Macromolecules 1993, *26*, 1244–1247

Synthesis and Photopolymerization of a Liquid-Crystalline Diepoxide

D. J. Broer,* J. Lub, and G. N. Mol

Philips Research, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands

Received July 23, 1992; Revised Manuscript Received October 22, 1992

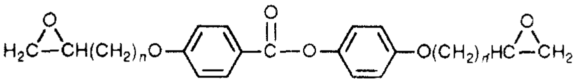
ABSTRACT: The synthesis of a liquid-crystalline diepoxide 4-[(3,4-epoxybutenyl)oxy]phenyl 4-[(3,4-epoxybutenyl)oxy]benzoate is described. The photoinitiated cross-linking of this molecule, uniaxially oriented in the nematic state, to form an ordered network is studied. This network shows an increased birefringence which is maintained at high temperatures.

Introduction

In previous investigations we demonstrated that the photoinitiated bulk polymerization of various liquid-crystalline diacrylates in their oriented state leads to densely cross-linked oriented polymer networks.[1-3] Macroscopic single liquid-crystal orientation of the low viscous nematic monomers is achieved on a substrate coated with a unidirectionally rubbed thin polymer film, e.g., polyimide. Subsequently, the monomeric alignment is permanently fixed by the fast photoinitiated chain cross-linking of the diacrylates. The resulting films exhibit highly anisotropic optical,[1-3] thermal,[4] and mechanical[5] properties.

Most of these diacylates have a melting temperature well above 80 °C.[3] Lower melting diacrylates, which may have advantages for processing of these materials, are difficult to prepare. The monomers obtained with lower melting temperatures exhibit the nematic mesophase only in the supercooled state or exhibit other mesophases (e.g., S_A). With these materials it is difficult to retain the alignment during polymerization. Therefore, we started to look at other polymerizable systems such as epoxides.

A known liquid-crystalline diepoxide is 4-[(2,3-epoxypropenyl)oxy]phenyl 4-[(2,3-epoxypropenyl)oxy]benzoate (**1a**).[6] This liquid crystal still has a relatively high melting temperature (T_m = 118 °C) and exhibits only a monotropic nematic phase (T_c = 93 °C). From nonreactive liquid crystals of similar structure (e.g., the series of 4-*n*-alkoxyphenyl 4-*n*-alkoxybenzoate molecules) it is known that with increasing length of the alkoxy group the melting temperature decreases more than the clearing temperature.[7] Therefore, we decided to prepare a liquid-crystalline diepoxide with an additional methylene group between the epoxide moiety and the mesogenic group s.e. **1b**, hoping to obtain a thermotropic nematic phase.



1a, *n* = 1; **1b**, *n* = 2

To perform isothermal cationic photopolymerization, we chose as initiator diphenyliodonium hexafluoroarsenate.[8] Because the aromatic rings of the mesogenic group in **1b** make it impossible to use the deep-UV radiation necessary to photolyze the diphenyliodonium group, α,α-dimethoxydeoxybenzoin can be added. The last compound is capable of activating the diphenyliodonium group and absorbs in the near UV (300–400 nm).

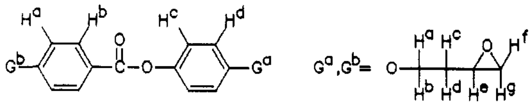
Experimental Section

Synthesis. (a) 4-(3-Butenyloxy)benzoic Acid (2). A mixture of 33.2 g of ethyl 4-hydroxybenzoate (0.2 mol), 22.5 mL of 4-bromo-1-butene (0.22 mol), 42 g of K_2CO_3 (0.3 mol), and 200 mL of acetone is boiled for 24 h. After filtration and evaporation of the acetone, 200 mL of diethyl ether is added followed by 100 mL of water. After separation, the ethereal layer is extracted twice with 100 mL of a 10% aqueous solution of NaOH. The residue obtained after evaporation of the diethyl ether is boiled with 300 mL of a 1:2 ethanol/water mixture containing 30 g of KOH. After obtainment of a clear solution, this solution is cooled and a 6 N HCl aqueous solution is added with intense stirring until pH 2. The crude product is obtained by filtration, washed for 30 min with 300 mL of water, and crystallized from ethanol. Yield: 15.5 g of white plates (40%).

(b) 4-(3-Butenyloxy)phenol (3). To a boiling solution of 33 g of hydroquinone (0.3 mol) and 20 mL of 4-bromo-1-butene in 100 mL of ethanol is added over a period of 1 h 40 mL of an aqueous solution containing 13 g of KOH. After additional boiling for 4 h, the mixture is poured onto a mixture of 400 mL of water and 200 g of ice. An oil separates which is extracted with 100 mL of diethyl ether. The diethyl ether solution is extracted twice with 100 mL of deaerated 10% aqueous KOH solution. After extraction of the combined aqueous solution with 100 mL of diethyl ether, it is acidified with a 6 N aqueous HCl solution upon which an oil separates. The oil is extracted twice with 50 mL of dichloromethane. The combined dichloromethane solutions are washed with 50 mL of a saturated aqueous NaCl solution, dried over $MgSO_4$, and evaporated. The resulting oil is vacuum distilled. Yield: 5.4 g (16%) as a clear oil (bp 85 °C at 1 mmHg), which crystallizes when kept in the refrigerator.

(c) 4-(3-Butenyloxy)phenyl 4-(3-Butenyloxy)benzoate (4). A mixture of 4.2 g of **2** (22 mmol), 20 mL of $SOCl_2$, and 3 drops of DMF is stirred for 1 h. The excess of $SOCl_2$ is distilled off, first at 40 °C at the water aspirator, the last traces at 10^{-2} mmHg. Sixteen milliliters of pyridine is added. The mixture is cooled in an ice bath, and 3.3 g of **3** (20 mmol) is added. After stirring for 2 h at room temperature, the mixture is poured onto a mixture of 150 mL of water and 20 mL of concentrated HCl solution. The crude product obtained after filtration is washed successively with 150 mL of a 10% aqueous Na_2CO_3 solution, 150 mL of water, and 100 mL of cold ethanol. After drying, 5.0 g of the product (74%) is obtained as a white powder.

(d) 4-[(3,4-Epoxybutenyl)oxy]phenyl 4-[(3,4-Epoxybutenyl)oxy]benzoate (1b). A solution of 5 g of **4** (15 mmol) and 8 g of 75% pure 3-chloroperoxybenzoic acid (35 mmol) in 50 mL of dichloromethane is stirred at room temperature for 7 days. After filtration, the dichloromethane solution is extracted successively with 70 mL of a 5% aqueous solution of Na_2SO_3, 50 mL of a 5% aqueous solution of Na_2CO_3, and 50 mL of a concentrated aqueous NaCl solution. After drying over $MgSO_4$ and evaporation of the dichloromethane, the crude product is obtained; 3.2 g of the pure product (61%) is obtained after two crystallizations at −18 °C from 2-propanol. Its ^1H NMR spectrum (the data for which are given below) is in accordance with its structure. The protons are numbered as follows:



0024-9297/93/2226-1244$04.00/0

Scheme I
Synthetic Route to 4-[(3,4-Epoxybutenyl)oxy]phenyl 4-[(3,4-Epoxybutenyl)oxy]benzoate (1b)

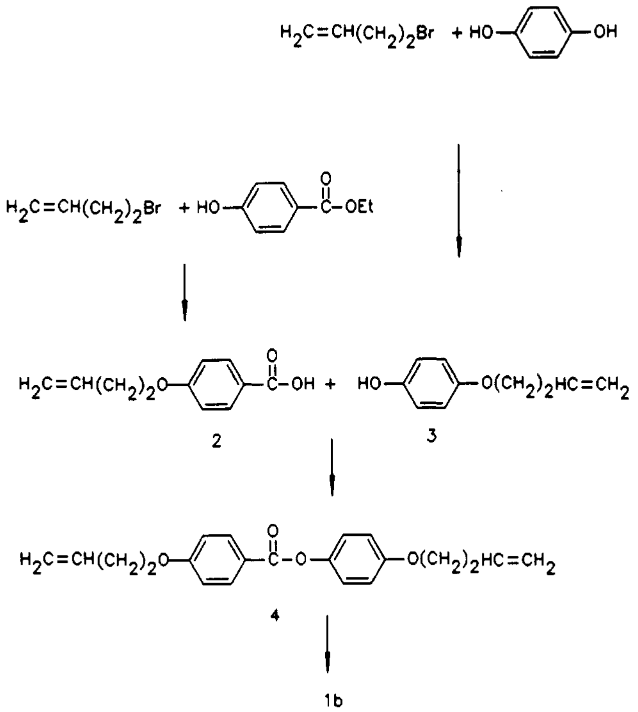


Table I
Transition Temperatures of the Compounds Shown in Scheme I, Measured with DSC

	T_m (°C)	T_c (°C)		T_m (°C)	T_c (°C)
1b	45	61	**3**	10	—
2	120	141	**4**	52	(48)

^{1}H NMR (300 MHz, $CDCl_3$, tetramethylsilane as internal standard):

Aromatic system, 8.13 (H^b, d, $J_{a,b}$ = 8.6 Hz), 7.11 (H^c, d, $J_{c,d}$ = 8.6 Hz), 6.97 (H^a, d, $J_{a,b}$ = 8.6 Hz), 6.93 (H^d, d, $J_{c,d}$ = 8.6 Hz).

Group G^a, 4.13 (H^a, m, $J_{a,b}$ = 9.5 Hz, $J_{a,c}$ = 7.0 Hz, $J_{a,d}$ = 5.9 Hz), 4.11 (H^b, m, $J_{a,b}$ = 9.5 Hz, $J_{b,c}$ = 5.9 Hz, $J_{b,d}$ = 5.3 Hz), 3.15 (H^e, m, $J_{c,e}$ = 4.7 Hz, $J_{d,e}$ = 6.9 Hz, $J_{e,f}$ = 2.8 Hz, $J_{e,g}$ = 4.1 Hz), 2.83 (H^g, dd, $J_{e,g}$ = 4.1 Hz, $J_{f,g}$ = 5.4 Hz), 2.57 (H^f, dd, $J_{e,f}$ = 2.8 Hz, $J_{f,g}$ = 5.4 Hz), 2.11 (H^c, m, $J_{a,c}$ = 7.0 Hz, $J_{b,c}$ = 5.9 Hz, $J_{c,d}$ = 15.4 Hz, $J_{c,e}$ = 4.7 Hz), 1.94 (H^d, m, $J_{a,d}$ = 5.9 Hz, $J_{b,d}$ = 5.3 Hz, $J_{c,d}$ = 15.4 Hz, $J_{d,e}$ = 6.9 Hz).

Group G^b, 4.22 (H^a, m, $J_{a,b}$ = 9.5 Hz, $J_{a,c}$ = 7.0 Hz, $J_{a,d}$ = 5.9 Hz), 4.19 (H^b, m, $J_{a,b}$ = 9.5 Hz, $J_{b,c}$ = 5.9 Hz, $J_{b,d}$ = 5.3 Hz), 3.16 (H^e, m, $J_{c,e}$ = 4.7 Hz, $J_{d,e}$ = 6.9 Hz, $J_{e,f}$ = 2.8 Hz, $J_{e,g}$ = 4.1 Hz), 2.85 (H^g, dd, $J_{e,g}$ = 4.1 Hz, $J_{f,g}$ = 5.4 Hz), 2.59 (H^f, dd, $J_{e,f}$ = 2.8 Hz, $J_{f,g}$ = 5.4 Hz), 2.17 (H^c, m, $J_{a,c}$ = 7.0 Hz, $J_{b,c}$ = 5.9 Hz, $J_{c,d}$ = 15.4 Hz, $J_{c,e}$ = 4.7 Hz), 1.94 (H^d, m, $J_{a,d}$ = 5.9 Hz, $J_{b,d}$ = 5.3 Hz, $J_{c,d}$ = 15.4 Hz, $J_{d,e}$ = 6.9 Hz).

Physical Measurements and Polymerization. The polymerization mixture was made by dissolving 98% of **1b**, 1% of the iodonium salt, and 1% of α,α-dimethoxydeoxybenzoin in dichloromethane and subsequent evaporization.

The polymerization experiments and physical measurements were performed as described earlier.[1-4]

Results and Discussion

The synthetic route to **1b** is outlined in Scheme I. The melting and clearing temperatures of **1b** and its intermediates measured by DSC are shown in Table I. **1b**, **2**, and **4** exhibit the nematic phase as revealed by polarizing microscopy. Comparison of the transition temperatures of **4** with those of 4-(butyloxy)phenyl 4-(butyloxy)-benozate[7] (T_m = 86 °C; T_c = 91 °C) reveals a considerable effect of the unsaturation in the side chains on these transition temperatures.

Monomer **1b** can be macroscopically oriented in a glass test cell provided with rubbed polyimide layers. The cell is filled either by capillary flow at elevated temperatures (>45 °C) or by pressing the molten monomer between two preheated rubbed glass substrates. The film thickness has been varied between 6 and 60 μm. These methods yield uniaxially oriented monomer films which are virtually defect-free over several square centimeters, as observed by polarizing microscopy. The presence of the photoinitiator system decreases the clearing temperature to 56 °C but does not affect the molecular ordering in the nematic region. Upon irradiation with a UV lamp, the oriented nematic monomer polymerizes, yielding transparent polymeric films with perfect macroscopic orientation. The polymerization can be performed in the stable thermotropic nematic phase above the melting point of the monomer and also in the monotropic nematic phase below this melting point. During supercooling to room temperature it is a long time before crystallization sets in, allowing polymerization without crystal formation. In all cases the films are clear and highly birefringent and show no liquid-crystalline transitions in the temperature range from room temperature to 300 °C. They adhere strongly to the polyimide.

Figure 1 displays the ordinary $(n_o)_m$ and extraordinary $(n_e)_m$ refractive index of monomer **1b** in the presence of the photoinitiator and sensitizer. Above T_c at 56 °C, the isotropic refractive index $(n_i)_m$ is measured. The order parameter $\langle P_2 \rangle$ of **1b** in its nematic state is estimated from the refractive indices using the Haller extrapolation[9] and is displayed in Figure 2. With descending temperature, the monomeric order parameter increases from about 0.5 near T_c to 0.75 at room temperature. When compared at equal reduced temperatures, these values appear to be somewhat higher than those found for the liquid-crystalline diacrylate monomers,[3] which might be explained by the more extended conformation of the epoxide endgroups.

Upon polymerization, an increase of the average refractive index of 2% is measured as a result of a change in the molecular packing, due to polymerization shrinkage. Simultaneously, the birefringence (Δn) of the sample increases due to an increase of the degree of ordering during polymerization. Figure 3 shows an increase of Δn from 0.10 to 0.15 during polymerization at 50 °C. After polymerization, the Δn has become almost temperature-independent up to 140 °C, and the oridinary $(n_o)_p$ and extraordinary $(n_e)_p$ refractive indices of the anisotropic network change only because of a decreasing density with temperature. Of special interest for practical applications of the material is the high $(n_e)_p$ value, which is somewhat higher than those described for networks based on liquid-crystalline diacrylates.[3] The polymeric order parameter estimated from the refractive indices is displayed in Figure 2, confirming the high ($\langle P_2 \rangle \geq 0.8$) and nearly temperature-independent degree of order.

The increase of the order parameter during polymerization is much higher for the diepoxide than for the LC diacrylates.[2] In the latter case the molecular packing of the central aromatic core is constrained by the polyacrylate main chains, containing two carbon atoms per repeating unit, especially at shorter spacer lengths. In the case of poly(**1b**), the length of the repeating unit of the polymer main chain is now three atoms, one of which is a flexible ether linkage. This apparently gives less steric hindrance to the molecular packing of the mesogenic units even in the case of poly(**1b**) containing short spacers which consist

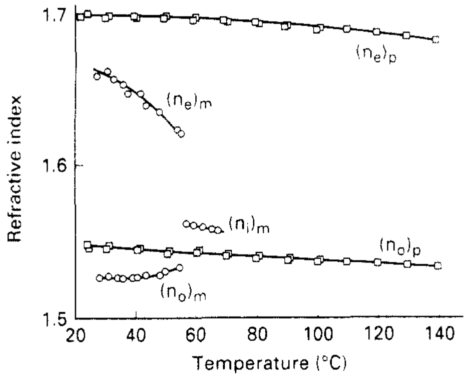


Figure 1. Ordinary, extraordinary, and isotropic refractive indices (at wavelength $\lambda = 589$ nm) vs temperature of **1b** mixed with the initiating system before (○) and after photopolymerization (□). The polymerization temperature was 50 °C.

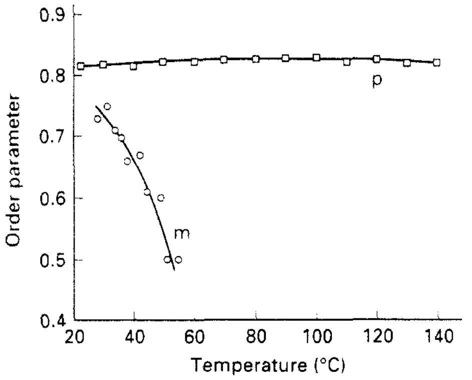


Figure 2. Order parameter vs temperature of **1b** mixed with the initiating system before (○) and after photopolymerization at 30 °C (□).

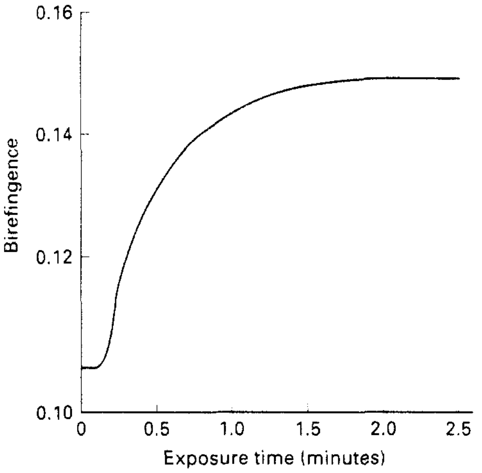


Figure 3. Increase of birefringence during polymerization of **1b** at 50 °C. At $t = 0$ the photoinitiated polymerization is started (UV source: medium-pressure Hg lamp; intensity at 365 nm, 100 mW/cm^2).

of two carbon atoms. The invariable order parameter up to 140 °C points to a glass transition temperature higher than this temperature.

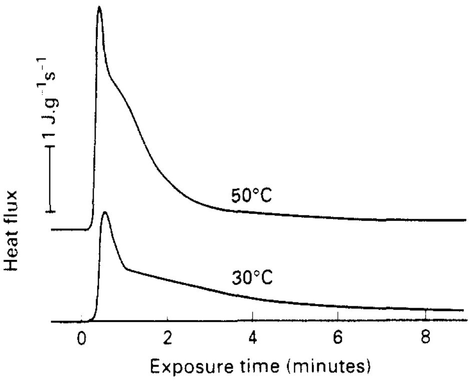


Figure 4. Isothermal DSC traces of the photoinitiated polymerization of **1b** (UV source: fluorescent lamp; $\lambda = 340$ nm; intensity, 6 mW/cm^2).

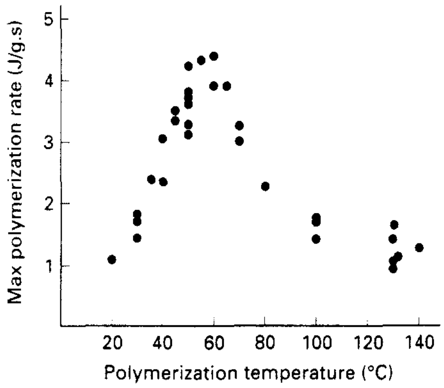


Figure 5. Maximum polymerization rate of **1b** vs temperature measured with DSC (UV source: see Figure 4).

Despite the advantages of the LC diepoxides over LC diacrylates (higher degree of order, less polymerization shrinkage, and better adhesion to various substrates), there is a serious drawback. In general, the photoinitiated polymerization of diepoxides proceeds much more slowly and takes several minutes, whereas the diacrylates cure within seconds under identical conditions.[2] The photoinitiated polymerization of the isotropic diglycidyl ether of Bisphenol A (DGEBA) proceeds about a factor of 3 faster than that of **1b** at equal temperatures. A conclusion on the influence of the nematic order on the rate of polymerization may, however, not be drawn because of the difference in the local chemical environment of the reactive oxirane ring. Figure 4 shows two isothermal DSC curves of the photoinitiated polymerization of **1b** in the nematic phase at 30 and 50 °C, respectively. Although irradiated for more than 8 min, the polymerization still continues at a rate close to the detection limit of the DSC. At the onset of the polymerization, three stages can be observed. First, there appears to be an induction period of several seconds which can also be observed in Figure 3, displaying the change in birefringence during the reaction. The nature of the induction period is not readily apparent, but it is not inherent to epoxide curing as it is not observed for the DGEBA curing. In the second stage, the polymerization rate increases rapidly to its maximum. The sharp drop in rate may be explained by the combined action of monomer depletion, monomer immobilization (when one reactive end has been reacted), and hindered monomer diffusion during vitrification of the sample. During the third stage of the reaction, the rate decreases slowly to an end-conversion of 75–85% after prolonged irradiation (>20 min) as measured by FTIR.

The influence of the nematic molecular order on the rate of polymerization can be deduced from Figure 5, showing the maximum rate vs the polymerization temperature. At low temperatures the rate increases with temperature due to an increased diffusional mobility. When the polymerization is conducted above the clearing temperature of the monomer, the polymerization rate decreases rapidly. However, it should be noted that the polymerization in the isotropic phase up to about 100 °C is affected by the transition to the mesophase as the mean molecular weight of the system increases during polymerization. The transition occurs at higher conversion as the polymerization temperature is increased. This means that although the initial monomeric state was isotropic, part of the polymerization is still carried out in the LC phase. An exact analysis of the observed polymerization phenomena above T_c is difficult. The sample becomes turbid because of the formation of LC domains when polymerization is initiated in an initially unoriented sample. This affects the UV intensity distribution over the sample thickness as well as the heat emission of the sample in the DSC.

Conclusions

A liquid-crystalline diepoxide with a thermotropic nematic phase is synthesized. The photoinitiated cross-linking of this material, aligned on a rubbed surface, results in a densely cross-linked uniaxial polymeric network. The anisotropic properties of the aligned molecules are transferred to the network. Upon polymerization at a reduced temperature of 0.97 the order parameter increases from 0.55 to 0.82 as measured with the aid of the refractive indices. This order is higher than that in similar networks obtained from liquid-crystalline diacrylates.

References and Notes

(1) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 2255.

(2) Broer, D. J.; Hikmet, R. A. M.; Challa, G. *Makromol. Chem.* **1989**, *190*, 3201.

(3) Broer, D. J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1991**, *192*, 59.

(4) Broer, D. J.; Mol, G. N. *Polym. Eng. Sci.* **1991**, *31*, 625.

(5) Hikmet, R. A. M.; Broer, D. J. *Polymer* **1991**, *32*, 1627.

(6) Meier, H. M.; Kirchmeyer, S.; Müller, H. P.; Karbach, A.; Dhein, R. In *Proceedings of the fourth annual international conference on crosslinked polymers, Luzern, 1990*; State University of New York at New Paltz, New Paltz, NY, 1990; p 167.

(7) Demus, D.; Demus, H.; Zaschke, H. *Flüssige Kristalle in Tabellen*; VEB Deutcher Verlag für Grundstoffindustrie: Leipzig, 1974; p 65.

(8) Lohse, F.; Zweifel, H. *Adv. Polym. Sci.* **1986**, *78*, 61.

(9) Haller, I.; Huggins, H. A.; Lilienthal, H. R.; McGuire, T. R. *J. Phys. Chem.* **1973**, *77*, 950.