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THERMAL PROPERTIES OF LIQUID-CRYSTALLINE DIOLS AND CORRESPONDING BIS-URETHANES WITH MESOGENIC GROUPS OF VARIOUS STRUCTURES IN SIDE CHAINS

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The liquid-crystalline diols with mesogenic groups of different structures were synthetized and their temperature behavior and existence of mesophases were determined. These compounds were also reacted with phenylisocyanate to form bis-urethanes at the ratio of reactive groups [OH]/[NCO] = 1/1. The changes of phase transition temperatures due to the change of H–O–H to H–N–H interactions have been investigated. Generally, the introduction of a phenylurethane group into the molecule suppresses the occurence of mesophases; in the case of simple mesogens the mesophases disappear completely. Stiff substituents bound to mesogen as end groups (such as the phenyl group, alkoxy group, etc.) stabilize the mesophases to such a degree that the negative influence of urethane group is compensated and the LC properties are recovered.

Keywords: liquid-crystalline diols; phenylisocyanate; mesophases; phenylurethanes

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INTRODUCTION

Thermotropic liquid crystalline (LC) polymers with alternating rigid (mesogenic) and flexible (spacer) units in the chain have attained considerable attention in literature [1,2]. Systems such as polyesters, polyethers, polycarbonates, etc. have been investigated. Less attention was devoted to LC polyurethanes, as their LC/isotropic transition is located at high temperatures. In LC polyurethanes the mesogenic groups were usually introduced into polyols or polyisocyanates [3,4]. Recently LC networks (LCNs) also have been investigated [5,6]. In the isotropic state the LCNs exhibit the mechanical behavior of conventional networks, whereas in the LC state a complex behavior reflecting a coupled response of ordered mesogens to the applied force has been found [7,8]. Both types of the LCNs, with mesogens in the main or in the side chains, have been investigated. The DSC measurements of polyurethanes having the mesogenic part in the main chain revealed that the transition temperatures in LC polyurethanes qualitatively corresponded to those in LC diols [8]. The advantage of LCNs prepared from polyols with mesogens in side chains is in their lower melting temperatures, so that the behavior corresponding to classical elastomers can be obtained. A modification of the structure of initial reactants could influence the thermal and mechanical properties of the corresponding polyurethane systems.

We have synthetised LC diols of various structures with two or three aromatic rings in the side chain. We investigated the relation between the type of the side substituent (structure of mesogen and/or spacer) and the mesogenic behavior of the diols.

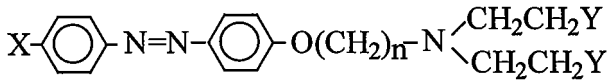
By the reaction of diols with phenylisocyanate in the stoichiometric ratio of reactive groups ([OH]/[NCO] = 1) bis-urethanes were prepared. The mesomorphic properties of the bis-urethanes have been established and compared with those of corresponding diols. The aim was to find a bis-urethane with a wide temperature range of mesophase, overlapping the mesophase range of the corresponding diol, that could be used for preparation of LC polyurethanes by the polymerization in LC state.

EXPERIMENTAL

Structure of Diols and Related Phenylisocyanates

A series of diols, with two or three aromatic rings in the side chain bound to the two terminal hydroxy groups in the main chain, have been synthesized (compounds **1**–**6**, Y = OH). All these diols were reacted with phenylisocyanate at the ratio [OH]/[NCO] = 1. In this way a series of bis-urethanes

has been prepared where both the –OH groups have been substituted by phenylisocyanate groups (compounds **1**–**6**, Y = OCONHphenyl).



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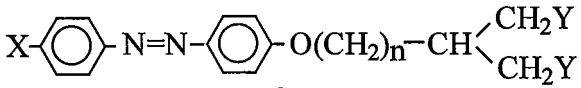

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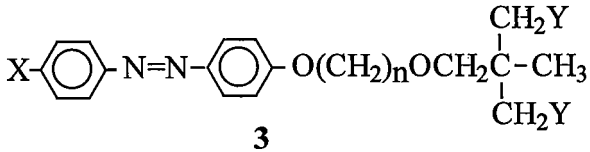

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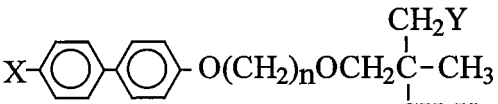

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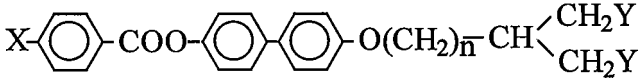

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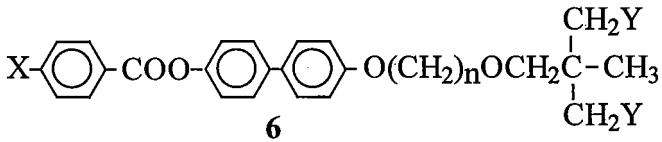
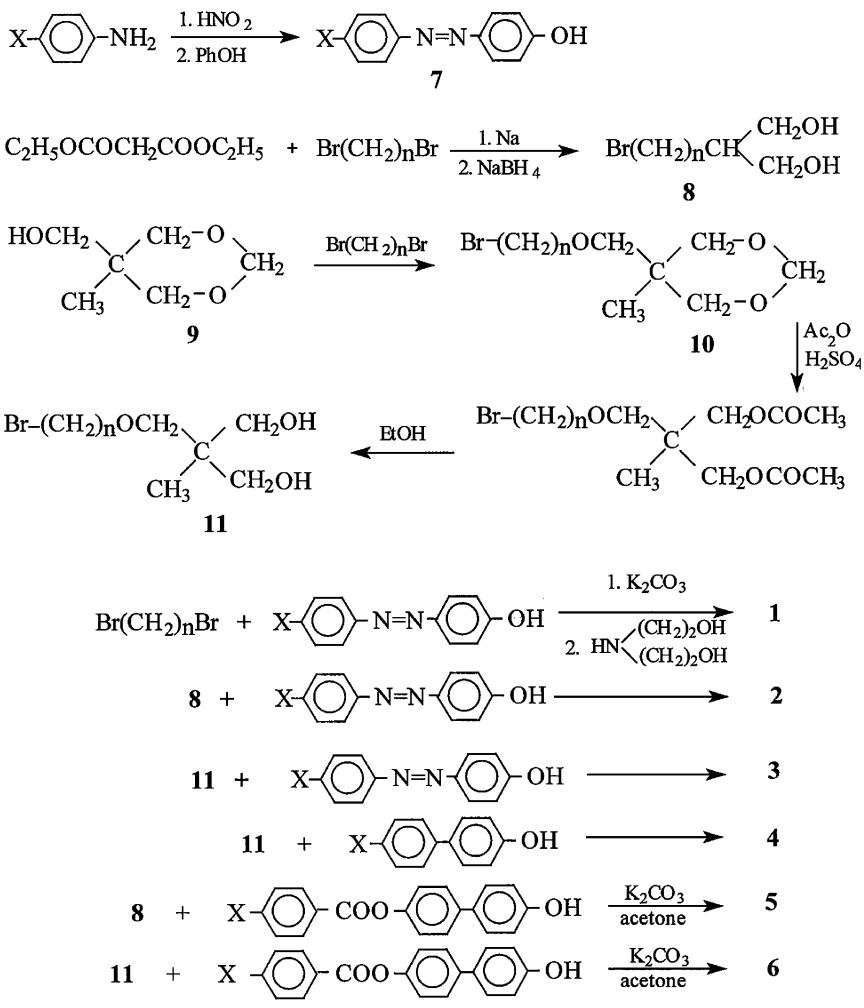


6

n = 5, 6; X = H, O_2N, NC, $H_{13}C_6O$, $H_{15}C_7O$, $H_{17}C_8O$, $H_{21}C_{10}O$, or phenyl; Y = OH or OCONHphenyl

Synthesis of Diols

The synthesis of materials was carried out according to the Scheme 1. Starting phenols (7) were obtained by diazotation and copulation of corresponding anilins with phenol.



SCHEME 1 Synthesis of diols with mesogenic groups.

Preparation of 2-(6-bromhexyl)-1,3-propandiol (8)

30 g (1.3 M) of sodium was dissolved in 500 ml of absolute ethanol under cooling. Then 260 g (1.625 M) of dried diethylmalonate and 407 g (1.668 M) of dried 1,6-dibromhexane were added under vigorous stirring and refluxed for 90 min. The mixture was cooled down and distilled under reduced pressure. Boiling point of the product was 145–150°C/1.5 mm. The yield was 198.5 g, $n^{20} = 1.4600$. For the next reaction, 185 g of this compound was dissolved in 4000 ml of methanol and heated to the boiling point.

During 2 h, 183 g (4.82 M) of natriumborohydride were added slowly under stirring. After cooling of the mixture, 2000 ml of water was added and vigorously stirred for 1 h. Methanol was distilled under reduced pressure, and the remaining water phase was extracted three times by diethylether. Sixty one g of yellowish oil was dissolved in 500 ml of heptane and 400 ml of ethyl acetate and cooled down to −80°C. Crystals were separated on cooled fritted glass. After heating to laboratory temperature they melted into yellow viscous liquid (**8**), yield 27 g.

Products were characterized by ^{1}H-NMR spectroscopy using a Varian NMR spectrometer Gemini 200 at 25°C.

^{1}H-NMR ($CDCl_3$, 200 MHz): 3.70 dd and 3.55 dd (2H+2H, CH_2OH); 3.34 t (2H, CH_2Br); 3.22 s (2H, OH); 1.79 quint (2H, $\boldsymbol{CH}_2CH_2Br$); 1.65 m (1H, CH); 1.1–1.4 m (8H, CH_2).

Acetal (**9**) was prepared from 1.1 M (132 g) of 1,1,1-tris(hydroxymethyl)ethane, 1 M (30 g) paraformaldehyde, and 30 g $CaCl_2$ in 100 ml dioxane, with 1 ml HCl used as a catalyst. The mixture was refluxed for 10 h, and then the organic layer was separated, dried by calcium chloride, and distilled. Boiling point of the product was 103°C/10 mm.

*Preparation of acetal (***10***)*

Twenty three g of sodium was pulverized in 300 ml of xylene. After cooling to 100°C, 150 g of acetal (9) was added dropwise under vigorous stirring. The mixture was then stirred for 2 h under the reflux. After cooling to room temperature, 200 ml of dioxane, 488 g of 1,6-dibromhexane, and 2 ml 15-crown-5 were added. The reaction mixture was stirred for 1 h at room temperature and then slowly heated to boiling point. Then the mixture was refluxed for 2 days and left to stand overnight. The precipitated natrium bromide was separated by filtration and extracted by hot dioxane. Then the dioxane was evaporated and the yellow residue was distilled (b.p. 145–150°C/3 mm) to obtain 110 g of colorless liquid (**10**).

^{1}H-NMR ($CDCl_3$, 200 MHz): 4.9 and 4.65 dd (2H, -O-CH_2-O-); 3.8 and 3.4 dd (4H ,C-CH_2-O); 3.45 m (6H, CH_2Br and CH_2OCH_2); 1.85 quint. (2H, $\boldsymbol{CH}_2CH_2Br$); 1.58 quint. (2H, $\boldsymbol{CH}_2CH_2O$); 1.40 m (4H, CH_2); 0,85 s (3H, CH_3).

*Preparation of diol (***11***)*

Hydrolysis of very stable acetal ring was carried in two steps: Acetal (**10**) (50 g) was mixed with an excess of acetanhydride and 1 ml of concentrated sulphuric acid. The resulting solution was heated in a water bath for 10 h. The acetanhydride was removed by evaporation under reduced pressure and the residue was diluted by ethanol. Then the solution was refluxed for several hours and evaporated under reduced pressure to dryness. Then the

procedure of addition of new portion of alcohol, refluxing, and evaporating was repeated three times. The residue was diluted with water (100 ml) and extracted twice with ether. The combined extracts were dried over anhydrous potassium carbonate. The ether was evaporated. The product (**11**) is yellow viscous liquid (yield 41 g).

^{1}H-NMR ($CDCl_3$, 200 MHz): 3.5–3.7 dd (4H, CH_2OH); 3.4 m (6H, CH_2Br, CH_2OCH_2), 1.8 quint (2H, $\boldsymbol{CH}_2CH_2Br$); 1.55 quint. (2H, $\boldsymbol{CH}_2CH_2O$); 1.40 m (4H, CH_2), 0.8 s (3H, CH_3).

Preparation of final diols

Diols (**1**) were obtained by heating of corresponding phenols to the temperature of 60°C with fivefold excess of 1,5-dibrompentane resp. 1,6-dibromhexane in the excess of anhydrous potasium carbonate in acetone for 48 h. Products were crystallized from acetone and then heated with excess of diethylamine in isopropanol for 48 h at 85°C. The final diols (**1**) were crystallized twice from toluene.

^{1}H-NMR ($CDCl_3$, 200 MHz):

diol **1** (X = CN, n = 6, Y = OH): 7.89 d (4H, HAr ortho to –N); 7.73 d (2H, HAr ortho to CN); 6.95 d (2H, HAr ortho to –OR); 3.99 t (2H, CH_2OAr), 3.65 t (4H, CH_2OH); 2.60 t (4H, $\boldsymbol{CH}_2CH_2O$); 2.49 t (2H, CH_2N); 1.77 quint (2H, $\boldsymbol{CH}_2CH_2OAr$); 1.3–1.46 m (6H, CH_2).

diol **1** (X = NO_2, n = 5, Y = OH): 8.28 d (2H, HAr ortho to NO_2), 7.88 m (4H, HAr ortho to –N); 6.93 d (2H, HAr ortho to –OR); 3.99 t (2H, CH_2OAr); 3.55 t (4H, CH_2OH); 2.59 t (4H, $\boldsymbol{CH}_2CH_2O$); 2.50 t (2H, CH_2N); 1.77 quint (2H, $\underline{CH_2}CH_2OAr$); 1.45 m (4H, CH_2).

Diols (**2**) were obtained by heating of corresponding phenols with 1.1 excess of (**8**) in acetone in excess of dried potassium carbonate at 60°C for 48 h. The final diol (**2**) was filtered and recrystallized from toluene.

^{1}H-NMR ($CDCl_3$, 200 MHz):

diol **2** (X = C_6H_5, n = 6, Y = OH): 7.06–7.89 m (13H, HAr); 4.05 (2H, CH_2OAr); 3.4 dd (4H, CH_2OH); 3.1 t (2H, –OH); 1.72 m (1H, CH); 1.23–1.44 (10H, CH_2).

The final diols (**3**), (**4**), (**5**), and (**6**) were obtained by reaction with mesogenic phenols in acetone in the presence of anhydrous potassium carbonate and potassium iodide as catalysts. Mesogenic phenols were synthesized by usual methods or by the method described in Kašpar et al. [9]. All products were crystallized from acetone and purified by column chromatography on silica gel (Kieselgel 60, Merck Darmstadt) using CH_2Cl_2 with 5% of ethanol as an eluent. The purity of products was determined by HPLC carried out with chromatograph Ecom using Tessek C18 column with mixture of methanol and toluene (90:10) as the eluent and detection of eluting products by UV-VIS detector ($\lambda = 290$ nm).

^{1}H-NMR ($CDCl_3$, 200 MHz):

diol **3** (X = $C_6H_{13}O$, n = 6, Y = OH): 8.15 d (2H, HAr ortho to –COO); 7.50 m (4H, HAr); 7.25 d (2H, HAr ortho to –OCO); 6.98 d (4H, HAr ortho to –O–); 4.00 m (4H, CH_2OAr); 3.60 q (4H, $–CH_2OH$); 3.42 m (4H, CH_2OCH_2); 2.3 brs (2H, OH); 1.8 m (4H, CH_2 CH_2OAr); 1.2–1.6 m (12H, CH_2); 0.9 t (3H, CH_3); 0.8 s (3H, CH_3).

diol **4** (X = $C_8H_{17}O$, n = 6, Y = OH): 7.45 d (4H, HAr meta to –O–); 6.95 d (4H, HAr ortho to –O–); 4.0 t (4H, CH_2OAr); 3.5–3.7 dd (4H, CH_2OH); 3.44 m (4H, CH_2OCH_2), 2.2 brs (2H, OH); 1.8 quint (4H, $\underline{CH_2}CH_2OAr$); 1.2–1.7 m (16H, CH_2); 0.9 t (3H, CH_3); 0.8 s (3H, CH_3).

diol **4** (X = $C_7H_{15}CO$, n = 6, Y = OH): 8.0 d (2H, HAr ortho to –CO); 7.6 dd (4H, HAr); 7.0 d (2H, HAr ortho to –O); 4.0 t (2H, CH_2OAr); 3.5–3.7 q (4H, CH_2OH); 3.42 m (4H, CH_2OCH_2); 2.95 t (2H, CH_2CO); 2.4 brs (2H, OH); 1.8 quint (2H, $\underline{CH_2}CH_2OAr$); 1.2–1.6 m (14H, CH_2); 0.9 t (3H, CH_3); 0.8 s (3H, CH_3).

diol **6** (X = $C_6H_{13}O$, n = 6, Y = OH): 7.85 d (4H, HAr ortho to N); 7.0 d (4H, HAr ortho to –O); 4.0 t (4H, CH_2OAr); 3.5–3.7 q (4H, CH_2OH); 3.4 m (4H, CH_2OCH_2); 2.7 brs (2H, OH); 1.8 quint (H, CH_2CH_2OAr); 1.2–1.6 m (12 H, CH_2); 0.9 t (3H, CH_3); 0.8 s (3H, CH_3).

Preparation of bis-urethanes

Corresponding diols were refluxed in toluene with twofold excess of phenylisocyanate for 60 min. After cooling down, the precipitate was filtered and crystallized from toluene.

^{1}H-NMR ($CDCl_3$, 200 MHz):

bis-urethane **1** (X = NO_2, n = 6, Y = $OCONHC_6H_5$): 8.29 d (2H, HAr ortho to NO_2); 7.23 m (7H, HAr); 6.93 m (5H, HAr); 4.19 t (4H, CH_2OCO); 3.96 t (2H, CH_2OAr); 2.76 t (4H, $\underline{CH_2}CH_2OCO$); 2.52 t (2H, CH_2N); 1.73 quint (2H, CH_2CH_2OAr); 1.28–1.43 m (6H, CH_2).

bis-urethane **2** (X = C_6H_5, n = 6, Y = $OCONHC_6H_5$): 7.06–7.89 m (23H, HAr); 4.26 dd (4H, $–CH_2OCO$); 3.99 t (2H, CH_2OAr); 1.72 quint (1H, CH); 1.23–1.44 m (10H, CH_2).

bis-urethane **3** (X = $C_6H_{13}O$, n = 6, Y = $OCONHC_6H_5$): 8.15 d, (2H, HAr otho to –COO); 7.50 m (4H, HAr); 7.3 m (10 H, HAr ortho to –OCO, HAr meta and ortho to NH); 7.0 m (6H, HAr ortho to –O–, HAr para to –NH); 6.6 s (2H, NH); 4.15 m (4H, CH_2OCONH); 4.0 m (4H, $\boldsymbol{CH_2}CH_2OAr$); 1.2–1.6 m (12H, CH_2); 1.0 s (3H, CH_3); 0.9 t (3H, CH_3).

Methods of Measurements

Phase transition temperatures and the sequence of mesomorphic phases were determined from characteristic textures and their changes were observed under a polarizing microscope Eclipse E-600 Nikon. The samples were filled into glass plates in the isotropic state. For temperature control

the heating stage Linkam was used. The temperature changed usually at a rate of 2–5 K/min.

Most of materials were also studied by differential scanning calorimetry carried out by Perkin-Elmer DSC-7 equipment using the 5–10 K/min heating and cooling rate.

RESULTS AND DISCUSSION

Phase transition temperatures established from texture changes during observation in polarizing microscope are in good agreement with the positions of peaks in DSC plots. Data for all studied materials are summarized in Table 1. In the starting diols as well as in the bis-urethanes the existence of mesophases depends strongly on the type of substituent X.

For diols **1** with X = H the mesophases do not occur. If X = CN, the nitril group increases the longitudinal dipole moment of the molecule, which causes higher intermolecular interactions and the smectic mesophase appears on cooling. This mesophase partially crystallizes during heating (see Figure 1). All bis-urethanes **1** with X = H or X = CN did not have any mesophase and went into an amorphic phase during cooling.

TABLE 1 Phase Transition Temperatures for Diols and Bis-Urethanes

			Diol							Bis-urethane					
Formula	X	n	m.p.	Iso		N		Sm	Cr	m.p.	Iso		N		Cr
1	H–	5	77	•		–		–	56 •	77	•		–		xx
1	H–	6	92	•		–		–	77 •	78	•		–		xx
1	NC–	5	103	•	106	–		•	(99) x	101	•		–		xx
1	NC–	6	102	•	97	–		•	(59) x	86	•		–		xx
1	O_2N–	5	90	•	128	•	125	•	69 •	105	•		–		xxx
1	O_2N–	6	102	•	130	•	123	•	68 •	82	•		–		xxx
1	$C_8H_{17}O$–	5	1	•	114	•	52	•	−18 •	100	•		–	50	•
1	Ph–	6	137	•	146	•	138	•	133 •	55	•	126	•	48	•
2	Ph–	6	168	•	180	•	168	•	164 •	121	•	152	•	121	•
3	$C_6H_{13}O$–	6	105	•		–		–	102 •	118	•		–	< 20	•
4	$C_8H_{17}O$–	6	117	•	120	•		–	105 •	116	•		–	23	•
4	$C_7H_{15}CO$	6	96	•	112	•		–	89 •	48	•		–	(46)	x
5	$C_{10}H_{21}O$–	6	107	•	174	•	156	•	94 •	149	•	153	•	140	•
6	$C_6H_{13}O$–	6	129	•	171	•	139	•	114 •	86	•	159	•	78	•
6	$C_{10}H_{21}O$–	6	120	•	163	•	152	•	107 •	75	•	138	•	75	•

x Material partially crystalizes during heating.

xx Material does not crystallize and continuously goes into an amorphic phase.

xxx Decomposition.

•Phase exists.

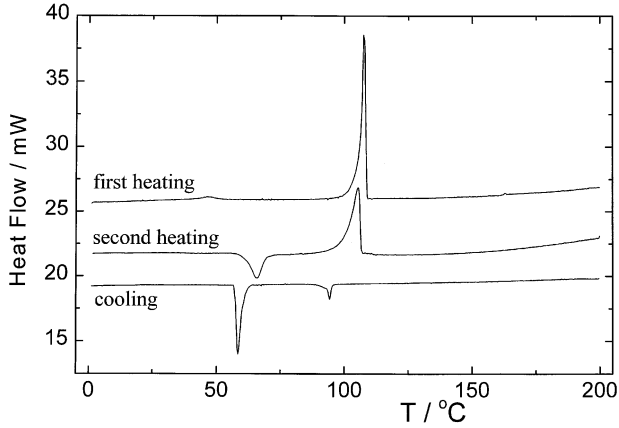


FIGURE 1 DSC plots for diol **1** (X = CN, n = 6, Y = OH). Heating (cooling) rate is 5–10 K/min.

The nitro group as a substituent polarizes mesogenic core of the molecule even stronger. In addition, the nematic phase appears and the temperature range of mesophases is expanded. Unfortunately after substitution of the –OH groups of diols by phenylurethanes, the decomposition of materials occurs after melting. The strong oxidation effect of nitro group also contributes to this decomposition. Therefore, the nitro and cyano groups have not been introduced as the substituents to the molecule of more complicated compounds having three aromatic rings. We observed for diol **1** substituted by nitro group two mesophases in contradiction to diol **1** substituted by CN group. Similar behavior was observed in a case of terminally substituted mesogens with azo group in mesogenic core [10]. The author mentioned nematic mesophase for compound substituted by CN group whereas we found smectic mesophase. This different behavior may be connected with the fact that compounds in Petrov and Shimizu [10] had no free hydroxy groups. The mesogenic behavior of diol **1** ($X = NO_2$) corresponds to the compounds with terminal NO_2 group that were described before [10,11].

Longer alkoxy substituent in the compound **1** leads to expected decrease of melting point due to lowering of the dipole moment of the molecule. However, mesophases of corresponding bis-urethane disappeared in spite of the fact that the starting diol had smectic mesophase, which crystallizes at very low temperature (see Figure 2), and the liquid crystalline behavior existed within the temperature range of about 130 degrees. Introduction of a nonsubstituted phenyl ring into the X position of the compound **1** stabilized the mesophases, and a nematic phase also

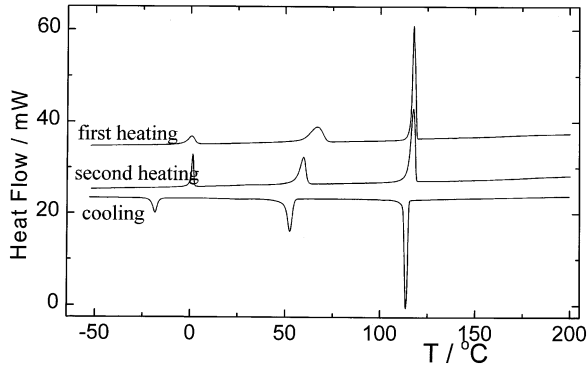


FIGURE 2 DSC plots for diol 1 ($X = C_8H_{17}O$, $Y = OH$). Heating (cooling) rate is 5–10 K/min.

appeared in the corresponding bis-urethane in spite of the fact that a partial decomposition of the material takes place.

Compound **2** differs from compound **1** by the diol type. When the phenyl ring was used in the X position of the diol **2**, similar behavior of monotropic phases was observed at higher temperatures than in the case of the diol **1**. Bis-urethane with the structure **2** has the nematic phase in the temperature range that is much narrower than that for the bis-urethane **1**.

Modification of diol structure using more branched alkyl chain (formulas **3** and **4**) did not lead to a substantial widening of the temperature range of mesophases. For both, diol **3** and bis-urethane **3** mesophases disappeared. For the diols **4** with biphenyl moiety in the core, only a nematic phase was observed. It differs from similar amphiphilic biphenyl derivatives with another type of diol unit described by Tschierske et al. [12] that exhibited smectic C and smectic A phases. The diol of similar structure having biphenyl mesogenic core was also studied by Akiyama and Koide [13]. Their diol had methoxy group in para position and less branched alkyl chain. They observed one enantiotropic mesophase for diol and one or two mesophases for related polyurethanes. The corresponding bis-urethanes 4 did not have any mesophase. The compound was relatively stable, and no symptoms of decomposition were observed even after multiple heatings. The longitudinal dipole moment of mesogene for aliphatic X = RO is very low, and the differences in electron densities on aromatic rings are probably not sufficient to create strong enough donor–acceptor interactions that could create ordered structure. The strong hydrogen bonds of urethane groups dominate and probably disturb parallel ordering of molecules.

Even increasing of the molecule polarity due to introduction of a keto group to the molecule of formula **4** ($X = C_7H_{15}CO$) did not bring

improvement. In spite of the fact that diol **4** exhibits a nematic phase, bis-urethane **4** has no mesophase and low melting point.

Since the best results were obtained for the compounds **1** and **2** *with the substitution by phenyl ring*, we prepared and studied materials containing three aromatic rings connected by ester group in the mesogenic core (formulas **5** and **6**). It is known that the presence of the ester group in molecule for some type of LC compounds could lead to a decrease of the phase transition temperatures [9,14] and simultaneously could disturb compensation of the dipole moment by a symmetric substitution by the alkyl groups (formula **4**, X = RO). All the three studied diols with formulas **5** and **6** show wide mesophase temperature ranges. After the addition of phenylisocyanate to the diol **5**, the smectic mesophase disappears and only the narrow nematic phase remains. The bis-urethanes derived from the structure **6** have nematic phases in wide temperature range regardless of the alkyl chain length. This fact confirms that the presence of three aromatic rings is substantial for formation of mesophases in bis-urethanes. Photos of a texture in smectic phase of diol **5** ($X = C_{10}H_{21}O$) and in mesophase of corresponding bis-urethane **5** ($X = C_{10}H_{21}O$) are shown in Figures 3 and 4 respectively. We cannot distinguish the type of the smectic

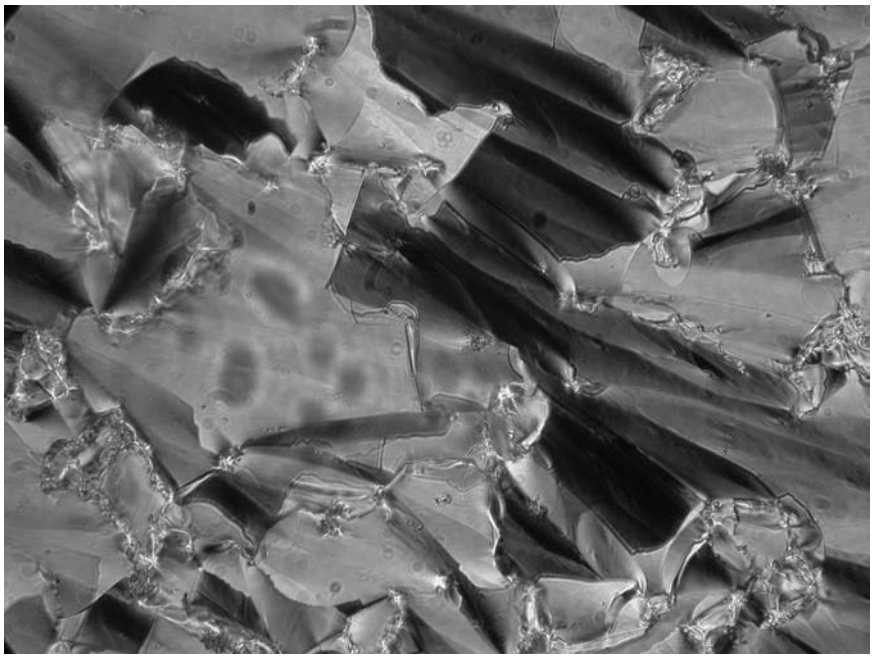


FIGURE 3 Texture of the diol **5** ($X = C_{10}H_{21}O$, Y = OH) in smectic phase at the temperature 150°C. (See Color Plate I).

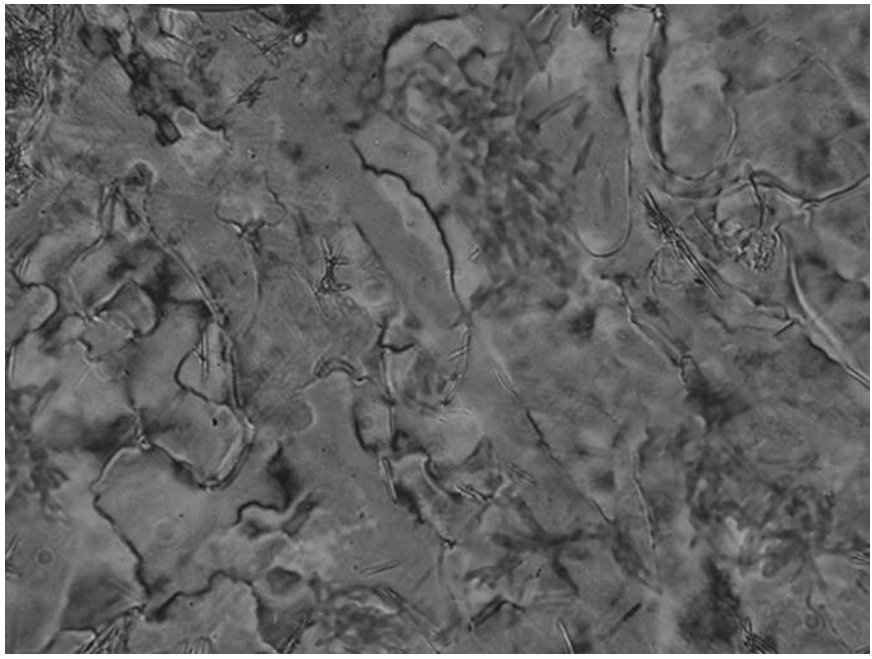


FIGURE 4 Texture of the bis-urethane 5 ($X = C_{10}H_{21}O$, $Y = OCONHC_6H_5$) in a mesophase at the temperature 147°C. (See Color Plate II).

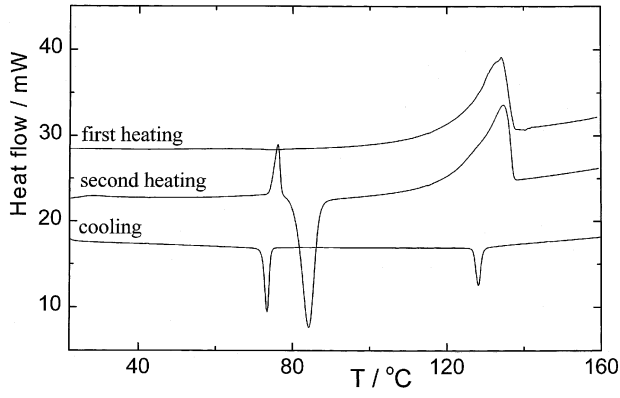


FIGURE 5 DSC plots for bis-urethane 6 ($X = C_{10}H_{21}O$, $Y = OCONHC_6H_5$). Heating (cooling) rate is 5–10 K/min.

mesophase from observed texture for diols **5** and **6**. It seems to be partially homeotropically aligned. Bis-urethane 6 ($X = C_{10}H_{21}O$) shows a postponed crystallization, which takes place during heating after the phase transition (Figure 5). This phenomenon has not been studied in detail so far.

CONCLUSION

Great differences in mesogenic behavior of diols and bis-urethanes are caused by the distinct character of inter- and intra-molecular hydrogen bonds [15,16,17]. Hydrogen bond O . . . H . . . O supports a stronger aggregation of molecules of diols and by this the existence of mesophases instead of weaker bonds N . . . H . . . N in bis-urethanes. We have found promising materials for preparation of grafted LC polyurethanes with urethane group in the main chain. Bis-urethanes **6** with three phenyl rings in the core and the long alkyl chains as substituents ($X = C_6H_{13}O$ or $X = C_{10}H_{21}O$) have wide mesophase temperature ranges (about 80 degrees) that overlap with those of the mesophases of the corresponding diols. We assume that in the middle of these intervals the whole system could not pass to the crystalline or isotropic state during polymerization. The physical properties of such LCN polyurethanes are now under study.

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