Anisotropic Network Formation by the Photopolymerization of New Monomers Derived from 4-Hydroxybenzenethiol

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ABSTRACT: New polymerizable difunctional liquid crystals of monomers derived from 4-hydroxybenzenethiol were synthesized, characterized, and photopolymerized by the formation of anisotropic films. These films were obtained by the irradiation of the monomers in the mesophase with UV light before they were macroscopically oriented in glasses treated on the surface with polyimide and uniaxially rubbed. The monomers showed smectic and nematic mesophases. The thin films, uniaxially oriented, were optically transparent. The orientation was verified by IR dichroism, which showed a preferential order of mesogens. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1812–1817, 2005

Key words: networks; orientation; thin films

INTRODUCTION

Mesogens with direactive functional polymerizable groups have been used for a long time in the formation of anisotropic networks[1–4] obtained by photochemical polymerization. These anisotropic networks have many potential uses, such as polarizers, fiber-optic cables, and interference filters.[5–7] This method of photopolymerization of liquid-crystal molecules involves the macroscopic orientation of mesogens by surface mechanical forces, electric fields, or magnetic fields, followed by the photoinduced polymerization of reactive functional groups such as acrylates, vinyls, or epoxies under the action of UV light.[8–10] During the photopolymerization process, the mesogens, macroscopically oriented in the mesophase, are fixed, yielding uniaxially crosslinked networks, which exhibit highly anisotropic optical and mechanical properties. The crosslinking reactions of these mesogens lead to materials that combine the typical properties of liquid crystals and thermostable polymers.[11] A high mechanical modulus, a thermal expansion minor coefficient, and greater ease of processing before crosslinking are some of the advantages of these useful materials in high technology with respect to conventional liquid-crystal polymers.[12]

The global molecular orientation of molecules of this kind of system can be quantified with the order parameter S, which is determined by different methods, such as birefringence and X-rays. Moreover, the molecular orientation in some specific parts of the molecules can be determined by Fourier transform infrared (FTIR) dichroism.[13]

Diacrylate monomers are among the most studied because of their versatility in synthesis, which enables structural modifications, and the possibility of crosslinking at different temperatures. In addition, these monomers allow the preparation of organized networks with high order parameters, high birefringence, and good substrate adhesion. However, most reported liquid-crystal monomers exhibit a mesophase at high temperatures, and this hinders the preparation of films.[14]

Here we describe the synthesis, thermotropic properties, and photoinitiated polymerization of liquid-crystal diacrylates under UV light for the preparation of anisotropic networks. Moreover, the dichroic ratio for specific groups of the networks were determined with FTIR linear dichroism.
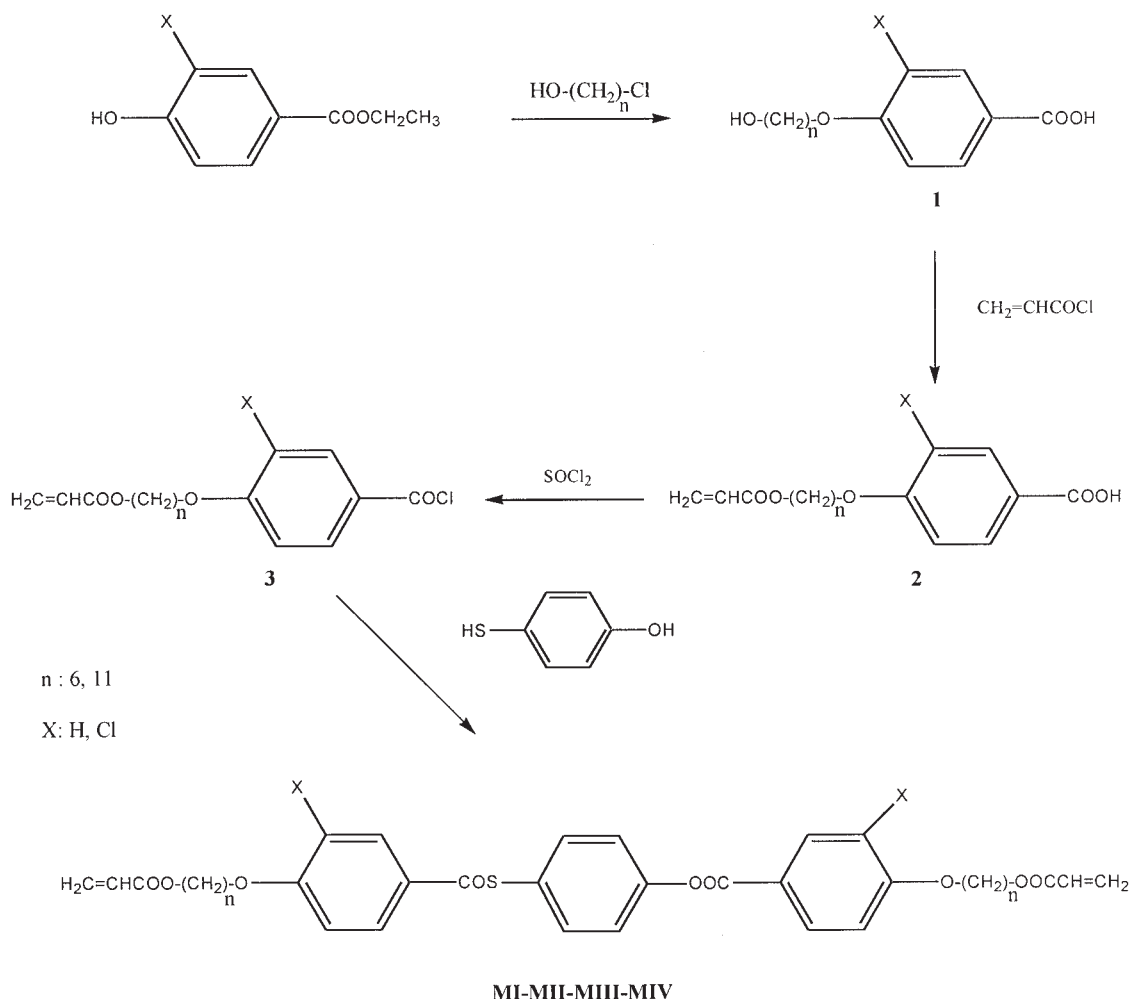
EXPERIMENTAL

Materials

All the solvents were dried before use. They were obtained from Merck (Whitehouse Station, NJ). Acryloyl chloride was distilled twice before use. All chemicals were obtained from Aldrich (Madison, WI) and used with no purification.

Scheme 1 Synthetic route of the mesogens.

Measurements

^{1}H-NMR spectra were recorded on a Bruker CA250 spectrometer (Karlsruhe, Germany). The chemical shifts were calibrated from tetramethylsilane. IR measurements were carried out with a Nicolet Magma-IR 550 Fourier transform instrument with a CaF_2/Al grid polarizer. Polarized IR measurements were carried out at the environmental temperature at polymer homogeneous alignment.

An STA 625 differential scanning calorimeter (Surrey, UK) was used to determine the thermal transitions. All heating and cooling rates were 10°C/min under nitrogen.

A Leitz Ortholux II Pol-BK optical polarized microscope (Wetzlar, Germany) equipped with a hot stage was used to observe the thermal transitions and textures. Photopolymerization was initiated with a 350-W mercury lamp. The samples were heated in a Linkam model TP91 furnace (Surrey, UK). The intensity of the radiation over the diacrylate monomers was detected with a Cole–Parmer radiometer (Vernon Hills, IL).

Synthesis

The synthetic routes for the diacrylates are shown in Scheme 1.

4-(6-hydroxyhexyloxy)benzoic acid (**1**)

To a mixture of ethyl-4-hydroxybenzoate (16.6 g, 0.10 mol) and potassium carbonate (27.6 g, 0.20 mol) in 150 mL of cyclohexanone, 6-chlorohexanol (16.2 mL, 0.12 mol) was added. Then, the mixture was refluxed with vigorous stirring for 16 h and hot-filtered. The remaining K_2CO_3 was washed several times with cyclohexanone, and then the solvent was removed. The residual oil was dissolved in 150 mL of methanol, and a solution of 22.45 g (0.4 mol) of potassium hydroxide in 50 mL of water was added. The mixture was refluxed for 16 h. Then, the solvent was removed under reduced pressure. The solid was dissolved in water and acidified with a 6 N hydrochloric acid solution with vigorous stirring. The crude product, obtained after filtration as a white solid, was further purified by

recrystallization from ethanol to give colorless crystals [yield = 19.94 g (84%)].

FTIR (KBr, cm^{-1}): 3100, 2900, 1710, 1597, 1503, 1456, 1412. ^{1}H-NMR (CDCl$_3$, ppm): 8.0 (d, 2H, aromatic), 7.2 (d, 2H, aromatic), 4.1 (t, 2H, OCH$_2$), 4.0 (t, 2H, ArOCH$_2$), 1.8–1.3 (m, 8H, CH$_2$).

4-(6-acryloyloxyhexyloxy)benzoic acid (2)

1 (10.0 g, 0.039 mol) was added to a solution of *N,N*-dimethylaniline (4.90 mL, 0.039 mol) in 200 mL of 1,4-dioxane. At 60°C, acryloyl chloride (2.70 mL, 0.003 mol) was added in small quantities with stirring for about 15 min. The stirring was continued for 2 h; during this period, the product precipitated, was separated by filtration, and was recrystallized from a 2-propanol/water mixture [80/20 v/v; yield = 6.0 g (53%)].

FTIR (KBr, cm^{-1}): 3100, 2900, 1729, 1684, 1610, 1555, 1412. ^{1}H-NMR (CDCl$_3$, ppm): 8.0 (d, 2H, aromatic), 7.2 (d, 2H, aromatic), 6.5 (d, 1H, vinyl), 6.2 (d, 1H, vinyl), 5.8 (d, 1H, vinyl), 4.1 (t, 2H,OCH$_2$), 4.0 (t, 2H, ArOCH$_2$), 1.8–1.3 (m, 8H, CH$_2$).

Bis{4-[6-(acryloyloxy)hexyloxy]benzoyl}-1-thio-4-oxyphenylene (**mi**)

4-Hydroxythiophenol (0.4 g, 0.0029 mol) was dissolved in 5 mL of dry tetrahydrofuran (THF) containing 3 mL of triethylamine. The mixture was cooled to −5°C. Then, 4-(6-acryloyloxyhexyloxy)benzoyl chloride (2.0 g, 0.0058 mol) in 10 mL of dry THF was added dropwise. After 10 h of stirring at room temperature, the solvent was evaporated, and the product was purified by column chromatography [silica gel, ethyl acetate/*n*-hexane (75/15 v/v) as an eluent]. The product was isolated by the evaporation of the eluent *in vacuo* at room temperature. Further purification was done by recrystallization from a methanol/chloroform mixture [80/20; yield = 1.7 g (40%)].

FTIR (KBr, cm^{-1}): 2941, 2863, 1730, 1590 1503, 1463, 1402, 1262. ^{1}H-NMR (CDCl$_3$, ppm): 8.1 (d, 4H, aromatic), 7.2 (d, 2H, aromatic), 7.0 (d, 2H, aromatic), 6.6 (d, 4H, aromatic), 6.3–5.6 (m, 6H, vinyl), 4.1 (t, 4H, COOCH$_2$), 4.0 (t, 4H, ArOCH$_2$), 1.8–1.2 (m, 16H, aliphatic). ^{13}C-NMR (CDCl$_3$, ppm): 161.8, 162.1, 148.8, 146.7, 132.0, 127.1, 125.9, 123.8, 119.8, 116.4, 73.0, 66.1, 30.2, 23.9.

Thin-film preparation

Oriented photopolymerized films were produced by an oriented rubbing method. The liquid-crystal diacrylate was provided with 1% 2,2-dimethoxy-2-phenylacetophenone (photoinitiator) and with 100 ppm 4-methoxyphenol (thermal inhibitor). To thoroughly mix the compounds, the monomer, photoinitiator, and

TABLE I
Phase-Transition Tempereatures

n	X	Monomer	Temperatures (°C)[a]
6	H	**MI**	Cr 79 N 172 I
11	H	**MII**	Cr 61 Sm$_c$ 78 N 120 I
6	Cl	**MIII**	Cr 75 N 85 I
11	Cl	**MIV**	Cr 65 N 78 I

Cr, crystalline phase; N, nematic phase; I, isotropic phase; Sm$_c$, smectic phase.
[a] The diacrylates **MI** and **MII** were stabilized by 100. ppm 2,6-di-*tert*-butyl-4-methylphenol to avoid thermal polymerization.

thermal inhibitor were dissolved in methylene chloride. Then, the solvent was evaporated. The resulting solid was dried *in vacuo* overnight. In the monomeric phase, the liquid-crystalline mixture was aligned in a cell consisting of two polyimide-coated microscopic cover glasses, which were repeatedly rubbed in one direction.

The photopolymerization was initiated by irradiation for 15 min with a fluorescent lamp with an intensity of 0.5 mW/cm^2 (measured at 350 nm). Thus, the thin films were all transparent.

RESULTS AND DISCUSSION

Synthesis of bis{4-[*n*-(acryloyloxy)hexyloxy]benzoyl}-1-thio-4-oxyphenylene and chlorine derivates

The chemical structure of the molecules is shown in Scheme 1. All the synthesized monomers consist of three aromatic rings interlaced by thioester and ester groups. The functional acrylate groups are interlaced with the mesogen units by 6/11 flexible carbon chains. The process guarantees a high density of crosslinking after the photopolymerization. We have synthesized the monomers with a well-known synthetic route that leads to high yields of 4-(*w*-hydroxyalkyloxy)benzoic acid derivatives. The incorporation of reactive groups is obtained by an acryloyl chloride reaction with **2**. Finally, the monomers are obtained by the esterification of **3** with 4-hydroxybenzenethiol in yields of 40–65%.

Phase behavior

The transition temperatures of the liquid-crystal diacrylates are given in Table I. Diacrylates **MI** and **MII** are colorless, crystalline materials that exhibit broad enantiotropic ranges (93 and 59°C, respectively). For chlorine derivatives **MIII** and **MIV**, they are as expected. It is well known that introducing lateral substituents into an aromatic ring of a liquid-crystalline compound normally lowers the nematic–isotropic transition temperatures.[15] The two chlorine atoms po-
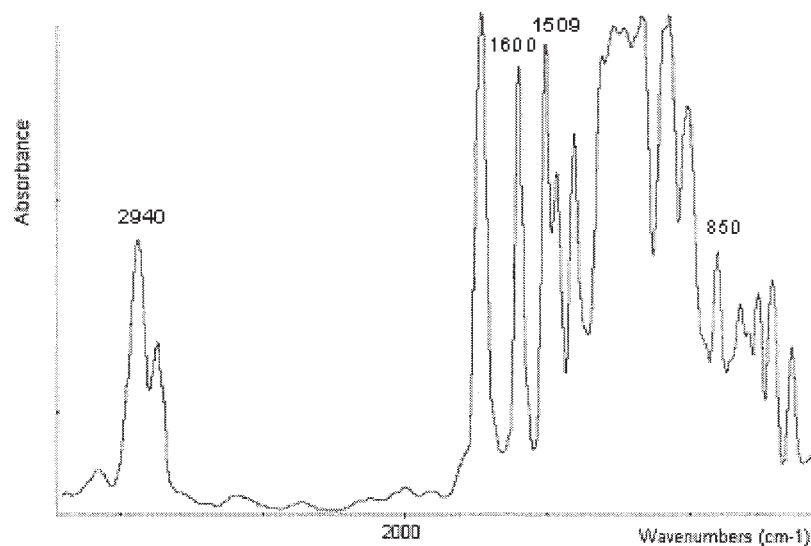
Figure 1 FTIR spectrum of **MI**.

sitioned on the lateral aromatic rings have a broadening effect on the molecule, and this result in reduced intermolecular attractions. Thus, these reduced intermolecular attractions result in lower melting and clearing points. Another fact to be considered is the influence of the molecular geometry. Steric and repulsive interactions caused by the chlorine atoms by the substitution on the lateral aromatic rings lead to a larger twist than that in the unsubstituted molecule. This larger twist tends to reduce anisotropic polarizability, thus reducing the thermal stability.

Diacrylates **MIII** and **MIV** exhibit much smaller enantiotropic ranges (10 and 13°C, respectively). Orthoscopic measurements have revealed that all the diacrylates are in the nematic phase, having the characteristic schlieren texture, which coexists with the homeotropic alignment.

An increase in the number of carbon atoms in the terminal methylene group from 6 to 11 for **MII** produces the formation of a smectic C phase in the lower temperature region of 61–78°C (see Table I) and a nematic phase in the higher temperature region of 78–120°C. The identity of the smectic C phase has been assigned on the basis of the optical textures. The characteristic focal–conic and homeotropic texture of the smectic C phase has been clearly identified in the cooling process. No smectic properties have been observed, even in the higher homologue **MIV**.

MI is by far the synthesized monomer that meets the requirements for photopolymerization. The mesophase is always present even if a thermal inhibitor and initiator are incorporated to make UV polymerizations. It also has a high mesophase range, which enables us to choose an optimal temperature for photopolymerization.

Photopolymerization and FTIR dichroism

The monomers were macroscopically oriented in a nematic phase and maintained on cells of 5 μm with pretreated polyimide and unidirectionally rubbed. On the cell, the monomers were irradiated with UV light with an intensity of 0.5 mw/cm^2 at 350 nm for 15 min, and optically transparent films were obtained. Freestanding films 5 μm thick were aligned under a polarizing microscope parallel to the IR polarizer and measured in the spectrophotometer.

IR analysis without a polarizer revealed a complete disappearance of the vinyl absorption band at 1635 and 843 cm^{-1} for all the monomers. The absorbance measured by the **MI** film is presented in Figure 1.

Here we studied various absorption bands of anisotropic networks (photopolymerization of **MI**) by IR dichroism to compare the orientations of the mesogenic units and the flexible spacers, which are listed in Table II.

In the spectrophotometer, the film was oriented in such way that the average orientation of the aromatic core under discussion was almost parallel to the transition dipole moments and long molecular axis and parallel to the light polarization vector with a 0° angle.

TABLE II
Polarized FTIR Peak of the Studied Absorption Bands

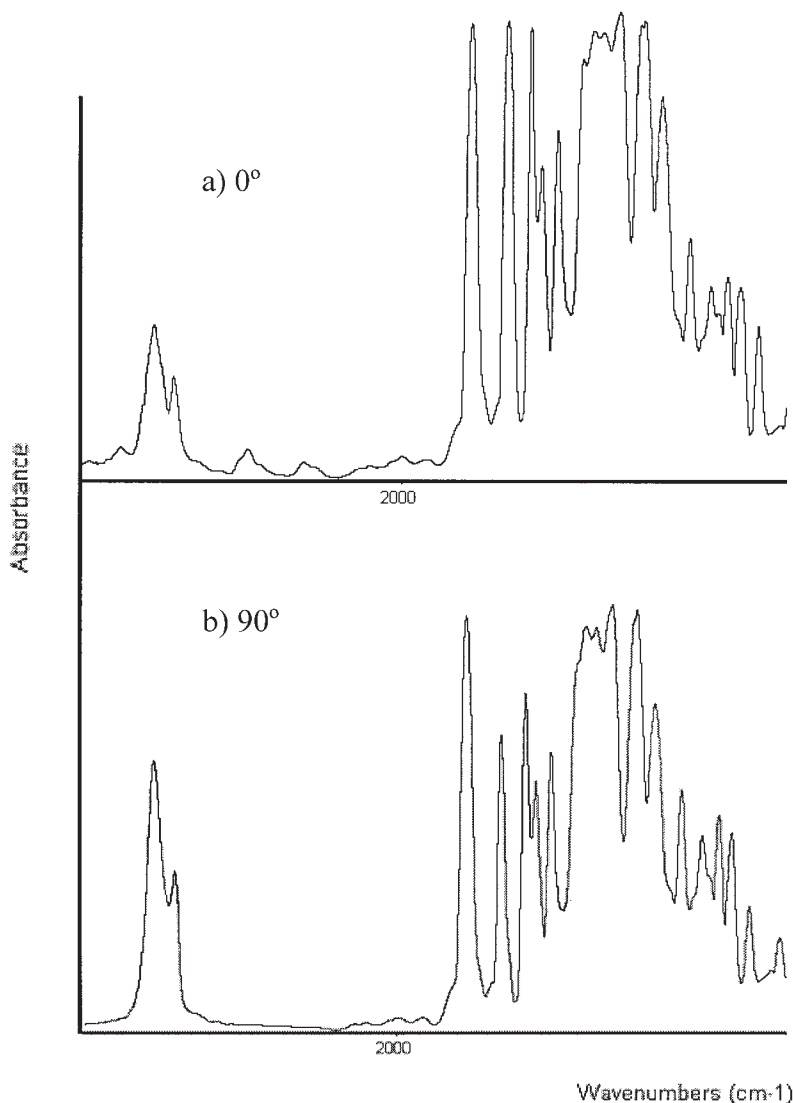| Frequency (cm^{-1})	Assignment	Moiety
2940	ν_sCH$_2$	Stretching spacer
1600	νC$=$C	Stretching benzene ring
1509	νC$=$C	Asymmetric benzene ring
850	δCH	Aromatic CH out-of-plane vibration

Figure 2 FTIR spectra when the polarizers are rotated from (a) 0 and (b) 90° in the homogeneously aligned film.

Afterwards, the polarizer was turn round at 90°. A rise or decrease in the intensity of some typical studied bands was observed when the polarizer was rotated from 0 to 90° angles in FTIR spectra (Fig. 2).

To show the difference in the intensity of the polymer absorption bands, it can be observed that the absorbance at 1600 cm^{-1}, assigned to a C=C band on the benzene ring, and at 1509 cm^{-1}, assigned to a C=C band on the asymmetric benzene ring, gradually lowers when the polarization angle rises.

On the other hand, there is an increase in the magnitude of the absorbance at 2940 (stretching CH$_2$ groups) and 850 cm^{-1} (aromatic CH absorption bands, out-of-plane vibrations perpendicular) as a function of the polarization angle from 0 to 90°.

Information about the direction and preferential order of the individual units can be determined by the dichroic ratio R, which is defined as the optic density quotient measured with parallel (A_{max}) and perpen-

dicular (A_{min}) linear polarized light (Table III). The peak intensity is determined as the difference in the absorbance at a band maximum and at a baseline level, corrected for the polarizer efficiency:[13]

$$R = A_{max}/A_{min}$$

The results show that the film of **MI** has a preferential degree orientation. The orientation of C=C aromatic

TABLE III
R Values of Monomer MI

Specific group	$R = A_{max}/A_{min}$
$\nu_s CH_2$	4.68
$\nu C=C$	5.12
$\nu C=C$	5.35
δCH	4.76

rings indicates that the direction of the transition moment of the C$=$C vibrations is preferentially parallel to the direction of orientation, whereas the —CH$_2$ groups and aromatic-ring —CH vibrations are perpendicular to the direction. The results agree with those presented in the literature.[16]

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