New Liquid-Crystal Polymer with a 1,3-Dithiane Ring

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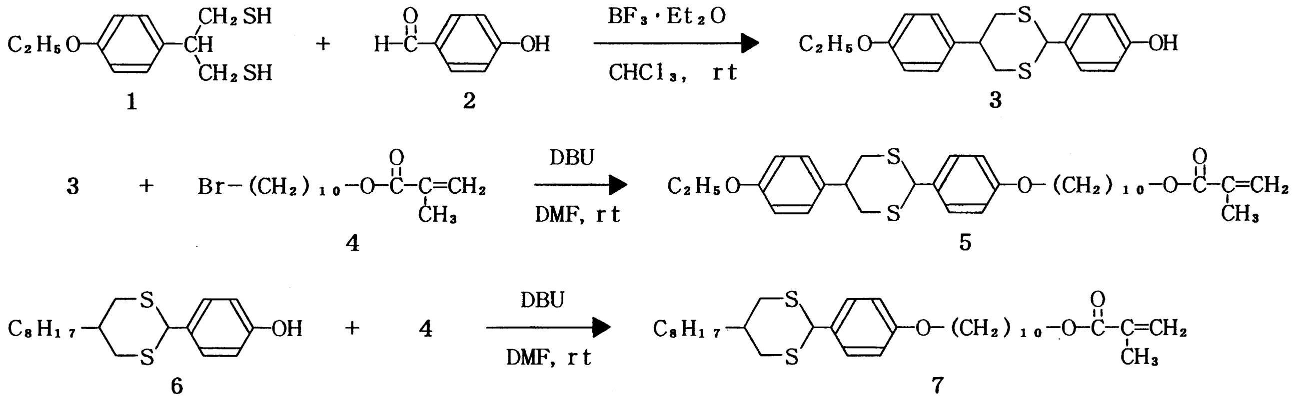
New polymerizable liquid crystal materials, 10-{4-[5-(4'-ethoxyphenyl)-1,3-dithian-2-yl]phenoxy}decyl methacrylate (5) and 10-{4-[5-octyl-1,3-dithian-2-yl]phenoxy}decyl methacrylate (7) have been synthesized and converted into polymers. Since these polymers (5', 7') show the schlieren texture of a nematic phase (e.g. 5': G 5 N 63 I), they are a new type of liquid crystal polymer having a 1,3-dithiane ring in their mesogen units.

For the last fifteen years, 2,5-disubstituted-1,3-dithianes, 1,3-oxathianes, and 1,3-dioxanes have been reported as new types of liquid crystal materials.[1-8] For the past several years, liquid crystal polymers have been noticed as functional materials and various liquid crystal polymers were synthesized. However, dithiane type liquid crystal polymers have not been reported. Accordingly, we have synthesized new various 1,3-dithiane type liquid crystal monomers with a polymerizable double bond, but the corresponding polymers were found difficult to exhibit the mesomorphic phase. In this study, we have synthesized two new types of 1,3-dithiane polymers and they exhibited the nematic liquid crystal phase at around room temperature. This letter reports the syntheses and mesomorphic behaviors of these new types of polymers with a 1,3-dithiane ring.

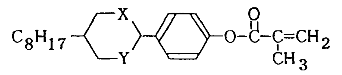
Compounds 5 and 7 were synthesized by the route shown in Scheme 1.

In the syntheses of compound 3, only a trans isomer was produced as judged from ^{1}H-NMR data. Therefore, separation of trans and cis isomers was not necessary. Compound 4 was synthesized from 1,10-dibromodecane and methacrylic acid. Compound 5 was purified by column chromatography and subsequent repeated recrystallizations (hexane:ether=2:1). Judging from ^{1}H-NMR data, only a trans isomer was obtained. This result is in accordance with a previous result.[4] Compounds 6 were synthesized from 2-alkyl-1,3-propanedithiol and p-hydroxybenzaldehyde. As trans and cis isomers were produced which differed at the C5 position of the 1,3-dithiane ring, repeated recrystallizations were required to get the trans isomer. As the C2 proton signals of trans and cis isomers appear at δ=5.20 and 5.15, respectively, in the ^{1}H-NMR spectra, removal of cis isomer can be checked by the disappearance of the cis isomer's peak. Side chain polymers were synthesized by the free radical polymerization of the monomers (5, 7). The number and weight average molecular weights (Mn and Mw) were determined using a Toso high speed GPC system HLC 8020. These values indicated the production of polymers (Table 1). Measurements of transition temperatures and assignments of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers, a Mettlar DSC system, and an X-ray system. Phase identification was made by comparing the observed textures with



Scheme 1. Synthetic pathway for the compounds 5 and 7.

Table 1. Transition Temperatures for Monomers 5, 7 and the corresponding polymers

		Phase transition temperatures (°C)[a] (Monomer)	(Polymer)	Mn[b] (Mw)
5		$C \underset{72}{\overset{80}{\rightleftarrows}} N \underset{98}{\overset{98}{\rightleftarrows}} I$	$G \xrightarrow{5} N \xrightarrow{63} I$	19000 (45000)
7		$C \underset{15}{\overset{95}{\rightleftarrows}} I$	$G \xrightarrow{30} N \xrightarrow{76} I$	18000 (39000)
			(8, 9, 10)	
	X Y	Phase transition temperatures (°C)[a] (Monomer)	(Polymer)	Mn[b] (Mw)
8	O O	$C \xrightarrow{70} I \overset{65}{\rightleftarrows} SmB \xrightarrow{46} C$	$G \xrightarrow{79} N \xrightarrow{164} I$	33000 (85000)
9	S O	$C \underset{36}{\overset{77}{\rightleftarrows}} I$	$G \xrightarrow{81} N \xrightarrow{140} I$	21900 (96000)
10	S S	$C \underset{61}{\overset{85}{\rightleftarrows}} I$	$C \xrightarrow{250}$ (dec.)	21600 (60700)

[a] C:Crystal, N:Nematic, Sm:Smectic, I:Isotropic, G: Glass, dec. : decomposed.

[b] Mn:number average molecular weight, Mw:weight average molecular weight. Mn and Mw were determined using a Toso high speed GPC system (solvent: THF, standard: polystyrene).

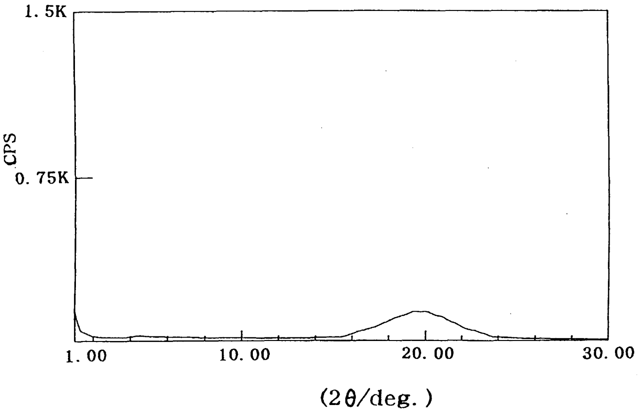


Figure 1. X-ray diffraction pattern of liquid crystal polymer 7'.
X-ray diffraction was measured with a Rigaku X-ray Rad 2B system using Ni-filtered CuKα radiation.

those in the literature,[9] and the result of X-ray diffraction. Phase transition temperatures for monomers (5, 7), the corresponding dithiane polymers (5', 7'), and related polymers are given in Table 1. Though polymers 8', 9' exhibited the nematic phase, the corresponding 1,3-dithiane polymer 10' did not exhibit any liquid crystal phases.[7,8] These facts may indicate that 1,3-dithiane type polymer is more difficult to exhibit the liquid crystal phase than 1,3-dioxane or 1,3-oxathiane type polymer. Therefore, polymer 7' having an alkyl chain as a spacer and a three ring type polymer 5' having a same spacer were synthesized. Both polymers 7' and 5' having a 1,3-dithiane ring in their principal structure exhibited the schlieren texture of nematic liquid crystal phase. The result of X-ray diffraction also supports this result. That is, there is a very broad peak at around 20°, but no peaks are seen at smaller angles as shown in Fig 1. Therefore, these polymers are the first liquid crystal polymers with 1,3-dithiane ring. The principal features of the mesomorphic behavior of 1,3-dithiane type liquid crystal polymer are (1) to exhibit the nematic liquid crystal phase at around room temperature, and (2) lower nematic-isotropic transition temperatures (5': 63°C, 7': 76°C) than those of ordinary methacrylate type liquid crystal polymer having alkoxy type side chains.[10]

References and Notes

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