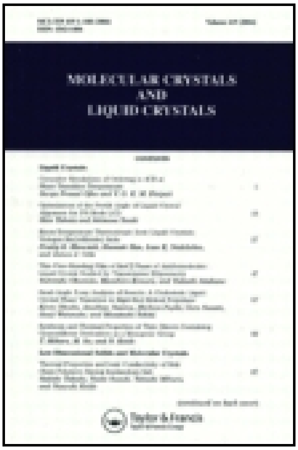

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Liquid Crystalline Epoxide Thermosets Copolymerization with aromatic diamines

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Liquid Crystalline Epoxide Thermosets

Copolymerization with aromatic diamines

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Highly ordered networks were produced by copolymerization of a low molecular weight liquid crystalline (LC) diepoxide with an aromatic diamine. A series of aromatic diamines was synthesized and their Polymerization reaction with the LC-diepoxide was studied by means of differential scanning calorimetry. By adjusting the melting point of the crosslinking agents an eutectic LC mixture was found on which all the physical measurements were carried out. The degree of order of a certain dye guest in the polymer networks as determined by UV-dichroism was 0.76. Birefringence measurements have confirmed that about the same level of ordering can be maintained up to the thermal degradation point (i.e., 300°C). Microscopy and X-ray studies have revealed that the epoxy-amine mixture is transformed from a nematic to a smectic phase, as a result of the polymerization reaction at 120°C.

Keywords: Ordered networks, LC diepoxide, UV-dichroism, thermosets

1. INTRODUCTION

Recently many of the research activities in the field of liquid crystalline (LC) polymers have been focussed on the subject of ordered networks.[1–3] These materials are interesting, especially because of their excellent anisotropic optical[4] and mechanical[5] properties.

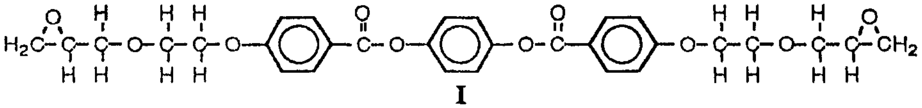
In the previous paper we described[6] the production of such networks by photo-initiated-polymerization of low molecular weight LC-diepoxides in the nematic phase. After the macroscopic orientation of the monomers with the aid of a known surface treatment technique (rubbed polyimide),[7] a chain-polymerization reaction was started by means of a cationic initiator sensitive to ultra violet (UV) light. This led to a network in which the LC order was maintained up to the degradation temperature. Although these systems are very well suited for application as thin layers, there are certain draw-backs, especially when preparing bulk materials. The first point of concern is the insufficient dissipation of the reaction heat during the rapid polymerization reaction which leads to a rise in temperature and consequently to a decrease of the degree of order of the reacting system.[8] However, there are ways to slow down the reaction and partly overcome this problem. Secondly, as it was shown in the previous paper,[6] after retardation of the reaction rate, the chain-polymerization tends to continue in the dark almost to completion. This makes controlling of, e.g., mechanical properties very difficult. These limitations also apply to the photoinitiated polymerization of LC-diacrylates.[4,5]

An alternative way for the production of such networks is the copolymerization of the LC-diepoxide with diamine monomers. This reaction proceeds in a slower and much more controllable fashion.[9]

Müller and co-workers[10,11] were the first to demonstrate that the mesophase of a LC-diepoxide can be frozen in by the reaction with an aromatic diamine. However, no attempts were made to orient the material macroscopically in order to determine the anisotropic properties. Simultaneously with our work, Barclay *et al.* also published two papers on this subject.[12,13] However, the resulting networks from their low molecular weight LC-diepoxide monomers displayed a very low degree of order.

We initially started to investigate the possibility of producing macroscopically ordered epoxy-amine networks as thin films. By selecting a suitable LC mixture, we were able to produce highly ordered materials. Subsequently, we made a successful attempt to prepare such materials in the bulk by means of polymerization under the influence of a magnetic field. These results will be published in the near future.

The LC-diepoxide (I) we have chosen demonstrates a broad nematic phase and a good reactivity towards amines:



I

$$\text{crystal} \xrightarrow{124} \text{nematic} \xrightarrow{186^\circ\text{C}} \text{isotropic}$$

In contrast to the LC-diepoxides studied by other investigators,[10-13] the above compound contains a short spacer segment connecting the epoxy group with the mesogenic part. The function of the spacer is to prevent the possible distortion of the molecular order as a result of the crosslinking reaction. The synthesis and photo-initiated-polymerization of this compound was published previously.[6]

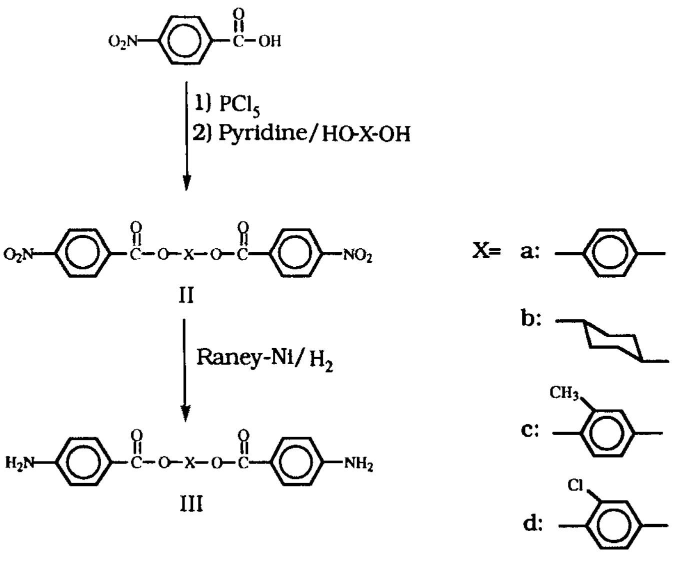
As curing agents we used a series of aromatic diamines, newly synthesized and some others which were commercially available. Dynamic mechanical and rheological measurements were conducted on one particular epoxy–amine mixture in which the LC ordering was maintained during the reaction. The degree of order was determined by UV-dichroism and birefringence (Δn) measurements. Finally morphological studies have been carried out to characterize the structure of the networks.

2. EXPERIMENTAL

A. Synthesis of Aromatic Diamines and Epoxy Compound I

The general route for the synthesis of epoxy compound I has been presented earlier.[6] 4,4′-Azodianiline (see Table 1, compound IIIe) was supplied by Eastman Kodak (Rochester/USA) and 4,4′-diaminobiphenyl (IIIf) by RPL (Leuven, Belgium). Both compounds were used without further purification. The synthetic route for the remaining diamines is outlined in Scheme 1 and a general synthetic procedure is described below:

To a 500 ml flask containing 100 ml of pyridine was added 7 g (38 mmol) of p-nitrobenzoyl chloride synthesized according to Reference 14. After adding 19 mmol of the appropriate diol, the mixture was stirred for 24 hours. (In the case of the compound IIIb, trans-1,4-dihydroxycyclohexane was prepared as described in Reference 15.) Then 400 ml of water was added and the precipitate was filtered off. The crude product was stirred for 1 hour with 250 ml of a 5% Na_2CO_3 solution and then washed with 200 ml water. The dinitro compounds (IIa–d) were obtained after recrystallization from a suitable solvent (see Table 1). The reduction of these compounds to the corresponding diamines was carried out in a autoclave using Raney–Nickel (Ni) as



SCHEME 1 Synthetic route to the aromatic diamines.

TABLE I

Data Concerning all the Aromatic Diamines Studied in this Paper

Compound[a]	T_m^b (°C)	ΔH (kJ/mol)	Recrystallization solvent	Yield (%)	Solvent[c]
III (II) a	319.4 (262.9)[d]	42.3 (35.1)	1-Butanol/DMF (DMF)	94 (66)	DMF
III (II) b	297.7 (261.2)	51.4 (48.1)	Butylacetate/DMF (DMF)	74 (48)	DMF
III (II) c	272.0 (273.8)	34.3 (53.6)	Dioxane/DMF (DMF)	58 (78)	THF
III (II) d	260.7 (256.6)	36.9 (38.9)	Dioxane/DMF (DMF)	40 (67)	THF
III e	248.7	23.9			DCM
III f	130.7	21.9			DCM

[a] Data reported in (···) are from the corresponding dinitro compounds.

[b] Because of the high melting point (T_m), the values reported here are derived from the first heating scan.

[c] These are the solvents used for preparing the polymerization mixture.

[d] This dinitro compound has a nematic–isotropic transition at 266°C (Reference 28).

catalyst. Thus a 500 ml reaction vessel was filled with 25 mmol of a dinitro compound, 200 ml of *N*, *N*-dimethyformamide (DMF) and a sufficient amount of Raney–Ni. After 16 hours at 50°C (operating pressure approx. 20 bar), the mixture was filtered and the filtrate was treated with active carbon. Subsequently the solvent was evaporated and the residue was recrystallized (see Table 1).

(IIIa): 1,4-Phenylene-di-4-aminobenzoate

^{1}H NMR (DMSO-d_6): δ6.2 ppm (4H, s) 6.6 (4H, d, $J = 8.9$ Hz), 7.3 (4H, s), 8.0 (4H, d, $J = 8.6$ Hz)

(IIIb): Trans-cyclohexane-1,4-diyl-di-4-aminobenzoate

^{1}H NMR (DMSO-d_6): δ1.65 ppm (4H, m), 2.01 (4H, d, $J = 7.88$ Jz), 4.93 (2H, m), 5.95 (4H, s), 6.58 (4H, d, $J = 8.6$ Hz), 7.66 (4H, d, $J = 8.6$ Hz)

(IIIc): 2-Methyl-1,4-phenylene-di-4-aminobenzoate

^{1}H NMR (DMSO-d_6): δ2.1 ppm (3H, s), 6.176 (2H, s), 6.183 (2H, s), 6.653 (2H, d, $J = 3.66$ Hz), 6.622 (2H, d, $J = 3.66$ Hz), 7.06 (1H, dd), 7.16 (2H, m), 7.78 (2H, d, $J = 8.61$ Hz), 7.83 (2H, d, $J = 8.79$ Hz)

(IIId): 2-Chloro-1,4-phenylene-di-4-aminobenzoate

^{1}H NMR (DMSO-d_6): δ6.224 ppm (2H, s), 6.256 (2H, s) 6.629 (2H, d, $J = 4.06$ Hz), 6.661 (2H, d, $J = 4.06$ Hz), 7.3 (1H, dd), 7.43 (1H, d, $J = 8.63$ Hz), 7.55 (1H, d, $J = 2.79$ Hz), 7.791 (2H, d, $J = 7.62$ Hz), 7.832 (2H, d, $J = 7.36$)

The ^{1}H NMR spectra were measured with a Varian VXR-400 S NMR spectrometer. The spectra of the intermediate compounds were in all cases in accordance with the structures. TMS was used as the internal standard.

B. Physical Measurements

To prepare the polymerization mixture, stoichiometric amounts of diepoxide (2 mol) and a diamine (1 mol) were dissolved in a suitable solvent (see Table 1). The solvent was then removed under reduced pressure at room temperature (RT). The epoxy value of compound I was determined by potentiometric titration:

3.48 equivalent/kg, theoretical value: 3.63

Thermal characterization was carried out on a Perkin–Elmer DSC-7 calorimeter (scanning rate 10°C/min) using indium metal for the calibration of the apparatus. Samples were weighed (ca. 4–6 mg) in aluminium pans and run under nitrogen atmosphere. In the case of reactive epoxy-amine systems, the base line was established by running a similar second scan as the first one.

To determine the weight loss of the materials as a function of the temperature, samples were heated at a rate of 5°C/min under a nitrogen atmosphere in a Perkin–Elmer TGA-7 thermogravimetric analyzer.

Morphological characterization was performed with a Jenapol (Jena) microscope, provided with a Mettler FP82 hot stage and a FP80 central processor. Using a Kipp-compensator (0–6λ) the optical retardation (L) was measured digitally with the aid of a RETARMET 2 (Carl Zeiss/Jena) at a wave length of 546.1 nm. L could be measured very accurately ($\pm 1\%$). To calculate Δn, the cell thickness was also needed, which was determined interferometrically. In our case, this introduced an estimated inaccuracy of about 3% in the absolute Δn values.

The degree of order is described by the average value of the second order Legendre polynomial $\langle P_2 \rangle = (3\cos^2\theta - 1)/2$, where θ is the angle between the molecular long axis and the director. In order to obtain $\langle P_2 \rangle$, the polymerization mixture with approximately 0.5% (w/w) azo dye D_2 (Merck Ltd/Poole) was melted between two glass plates in the Mettler hot stage at the required temperature (i.e., 120°C). The reaction was allowed to continue for one hour. To ensure a macroscopic planar orientation of the monomers as for Δn measurements, the inner surfaces of the plates were coated with a uniaxially rubbed thin polyimide film. The sample thickness was controlled by glass fibre threads, having a diameter of 8.5 μm. The optical absorbance was measured at room temperature (RT), both parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the director of the planar LC layer, using a Shimadzu UV-Visible recording spectrophotometer type UV-160. The spectra were corrected for the internal anisotropic polarization of the apparatus. $\langle P_2 \rangle$ was calculated according to expression (1)[16]:

$$\langle P_2 \rangle = (A_\parallel - A_\perp)/(A_\parallel + 2A_\perp) \tag{1}$$

The polarizer angle was adjusted to obtain the maximum value for $A_\parallel$ at $\lambda_{\max}$(500 nm) and realigned through 90° to measure the minimum value, $A_\perp$. The local field corrections have been ignored.[6,17,18]

X-ray diffraction patterns were made with a flat film (Kiessig pine hole camera) using Ni-filtered CuK$_\alpha$ radiation. The sample to film distance was 50 mm.

Rheological measurements were performed with the aid of a Rheometrics RMS-800 dynamic mechanical spectrometer using parallel-plate (8 mm in diameter) geometry. The storage (G') and loss (G'') moduli were determined at a frequency of 15 Hz.

Mechanical behaviour from the glassy to rubbery region was studied using a Perkin-Elmer dynamic mechanical Analyzer (DMA-7). The storage (E'), loss (E'') Young moduli and loss tangent (tan delta $= E''/E'$) were determined in the three point bending mode at a heating rate of 5°C/min and a fixed frequency of 1 Hz.

3. RESULTS AND DISCUSSION

A. Copolymerization of the Diepoxide I with Various Diamines as Studied by Differential Scanning Calorimetry (DSC)

In order to produce ordered networks, an aromatic diamine is needed, having the ability to form a LC phase in a mixture with the diepoxide I. An aromatic diamine is favoured over an aliphatic diamine, because the latter is already reactive at RT,[9] which is well below the nematic temperature range of compound I. In searching for a suitable compound, considering the structure of the diepoxide, an aromatic diamine with the same mesogenic group seems to be a logical choice. Figure 1a shows a DSC scan of a stoichiometric mixture of the diepoxide I with the corresponding diamine IIIa. On the

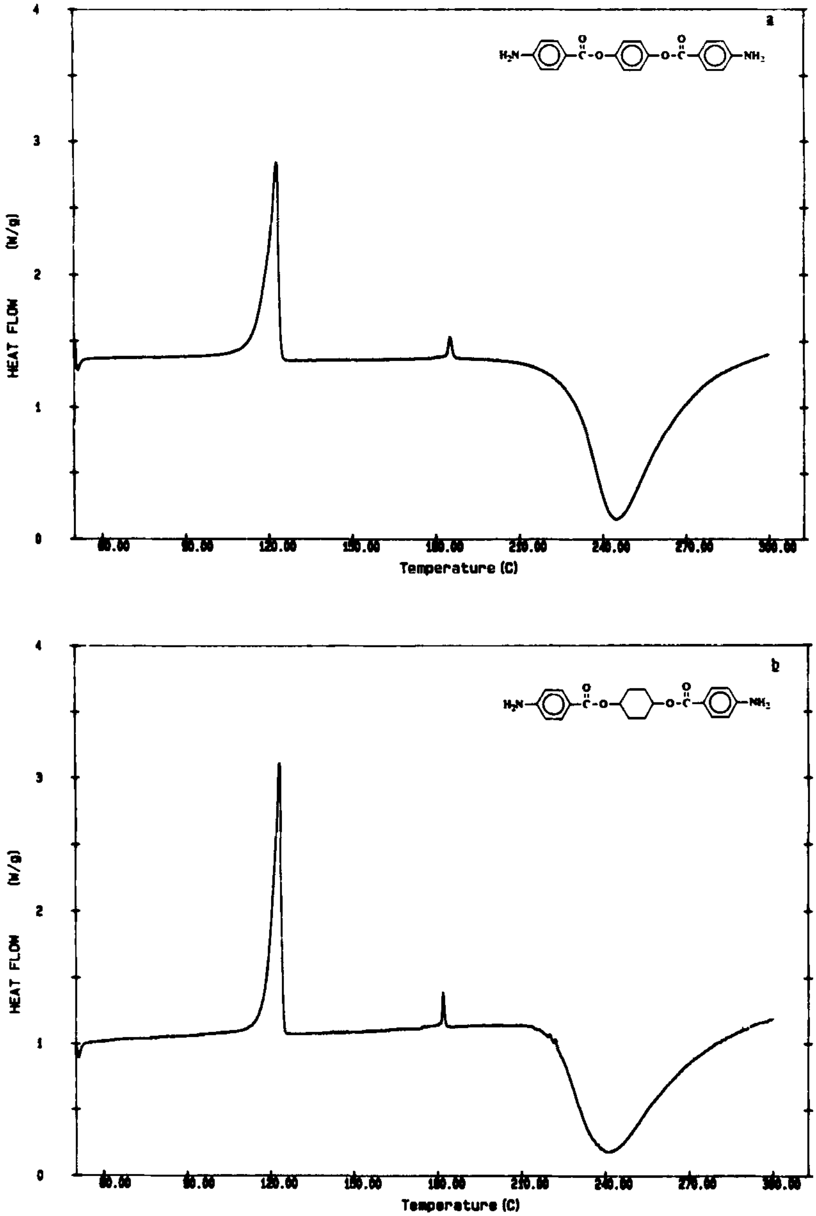


FIGURE 1 DSC traces of the thermal polymerization of diepoxide I with various aromatic diamines. For a matter of convenience the structures of the corresponding diamines are also displayed.

basis of this thermogram one can conclude that this mixture consists of two immiscible solids, forming two almost completely separate phases. During the thermal scan initially the phase rich in the diepoxide melts at 122.7°C. Above the nematic to isotropic transition temperature (T_i) at 185.2°C, the second phase mainly consisting of diamine IIIa starts to melt. However, due to the subsequent exothermic reaction no endothermic

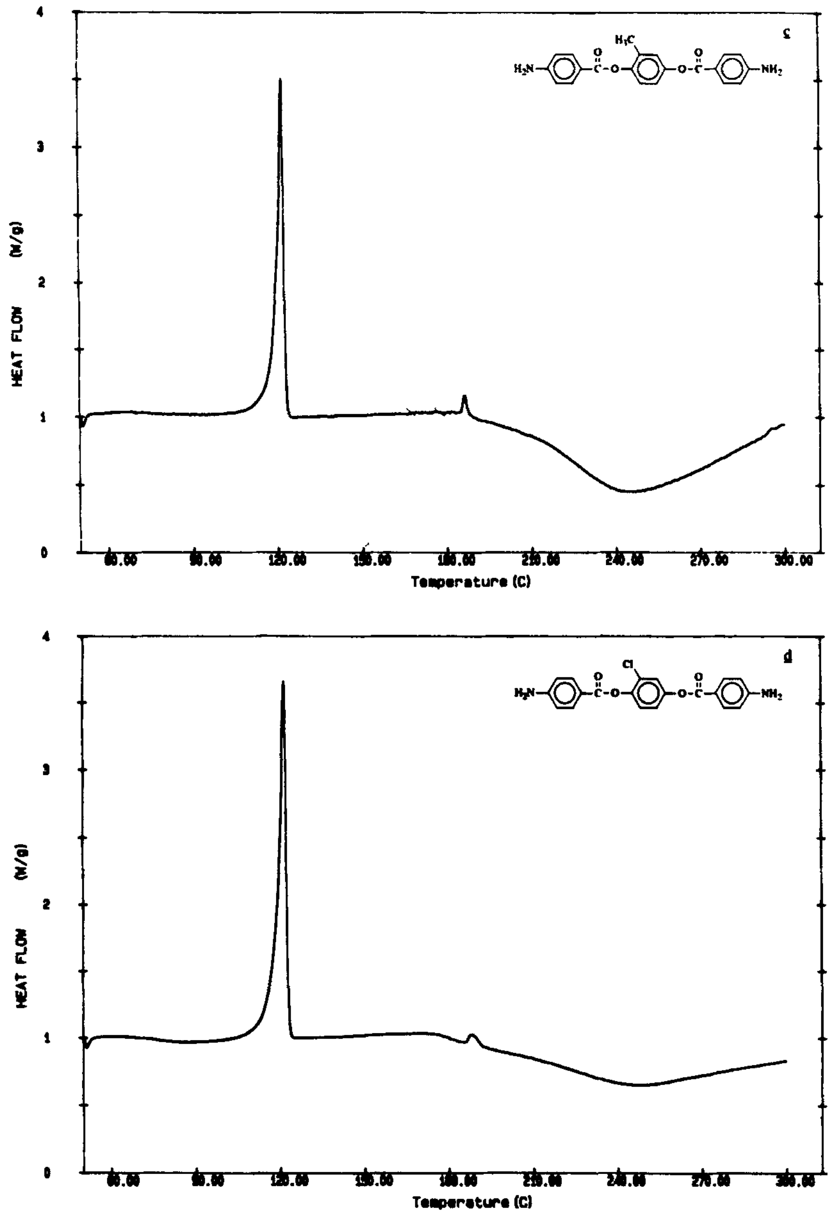


FIGURE 1c–d (*Continued*).

melting peak (T_m) can be observed. It is obvious that curing agent IIIa is not suitable for network formation within the nematic phase. This might be attributed to the high T_m of 319.4°C for this compound (see Table 1). The replacement of the central aromatic ring of IIIa by trans-1,4-cyclohexane[19] leads to a decrease of T_m by more than 20°C (see diamine IIIb). However, Figure 1b shows that the reaction still occurs well above the nematic temperature range. A further decrease of T_m can be realized by introducing

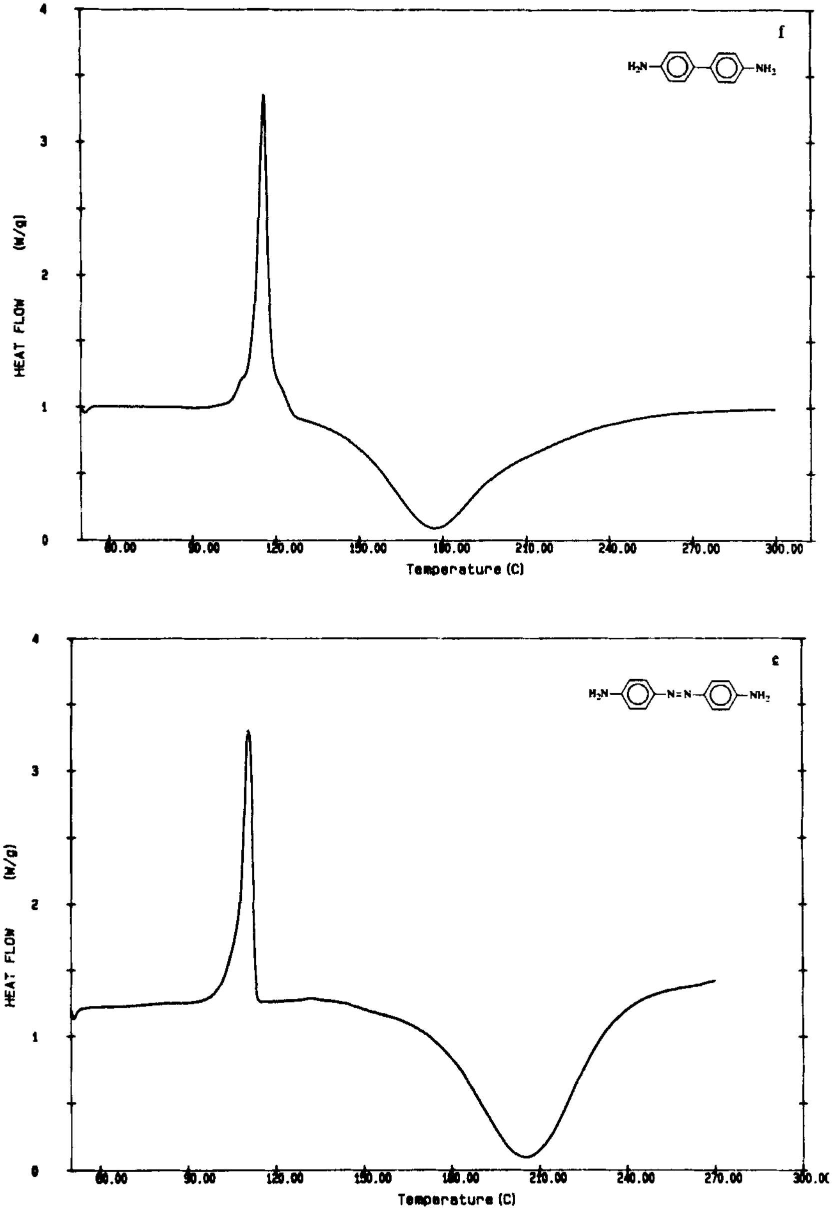


FIGURE 1e–f (*Continued*).

a methyl group (IIIc) or chloro atom (IIId) into the central ring of IIIa.[20] With IIIc (T_m = 272.0°C) reaction occurs just outside and with IIId (T_m = 260.7°C), just inside the nematic phase (Figures 1c and 1d resp.). Although IIId seems to be suitable in principle for freezing in the LC phase, a further decrease of T_m is desirable because a lowering of the cure temperature (T_{cure}) would lead to an increase of the initial degree of order. This can be achieved by using the two ring aromatic diamines like 4,4′-azodianiline (IIIe) or 4,4′-diaminobiphenyl (IIIf) instead of the three ring systems. From Figures 1e and 1f one can conclude that compound IIIf is the most suitable curing agent. The mixture of this diamine with the diepoxide I is actually an eutectic mixture with the T_m at 115.9°C. This is confirmed by the observation that a small deviation from the 2:1 molar ratio between the compounds I and IIIf causes a second peak to appear at a higher temperature, the 115.9°C peak always remaining the lowest. The mixture with diamine IIIf is additionally favoured because an eutectic is an intimate mixture of fine crystals whereas the crystals that are formed above the eutectic temperature are coarse.[21] This fine texture may accelerate the mixing of the reactive compounds upon melting.

No thermal transitions can be observed after the mixtures have been cured. This agrees well with the previous studies[6,22,23] and morphological observations conducted on the present systems (see also section IIIB).

In conclusion, by adjusting the T_m of the curing agent it was possible to find a suitable mixture (diepoxide I/diamine IIIf) for preparing the network in an ordered state. All further physical measurements have been carried out on the mixture I–IIIf.

B. UV-Dichroism and Birefringence Measurements

The polymerization reaction is conducted for one hour at 120°C, just above the eutectic T_m where the initial state of ordering is highest. As will become clear (below), after this time the reaction does not proceed further. After 1 hour of curing at 120°C the order parameter $\langle P_2 \rangle$ of the dichroic dye D_2 at RT is 0.76 ± 0.02. This is a measure of the average molecular orientation of the network with emphasis on the aromatic mesogenic moieties (see Figure 2). Unfortunately UV-dichroism is not a suitable technique for investigating the level of ordering at higher temperatures. This is due to the low thermal stability of the dichroic dyes. As an alternative method we have measured birefringence (Δn) which is directly proportional to $\langle P_2 \rangle$.[17] During one hour of reaction time at 120°C Δn rose from 0.10 to 0.17 due to the improvement of the molecular packing by polymerization.

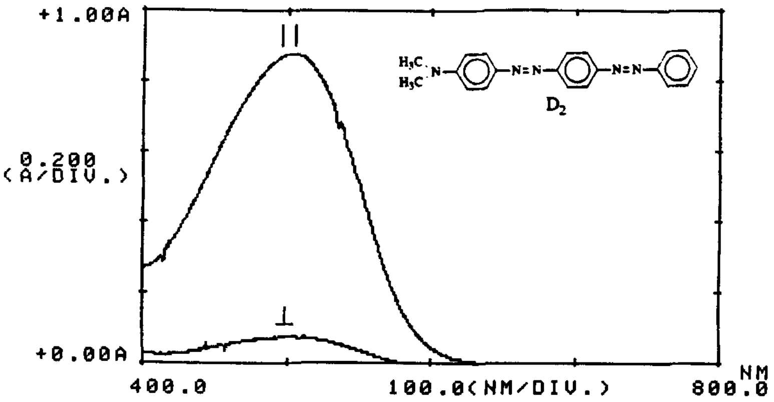


FIGURE 2 Absorption spectra of dye D_2 in the mixture I–IIIf after one hour at 120°C. The spectra are measured at RT both parallel (||) and perpendicular (⊥) to the alignment direction.

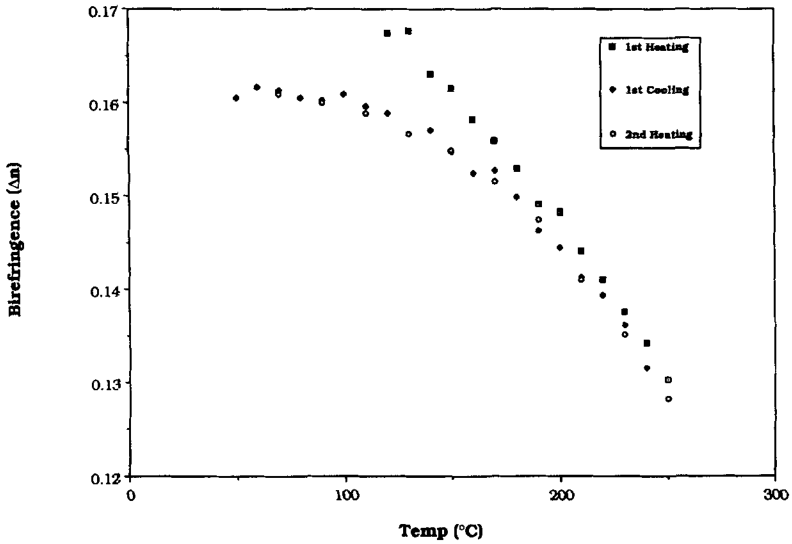


FIGURE 3 The change of birefringence as a function of temperature (10°C/min) for the mixture I–IIIf after one hour at 120°C.

A slow heating scan from 120°C to 250°C causes Δn to decrease by more than 22% [see Figure 3]. However, upon subsequent cooling to 120°C Δn almost returns to its starting value and does not change after further cooling to RT. This process can be repeated. Thus, it is clear that the material, as far as the degree of order is concerned, has become highly stable. The reversible variation of Δn as a function of temperature is connected with the change of degree of order and density of the sample. Figure 4 displays the dynamic mechanical properties after one hour at 120°C. The transition from the rubbery to glassy state (maximum in tan delta) takes place at 95°C. Raising the temperature to 250°C leads to an increase of this transition for almost 25°C. The existence of a rubbery region with a stable and high E' value (6×10^7 Pa)* suggests that the material has gelled during the polymerization at 120°C. The occurrence of gelation can also be deduced from Figure 5 where the evolution of the dynamic storage (G') and loss (G'') moduli is monitored as a function of time, again at $T_{\mathrm{cure}} = 120$°C. Initially both $G'(t)$ and $G''(t)$ start to rise and at a certain point the curves cross.

Before this crossover viscous properties are dominating ($G'' > G'$) while thereafter the elastic behaviour is predominant. It has been shown that for isotropic systems, with the stoichiometric ratio of the reactive groups, this crossover corresponds to the rheological gelpoint.[26,27] It is difficult to judge whether the gelation in our system occurs exactly at the crossover in Figure 5, but it seems reasonable to assume that somewhere before this point the mixture starts to gel. Analysis of the time dependencies of G' and G'' furthermore reveals that after one hour at 120°C, G' reaches a plateau value of about 3×10^7 Pa which corresponds to the rubber value of E' in Figure 4. The fact that both

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* The very high rubber modulus for some fully cured epoxy networks was attributed to the rigid character and low flexibility of the starting materials.[24,25]

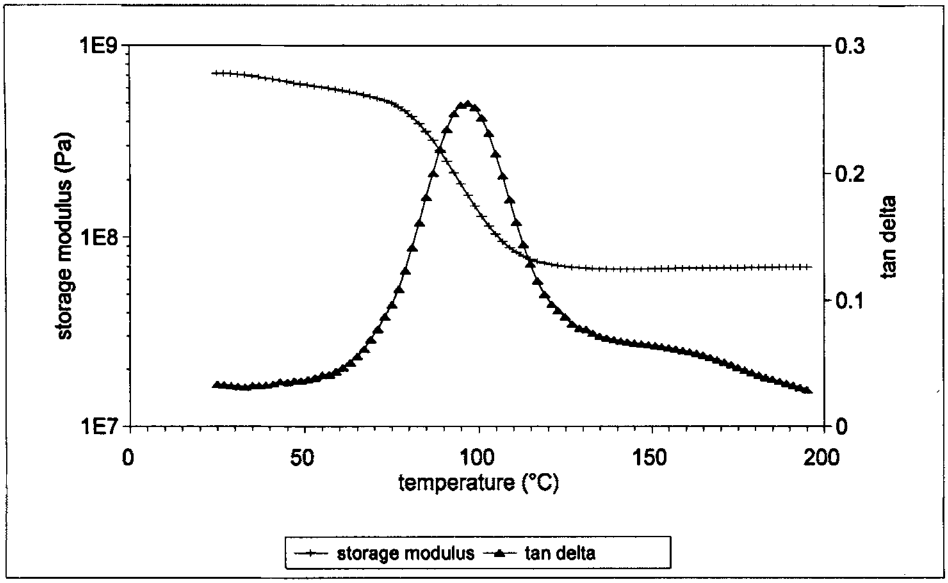

FIGURE 4 Dynamic mechanical properties for the mixture I–IIIf measured after one hour at 120°C.

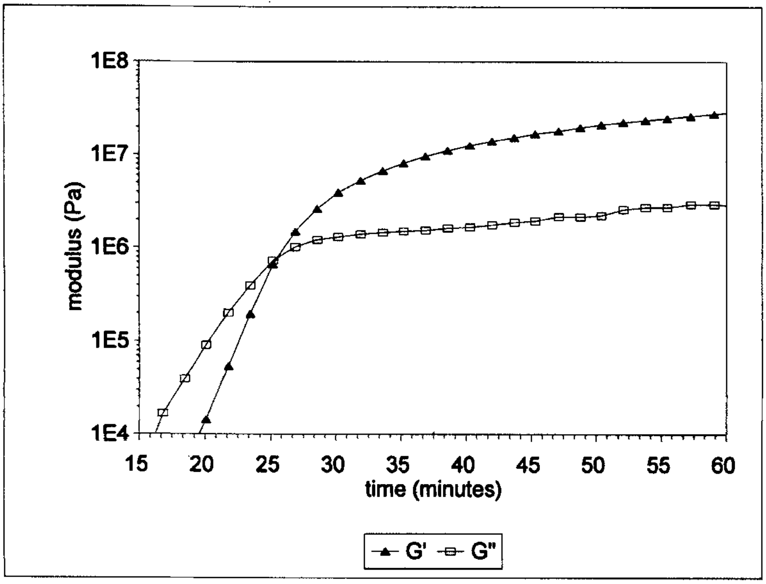

FIGURE 5 Evolution of the storage (G') and loss (G'') moduli during the reaction of the mixture I–IIIf measured at $f = 15$ Hz and $T = 120$°C.

G' and G'' level off indicates that no significant amount of reaction takes place after one hour at 120°C.

C. Microscopic, X-ray and Thermal Stability Investigations

Microscopic observations have revealed that a clear nematic to smectic transition takes place after 16–18 min of polymerization time at 120°C (see Figure 6). This is directly

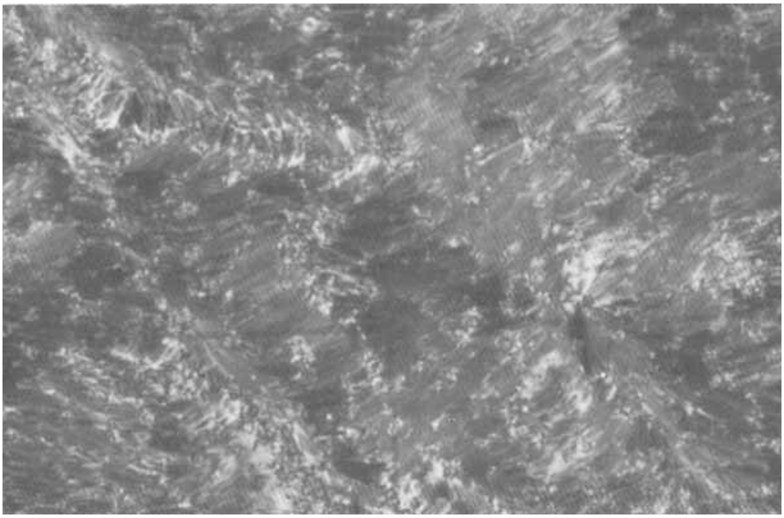

FIGURE 6 The polarization microscope photograph (× 180) of the mixture I–IIIf cured for one hour at 120°C and then heated to 200°C (measured at RT). See Color Plate IV.

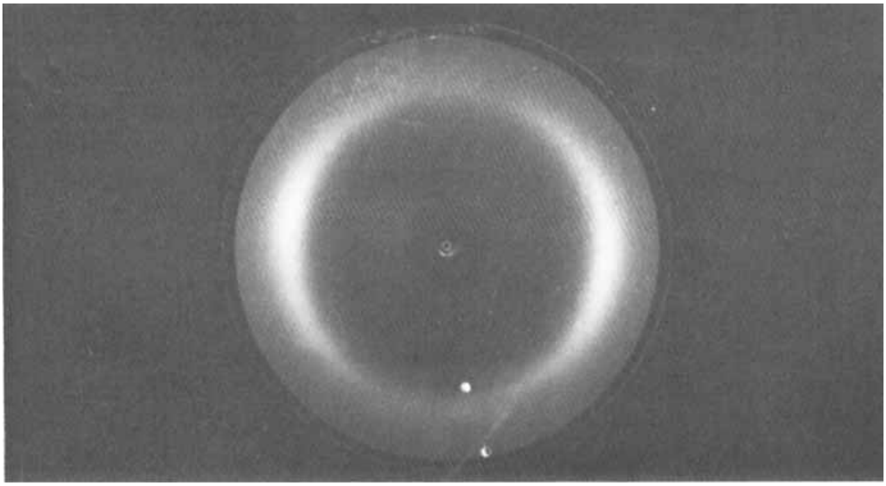

FIGURE 7 The X-ray diffraction pattern of the same material as in Figure 6 (measured at RT).

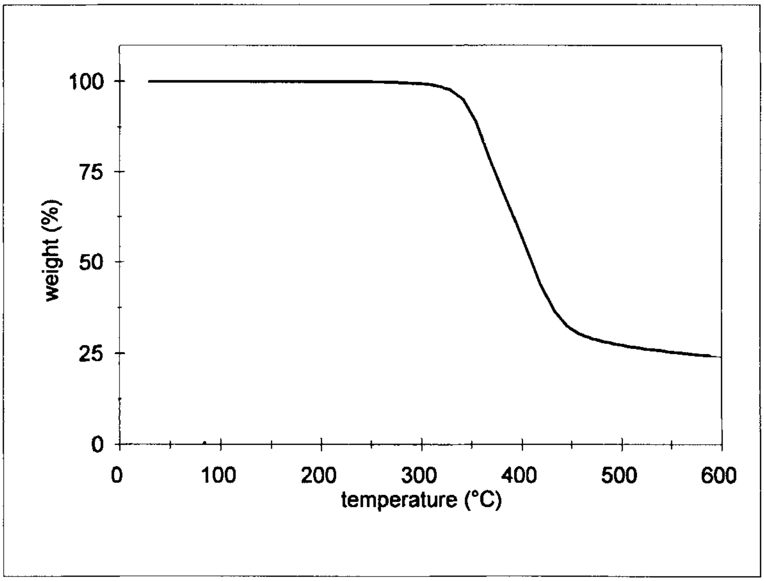

FIGURE 8 TGA trace of the mixture I–IIIf.

connected to the increase of the order (shifting of T_i to higher temperatures) as was observed by Δn measurements. The X-ray diffraction studies confirm the microscopic observations (see Figure 7). The diffuse ring at wide angle indicates that the lateral arrangement of the molecules is disordered and the very sharp reflections at small angle show the existence of extensive layer-like correlations. One can also recognize that some level of macroscopic orientation is induced by capillary action during the filling of the measuring cell. These features correspond to a S_A or S_C phase. However, the polarization microscope photograph (see Figure 6) showing the focal conic texture seems to indicate a S_A phase. The d-spacing measured for the wide angle diffraction ring is 4.5 Å which corresponds to the average distance between the neighbouring molecules. The layer thickness determined from the sharp reflections at small angle is 14.1 Å. This is much smaller than the layer spacing of 27 Å which is calculated, in analogy with low molecular weight LC-mixtures, from the molecular length of the epoxy in its extended conformation ($\approx$ 35 Å) and that of the diamine ($\approx$ 10 Å), taking into account the molar ratio of the two monomers. If the spacer segment of the epoxy compound is excluded from the calculations, a layer spacing of 14 Å is determined. This would then mean that the flexible parts are not participating in the lamellar structure. However, the actual situation is probably quite complicated and more investigations are needed in order to determine the molecular packing of the networks. The frozen-in focal conic texture hardly changes after heating the material up to the thermal degradation point which according to the TGA-thermogram lies around 300°C (see Figure 8).

4. CONCLUSION

By selecting crosslinking agents with appropriate melting points, it was possible to carry out the network formation between a LC-diepoxide and an aromatic diamine well inside the nematic phase which transformed to a smectic phase as a result of the polymerization reaction at 120°C. The order parameter of the resulting network as determined by UV-dichroism was about 0.76. The change of birefringence upon subsequent heating and cooling runs was quite reversible, characteristic of a stable network with a high degree of conversion.

Acknowledgements

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