL RESULTS AND DISCUSSION

Typical example of thermograms taken during DSC measurements are presented in Fig. 1.

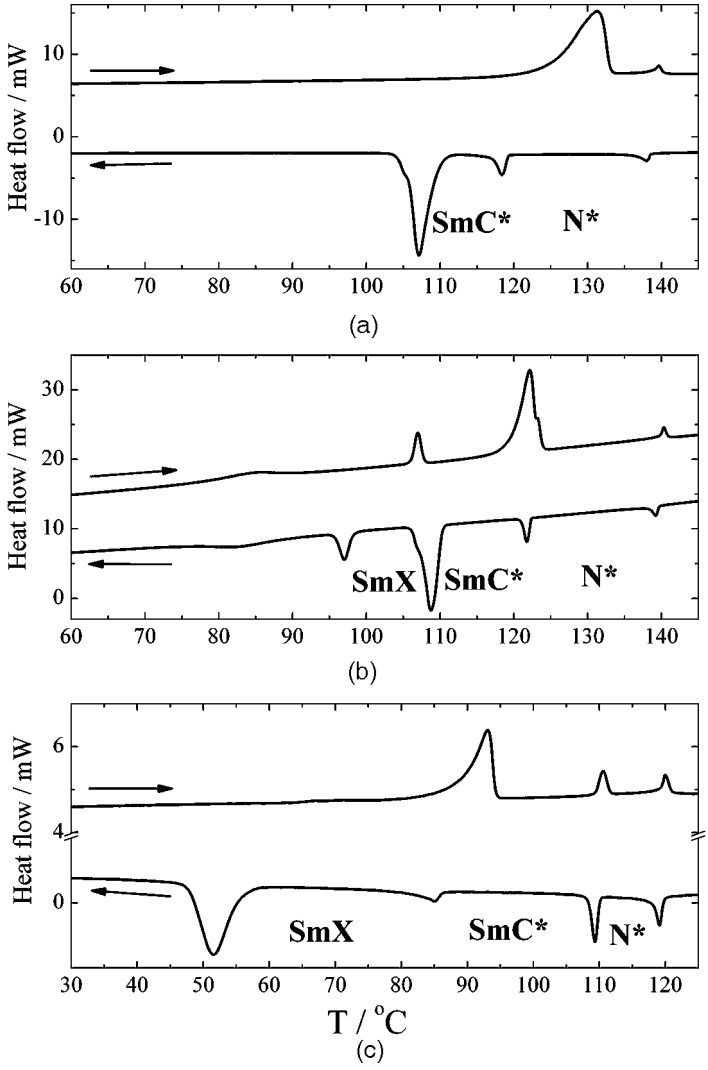


FIGURE 1 DSC plots for the studied monomers on heating/cooling runs: **1H** (a), **2H** (b), and **2CL** (c). Arrows show the direction of the temperature change.

Phase-transition temperatures established from texture changes during observation with the polarizing microscope are in good agreement with the position of peaks in DSC plots (see Fig. 1). Data for all studied materials are summarized in Table 1. The nonsubstituted (**1H** and **2H**) and chlorine-substituted (**1CL** and **2CL**) compounds

TABLE 1 Sequence of Phases, Melting Points (mp, °C), Phase-Transition Temperatures (°C), and Transition Enthalpies [ΔH (J/g)] from DSC Measured on Cooling (5 K min^{-1}) for all Studied Homologues

Compound	Substituent	mp	Cr.	°C	SmX	°C	SmC*	°C	N*	°C	BP	°C	Iso
1H	H	132 [67.9]	•		–	107 [–50.9]	•	119 [–5.7]	•	138 [–2.4]	•	145 [msc]	•
1M	CH_3	91 [0.5]	•	89 [–53.9]	•	107 [–1.4]	–		–		–		•
1MO	OCH_3	102 [1.4]	•	89 [–44.1]	•↑	117 [40.1]	–		–		–		•
1CL	Cl	86 [8.8]	•	47 [–0.2]	•	80 [–25.1]	•	113 [–7.3]	•	117 [–1.4]	•	119 [msc]	•
2H	H	85 [10.4]	•	82 [–7.6]	•	111 [–39.8]	•	122 [–4.2]	•	140 [–1.4]	•	142 [msc]	•
2M	CH_3	44 [15.6]	•	37 [–15.6]	–		•	56 [–2.6]	•	73 [–1.8]	–		•
2MO	OCH_3	105 [48.4]	•	76 [–35.9]	–		–		•	95 [–1.6]	•	96 [msc]	•
2CL	Cl	93 [25.9]	•	51 [–20.6]	•	85 [–1.5]	•	110 [–2.9]	•	119 [–2.3]	•	122 [msc]	•

•, the phase exists; –, the phase does not exist; •↑, the phase was detected upon heating only; [msc], determined from microscope only. SmX denotes low-temperature nontilted smectic phase or crystalline modification.

show the blue phase (BP), the cholesteric phase (N*), the ferroelectric phase (SmC*), and a low-temperature nontilted smectic phase (SmX). The temperature range of the blue phase was unusually broad, 1–7 K, depending on the material. In Fig. 2, a microphotograph of the phase transition from the blue phase to the cholesteric phase of the **1H** compound, taken at 138°C, is shown. A microphotograph of the cholesteric texture typical for the studied compounds is depicted in Fig. 3.

The lateral substitution by chlorine slightly decreases the phase-transition temperatures for both types of the substituted compounds. This typical behavior has been shown in our previous work dealing with rod-like liquid-crystalline materials [11].

The methoxy-substituted **1MO** compound shows some modification of the crystalline phase that appears upon heating only. No phase transitions were observed upon cooling from the isotropic phase. But in the case of methoxy substitution far from the chiral center in the **2MO** compound, the blue phase and the cholesteric phase were detected, which have monotropic characters.

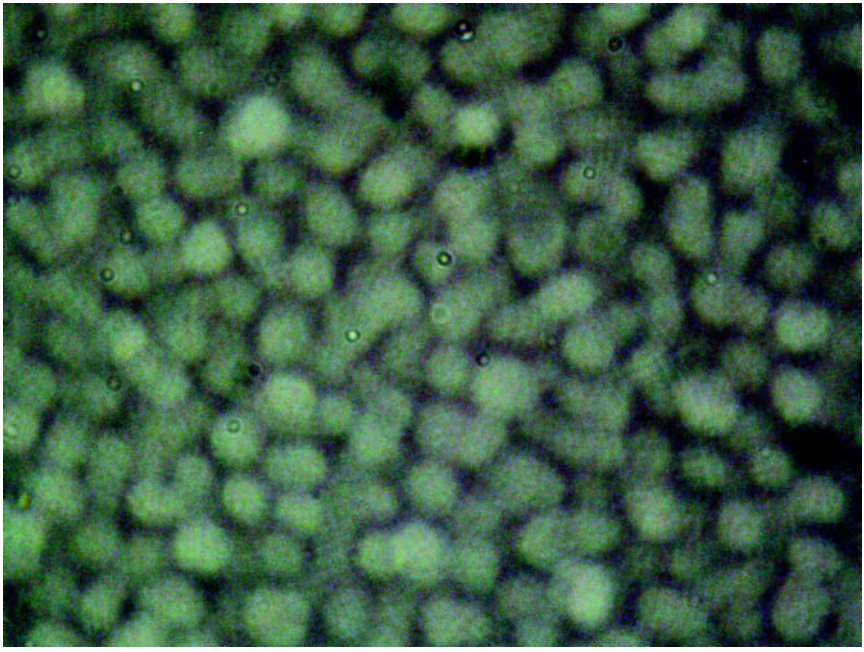


FIGURE 2 Microphotograph of the blue phase **2CL** compound taken at 121°C. The width of the photo is about 150 μm.

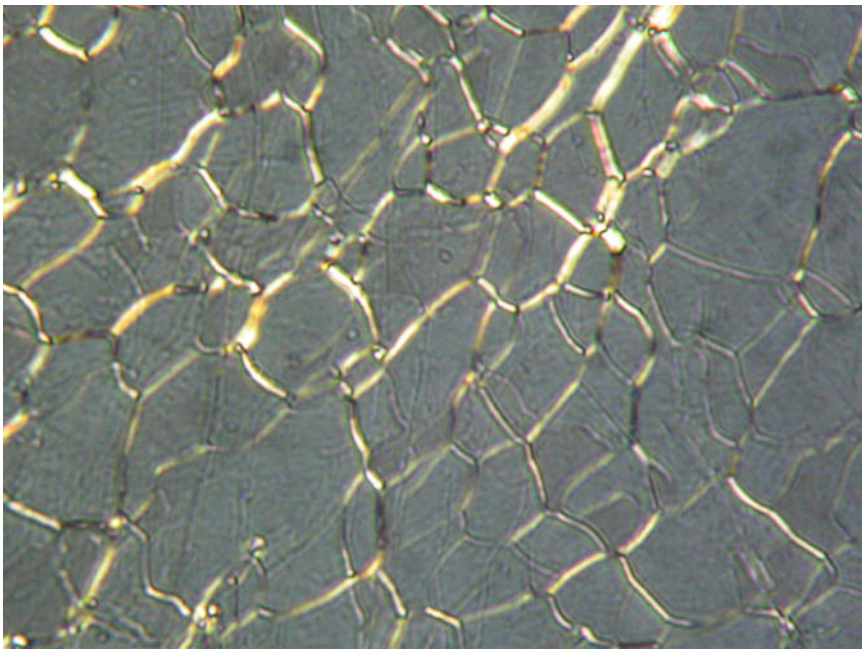


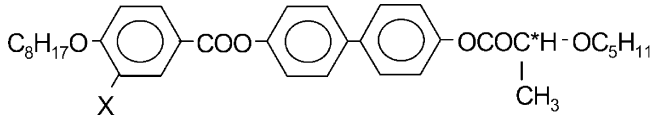
FIGURE 3 Microphotograph of the cholesteric texture of **2H** compound taken at 135°C. The width of the photo is about 300 μm.

In the case of methyl substitution in **1M** compound, only the low-temperature phase was detected. It can be either crystalline modification or the low-temperature nontilted smectic phase. X-ray studies are necessary for structure determination of this phase. The other type of the methyl-substituted **2M** compounds shows the cholesteric phase and the chiral SmC^* phase at significantly lower temperatures than analogous 2H, 2MO, and 2CL compounds. The chiral SmC^* phase shows bistable switching under an applied electric field (40 $kVcm^{-1}$, 1 Hz), which confirms ferroelectric behavior. Moreover, because of high values of the real part of complex permittivity (100–200, depending on the compound measured at 150 Hz), the antiferroelectric phase could be excluded.

The chiral center close to the side-substituted molecular core by a bulky group (CH_3 for **1M** compound or OCH_3 for **1MO** compound) probably leads to the hindrance of free rotation and, hence, to the nonexistence of the mesomorphic behavior. In the case of chlorine substitution, this effect does not occur. For comparison, in the case of the similar side substitution in another type of molecular core by the same

bulky CH_3 or OCH_3 groups near the chiral center of (S)-2-alkoxypropionic group, this does not prevent the existence of the ferroelectric SmC* phase [12] and leads only to the shift of the phase transitions to the lower temperatures and to the broadening temperature range of the SmC* phase in comparison with nonsubstituted compounds. In principle, it is necessary to take into account the change of the direction and absolute value of the dipole moment.

In our previous works, we have found a systematic occurrence of cholesteric mesophase in compounds with the same core.



For these compounds, sequence of phases and phase-transition temperatures are as follows:

for X = H, Cr 72°C SmC* 134°C N* 145 Iso [13];
for X = CH_3, Cr 10°C SmC* 89°C N* 104 Iso [14];
for X = Cl, Cr 50°C SmC* 113°C N* 114°C BP 115°C Iso [15]; and
for X = OCH_3, Cr 54°C SmC* 69°C SmA 79°C N* 80 Iso [16].

The existence of the cholesteric phase in **2H, 2M, 2MO**, and **2CL** compounds is probably connected with the character of the core and lateral-substituent position with respect to the chiral center.

Mesomorphic properties are probably mainly supported by a transversal dipole moment connected with the lateral substituent (group or atom). A series of the analogous compounds without –OH groups will be prepared and the influence of the hydrogen bonds of the diol group on the mesomorphic behavior of these compounds will be studied.

CONCLUSIONS

Two series of new ferroelectric liquid-crystalline diols with 1,3–propandiol group connected by a flexible spacer to the mesogenic part of the molecule have been synthesized. Both series are laterally substituted by methyl, methoxy, or chlorine substituents in the meta position to the carboxylic group of the 4-alkoxybenzoate unit.

The presence of a bulky substituent (methyl or methoxy groups) in close proximity to the chiral center causes sterical hindrance of free rotation on –O–CH_2–C* bonds of the chiral unit, which cannot take up conformation appropriate for the arrangement of the SmC* phase.

Compounds without lateral substitution (**1H** and **2H**) differ only insignificantly. Moreover, relatively small chlorine atoms also cannot cause the sterical hindrance (**1CL** and **2CL**).

The studied new series of diols are predestined for preparation of liquid-crystalline polyurethanes by bulk polymerization in the temperature range of the ferroelectric SmC^* phase [17].

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