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New side chain liquid crystalline polysiloxanes containing 1,3-dithiane or 1,3-dioxane rings as mesogenic side groups

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New liquid crystal materials: 2-[*p*-(9-decenyloxy)phenyl]-5-(*p*-alkoxyphenyl)-1,3-dioxane (**11**) and 2-[*p*-(9-decenyloxy)phenyl]-5-(*p*-alkoxyphenyl)-1,3-dithiane (**12**) were synthesized. The mesomorphic behaviour of these compounds was determined. Though the 1,3-dioxane-type monomer exhibited both SmA and nematic phases, the 1,3-dithiane-type monomer only exhibited a nematic phase. By the hydrosilylation of poly(methylhydrosiloxane) and these monomers, side chain polysiloxanes were synthesized. For the monomers, the transition temperatures of the nematic to isotropic transitions of 1,3-dioxane-type compounds are higher than those of the corresponding 1,3-dithiane-type compounds. However, in the polysiloxane polymer this relation reversed.

1. Introduction

Over the last sixteen years, 2,5-disubstituted-1,3-dithianes, 1,3-oxathianes and 1,3-dioxanes have been reported as new types of liquid crystal materials [1–32]. Liquid crystal polymers have also been identified as important functional materials, and various liquid crystalline, side chain polymers have been synthesized [33]. However, while the effect of large sulphur atoms on the liquid crystal polymer system may be interesting, dithiane-type liquid crystal polymers have not been reported. In a previous paper we reported new methacrylate-type liquid crystal polymers containing a 1,3-dithiane ring. These polymers exhibited lower nematic–isotropic transition temperatures than those of ordinary methacrylate-type liquid crystal polymers. It would be interesting if such an effect would hold for polysiloxanes containing a 1,3-dithiane moiety. In this paper we wish to report the syntheses and the mesomorphic behaviour of such sulphur-containing polysiloxane compounds.

2. Results and discussion

2-[*p*-(9-Decenyloxy)phenyl]-5-(*p*-alkoxyphenyl)-1,3-dioxanes (**11**) and 2-[*p*-(9-decenyloxy)phenyl]-5-(*p*-alkoxyphenyl)-1,3-dithianes (**12**) were synthesized according to the scheme and is described below.

In the synthesis of ethyl *p*-ethoxyphenylacetate (**1**), both esterification and etherification were accomplished in one step from *p*-hydroxyphneylacetic acid. In step (**1**)–(**2**), it was necessary to keep the reaction temperature at 200–210°C for about 40 min under a reduced pressure (20–30 mmHg) for the complete evolution of carbon monoxide. In the bromination of the diol (**3**), a large excess of PBr_3 was required to yield the dibromide as the main product: mono and di-bromides were produced, however, separation of them was not carried out in this step. Therefore, in the synthesis of the mercaptan (**6**), a mixture of mono and di-bromide was used. Compound **6** was purified by column chromatography (compound **6** eluted in a hexane fraction and **7** eluted separately). Compounds **11** and **12** were purified first by column chromatography (Wakogel C-300, benzene : ether = 5 : 1), and then by recrystallization from hexane–ether (2 : 1).

In the hydrosilylation of poly(emthylhydrosiloxane) and the synthesized monomers, chloroplatinic acid was used as a catalyst. The synthesized monomers (**11** and **12**) were soluble in hexane, thus separation of the polymer was performed by reprecipitation in hexane. The resultant polymers were purified by column chromatography using chloroform as the eluent. The degree of hydrosilylation was estimated by the peak integration of the ^1H NMR spectrum. The disappearance of the Si–H peak in the ^1H NMR spectrum and the Si–H absorption peak in the IR spectrum confirmed the analysis.

Measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro-melting point apparatus equipped with polarizers, and a differential scanning calorimeter. Phase identification was made by comparing the observed textures with those in the literature [32, 34]. Phase transition temper-

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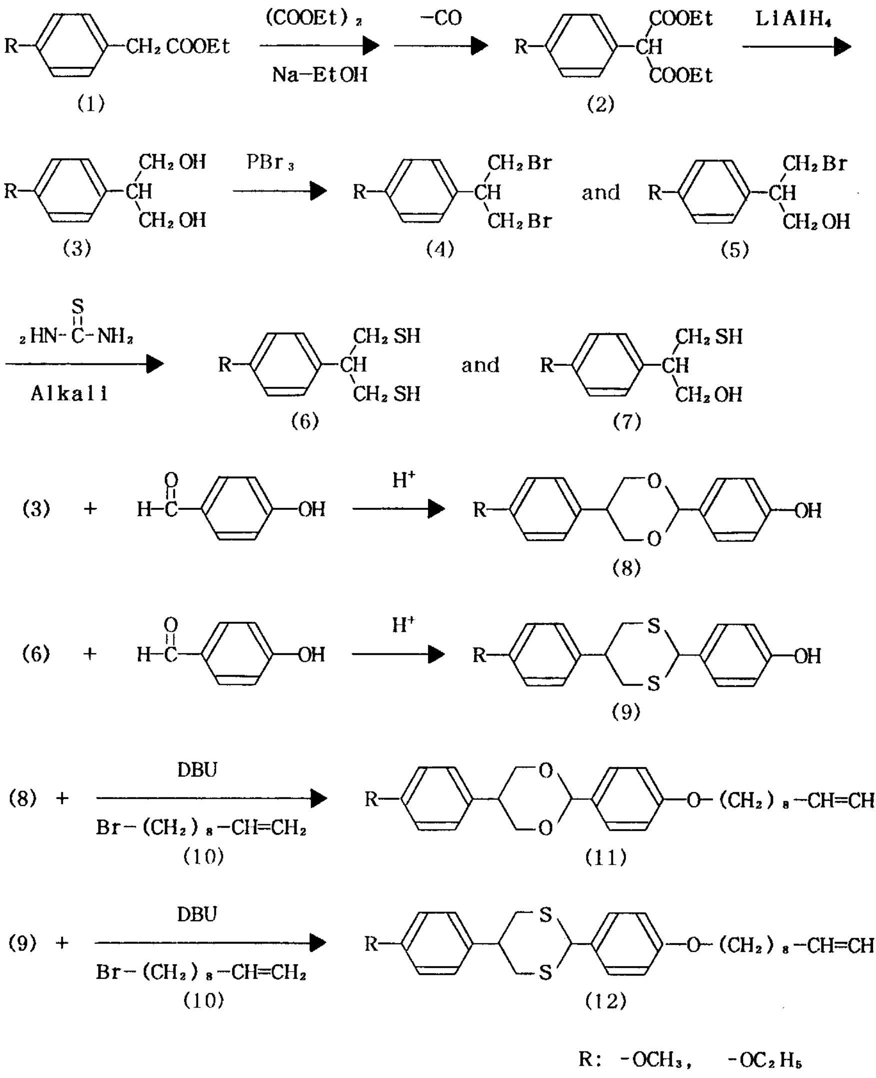
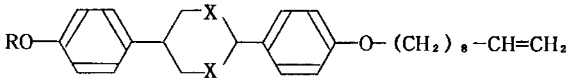


Scheme. Synthetic pathway for compounds **11** and **12**.

atures for the monomers **11** and **12**, the corresponding polymers (**Po-11**, **Po-12**), and related compounds are given in tables 1 and 2.

Though the 1,3-dioxane monomers (**11-1**, **11-2**) and polymers (**Po-11-1**, **Po-11-2**) exhibited SmA phases, the corresponding 1,3-dithiane monomers (**12-1**, **12-2**) and

Table 1. Phase transition temperatures for monomers **11** and **12**, and the corresponding polymers.

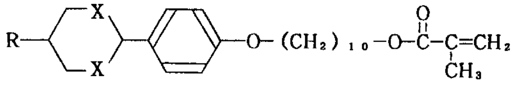


(**11**), (**12**)

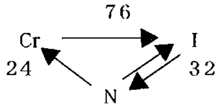
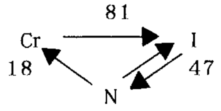
Compound	*R*	*X*	Phase transition temperatures/°C	
			Monomer	Polymer
11-1	CH_3	O	Cr 72 SmA 103 N 139 I	Cr 150 SmA 210 N 240 I
11-2	C_2H_5	O	Cr 98 SmA 146 N 161 I	Cr 140 SmA 203 N 235 I
12-1	CH_3	S	Cr 112 N 160 I	Cr 110 N 167 I
12-2	C_2H_5	S	Cr 114 N 179 I	Cr 134 N 210 I

Cr, Crystal; N, Nematic; Sm, Smectic; I, Isotropic.

Table 2. Phase transition temperatures for monomers **13** and **14**, and the corresponding polymers.



(13), (14)

Compound	*R*	*X*	Phase transition temperatures/°C	
			Monomer	Polymer
13-1	C_8H_{17}	O		Cr 80 SmA 101 I
13-2	$C_{10}H_{21}$	O		Cr 85 SmA 105 I
14-1	C_8H_{17}	S	$\mathrm{Cr} \underset{15}{\overset{95}{\rightleftarrows}} \mathrm{I}$	Cr 30 N 76 I
14-2	$C_{10}H_{21}$	S	$\mathrm{Cr} \underset{20}{\overset{112}{\rightleftarrows}} \mathrm{I}$	Cr 21 N 81 I

Cr, Crystal; N, Nematic; Sm, Smectic; I, Isotropic.

polymers (**Po-12-1**, **Po-12-2**) did not. This indicates that 1,3-dioxane-type compounds are preferred in promoting smectic behaviour than the 1,3-dithiane-type compounds. The temperatures of the liquid crystal to isotropic ($T_{\mathrm{LC-I}}$) phase transitions of the 1,3-dioxane monomers are lower than those of the corresponding 1,3-dithiane monomers. However, this relation was reversed for the corresponding polymers, that is, the $T_{\mathrm{LC-I}}$s for the 1,3-dioxane polymers are higher than those for the corresponding 1,3-dithiane polymers. This relation also fits for the methacrylic compounds **13** and **14**, that is, for polymer liquid crystals, the thermal stability of the 1,3-dithiane-type liquid crystal is lower than that of the corresponding 1,3-dioxane-type liquid crystal.

Generally large atoms have large dispersion forces, therefore, the transition temperatures of the 1,3-dithiane-type liquid crystal monomers are higher than those of the corresponding 1,3-dioxane-type liquid crystal monomers [11]. On the other hand, larger atoms have larger volumes and therefore make the LC molecule wider. In the liquid crystal monomers of 1,3-dithiane and 1,3-dioxane, dispersion force effect is prominent. For the liquid crystal polymers, the volume effect may be larger than the dispersion force effect. This can be rationalized in that the distances between the mesogens of the polymeric system must be greater than in the corresponding monomers, and this may weaken the effect of the dispersion force of the sulphur atoms between the mesogens.

The principal feature of the mesomorphic behaviour of 1,3-dithiane-type polymers is to exhibit the nematic liquid crystal phase, and to possess lower nematic–isotropic transition temperatures than the corresponding 1,3-dioxane-type polymers.

3. Experimental

3.1. *Analysis*

IR, H NMR and mass spectra were obtained with a Hitachi 215 spectrometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80B spectrometer, respectively. Elemental analyses were carried out with a Perkin–Elmer 250 instrument. The transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro-melting point apparatus equipped with polarizers and a Mettler DSC20 system, respectively.

3.2. *Synthesis of the diethyl* p-*alkoxy malonates* (**2**)

A conventional procedure was used for the syntheses of **2** [36].

3.2.1. *Diethyl* p-*methoxyphenylmalonate* (**2**)

Yield 60–70 per cent. B.p. 165–170°C (2–5 mmHg). IR ($CHCl_3$), 2850–3000 (alkyl), 1740 (C=O), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 1·3$ (t, 6 H, CH_3), 3·8 (s, 1 H, OCH_3), 4·25 (q, 4 H, OCH_2), 4·6 (s, 1 H, CH), 7·2 (q, 4 H, ArH).

3.2.2. *Diethyl* p-*ethoxyphenylmalonate* (**2′**)

Yield 50–60 per cent. B.p. 165–175°C (3–5 mmHg). IR ($CHCl_3$), 2850–3000 (alkyl), 1740 (C=O), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 1·3$ (q, 9 H, CH_3), 3·9–4·5 (m, 6 H, OCH_2), 4·6 (s, 1 H, CH), 7·2 (q, 4 H, ArH).

3.3. *Synthesis of the 2-(*p-*alkoxyphenyl)-1,3-propanediols* (**3**)

3.3.1. *2-(*p-*Methoxyphenyl)-1,3-propanediol* (**3**)

$LiAlH_4$ reduction of **2** in ether at 35°C for 18 h provided **3**. Yield 90–95 per cent. IR ($CHCl_3$), 3600 (OH), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 2·3$ (b, 2 H, OH), 3·0 (m, 1 H, CH), 3·8 (s, 3 H, OCH_3), 3·9–4·1 (m, 4 H, OCH_2), 7·05 (q, 4 H, ArH).

3.3.2. *2-(*p-*Ethoxyphenyl)-1,3-propanediol* (**3′**)

Yield 90–95 per cent. IR ($CHCl_3$) 3600 (OH), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 1·4$ (t, 3 H, CH_3), 2·5–4·3 (m, 9 H, CH_2O, CH, OH), 7·05 (q, 4 H, ArH).

3.4. *Synthesis of the 2-(*p-*alkoxyphenyl)-1,3-propanedithiols* (**6**)

3.4.1. *2-(*p-*Methoxyphenyl)-1,3-propanedithiol* (**6**)

To a solution of thiourea (0·07 mol, 5·3 g) in triethylene glycol (20 ml) kept at 75°C was added a mixture of **4** and **5** (6·4 g) under a nitrogen atmosphere, followed by stirring at 75°C for 18 h. Tetraethylenepentamine (0·02 mol) was then added, and the mixture was stirred at 75°C for 2 h under a nitrogen atmosphere. The reaction mixture was poured into ice–water (200 g) and extracted twice with ether (2 × 300 ml). The extract was dried over anhydrous Na_2SO_4, and evaporated *in vacuo* at 40°C. Compound **6** was purified by column chromatography (Wakogel C-300), with hexane as eluent. IR ($CHCl_3$), 2850–3000, 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 1·0–1·6$ (b, 2 H, SH), 2·6–3·1 (m, 5 H, CH_2S, CH), 3·8 (s, 3 H, OCH_3), 7·05 (q, 4 H, ArH).

3.4.2. *2-(*p-*Ethoxyphenyl)-1,3-propanedithiol* (**6′**)

IR ($CHCl_3$), 2850–3000, 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 1·0–1·6$ (m, 5 H, SH, CH_3), 2·6–3·0 (m, 5 H, CH_2, CH), 4·05 (q, 2 H, OCH_2), 7·05 (q, 4 H, ArH).

3.5. *Synthesis of 2-(4-hydroxyphenyl)-5-(4-methoxyphenyl)-1,3-dioxane* (**8**)

To a solution of compound **3** (0·005 mol) and *p*-hydroxybenzaldehyde (0·005 mol) in anhydrous $CHCl_3$ (300 ml) cooled in an ice bath were added BF_3 $(C_2H_5)_2O$ (0·5 g) and a molecular sieve (3 A, 1/16, 3 g). The mixture was stirred at 0–5°C for 8 h and then at 20–25°C for 18 h. The solution was washed with cold 10 per cent aqueous $NaHCO_3$ (200 ml), dried over anhydrous Na_2SO_4, and evaporated *in vacuo* at 40°C. The crude product was purified by column chromatography (Wakogel C-300) and recrystallized. Yield 30–40 per cent. IR ($CHCl_3$), 3600 (OH), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta =$ 2·5–4·5 (m, 8 H, CH_2O, CH, OCH_3), 5·6 (s, 1 H, CH), 6·8–7·7 (m, 8 H, ArH), 9·1 (b, 1 H, OH).

3.6. *Synthesis of 2-(4-hyroxyphenyl)-5-(4-methoxyphenyl)-1,3-dithiane* (**9**)

Compounds **9** were synthesized by following the same procedure as for compounds **8** using **6** instead of **3**. Yields 25–40 per cent. IR ($CHCl_3$), 3600 (OH), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 2·5–4·5$ (m, 8 H, CH_2S, CH, OCH_3), 5·1 (s, 1 H, CH), 6·8–7·6 (m, 8 H, ArH), 9·2 (b, 1 H, OH).

3.7. *Synthesis of the 2-[4-(9-decenyloxy)phenyl]-5-(4-alkoxyphenyl)-1,3-dioxanes* (**11**)

3.7.1. *2-[4-(9-Decenyloxy)phenyl]-5-(4-methoxyphenyl)-1,3-dioxane* (**11-1**)

A solution of compound **8** (0·005 mol), compound **10** (0·005 mol), and 1,8-diazabicyclo[5·4·0]undec-7-ene (0·005 mol) and phenothiazine (0·05 g) in anhydrous DMF (50 ml) was stirred at 30°C for 18 h under a nitrogen atmosphere. The solution was poured into ice–water and extracted twice with ether (2 × 200 ml). The extract was washed and dried over anhydrous Na_2SO_4, and evaporated *in vacuo* at 40°C. The crude product was purified by column chromatography (Wakogel C-300) and recrystallized. Yield 52 per cent. IR ($CHCl_3$), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta = 0·9–2·1$ (m, 14 H, CH_2), 2·5–4·5 (m, 10 H, CH_2O, CH, OCH_3), 4·8–6·2 (m, 4 H, CH, $-CH=CH_2$), 6·7–7·7 (m, 8 H, ArH). Found: C, 76·35; 8·53 per cent. Calculated for $C_{27}H_{36}O_4$: C, 76·3; H, 8·55 per cent. Mass 424 (M^+).

3.7.2. *2-[4-(9-Decenyloxy)phenyl]-5-(4-ethoxyphenyl)-1,3-dioxane* (**11-2**)

Yield 46 per cent. IR ($CHCl_3$), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta =$ 0·9–2·1 (m, 17 H, CH_2, CH_3), 2·5–4·5 (m, 9 H, CH_2O, CH), 4·8–6·2 (m, 4 H, CH, $-CH=CH_2$), 6·7–7·7 (m, 8 H, ArH). Found: C, 77·08; H, 9·10 per cent. Calculated for $H_{28}H_{38}O_4$: C, 76·67; H, 8·73 per cent. Mass 438 (M^+).

3.8. *Synthesis of the 2-[4-(9-decenyloxy)phenyl]-5-(4-alkoxyphenyl)-1,3-dithianes* (**12**)

3.8.1. *2-[4-(9-Decenyloxy)phenyl]-5-(4-methoxyphenyl)-1,3-dithiane* (**12-1**)

Yield 39 per cent. IR ($CHCl_3$), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta=$ 0·9–2·2 (m, 14 H, CH_2), 2·7–3·5 (m, 5 H, CH_2S, CH), 3·7–4·1 (m, 5 H, CH_2O, OCH_3), 4·7–6·2 (m, 4 H, CH, $-CH=CH_2$), 6·7–7·7 (m, 8 H, ArH). Found: C, 71·17; H, 7·74 per cent. Calculated for $C_{27}H_{36}S_2O$: C, 71·01; H, 7·95 per cent. Mass 456 (M^+).

3.8.2. *2-[4-(9-Decenyloxy)phenyl]-5-(4-ethoxyphenyl)-1,3-dithiane* (**12-2**)

Yield 47 per cent. IR ($CHCl_3$), 2850–3000 (alkyl), 1600 (Ar), 1280 (ether) cm^{-1}. ^1H NMR ($CDCl_3$), $\delta=$ 0·9–2·2 (m, 17 H, CH_2, CH_3), 2·7–3·5 (m, 5 H, CH_2S, CH), 3·8–4·3 (m, 4 H, CH_2O), 4·7–6·2 (m, 4 H, CH, $-CH=CH_2$), 6·7–7·7 (m, 8 H, ArH). Found; C, 71·95; H, 8·18 per cent. Calculated for $C_{28}H_{38}S_2O_2$: C, 71·44; H, 8·14 per cent. Mass 470 (M^+).

3.9. *Synthesis of polysiloxanes*

Poly(methylhydrogensiloxane) (0·2 g) and 20 mol % excess of the monomer (versus the Si–H groups present in polysiloxane) were dissolved in 20 ml of dry distilled toluene. 1 mg of H_2PtCl_6 catalyst in isopropanol solution was then added with a micropipette. The reaction mixture was heated to 80°C for 18 h, then 110°C for 12 h under a nitrogen atmosphere. The polymers were separated by reprecipitation from hexane.

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