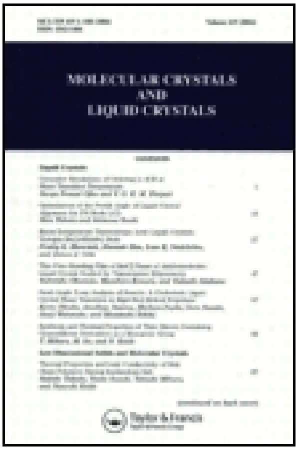

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New Polymerizable Liquid Crystal Materials with 1,3-Dioxane or 1,3-Dithiane Ring

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New Polymerizable Liquid Crystal Materials with 1,3-Dioxane or 1,3-Dithiane Ring

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New polymerizable liquid crystal materials: 4-(5-Alkyl-1,3-dioxan-2-yl)-phenyl acrylate (7) and 4-(5-alkyl-1,3-dithiane-2-yl)phenyl acrylates (8) have been synthesized. The corresponding methacrylates were also synthesized. The mesomorphic behavior of these compounds was measured. Though compounds (7) and (7′) exhibit the smectic phase, compounds (8) and (8′) did not exhibit the smectic phase. This must cause by the wider molecular width of compounds (8) and (8′) having two big sulfur atoms.

Monomers (7), (7′), (8), and (8′) were polymerized and new liquid crystal polymers were obtained. Though dioxane type polymers (Po-7, Po-7′) exhibited the nematic liquid crystal phase, the corresponding 1,3-dithiane type polymers did not.

Keywords: 1,3-Dioxane, 1,3-Dithiane, liquid-crystal polymer

INTRODUCTION

In the last fifteen years, 2,5-disubstituted-1,3-dioxanes, 1,3-oxathianes, and 1,3-dithianes have been reported successively as new types of liquid crystal materials.[1–24] On the other hand, liquid crystal polylmers have been noticed as functional materials and many studies have been done.[25,26]

This time we synthesized 1,3-dioxane and 1,3-dithiane type new liquid crystal monomers with polymerizable double bond and porymerized them. In these polymers, the 1,3-Dioxane type polymer exhibited the liquid crystal phase. Generally, side chain type liquid crystal polymer has a aliphatic chain as a flexible spacer between principal chain and mesogen group. A flexible spacer can ease off the viblation of principal chain, so that mesogen groups can orientate each other.

Without the spacer most of liquid crystal polymer cannot exhibit a liquid crystal phase. Therefore, this is a case to exhibit a liquid crystal phase without a spacer. In the present paper, we wish to report the syntheses of these new liquid crystal materials and comparison of the mesomorphic behavior between these two materials.

RESULTS AND DISCUSSION

Monomers, 4-(5-alkyl-1,3-dioxan-2-yl)phenyl acrylate and 4-(5-alkyl-1,3-dithiane-2-yl)phenyl acrylate were synthesized by the following route. Though, in the bromination step both mono and di-bromide were produced, separation of them was not carried out in this step. So that, in the syntheses of mercaptane, a mixture of compounds (2) and (3) was used.

Compound (4) was separated by the column chromatography, in which it eluted with hexane solvent (wako gel C-300). Synthesized monomers (7) and (8) contain trans and cis isomers, respectively. Therefore, (7) and (8) were purified by the column chromatography (Wakogel C-300, benzene: hexane = 2:1) and several time recrystallizations (hexane: ether = 5:1), respectively.

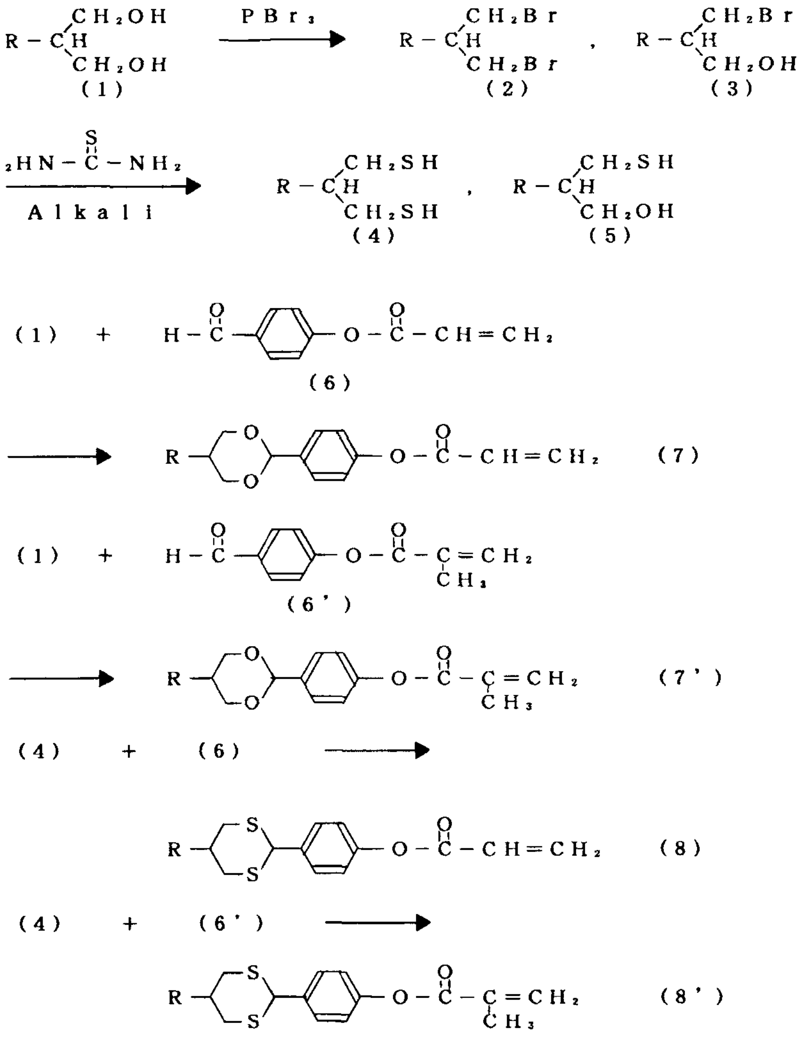
In the ^{1}H-NMR data for monomers 8 and 8′, the C-2 proton signals of the 1,3-dithiane ring for the trans and cis isomers appeared at 5.20 ppm and 5.15 ppm, respectively. Therefore, the removal of cis isomer by purification could be checked by the disappearance of this cis isomer's peak. In the same way, in the ^{1}H-NMR data for monomers 7 and 7′, the C-2 proton signals of the 1,3-dioxane ring for the trans and cis isomers appeared at 5.45 ppm and 5.50 ppm, respectively. Therefore, in the case of monomers 7 and 7′, the check of purity of trans isomer could be done in the same manner as for monomers 8 and 8′.

Polymers with pendant functional groups were prepared by the free radical polymerization of monomers, respectively. To decide the proper solvent for the polymerization, dioxane, benzene, and N,N-dimethylformamide were used. The comparative result is given in Table I. Though in the acrylate type polymer the number average molecular weight (*Mn*) and the weight average molecular weights (*Mw*) for Po-2 are lower than those for Po-1 and Po-3, in the methacrylate type polymer the *Mn* and *Mw* for Po-5 is higher than those for Po-4 and Po-6. And the values of *Mw*/*Mn* for Po-2 and Po-5 are small. Though Po-2 and Po-5 are white powder, other polymers have an orange color. On account of the results written above, dioxane was selected.

Measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers. Phase identification was made by comparing the observed textures with those in the literature.[27,28] Phase transition temperatures for monomers (7) and (8) are given in Table II.

Monomers 7′ exhibit the SmB phase. Judgement of SmB phase was carried out by DSC and observation of liquid crystal phase. That is, the value of transition enthalpy for isotropic to smectic is 7.80 KJ/mol (7′–3). Generally, ΔH of isotropic to SmA is 4–6 KJ/mol and ΔH of isotropic to SmB is 4–8 KJ/mol.[28] Therefore, this value belongs to that of SmB. And SmB textures with lancets were observed.

Though monomers 7–2 and 7–3 exhibit SmA phase, the corresponding 8–2 and 8–3 exhibit the nematic phase. And monomers 7′ exhibit the SmB phase but the



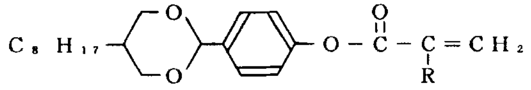
R : $n-C_6H_{13}$, $n-C_8H_{17}$, $n-C_{10}H_{21}$.

FIGURE 1

corresponding monomers 8′ did not exhibit any liquid crystal phases. Monomers 8 and 8′ have two sulfur atoms instead of two oxygen atoms in monomers 7 and 7′. Sulfur atoms are bigger than oxygen atoms, so that the molecular width of monomers 8 and 8′ are wider than that of monomers 7 and 7′. This must cause the results written above. And this also implies that the width near the long alkyl chain is important to exhibit the smectic phase. Because the molecular width of monomers 7′ is also wider than that of monomers 7 but in this case 7′ also exhibits the smectic phase. (7′ have a methacryloyl group which contains a methyl group

TABLE I

Selection of solvent for polymerization



	R	solvent	Mn	Mw	Mw/Mn
Po-1	H	benzene	9800	23400	2.39
Po-2	H	dioxane	8200	16900	2.06
Po-3	H	DMF	10200	26500	2.60
Po-4	CH_3	benzene	14400	56900	3.95
Po-5	CH_3	dioxane	33000	85000	2.58
Po-6	CH_3	DMF	24400	61600	2.52

Mn : number average molecular weight.
Mw : weight average molecular weight.

and this methyl group makes a difference of molecular width at the far position from the long alkyl chain.)

Some mesomorphic data for the polymerized 7, 7′, 8, and 8′ are also given in Table III.

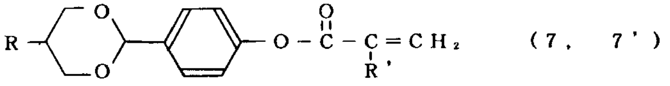
Though the dioxane type polymer (Po-7, Po-7′) exhibited the nematic liquid crystal phase, the corresponding dithiane type polymer (Po-8, Po-8′) did not. As the main difference of these two types of polymer is the molecular width of mesogenic side group, this may affect the appearance of mesophase. ΔH_{N-I} for Po-7′ was 3.2 J/g. This value was smaller than that for other methacrylate type liquid crystal polymer.[29]

EXPERIMENTAL

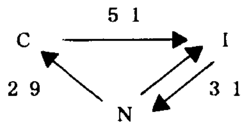
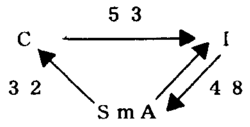
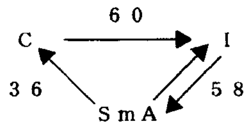
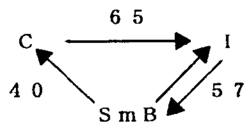
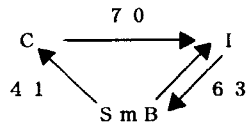
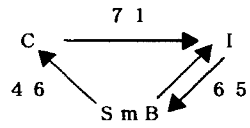
IR, ^{1}H-NMR, and mass spectra were obtained with a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi M-80B spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Transition temperatures and mesomorphic phases were determined by means of a Mitamura Riken micro melting point apparatus equipped with polarizers and a Mettler DSC 20 system, respectively. The number and weight average molecular

TABLE II

Transition temperature for compounds 7, 7′, 8, and 8′



(7, 7′)

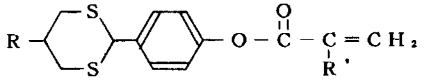
	R	R′	TRANSITION TEMPERATURES (°C) a)
7 – 1	C_6H_{13}	H	
7 – 2	C_8H_{17}	H	
7 – 3	$C_{10}H_{21}$	H	
7′ – 1	C_6H_{13}	CH_3	
7′ – 2	C_8H_{17}	CH_3	
7′ – 3	$C_{10}H_{21}$	CH_3	

weights (*Mn* and *Mw*) were determined using a Toso high speed GPC system (solvent: THF, standard: polystyrene).

4-Formylphenyl Acrylate (6) and 4-formylphenyl Methacrylate (6′)

To a solution of 4-formylphenol (0.03 mol) and 1,8-diazabicycro-[5.4.0]-undec-7-ene (0.03 mol) and phenothiazine (0.1 g) in anhydrous N,N-dimethyl-formamide (50 ml) was added methacryloyl chloride (0.03 mol) in a nitrogen atmosphere,

TABLE II (*continued*)



(8, 8')

	R	R'	TRANSITION TEMPERATURE (°C) [a]
8 −1	C_6H_{13}	H	$C \underset{35}{\overset{77}{\rightleftarrows}} I$
8 −2	C_8H_{17}	H	$C \xrightarrow{92} I \xrightarrow{61} N \xrightarrow{50} C$
8 −3	$C_{10}H_{21}$	H	$C \xrightarrow{75} I \xrightarrow{56} N \xrightarrow{45} C$
8' −1	C_6H_{13}	CH_3	$C \underset{59}{\overset{95}{\rightleftarrows}} I$
8' −2	C_8H_{17}	CH_3	$C \underset{61}{\overset{85}{\rightleftarrows}} I$
8' −3	$C_{10}H_{21}$	CH_3	$C \underset{75}{\overset{75}{\rightleftarrows}} I$

a) C : Crystal, I : Isotropic,
Sm : Smectic, N : Nematic.

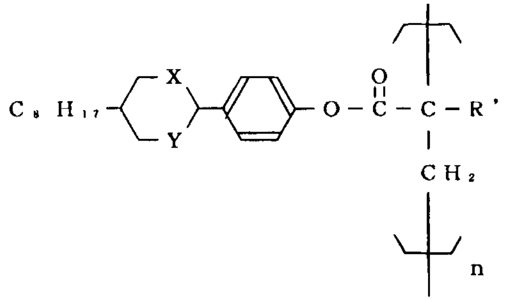
followed by stirring at 30°C for 18 h. The solution was poured into ice water (400 ml) and extracted twice with ether (each 200 ml). The ether solution was dried over anhyd. Na_2SO_4 and evaporated in vacuo at 40°C. The transparent liquid was obtained in a 50–60% yield.

Compound 6: IR ($CHCl_3$) 1700, 1740 (C=O), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 6.0–6.7 (m, 3H, —C=CH_2), 7.2–8.2 (q, 4H, ArH), 10.0 (s, 1H, CHO).

Compound 6': IR ($CHCl_3$) 1700, 1740 (C=O), 1600 (Ar) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 2.0 (s, 3H, CH_3), 5.8, 6.4 (s, 2H, =CH_2), 7.2–8.1 (q, 4H, ArH), 10.0 (s, 1H, CHO).

TABLE III

Transition temperatures for polymers



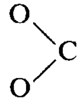
	R'	X	Y	TRANSITION TEMPERATURE (°C)[a)]	Mn	Mw[b)]
Po-7	H	O	O	g 35 N 140 I	8200	16900
Po-7'	CH_3	O	O	g 79 N 164 I	33000	85000
Po-8	H	S	S	C 147 I	7600	10400
Po-8'	CH_3	S	S	C 250 (dec.)	21600	60700

a) : g : glass, N : Nematic, C : Crystal, I : Isotropic,
dec. : decomposed.

b) : Mn : number average molecular weight,
Mw : weight average molecular weight.

4-(5-Alkyl-1,3-Dioxan-2-yl)phenyl Acrylate (7) and 4-(5-Alkyl-1,3-Dioxan-2-yl)phenyl Methacrylate (7')

To a solution of compound (1) (0.01 mol), (6) (0.01 mol), and phenothiazine (0.1 g) in anhyd. $CHCl_3$ (200 ml), cooled in an ice bath were added BF_3 $(C_2H_5)_2O$ (0.5 g) and molecular sieves (3A, 1/15, 3 g). This mixture was stirred at 0–5°C for 8 h and then at 20–25°C for 16 h. The solution was washed with 10% aqueous $NaHCO_3$ (400 ml), dried over anhyd. Na_2SO_4, and evaporated in vacuo at 40°C. The crude product was purified by column chromatography and recrystallizations from hexane.

The purified trans isomer was obtained as a white powder. IR ($CHCl_3$) 2950–2800 (alkyl), 1750 (C=O), 1610 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ monomers 7: 0.7–2.5 (m, R—CH), 3.3–4.4 (m, 4H, CH_2O), 5.45 (s, 1H,  ${}^{O}_{O}\rangle CH$), 5.75–6.60 (m, 3H, $CH{=}CH_2$), 7.0–7.75 (q, 4H, ArH). Monomers 7': 0.7–2.5 (m, R—CH, CH_3), 3.3–4.4 (m, 4H, CH_2O), 5.45 (s, 1H, $\begin{array}{l}O\diagdown\\ \quad CH\\ O\diagup\end{array}$), 5.8, 6.4 (d, 2H, $=CH_2$), 7.0–7.75 (q, 4H, ArH).

4-(5-Alkyl-1,3-Dithian-2-yl)phenylacrylate (8) and 4-(5-Alkyl-1,3-Dithian-2-yl)phenylmethacrylate (8′)

Monomers 8 and 8′ were synthesized according to the same procedure as that for compounds 7. IR ($CHCl_3$) 2950–3000 (alkyl), 1750 (C=O), 1600 (Ar) cm^{-1}. ^1H-NMR ($CDCl_3$) δ Monomers 8: 0.7–2.3 (m, R—CH), 2.7–3.9 (m, 4H, CH_2S), 5.2 (s, 1H, $\begin{array}{l}S\diagdown\\ \quad CH\\ S\diagup\end{array}$), 5.9–6.6 (m, 3H, $CH=CH_2$), 7.0–7.7 (q, 4H, ArH).

Monomers 8′: 0.7–2.3 (m, R—CH, CH_3), 2.7–3.0 (m, 4H, CH_2S), 5.2 (s, 1H, $\begin{array}{l}S\diagdown\\ \quad CH\\ S\diagup\end{array}$), 5.8, 6.4 (d, 2H, =CH), 7.0–7.7 (q, 4H, ArH).

7-1: Yield, 48%. Found: C, 72.14; H, 8.18%. Calcd for $C_{19}H_{26}O_4$: C, 71.67 H, 8.23%. Mass 318 (M^+).

7-2: Yield, 36%. Found: C, 72.81; H, 8.73%. Calcd for $C_{21}H_{30}O_4$: C, 72.80 H, 8.73%. Mass 346 (M^+).

7-3: Yield, 37%. Found: C, 74.07; H, 9.05%. Calcd for $C_{23}H_{34}O_4$: C, 74.07 H, 9.15%. Mass 374 (M^+).

7′-1: Yield, 41%. Found: C, 72.37; H, 8.48%. Calcd for $C_{20}H_{28}O_4$: C, 72.37 H, 8.48%. Mass 332 (M^+).

7′-2: Yield, 42%. Found: C, 73.76; H, 9.81%. Calcd for $C_{22}H_{32}O_4$: C, 73.30 H, 8.95%. Mass 360 (M^+).

7′-3: Yield, 36%. Found: C, 74.19; H, 9.34%. Calcd for $C_{24}H_{36}O_4$: C, 74.19 H, 9.34%. Mass 388 (M^+).

8-1: Yield, 7%. Found: C, 65.06; H, 7.48%. Calcd for $C_{19}H_{26}O_2S_2$: C, 65.06 H, 7.48%. Mass 350 (M^+).

8-2: Yield, 16%. Found: C, 66.43; H, 8.01%. Calcd for $C_{21}H_{30}O_2S_2$: C, 66.62 H, 7.99%. Mass 378 (M^+).

8-3: Yield, 12%. Found: C, 68.31; H, 8.68%. Calcd for $C_{23}H_{34}O_2S_2$: C, 67.93 H, 8.43%. Mass 406 (M^+).

8′-1: Yield, 8%. Found: C, 65.89; H, 7.87%. Calcd for $C_{20}H_{28}O_2S_2$: C, 65.89 H, 7.74%. Mass 364 (M^+).

8′-2: Yield, 15%. Found: C, 67.05; H, 8.25%. Calcd for $C_{22}H_{32}O_2S_2$: C, 67.30 H, 8.22%. Mass 392 (M^+).

8′-3: Yield, 12%. Found: C, 68.82; H, 9.07%. Calcd for $C_{24}H_{36}O_2S_2$: C, 68.52 H, 8.63%. Mass 420 (M^+).

Syntheses of Polymers

Polymers Po-7, 7′, 8, and 8′ were synthesized by the free radical polymerization of a solution of the corresponding monomers (0.5 mol/l) and AIBN (0.02 mol/l) as initiator in dioxane (2 ml) at 70°C for 72 h, deaerated ampules being employed. As monomers are soluble in hexane solvent, polymers were obtained by reprecipitation with hexane. And then a reprecipitation from tetrahydrofuran solution was carried out.

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