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PREPARATION AND CHARACTERIZATION OF CROSSLINKED LIQUID CRYSTALLINE POLYMER FILMS AS NONLINEAR OPTICAL MATERIALS

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ABSTRACT

Liquid crystalline monomers have been synthesized and characterized in purpose to make polymeric second-order nonlinear optical (NLO) materials. Crosslinked polymers have been made to thermally stabilize the orientation created in aligned samples. The orientation has been measured by means of x-ray scattering and infrared dichroism. Oriented, crosslinked poly(vinyl ether)s were made by cationic polymerization whereas crosslinked, nonlinear optical poly(acrylate)s were made by radical polymerization. Polymerization was initiated both thermally and photochemically. The NLO activity of the poly(acrylate)s was measured as the Pockels effect and the second harmonic generation signal, giving values of 0.15 pm/V and 0.40 pm/V, respectively.

INTRODUCTION

This paper reviews some of the work carried out on the in-situ photopolymerization of liquid crystalline monomers reported in four recent papers [1-4]. The work of our group has been focused on preparing nonlinear optical (NLO) liquid crystalline polymers (LCP)s with a thermally stable organization. The research was initially directed toward understanding how to prepare oriented LCPs with thermal stability. At a later stage the use of this knowledge was combined with the incorporation of NLO-functional groups, which ultimately produced functional materials.

The monomers presented in this study were synthesized as described in earlier papers [1-4], and the structures are shown in Fig. 1.

ORIENTED AND CROSSLINKED FILMS [1, 2]

Oriented Films

Thermal stabilization of low molar mass self-organizing molecules is achieved using in-situ photopolymerization of liquid crystalline monomers [5, 6]. A high degree of quadrupolar order is obtained in the liquid crystalline monomer phase, simply by contacting the monomer with a unidirectionally rubbed polyimide film. During polymerization, the high degree of order is retained and a highly oriented polymer film is produced. Photoinitiation offers an advantage over thermal initiation in that the polymerization temperature can be freely chosen. This is important when polymerizations are performed within the mesophase range of the monomer.

Oriented polymer films were obtained by cationic photopolymerization of **1** in the mesophase. Wide-angle x-ray diffraction measurements were performed in order to assess the degree of order obtained in the films. Values around 0.9 for the order parameter were obtained [1].

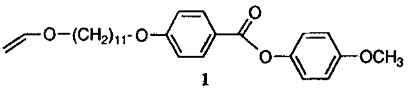
The oriented films of poly(**1**) showed smectic mesomorphism and possessed an isotropization temperature around 130°C. By heating the films above this temperature and then subsequently cooling them again, the previously oriented samples became globally unoriented. The orientation was completely lost, showing the need for thermal stabilization of the macroscopic organization.

Crosslinked Films

In trying to prepare a side-chain liquid crystalline polymer with a thermally stable mesophase, two different types of bifunctional vinyl ether monomers, denoted **2** and **3** respectively, were used. Each of the two compounds were mixed in relatively low concentrations (10-20 mol%) with the monofunctional monomer **1**, and the mixtures were subsequently polymerized, both thermally at 80°C in the DSC and photochemically in the microscope hot-stage at the same temperature. The different structures of the bifunctional monomers were believed to cause differences in the properties of the formed polymers. At this stage, no attempts were made to produce oriented structures.

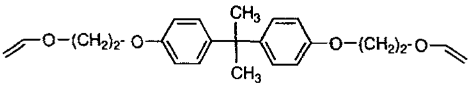
Compound **2** is a nonmesogenic monomer and, at low concentrations in polymerization with **1**, mainly acts as an impurity, which is demonstrated by the observed decrease in isotropization temperature with increasing content of **2** (Table 1). Crosslinks always connected backbone chains and were probably located between the smectic layers in poly(**1**). The side-chains were free to move but were somewhat disturbed by the new compound present. At sufficiently high concentration of **2**, the polymer became fully amorphous and no first-order transitions were observed [1].

The bifunctional mesogenic monomer **3** was considered to be more promising since the structure is quite similar to **1** and should fit better than **2** into the smectic structure of poly(**1**). The results (Table 1) clearly show that this was the case. Only 10 mol% of the bifunctional monomer **3** was needed to give a polymer with a k70i i60n44s_A20k



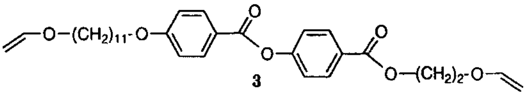
1

k55i i25k



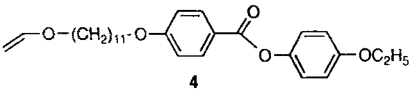
2

k55i i23n17k



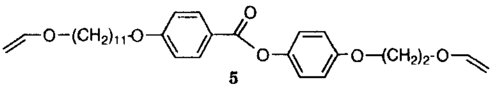
3

k66n76i i70n59s_A38k



4

k64s_A66n70i i66n63s_A48s_B25k



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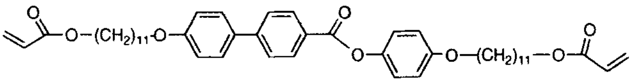
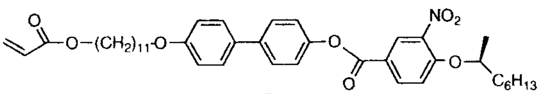
k42s_E89s_C118s_A128i i125s_A115s_C81s_E58k



6

k56s_A*62i i61s_A*11k



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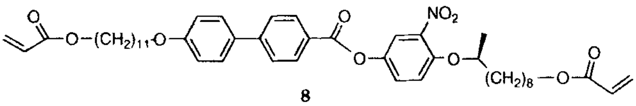

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FIG. 1. Liquid crystalline monomers discussed in this paper.

TABLE 1. Isotropization Temperature (T_i)[a] and Texture[b] for Some Polymers. A Dash Indicates no Transition Was Observed.

Polymer	Monomer feed	T_i, °C	Texture
1	100/0	126	Smectic
1/2	90/10	109	Smectic
1/2	80/20	–	Amorphous
1/3	90/10	–	Smectic

[a] From 1st heating scan in the DSC.
[b] As observed in the microscope.

thermally stabilized mesophase [1]. This polymer showed a texture resembling focal conic domains, indicative of a smectic liquid crystalline phase. The DSC traces of poly(**1**) and its crosslinked equivalent, containing 10 mol% of **3**, are shown in Fig. 2, and it can be seen that the endothermic isotropization peak is not present in the crosslinked polymer.

Films with Orientational Thermal Stability

In this part of the work the goal was to prepare an oriented side-chain liquid crystalline polymer film possessing thermal stability with respect to the orientation of the mesogenic groups. To meet these requirements and use the methods described earlier, it was necessary to find a bifunctional mesogenic monomer miscible with **1** in the mesophase. A mixture of **1** with **2** could not be oriented since the bifunctional monomer crystallized before any mesophase was formed on cooling the isotropic monomer mixture. This excluded the possibility of using monomer **2**.

The mixture of **1** and **3** (10 mol%) formed at 52°C on cooling a stable and potentially orientable nematic phase. The occurrence of this mixed mesophase was probably due to the similarity of the monomer structures. Polymerization of the

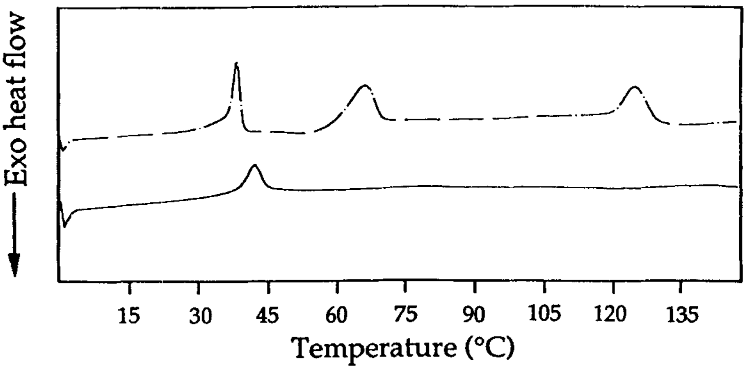

FIG. 2. DSC thermogram of poly(**1**) (-·) and its crosslinked equivalent (——) containing 10 mol% of **3**. Data from Ref. 1. With permission from Elsevier Sciences Ltd., UK.

monomer mixture **1** and **3** at 50°C with photochemical initiation in a 20-μm thick glass cell coated with a rubbed polyimide film resulted in a highly ordered polymer film that could be heated up to 200°C and then subsequently cooled down again, resulting in almost complete recovery of the orientation [1]. The film was completely transparent at room temperature and showed a texture of macroscopically ordered focal conical domains, indicating smectic mesomorphism. The high degree of orientation was verified by small-angle x-ray scattering, showing only arc-shaped outer and spot-like inner reflexes.

No isotropization peak for the crosslinked poly(**1**/**3**) was observed (Fig. 2). Isotropization is impossible due to the presence of crosslinks. However, an infrared dichroic investigation [2] of a similar material, poly(**4**/**5**), showed that the order parameter decreased to reach a value of zero at 200°C. Upon cooling, the order parameter increased again and was almost completely regained when the material reached room temperature. The explanation was that the crosslinks originating from the bifunctional monomer gave the material a memory which resulted in a regain of the orientation after cooling to room temperature. The reason that complete regain of the orientation was not obtained was explained by the hypothesis of incomplete polymerization. The photopolymerization of the aligned monomers was carried out at a temperature lower than the glass transition temperature (T_g) of the ultimate polymer network, which resulted in vitrification of the material. When the films were heated to above T_g, the unreacted monomers continued to polymerize due to an acid residue acting as a thermal initiator. Consequently, these monomers were locked-in with an isotropic organization and the order parameter of the sample permanently decreased. This hypothesis was supported by the fact that the order parameter of the crosslinked samples regained the same value after the second heating and cooling cycle. The films exhibited the same behavior over ten consecutive heating–cooling scans [2].

On a molecular level, the reorientation of the side groups in the polymer network can be described as in Fig. 3. When heating the sample, the mesogens in the side groups which are linked to the network at one end are free to move and may reach an "isotropic" state, while the mesogens that are linked to the network at both ends are fixed in one position. On lowering the temperature, the mesogens in the "isotropic" side groups organize in the direction of the crosslinked mesogens. The

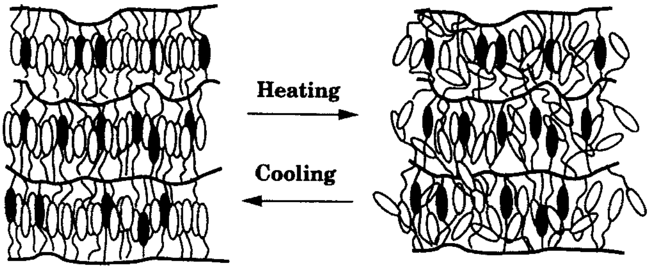

FIG. 3. Schematic representation of the reorganization of an organized network [poly(**4**/**5**) of molar ratio 90/10] during heating and cooling. Data from Ref. 2. With permission from Elsevier Sciences Ltd., UK.

more side groups linked to the network in both ends, the lower the reduction of the order parameter at elevated temperatures.

CROSSLINKED NLO FUNCTIONAL POLYMER FILMS [3, 4]

In the past decade, considerable effort has been directed toward the design, synthesis, and characterization of organic materials for second-order nonlinear optics. The advantages of using organic materials in electrooptical applications are their rapid response and their high intrinsic molecular hyperpolarizability [8]. Second-order nonlinear optical properties can only be obtained in materials with a polar order. Currently available organic nonlinear optical materials have many desired properties but normally they all suffer from a low polar order which is usually unstable with time.

The second-order susceptibility $\chi^{(2)}$ is given by

$$\chi^{(2)} = N < \beta > \qquad (1)$$

where N is the number of molecules per unit volume and $<\beta>$ is the average value of the hyperpolarizability with consideration taken of the degree of order. A requirement for second-order nonlinear optical effects is that $\chi^{(2)} \neq 0$. In nematic and smectic liquid crystalline phases, $\chi^{(2)} = 0$ because β is averaged out along the direction of the molecule. This is because liquid crystals are normally nonpolar materials and have the wrong kind of internal order, quadrupolar instead of dipolar. Along the director the liquid crystalline order is strictly nonpolar; however, perpendicular to the director, the polar order can be induced. The local polarization, $\mathbf{P} \perp \mathbf{n}$, has the advantage of being thermodynamically stable. This can only be realized in tilted chiral smectic phases and particularly in the chiral smectic C (s_C*) state [7]. Furthermore, a macroscopic polarization can be obtained in the surface-stabilized ferroelectric state. Along the direction perpendicular to the director, $<\beta> \neq 0$, and thus $\chi^{(2)} \neq 0$ and the materials may therefore exhibit a second-order nonlinear optical response.

Materials for nonlinear optics must combine their unique optical properties with good mechanical and thermal properties. Low molar mass and polymeric ferroelectric liquid crystals are ferroelectric in the s_C* phase, and their polar order is limited to that state. However, we have showed that it is possible to thermally and mechanically stabilize the polar organization of a s_C* phase using the in-situ photopolymerization technique [3, 4]. This stabilization required a novel crosslinkable ferroelectric monomer mixture. We used a mixture of **6** and **7** in the proportions 70/30 mol%.

The crosslinkable ferroelectric monomer mixture could be designed in several ways, but independent of design it should result in a nonlinear optical material which after crosslinking is pyroelectric and no longer ferroelectrically switchable.

Preparation of the Crosslinked Liquid Crystals

Cells of a conventional sandwich type, consisting of two parallel glass substrates separated a distance of either 2 or 4 μm by evaporated SiO_x spacers, were used for the ferroelectric, poling, polymerization, and nonlinear optical experiments. The substrates were prepared from ITO-coated glass sheets (Balzers Baltracon) on which an electrode pattern was formed. An insulating layer of SiO_x of about 1000 Å thickness was deposited onto the electrodes. The uniform bookshelf alignment of the liquid crystal material in the cell was achieved by using a thin, unidirectionally rubbed polyimide aligning layer deposited on top of the insulating layer.

The liquid crystalline mixture (**6**/**7**) was introduced into the cell in the s_A* or in the isotropic phase by capillary forces. The cell was inserted into a hot stage with the temperature controlled to an accuracy of 0.1°C. The liquid crystalline substances were examined in a polarizing microscope (crossed polarizers). At the temperatures ($\approx$ 92°C) at which the ferroelectric electrooptic response indicated that the s_C* phase was fully developed, a dc electric field ($E \approx$ 30 V/m) was applied in order to orient the spontaneous polarization in the whole cell in one direction. After obtaining a ferroelectric monodomain structure for the 70/30 blend, mixed with photoinitiator, the cell was irradiated with UV light for about 10 minutes while keeping the dc-field on, during which the liquid crystalline mixture underwent radical polymerization. The ratio of photoinitiator to monomer was 1/250 (0.4 mol%).

Properties of the Crosslinked Liquid Crystals

As a consequence of the polymerization process, the texture of the sample was changed slightly after illumination. The initially uniform bookshelf texture was disturbed by stripes oriented perpendicular to the smectic layers. Although the initial uniformity of the texture was changed after illumination, only a small difference was found in the position of the optical axis before and after polymerization. The crosslinked polymers did not exhibit any ferroelectric response. Instead, a very weak linear electrooptical response was recorded, probably corresponding to a small deviation of the molecules around their fixed position on the cone. The absence of ferroelectric switching indicates that the uniform molecular tilt in the s_C* phase was fixed during polymerization and that the macroscopic polarization of the sample (in a direction perpendicular to the cell glass plates) was made permanent.

The polymer network organization showed good thermal stability. Heating above the isotropization temperature of the nonpolymerized liquid crystal material caused no changes in the molecular tilt of the network. DSC showed, however, a distinct endothermic peak close to 45°C. This transition, which was observed on first and second heating and on first cooling, caused no textural changes as revealed by polarized light microscopy. The transition has also been observed in s_A and s_B networks but is presently not understood. Earlier studies showed that the enthalpy of the transition decreases with an increasing degree of crosslinking [1, 2].

Nonlinear Optical Properties

Two types of experiments were performed in order to confirm the presence of second-order nonlinear optical activity in the crosslinked poly(**6**/**7**): Pockels measurement [4] and second-harmonic generation measurement [7]. The Pockels measurement was carried out in a standard setup with a HeNe laser (633 nm), polarizer, sample, Soleil-Babinet compensator, analyzer, and detector. In Fig. 4 the

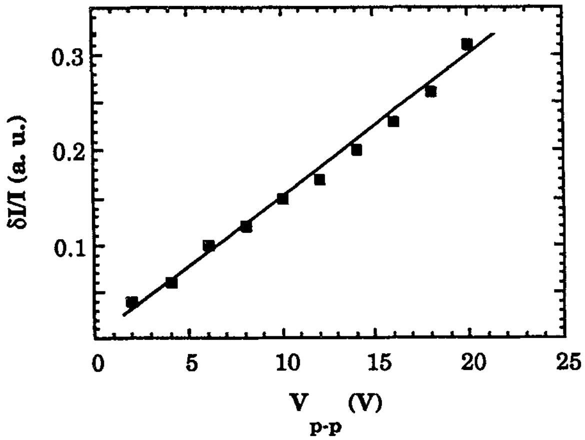

FIG. 4. The modulated intensity as a function of voltage in poly(6/7) (70/30 mol%) measured at room temperature. Data drawn after Fig. 9 in Ref. 4.

intensity modulation $\delta I/I$ is plotted as a function of the electric field; it is found to be linear as expected. I is the intensity transmitted through the setup when $E = 0$. The linearity in Fig. 4 can, however, also arise from a motion of the optic axis linear in the electric field. This may arise if the chiral units are not frozen-in completely by the polymer network. Therefore, it is necessary to investigate explicitly the origin of the result in Fig. 4.

For the second-harmonic generation measurement, the sample was mounted on a stage which could be rotated by means of a step motor so that the angle of incidence could be varied. The SHG experiment was performed with a Q-switched Nd:YAG laser operating at 1064 nm wavelength with a pulse width of about 7 ns and a 10-Hz repetition rate. The SHG signal (532 nm) was separated from the fundamental beam by an edge filter after the sample, transmitted only wavelengths <700 nm, and detected by a photomultiplier. It was also explicitly checked that there was no contribution to the detected signal from the fundamental beam.

The SHG signal is presented in Fig. 5 as a function of the angle of incidence. Due to the planar (bookshelf) geometry of the samples, the signal exhibited a minimum at normal incidence. The SHG signal was compared to that of a quartz reference at the corresponding angle of incidence, and was about 1000 times weaker. Considering the small thickness of the cell and the quadratic dependence of the SHG signal on the cell thickness up to the coherence length of the laser beam, our material should have NLO d-coefficients (essentially $\chi^{(2)}$ values) of the same order as those of quartz (i.e., in the range of 0.4 pm/V).

WORK IN PROGRESS

Obtained results confirm the correctness of the idea of making thermally stable, NLO active polymers via photocrosslinking of liquid crystalline monomers. However, it is possible to enhance the NLO activity and the thermal stability of the

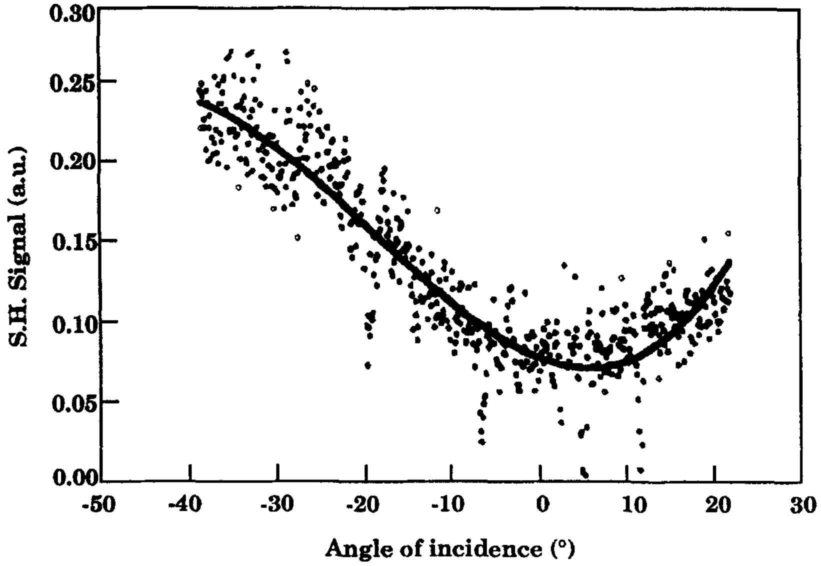

FIG. 5. Second harmonic signal as a function of angle of incidence for poly(6/7) (70/30 mol%). Data drawn after Fig. 6 in Ref. 7.

material by using other monomers. The present work focuses on the development of **8**, which increases the amount of NLO active chromophores in the material and also improves the thermal stability since only monomers with crosslinking ability are used.

ACKNOWLEDGMENTS

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