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New chiral thiols possessing biphenyl and phenyl moieties as well as ester linkage groups in the molecular core have been synthesised and grafted on polybutadiene diol backbones. The resulting diols possess OH end groups that enable the possibility for preparation of ordered liquid crystal networks. The mesomorphic properties of the synthesised thiols and resulting diols have been studied by polarising optical microscopy and differential scanning calorimetry. Chiral thiols as well as the resulting side-chain diols exhibit liquid crystalline behaviour, with a very broad paraelectric smectic A phase. The effects of side-chain structure of the ester thiols and density of grafting of the polybutadiene diols on mesomorphic properties were determined and are discussed.

Keywords: chiral thiols; polybutadiene diols; Bunte salts; side-chain polymers; liquid crystal polymers

1. Introduction

For the last two decades, thermotropic liquid crystalline polymers (LCPs) with alternating rigid (mesogenic) and flexible units (spacer) in their side-chains have attained considerable attention as they present a unique combination of the properties typical for conventional monomeric liquid crystals with those peculiar to polymers. This class of materials has also been systematically studied owing to properties that meet the demands of various applications. Intro duction of rigid mesogenic groups (side-chain) into the polymer chain (backbone) usually leads to LCPs that exhibit an intermediate state of aggregation between crystalline and amorphous structures (*1*).

Since 1984 (*2*), the development of LCPs with chiral side-chains, and especially those exhibiting ferroelectric behaviour, has been an active area in the field of liquid crystal research. Most of the work has been devoted to studies on polyacrylates (*3, 4*) and polysiloxanes (*5–11*). In order to study polar properties, LCPs need to be designed in such a way that mesogenic groups are separated from the polymer backbone by a flexible spacer chain so that the motion of the side-chains is decoupled from that of the backbone (*12*). Tilted smectic phases are typically exhibited by LCPs where the length of the flexible spacer is greater than six methylene units. It has also been shown that an increase of the backbone flexibility results in preferential tendency for tilted smectic phases to be exhibited (*5, 13*). Even for polymers possessing the chiral ferroelectric smectic C (SmC*) phase, the flexibility of the polymer backbone is an important factor in determining the response time of the polymer in an applied electric field. Polymers with more flexible backbones respond to the applied electric field much faster than those with more rigid backbones (*14*).

Polybutadiene diols grafted with LC side-chains of different structure offer new possibilities for the design and synthesis of novel linear and cross-linked materials, which might exhibit properties that meet demands of photonic applications. On the other hand, 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 cross-linking in the LC state on development, final structure and physical properties of such systems. Possible cross-linking in magnetic or electric fields allows preparation of macroscopically oriented structures and determination of the effect of orientation on physical properties.

Recently, several types of the chiral thiols with two aromatic rings have been synthesised and grafted on polybutadiene diol backbones. Only few of the resulting polymers possess LC behaviour and the viscosity was high, which made advanced studies impossible (*15, 16*). In order to improve the mesomorphic and physical properties, three phenyl rings with different linkage groups together with longer hydrocarbon chain in the chiral part of the molecule have been used (*17*).

In this paper, a synthetic procedure and mesomorphic characterisation are described of a new

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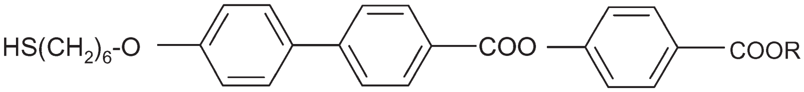
Table 1. Chemical formula of the ester thiols and related grafted polybutadiene diols.



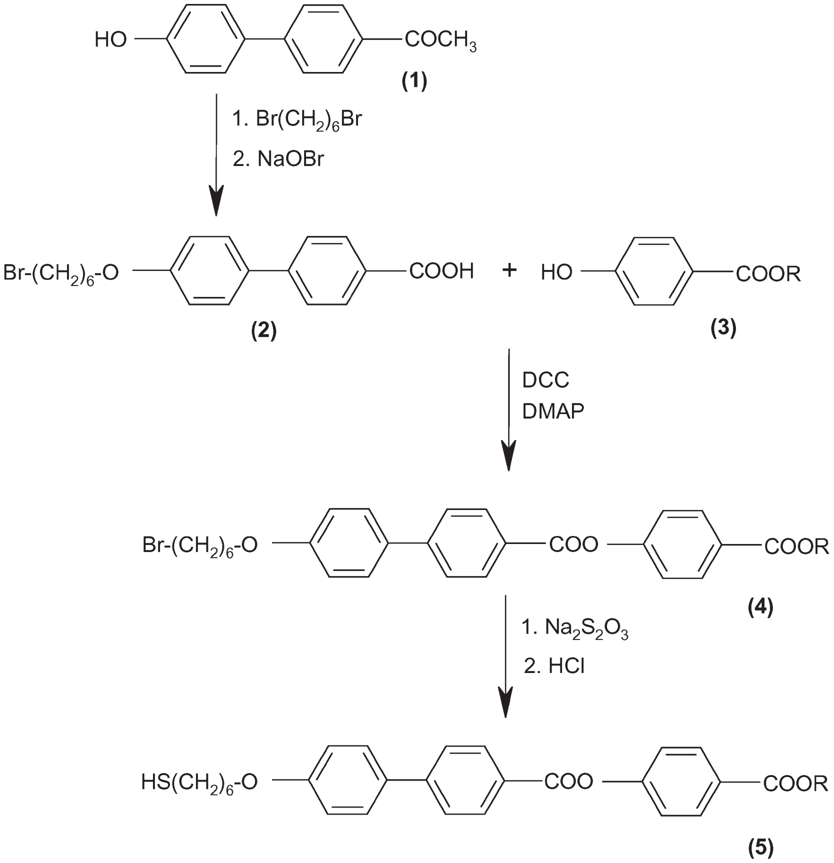
Monomer	Polymer	R
MK10	**PK10**	$–C^*H(CH_3)COO(CH_2)_3CH_3$
MK11	**PK11**	$–CH_2C^*H(CH_3)CH_2CH_3$
MK17	**PK17**	$–C^*H(CH_3)COOCH_2C^*H(CH_3)CH_2CH_3$

series of chiral thiols with three aromatic rings possessing an ester group in the molecular core. The effects of the ester thiol structure and density of grafting on the polybutadiene diols have been studied and discussed. General chemical formulae and corresponding abbreviations for the ester thiols with three phenyl rings in the molecular core, i.e. butyl (*S*)-2-{4-[4′-(6-mercaptohexyloxy)biphenylcarbonyloxy]-phenylcarbonyloxy}propionate (denoted **MK10**), (*S*)-2-methylbutyl 4-[4′-(6-mercaptohexyloxy)biphenylcarbonyloxy]benzoate (denoted **MK11**) and (*S*,*S*)-2-methylbutyl 2-{4-[4′-(6-mercaptohexyloxy)-biphenylcarbonyloxy]-phenylcarbonyloxy}propionate (denoted **MK17**) and the related polybutadiene diols are shown in Table 1. All chiral centres are in the *S*-configuration.

2. Synthesis of chiral thiols

All chiral thiols with three aromatic rings possessing ester groups in the molecular core were synthesised by a similar method. The general synthetic procedure is presented in Scheme 1.

4,4′-hydroxybiphenylmethylketone (**1**) was obtained from 4-acetyloxybiphenyl according to the procedure described previously (*5*). Ketone **1** was



Scheme 1. General procedure for synthesis of the monomers with ester groups (see also Table 1 for the R-chain structure).

converted by alkylation with 1,6-dibromohexane into the ether and by reaction with NaOBr using standard conditions that resulted in the desired 4[-(6-bromohexyloxy)-4'-biphenylcarboxylic acid (**2**). The phenols (**3**) were prepared from alkyl lactates and *p*-hydroxybenzoic acid according to the procedure described elsewhere (*18*). The acid **2** was condensed with the appropriate phenol **3** using dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) in methylene chloride as the condensation agent, yielding the mesogenic bromide (**4**).

The preparation of the thiols from thiouronium salts is impossible due to the hydrolysis of the ester group. However, the creation of the thiol group can be proceeded efficiently through the so-called Bunte salts ($RSSO_2ONa$) (*19*) prepared by the following procedure.

Sodium thiosulfate (0.1 mol) and potassium iodide (1 g) were dissolved in 50 ml of hot water. A solution of 0.1 mol of mesogenic bromide **4** in 200 ml of the ethanol was added with rigorous stirring and then the mixture was refluxed for 12 h. After this reaction, the salt was filtered off, washed with hot ethanol and water. Without drying, the crude product was placed into a flask with 150 ml of ethanol and 150 ml of chloroform. The flask was flushed with argon for 10 min. Then the mixture was stirred and 50 ml dilute hydrochloric acid (1:3) was added. The reaction mixture was stirred continuously under argon at room temperature for 3 h. After that, 400 ml of water was added and the organic layer was separated (still under argon), dried using sodium sulfate, filtered and dried by vacuum evaporation. The residue was recrystallised under argon from the mixture of ethanol or tetrahydrofuran and water. As a result, white crystals of thiol **5** were obtained. The yield was 30–40%.

The structures of the intermediates and all final products were checked via ^1H NMR spectroscopy using Varian NMR (300 MHz) spectrometer and solutions in $CDCl_3$ or perdeuterated dimethylsulfoxide (DMSO) with tetramethylsilane as an internal standard.

For 4,4′-(6-bromohexyl)oxybiphenylcarboxylic acid (**2**), ^1H NMR (300 MHz, $CDCl_3$): 7.98 (d, 2H, ortho to –COOH), 7.60–7.80 (dd, 4H, ortho to –Ar), 7.02 (d, 2H, ortho to –O), 4.00 (t, 2H, CH_2O), 3.50 (t, 2H, CH_2Br), 1.40–1.40 (m, 8H, CH_2).

For bromide **4** (R=–$C^*H(CH_3)COOC_4H_9$), ^1H NMR (300 MHz, $CDCl_3$): 8.20 (dd, 4H, ortho to –COO), 7.70 and 7.60 (d+d, 4H, ortho to –Ar), 7.35 (d, 2H, ortho to –OCO), 7.00 (d, 2H, ortho to –OCH_2), 5.35 (q, 1H, C*H), 4.20 (t, 2H, $COOCH_2$), 4.02 (t, 2H, CH_2OAr), 3.42 (t, 2H, CH_2Br), 1.20–2.00 (m, 15H, CH_2+CH_3C^*), 0.90 (t, 3H, CH_3).

For the Bunte salt (R=–$C^*H(CH_3)COOC_4H_9$), ^1H NMR (300 MHz, DMSO): 8.10 (dd, 4H, ortho to –COO), 7.85 and 7.70 (d+d, 4H, ortho to –Ar), 7.48 (d, 2H, ortho to –OCO), 7.03 (d, 2H, ortho to –OCH_2), 5.22 (q, 1H, C*H), 4.10 (t, 2H, $COOCH_2$), 4.00 (t, 2H, CH_2OAr), 2.81 (t, 2H, CH_2S), 1.20–1.80 (m, 15H, CH_2+CH_3C^*), 0.85 (t, 3H, CH_3).

For thiol **MK10** (**5** with R=–$C^*H(CH_3)CO$-OC_4H_9), ^1H NMR (300 MHz, $CDCl_3$): 8.20 (dd, 4H, ortho to –COO), 7.70 and 7.58 (d+d, 4H, ortho to –Ar), 7.35 (d, 2H, ortho to –OCO), 7.00 (d, 2H, ortho to –OCH_2), 5.35 (q, 1H, C*H), 4.20 (t, 2H, $COOCH_2$), 4.02 (t, 2H, CH_2OAr), 2.70 (t, 0.02H, residual CH_2SSCH_2), 2.55 (m, 2H, CH_2SH), 1.20–1.90 (m, 15H, CH_2+CH_3C^*), 0.90 (t, 3H, CH_3).

For thiol **MK11** (**5** with R=–$CH_2C^*H(CH_3)$-CH_2CH_3), ^1H NMR (300 MHz, $CDCl_3$): 8.20 (dd, 4H, ortho to –COO), 7.70 and 7.58 (d+d, 4H, ortho to –Ar), 7.35 (d, 2H, ortho to –OCO), 7.00 (d, 2H, ortho to –OCH_2), 4.20 (m, 2H, $COOCH_2$), 4.02 (t, 2H, CH_2OAr), 2.55 (m, 2H, CH_2SH), 1.20–1.90 (m, 11H, CH_2+CH), 0.95 (m, 6H, CH_3).

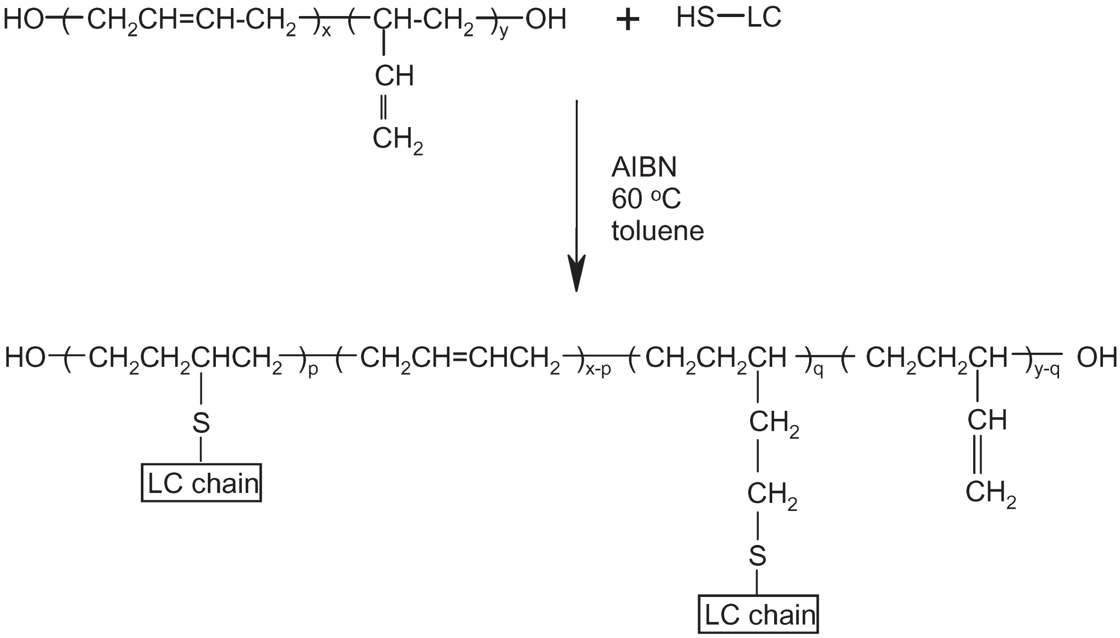
For thiol **MK17** (**5** with R=–$C^*H(CH_3)CO$-$OCH_2C^*H(CH_3)CH_2CH_3$), ^1H NMR (300 MHz, $CDCl_3$): 8.20 (dd, 4H, ortho to –COO), 7.70 and 7.58 (d+d, 4H, ortho to –Ar), 7.35 (d, 2H, ortho to –OCO), 7.00 (d, 2H, ortho to –OCH_2), 5.35 (q, 1H, C*H), 4.05 (m, 2H, $COOCH_2$), 4.02 (t, 2H, CH_2OAr), 2.55 (m, 2H, CH_2SH), 1.20–1.90 (m, 14H, CH_2+CH), 0.95 (m, 6H, CH_3).

3. Synthesis of polybutadiene diols

General scheme of preparation of the polybutadiene diols with chiral thiols side-chains is presented in Scheme 2. Side-chain LC polybutadienes have been prepared by the addition of a mesogenic thiol to double bonds of OH-terminated telechelic polybutadiene Krasol 3000 at 80°C in the presence of azoisobutyronitrile (AIBN) as initiator.

After dissolving, reaction mixtures consisting of thiol, OH-terminated polybutadiene Krasol 3000, AIBN and toluene as solvent were placed into glass ampoules. Then the reaction mixture was bubbled with nitrogen for 10 min and the ampoules sealed. The addition proceeded at temperature 60°C for 48 h. Then the reaction mixtures were poured into an excess of methanol and precipitated products were purified by re-precipitation from chloroform solutions to methanol.

Final polymers were purified from residual thiols by stirring with Ag_2O pulver in tetrahydrofuran solutions for several hours. Then the solutions were filtered and poured into water. The precipitates were



Scheme 2. General procedure for preparation of the resulting side-chain polymers – the polybutadiene diols (LC chain–S stands for **MK10**, **MK11** and **MK17**).

separated by suction. The density of grafting, *G*, was confirmed by NMR spectroscopy of the respective polybutadiene diols; calculations were carried out according to the procedure described by DelaCampa and Pham (*20*). For all studied cases, the polar ratio of 1,2 and 1,4 grafting (see Scheme 2) was about $q/p \approx 0.40$ and the ratio of the residual unsaturated segments $(y-q)/(x-p) \approx 0.55$ independently on the density of grafting.

4. Experimental

For the studied thiols and related polybutadiene diols, the 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 (Nikon Eclipse E600POL). Due to the relatively high viscosity of all prepared polymers it was necessary to use the shearing technique (*21*). In that case, the sample was 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 the present case the overlapping area was 16.8 mm^2). The distance between the glass plates was 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 (*21*). A 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 a rate of 10 K min^{-1}. Samples weighing 4–12 mg hermetically sealed in aluminium pans were placed in a nitrogen atmosphere and the temperature was calibrated on extrapolated onsets of melting points of water, indium and zinc. The enthalpy change was calibrated on enthalpies of melting of water, indium and zinc.

5. Mesomorphic properties

The mesomorphic properties of the studied thiols and the resulting diols are summarized in Table 2. Due to the active hydrophilic SH end chain of the studied thiols, it was complicated to study the mesomorphic properties in detail. However, a very broad paraelectric orthogonal smectic A (SmA) phase is clearly identified by characteristic textures and their changes with temperature for all studied thiols. Microphotographs of growth of the SmA bâtonnets from the isotropic melt (at 138°C) and resulting typical fan-shaped texture of the SmA phase (at 98°C) for thiol **MK17** are shown in Figures 1(a) and 1(b), respectively. A broad enantiotropic SmA phase

Table 2. Sequence of phases and phase transition temperatures (°C) measured on cooling and melting points, m.p. (°C), and clearing points, c.p. (°C), measured on heating (10 K min^{-1}) by DSC for the studied chiral thiols and related polybutadiene diols. (G is the density of grafting (mol. %), "•" indicates the phase exists).

	G	m.p. [ΔH /J g^{-1}]	c.p. [ΔH /J g^{-1}]	Cr	T_c [ΔH /J g^{-1}]	SmA	T_c [ΔH /J g^{-1}]	I
MK10	–	43.2 [+50.1]	87.2 [+5.3]	•	33.2 [−44.0]	•	77.1 [−3.1]	•
PK10-10	10	71.4 [+3.1]	165.9 [+3.0]	•	64.2 [−3.0]	•	164.1 [−3.1]	•
PK10-20	20	70.5 [+6.2]	163.8 [+5.5]	•	63.2 [−5.3]	•	161.4 [−5.6]	•
PK10-30	30	70.8 [+6.3]	163.7 [+6.2]	•	64.0 [−6.3]	•	163.1 [−6.3]	•
MK11	–	60.2 [+5.5]	204.8 [+9.9]	•	38.1 [−1.3]	•	204.6 [−10.9]	•
PK11-30	30	66.4 [+21.9]	217.7 [+5.2]	•	54.0 [−1.8]	•	211.9 [−8.8]	•
MK17	–	88.8 [+8.8]	141.5 [+5.3]	•	78.3 [−7.5]	•	138.1 [−5.1]	•
PK17-15	15	69.4 [+2.0]	105.0 [+2.6]	•	62.3 [−1.0]	•	102.7 [−1.1]	•
PK17-30	30	72.8 [+4.0]	116.1 [+5.7]	•	69.5 [−3.2]	•	115.1 [−3.3]	•
PK17-45	45	63.6 [+3.7]	109.8 [+4.8]	•	58.3 [−1.8]	•	106.2 [−3.8]	•

spanning more than 140 K was detected for thiol **MK11**. The lowest melting point was found for thiol **MK10**, but the width of the mesophase is only about 35 K (see Table 2). DSC plots on heating/cooling runs for all newly synthesised thiols are shown in Figure 2.

Commercial OH-terminated telechelic polybutadiene Krasol 3000, which was used for the polymer preparation, possesses a glass transition temperature at −41°C (as detected by DSC). The prepared polybutadiene diols grafted by three phenyl ring side-chain thiols of different structure (see Table 2) also possess a broad temperature range of the paraelectric smectic A phase that have been clearly identified from the characteristic textures and their changes with temperature on cooling (see Figure 1c for polybutadiene diol **PK10-20** at 148°C). Improvement of the alignment has been reached by the shearing of the top glass of the sample cell. For polybutadiene diol **PK17-30**, microphotographs of the texture before and after the shearing showing the improvement of the alignment are depicted in Figures 1e and 1f, respectively. Characteristic texture of the high ordered crystal phase is shown in Figure 1d for polybutadiene diol **PK10-20** (at 51°C). The prepared polybutadiene diols all exhibit an electro-optical response to an applied electric field, indicating the electro-clinic effect connected with the fluctuations on the molecules in the tilt direction. For polybutadiene diols, an example of the DSC plots on heating/cooling runs is shown in Figure 3 for **PK17-15**, **PK17-30** and **PK17-45**. The phase transitions peaks on DSC scans are very broad, reaching 15–30 K for some of the studied polymers.

The effect of grafting of the side-chains on the mesophase behaviour was checked carefully, but no pronounced dependence of the mesomorphic properties on the density of grafting was detected. It should be mentioned that independently on the density of grafting, the clearing point increases for **PK10** with respect to thiol **MK10** by about 80 K, whereas it decreases by about 30 K for **PK17** with respect to thiol **MK17**. In order to explain such behaviour, advanced structural studies together with modelling are in progress and will be presented elsewhere.

6. Summary and conclusions

Three new types of chiral thiols possessing biphenyl and phenyl moieties as well as ester linkage groups in the molecular core have been synthesized and grafted on polybutadiene diol backbones. The preparation of the thiols from thiouronium salts (standard method) was impossible in the present case due to the hydrolysis of the ester group. In order to solve that problem, new method of synthesis of the chiral thiols with the ester linkage groups through the so-called Bunte salts has been successfully developed. All newly synthesised chiral thiols as well as the related polybutadiene diols possess liquid crystalline behaviour, i.e. a paraelectric orthogonal SmA phase over a very broad temperature range.

The effect of structural changes in the mesogenic thiols has been detected with respect to the mesomorphic properties of the resulting diols. For the **MK10** thiol and related **PK10** polybutadiene diols a significant broadening of the temperature range of the mesophase has been found. However, no pronounced effect of the density of grafting for the **PK10** and **PK11** diols occurs. The increase of the phase transition temperatures and slight broadening of the SmA phase with respect to the related thiol **MK17** was detected for **PK17** diols possessing two chiral centres. The density of grafting effect has been studied: the mesomorphic behaviour of the studied compounds increases with an increase density of grafting.

Recently, compounds with chemical structure similar to the thiols studied here have been presented.

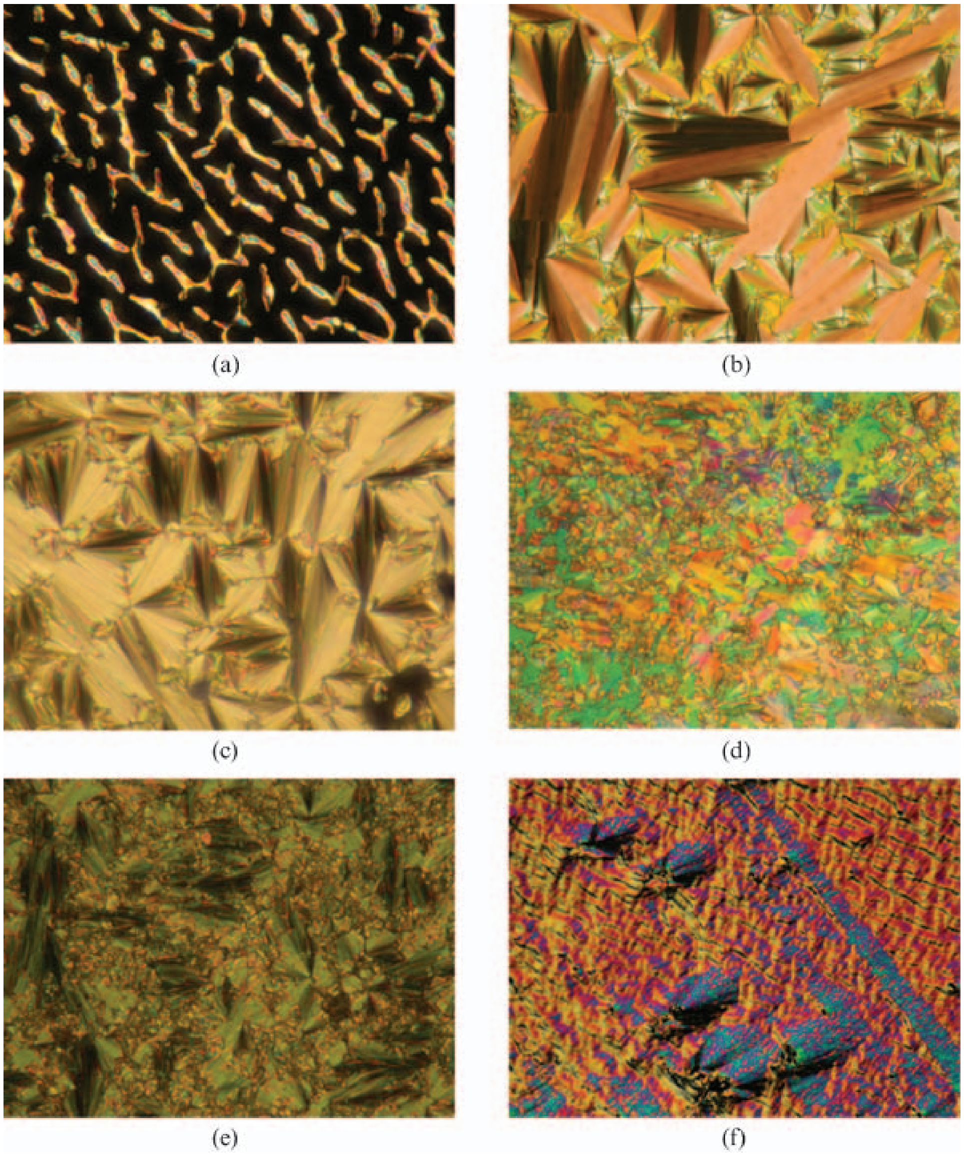


Figure 1. Microphotographs obtained on cooling: (a) growth of the SmA bâtonnets from the isotropic melt at 138°C for thiol **MK17**; (b) typical fan-shaped texture of the SmA phase at 98°C for thiol **MK17**; (c) texture of the SmA phase at 148°C for polybutadiene diol **PK10-20**; (d) texture of the highly ordered crystal phase at 51°C for polybutadiene diol **PK10-20**; (e) texture of the SmA phase at 109°C for polybutadiene diol **PK17-30**; (f) texture of the SmA phase after the shearing at 100°C for polybutadiene diol **PK17-30**. The width of the pictures is about 200 μm.

The only difference is in the non-chiral chain: the alkyl chain (C_nH_{2n+1}) (*22*) or the terminal double bond (–CH=CH$_2$) (*23*) instead of the –SH group. Both series of compounds (*22, 23*) possess a very broad ferroelectric SmC* phase below the orthogonal paraelectric SmA phase. However, none of the thiols in this work exhibit a ferroelectric tilted SmC* phase. It can be concluded that strong steric influence of the bulky end-chain group (as SH) can affect and suppress the formation of the tilted ferroelectric phase due to possibility of existence of the additional hydrogen bond.

Nevertheless, the chiral thiols and related polybutadiene diols described in this paper could be used as dopants for the multicomponent mixtures with high potential applicability in various electro-optical applications in photonics as well as giving a possibility for preparation of the liquid crystal ordered networks (*24*). Moreover, the chiral terminally thiol-functionalized mesogens studied in this work can be taken as precursor molecules for the preparation special liquid crystalline materials to be attached to gold nanoparticles (*25–27*).

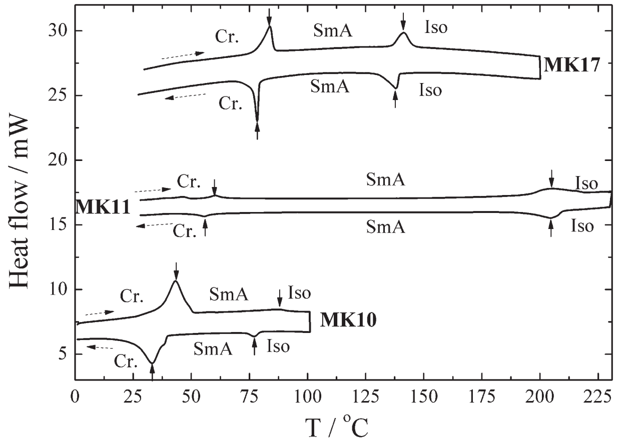


Figure 2. DSC plots on heating/cooling runs (indicated by dashed arrows) for thiols **MK10**, **MK11** and **MK17**. Solid vertical arrows indicate the peaks corresponding to phase transitions on heating/cooling.

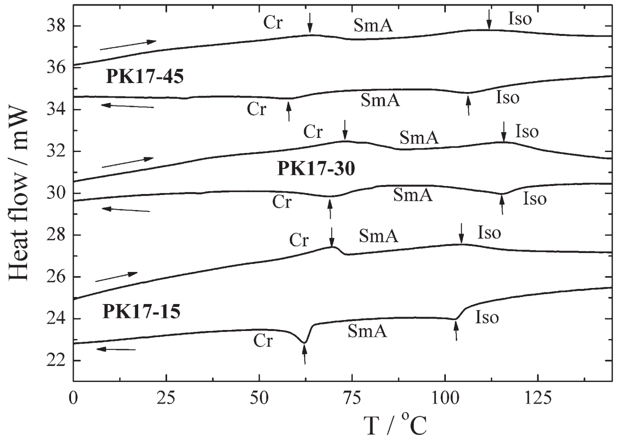


Figure 3. DSC plots on heating/cooling runs (indicated by dashed arrows) for the polybutadiene diols **PK17-15**, **PK17-30** and **PK17-45**. Solid vertical arrows indicate the peaks corresponding to phase transitions on heating/cooling.

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References

(1) De Genes P.G. *The Physics of Liquid Crystals*; Oxford University Press: Oxford, 1974.
(2) Shibaev V.P.; Kozlovsky M.V.; Beresnev L.A.; Blinov L.M.; Plate N.A. *Polymer Bull.* **1984**, *12*, 299–306.
(3) Hahn B.; Percec V. *Macromolecules* **1987**, *20*, 2961–2968.
(4) Talroze R.V.; Zubarev E.R.; Kuptsov S.A.; Merekalov A.S.; Yuranova T.I.; Plate N.A.; Finkelmann H. *React. Funct. Polym.* **1999**, *41*, 1–11.
(5) Bubnov A.; Kašpar M.; Hamplová V.; Glogarová M.; Samaritani S.; Galli G.; Andersson G.; Komitov L. *Liq. Cryst.* **2006**, *33*, 559–566.
(6) Svensson M. Chiral Liquid Crystalline Side-Chain Polymers: Design, Synthesis and Properties. Ph.D. Thesis, Chalmers University of Technology, Göteborg, Sweden (1997).
(7) Olsson N. Liquid Crystalline Siloxane Dimers and Polymers – Advanced Materials with Enhanced Properties. Ph.D. Thesis, Chalmers University of Technology, Göteborg, Sweden (2006).
(8) Galli G.; Ragnoli M.; Chiellini E.; Komitov L.; Andersson G. *Ferroelectrics* **2002**, *276*, 37–44.
(9) Galli G.; Di Bona M.R.; Fodor-Csorba K.; Gallot B.; Chiellini E. *Mol. Cryst. Liq. Cryst.* **1999**, *336*, 101–110.
(10) Cesarino C.; Komitov L.; Galli G.; Chiellini E. *Mol. Cryst. Liq. Cryst.* **2001**, *372*, 217–227.
(11) Zhang B.-Y.; Meng F.-B.; Tian M.; Xiao W.-Q. *React. funct. Polym.* **2006**, *66*, 551–558.
(12) Finkelmann H.; Happ M.; Portugall M.; Ringsdorf H. *Makromol. Chem.* **1978**, *179*, 2541–2549.
(13) Hsu C.H.; Jin J.H.; Chou L.R.; Hsuie G.H. *Macromolecules* **1992**, *25*, 7126–7134.
(14) Hachiya S.; Tomoika K.; Yuasa K.; Togawa S.; Sekiya T.; Takahashi K.; Kawasaki K. *J. Soc. Inf. Display* **1993**, *295*, 143–147.
(15) Kašpar M.; Bubnov A.; Hamplová V.; Novotná V.; Lhotáková Y.; Havliček J.; Ilavský M. *Mol. Cryst. Liq. Cryst.* **2005**, *428*, 49–63.

(16) Bubnov A.; Kašpar M.; Sedláková Z.; Garić M.; Obadović D.Ž.; Ilavský M. In *Proceedings of the XVI Conference on Liquid Crystals: Chemistry, Physics and Applications,* pp. 11, Perkowski P., *et al.,* Eds.; Garmond: Warsaw, 2007.
(17) Kašpar M.; Bubnov A.; Sedláková Z.; Stojanović M.; Havlíček J.; Obadović D.Ž.; Ilavský M. *Eur. Polym. J.* **2008**, *44*, 233–243.
(18) Kašpar M.; Hamplová V.; Novotná V.; Glogarová M.; Pociecha D.; Vanek P. *Liq. Cryst.* **2001**, *28*, 1203–1209.
(19) Westlake H.E., Jr.; Dougherty G. *J. Am. Chem. Soc.* **1945**, *67*, 1861.
(20) DelaCampa J.G.; Pham Q.T. *Macromol. Chem* **1981**, *182*, 1415–1419.
(21) Skarp K.; Andersson G. *Ferroelectrics Lett.* **1986**, *6*, 67–74.
(22) Taniguchi H.; Ozaki M.; Yoshino K.; Satoh K.; Yamasaki N. *Ferroelectrics* **1988**, *77*, 137–144.
(23) Bubnov A.; Hamplová V.; Novotná V.; Kašpar M.; Glogarová M. In *Proceedings of the XVI Conference on Liquid Crystals: Chemistry, Physics and Applications,* pp. 83, Perkowski P., *et al*., Eds.; Garmond: Warsaw, 2007.
(24) Urayama K.; Luo Z.-H.; Kawamura T.; Kohjiya S. *Chem. Phys. Lett.* **1998**, *287*, 342–346.
(25) Kumar S.; Lakshminarayanan V. *Chem. Commun.* **2004**, 1600–1601.
(26) Kumar S.; Pal S.K. *Liq. Cryst.* **2005**, *32*, 659–661.
(27) Dobbs W.; Suisse J.-M.; Douce L.; Welter R. *Angew. Chem.* **2006**, *45*, 4179–4182.