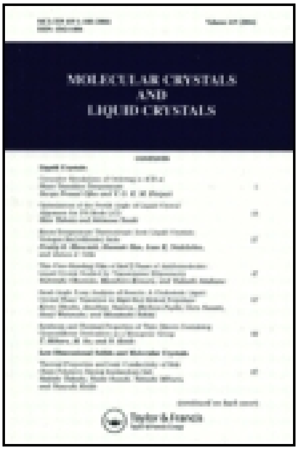


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

New Chiral Thiols and Related Side Chain Liquid Crystalline Polymers

Alexej Bubnov [a] , Miroslav Kašpar [a] , Zdena Sedláková [b] & Michal Ilavský [b] [c]

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

[b] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

[c] Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Version of record first published: 22 Sep 2010

To cite this article: Alexej Bubnov, Miroslav Kašpar, Zdena Sedláková & Michal Ilavský (2007): New Chiral Thiols and Related Side Chain Liquid Crystalline Polymers, Molecular Crystals and Liquid Crystals, 465:1, 93-107

To link to this article: http://dx.doi.org/10.1080/15421400701205628

Mol. Cryst. Liq. Cryst., Vol. 465, pp. 93–107, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701205628

New Chiral Thiols and Related Side Chain Liquid Crystalline Polymers

Alexej Bubnov
Miroslav Kašpar
Institute of Physics, Academy of Sciences of the Czech Republic,
Na Slovance, Prague, Czech Republic

Zdena Sedláková
Institute of Macromolecular Chemistry, Academy of Sciences of the
Czech Republic, Prague, Czech Republic

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

New series of chiral thiols with three aromatic rings and the $N = N$ group in the molecular core have been synthesized and grafted on polybutadiene diols backbone. The resulting polymers possess the OH end groups for possible preparation of the liquid crystal ordered networks. Basic properties of the thiols and resulting polybutadiene diols have been studied by polarizing microscopy and differential scanning calorimetry. The resulting diol-based polymers show the liquid crystalline behaviour in a broad temperature range. The effect of the side chain structure and density of grafting on the properties of polybutadiene diols has been studied and discussed.

Keywords: chiral thiols; differential scanning calorimetry; diols; liquid crystal; polarizing optical microscopy; polybutadiene

This work was supported by Grants No. IAA4112401 from the Grant Agency of the Academy of Sciences of the Czech Republic; No. 202/05/0431 from the Czech Science Foundation and ESF-COST Action D35 WG0013/05.

Address correspondence to Dr. 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. E-mail: bubnov@fzu.cz

INTRODUCTION

Thermotropic liquid crystalline (LC) polymers with alternating rigid (mesogenic) and flexible (spacer) units in the side chain have attained considerable attention in literature as they present a unique combination of the properties typical for monomeric liquid crystals with those peculiar to polymers [1,2].

Since 1984 [3], the development of the side chain ferroelectric LC polymers is an active research subject in the liquid crystal research. Most of the work was devoted to studies on polyacrylates [4] and polysiloxanes [5–9]. In order to study the polar properties, LC polymers need to be designed in such a way that mesogenic groups are separated from the polymer backbone by a flexible spacer chains so that the motion of the side chains is decoupled from that of the backbone [10]. Tilted smectic phases are typically exhibited by LC polymers where the length of the flexible spacer is greater than six methylene units. It was also shown that an increase of the backbone flexibility results in the preferential tendency for tilted smectic phases to be exhibited [11]. The polymers with flexible backbones are responding on the applied electric field much faster than those with more rigid backbones [12].

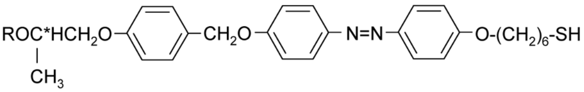
In recent years, the azobenzene containing LC polymer systems have received increasing attention because of their unique properties that allow various applications triggered by light. A variety of LC azo polymers has been synthesized in which the azobenzene moiety plays roles as both mesogene and photosensitive chromophore [13–19].

Polybutadiene diols grafted with liquid crystalline side chains of different structure offer the design and synthesis of novel linear and crosslinked materials, which might exhibit properties that respond demands photonics applications. On the other hand, the network formation based on well-defined polyols and polyisocyanates leads to controlled chain construction with well predictable final network structure. In that case, it is possible to determine the effect of crosslinking in the LC-state on development, final structure and physical properties of such systems. Possible crosslinking in magnetic or electric fields allows to prepare macroscopically oriented structure and to determine the effect of orientation on physical properties.

A very promising type of flexible backbone (but not well studied until now) can be based on dienes such as polybutadiene. In this case, the double bond exists in each 1.4 or 1.2 monomeric unit and these double bonds can be used for further chemical reactions so that various LC monomers can be grafted on polybutadiene backbone. The grafting can be proceeded through the terminal thiol group attached to the end of flexible spacer of the LC molecule. As the OH terminated polybutadiene diols with various length (molecular weights within 500–20,000) are commercially available, their grafted analogues can be used for preparation of linear or crosslinked LC liquid crystalline polymers. Our preliminary results have shown that approximately 50 mole percent of double bonds of polybutadiene diols can be used for grafting and concentration of the OH groups (functionality of diols) is practically unaffected by grafting reaction [20,21]. High flexibility of polybutadiene backbone together with the absence of the polar groups (that could interact with mesogens) suggests that the LC ordering of the side chain segments will not be affected by the backbone. Several types of the chiral thiols with two aromatic rings have been synthesized and grafted on polybutadiene diols backbone. Only few of the resulting polymers possess the liquid crystalline behaviour and the viscosity was high that makes impossible the advanced studies [13,20,22]. In order to improve the mesomorphic and physical properties, longer hydrocarbon chain in the chiral part of the molecule should be used.

In present work, the effect of structural changes in the mesogenic thiols possessing three benzene rings and the photosensitive N=N group in the molecular core has been investigated with respect to the mesomorphic properties of the resulting polymers. Several types of rod-like liquid crystalline molecules with thiol group attached to flexible spacer end and with the chiral group, based on (S)–2–methylbutanol or (S)–2–methyl–2–alkyloxyethanol have been synthesized. The effect of the side chains structure, type of chiral group and density of grafting (G) on the polybutadiene diols has been studied. General chemical formulae and corresponding abbreviations for the side chain units (monomers) and respective polymers are presented in Table 1.

TABLE 1 Chemical Formula of the Side Chain Unit with Three Phenyl Rings Molecular Core Incorporating the N=N group



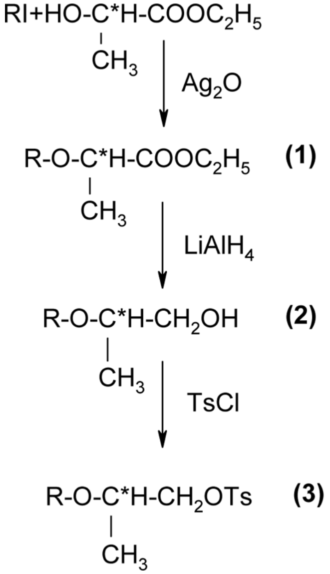
Monomer	R	Polymer
MK16	$CH_3CH_2C^*H(CH3)CH2$	**K16**
MK15	C_6H_{13}	**K15**
MK12	C_9H_{19}	**K12**
MK13	$C_{12}H_{25}$	**K13**

Synthesis

The whole synthetic procedure for the polymers with side chain units possessing three phenyl rings and the azo group in the core is divided in several parts, namely, (i) preparation of the chiral chains for the thiols; (ii) synthesis of the chiral thiol units; (iii) preparation of the butadiene polymers with side chain thiol units. The structures of intermediates and final products were characterised by ^{1}H–NMR spectroscopy using a 200 MHz Varian NMR spectrometer and solutions in $CDCl_3$ with tetramethylsilane as an internal standard.

Chiral Chains for Thiols

General procedure for synthesis of the chiral chains is presented in Scheme 1. The ethyl-(S)-lactate (500 mmol) was alkylated by corresponding alkyl iodide (300 mmol) in diethylether in the presence of silver (**1**) oxide (300 mmol). The reaction was carried out under vigorous stirring for 48 hours. The solid residue was removed by filtration; diethylether was evaporated and resulting liquid was distilled in vacuum. The product (**1**) was added slowly drop wise to an ether suspension of excess lithiumaluminium hydride ($LiAlH_4$). After that the



SCHEME 1 General procedure for synthesis of the chiral chains (R is C_6H_{13} – (n-hexyl); C_9H_{19} – (n-nonyl); $C_{12}H_{25}$ – (n-dodecyl); and $CH_3CH_2C^*H(CH3)$ CH2 – ((S)-2-methylbutyl)).

mixture was stirred for 8 hours and the excess of $LiAlH_4$ was removed by addition of the ethyl acetate. Then, water was added dropwise under ice cooling. The solid was separated by filtration and extracted with ether. After drying by sodium sulphate, the ether was evaporated in order to obtain (**2**) – the light yellow liquid. The tosylate (**3**) was prepared by usual method with tosylchloride (TsCl) in dry pyridine at 0°C.

^{1}H-NMR data (200 MHz, $CDCl_3$) for (**1**) with R = (S)-2-methylbutyl: 4.15 q (2H, $COOCH_2$); 3.95 q (1H, $C^*H{-}COO$); 3.10 m and 3.40 m (2H, CH_2O); 1.40 d (3H, $CH_3C^*{-}COO$); 1.20–1.70 m (3H, $C^*H{-}CH_2$); 1.25 t (3H, $\underline{CH_3}CH_2{-}OCO$); 1.40 d (3H, $CH_3{-}C^*{-}COO$); 0.90 t (3H, CH_3).

^{1}H-NMR data (200 MHz, $CDC1_3$) for (**3**) with R = (S)-2-methylbutyl: 7.80 and 7.30 d + d (4H, arom.); 3.90 (2H, $S{-}O{-}CH_2$); 3.55 m (1H, $C^*H{-}O$); 3.20 d (2H, $O{-}CH_2$); 2.40 s (3H, CH_3Ar); 1.60 and 1.40 and 1.20 m + m + m (3H, C^*HCH_2); 1.10 d (3H, $CH_3C^*{-}O{-}$); 0.80 t (3H, $\underline{CH_3}CH_2$).

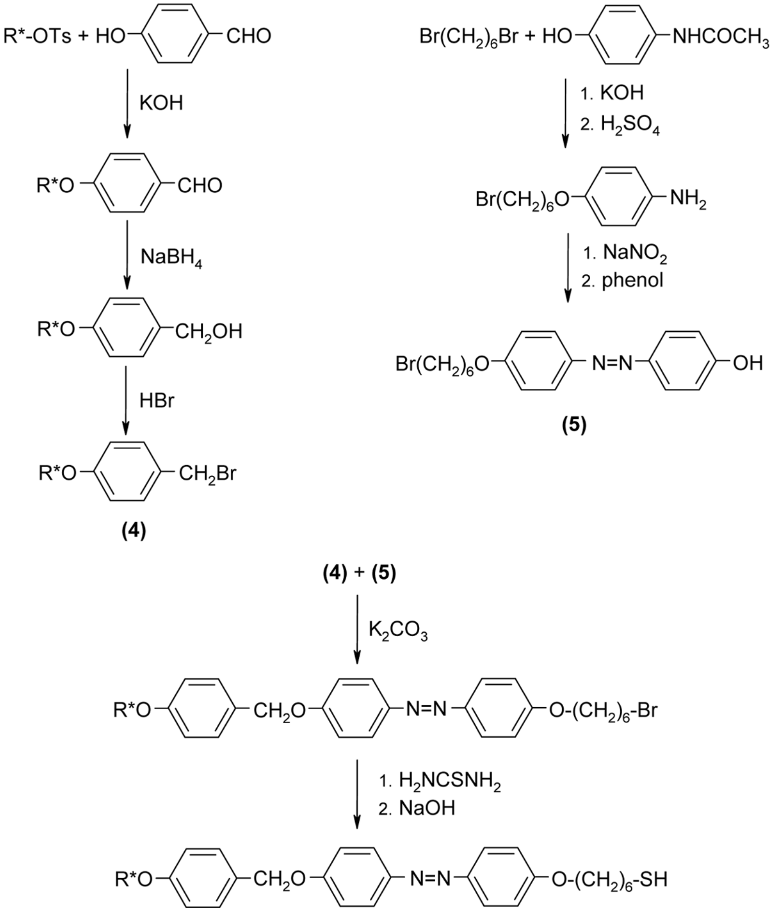
Chiral Thiols Units

All three-ring side chain units incorporating the N=N group were synthesized according to the procedure presented in Scheme 2.

4-hydroxybenzoldehyde was alkylated by corresponding tosylate (**3**) and potassium hydroxide in the ethanol/water solution at reflux for 10 days. The solvents were evaporated; the residue was poured into water and extracted by dichloromethane. The organic extract was dried by potassium hydroxide, filtered and evaporated. The residual liquid was reduced by sodium borohydride in dioxane at 70°C for 3 hours. Then the reaction mixture was poured into a very dilute hydrochloride acid (HCl) (1–2%) and extracted twice with dichloromethane. The organic extract was washed with water and then evaporated. This compound was heated at 80°C in excess of concentrated hydrobromic acid for 2 hours without further purification. The reaction mixture was poured in a water/ice mixture, extracted with dichloromethane, dried over calcium chloride ($CaCl_2$) and evaporated in vacuum.

4-ω-bromhexyloxy-4′-hydroxyazobenzene (**5**) was obtained from 4-acetamidophenol using standard methods of alkylaltion, diazotation and coupling with phenol. The crude product was crystallized from ethanol.

Intermediates (**4**) and (**5**) were reacted in acetonitrile in the presence of an excess of dry potassium carbonate at room temperature for about 12 hours. The reacted mixture was poured into excess of water; the precipitate was filtered off and washed with ethanol. The product was heated at reflux for 10 hours with thiourea in dry ethanol. The resulting thiouronium salt was crystallized from ethanol/tetrahydrofuran mixture. The yellow product was hydrolyzed with NaOH in ethanol/water mixture for 8 hours under argon atmosphere



SCHEME 2 General procedure for synthesis of the three-rings side chain units, where R* is the (S)-2-methyl-2-[(S)-2-methylbutyloxy]-ethyl (denoted as **MK16)**, (S)-2-methyl-2-hexyloxyethyl (denoted as **MK15)**; (S)-2-methyl-2-nonyloxyethyl (denoted as **MK12)** (S)-2-methyl-2-dodecyloxyethyl (denoted as **MK13)**.

under reflux. Then it was cooled down in refrigerator and the product was collected by filtration under argon and dried in vacuum at 50°C. The sodium mercaptide was acidified by HCl and mercaptane was isolated by extraction with dichloromethane; both operations were carried out under the argon atmosphere.

^{1}H-NMR data (200 MHz, $CDCl_3$) for (**4**) with R* = (S)-2-methyl-2-[(S)-2-methylbutyloxy]-ethyl-: 7.25 d (2H, HAr ortho to CH_2Br);

6.87 d (2H, HAr ortho to $-O$); 4.50 s (2H, CH_2Br); 3.70–4.00 m (3H, $-OC^*H-CH_2-O-$); 3.35 m (2H, $C^*-CH_2OC^*$); 1.30–1.60 m (3H, $\underline{CH_2–C^*H}-CH_2$); 1.22 d (3H, CH_3C^*-O-); 0.90 m (6H, $2xCH_3$).

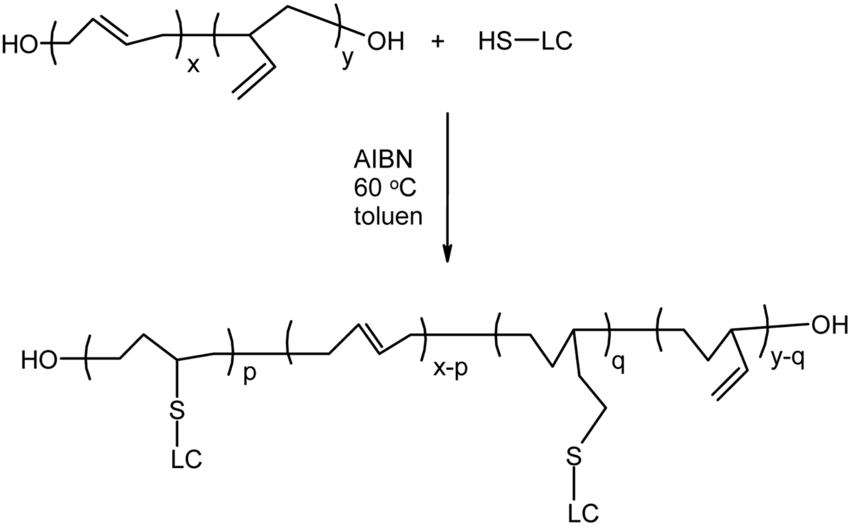
^{1}H-NMR data (200 MHz, $CDC1_3$) for (5): 7.82 dd (4H, HAr ortho to $-N{=}N-$); 6.95 dd (4H, HAr, ortho to $-O-$); 4.05 t (2H, CH_2-O-); 3.42 t (2H, CH_2Br); 1.80 m (4H, CH_2); 1.50 m (4H, CH_2).

^{1}H-NMR data (200 MHz, $CDC1_3$) for final product **MK16**: 7.87 d (4H, HAr ortho to $-N{=}$); 7.38 d (2H, HAr ortho to $-CH_2$); 6.90–7.10 d + d + d (6H; HAr ortho to $-O-$); 5.02 s (2H, $Ar-CH_2$); 4.00 t (4H, CH_2OAr); 3.70–3.90 m (1H, $-O-C^*H$); 3.35 m (2H, CH_2-O-C^*); 2.52 m (2H, CH_2SH); 1.30–1.80 m (11H, CH_2, CH); 1.25 d (3H, CH_3C^*-O); 0.90 m (6H, $2xCH_3$).

^{1}H-NMR data (200 MHz, $CDCl_3$) for final product **MK13**: 7.86 d (4H, HAr ortho to $-N{=}$); 7.38 d (2H, HAr ortho to $-CH_2$); 6.90–7.10 d+d+d (6H HAr ortho to $-O-$); 5.03 s (2H, $Ar-CH_2$); 4.00 m (4H, CH_2OAr); 3.70–3.90 m (1H, $-O-C^*H$); 3.55 t (2H, CH_2OC^*); 2.52 m (2H, CH_2SH); 1.30–1.80 m (31H, CH_2, CH_3); 090 t (3H, CH_3).

Polymers with Side Chain Thiol Units

General scheme of preparation of the polymers with chiral thiols side chains is presented in Scheme 3. Side chain liquid crystalline polymers had been prepared by the addition of a mesogenic thiol to



SCHEME 3 General procedure for preparation of the side chain polymers.

double bonds of OH-terminated telechelic polybutadiene Krasol 3000 at 80°C in the presence of azoisobutyronitril (AIBN) as initiator.

After dissolving, reaction mixtures consisting of thiol, HO-terminated polybutadiene Krasol 3000, AIBN and toluene as solvent were placed into glass ampoules. Then, the reaction mixture was bubbled by nitrogen for 10 min. and ampoules were sealed. The addition proceeded at temperature 60°C for 48 hours. Then, the reaction mixtures were poured into an excess of methanol and precipitated products were purified by reprecipitation from chloroform solutions to methanol. As the ^{1}H-NMR spectra are very similar for the synthesised polymers, the representative one is presented below.

^{1}H-NMR data (200 MHz, CDCl3) for (**K12**): 7.90 (4H, HAr ortho to $-$N=N$-$); 7.38 (2H, HAr ortho to $-CH_2$); 6.90–7.10 d+d+d (6H, HAr ortho to $-$O$-$); 5.40 m (1.8H, $-$CH=); 5.00 m (3.1H, =CH_2 and CH_2O); 4.00 m (4H, CH_20Ar); 3.70–3.90 m (1H, $-O-C^*H$); 3.55 t (2H, CH_2OC^*); 2.55 m (4H, CH_2-S-); 2.05 m (3.7H, $\underline{CH_2}-CH=CH_2$); 1.10–1.90 m (43H, CH_2, CH_3); 0.90 t (3H, CH_3).

METHODS OF STUDY

For side chain units (monomers), sequence of phases and phase transition temperatures were determined on cooling from characteristic textures and their changes observed on planar cells of different thickness in the polarising microscope (NICON ECLIPSE E600POL). Due to relatively high viscosity of the prepared polymers it was necessary to use the shearing technique [23]. In that case, the sample is prepared between two ITO coated glass plates provided with a special electrode pattern by etching in order to have a well-defined overlapping area (in present case the overlapping area is 16.8 mm^2). The distance between the glass plates is maintained by evaporated silicon-monoxide spacers of 3 μm thickness. The orientation of the smectic layers is such that they are mutually parallel with the layer normal parallel to the glass plates. This orientation is achieved by shearing the plates relative to each other in a specially constructed shear cell-holder. The LINKAM LTS E350 heating stage with TMS 93 temperature programmer was used for the temperature control, which enabled temperature stabilisation within ± 0.1 K. The phase transition temperatures were checked by differential scanning calorimetry (DSC - Pyris Diamond Perkin-Elmer 7) on cooling/heating runs at rates of 5K min^{-1} and 10K min^{-1} for monomers and polymers, respectively. The samples of 4–10 mg hermetically sealed in aluminium pans were placed in a nitrogen atmosphere.

EXPERIMENTAL RESULTS AND DISCUSSION

Sequence of phases and phase transition temperatures for the three phenyl ring side chain thiol units and resulting polymers determined on cooling for the isotropic phase obtained by observation in polarizing microscope and checked by DSC are summarized in Table 2.

Due to active hydrophilic SH end chain of the studied side chain units it was not possible to study the mesomorphic properties details. Nevertheless, by means of texture observations in Polarizing Microscope the liquid crystalline phases for the side chain units were identified. Typical microphotographs of the textures corresponding to the paraelectric SmA phase, ferroelectric SmC* phase and low temperature non-tilted smectic phase are shown on Figure l(a-d) for the monomer **MK12**. This monomer is the only one that shows the SmA phase on the transition from the isotropic phase. Monomers **MK16**, **MK15** and **MK13** possess the chiral nematic phase (typical texture is presented on Figure 2(a)) and a polar tilted SmX* phase (ferroelectric switching under low frequency electric field was observed). In order to identify the type of this phase, further studies are necessary.

Commercial OH-terminated telechelic polybutadiene Krasol 3000 that was used for polymers preparation possess the glass transition temperature at -41°C (detected by DSC). The prepared three phenyl ring polymers with indicated density of grafting show the mesomorphic behaviour. A variety of highly ordered smectic phases (denoted as SmX or/and LCX) and some crystal modifications (denoted as CrX) are detected by texture observation in polarizing microscope (see Table 2). Microphotographs of the textures typical for the prepared polymers are presented on Figure 2(b–d) for polymer **K15–50** and on Figure 3 for polymer **K13–30**. These textures are very similar to those presented in Ref. 22 for the non-tilted smectic phase that was proved by X-ray diffraction on non-oriented samples.

On Figures 4–5, the representative DSC plots on cooling runs are presented for the indicated side chain units and related polymers. While compare the DSC curves for the monomers and for the polymers, it can be mentioned that the peaks are broader for the polymers. Relatively high viscosity of the polymers and the phase coexistence region was detected for some of the polymeric materials.

As one of the aims of the present paper was to check the influence of the length of the chiral chain of the monomer on the density of grafting, we regret to mention that no pronounced effect was found for these series of new polymeric liquid crystalline compounds.

TABLE 2 Sequence of Phases and Phase Transition Temperatures T (°C) Measured on Cooling from the Isotropic Phase by DSC; Melting Points, m.p. (°C) and Clearing Points, c.p. (°C), Measured on Heating by DSC for the Studied Monomers (Thiols) and Resulted Diol-Based Polymers (G is the Density of Grafting (mol%)). The Heating/Cooling Rate was 5 K min^{-1} and 10 K min^{-1} for Monomers and Polymers, Respectively

Material	G	m.p. ΔH	c.p. ΔH		T ΔH		T ΔH		T ΔH		T ΔH		T ΔH	
MK16		69.8 [+13.6]	128.7 [+4.5]	Cr	51.5 [−4.7]	CrX	84.8 [−0.4]	CrX	103.0 [−6.9]	SmX*	116.5 [−1.1]	N*	126.8 [−4.9]	Iso
K16–30	30	75.0 [+13.2]	135.4 [+4.8]			Cr	64.0 [−9.4]	CrX	79.1 [−8.1]	LCX	111.3 [−0.9]	LCX	123.6 [−4.0]	Iso
K16–50	50	74.8 [+11.6]	143.1 [+7.9]			Cr	66.3 [−7.5]	CrX	84.9 [−6.3]	LCX	126.3 [−0.1]	LCX	133.7 [−3.4]	Iso
MK15	–	66.2 [+6.7]	120.7 [+1.3]	Cr	57.5 [−5.8]	CrX	94.4 [−4.1]	SmX	97.0 [−0.1]	SmX*	102.9 [−0.5]	N*	117.0 [−2.9]	Iso
K15–30	30	62.1 [+11.9]	131.2 [+4.5]			Cr	60.6 [−0.1]	CrX	74.8 [−1.9]	LCX	102.1 [−0.1]	SmX	121.3 [−3.9]	Iso
K15–50	50	57.4 [+10.1]	140.0 [+8.1]			Cr	65.2 [−7.8]	CrX	77.2 [−1.3]	LCX	110.0 [−0.1]	SmX	133.7 [−6.8]	Iso
MK12	–	69.0 [+10.3]	129.0 [+9.6]			Cr	63.4 [−8.5]	CrX	91.0 [−4.5]	SmC*	102.4 [−2.0]	SmA*	126.9 [−10.6]	Iso
K12–20	20	36.8 [+2.0]	115.3 [+1.5]			Cr	− 15.4 [−2.0]	LCX	52.6 [−0.6]	LCX	80.1 [−0.3]	LCX	114.8 [−1.3]	Iso
K12–30	30	63.5 [+2.6]	121.2 [+4.5]					Cr	52.7 [−1.4]	LCX	100.9 [−0.2]	LCX	119.4 [−0.6]	Iso
K12–40	40	−1.3 [+5.4]	122.6 [+1.4]			Cr	− 5.9 [−4.1]	CrX	83.8 [−2.6]	LCX	90.2 [−0.2]	LCX	115.8 [−1.9]	Iso
MK13	–	65.6 [+11.6]	118.6 [+4.8]	Cr	0.3 [−4.2]	Cr	56.5 [−7.0]	CrX	92.0 [−5.4]	SmX*	95.8 [−0.1]	N*	116.9 [−4.9]	Iso
K13–20	20	38.6 [+2.6]	137.8 [+5.7]			Cr	69.8 [−0.9]	CrX	92.7 [−6.0]	LCX	96.9 [−0.1]	LCX	131.5 [−6.7]	Iso
K13–30	30	60.6 [+8.0]	126.7 [+2.1]	Cr	− 3.4 [−1.7]	CrX	80.4 [−1.3]	CrX	89.0 [−1.9]	LCX	115.1 [−1.9]	SmX	121.4 [−1.3]	Iso
K13–40	40	70.4 [+12.8]	120.1 [+2.2]							Cr	84.4 [−7.3]	SmX	111.9 [−0.7]	Iso

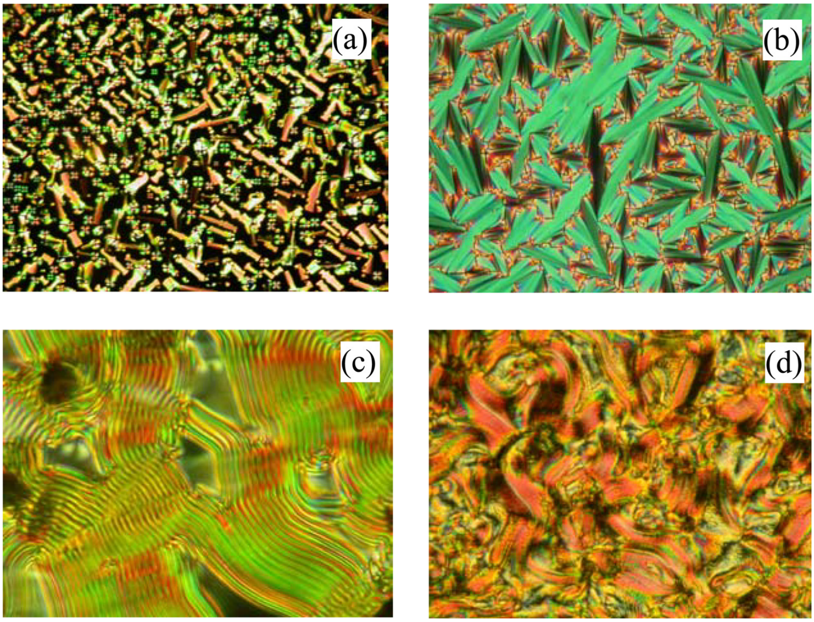


FIGURE 1 Microphotographs of the textures for monomer **MK12** obtained on cooling: the isotropic SmA phase transition at 126.5°C (a); fan-shaped texture of the SmA phase at 120°C (b); texture of the ferroelectric SmC* phase with disclination lines at 99°C (c); the crystal CrX phase at 85°C (d). The width of the pictures is about 300 μm. (See COLOR PLATE IV)

SUMMARY AND CONCLUSION

Several types of new chiral thiols with three aromatic rings possessing the N=N group and differing in the length of the chiral chain have been synthesized. Depending on the side chain length, the synthesized monomers (thiols) possess the chiral nematic phase, the paraelectric SmA phase, a polar tilted smectic phase (probably the ferroelectric SmC* phase) and the non-tilted low temperature smectic phase. The phases were identified basically by the textural observations in polarizing microscope. Due to active hydrophilic SH end chain it was not possible to study the properties in details.

Using the synthesized thiols, respective side chain polymers have been prepared and studies by Differential Scanning Calorimetry and Optical Polarizing Microscopy. The effect of structural changes in the mesogenic thiols has been investigated with respect to the mesomoiphic properties of the resulting polymers. The resulting polymers

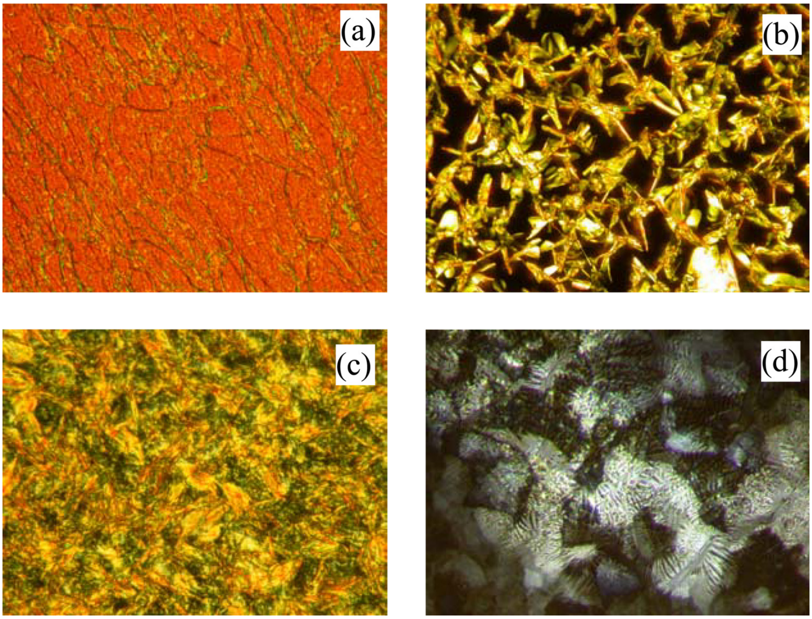


FIGURE 2 Microphotographs of the textures obtained on cooling for: oily streak texture of the N*phase at 121°C for monomer **MK16** (a); the isotropic-SmX phase transition at 133°C for polymer **K15–50** (b); texture of the low temperature orthogonal SmX phase at 124°C for polymer **K15–50** (c); highly ordered crystal phase at 64°C for polymer **K15–50** (d). The width of the pictures is about 300 μm. (See COLOR PLATE V)

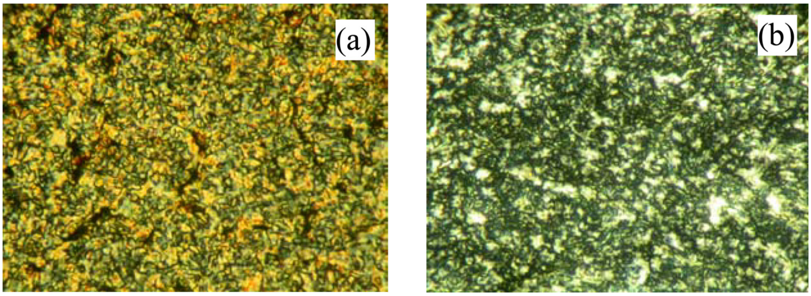


FIGURE 3 Microphotographs of the textures obtained on cooling for polymer **K13–30**: texture of the low temperature orthogonal SmX phase at 119°C (a) and highly ordered crystal phase at 110°C (b). The width of the pictures is about 300 μm. (See COLOR PLATE VI)

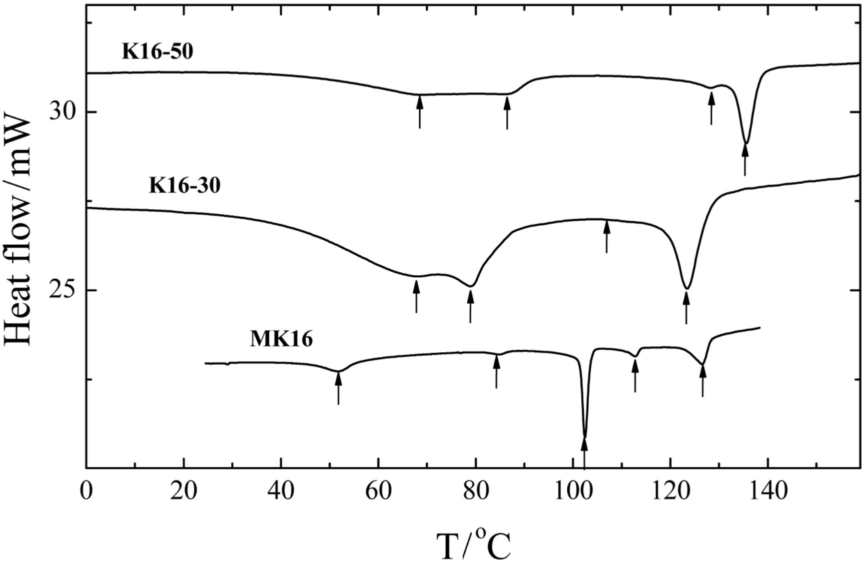


FIGURE 4 DSC plots on cooling runs for: monomer **MK16** and polymers **K16–30** and **K16–50** as indicated. Arrows indicate the pronounced changes in Cp.

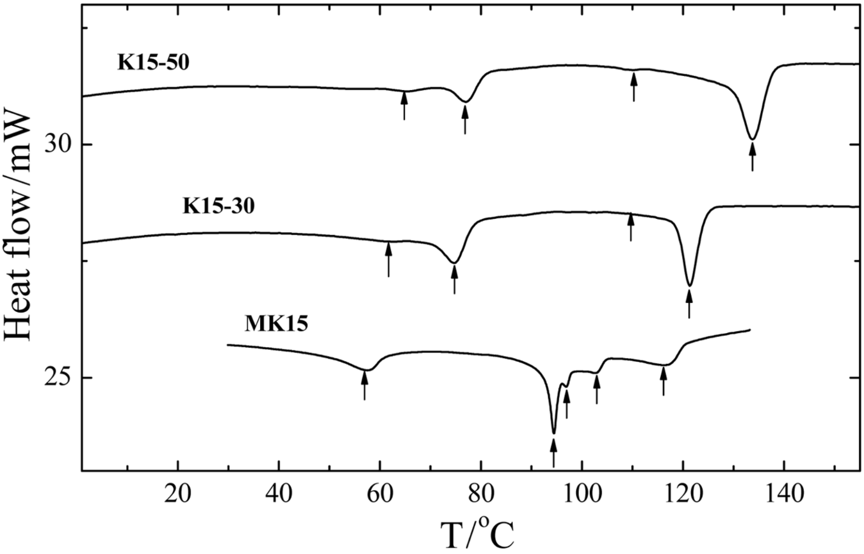


FIGURE 5 DSC plots on cooling runs for: monomer **MK15** and polymers **K15–30** and **K15–50** as indicated. Arrows indicate the pronounced changes in Cp.

possess the liquid crystalline phases, probably of the smectic type that need to be confirmed by X-ray studies. Density of grafting effect on mesomorphic behaviour has been checked. The mesomorphic behaviour of the studied polymers increases with density of grafting. The main disadvantage of the studied polymers is a very high viscosity that makes impossible detailed studies. Nevertheless, probably a slight modification of the monomer's structure can improve the properties of this class of materials and make it possible to use them for applications. One of the possibilities is to increase the polarity of the molecule by attaching additional chiral centre to the molecule.

The present paper presents mostly the synthetic work and the preliminary studies of the mesomorphic properties of the newly synthesized liquid crystalline side chain units and the related polymers. Further studies (results of dielectric spectroscopy and electro-optics, X-ray and photoferroelectric effect studies) of the synthesized polymers are in progress now and will be presented elsewhere in order to identify precisely type of the detected polymer's mesophases and their structural and electro-optic properties.

REFERENCES

[1] Ciferri, A., Krikbaum, W. R., & Meyer, R. B. (Eds.), (1982). *Polymer Liquid Crystals*, Academic Press: New York.

[2] Aharoni, S. M. & Edvards, S. F. (1994). *Rigid Polymer Networks*, Advances in Polymer Science 118: Springer Verlag.

[3] Shibaev, V. P., Kozlovsky, M. V., Beresnev, L. A., Blinov, L. M., & Plate, N. A. (1984). *Polymer Bull. (Berlin)*, *12*, 299.

[4] Hahn, B. & Percec, V. (1987). *Macromolecules*, *20*, 2961.

[5] Svensson, M. (1997). "Chiral liquid crystalline side chain polymers: Design, synthesis and properties" *PhD. Thesis*, Chalmers University of Technology, Gothenburg, Sweden.

[6] Galli, G., Di Bona, M. R., Fodor-Csorba, K., Gallot, B., & Chiellini, E. (1999). *Mol. Cryst. Liq. Cryst.*, *336*, 101.

[7] Cesarino, C., Komitov, L., Galli, G., & Chiellini, E. (2001). *Mol. Cryst. Liq. Cryst.*, *372*, 217.

[8] Galli, G., Ragnoli, M., Chiellini, E., Komitov, L., & Andersson, G. (2002). *Ferroelectrics*, *276*, 37.

[9] Bubnov, A., Kašpar, M., Hamplová, V., Glogarová, M., Samaritani, S., Galli, G., Andersson, G., & Komitov, L. (2006). *Liquid Crystals*, *33*, 559.

[10] Finkelmann, H., Happ, M., Portugall, M., & Ringsdorf, H. (1978). *Makromol. Chem.*, *179*, 2541.

[11] Hsu, C. H., Jin, J. H., Chou, L. R., & Hsuie, G. H. (1992). *Macromolecules*, *25*, 7126.

[12] Hachiya, S., Tomoika, K., Yuasa, K., Togawa, S., Sekiya, T., Takahashi, K., & Kawasaki, K. (1993). *J. Soc. Inf. Disp.*, *295*, 143.

[13] Ikeda, T. & Tsutsumi, O. (1995). *Science*, *268*, 1837.

[14] Ulysse, L., Cubillos, J., & Chmielewski, J. (1995). *J. Am. Chem. Soc.*, *117*, 8466.

[15] Brecl, M. & Malavasic, T. (1997). *J. Pol. Science: Part A: Polymer Chemistry*, *35*, 2871.

[16] Wu, Y., Mamiya, J., Shiono, T., Ikeda, T., & Zhang, Q. (1999). *Macromolecules*, *32*, 8829.

[17] Ho, Ch.-H., Yang, K.-N., & Lee, S.-N. (2001). *J. Pol. Science: Part A: Polymer Chemistry*, *39*, 2296.

[18] Liu, J.-H. & Hsieh, Ch.-D. (2006). *J. Appl. Pol. Science*, *99*, 2443.

[19] Tsutsumi, O., Kitsunai, T., Kanazawa, A., Shiono, T., & Ikeda, T. (1998). *Macromolecules*, *31*, 355.

[20] Kašpar, M., Bubnov, A., Hamplová, V., Novotná, V., Lhotáková, Y., Havlicek, J., & Ilavsky, M. (2005). *Mol. Cryst. Liq. Cryst.*, *428*, 49.

[21] Kašpar, M., Hamplová, V., Novotná, V., Studenovský, M., & Ilavsky, M. (2003). *Mol. Cryst. Liq. Cryst.*, *390*, 17.

[22] Bubnov, A., Kašpar, M., Sedláková, Z., Garić, M., Obadović, D. Ž., & Ilavský, M. (2006). *Proceedings of SPIE*, in print.

[23] Skarp, K. & Andersson, G. (1986). *Ferroelectrics Letters*, *6*, 67.