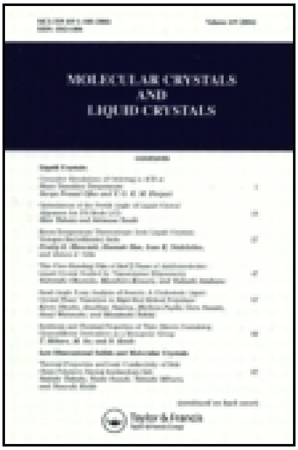

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The Synthesis and Polymerisation of a Liquid Crystalline Crosslinkable Thiol-Ene Molecule

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The Synthesis and Polymerisation of a Liquid Crystalline Crosslinkable Thiol-Ene Molecule

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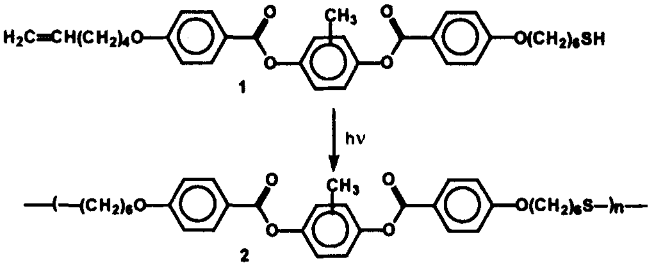
In order to stabilise the alignment of liquid crystalline main chain polymers obtained by photopolymerisation of liquid crystalline thiol-ene molecules, a crosslinkable liquid crystalline thiol-ene molecule was made. Upon polymerisation of mixtures of both molecules, polymers were formed which suffer less from domain formation due to phase separation, crystallisation and shrinkage compared to polymers made from non-crosslinkable thiol-ene molecules. Due to this stabilisation, materials with high birefringence could be prepared.

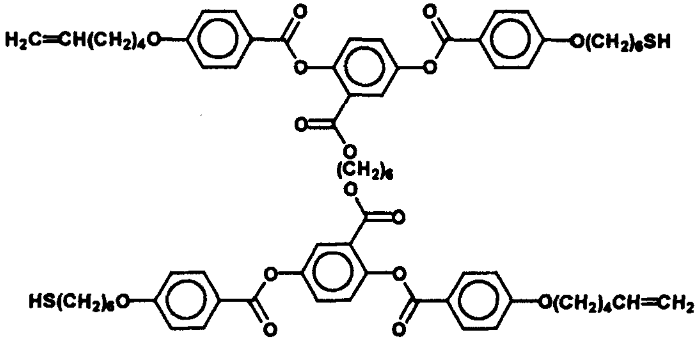
Keywords: liquid crystalline main chain polymers; photopolymerisation

Introduction

Highly oriented polymeric films can be obtained through photopolymerisation of aligned liquid crystals containing two polymerisable groups such as acrylates, methacrylates, vinylethers and epoxides[1,2]. A limitation of the so-called liquid-crystalline networks, which are basically of the side-chain polymer type, is that the order parameter *S*, when polymerised in the easy-to-process nematic (N) phase, remains below 0.8, which also imposes its limits to 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 realised than with liquid-crystalline side-chain polymers. For that reason we designed and synthesised molecules like **1** or others similar molecules[3,4] which upon photopolymerisation in the liquid crystalline state form main-chain polymers in a radical chain addition polymerisation reaction.



Thus, by sequential addition of the thiol group to the double bond, polymer **2** is formed. The optimum polymerisation temperature lies around 90°C. At lower temperatures the polymerisation rate and conversion is hindered by crystallisation. At higher temperatures, the ceiling temperature[5] becomes increasingly more important. Polymer **2** shows a degree of polymerisation of about 25. It exhibits a substantial higher birefringence than materials made by photopolymerisation of corresponding diacrylates, vinyl ethers or diepoxides[3]. It is believed that this is due to a higher ordering in this polymer as discussed before. A drawback of this material is that the initial alignment of **1** is partly lost during photopolymerisation resulting in opaque polymeric films of **2**. On cooling, the material becomes completely scattering. Polymerisation shrinkage, phase separation and crystallisation are the main causes of the disturbance of the macro alignment. In order to overcome these problems and to make material with better optical properties, it was decided to introduce some crosslinks in the polymer. These crosslinks will suppress molecular mobility and the accessibility for molecular rearrangements, and thus phase separations. For that reason crosslinkable liquid crystalline monomer **3** was designed. It contains two thiol groups and two olefinic groups making crosslinks possible. It has some structural similarities with monomer **1**, which will be helpful to mix them, and intermediates for the synthesis of **1** can also be used for the synthesis of **3**.



3

Experimental

Synthesis of **3** (see scheme on page 5).

4-(5-hexenyloxy)benzoyl chloride (**6**) and 4-(6-mercaptohexyloxy)benzoic acid (**9**) were prepared according to references 6 and 3, respectively. All compounds exhibited ^{1}H-NMR and ^{13}C-NMR spectra in accordance with their structures.

5-(tetrahydropyran-2-yloxy)-hydroxybenzoic acid (**4**). 22 ml of 3,4-dihydropyran (0.24 mole) was added drop wise to a mixture of 30.8 g of 2.5-dihydroxybenzoic acid (0.2 mole), 2 g of pyridinium 4-toluenesulfonate and 100 ml of dichloromethane. After stirring the mixture overnight at room temperature, it was filtered and extracted twice with 50 ml of half saturated brine. After drying over magnesium sulphate it was evaporated. The remaining solid was washed twice thoroughly with 200 ml of ligroin. 35.2 g of the product (74%) was obtained as a white solid.

hexamethylene-di-(2-hydroxy-5-(tetrahydropyran-2-yloxy)benzoate) (**5**). A mixture of 11.9 g of 5-(tetrahydropyran-2-yloxy)-hydroxybenzoic acid (**4**, 50 mmole), 4.2 g *of sodium bicarbonate* (50 *mmole) and* 25 *ml of* dimethylacetamide was heated at 90°C until the evolution of carbon dioxide had ceased. 3.5 ml of 1,6-dibromohexane (25 mmole) was added and the reaction was continued for 3 hours at the same temperature. After cooling to room temperature, the crude product precipitated. It was washed thoroughly with water crystallised from 2-propanol and dried at 60°C under vacuum. 10.2 g of the product (73%) was obtained as a white solid.

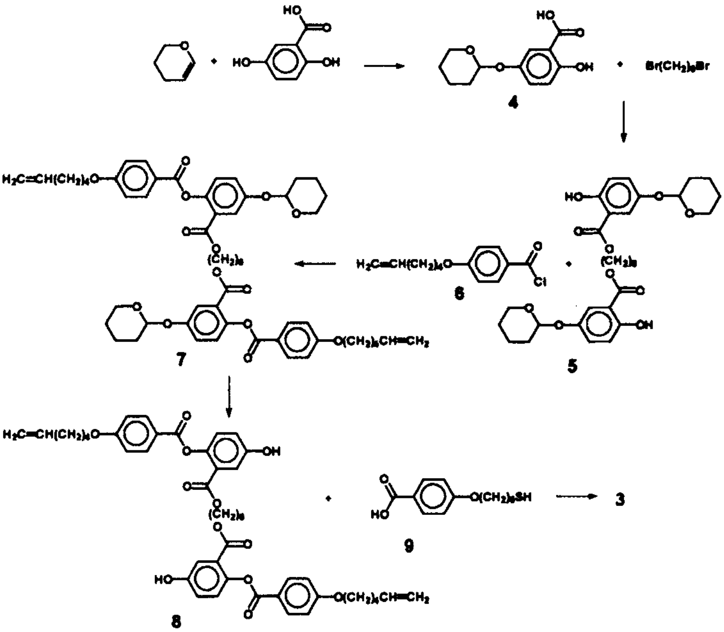
hexamethylene-di-(-(4-(5-hexenyloxy)benzoyloxy)-5-hydroxybenzoate) (**8**). A solution of 8.6 g of 4-(5-hexenyloxy)benzoyl chloride (**6**, 36 mmole) in 50 ml of dichloromethane was added drop wise to a solution of 10 g of hexamethylene-di-(2-hydroxy-5-(tetrahydropyran-2-yloxy)benzoate) (**5**, 18 mmole) and 7 ml of triethylamine (50 mmole) in 100 ml of dichloromethane. After the addition, the mixture was stirred for one night and then evaporated. The resulting solid was washed twice with 100 ml of ethanol. The intermediate product 7 thus obtained was mixed with 70 ml of ethanol and 0.7 g of pyridinium 4-toluenesulfonate. The mixture was stirred for 2 hours at 60°C. After cooling in an ice bath, the product precipitated. It was dried at 70°C under vacuum. 9.5 g of the product (67%) was obtained as a white solid.

hexamethylene-di-(2-(4-(5-hexenyloxy)benzoyloxy)-5-(4-(6-mercaptohexyloxy)benzoyloxy)benzoate) (**3**). To a mixture of 6 g of hexamethylene-di-(-(4-(5-hexenyloxy)benzoyloxy)-5-hydroxybenzoate) (**8**) 7.5 mmole), 3.8 g of 4-(6-mercaptohexyloxy)benzoic acid (**9**, 15 mmole), 0.2 g of 4-N,N-dimethylaminopyridine and 50 ml of dichloromethane, cooled in an ice bath, was added 3.1 g of N,N'-dicyclohexyl carbodiimide. The mixture was stirred overnight at room temperature and then filtered over a small silica pad. After evaporation, the product was recrystallised from ethyl acetate. 4.8 g of the product (50%) was obtained as a fine white powder.

Polymerisation and characterisation experiments These experiments were performed as described in references 3 and 4.

Results and discussion.

The synthesis of crosslinkable monomer 3 is outlined below.



In order to make a crosslinkable molecule with structural similarities to **1**, our approach is to connect the middle rings of two molecules to create a twin molecule. For that reason, molecule **5** was made containing two protecting groups to couple the vinyl ('ene') and thiol containing groups sequentially. The steps from **5** to the product **3** are the same used for the synthesis of **1**[3]. **5** was made by coupling of acid **4** with 1,6-dibromohexane and **4** was made from 2,5-dihydroxybenzoic acid and 3,4-dihydropyran. In this reaction, the reactivity of the 2-hydroxy group turned out to be much higher than that of the other hydroxy group or the carboxylic group which made purification easy and the yield rather high. Monomer **3** exhibits a melting point of 124°C and a nematic to isotropic transition of 145°C. It is easily miscible with monomer **1**.

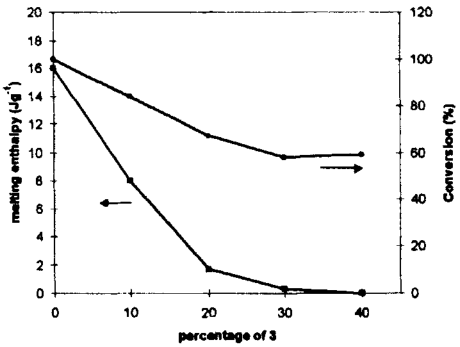


FIGURE 1. Melting enthalpy of copolymers of **1** and **3** as a function of the amount of **3** (weight percentage). (left). Conversion of reactive groups during the polymerisation of a mixture of **1** and **3** as a function of the amount of **3** (weight percentage) measured with photo DSC. (right).

To find out whether addition of compound **3** could suppress the crystallisation of the polymer during photopolymerisation and upon cooling, mixtures of **1** and **3** were photopolymerised at 90°C. Subsequently, they were stored at room temperature for one week and the melting enthalpy of the polymers was measured by DSC. Figure 1 shows that 40% of **3** in the copolymer completely suppressed crystallisation. The same figure also shows that the conversion decreases with increasing amount of **3**. Amounts higher than 40% of **3** gave less reproducible results and phase separation appeared to occur again. Figure 2 shows the effect of temperature on the birefringence for monomer **1** and polymers with various amounts of **3**, prepared at 90°C in a cell with rubbed polyimide layers. The non-crosslinked polymer **2** shows a strong temperature dependence of the birefringence. Above 240°C the polymer became isotropic and below 80° it crystallised.

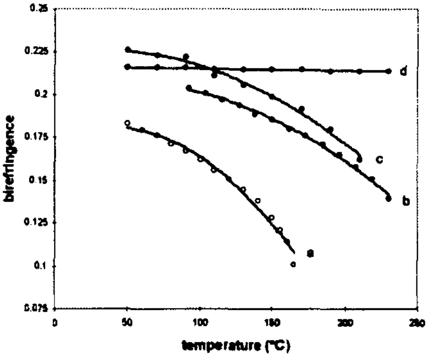


FIGURE 2. Effect of temperature on the birefringence of monomer **1** (a), and of polymers made from **1** (b), from a 2:8 mixture (w/w) of **3** and **1** (c) and from a 4:6 mixture (w/w) of **3** and **1** (d).

The polymer containing 20% of **3** showed a higher birefringence than the latter one but it was still temperature dependent. Probably a higher ordering was sustained due to the presence of the crosslinks. The polymer containing 40% of **3** showed a temperature independent birefringence showing the stability of this material. The value of the birefringence is lower than that of the polymer with 20% of **3**. This might be due to the effect of higher crosslink density which makes the polymer less main-chain-like.

As stated in the introduction, polymer **2**, made from **1** suffers from strong scattering. This is probably caused by domain formation as a result of the disturbance of the macro alignment due to polymerisation shrinkage and/or phase separation. At room temperature, crystallisation of **2** caused the transparency to drop even more to a value of less than 5%[3]. In the case of the polymer containing 40% of **5** a transparency of about 80% was observed at room temperature. Although this is a strong improvement, this value is still lower than that of polymer films made out of acrylates. Future investigations will deal with better transparency and materials processable at lower temperatures.

Conclusions

Crystallisation of liquid crystalline main chain polymers made by photopolymerisation of liquid crystalline thiol-ene molecules can be suppressed by the addition of crosslinkable monomers before polymerisation. The polymers obtained have higher birefringence values than those obtained by photopolymerisation of liquid-crystalline diacrylates or vinyl ethers, and hence are believed to have higher order parameters.

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