Synthesis and photoinitiated polymerization of liquid crystalline diepoxides

S. Jahromi*
Department of Polymer Technology, Faculty of Chemical Engineering and Materials Science, Delft University of Technology, PO Box 5045, 2600 GA Delft, The Netherlands

and J. Lub and G. N. Mol
Philips Research Laboratories, PO Box 80 000, 5600 JA Eindhoven, The Netherlands
(Received 4 January 1993; revised 21 May 1993)

Four different liquid crystalline diepoxides were synthesized. Replacement of a methylene group by an oxygen atom in the spacer segment of the molecule decreased the thermal stability of the mesophase. In order to produce highly anisotropic networks, these compounds were cationically photopolymerized in the nematic phase. Differential scanning calorimetry and Fourier transform infra-red were used to monitor the polymerization. The degrees of conversion calculated from both techniques were in good agreement with each other. The replacement of a methylene group by an oxygen atom in the spacer part of the molecule also increased the rate of the polymerization reaction. Post-curing was sometimes necessary to produce highly stable networks. Furthermore, some results suggest that liquid crystalline nematic ordering increases the polymerization rate.

(Keywords: ordered networks; liquid crystalline epoxides; photoinitiated polymerization)

INTRODUCTION

Ordered networks are of great interest owing to their anisotropic optical and mechanical properties. The basic idea in the production of highly ordered and highly crosslinked networks is to orient low-molecular-weight liquid crystalline monomers uniaxially and subsequently freeze in the orientation by polymerization[1-5].

Liebert and Strzelecki[1,2] were the first to use diacrylates which were thermally polymerized in the mesophase. Recently, Broer and Hikmet and their various coworkers[6-8] have shown that a more convenient way of producing ordered networks is by photoinitiated polymerization of liquid crystalline diacrylates. The most important advantage of this method over the thermally induced polymerization is the possibility to polymerize within the mesophase at nearly any temperature. In this way the degree of order and consequently the anisotropic properties of the network can be adjusted as desired.

Recently, Broer *et al.*[9] also published some preliminary results concerning the photoinitiated polymerization of a liquid crystalline diepoxide. This is of interest in view of the better mechanical and thermal stabilities of polyepoxides over polyacrylates[10]. Epoxides also show superior adhesive properties when compared with acrylates.

In the present paper we explore further the possibility of using the epoxide group as the polymerizing unit. The synthesis of four diepoxides will be described. The compounds, shown in *Scheme 1*, consist of either two rings (**7a** and **7b**) or three rings (**9a** and **9b**). The influence of a methylene group or an oxygen atom in the spacer part of the molecule on the liquid crystalline properties and rate of polymerization will be discussed.

To determine the stability of the networks, as far as the level of ordering is concerned, birefringence measurements were carried out.

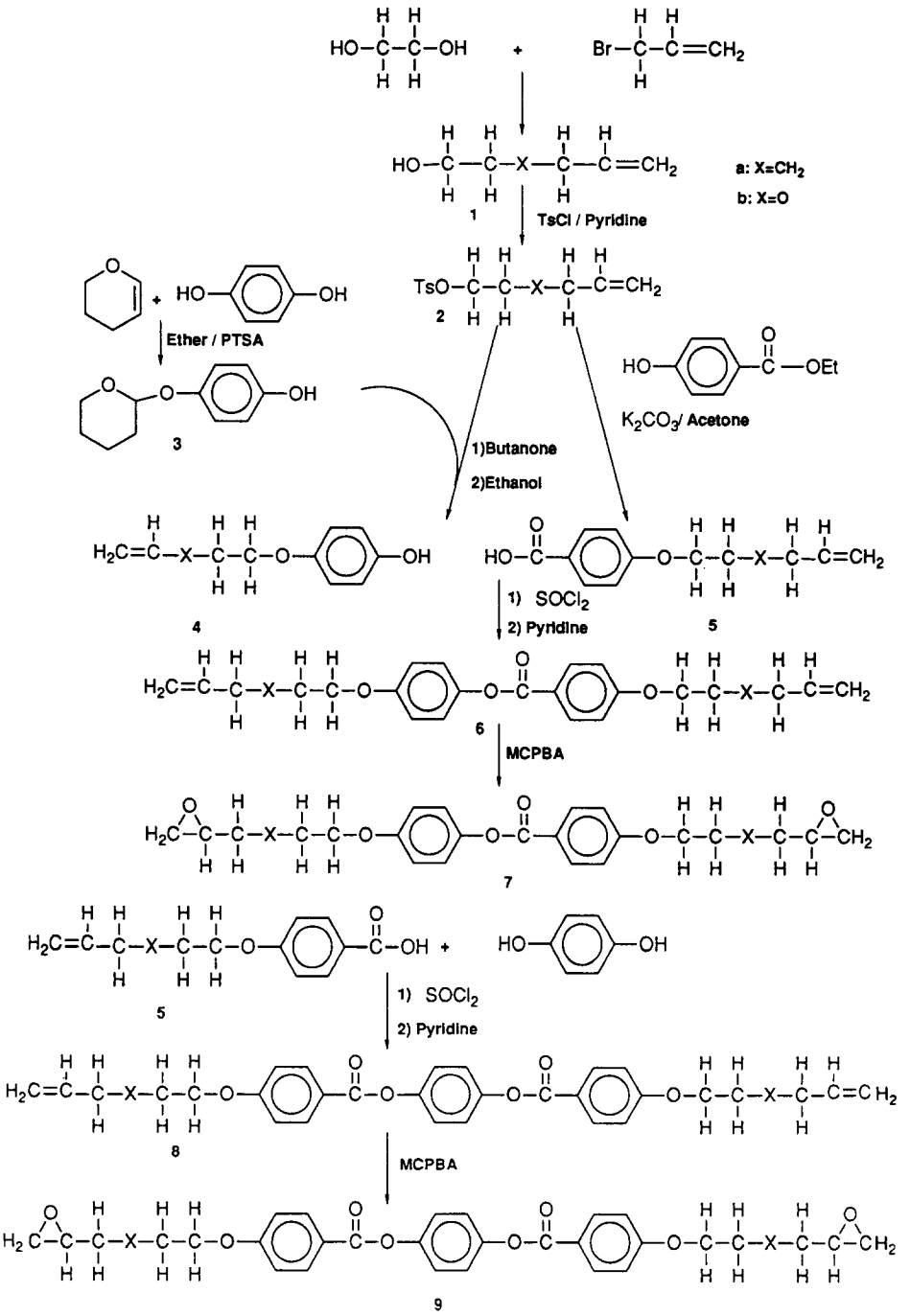
EXPERIMENTAL

Synthesis of monomers

The synthetic route used in our study is outlined in *Scheme 1*. 5-Hexen-1-ol **1a** was supplied by Aldrich Chemical Co. Allyl 2-hydroxyethyl ether was synthesized according to details given in the literature[11]. The tosylates 5-hexen-1-yl *p*-toluenesulfonate **2a** and 2-(allyloxy)ethyl *p*-toluenesulfonate **2b** were prepared according to details given in the literature[12]. The synthetic procedures of the remaining compounds with $X=CH_2$ and $X=O$ are similar and are described below.

Synthesis of 4-(tetrahydropyran-2-yloxyl)phenol 3. Over a period of 30 min, 2 ml of dihydropyran (0.1 mol) were added to a mixture of 11 g of hydroquinone (0.1 mol) and 0.2 g of *p*-toluenesulfonic acid (PTSA) in 100 ml of ether. During the reaction the hydroquinone dissolved completely. After stirring for 1 h, the ethereal solution was extracted twice with 40 ml of a deaerated aqueous solution of 3 g of NaOH (75 mmol) and 0.3 g of $NaHSO_3$. The combined aqueous layers were washed

*To whom correspondence should be addressed
0032-3861/94/030622-08



Scheme 1 Synthetic route to all the monomers

with 25 ml ether, cooled with ice and carefully acidified with acetic acid. The precipitated product was collected by filtration, washed with 50 ml of water and dried over SiO_2. The yield was 8.4 g (43%).

Synthesis of 4-(5-hexen-1-yloxy)phenol ***4a*** *and 4-[2-(allyloxy)ethoxy]phenol* ***4b.*** Around 9.5 g (0.049 mol) of 4-(tetrahydropyran-2-yloxy)phenol **3** were added to a mixture of 2.6 g (0.049 mol) of NaOMe in 100 ml 2-butanone, upon which a clear solution was obtained. After the addition of 0.044 mol of tosylate **2** the mixture was stirred for 12 h at 60°C. The mixture was filtered and the filtrate was evaporated to dryness. The residue was then dissolved in 60 ml of ether and 40 ml of water were added. The ether solution was washed twice with 50 ml of a 10% aqueous solution of NaOH. After evaporation of the ether, 40 ml of a 1:1 ethanol/water solution and 2 g of PTSA were added. The mixture was then refluxed for 2 h. After addition of 100 ml of water, the solution was extracted twice with 100 ml of ether. The ether solution was then extracted with 100 ml of a 10% aqueous solution of NaOH. After acidification of the water layer with concentrated HCl to a pH of 3, the water layer was extracted twice with 100 ml of ether. The ether solution was then washed with 100 ml of a saturated aqueous NaCl solution, dried over $MgSO_4$ and evaporated to give **4a** (81%) or **4b** (67%) as an oil. The oils were used without further purification.

Synthesis of 4-(5-hexen-1-yloxy)benzoic acid ***5a*** *and 4-(2-allylethoxy)benzoic acid* ***5b.*** A two-necked flask equipped with a reflux condenser was charged with 60 ml of acetone, 7.40 g (0.060 mol) of K_2CO_3, 5.95 g (0.035 mol) of 4-hydroxy ethyl benzoate and 0.035 mol of tosylate **2**.

The mixture was heated under reflux for 24 h. After filtration and evaporation of the acetone, 100 ml of ether and 50 ml of water were added. The ether solution was separated and subsequently extracted with 100 ml of a 10% aqueous solution of NaOH. After evaporation of the ether, the residue was heated under reflux in 100 ml of a 1:2 ethanol/water mixture containing 0.18 mol of KOH. After obtaining a clear solution, the heating was continued for an additional 15 min. The solution was acidified after cooling with concentrated HCl to a pH of 3. The crude product obtained by filtration was washed with 100 ml of water and recrystallized from a 1:1 ethanol/water solution to give **5a** (76%) or **5b** (66%). Compound **5b** had a melting point of 119°C and showed no liquid crystallinity. Compound **5a** had a melting point of 98°C and shared a nematic to isotropic transition at 143°C. In addition, a monotropic smectic transition at 82°C could be observed for this compound.

*Synthesis of 4,4'-bis(5-hexen-1-yloxy) phenyl benzoate **6a** and 4,4'-bis[2-allyloxy)ethoxy] phenyl benzoate **6b**.* A 250 ml flask was charged with 0.02 mol of **5**, 20 ml of $SOCl_2$ and three drops of dimethylformamide (DMF). After stirring for 1 h at room temperature the excess $SOCl_2$ was removed under vacuum at 10^{-2} mmHg. Then 16 ml of pyridine followed by 0.02 mol of **4** were added and the solution was stirred for 24 h at room temperature. After addition of 50 ml of water and 80 ml of dichloromethane under constant stirring, the organic layer was washed with 50 ml of a 1:6 HCl/water solution. To ensure that all the pyridine was removed, the solution was extracted with 50 ml of 1 N HCl aqueous solution. After working up according to the synthesis of **4** and recrystallization from isopropanol, a 62% yield of **6a** (57% yield of **6b**) was obtained.

*Synthesis of 4,4'-bis(5,6-epoxyhexen-1-yloxy) phenyl benzoate **7a** and 4,4'-bis[2,3-epoxypropyl)ethoxy] phenyl benzoate **7b**.* Under continuous stirring, 5.0 g (0.022 mol) of *m*-chloroperoxybenzoic acid (MCPBA) were added to a solution of 0.01 mol of the diolefin **6** in 80 ml of dichloromethane. The mixture was then refluxed for 48 h. After cooling and subsequent filtration, the mixture was washed with 80 ml of a 5% aqueous solution of Na_2SO_3, 80 ml of a 5% aqueous solution of $NaHCO_3$ and 50 ml of a 30% aqueous solution of NaCl. The dichloromethane layer was dried over $MgSO_4$ and evaporated. After recrystallization from isopropanol, a 72% yield of **7a** (77% yield of **7b**) was obtained.

7a: ^{1}H n.m.r. ($CDCl_3$), δ (ppm) 1.6 (8H, m, CH_2 of butyl), 1.9 (4H, m, CH_2 of butyl), 2.5 (2H, m, CH_2 of epoxy), 2.8 (2H, t, CH_2 of epoxy), 3.0 (2H, m, CH of epoxy), 4.0 (2H, t, CH_2 of butyl), 4.1 (2H, t, CH_2 of butyl), 6.2 (2H, d, aromatic), 7.0 (2H, d, aromatic), 7.1 (2H, d, aromatic), 8.1 (2H, d, aromatic).

7b: ^{1}H n.m.r. ($CDCl_3$), δ (ppm) 2.6 (2H, dd, CH_2 of epoxy), 2.8 (2H, dd, CH_2 of epoxy), 3.2 (2H, m, CH of epoxy), 3.5 (2H, m, CH_2 of glycidyl), 3.9 (6H, m, CH_2 of glycidyl and CH_2 of ethyl), 4.1 (2H, t, CH_2 of ethyl), 4.2 (2H, t, CH_2 of ethyl), 6.9 (2H, d, aromatic), 7.0 (2H, d, aromatic), 7.1 (2H, d, aromatic), 8.1 (2H, d, aromatic).

Synthesis of p-*phenylene di[4-(5-hexen-1-yloxy)benzoate] **8a** and* p-*phenylene di{4-[2-(allyloxy)ethoxy]benzoate} **8b**.* Around 0.01 mol of **5** was converted to its acid chloride as described for the synthesis of **6**. The acid chloride was mixed with 8 ml of pyridine. After adding 0.55 g of hydroquinone, the mixture was stirred for 24 h. Then, 25 ml of water were added and the precipitate was filtered. The crude product was stirred for 1 h with 150 ml of a 5% aqueous Na_2CO_3 solution and then washed with 100 ml of water. The residue was recrystallized from a 1:1 mixture of ethanol and ethyl acetate to give **8a** (82%) or **8b** (76%).

Synthesis of p-*phenylene di[4-(5,6-epoxyhexen-1-yloxy)benzoate] **9a** and* p-*phenylene di{4-[2-(2,3-epoxypropyl)ethoxy]benzoate} **9b**.* These compounds were prepared in the same manner as described for the synthesis of **7**. Compound **9a** was recrystallized from a 1:1 mixture of ethanol and ethyl acetate (77%), whereas compound **9b** was recrystallized from ethyl acetate (56%).

9a: ^{1}H n.m.r. ($CDCl_3$), δ (ppm) 1.6 (8H, m, CH_2 of butyl), 1.9 (4H, m, CH_2 of butyl), 2.5 (2H, dd, CH_2 of epoxy), 2.7 (2H, dd, CH_2 of epoxy), 2.9 (2H, m, CH of epoxy), 4.1 (4H, t, CH_2 of butyl), 7.0 (4H, d, aromatic), 7.1 (4H, s, aromatic), 8.1 (4H, d, aromatic).

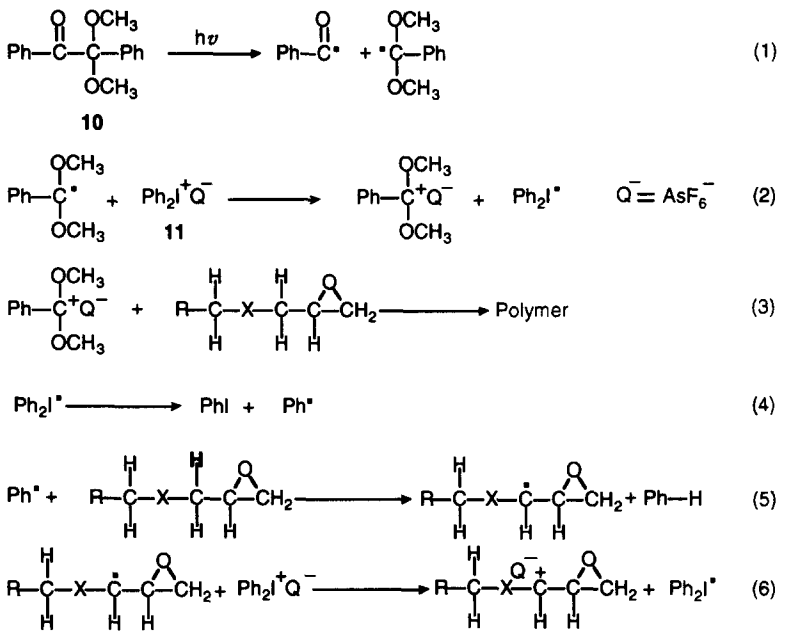
9b: ^{1}H n.m.r. ($CDCl_3$), δ (ppm) 2.7 (2H, dd, CH_2 of epoxy), 2.8 (2H, dd, CH_2 of epoxy), 3.2 (2H, m, CH of epoxy), 3.5 (2H, dd, CH_2 of glycidyl), 3.9 (6H, m, CH_2 of glycidyl and CH_2 of ethyl), 4.2 (4H, t, CH_2 of ethyl), 7.0 (4H, d, aromatic), 7.3 (4H, s, aromatic), 8.1 (4H, d, aromatic).

The ^{1}H n.m.r. spectra of the intermediate compounds were measured with a 80 MHz Brucker n.m.r. spectrometer and were in all cases in accordance with their structures. For all the final products the spectra were recorded on a 200 MHz Nicolet n.m.r. spectrometer. Tetramethysilane (TMS) was used in all cases as the internal standard and $CDCl_3$ as the solvent.

Photoinitiated polymerization and physical measurements

The cationic photoinitiator diphenyliodonium hexafluoroarsenate **11** (see *Scheme 2*) was synthesized in the same manner as described by Crivello *et al.*[13]. The free radical promoter, 2,2-dimethoxy-2-phenylacetophenone (DMPA) **10** (see *Scheme 2*) was obtained from Ciba Geigy (Basel, Switzerland) under the tradename IRGACURE 651 and was used without further purification. To prepare the polymerization mixture, 98.5% (w/w) of the diepoxide, 1% (w/w) of **11** and 0.5% (w/w) of **10** were dissolved in dichloromethane. After evaporation of the solvent, the resulting solid was dried in vacuum overnight.

A Perkin–Elmer differential scanning calorimeter (DSC-2C) was modified[14] for the study of photoinitiated polymerization. The u.v. irradiation was carried out using a PL10W/10 lamp ($\lambda_{max} = 365$ nm). The light intensity, measured with an International Light 745A u.v. curing radiometer, was 6 mW cm^{-2}. To ensure a dry atmosphere and a good heat transfer both sample and reference compartments were continuously flushed with dry nitrogen. The sample weight was 0.9–1.3 mg. The conversions (α) using the differential scanning calorimetry (d.s.c.) data were calculated by dividing the measured enthalpies (ΔH) by the experimentally found value for 100% conversion[15] of the epoxide group in chemically pure phenyl glycidyl ether ($\Delta H = 93$ kJ eq^{-1} epoxide group). The assumption is that this value also applies to full conversion of the epoxide groups in the compounds investigated by us. To justify this we have determined α by a second technique, Fourier transform infra-red



Scheme 2 Simplified reaction mechanism of the photoinitiated cationic polymerization of epoxides

(*FT*i.r.). The accuracy of the α values measured by d.s.c. was about 5%, whereas the rate of polymerization could be determined much less accurately (maximum 10%).

*FT*i.r. studies were performed using a Mattson Polaris (Icon software) spectrometer. During 20 s, eight scans were collected with a resolution of 4 cm^{-1}. To monitor the reaction, the polymerizing mixture was sandwiched between two polyethylene plates with a spacing of approximately 100 μm. These plates were mounted in a Specac P/N 20125 temperature controller.

The degree of conversion (α) was monitored by recording an *FT*i.r. spectrum after every period of irradiation. The peak area of the epoxide ring absorption was measured between 976 and 890 cm^{-1} relative to the carbonyl stretch area between 1770 and 1659 cm^{-1}, which was chosen as the reference band. All the absorptions were measured in the region between 0.2 and 2 absorbance units where there is, assuming that Beer's law applies, a linear relationship between absorption and concentration of the chromophore.

The macroscopic orientation of the liquid crystal monomers was achieved in a glass cell of which both inner surfaces were coated with a uniaxially rubbed, thin polyimide film. Upon filling by capillary action this led to a planar orientation of the monomers.

Morphological characterization was performed with a Leitz microscope, type Laborlux 12 Pol, provided with a Mettler FP82 hot stage and FP80 central processor. Using a rotary compensator, type K, equipped with calcite compensator plates, the optical retardation (L) was measured using the glass cells described above. L could be measured very accurately (>99%). To determine the birefringence Δn, the cell thickness was needed. This was measured interferometrically. In our case this introduced an estimated inaccuracy of about 3% in the absolute Δn values.

Thermal characterization was carried out in a Perkin–Elmer DSC-2C (scanning rate 10°C min^{-1}).

Table 1 Transition temperatures and enthalpies of the monomers

	C→N		N→I	
Compound	Temperature (°C)	ΔH (kJ mol^{-1})	Temperature (°C)	ΔH (kJ mol^{-1})
7a	46 (52)[a]	34.9	66 (58)	2.0
7b	53 (43)	40.9	18	1.1
9a	119 (129)	22.4	213 (204)	0.9
9b	124 (120)	29.4	186 (180)	0.5

[a] Data in parentheses are from the corresponding diolefins

RESULTS AND DISCUSSION

Mesomorphic properties of the monomers

The transition temperatures, enthalpies and phase behaviours of the four compounds investigated are given in *Table 1*. The compounds can be classified into two groups, one containing a two-ring system (**7a** and **7b**) and the other a three-ring system (**9a** and **9b**). The compounds in each series differ only in the nature of group X (CH_2 or O, as in *Scheme 1*) placed at the β position with respect to the epoxide ring. In both series, replacement of a methylene group by an oxygen atom has a drastic effect on the thermal stability of the nematic phase. Comparison of the three-ring systems (**9a** and **9b**) reveals that the oxygen-containing **9b** has a thermotropic nematic range which is 32°C smaller than that of **9a**. The destabilizing effect of the O atom in the spacer is probably also responsible for the fact that the two-ring system **7b** exhibits only a monotropic nematic phase while **7a** exhibits a thermotropic nematic phase of 20°C. For the corresponding diolefins we observe the same phenomenon. This destabilizing effect of the oxygen atom in the spacer on the nematic phase has been known for a long time, and attempts have been made to explain it mainly in terms of a change in the polarity of the spacer resulting from the introduction of the oxygen atom. Also, conformational differences might play a role[16,17].

Figure 1 shows the birefringence (Δn) of the compounds

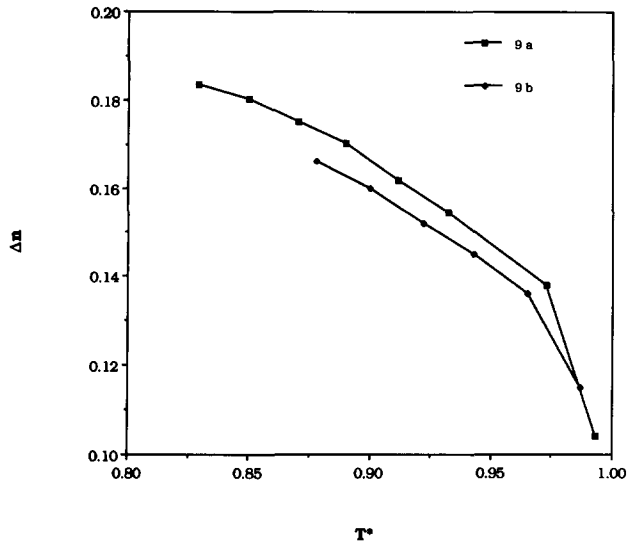


Figure 1 Birefringence (Δn) of compounds **9a** and **9b** plotted against the reduced temperature (T^*)

9a and **9b** plotted against the reduced temperature defined as $T^* = T/T_i$, where T is the actual temperature in Kelvin and T_i is the nematic to isotropic transition temperature. In treating these Δn data and also subsequent data in this text, we assume that

$$\Delta n(T) \propto \langle P_2(T) \rangle$$

This means that for a certain compound the measured Δn as a function of temperature is directly proportional to the average value of the second-order Legendre polynomial $\langle P_2 \rangle$, which is also denoted by S. In relating $\langle P_2 \rangle$ to the Δn measurements, local field corrections have been ignored, which seems, according to Dalmolen and De Jeu[18], a reasonable approximation. Furthermore, in order to determine $\langle P_2 \rangle$ values by probing Δn, the anisotropic polarizability of the compounds should be known and again certain assumptions are to be made[19]. Because of these difficulties we have refrained from measuring the absolute $\langle P_2 \rangle$ values. However, it is noteworthy that the Δn values measured by us are somewhat higher than the Δn values obtained for the networks made from photoinitiated polymerization of the corresponding liquid crystalline diacrylates[8].

As can be seen in *Figure 1*, compounds **9a** and **9b** have a small difference in Δn which remains constant nearly up to the T_i. If this is of any statistical significance it can therefore be attributed to a difference in anisotropic polarizability between the compounds, caused by the replacement of a methylene group (in **9a**) by an oxygen atom (in **9b**).

Photoinitiated polymerization

The initiating system used in our study consists of a diaryliodonium salt **11** and the free radical initiator DMPA **10**. Based on a detailed study conducted on the photoinitiated cationic polymerization of tetrahydrofuran[20–22] using the same initiating system, the following mechanism can be given for the photoinitiated polymerization of the epoxides (see *Scheme 2*).

Upon irradiation DMPA decomposes into free radical fragments (equation (1)). Owing to the favourable reduction potential of the iodonium salt **10** an electron transfer process can then take place (equation (2)). The carbocation thus formed directly initiates the polymerization (equation (3)). Subsequently, the phenyl radicals generated (equation (4)) can abstract a hydrogen atom from a methylene group near the epoxide ring, leading to a chain reaction (equation (5)). The exact position of the H abstraction obviously depends on the nature of group X (in the example shown in *Scheme 2* the H abstraction is at the α position with respect to the epoxide group). Following the reaction shown in equation (6), a carbocation is again produced.

It must be emphasized that the actual reaction path can be much more complicated than the one depicted in *Scheme 2*. For example, direct excitation of the iodonium salts at a short wavelength can lead to the production of the powerful Brönsted acid HQ, which is also capable of initiating the cationic polymerization[23]. In our case, we assume that all these processes are of secondary importance. This is partly justified owing to the fact that in our system the polymerization rates are extremely low in the absence of a free radical promoter.

The radical species formed in the reaction shown in equation (5) can be stabilized by the oxygen atom positioned β to the epoxide ring (X=O)[24]. This could then have an effect on the rate of polymerization (v). A comparison of the reactivities of compounds **7a** and **7b** in the isotropic phase at 100°C suggests that v_{max} actually increases after substitution of a methylene group by an oxygen atom (see *Table 2*). However, the reactivities are completely reversed at 50°C, where compound **7a** is liquid crystalline and compound **7b** is isotropic. Furthermore, polymerization of the oxygen-containing compound **9b** in the nematic phase at 120°C led to a conversion of 72% with a maximum polymerization rate of 0.22 kJ eq^{-1} s^{-1}, whereas the data concerning the polymerization of compound **9a** at about the same reduced temperature could not be determined with acceptable accuracy. It was, however, obvious that the polymerization rate for compound **9a** was much lower than that for compound **9b**. The difficulty in polymerizing **9a** was probably due to the combination of a low polymerization rate and a high temperature. The low rate and the high temperature might have caused secondary reactions to occur (e.g. between the initiator and the epoxide compound), leading to a change of colour in the material from colourless to yellow upon polymerization. Hence, one may conclude from these observations that the molecular ordering in the nematic phase increases the rate of polymerization. Further evidence for this phenomenon is provided in *Figure 2*. This figure shows the d.s.c. curves of isothermal measurements at various

Table 2 Conversions (α) and rates of polymerization determined by d.s.c. for compounds **7a** and **7b** at different temperatures

	7a		**7b**	
Temperature (°C)	v_{max} (kJ eq^{-1} s^{-1})	α^a (%)	v_{max} (kJ eq^{-1} s^{-1})	α (%)
50	0.32	49.3	0.10	27.6
80[b]	0.23	45.1	0.21	40.0
100	0.12	47.1	0.31	50.7

[a] Samples were irradiated as long as a heat flux could be detected by d.s.c.
[b] For the second peak $v_{max} = 0.21$ kJ eq^{-1} s^{-1}

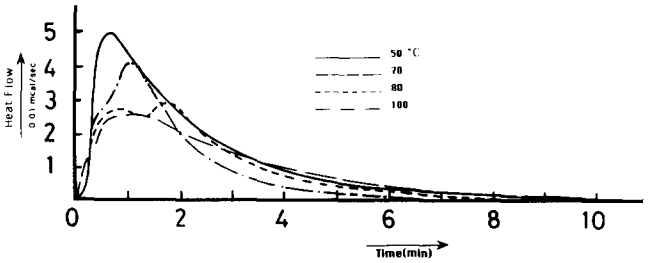


Figure 2 Isothermal d.s.c. traces of the photoinitiated polymerization of **7a** at various temperatures. Data are not normalized for the differences in sample weights

temperatures during u.v. irradiation of compound **7a**. In contrast with the polymerization in the liquid crystalline phase at 50°C, the d.s.c. curve at 70°C shows a discontinuity at the beginning of the reaction. Apparently, after a short period of time a second peak appears which is shifted to a higher temperature upon polymerization at 80°C and which completely disappears at 100°C.

It is now known that polymerization in the isotropic phase can sometimes lead to an increase of the T_i. This has been observed upon photoinitiated polymerization of the liquid crystalline diacrylates above the T_i[8,25]. So, it is probable that the transition to the liquid crystalline phase is accompanied by an increase in the rate of polymerization, leading to a second maximum as seen in the d.s.c. curve at 80°C. This is partly confirmed by the observation that sample **7a**, which was initially transparent at 70°C (i.e. isotropic) and also at 80°C, became turbid (i.e. anisotropic) during polymerization. The reason for this turbidity after the transition to the liquid crystalline phase is further discussed by Broer *et al.*[8,25]. At 100°C there was no transition to the liquid crystalline phase. Consequently, the sample remained clear during the irradiation, and also no discontinuity in the d.s.c. curve was observed (see *Figure 2*).

From the effect of the nematic ordering on the rate of polymerization we might infer that the value of the activation energy for propagation is lower if the monomeric phase is ordered. This can lead to an increase in the polymerization rate[26].

FT*i.r. and birefringence measurements*

It is well known that termination reactions are less likely to occur in cationic polymerization. Owing to the living character of the system, the polymerization will continue in the dark[23,27]. In order to determine the extent of this post-cure reaction, real-time *FT*i.r. measurements were conducted with compound **7a**. During the irradiation the polymerization was monitored by quasi-real-time *FT*i.r. spectroscopy. As can be seen in *Figure 3*, the conversion of the epoxide group after 10 min of irradiation has reached a value of 53%, which agrees well with the d.s.c. data*. Thereafter, the rate of polymerization falls to below the detection limit of d.s.c., but, as detected with the aid of *FT*i.r., the reaction

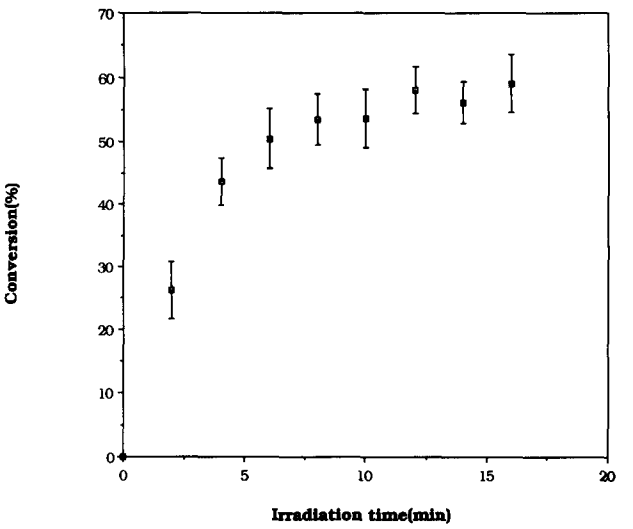


Figure 3 Conversion monitored by quasi-real-time *FT*i.r. as a function of irradiation time for compound **7a** at 50°C

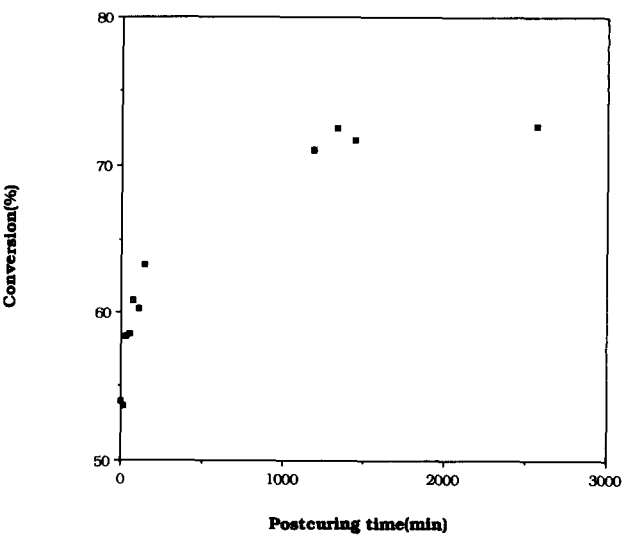


Figure 4 Conversion as a function of post-curing time (at 50°C) after 16 min of irradiation (at 50°C) monitored by real-time *FT*i.r.

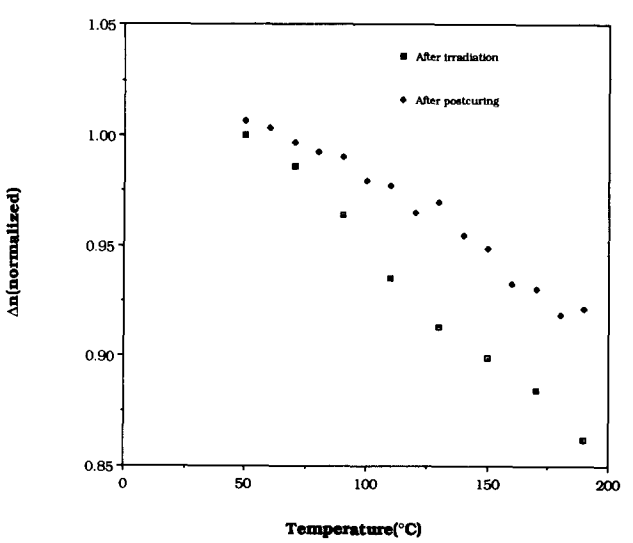


Figure 5 The temperature dependence of birefringence just after irradiation (16 min at 50°C) and after an additional post-curing treatment (25 h at 50°C) for compound **7a**. Data are normalized for Δn at $T = 50$°C

* To be able to compare the d.s.c. data with the *FT*i.r. results the conditions for both sets of measurements should be identical. Therefore, the light intensity was kept the same and although the sample thickness for *FT*i.r. measurements varied by up to 100 μm, it was shown by d.s.c. that the conversion did not depend on the thickness in this range

continues to proceed in the dark (see *Figure 4*). The fact that the reaction does not proceed to full conversion but levels off at 73% could be attributed to the possible inhomogeneous character of the system.

The effect of the reaction in the dark on the stability of the ordered networks made from compound **7a** is demonstrated in *Figure 5*, where Δn is followed during the thermal scan just after the irradiation and after the network has undergone an additional post-curing treatment.

During irradiation Δn increased by almost 20%, which results from an improvement in the molecular packing as the crosslinking reaction proceeds[8]. However, Δn did not change during post-curing at 50°C as a function of time, but, as can be seen in *Figure 5*, its temperature dependence is much less pronounced upon heating compared with the non-post-cured sample. Besides, for the non-post-cured sample Δn hardly changed upon cooling. This means that the heating of **7a** just after irradiation causes the degree of disorder to be fixed irreversibly by further network formation. On the other hand, the reversible change of Δn for the post-cured network is demonstrated in *Figure 6*, where the sample has been exposed to subsequent heating and cooling runs. During the first heating there is still a small amount of polymerization of **7a**. Probably a somewhat too rapid heating during this run (10°C min^{-1}) may have caused the slight difference in Δn values upon cooling when compared to the initial heating scan. However, once the network has been fixed at 200°C one still observes the reversible change in Δn connected to the changes in density and state of order.

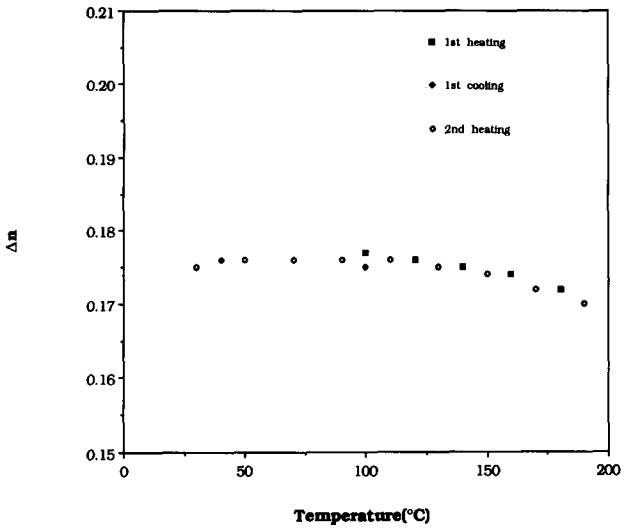


Figure 8 Birefringence as a function of temperature (10°C min^{-1}) after 10 min of irradiation at $T^* = 0.92$ of the compound **9b** (after the irradiation Δn had increased by 12%)

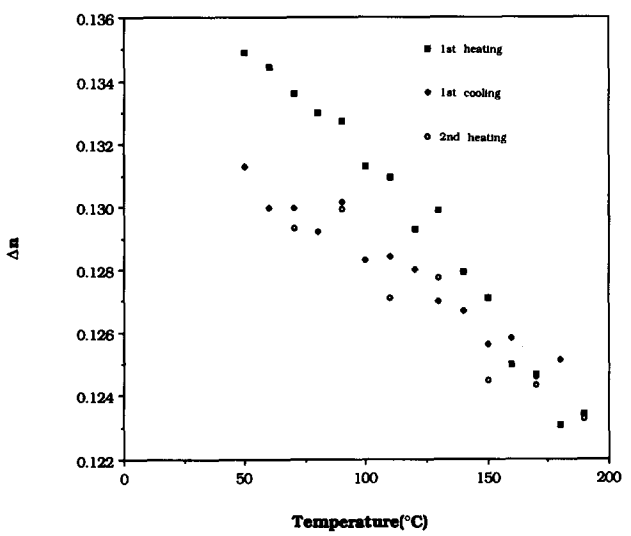


Figure 6 Birefringence of compound **7a** as a function of temperature (10°C min^{-1}) after 16 min of irradiation and 25 h of post-curing at 50°C

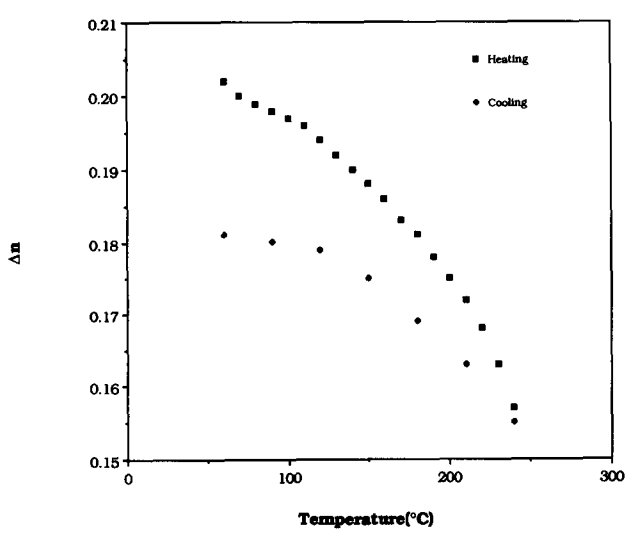
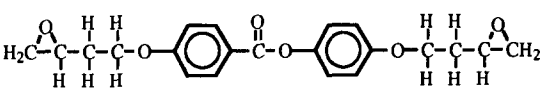


Figure 7 Birefringence as a function of temperature (10°C min^{-1}) after 10 min of irradiation at $T^* = 0.86$ of the compound **9a**

Broer *et al.*[9] performed the photoinitiated polymerization on a similar type of liquid crystalline diepoxide with a shorter spacer segment, namely



4,4'-Bis(3,4-epoxybuten-1-yloxy) phenyl benzoate 12

They also carried out the polymerization in the nematic phase at 50°C using the same initiating system and concluded that highly ordered networks, maintaining their stability to higher temperatures, were obtained just after the irradiation[9]. This is in direct contrast with the results presented here, which illustrate the necessity for an additional post-curing treatment in order to freeze in the orientation. An explanation for the effect of post-curing and the discrepancy in the experimental results is given in the following discussion.

Generally, during the isothermal network formation the reaction kinetics will enter a diffusion-controlled mode once the glass transition temperature (T_g) of the material has reached the isothermal cure temperature (T_{cure})[28]. At this point vitrification is said to occur. In our case it is difficult to determine whether this phenomenon also applies to photoinitiated polymerization of liquid crystalline diepoxides. However, it seems reasonable to assume, especially at these low polymerization temperatures, that vitrification will play a major role in retardation of the reaction rates. Hence, the non-post-cured sample **7a** cured at 50°C has a T_g of about

50°C just after the irradiation, and upon heating above this temperature Δn would tend to decrease owing to the higher mobility of the molecules. Simultaneously, this lower degree of order would be fixed by further polymerization. However, for the post-cured samples the T_g has increased because of the continuation of the reaction in the glassy state, as followed by *FT*i.r. (see *Figure 4*), and so Δn shows less tendency to decrease upon heating (see *Figure 5*). For the photoinitiated polymerization of isotropic diacrylates this continuation of reaction in the glassy state has led to a difference of more than 70°C between T_{cure} and T_g as determined by dynamic mechanical thermal analysis[29]. We have taken d.s.c. measurements to determine the T_g, but no real transition could be observed. This observation can be attributed to the high crosslink density of the samples[31]. Also, no residual reaction heat during the thermal scan just after the isothermal run could be detected by d.s.c.

Broer *et al.*[9] claimed in their publication that after the polymerization of **12** at 50°C Δn had become almost temperature independent up to 140°C. They derived from this observation that the T_g of the material was even higher than 140°C. However, these experiments were conducted with the aid of a medium pressure Hg lamp (intensity at 365 nm = 100 mW cm^{-2}). It can be argued that this high intensity u.v. light could have led to a rise in temperature and consequently to an unintentional thermal post-curing of the sample.

As mentioned before, the degree of conversion for compound **9a** was low, as reflected in the Δn stability of the network prepared from this monomer (see *Figure 7*). The measurement of Δn became somewhat difficult as the uniaxial texture of the monomer changed upon polymerization. Microscopic observations revealed that in all other monomers no change in texture took place after the polymerization. On the other hand, the conversion of epoxide groups in compound **9b** was as high as 72%, which led to the high stability of the networks (see *Figure 8*).

CONCLUSIONS

Ordered networks are produced upon photoinitiated polymerization of low-molecular-weight liquid crystalline diepoxides. Post-curing reactions improve the thermal stability of the networks owing to an increase in T_g. The oxygen atom in the spacer part of the molecule has a pronounced effect on the liquid crystalline properties and the rate of polymerization. It was also shown in a qualitative manner that in our case the nematic order increases the rate of polymerization.

REFERENCES

1 Liebert, L. and Strzelecki, L. *Bull. Soc. Chim. Fr.* 1973, **2**, 597
2 Liebert, L. and Strzelecki, L. *C. R. Hebd. Seances Acad. Sci., Ser. C* 1973, **276**, 647
3 Clough, S. B., Blumstein, A. and Hsu, E. C. *Macromolecules* 1976, **2**, 123
4 Hoyt, A. E. and Benicewicz, B. C. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 3403
5 Clough, S. B., Blumstein, A. and Hsu, E. C. *Macromolecules* 1976, **2**, 3417
6 Broer, D. J., Hikmet, R. A. M. and Challa, G. *Makromol. Chem.* 1989, **190**, 3201
7 Hikmet, R. A. M., Lub, J. and Broer, D. J. *Adv. Mater.* 1991, **3**, 392
8 Broer, D. J., Boven, J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1989, **190**, 2255
9 Broer, D. J., Lub, J. and Mol. G. N. *Macromolecules* 1993, **26**, 1244
10 Soane, D. S. and Martynenko, Z. 'Polymers in Microelectronics', Elsevier, Amsterdam, 1989, p. 66
11 Hurd, C. D. *J. Am. Chem. Soc.* 1938, **60**, 1905
12 Mori, K. *Tetrahedron* 1981, **37**, 1329
13 Crivello, J. V., Lam, J. H. W. and Valante, C. N. *J. Rad. Curing* 1977, **4**, 2
14 Kloosterboer, J. G., Van de Hei, G. M. M., Gossink, R. G. and Dortant, G. C. M. *Polym. Commun.* 1984, **25**, 322
15 Klute, C. H. and Viehmann, W. *J. Appl. Polym. Sci.* 1961, **5**, 86
16 Gray, G. W. 'Molecular Structure and the Properties of Liquid Crystals', Academic Press, London, 1962
17 Gray, G. W. in 'The Molecular Physics of Liquid Crystals' (Eds G. R. Luckhurst and G. W. Gray), Academic Press, London, 1979
18 Dalmolen, L. G. P. and De Jeu, W. H. *J. Chem. Phys.* 1983, **78**, 7353
19 Haller, L., Huggins, H. A., Lielienthal, H. R. and McGuire, T. R. *J. Phys. Chem.* 1973, **22**, 950
20 Yagci, Y. *J. Rad. Curing* 1989, **16**, 9
21 Yagci, Y. and Ledwith, A. *J. Polym. Sci., Polym. Chem. Edn* 1988, **26**, 1911
22 Abdul-Rasoul, F. A. M. and Ledwith, A. *Polymer* 1978, **19**, 1219
23 Pappas, S. P. 'UV Curing Science & Technology', Vol. II, Stanford, New York, 1985
24 Viehe, H. G. 'Substituent Effects in Radical Chemistry', Reidel, Dordrecht, 1986
25 Broer, D. J., Mol, G. N. and Challa, G. *Makromol. Chem.* 1989, **190**, 19
26 Odian, G. 'Principles of Polymerization', 2nd Edn, Wiley, New York, 1981, p. 259
27 Decker, C. and Moussa, K. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 3429
28 Oleinik, E. F. *Adv. Polym. Sci.* 1986, **80**, 49
29 Kloosterboer, J. G. and Lijten, G. F. C. M. *Polymer* 1990, **31**, 95