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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Lub, J. , Broer, D. J. , Antonio, M. E. Martinez and Mol, G. N.(1998) 'The formation of a liquid crystalline main chain polymer by means of photopolymerization', *Liquid Crystals*, 24: 3, 375 – 379

To link to this Article: DOI: 10.1080/026782998207181

URL: <http://dx.doi.org/10.1080/026782998207181>

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The formation of a liquid crystalline main chain polymer by means of photopolymerization

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(Received 9 June 1997; accepted 3 September 1997)

A nematic liquid crystal material containing a mercapto group and an olefinic group was synthesized. Photopolymerization of this compound in the liquid crystalline state resulted in a liquid crystalline main chain polymer which showed a relatively high birefringence. Due to scattering, the material had a low transmission at ambient temperatures.

1. Introduction

Highly oriented polymeric films can be obtained through photopolymerization of aligned liquid crystals containing two polymerizable groups such as acrylates, methacrylates, vinyl ethers and epoxides [1]. A limitation of the so-called liquid crystalline networks, which are basically of the side group polymer type, is that, when polymerized in the easy-to-process nematic (N) phase, the order parameter S remains below 0.8, which also imposes its limits on the optical anisotropy. The limitation of S is explained mainly by steric factors in the networks. It is known that, because of the larger aspect ratio of liquid crystalline main chain polymers, a higher S can be realized than with liquid crystalline side group polymers. It is therefore of interest to design liquid crystalline monomers which upon photopolymerization would align the mesogenic cores in a main chain type of molecular arrangement. The photo-induced addition of thiols onto olefins is a well-known reaction for non-liquid crystalline systems, resulting in linear polymers [2]. Scheme 1 explains how this addition reaction may result in main chain liquid crystalline polymers. Monomer A, which contains a mercapto group as well as an olefinic group, reacts with the photo-initiator to form thiyl radical B. This radical adds to the double bond of another molecule of A, forming structure C, which contains a carbon-centred radical. After abstraction of a hydrogen from A, oligomeric species D is formed and another thiyl radical B. In this way a radical chain is operative leading to high molecular mass species.

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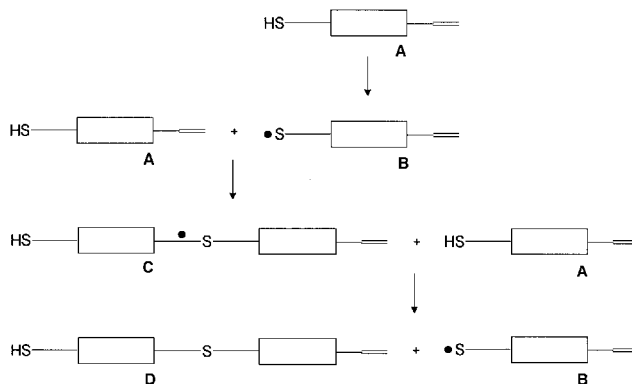
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This paper describes the synthesis of a mesogenic monomer containing an olefinic and a thiol functional group, and its photopolymerization behaviour. The monomer we selected was a mixture of 4-[4-(5-hexenyloxy)benzoyloxy]-1-[4-(5-mercaptopentyloxy)benzoyloxy]-2- and 3-methylbenzenes (**1**) (see scheme 2). The mesogenic group is derived from methylphenylene bisbenzoate, one end group being hexenyl and the other mercaptopentyl. The molecule resembles the non-reactive 2,5-dimethylphenylene bis(4-hexyloxybenzoate), which exhibits an enantiotropic nematic phase between 88 and 172°C [3]. It was expected that **1** would also exhibit a broad range nematic mesophase facilitating our study of the polymerization in the nematic phase over a broad temperature range.

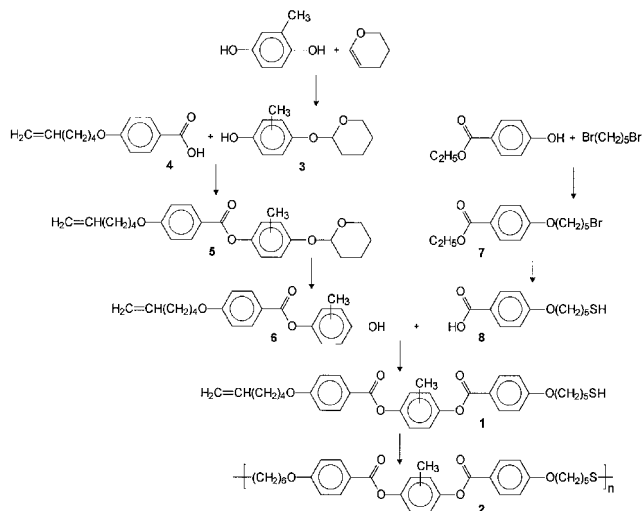
2. Experimental

2.1. Characterization and source materials

¹H NMR and ¹³C NMR spectra were measured using a Bruker DPX 300 spectrometer and a solution in



Scheme 1. Representation of the thiol-ene polymerization reaction.



Scheme 2. Synthesis of 4-[4-(5-hexenyloxy)benzoyloxy]-1-[4-(5-mercaptopentylloxy)benzoyloxy]-2- and 3-methylbenzenes (1) and formation of its polymer (2).

CDCl₃ with TMS as an internal standard. The products gave ¹H NMR spectra that were in accordance with their structures. Phase transitions were measured using a Perkin Elmer DSC-7 apparatus. A Reichert optical microscope coupled with a Mettler FP52 hot stage was used for texture analysis. The photopolymerization experiments were performed in the same manner as those with diacrylates as described previously [4]. Irradiation was carried out for 180 minutes with a Philips PL-10 lamp in dry air. Cells provided with rubbed polyimide were filled by capillary action using the molten monomer–initiator mixture. The birefringence and the changes in the birefringence and transmission during polymerization were measured using a UV–Vis spectrophotometer, in which the cell was placed between two crossed polarizers with its orientation axis at 45° to the polarizers as described in references [5] and [6].

The size exclusion chromatography experiments were performed using solutions in chloroform (0.2–0.5 mg g⁻¹). After filtration (Millex-LCR 0.5 μm filter), 25 μl samples of the solutions were injected into a GPC column (PL gel-5 μm-mixed-c column, 300 × 7.5 mm², linear range 200 to 3 × 10⁶, with guard column 50 × 7.5 mm²) and eluted with chloroform at a flow rate of 1.0 ml min⁻¹. Detection occurred at 254 nm. The equipment was calibrated with the aid of a series of 16 narrow dispersion polystyrene standards (Mw: 580–3 × 10⁶).

All the solvents were obtained from E. Merck. All other chemicals were obtained from Janssen Chimica. 4-(5-hexenyloxy)benzoic acid (4) was prepared according to a procedure described in the literature [7].

2.2. Synthesis of 4-(tetrahydropyran-2-yloxy)methylphenols; mixture of the 2- and 3-methyl isomers (3)

To a solution of 126 g of methylhydroquinone and 5 g of 4-toluenesulphonic acid in 11 of diethyl ether was added 90 ml of dihydropyran over a period of 30 min, with stirring. After stirring had continued for another 2 h, nitrogen was bubbled through and a nitrogen-purged solution of 45 g of sodium hydroxide in 500 ml of water was added. After separation, the aqueous layer was acidified by purging with carbon dioxide. The crude product separated as a brown oil, which was extracted into 300 ml of carbon tetrachloride. After evaporation, the brown oil crystallized slowly. The solid was ground and washed twice with 300 ml of water. After drying over silica gel under vacuum, 59 g (28%) of 3 was obtained as a light brown powder. As deduced from ¹H NMR, it was a 1:1 mixture of the 3- and 2-methyl isomers. The acetalic C–H protons were observed separated at 5.30 and 5.35 ppm.

2.3. Synthesis of 4-[4-(5-hexenyloxy)benzoyloxy]methylphenols; mixture of the 2- and 3-methyl isomers (6)

A mixture of 22 g of 4-(5-hexenyloxy)benzoic acid (4), 20.8 g of 4-(tetrahydropyran-2-yloxy)methylphenol (3), 1.2 g of 4-*N,N*-dimethylaminopyridine and 150 ml of dichloromethane was cooled in an ice bath with magnetic stirring. 21 g of *N,N'*-dicyclohexylcarbodiimide was added and stirring was continued for 1 h. After the ice bath had been removed, stirring was continued for 16 h at room temperature. Intermediate 5 was obtained as an oil after filtration and evaporation of the dichloromethane. It crystallized overnight and was washed twice with 150 ml of ethanol. This product was mixed with 400 ml of ethanol and 4 g of pyridinium 4-toluenesulphonate. After this mixture had been stirred at 60°C for 2 h, it was added dropwise to a mixture of 100 g of ice and 700 ml of water. The precipitated product was washed with 300 ml of water and dried over silica gel under a vacuum. 18.0 g of 6 (61%) was obtained as a light yellow powder.

2.4. Synthesis of ethyl 4-(5-bromopentylloxy)benzoate (7)

A mixture of 100 ml of 1,5-dibromopentane, 108 g of ethyl 4-hydroxybenzoate, 134 g of potassium carbonate and 500 ml of 2-butanone was refluxed for 16 h. After cooling and filtration, the 2-butanone was evaporated. The residue was dissolved in 400 ml of diethyl ether and the solution washed twice with 300 ml of 10% sodium hydroxide solution. After shaking with 200 ml of a saturated sodium chloride solution and drying over magnesium sulphate, the diethyl ether was evaporated. To separate the product from the excess of 1,5-dibromohexane and the by-product, bisethyl 4-(1,5-pentylene-dioxy)benzoate, the mixture was fractionated in a

Kugelrohr apparatus. ($T = 140^{\circ}\text{C}$, $P = 0.05$ mb). 60.0 g of the product (29%) was obtained as a white solid.

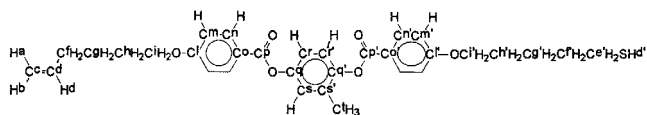
2.5. Synthesis of 4-(5-mercaptopentyl)benzoic acid (**8**)

A mixture of 60.0 g of ethyl 4-(5-bromopentyl)benzoate (**7**), 22.0 g of thiourea and 40 ml of water was stirred for 2 h at 110°C . After cooling, 360 ml of 10% sodium hydroxide solution was added. After heating under reflux for 2 h, the hot solution was treated with 2.5 M hydrochloric acid and vigorously stirred until $\text{pH} = 1$. The crude precipitated product was washed with 400 ml of water and dried at 60°C under vacuum giving 31 g of the product (68%) after recrystallization from chloroform. Cr– 120°C –N– 151°C –I.

2.6. Synthesis of 4-[4-(5-hexenyloxy)benzoyloxy]-1-[4-(5-mercaptopentyl)benzoyloxy]-2- and 3-methylbenzenes (**1**)

A mixture of 24.0 g of 4-(5-mercaptopentyl)benzoic acid (**8**), 50.0 g of the 4-[4-(5-hexenyloxy)benzoyloxy]-methylphenols (**6**), 1.2 g of 4-*N,N*-dimethylaminopyridine and 150 ml of dichloromethane was cooled in an ice bath with magnetic stirring. 21 g of *N,N'*-dicyclohexylcarbodiimide was added and stirring was continued for 8 h in the ice bath. After removal of the ice bath, stirring was continued for 16 h at room temperature. The crude product was obtained after elution of the mixture from a small silica column. 36.8 g of **1** (67%) was obtained as a white powder after two crystallizations from a 1:1 mixture of 2-propanol and ethyl acetate. It was contaminated with about 5% of a by-product as a result of thioesterification. Cr– 64°C –N– 170°C –I.

^1H NMR: 8.16 (d, 2H, $J = 8.6$, H^{m}), 8.14 (d, 2H, $J = 8.6$, H^{n}), 7.17 (d, 1H, $J = 8.5$, H^{r}), 7.13 (d, 1H, $J = 2.5$, H^{s}), 7.08 (dd, 1H, $J_1 = 8.5$, $J_2 = 2.5$, H^{t}), 6.99 (d, 2H, $J = 8.6$, $\text{H}^{\text{m'}}$), 6.96 (d, 2H, $J = 8.6$, H^{m}), 5.84 (m, 1H, $J_1 = 17.0$, $J_2 = 10.2$, $J_3 = 6.5$, H^{d}), 5.05 (d, 1H, $J = 17.0$, H^{a}), 4.98 (d, 1H, $J = 10.2$, H^{b}), 4.05 (t, 4H, $J = 6.5$, H^{i} , $\text{H}^{\text{i'}}$), 2.58 (q, 2H, $J = 7.5$, H^{e}), 2.24 (s, 3H, H^{l}), 2.15 (q, 2H, $J = 6.5$, H^{f}), 1.9–1.5 (m, 10H, H^{g} , H^{h} , $\text{H}^{\text{i'}}$, $\text{H}^{\text{g'}}$, $\text{H}^{\text{h'}}$), 1.35 (t, 1H, $J = 7.5$, $\text{H}^{\text{d'}}$).

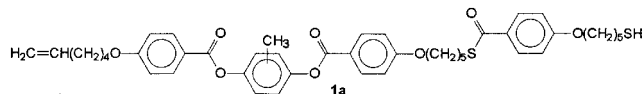


^{13}C NMR: 164.9 (C^{p}), 164.5 ($\text{C}^{\text{p'}}$), 163.5 (C^{l} and $\text{C}^{\text{l'}}$), 148.4 (C^{q}), 147.1 ($\text{C}^{\text{q'}}$), 138.8 (C^{d}), 132.3 (C^{n} and $\text{C}^{\text{n'}}$), 131.8 ($\text{C}^{\text{s'}}$), 124.1 (C^{s}), 122.9 ($\text{C}^{\text{r'}}$), 121.4 and 121.6 (C^{o} and $\text{C}^{\text{o'}}$), 120.0 (C^{r}), 115.3 (C^{c}), 114.3 (C^{m} and $\text{C}^{\text{m'}}$), 68.5 (C^{i} , $\text{C}^{\text{i'}}$), 34.0 ($\text{C}^{\text{f'}}$), 33.8 (C^{f}), 29.0 ($\text{C}^{\text{h'}}$), 28.9 (C^{h}), 25.7 (C^{g}), 25.3 (C^{e}), 24.9 ($\text{C}^{\text{e'}}$), 16.4 (C^{l}).

3. Results and discussion

3.1. Synthesis of **1**

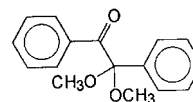
The synthesis of **1** is outlined in scheme 1. In order to esterify only one phenolic group of methylhydroquinone, its mono THP ether **3** was prepared. This compound was obtained as an equimolar mixture of the 2- and 3-methyl isomers. No attempts were made to separate them. After esterification with acid **4** and deprotection, the phenolic compounds **6** were obtained, also as a mixture of the 2- and 3-methyl isomers. Compounds **6** were esterified with acid **8**, which was obtained by interaction of ester **7** with thiourea, followed by saponification. When using equimolar amounts of **6** and **8** to form **1**, appreciable amounts of the following by-product **1a** were formed:



This compound could be easily detected in the ^1H NMR spectra of the reaction product at 3.1 ppm (the methylene group next to the thiocarboxy moiety) and at 7.9 ppm in the aromatic region. It is the results from the esterification of the mercapto groups by benzoic acid **8**. A 1.7 times excess of phenolic compound **6** was used to suppress the esterification of these mercapto groups. In this way only about 5% of **1a** was formed, which could not be separated from **1** by repeated crystallization. Because compound **1a** contains both reactive groups it will also react as structure **A** of scheme 1 in the polymerization reaction. **1** exhibits an enantiotropic nematic phase between its melting point at 64°C and its clearing point at 170°C . Its liquid crystalline properties indeed resemble those of the non-reactive 2,5-dimethylphenylene bis(4-hexyloxybenzoate) (see Introduction).

3.2. Photopolymerization of **1**

In order to photopolymerize **1**, it was mixed with 1 wt % of photo-initiator 2,2-dimethoxy-2-phenylacetophenone **9**:



Samples of this mixture were photopolymerized at various temperatures above the melting point of **1**. In all cases a good conversion of monomer **1** to polymer **2** (see scheme 2) was confirmed by ^1H NMR spectroscopy. The original signals of the olefinic moiety, at 2.2, 5.0 and 5.8 ppm, and the mercapto hydrogen at 1.3 ppm had disappeared. ^{13}C NMR also showed disappearance of the olefinic signals at 138.8 and 115.3 ppm and of the

methylene group linked to the thiol group at 25.3 ppm. In addition, new signals were observed, among which was a signal at 32.5 ppm which can be attributed to the methylene groups linked to the sulphur atom in the polymer. In order to obtain a more quantitative understanding of the conversion, the molecular masses of the samples were determined by means of GPC. These data are presented in the table. All the samples had number average molecular masses of about 10^4 . This implies an average degree of polymerization of about 20. The highest molecular masses were found between 100 and 120°C; it is not yet clear which factors determine this temperature dependence. The sample polymerized at 100°C was subjected to further analysis. DSC investigation of this sample showed a melting point of 150°C; above this temperature, a nematic phase was confirmed by means of optical microscopy; above 250°C the material entered the isotropic state. Upon cooling to room temperature the sample started to crystallize.

4. Optical measurements

In order to measure the birefringence (Δn) the monomer containing 1% of the initiator was introduced into a glass cell, provided with rubbed polyimide for macroscopic alignment, at 100°C. Figure 1 shows the UV-Vis transmission spectrum of a filled cell measured between crossed polarizers and oriented at 45° with respect to the rubbing direction. From the maxima and minima of the curve, the birefringence at these wavelengths (λ) was deduced according to:

$$T = \sin^2(\pi d \Delta n / \lambda)$$

where T is the transmission and d the thickness of the cell [5]. $d \Delta n / \lambda$ should be an integer plus 1/2 at the maxima and an integer at the minima. The data from figure 1 were used to construct figure 2, which shows the wavelength dependence of the birefringence. After polymerization by means of UV irradiation for 180 s the other curve of figure 1 was obtained. This curve was

Table. Number average molecular mass, weight average molecular mass and molecular mass dispersion as a function of the polymerization temperature of **1**.

Polymerization temperature °C	$\langle M_n \rangle \times 10^{-3}$	$\langle M_w \rangle \times 10^{-3}$	D
70	7.4	19	2.6
80	11	24	2.2
90	13	29	2.2
100	15	35	2.3
110	14	35	2.5
120	15	34	2.3
130	12	30	2.6
140	9.8	23	2.5

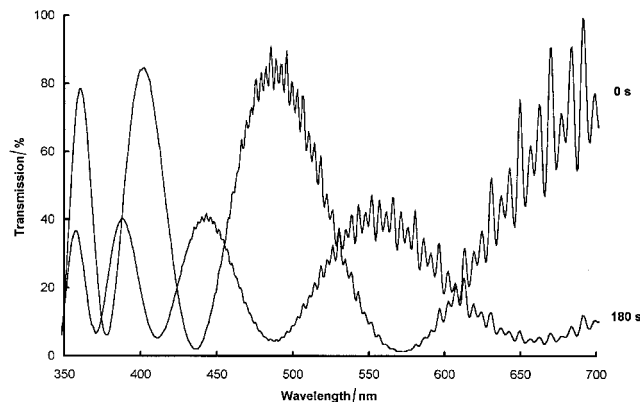


Figure 1. Transmission of a film of a mixture of 4-[4-(5-hexenyl-oxo)benzoyloxy]-1-[4-(5-mercaptopentyl-oxo)benzoyloxy]-2- and 3-methylbenzenes (**1**) and 2,2-dimethoxy-2-phenylacetophenone **9** before and after polymerization.

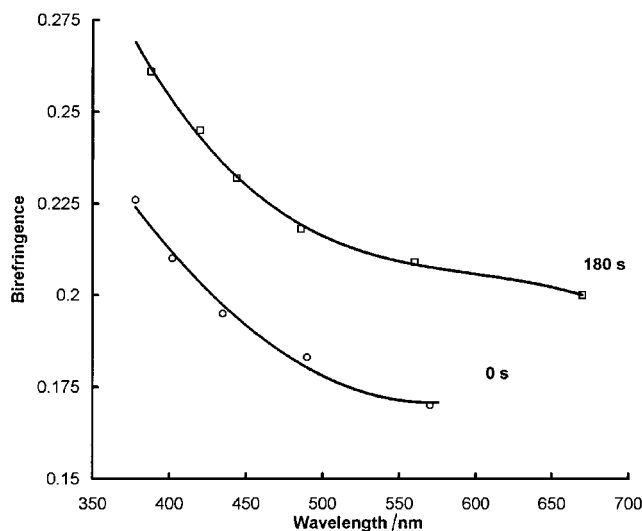


Figure 2. Dispersion of the birefringence of monomer (**1**) before and after polymerization at 100°C.

used to construct, the wavelength dependence of the birefringence of the polymer which resulted in much higher birefringence (figure 2). With the aid of the data in figure 2 and intermediate measurements at 10 and 60 s, the birefringence at 589 nm (sodium D-line) was interpolated and plotted in figure 3. This figure shows a rapid increase in birefringence until about 60 s. The end value, well above 0.20, is much higher than values obtained for liquid crystalline networks obtained from corresponding diacrylates [7, 8] or divinyl ethers [9]. The higher birefringence can be explained assuming that the conformation of the liquid crystalline main chain leads to higher order parameters in the polymer film than those of side group polymer based networks.

From figure 1 it is also apparent that the transmission of the polymer was much poorer than that of the

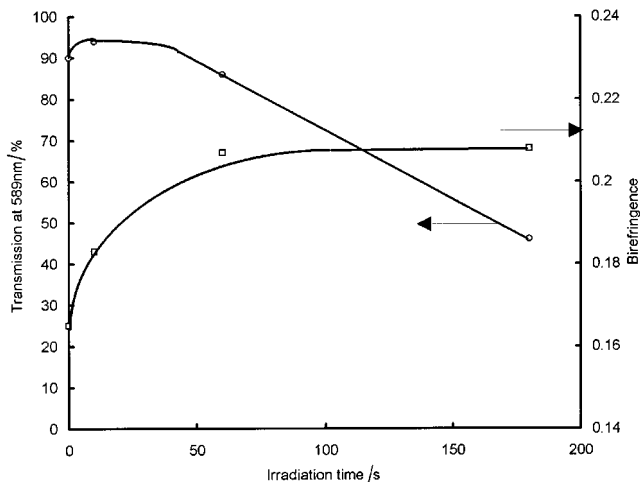


Figure 3. Change in birefringence (right) and transmission (left) during polymerization of monomer (1) at 100°C.

monomer. The effect of polymerization on transmission has also been plotted in figure 3 for all these experiments. The figure shows a decrease in the transmission with ongoing polymerization. The sample became opaque. Scattering due to domain formation is probably responsible for this effect. The macro-alignment of the cells may also have been disturbed as a result of polymerization shrinkage and/or phase separation. As no crosslinks were formed in this system, the polymer chains were still mobile. Cooling the cell obtained after polymerization for 180s to room temperature caused the transmission to drop to almost 5%. Again crystals were formed.

Future studies will focus on thiol-ene molecules having different structures [10], which are for example processable at lower temperatures, and on crosslinking molecules. In particular, in the case of the latter types of compound it may be possible to suppress the domain

formation and crystallization of the polymer. If so, it will be possible to use these materials to manufacture stable optical components.

5. Conclusion

A liquid crystalline monomer with a broad range nematic mesophase that can be used for so-called thiol-ene photopolymerization has been prepared. This monomer can be photopolymerized in the bulk. The polymer formed in this way exhibits mesomorphic behaviour at high temperatures and crystallizes at ambient temperature. The polymer has higher birefringence values than those obtained by photopolymerization of liquid crystalline diacrylates or vinyl ethers, and hence is believed to have a higher order parameter.

This work was supported by the European Community under Brite Project BE-5363.

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