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Synthesis and Polymerization of Liquid Crystals Containing Vinyl and Mercapto Groups

Johan Lub*, Dirk Jan Broer, and Nel van den Broek

Philips Research Laboratories,
Prof. Holstlaan 4, NL-5656 AA Eindhoven, The Netherlands

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Introduction

Polymers with a well-defined molecular order are of interest because of their optical and electro-optical properties. A convenient method for producing thin films of these polymers involves photo-initiated chain-crosslinking of liquid-crystalline monomers. The different liquid-crystalline states of low-molecular-mass reactive mesogens show a wide variety of molecular order, all of which may be used for fixation in the polymerization process. Various known techniques for establishing monolithic molecular order in liquid crystals can be applied or can be combined with one another to create films with complicated molecular architectures that are optically free of defects. The monomers have a large degree of freedom in their molecular structure allowing the tailoring of the properties in the mesomorphic state and the mechanical and optical properties of the films.

The first reports of bulk photopolymerization of reactive liquid crystals were related to monoacrylates forming liquid-crystalline side-chain polymers. The linear polymers formed exhibited various mesophases, although their transition temperatures differed from those of the initial monomer. Liquid-crystalline phase transitions therefore took place during the polymerization process or during cooling to ambient temperature and the molecular order changed as a result of the polymerization. To overcome this problem, bulk photopolymerization of functional liquid-crystalline monomers was attempted (photocrosslinking liquid crystals). Early experiments involved the free-radical-based photopolymerization of monolithically ordered nematic liquid-crystalline diacrylates, which resulted in stable polymers, denoted as liquid-crystalline networks, having the same texture and almost the same degree of molecular orientation. However, the use of liquid-crystalline diepoxides and liquid-crystalline divinylethers photopolymerized using photocationic mechanisms leads essentially to the same results.

A limitation of side-chain liquid-crystalline networks is that when the polymerization is carried out in the easy-to-process nematic (N) phase, the order parameter S remains below 0.8, which imposes limits on the anisotropy of, for instance, the optical properties. The limitation of S is mainly attributed to steric factors in the networks. Although thermal vibrations of the mesogenic cores are thought to become restricted when embedded in the network structure, which should lead to higher values of S (also because their virtual transition to the isotropic state has been shifted to higher temperatures), the distribution of their long axes remains rather wide as their tendency to parallelism is hindered by the polymer chain. This hypothesis is supported by the fact that S tends to decrease even more with (a) shorter spacers between the polymer chain and the mesogenic core, and (b) bulky substituents at the core moieties. This hypothesis is further supported by the fact that higher S values were found for epoxide networks, in which the mesogenic crosslinks are separated by a periodicity of three atoms in the polymer chain, than for liquid-crystalline acrylate and vinyl networks with a polymer chain periodicity of two atoms. It is known that, because of the larger aspect ratio of a liquid-crystalline main-chain polymer, in general, a higher value of S can be realized than with a liquid-crystalline side-chain polymer.

It is therefore of both theoretical and practical interest to design liquid-crystalline monomers which upon photopolymerization align the mesogenic cores in a main-chain type of molecular arrangement. This principle is schematically...
shown in Figure 1, which compares: (a) the photoinduced chain-crosslinking reaction with (b) a photoinduced liquid crystal main-chain formation. In the first process the polymer chain grows in a more or less perpendicular manner, independently of the stiff cores, whereas in the latter process the stiff cores are incorporated in the polymer chains themselves. It is expected that the latter process yields photo-crosslinked polymers, depending on the monomer functionality. The general reaction involving a photo-dissociating initiator is shown in Scheme 1.

Scheme 1. General reaction scheme showing the formation of sulphide bonds by photoinduced addition of mercapto groups to vinyl groups

The photo-induced addition of thiols to olefins is a well-known reaction for non-liquid-crystalline systems, which leads to linear\(^{[13]}\) or crosslinked\(^{[13]}\) polymers, depending on the monomer functionality. The general reaction involving a photo-dissociating initiator is shown in Scheme 1.

Scheme 1. General reaction scheme showing the formation of sulphide bonds by photoinduced addition of mercapto groups to vinyl groups

The new materials described in this paper are designed so that groups R and R' are responsible for the mesomorphic behaviour; they have to be polyfunctional to form polymers. With a functionality of two, linear polymers are formed; higher functionalities lead to polymer networks. Here we have restricted ourselves to a functionality of two, with the aim of obtaining linear polymers. With this restriction two different systems may be used: (a) monomer blends consisting of a 1:1 ratio of di-vinyl and di-mercaptop liquid-crystalline monomers, or (b) a monomer which carries both the mercapto and the vinyl functionality. If groups R and R' are appropriately chosen both systems yield liquid-crystalline polymers which have the same chemical structure. This paper describes the synthesis and the properties of these types of monomer systems and their photopolymerization behaviour.

Results and Discussion

### 1. Synthesis and Properties of 1, 2, and 11a

In order to obtain high-molecular weight materials in polymerization experiments, an exact stoichiometric olefin-thiol ratio is needed, as outlined in the introduction. One way of realizing this is by mixing a liquid-crystalline di-olefin with a liquid-crystalline di-thiol. We synthesized both compounds as derivatives of the mesogenic group which had previously successfully been used with acrylates\(^{[14]}\), epoxides\(^{[13]}\), and vinyl ethers\(^{[16]}\) (see Scheme 2). Di-olefin 1 was prepared through esterification of hydroquinone with 4-(5-hexenyl)benzoic acid (3) with the aid of dicocohexylcarbodiimide and dimethylaminopyridine. To enable the introduction of the sulphur atoms ultimately resulting in the formation of di-thiol 2, di-olefin 1 was made to react with thiaoctic acid in a radical process initiated by azobisobutyronitrile to form di-thio acetate 4\(^{[10]}\). Attempts to form the desired di-thiol 2 by removing the acetyl groups of 4 failed. In order to remove these acetyl groups, the basic or acidic conditions needed (4-toluenesulphonic acid in ethanol, potassium hydroxide or ammonia in ethanol) were too strong and partially decomposed the mesogenic group, resulting in materials which could not be purified.

Scheme 2. Synthesis of 1,4-di-[4-(5-hexenyl)benzoic acid]benzene (1) and attempted synthesis of 1,4-di-[4-(6-mercaptohexyl)benzoic acid]benzene (2)

Scheme 3 shows an alternative way of obtaining di-thiol 2. Use was made of 4-(6-mercaptohexyl)benzoic acid (6), which was prepared by reaction of ethyl 4-(6-bromohexyl)benzoate (5) with thiourea, followed by hydrolysis. Esterification of hydroquinone with acid 6 in the same way as described for the synthesis of di-olefin 1 resulted in the formation of di-thiol 2 contaminated with appreciable amounts of di-thiol 2a. In this compound part of the mercapto groups had reacted with acid 6. This by-product could easily be detected and quantified from the \(^1\)H-NMR spectrum. The methylene group next to the thiocarboxy moiety appeared as a triplet at \(\delta = 3.1\) and the aromatic protons appeared as two doublets at \(\delta = 7.9\) and 6.9. In order to suppress the formation of 2a, the esterification reaction was carried out at 0°C using an excess of hydroquinone. 6% of 2a was, however, formed which could not...
be separated by means of crystallization. Separation by column chromatography (silica/dichloromethane) was not possible either. In attempts to purify 2 by column chromatography small amounts of disulphide were formed. The disulphide was detected by 1H-NMR in the form of a triplet at \( \delta = 2.65 \). Apparently, oxidation of 2 in dichloromethane solution is catalyzed by silica. The presence of 2, in principle, implies no problems in the polymerization reaction as it is also a dithiol. This should be taken into account when the stoichiometric mixtures of 1 and 2 are prepared for the polymerization experiments.

Another way of achieving an exact stoichiometry for the olefin and mercapto groups is by using compound 11a, which contains one olefinic group and one mercapto group. The synthesis of this compound is shown in Scheme 5. Hydroquinone has to be subsequently esterified by 4-(5-hexenyl)benzoic acid (3) and 4-(6-mercaptohexyloxy)benzoic acid (6). Monoprotected hydroquinone 8a was used in order to avoid laborious purification methods. This compound can be easily prepared and purified and has proved very useful in the preparation of asymmetric liquid-crystalline diacrylates[5][12] and epoxides[13]. Thus, after the esterification of 8a with 3 and deprotection of intermediate 9a, phenolic compound 10a was obtained. This compound was in turn esterified with 6. Both esterification reactions were carried out with the aid of dicyclohexylcarbodiimide and dimethylaminopyridine. In these cases too, an excess of 10a was used to suppress thioester formation. Nevertheless, about 3% of a compound similar to 2a was formed. Fortunately, this has no effect on the olefin–thiol ratio. Therefore this compound is more preferable than the mixture of 1 and 2. Compound 11a was found to have a melting point of 104°C (see Table 1), which means that the polymerization had to be carried out well above 100°C.

Table 1. Phase transitions of liquid crystals 1, 2, 11a, 11b, and 14

<table>
<thead>
<tr>
<th>Compound</th>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( R^3 )</th>
<th>Phase transitions/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( H_2C=CH )</td>
<td>( HC=CH_2 )</td>
<td>H</td>
<td>Cr=129—N=204—I</td>
</tr>
<tr>
<td>11a&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>( HS(CH_2)_2 )</td>
<td>( SH(CH_2)_2 )</td>
<td>H</td>
<td>Cr=100—N=194—I</td>
</tr>
<tr>
<td>11b&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>( H_2C=CH )</td>
<td>( CH_2=CH )</td>
<td>( CH_3 )</td>
<td>Cr=82—N=161—I</td>
</tr>
<tr>
<td>14&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>( HS(CH_2)_2 )</td>
<td>( HC=CH_2 )</td>
<td>H</td>
<td>Cr=43—N=80—I</td>
</tr>
</tbody>
</table>

<sup>[a]</sup> All these compounds are contaminated with small amounts of a thio-ester byproduct, see text.

2. Photopolymerization of 1, 2, and 11a

To study the polymerization behaviour of 11a, a mixture containing 1% of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone was prepared. Irradiating of this mixture in a DSC apparatus at 120°C and 130°C after melting resulted in the graphs shown in Figure 2. The presence of two peaks is explained by the subsequent occurrence of a reaction ex-
Scheme 5. Synthesis of 4-[4-(5-hexenyloxy)benzoyloxy]-4-(6-mercaptohexyloxy)benzene (11a) and 4-[4-(5-hexenyloxy)benzoyloxy]-1-[4-(6-mercaptohexyloxy)benzoyloxy]methylbenzene (11b).  

otherm and a crystallization exotherm. The first peak, attributable to the reaction exotherm, shows that the polymerization starts soon after the beginning of the irradiation. The second peak indicates crystallization of the reaction mixture, which will have an effect on the polymerization behaviour. At 130°C crystallization occurred at a later stage than at 120°C, which is understandable in terms of crystallization kinetics and thermodynamics. Owing to crystallization, results of calculations of the degree of conversion based on the integrated DSC curves would have been unreliable. For that reason we used 1H-NMR spectroscopy to obtain the conversion data. The new methylene groups of the sulphide bond were observed as a triplet at δ = 2.60. The original mercapto hydrogen and olefinic signals were still observed. A conversion of about 70% of the reactive groups was deduced from the integral values of the samples taken at both polymerization temperatures.

DSC analysis of the product obtained at 120°C showed that it melted between 160 and 175°C and became isotropic at about 260°C. Upon cooling, it crystallized around 140°C. In view of this crystallization temperature it is possible that the sample started to crystallize during polymerization. Crystallization is known to retard the polymerization reaction due to a reduced monomer mobility, which explains the relatively low conversion. These results were confirmed by size exclusion chromatography, which revealed an oligomeric material with a broad molecular weight distribution around 2000 and a relatively high monomer content.

Similar results were obtained with mixtures of 1 and 2. The method employed, though somewhat different than that used for 11a, resulted in the formation of polymer 12 with the same chemical structure (see Scheme 6).

1H-NMR analysis of a 1% mixture of the photoinitiator di-olch after irradiation, revealed no conversion of the double bonds. Therefore it can be concluded that homopolymerization of the olefinic bonds is not an important side reaction during the thiol-ene polymerization.


Breaking the molecular symmetry by incorporating a methyl substituent in the central ring of three ring liquid crystals monomers, results in a decrease in the melting point and suppression of crystallization. It was expected that this is also the case for the thiol-ene monomers and polymers. This would enable polymerization at lower temperatures with a higher degree of conversion. For that reason monomer 11b was prepared. The synthesis was similar to that of 11a (see Scheme 5), except that a mixture of products was obtained due to the fact that the starting compound 8b was a mixture of the 2- and 3-methyl isomers. When 10b was esterified with 6 in the same way as 10a, product 11b was found to be contaminated with appreciable amounts of the thioester byproduct. The 2-methyl isomer of 10b was undoubtedly sterically hindered, which had a
favourable effect on the thioesterification side reaction. The reaction with 6 was therefore carried out with 1.6 equivalents of 10b instead of 1.2 equivalents. This resulted in less than 4% by-product.

The liquid-crystalline properties of 11b are presented in Table 1. As expected, its melting and clearing points are lower than those of 11a. Whereas 11a started to crystallize below 90°C, 11b could be supercooled to room temperature before it started to crystallize slowly.

4. Photopolymerization of 11b

Only one exothermic peak was obtained in the photopolymerization of 11b at 90°C in a DSC apparatus in the same way as performed with 11a. An exotherm of about 80 kJ/mol was measured, close to the theoretical value of 79 kJ/mol[17]. The 1H-NMR spectrum of the photopolymerized product shows the absence of the original vinylic and mercapto protons. This means that the degree of conversion of 11b is higher than that of 11a. Size exclusion chromatography of the polymer revealed an average molecular weight (Mn) of 14·10^3 and a broad molecular weight distribution (Mw/Mn) of 2.6. Figure 3 shows that lower reaction enthalpies were obtained at polymerization temperatures below and above 90°C. At higher temperatures, the polymerization takes place closer to the ceiling temperature[23] resulting in incomplete conversion. At lower temperatures crystallization probably occurs. The result at 90°C shows the superiority of 11b over 11a, which is probably attributable to suppression of crystallization of the polymer. DSC analysis of the photopolymerization product of 11b at 90°C revealed a broad melting range between 130°C and 140°C and an isotropic transition at about 240°C. Upon cooling, crystallization started between 80°C and 60°C. The latter temperatures are lower than the actual melting temperature of 90°C, which explains the high degree of conversion, inspite of the fact that polymerization took place below the actual melting temperature.

Figure 3. Photopolymerization exotherm as a function of the polymerization temperature measured by DSC of 11b

6. Photopolymerization of 14

After photopolymerization of 14 at 60°C, in the nematic phase, the 1H-NMR spectra of the photopolymerized product 15 (see Scheme 7) revealed the absence of the original vinylic and mercapto protons. This means that the conversion for 14 is more complete than with 11a. Only one exothermic peak was obtained in the DSC apparatus. Size exclusion chromatography revealed an average molecular weight of 8·10^3 which is somewhat lower than that obtained with 11b. The molecular weight distribution was 2.7. Polymer 15 showed rather complex melting behaviour between 130 and 145°C after which it became liquid-crystalline. It became isotropic above 160°C. Upon cooling, the sample became liquid-crystalline again below 155°C and crystallization occurred at about 120°C. This crystallization did not seem to affect the polymerization at the relatively low temperature of 60°C; it probably sets in at a later stage. The morphology of the liquid-crystalline phase observed by polarizing microscopy points to a nematic phase. This is in agreement with the nematic phase observed for main-chain polymers containing the same mesogenic group connected by alkene spacers[18].

7. Molecular Orientation and Optical Properties of the Monomers and Polymers

The monomers were monolithically aligned in the nematic state between two glass substrates separated by 6 µm spacers and provided with a 200 nm rubbed polyimide coat-
ing. The monomer films were clear, colourless, and highly birefringent. Due to its poor conversion, monomer 11a was not used for the optical measurements. Figure 4 shows the birefringence as a function of the temperature for monomer 11b. At low temperatures, above the crystallization temperature, higher birefringences were measured than with the corresponding nematic diacrylates. This is explained by the existence of a broad mesophase and a better rod-like molecular conformation of the thiolene molecules due to the absence of the acrylate end-groups. Photopolymerization of the nematic monomer film of 11b at 90°C caused the birefringence to increase considerably, as can be seen in Figure 5. In the same figure it can be observed that, unfortunately, the transmission had decreased considerably. Scattering due to domain formation is probably responsible for this effect. The macro alignment of the material may have been disturbed as a result of polymerization shrinkage, phase separation and crystalization with ongoing polymerization. The end value of the birefringence above 0.2 is much higher than the values obtained with the corresponding LC networks obtained from LC diacrylates[6]. As predicted in the introduction, the conformation of the LC main chain leads to higher order parameters in the polymer films and thus to higher birefringences. Figure 4 also shows the birefringence of a thin polymer film polymerized at 90°C as a function of the temperature. The plot only shows data measured between 90°C and the transition to the isotropic state at about 240°C. When the sample was cooled below 90°C it began to crystallize and it lost its transparency completely.

Monomer 14 formed a strongly scattering material upon polymerization and for that reason the birefringence could not be measured. Probably, in this type of experiments crystallization sets in earlier than measured by DSC. It was not investigated any further.

Future studies will be carried out with this new type of compounds. These studies will focus on the effect of polymerization on the order in the liquid-crystalline state, the effect of molecular weight and crosslinking on the polymer properties as ways for suppressing crystallization and suppressing other effects which cause a decrease in the transmission of the polymeric films.

Conclusions

Liquid-crystalline monomers that can be used for so-called thiol-ene photopolymerization have been prepared successfully. Mesophase behaviour is observed at elevated temperatures. These molecules can be photopolymerized in the bulk if it is ensured that the structure of the monomers prevents crystallization during polymerization. In general, the polymers exhibit mesomorphic behaviour at high temperatures and are crystalline at ambient temperature. These polymers have a higher order than those obtained by photopolymerization of liquid crystalline diacrylates, and they hence have higher birefringence values.

We wish to thank J. H. van der Veen, M. E. Martinez Antonio, A. Ruiz-Melo, and J. F. Allan for their assistance with the syntheses and G. N. Mol for her assistance during the polymerization experiments. This work was supported by the European Community under Brite Project BE-5363.

Experimental Section

General: 1H- and 13C-NMR spectra were measured on a Brucker DPX 300 spectrometer, in CDCl3 with TMS as internal standard. Chemical shifts are given in ppm, coupling constants J in Hz. The intermediate products exhibited 1H-NMR spectra that are in accordance with their structures. – Phase transitions were measured on a Perkin Elmer DSC-7 apparatus. A Reichert microscope provided with a Mettler FP52 hot stage was used for texture measurements. – The photopolymerization experiments were performed identically to those with diacrylates as previously described[11]. – The birefringence, change of the birefringence, and transmission during polymerization were measured by UV-Vis spectroscopy between two crossed polarizers as described in ref[11].

The size exclusion chromatography experiments were performed in chloroform (0.2–0.5 mg/g). After filtration (Millex-LCR 0.5 µm filter), 25 µl of the solutions were injected on 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 of 1.0 ml/min. Detection occurs at 254 nm. The equipment is calibrated with a series of 16 narrow dispersed PS standards (Mw: 580–3 × 10⁶).

All solvents were obtained from Merck. All other chemicals were obtained from Acros Organics. The following chemicals were prepared according to literature procedures: 4-(5-hexenyloxy)benzoic acid (3)¹³, 4-(tetrahydropyran-2-yloxy)phenol (8a)¹⁹, and 4-(5-hexenoyloxy)phenol (13)¹³.

1,4-Di-4-(5-hexenoyloxy)benzoyloxybenzene (1): A mixture of 22 g of 4-(5-hexenoyloxy)benzoic acid (3), 5.5 g of hydroquinone, 1.2 g of 4,N,N-dimethylaninopyridine 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 one hour in the ice bath. After removing the ice bath, stirring was continued for 16 hours at room temperature. The crude product was obtained after elution of the mixture over a small silica column. 17.5 g of 2 (60%) was obtained as a white powder after crystallization from ethyl acetate. It was contaminated with about 6% of the byproduct 2a. -¹H NMR: 8.14 (d, 4 H, J = 8.6, H²), 7.26, (s, 4 H, H⁴), 6.97 (d, 4 H, J = 8.6, H⁶), 5.84 (m, 2 H, J₁ = 17.0, J₂ = 0.2, J₃ = 6.5, H⁸), 5.05 (d, 2 H, J = 17.0, H⁸), 4.98 (d, 2 H, J = 10.2, H⁸), 4.05 (t, 4 H, J = 6.5, H²), 2.15 (q, 4 H, J = 6.5, H²), 1.85 (m, 4 H, J₁ = 6.5, J₂ = 7.0, H³), 1.60 (m, 4 H, J₁ = 6.5, J₂ = 7.0, H³). -¹³C NMR: 164.8 (C¹), 163.5 (C³), 148.4 (C⁴), 132.3 (C₆), 121.5 (C₇), 115.3 (C₂), 114.3 (C₈), 68.5 (C⁵), 33.8 (C₉), 28.9 (C₈), 25.7 (C₉).

1,4-Di-[4-(6-mercaptohexyloxy)benzyloxy]benzene (4): A mixture of 5.1 g of 1,4-di-[4-(5-hexenoyloxy)benzyloxy]benzene (1), 2.5 ml of thioacetic acid, 20 mg of azoisobutyronitrile, and 25 ml of toluene was heated to 90°C. The reaction was followed by TLC. When the reaction was cooled in an ice bath with magnetic stirring, 21 g of NN'-dicyclohexylcarbodiimide was added and stirring was continued for 8 hours in the ice bath. After removing the ice bath, stirring was continued for 16 hours at room temperature. The crude product was obtained after elution of the mixture over a small silica column. 17.5 g of 2 (60%) was obtained as a white powder after crystallization from ethyl acetate. It was contaminated with about 6% of the byproduct 2a. -¹H NMR: 8.14 (d, 4 H, J = 8.6, H²), 7.26, (s, 4 H, H⁴), 6.97 (d, 4 H, J = 8.6, H⁶), 5.05 (t, 4 H, J = 6.5, H²), 4.05 (t, 4 H, J = 6.5, H²), 2.15 (q, 4 H, J = 6.5, H²), 1.85 (m, 4 H, J₁ = 6.5, J₂ = 7.0, H³), 1.60 (m, 4 H, J₁ = 6.5, J₂ = 7.0, H³). -¹³C NMR: 164.8 (C¹), 163.5 (C³), 148.4 (C⁴), 138.8 (C⁵), 132.3 (C₆), 122.6 (C₇), 121.5 (C₈), 115.3 (C₂), 114.3 (C₉), 68.5 (C⁵), 33.8 (C₉), 28.9 (C₈), 25.7 (C₉).

4-(Tetrahydropyran-2-yloxy)methylphenol, Mixture of the 2- and 3-Methyl Isomers (8b): 90 ml of dihydropyran was added over a period of 30 minutes to a solution of 126 g of methylhydroquinone and 5 g of 4-toluenesulphonic acid in 1 l of diethyl ether. After stirring for another two hours, nitrogen was bubbled through and a deaerated solution of 45 g of sodium hydroxide in 500 ml of water was added. The aqueous layer obtained after separation was acidified by purging with carbon dioxide. The crude product separated as a brown oil, which was extracted with 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 under vacuum, 59 g (28%) of 8b was obtained as a light brown powder. It was an 1:1 mixture of the 3- and 2-methyl isomers as deduced from ¹H NMR; apart from a difference in the aromatic region, the acetate C-H protons of the two isomers were observed separated at δ = 3.30 and 3.35.

4-(5-Hexenoyloxy)benzoyloxyphenol (1a): A mixture of 22 g of 4-(5-hexenoyloxy)benzoic acid (3), 19.4 g of (4-tetrahydropyran-2-yloxy)phenol (8a), 1.2 g of 4,N,N-dimethylaninopyridine 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 one hour in the ice bath. After removing the ice bath, stirring was continued for 16 hours at room temperature. Intermediate 9a was obtained after filtration, evaporation of the dichloromethane and crystallization from ethanol. This product was mixed with 400 ml of ethanol and 4 g of pyridinium 4-toluenesulfonate. After stirring this mixture at 60°C for 2 hours, 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 under vacuum. 26.0 g of 10a (83%) was obtained as a white powder.

4-(5-Hexenoyloxy)benzoyloxy)methylphenol, Mixture of the 2- and 3-Methyl Isomers (10b): This reaction was performed in the

same way as described for 10a, starting with 20.8 g of 8b. Intermediate 9b was not recrystallized due to oil formation but washed with 150 ml of ethanol after it had crystallized slowly overnight. 18.0 g of 10b (61%) was obtained as a light yellow powder.

4-4-<5-Hexenoyloxybenzoxyl]-1-[4-<6-mercaptopexoxy]-benzlyoxybenzene (11a): A mixture of 25.4 g of 4-(6-mercaptopexoxy)benzoic acid (6), 34.3 g of 4-4-<5-hexenoyloxybenzoylphenol (10a), 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 NN'-dicyclohexylcarbodiimide was added and stirring was continued for 8 hours in the ice bath. After removing the ice bath, stirring was continued for 16 hours at room temperature. The crude product was obtained after elution of the mixture over a small silica column. 34.9 g of 11a (63%) was obtained as a white powder after crystallization from a 1:1 mixture of 2-propanol and ethyl acetate. It was contaminated with about 4% of a by-product as a result of thioesterification. Its NMR data are the same as those of a mixture of 1 and 2.

4-4-<5-Hexenoyloxybenzoxyl]-1-[4-<6-mercaptopexoxy>-benzlyoxybenzene, Mixture of the 2- and 3-Methyl Isomer (11b): This reaction was performed as described for the synthesis of 11a with the exception that instead of 1.1 equivalent of 10a, 1.6 equivalent of 10b was used. 11b was obtained in 48% yield as a white powder after crystallization from a 2:1 mixture of 2-propanol and ethyl acetate. It was also contaminated with about 3% of a by-product as a result of thioesterification. The NMR data which are different from those of 11a are given below: 'H NMR: 8.16 (d, 4 H, J = 8.6, H'), 8.14 (d, 4 H, J = 8.6, H'), 7.17 (d, 1 H, J = 8.5, H'), 7.13 (d, 1 H, J = 2.5, H'), 7.08 (dd, 1 H, J = 8.5, J = 2.5, H'), 6.99 (d, 4 H, J = 8.6, H'), 6.96 (d, 4 H, J = 8.6, H'), 4.07 (t, 4 H, J = 6.5, H'), 4.50 (t, 4 H, J = 6.5, H'), 2.24 (s, 3 H, H'), -13C NMR: 164.9 (C°), 164.5 (C°), 163.5 (C° and C'), 148.4 (C°), 147.1 (C°), 132.3 (C° and C'), 131.8 (C°), 124.1 (C°), 122.9 (C°), 121.4 and 121.6 (C° and C'), 120.0 (C°), 114.3 (C° and C'), 68.5 (C° and C'), 16.4 (C°).

4-4-<6-Mercaptopexoxy]-benzlyoxy]<5-hexenoyloxybenzene (14): A mixture of 25.4 g of 4-(6-mercaptopexoxy)benzoic acid (6), 21.1 g of 4-4-<5-hexenoyloxyphenol (13), 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 hours in the ice bath. After removing the ice bath, stirring was continued for 16 hours at room temperature. The crude product was obtained after elution of the mixture through a small silica column. 20.9 g of 14 (49%) was obtained as a white powder after crystallization from ethanol at 0°C. It was contaminated with about 10% by-product as a result of thioesterification. -1H NMR: 8.14 (d, 2 H, J = 8.6, H'), 7.10, (d, 2 H, J = 8.5, H'), 6.95 (d, 2 H, J = 8.6, H'), 6.91 (d, 2 H, J = 8.6, H'), 5.84 (m, 1 H, J = 17.0, J = 10.2, J = 6.5, H'), 5.05 (d, 1 H, J = 17.0, H'), 4.98 (d, 1 H, J = 10.2, H'), 4.04 (t, 2 H, J = 6.5, H'), 3.97 (t, 2 H, J = 6.5, H'), 2.55 (q, 2 H, J = 7.5, H'), 2.13 (q, 2 H, J = 6.5, H'), 1.9-1.4 (m, 20 H, Hg, Hg', H°, H', Hb, Hb', Hc, Hc'), 1.35 (t, 1 H, J = 7.5, H'). -13C NMR: 165.3 (C°), 165.3 (C°), 156.8 (C°), 144.4 (C°), 138.5 (C°), 132.2 (C°), 122.5 (C°), 121.8 (C°), 115.1 (C°), 114.8 (C°), 114.3 (C°), 68.1 + 68.2 (C° + C'), 34.9 (C°), 33.4 (C°), 29.1 (C°), 28.7 (C°), 28.1 (C°), 25.5 (C°), 25.3 (C°), 24.5 (C°).

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