ORDERED EPOXY NETWORKS
Synthesis and Physical Properties
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Amir Shahab KOKABI JAHROMI

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Dit proefschrift is goedgekeurd door de promotoren:
Prof. dr. W. J. Mijs
Prof. dr. ir. A. Posthuma de Boer

Samenstelling van de promotiecommissie:

De Wnd. Rector Magnificus
Prof. dr. W. J. Mijs
Prof. dr. ir. A. Posthuma de Boer
Prof. dr. ir. H. Van Bekkum
Prof. dr. J. Feijen
Prof. dr. G. R. Luckhurst
Dr. M. Ilavsky
Dr. D. J. Broer

Technische Universiteit Delft
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University of Southampton
Academy of Sciences of the Czech Republic
Philips research Eindhoven
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CHAPTER I- General Introduction

Chain segment ordering can be introduced in conventional polymeric networks by uniaxial deformation. Such deformations are generally completely recoverable. Occasionally, the segmental order of the network chains becomes frozen-in, for example, as a result of stress-induced crystallization. Both experimental and theoretical aspects of deformation induced orientation in elastic networks have been investigated for a long time\textsuperscript{1}). This thesis deals with a relatively new concept for preparing ordered networks which is based on the fixation of the molecular order in a liquid crystalline phase by crosslinking reaction.

The term liquid crystal (LC) represents an intermediate state of aggregation between the crystalline solid and the amorphous liquid. LC-materials are quite complex anisotropic fluids and since their discovery in 1988, they have been subject of very intensive research both from the scientific and technological point of view\textsuperscript{2}). The latter activities are mainly motivated by the very interesting electro-optical properties of LC-materials and they have already led to their large scale application in display devices, for example.

Generally, liquid crystals can be divided into two major classes based on the structure of the ordered state, also called the mesophase: 1- The nematic phase where only long-range orientational order is present, i.e., the molecules are oriented with their long axis approximately parallel to each other. 2- Smectics phases, which are characterised in addition by a positional order in at least one dimension where the center of the molecules are arranged on average in equidistant planes. Based on the molecular arrangement, the smectic phases are subdivided into, for example, smectic A where the molecules are upright in each layer and smectic C where the molecules are inclined with respect to the layer normal. A more detailed description of these phases can be found in for example the classical books written by de Gennes\textsuperscript{3}) and Chandrasekhar\textsuperscript{4}) on the subject of liquid crystals.

Although, up to this moment, it is still not clear what are the exact requirements for materials to have LC properties, most of the conventional low molecular weight (LMW) LC materials consist of rigid rod like segments,
called mesogenic groups. LC properties have also been observed in polymers where the mesogenic groups are either incorporated in the main- or in the side-chain. In LC polymers similar phase structures can be observed as in LMW LC systems. These materials have also been extensively studied in the past two decades\textsuperscript{5,6}.

LC-ordered networks, which is the subject of this thesis, form a recent discipline in the field of LC materials, although the basic idea was already proposed by de Gennes\textsuperscript{7} in 1969 who predicted that polymerizing LMW mesogenic monomers could produce ordered networks with interesting stress-strain behaviour. As early as 1973, Strzelecki and coworkers\textsuperscript{8-10} thermally polymerized LMW LC diacrylates to form ordered networks which remained birefringent up to the decomposition temperature.

In recent years, LC-ordered networks have enjoyed a great renewed attention. This can partly be attributed to the fact that, although main-chain LC polymers have excellent properties, like high modulus, in the direction of the orientation, the properties transverse to the direction of orientation are rather poor. These problems can be overcome by the introduction of crosslinks between the chain which guarantees the dimensional stability of these ordered systems\textsuperscript{11-16}.

LC-ordered networks can be classified in several categories as is described below.

1- LC thermosets: These are ordered networks that, because of the high degree of crosslink density, display no thermal transitions like smectic to nematic or LC to isotropic. These materials are actually part of the much broader field of rigid rod networks that are presently being investigated both from the experimental, for example by Aharoni and coworkers\textsuperscript{17-22} and others\textsuperscript{23}, and theoretical aspects by the group in the Cavendish laboratories (Cambridge university)\textsuperscript{24-29}.

2- LC elastomers: These are lightly crosslinked either side\textsuperscript{30}- or main-chain\textsuperscript{31-34} LC polymers. LC elastomers are quite interesting systems owing to the fact that the macroscopic orientation can be achieved by applying mechanical fields\textsuperscript{35-39}. As a consequence, interesting opto-electronic properties can be realised by mechanical deformation and orientation\textsuperscript{40}. LC elastomers have also been theoretically studied by Warner and
coworkers\textsuperscript{41,43} in continuation of the original work of de Gennes\textsuperscript{44}, describing, for example, the stress-strain mechanical behaviour of these materials.

3- Anisotropic gels: These are ordered networks swollen either in an isotropic or anisotropic solvent. An example of the former kind was already reported by Samulski and Tobolsky\textsuperscript{45} in 1968 who crosslinked a solution of poly (γ-benzyl-L-glutamate) with the aid of γ-radiation. The phase behaviour of swollen networks in isotropic solvents are presently being investigated by Kishi\textsuperscript{46-47} et al. and others\textsuperscript{48-57}.

Ordered networks swollen in LMW LC solvents form another interesting class of LC materials because of, for example, their intriguing electro-optical properties. Hikmet and Zwerver\textsuperscript{58,59} prepared such networks by photoinitiated polymerization of a blend of LC diacylates and commercially available LMW LC compounds. A possible application of these materials in display devices was demonstrated\textsuperscript{60,61}. An open question is the phase behaviour of these LMW LC molecules dispersed in the ordered networks. It is suggested that there exist two populations of the LC molecules; one physically attached to the network and the other completely free. A further investigation into this phenomenon is required.

4- Networks with non-linear optical (NLO) properties: These are materials where NLO active molecules are chemically bonded to the network\textsuperscript{62-71}. Although these systems do not usually show LC properties, they do possess a macroscopic orientation of the NLO molecules which is normally induced by an external electric field, applied during the crosslinking reaction. The presence of crosslinks insure the orientational stability of these systems in contrast with the linear NLO polymeric materials where the degree of polar orientation of the NLO molecules usually decreases as a function of time. The orientational stability is essential in order to have materials which sustain their macroscopic NLO-properties over a long period of time.

This thesis deals with the first category, i.e., LC thermosets. These materials are interesting because of their excellent optical\textsuperscript{72} and mechanical\textsuperscript{73} properties. The basic idea in the production of highly crosslinked and highly ordered networks is to orient LMW LC monomers uniaxially and subsequently freeze in the orientation by polymerization and crosslinking. As the polymerizing unit a broad range of functional groups
are available like acrylates and bismaleimides\textsuperscript{74}). As mentioned earlier, Strzelecki and coworkers\textsuperscript{8–10} were the first to produce ordered networks by thermal polymerization of LMW LC diacrylates in the mesophase. Recently, Broer and Hikmet and their various coworkers\textsuperscript{75,76} have shown that a more convenient way of producing ordered networks is by photoinitiated polymerization of LMW LC diacrylates. This method offers the possibility of polymerizing isothermally in the LC phase at nearly any temperature. In this way the degree of order and consequently all anisotropic properties can be adjusted as desired.

Although networks, made by chain polymerization, 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 a decrease of the degree of order of the reacting system. However, there are ways to slow down the reaction and partly overcome this problem. Secondly, after retardation of the reaction rate, the photoinitiated chain polymerization reaction, generally, tends to continue in the dark almost to completion. This makes the controlling of, for example, mechanical properties very difficult. Moreover, the chemistry of chain polymerization is complex, because of the various side reactions that can occur during the network formation. In addition, these systems have a tendency to give structural inhomogeneities, like local vitrification during cure. These features of the chain polymerization reactions makes them unsuitable as model systems to study network formation in an ordered state which is actually the main objective of this thesis.

In this thesis, we will present, as an alternative, the crosslinking reaction of a series of LC diepoxide monomers. Conventional epoxy networks have better mechanical and thermal properties than their acrylate counterparts\textsuperscript{77}). Also, epoxides have the possibility to be polymerized either photochemically or thermally. Thermal polymerization is usually carried out with aliphatic or aromatic diamines. This step addition polymerization proceeds in a slower and much more controllable fashion. The chemical reactions involved are , in contrast with the chain polymerization described above, rather specific and free of side reactions\textsuperscript{78}). Indeed, conventional isotropic epoxy-amine networks have been frequently used to study the
crosslinking reactions in general\textsuperscript{79}. Thus, LC epoxy-amine systems are excellently suitable to investigate network formation in an ordered state.

Recently, several publications have appeared concerning the copolymerization of LC diepoxides with aromatic diamines\textsuperscript{80-87}. Some of these papers have actually been published simultaneously with our studies\textsuperscript{80-85}. As stated earlier, conventional epoxy networks have excellent mechanical and thermal properties. The objective of nearly all these investigations have been to improve these properties by incorporating LC like structures into these systems. A possible application of LC epoxide thermosets would be as encapsulation materials for integrated circuits. One of the major disadvantages of the current, mostly epoxy based, materials is their high coefficient of thermal expansion (CTE) in comparison with that of the chip. The thermal stress, caused by the expansion coefficient mismatch, leads to the occurrence of the cracks in the plastic package and the chip. Ordered networks, are promising materials for encapsulation purposes, because of their very low CTE values (see chapter VI).

Müller and coworkers\textsuperscript{86,87} were the first to demonstrate that the mesophase of a LC diepoxide can be frozen in by the reaction with an aromatic diamine. However, in this study and several other investigations\textsuperscript{80,81}, no attempts were made to orient the materials macroscopically in order to determine the anisotropic properties. Barclay et al.\textsuperscript{85} attempted to produce highly crosslinked and highly ordered networks by conducting the copolymerization of LMW LC diepoxides with a certain aromatic amine under the influence of a very strong magnetic field (13 T). However, the LC diepoxide monomers used, were so reactive that the polydomain structure became locked in by the polymerization reaction, before the macroscopic orientation could be fully achieved. As a result, only networks with a low degree of macroscopic order could be produced.

In this thesis, we will demonstrate, for the first time, that it is indeed possible to produce epoxy-amine networks with both a high degree of crosslink density and a high degree of macroscopic order.

As mentioned earlier, our main objective was to study in detail the physical properties of ordered networks. In this regard, there are two topics that are of primary importance. In the first place, of course, the state of order of these systems should be investigated. The question is how the level
of orientation changes as a function of the degree of polymerization and, especially, what the effect is of the crosslinking reaction. The second point of interest, is the elastic properties of these ordered systems. The rigid character of the monomers and the ordered structure are the two main factors which distinguish the present networks from conventional crosslinked polymers. In this thesis, we will describe the mechanical properties of macroscopically ordered networks in terms of both rigidity and degree of order, which we have analysed in detail.

The outline of this thesis is as follows:

In chapter II, we will describe the synthesis of a series of LMW LC diepoxides. The LC properties of these compounds, in terms of molecular structure will be discussed. Also, it will be demonstrated that highly ordered networks can be produced by photoinitiated polymerization of the LC diepoxides in the mesophase. The effect of the molecular structure and the liquid crystalline order on the rate of polymerization will be treated. It is shown that the polymerization reaction will continue in dark almost to completion. This phenomenon, which as stated earlier seriously hampers the controlling of, for example, mechanical properties, partly motivated the research in chapter III.

In chapter III, the crosslinking reaction of a certain LC diepoxide with a series of, newly synthesized and commercially available, aromatic diamines is described. It is shown that by systematically altering the structure of the diamine and by selecting those with the right melting point, it is possible to obtain an eutectic mixture. With the aid of standard techniques, like dichroism and birefringence measurements, we demonstrated, for the first time, that highly crosslinked and highly macroscopically ordered epoxy-amine networks can be produced. These networks possess, just like some of the systems described in chapter II, orientational stability up to the degradation point.

In chapter IV, the influence of chain extension and crosslinking reactions on the initial state of the order for a certain LC epoxy-amine mixture is described. Deuterium nuclear magnetic resonance ($^2$H-NMR) in combination with birefringence measurements has been used to monitor the orientational order as a function of the degree of polymerization separately for each of the reacting monomers. Furthermore, the results of the $^2$H-NMR
studies are compared with those obtained from the several other standard techniques like gel permeation chromatography.

In chapter V, the dynamic mechanical properties of a series of ordered and isotropic epoxy-amine systems are outlined. The reaction is followed in real time by frequency dependent rheological measurements in an attempt to determine the position of the gel point. The conversion of the epoxy groups at the gel point is compared with the results of the statistical theory for network formation in isotropic epoxy-amine systems. The dynamic mechanical properties of macroscopically ordered networks have been examined in terms of both rigidity and order. Comparisons are made between the experimental results and predictions of the "simple" rubber elasticity theory. A theory is presented, by T. Odijk, describing in a qualitative manner the influence of order on the mechanical properties. Also, the values of the coefficient of thermal expansion of these ordered networks have been determined.

Finally, in chapter VI, we will examine the possible application of LC epoxide thermosets as encapsulation materials for semiconductors. A new concept is proposed which, in principle, should lead to the reduction of the thermal stress in the integrated circuits.

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Chapter II- Synthesis and Photoinitiated Polymerization of Liquid Crystalline Diepoxides

Abstract: 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-infrared 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. Postcuring was sometimes necessary to produce highly stable networks. Furthermore, some results suggest that liquid crystalline nematic ordering increases the polymerization rate.

I. INTRODUCTION

Ordered networks are of great interest due 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\(^1\)-\(^3\).

Lierbert 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 photoinitiated polymerization of a liquid crystalline diepoxide. This is of interest in view of the better mechanical and thermal stability of poly-epoxides over poly-acrylates\(^10\). Epoxides also show superior adhesive properties when compared with acrylates.

\(^{*)}\) Based on: Jahromi, S., Lub, J., Mol. G.N., Polymer 1994, 35, 621
In this chapter, 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 molecules 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 the ordering is concerned, birefringence measurements were carried out.

Scheme 1. Synthetic route to all the monomers.
II. EXPERIMENTAL

A. Synthesis of monomers

The synthetic route used in our study is outlined in scheme 1. 5-Hexen-1-ol [1a] was supplied by Aldrich Chem. Co. Allyl-2-hydroxyethyl ether was synthesized according to details given in the literature\textsuperscript{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\textsuperscript{12}. The synthetic procedures of the remaining compounds with X = CH\textsubscript{2} and X = O are similar and are described below.

\textbf{-Synthesis of 4-(tetrahydropyran-2-yloxy)phenol [3].}\nOver a period of 30 minutes, 2 ml of dihydropyran (0.1 mol) is added to a mixture of 11 g of hydroquinone (0.1 mol) and 0.2 g of p-toluene sulfonic acid (PTSA) in 100 ml of ether. During the reaction the hydroquinone dissolved completely. After stirring for one hour, the ethereal solution is extracted twice with 40 ml of a deaerated aqueous solution of 3 g of NaOH (75 mmol) and 0.3 g of NaHSO\textsubscript{3}. The combined aqueous layers are washed with 25 ml ether, cooled with ice and carefully acidified with acetic acid. The precipitated product is collected by filtration, washed with 50 ml of water and dried over SiO\textsubscript{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 tosylate 2 the mixture was stirred for 12 hours at 60 °C. The mixture was filtrated and the filtrate was evaporated to dryness. The residue was then dissolved in 60 ml of ether and 40 ml of water was added. The ether solution was washed twice with 50 ml of 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 hours. After addition of 100 ml 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 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 MgSO₄ and evaporated to give 4a (81%) or 4b (67%) as an oil. These oils were used without further purification.

Synthesis of 4-(5-hexen-1-yloxy)benzoic acid [5a] and 4-(2-allyl ethoxy)benzoic acid [5b].

A two necked flask equipped with a reflux condensor was charged with 60 ml acetone, 7.40 g (0.060 mol) K₂CO₃, 5.95 g (0.035 mol) 4-hydroxy ethyl benzoate and 0.035 mol tosylate 2. The mixture was heated under reflux for 24 hours. After filtration and evaporation of acetone, 100 ml ether and 50 ml 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 minutes. The solution was acidified after cooling with concentrated HCl to 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 at 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-(allyoxy)ethoxy]phenyl benzoate [6b].

A 250 ml flask was charged with 0.02 mol of 5, 20 ml of SOCl₂ and 3 drops of DMF. After stirring for one hour at room temperature (RT) the excess of SOCl₂ 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 hours at RT. After addition of 50 ml water and 80 ml dichloromethane under constant stirring, the organic layer was washed with 50 ml of 1:6 HCl/water solution. To ensure that all pyridine was removed, the solution was extracted with 50 ml of 1N 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-(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 hours. After cooling and subsequent filtration, the mixture was washed with 80 ml of a 5% aqueous solution of Na₂SO₃, 80 ml of a 5% aqueous solution of NaHCO₃ and 50 ml of a 30% aqueous solution of NaCl. The etheral layer was dried over MgSO₄ and evaporated. After recrystallization from isopropanol, a 72% yield of 7a (77% of 7b) was obtained.

7a: ¹H-NMR (CDCl₃): δ1.6 ppm (8H, m, CH₂ of butyl), 1.9 (4H, m, CH₂ of butyl), 2.5 (2H, m, CH₂ of epoxy), 2.8 (2H, t, CH₂ of epoxy), 3.0 (2H, m, CH of epoxy), 4.0 (2H, t, CH₂ of butyl), 4.1 (2H, t, CH₂ of butyl), 6.2 (2H, d, aromatic), 7.0 (2H, d, aromatic), 7.1 (2H, d, aromatic), 8.1 (2H, d, aromatic).

7b: ¹H-NMR (CDCl₃): δ2.6 ppm (2H, dd, CH₂ of epoxy), 2.8 (2H, dd, CH₂ of epoxy), 3.2 (2H, m, CH of epoxy), 3.5 (2H, m, CH₂ of glycidyl), 3.9 (6H, m, CH₂ of glycidyl and CH₂ of ethyl), 4.1 (2H, t, CH₂ of ethyl), 4.2 (2H, t, CH₂ 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-allyoxy)ethoxy]benzoate [8b].

Around 0.01 mol of 5X, 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 hours. Then 25 ml of water was added and the precipitate was filtered. The crude product was stirred for one hour with 150 ml of a 5% aqueous Na₂CO₃ solution and then washed with 100 ml 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-yl)oxy]benzoate] [9a]
and p-phenylene di[4-(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 mixture of 1:1 ethanol and ethyl acetate (77%), whereas compound 9b was recrystallized from ethyl acetate (56%).

9a: ¹H-NMR (CDCl₃): d1.6 ppm (8H, m, CH₂ of butyl), 1.9 (4H, m, CH₂ of butyl), 2.5 (2H, dd, CH₂ of epoxy), 2.7 (2H, dd, CH₂ of epoxy), 2.9 (2H, m, CH of epoxy), 4.1 (4H, t, CH₂ of butyl), 7.0 (4H, d, aromatic), 7.1 (4H, s, aromatic), 8.1 (4H, d, aromatic).

9b: ¹H-NMR (CDCl₃): d2.7 (2H, dd, CH₂ of epoxy), 2.8 (2H, dd, CH₂ of epoxy), 3.2 (2H, m, CH of epoxy), 3.5 (2H, dd, CH₂ of glycidyl), 3.9 (6H, m, CH₂ of glycidyl and CH₂ of ethyl), 4.2 (4H, t, CH₂ of ethyl), 7.0 (4H, d, aromatic), 7.3 (4H, s, aromatic), 8.1 (4H, d, aromatic).

The ¹H NMR spectra of the intermediate compounds were measured with a 80 MHz Brucker NMR spectrometer and were in all cases in accordance with the structures. For all the final products the spectra were recorded on a 200 MHz Nicolet NMR spectrometer. Tetramethyldisilane was used in all cases as the internal standard and CDCl₃ as the solvent.

B. 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 promotor, 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\textsuperscript{14} for the study of photoinitiated polymerization. The UV-radiation was carried out using a PL10W/10 lamp (\( \lambda_{\text{max}} = 365 \) nm). The light intensity, measured with an International Light 745A UV 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 by dry nitrogen. The sample weight was 0.9-1.3 mg. The conversions (\( \alpha \)) using the DSC data were calculated by dividing the measured heat of enthalpy (\( \Delta H \)) by the experimentally found value for the 100% conversion\textsuperscript{15} of epoxide group in chemically pure phenyl glycidyl ether (\( \Delta H = 93 \) kJ/eq epoxide group)

The assumption is that this value also applies to full conversion of epoxide groups in the compounds investigated by us. To justify this we have determined \( \alpha \) by a second technique, fourier transform-infra red (FT-IR). The accuracy of \( \alpha \) values measured by DSC was about 5%, whereas the rate of polymerization could be determined much less accurately (max. 10%).

FT-IR studies were performed using a Mattson Polaris (Icon software) spectrometer. During 20 seconds 8 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 \( \mu \)m. These plates were mounted in a Specac P/N 20125 temperature controller series.

\( \alpha \) was monitored by recording a FT-IR spectrum after every irradiation time. The peak area of the epoxide ring absorption was measured between 976 and 890 cm\(^{-1}\) relative to the carbonyl stretch vibration 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 rotatory 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 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).

III. RESULTS AND DISCUSSION

A. Mesomorphic properties of the monomers

The transition temperatures, enthalpies and phase behaviour of the four compounds investigated are given in table 1. They 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 (CH₂ 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 system containing diepoxides 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 containing diepoxide 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 role¹⁶,¹⁷.
Table 1. Transition temperatures and enthalpies of the monomers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C → N</th>
<th>N → I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>Δ H (kJ/mol)</td>
</tr>
<tr>
<td>7a</td>
<td>46 (52)*</td>
<td>34.9</td>
</tr>
<tr>
<td>7b</td>
<td>53 (43)</td>
<td>40.9</td>
</tr>
<tr>
<td>9a</td>
<td>119 (129)</td>
<td>22.4</td>
</tr>
<tr>
<td>9b</td>
<td>124 (120)</td>
<td>29.4</td>
</tr>
</tbody>
</table>

*) Data between brackets are from the corresponding diolifins.

Fig. 1 shows the birefringence (Δn) of the compounds 9a and 9b plotted against the reduced temperature defined as $T^* = T/T_1$, where $T$ is the actual temperature in Kelvin and $T_1$ is the nematic to isotropic transition temperature. In treating these Δn data and also subsequent data in this text, we assume that:

$$\Delta n(T) \propto \langle P_2(T) \rangle$$  \hspace{1cm} (1)

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\(^\text{18}\), 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\(^\text{19}\). Because of these difficulties we have refrained from measuring the absolute $\langle P_2 \rangle$ values. However, it is noteworthy to state 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 \( \Delta n \) which remains constant nearly up to the \( T_1 \). If this is of any statistical significance it can therefore be attributed to a difference in anisotropic polarizibility between the compounds, caused by the replacement of a methylene group (in 9a) by an oxygen atom (in 9b).

B. Photoinitiated polymerization

The initiating system used in our study consists of a diaryliodonium salt [11] and a 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 in 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 \( \alpha \)-position with respect to the epoxide
Following reaction shown in equation 6, a carbocation is again produced.

\[
\text{Ph--C--C--Ph} \xrightarrow{h\nu} \text{Ph--C}^+ + \text{C--Ph} \quad (1)
\]

\[
\text{Ph--C}^+ + \text{Ph}_2^+Q^- \rightarrow \text{Ph}--C^+Q^- + \text{Ph}_2^+Q^- \quad (2)
\]

\[
\text{Ph}--C^+Q^- + \text{R--C--X--C--C--CH}_2 \rightarrow \text{Polymer} \quad (3)
\]

\[
\text{Ph}_2^+ \rightarrow \text{PhI} + \text{Ph}^* \quad (4)
\]

\[
\text{Ph}^* + \text{R--C--X--C--C--CH}_2 \rightarrow \text{R--C--X--C--C--CH}_2 + \text{Ph--H} \quad (5)
\]

\[
\text{R--C--X--C--C--CH}_2 + \text{Ph}_2^+Q^- \rightarrow \text{R--C--X--C--C--CH}_2 + \text{Ph}_2^+ \quad (6)
\]

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

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 Bronsted 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 reaction 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 reactivity of compounds 7a and 7b in the isotropic phase at 100 °C, suggests that \(v_{\text{max}}\)
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. Apparently, the rate of polymerization is increased so strongly, by the presence of the molecular order in the nematic phase, that it actually overshadows the effect of the oxygen atom.

Table 2. The conversion (a) and rate of polymerization as determined with DSC for compounds 7a and 7b at different temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>7 a</th>
<th>7 b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_{\text{max}}$(kJ/eq.sec)</td>
<td>$\alpha$(%)$^a$</td>
</tr>
<tr>
<td>50</td>
<td>0.32</td>
<td>49.3</td>
</tr>
<tr>
<td>80$^b$</td>
<td>0.23</td>
<td>45.1</td>
</tr>
<tr>
<td>100</td>
<td>0.12</td>
<td>47.1</td>
</tr>
</tbody>
</table>

a) Samples were irradiated as long as a heat flux could be detected by DSC.
b) For the second peak $v_{\text{max}}$=0.21 kJ/eq.sec.

The 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.sec whereas the data concerning polymerization of compound 9a at about the same reduced temperature could not be determined with acceptable accuracy. It was, however, obvious that the the polymerization rate for compound 9a was much lower than that of compound 9b. These observations confirm, once more, that the presence of the oxygen atom, positioned $\beta$ to the epoxide ring, indeed leads to the increase of the polymerization rate.

Further evidence for the effect of nematic order on the rate of polymerization is provided in figure 2. This figure shows the DSC curves of isothermal measurements at various temperatures during UV-irradiation of compound 7a. In contrast with the polymerization in the liquid crystalline phase at 50 °C, the DSC 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 diacylates above the $T_i^{28,25}$. So, it is probable that transition to the liquid crystalline phase is accompanied with an increase in the rate of polymerization, leading to a second maximum as seen in the DSC 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 liquid crystalline phase is further discussed by Broer et al. 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 DSC curve could be observed (see figure 2).

![Graph](image)

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

From the effect of the nematic order on the rate of polymerization we infer that the value of activation energy for propagation is lower if the monomeric phase is ordered. This can lead to an increase in the polymerization rate$^{26}$. 

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C. FT-IR and Birefringence measurements

It is well known that termination reactions are less likely to occur in cationic polymerization provided there are no nucleophilic impurities present. Since the system is still reactive, the polymerization will continue in the dark\textsuperscript{23,27}. In order to determine the extent of this postcure reaction, real-time FT-IR measurements were conducted with compound 7a. During the irradiation the polymerization was monitored by quasi real-time FT-IR spectroscopy. As can be seen in figure 3, the conversion of the epoxide group after 10 minutes of irradiation has reached a value of 53%, which agrees well with the DSC data\textsuperscript{4}). Thereafter, the rate of polymerization falls below the detection limit of the DSC, but, as detected with the aid of FT-IR, the reaction continues to proceed in the dark (see figure 4). The fact that the reaction does not proceed to full conversion and levels off at 73% could be attributed to the possibly inhomogeneous character of the system.

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

\textsuperscript{4}) To be able to compare the DSC with FT-IR 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-IR measurements varied by up to 100 μm, it was shown by DSC that the conversion did not depend on the thickness in this range.
Figure 4. Conversion as a function of postcuring time (at 50 °C) after 16 minutes of irradiation (at 50 °C) monitored by real-time FT-IR.

The effect of the dark reaction 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 postcuring treatment.

Figure 5. The temperature dependence of birefringence (Δn) just after the irradiation (16 minutes at 50 °C) and after an additional postcuring treatment (25 hr at 50 °C) for compound 7a. Data are normalized for Δn at T= 50 °C.

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 postcuring at 50 °C as a
function of time, but, as can be seen in fig. 5, its temperature dependence is much less pronounced compared to that of the non-postcured sample. Besides, for the non-postcured sample $\Delta n$ 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 $\Delta n$ for the postcured network is demonstrated in fig. 6, where the sample has been exposed to subsequent heating and cooling runs. During the first heating some additional polymerization of 7a, has occurred. Probably a somewhat too rapid heating during this run (10 °C/min) may have caused the slight difference in $\Delta n$ 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 of $\Delta n$ connected to the changes in density and state of the order.

![Graph showing birefringence as a function of temperature](image)

*Figure 6. Birefringence of compound 7a as a function of temperature (10 °C/min) after 16 minutes of irradiation and 25 hours of postcuring at 50 °C.*

Broer et al.\(^9\) performed the photoinitiated polymerization of a similar type of liquid crystalline diepoxide with a shorter spacer segment (compound [12]):

![Chemical structure of 4,4'-Bis(3,4-epoxybuten-1-yloxy)phenylbenzoate](image)

4,4'-Bis(3,4-epoxybuten-1-yloxy)phenylbenzoate [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\textsuperscript{9}). This is in direct contrast with the results presented here which illustrates the necessity for an additional postcuring treatment in order to freeze in the orientation. An explanation for the effect of postcuring 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 (T\text{g}) of the material has reached the isothermal cure temperature (T\text{cure})\textsuperscript{28}. At this point vitrification is occurring. 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-postcured sample 7a cured at 50 °C has a T\text{g} of about 50 °C just after the irradiation, and upon heating above this temperature Δn would tend to decrease due to the higher mobility of the molecules. Simultaneously, this lower degree of order would be fixed by further polymerization. However, for the postcured samples the T\text{g} has increased because of the continuation of the reaction in the glassy state as followed by FT-IR (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\text{cure} and T\text{g} as determined by dynamic mechanical thermal analysis. We have taken DSC measurements to determine the T\text{g}, but no real transition could be observed. This observation can be attributed to the high crosslink density of the samples\textsuperscript{29}). Also, no residual reaction heat during the thermal scan just after the isothermal run could be detected by DSC.

Broer et al.\textsuperscript{9}) claimed in their publication that after the polymerization of [12] at 50 °C Δn has become almost temperature independent up to 140 °C. They derived from this observation that the T\text{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\textsuperscript{2}). It can be argued that this high intensity UV light could have led to the rise of temperature and consequently to an unintentional thermal postcuring 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, conversion of epoxide groups in compound 9b was as high as 72%, which has led to the high stability of the networks (see figure 8).

Figure 7. Birefringence (Δn) as a function of temperature (10 °C/min) after 10 minutes of irradiation at T* = 0.86 for compound 9a.

Figure 8. Birefringence (Δn) as a function of temperature (10 °C/min) after 10 minutes of irradiation at T* = 0.92 for compound 9b (after the irradiation Δn increased by 12%).

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IV CONCLUSIONS

Ordered networks are produced upon photoinitiated polymerization of low molecular weight liquid crystalline diepoxides. Postcuring reactions improved the thermal stability of the networks due to an increase in Tg. 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.

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Chapter III- Liquid Crystalline Epoxide Thermosets: Copolymerization with aromatic diamines

Abstract: 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 crosslinking reaction with the LC-diepoxide was studied by means of differential scanning calorimetry. By selecting the crosslinking agents according to their melting point 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 epoxyamine mixture is transformed from a nematic to a smectic phase, as a result of the polymerization reaction at 120 °C.

I. INTRODUCTION

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

In the chapter II, we described\(^6\) the production of such networks by photoinitiated-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 chapter II\(^6\), after retardation of the reaction rate, the chain-polymerization tends to continue in the dark almost to completion. This makes controlling of, for example, 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 (see chapter V).

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

![Chemical Structure](image-url)

\[ \text{crystal} \rightarrow \text{nematic} \rightarrow 186 \degree \text{C isotropic} \]

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 photoinitiated-polymerization of this compound was described in chapter II\(^6\).

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.

II. EXPERIMENTAL

A. Synthesis of aromatic diamines

The general route for the synthesis of epoxy compound I has been presented earlier (see chapter II6). 4,4'-Azodianiline (see table 1, compound IIIe) was supplied by Eastman Kodak (Rochester/USA) and 4,4'-diaminobiphenyl (IIIff) 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:

\[ \text{O}_2\text{N}-\text{C}^\text{=O}-\text{OH} \]

1) \text{PCl}_5
2) Pyridine/ \text{HO-X-OH}

\[ \text{O}_2\text{N}-\text{C}^\text{=O-X-O-C}^\text{=O-NO}_2 \]

II

Raney-Ni/\text{H}_2

\[ \text{H}_2\text{N- C}^\text{=O-X-O-C}^\text{=O-NH}_2 \]

III

\[ \text{X=} \begin{array}{ll}
\text{a:} & \begin{array}{c}
\text{O}_2\text{N- C}^\text{=O-} \\
\end{array} \\
\text{b:} & \begin{array}{c}
\text{CH}_3 \\
\end{array} \\
\text{c:} & \begin{array}{c}
\text{Cl} \\
\end{array} \\
\text{d:} & \begin{array}{c}
\text{O}_2\text{N- C}^\text{=O-} \\
\end{array} \\
\end{array} \]

Scheme 1. Synthetic route to the aromatic diamines.
To a 500 ml flask containing 100 ml of pyridine was added 7 g (38 mmol) of p-nitrobenzoyl chloride synthesized according to ref. 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 ref. 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% Na₂CO₃ 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 catalyst. Thus a 500 ml reaction vessel was filled with 25 mmol of a dinitro compound, 200 ml of N,N-dimethylformamide (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

1H-NMR (DMSO-d₆): 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

1H-NMR (DMSO-d₆): δ1.65 ppm (4H, m), 2.01 (4H, d, J= 7.88 Hz), 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

1H-NMR (DMSO-d₆): 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)

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

1H-NMR (DMSO-d₆): 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 1H-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 1 was determined by the 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 lenght of 546.1 nm. L could be measured very accurately (±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 <P₂> = (3cos²θ-1)/2, where θ is the angle between the molecular long axis and the director. In order to obtain <P₂>, the polymerization mixture with approximately 0.5 % (w/w) azo dye D₂ (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∥) 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. $<P_2>$ was calculated according to expression (1)

$$<P_2> = \frac{(A_{\parallel} - A_\perp)}{(A_{\parallel} + 2A_\perp)}$$  \hspace{1cm} (1)

The polarizer angle was adjusted to obtain the maximum value for $A_{\parallel}$ at $\lambda_{\text{max}}$ (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.

III. 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 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 \( T_\text{N} \) at 185.2 °C, the second phase mainly consisting of diamine IIIa starts to melt. However due to the subsequent exothermic reaction no endothermic melting peak \( T_\text{m} \) 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 \( T_\text{m} \) of 319.4 °C for this compound (see table 1). The replacement of the central aromatic ring of IIIa by a trans-1,4-cyclohexane moiety\(^{19} \) leads to a decrease of \( T_\text{m} \) by more than 20 °C (see diamine IIIb). However, figure 1b shows that the reaction still occurs well above the nematic temperature range.

**Table 1. Data concerning all the aromatic diamines studied in this chapter.**

<table>
<thead>
<tr>
<th>Com. (^a)</th>
<th>( T_\text{m} ) (^b) (°C)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>Recrystallization Solvent</th>
<th>Yield (%)</th>
<th>Solvent (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>III (II) a</td>
<td>319.4 (262.9)(^d)</td>
<td>42.3 (35.1)</td>
<td>1-Butanol/DMF (DMF)</td>
<td>94 (66)</td>
<td>DMF</td>
</tr>
<tr>
<td>III (II) b</td>
<td>297.7 (261.2)</td>
<td>51.4 (48.1)</td>
<td>Butylacetate/DMF (DMF)</td>
<td>74 (48)</td>
<td>DMF</td>
</tr>
<tr>
<td>III (II) c</td>
<td>272.0 (273.8)</td>
<td>34.3 (53.6)</td>
<td>Dioxane/DMF (DMF)</td>
<td>58 (78)</td>
<td>THF</td>
</tr>
<tr>
<td>III (II) d</td>
<td>260.7 (256.6)</td>
<td>36.9 (38.9)</td>
<td>Dioxane/DMF (DMF)</td>
<td>40 (67)</td>
<td>THF</td>
</tr>
<tr>
<td>III e</td>
<td>248.7</td>
<td>23.9</td>
<td>DCM</td>
<td></td>
<td>DCM</td>
</tr>
<tr>
<td>III f</td>
<td>130.7</td>
<td>21.9</td>
<td>DCM</td>
<td></td>
<td>DCM</td>
</tr>
</tbody>
</table>

\(^a\) Data reported in (......) are from the corresponding dinitro compounds.

\(^b\) Because of the high melting point \( T_\text{m} \), 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 (ref 25).

A further decrease of \( T_\text{m} \) can be realized by introducing a methyl group (IIIc) or chloro atom (IIIId) into the central ring of IIIa\(^{20} \). With IIIc \( T_\text{m} = 272.0 °C \) reaction occurs just outside and with IIIId \( T_\text{m} = 260.7 °C \), just inside the nematic phase (figures 1c and 1d resp.). Although IIIId seems to be suitable in principle for freezing in the LC phase, a further decrease of \( T_\text{m} \) is desirable because a lowering of the cure temperature \( T_\text{cure} \) 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'-'diaminoazobenzene (IIIe) or 4,4'-'diaminobiphenyl (IIIi) instead of the three ring systems. From figure 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 \( T_\text{m} \) at 115.9 °C. This is confirmed by the observation that a
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.

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.
Figure 1c-d (Continued).

In conclusion, by selecting the curing agent with the right $T_m$, it was possible to find a suitable mixture (diepoxyde 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 $<P_2>$ of the dichroic
dye D₂ 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 <P₂>^{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.

![Diagram showing absorption spectra](image)

*Figure 2. Absorption spectra of dye D₂ in the mixture I-III after one hour at 120 °C. The spectra are measured at RT both parallel (||) and perpendicular (⊥) to the alignment direction.*

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.

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

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 (6x10^7 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_{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 gel-point^{23,24}. 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

*) The very high rubbery modulus for some fully cured epoxy networks was attributed to the rigid character of the starting materials^{21,22}.
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 $3 \times 10^7$ Pa which corresponds to the rubbery value of $E'$ in figure 4. The fact that both $G'$ and $G''$ levell off indicates that no significant amount of reaction takes place 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.
C. Microscopy, X-ray and thermal stability investigations

Microscopy 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 connected to the increase of the order (shifting of $T_1$ to higher temperatures) as was observed by $\Delta n$ measurements.

![Image](image.png)

*Figure 6. The polarization microscope photograph (x180) of the mixture I-IIIc cured for one hour at 120 °C and then heated to 200 °C measured at RT.*

The X-ray diffraction studies confirm the microscopy 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 favour 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 (~35 Å) and that of the diamine (~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.

![Image](image.png)

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

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).
IV. 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.

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Chapter IV- Liquid Crystalline Epoxide Thermosets: A deuterium nuclear magnetic resonance study

Abstract: The orientational order for a reactive liquid crystalline epoxy-amine mixture was monitored in real-time with the aid of deuterium nuclear magnetic resonance ($^2$H-NMR) and birefringence ($\Delta n$) measurements. The orientational order increased during the chain extension process, and it became irreversibly fixed as a result of the crosslinking reaction. The order parameter of the amine compound was more sensitive to the degree of the polymerization reaction than that of the epoxide. During the isothermal polymerization, the point where $\Delta n$ started to level off corresponded well with the point of gelation as determined by solubility experiments. The relative increase of the orientational order according to $^2$H-NMR agrees with the value extracted from birefringence measurements. X-ray diffraction measurements revealed that the orientation of the network hardly changes upon heating and cooling in the absence of the magnetic field. The reaction was also monitored in quasi-real time by gel permeation chromatography (GPC) and so the nature of various species, formed during the reaction, was determined. There was a good agreement between the reaction kinetics as determined by GPC and $^2$H-NMR experiments. The conversion ($\alpha$) of the epoxy groups at the gel point agreed well with the value predicted by the statistical theory for network formation in isotropic stoichiometric epoxy-amine mixtures, namely $\alpha=55\%$. In addition, good agreement was found between the experimentally determined increase in the number average molecular weight and theoretical predictions.

I. INTRODUCTION

Ordered networks can be prepared by polymerization of low molecular weight mesogenic monomers in the liquid crystalline (LC) phase. This concept has been used by many investigators, active in the rapidly growing field of ordered networks. As the polymerizing unit a broad range of functional groups have been used like acrylates\(^1,2\) or bismaleimides\(^3\). The possibility of using epoxy groups has also been recognized\(^4\). This is because in comparison with other materials, conventional epoxy polymers have proved to be among the best as far as their mechanical and electrical properties are concerned\(^5\).

In chapter II, we studied the LC-properties of a series of mesogenic diepoxide compounds. It was shown that highly macroscopically ordered networks can be prepared by photoinitiated chain polymerization of such materials in the LC-phase\(^6\). One of the aims of our investigation was to monitor the change of physical and material properties during network formation in an orientationally ordered state. Chain polymerization reactions often proceed very fast, which makes the monitoring of the reaction in real-time difficult. As an alternative we have investigated the

\(^{*)}\) Based on: Jahromi, S., Macromolecules, 1994, 27, 2804
copolymerization reaction of a LC diepoxide monomer with several aromatic diamines (see chapter III)\(^7\). This step-addition polymerization proceeds in a slower and much more controllable fashion. The chemical reactions involved are rather specific and usually free of side reactions\(^8\). These investigations indicated that the diepoxide (I) and the diamine (II) displayed in the upper section of figure 1 are very suitable for studying network formation in the LC-state; the polymerization reaction proceeds relatively slowly at low temperatures, allowing for various real-time measurements to be carried out. Figure 1 also shows the differential scanning calorimetric (DSC) trace of a stoichiometric mixture of the two compounds. The mixture is a eutectic with the melting point at 115.9 °C, above which a nematic phase is formed. With the aid of dichroism measurements, it was shown for the first time that epoxy-amine networks with high macroscopic order can be produced by conducting the polymerization just above the eutectic melting point (i.e., at 120 °C; chapter III)\(^7\).

![DSC trace of a stoichiometric mixture of compounds I and II.](image)

*Figure 1. DSC trace of a stoichiometric mixture of compounds I and II.*

It is the purpose of the present chapter to establish how the state of ordering for this particular mixture is affected by the polymerization reaction. In this regard two stages can be distinguished. The initial stage of the reaction consists of a chain extension process which results in the so-
called sol fraction. Depending on the polymerization conditions somewhere along the reaction path, a smooth transition from the sol to a gel state starts to take place. The possibility of a transition to a glassy state (vitrification) is present. Caruso et al. claimed that chain extension of a certain linear oligomer favoured an increase in the stability of the nematic phase, whereas crosslinks between the linear chains disfavoured it. They based these conclusion on the fact that the nematic to isotropic transition temperature (TNI), measured for the network, was lower than that found for the complete polymer and higher for the oligomer. Here we examine in real-time the effect of both processes on the order.

As a first measure of orientational order, we have measured the birefringence (Δn) during the polymerization. Δn is a measure of long range orientational order, and it also provides information concerning the macroscopic order. Deuterium nuclear magnetic resonance spectroscopy (2H-NMR), on the other hand, is a powerful technique to monitor the orientational order at a molecular level. 2H-NMR has already proved to be very useful for studying systems like low molecular weight LC-compounds, side chain and main chain LC-polymers, and strained elastomers. One of the most important advantages of the 2H-NMR technique is that the observed spectra in the LC-state are very well resolved in comparison with proton (1H)-NMR spectra for example. This is because the magnetic moments of deuterons are small, which leads to small dipolar interaction, and so they can be considered, at least in the first approximation, as isolated nuclei. The main feature which then dominates the 2H-NMR spectra is the electrostatic interaction between the quadrupole moment of the nucleus with the electric field gradient (efg) around it. Nevertheless, in order to study the orientational order of the system, it is also very useful to consider the interactions between the neighbouring deuterons (the dipole interactions). The other advantage of 2H-NMR is that by isotopic substitution of the protons the molecular order can be monitored in real-time separately for each of the reacting monomers. This will be illustrated in this chapter.

The nature of various species, formed during the polymerization reaction, is determined by gel permeation chromatography (GPC). Also, the system has been characterized by viscosity and X-ray measurements.
II. $^2$H-NMR: SOME BASIC RELATIONS

In anisotropic fluid media some anisotropic magnetic and electrostatic interactions are not averaged to zero by the molecular motion. In the case of deuterons the most important are the quadrupolar interaction ($v_q$) and the dipole-dipole interaction between neighbouring deuterons (D). These can be written as

$$v_q = \frac{3}{4} \frac{e^2 q Q}{h} S((3 \cos^2 \varphi) - 1)/2$$

(1)

$$D = d S((3 \cos^2 \alpha) - 1)/2, \quad \text{where} \quad d = -\frac{\frac{\gamma_D^2 \hbar}{2 \pi^2 \mu_D}}{2 \pi^2 \mu_D}$$

(2)

In these equations $\varphi$ and $\alpha$ are respectively the angle that the C-D bond and the radius vector $r_{DD}$ connecting the two deuterons make with the long molecular axis. The angular brackets denote the average over all molecular conformations. The quadrupolar coupling constant $\frac{e^2 q Q}{h}$ for deuterons bonded to unsaturated carbons is around 185 kHz[17]. In equation 2 with $r_{DD}=2.487 \ \AA$, $\frac{\gamma_D^2 \hbar}{2 \pi^2 \mu_D}=5663.\text{Hz.Å}^3$ (see ref. 18). $S$ denotes the orientational order parameter of the long molecular axis with respect to the director which is identified as the direction of the magnetic field when the magnetic susceptibility is positive. In writing these equations several assumptions have been adopted. (1) The efg tensor is axially symmetric around the C-D bond. (2) The symmetry of the liquid crystal is considered to be unaxial. (3) The LC-molecules can be approximated to a rigid cylindrical rod whose symmetry is parallel to the long molecular axis. The important issue is whether the last two assumptions will hold throughout the polymerization reaction. Some evidence in favour of these simplifications will be presented later in this paper. In the following we have also assumed that the effect of the director fluctuations is negligible.

The perturbation of the $^2$H-NMR spectra due to the dipolar interaction could be observed in one case at the start of the reaction where
the viscosity was still low, thus resulting in small linewidth. However, the spectra were usually dominated by quadrupolar interactions which resulted in the splitting of the signal coming from each type of deuterons into a doublet with the spacing of:

\[ \Delta = 2v_q = \frac{3 e^2 q Q}{2} \frac{S((3 \cos^2 \varphi) - 1)/2}{h} \]  

(3)

III. EXPERIMENTAL

The synthesis of epoxide compound I has been described chapter II\(^8\):
Epoxy value = 3.48 equivalent/Kg (theoretical value: 3.63 equivalent/Kg)
The deuterated diepoxide was synthesized by using hydroquinone-d\(_4\) (MSD ISOTOPES, Montreal, Canada). 4,4'-diaminobiphenyl (II) was supplied by RPL (Leuven, Belgium) and was used without further purification (purity >
98%). The deuterated diamine was supplied by MSD ISOTOPES (Montreal, Canada).

To prepare the polymerization mixture a stoichiometric amount of the diepoxide (2 mol) and the diamine (1 mol) was dissolved in dichloromethane. The solvent was then removed under reduced pressure at room temperature (RT). In order to ensure a homogeneous mixing of the two components, after evaporation of the solvent, the mixture was stirred mechanically for ca. 1 min. at 120 °C and then quenched to RT. For the \(^2\)H-
NMR measurements, nomally ca. 10 % (w/w) of the corresponding monomer was deuterated.

\(^2\)H-NMR spectra were recorded at 61.4 MHz on a Varian VXR-400 S spectrometer. The spectra were obtained by Fourier transformation of the free induction decay (FID). Typically 200 FIDs were accumulated. The polymerization mixtures were placed in a 5 mm tube. The NMR probe was equilibrated at the 120±1 °C before inserting the NMR tube and starting the measurements. The system was homogeneously aligned by the magnetic field (9.4 T) immediately after melting into the LC phase. This was manifested by the sharpness and symmetry of the NMR peaks\(^19\).

The conversion of epoxy groups up to the gel point was determined by \(^1\)H-NMR. The reaction mixtures, cured for various times at 120 °C, were dissolved in dimethylsulfoxide (DMSO). The spectra were measured with a
Varian VXR 400 S. The conversion was calculated from the decrease in the intensity of the epoxy ring protons at 2.77 ppm relative to the intensity of the aromatic part at 8.09 ppm (relative accuracy of 5%). The conversion beyond the gel point (87 % after 1 hour at 120 °C) was determined by potentiometric titration of the remaining epoxy groups.

Number average molecular weights (M_n) were determined by GPC with tetrahydrofuran as eluent using a UV-detector operating at 279 nm. At this wavelength the extinction coefficients for both diepoxide and diamine were equal. The Ultrastyragel column of 10^3 Å pore size was calibrated with monodisperse polystyrene standards. The experimental conditions for measurements of Δn (relative accuracy 2-3 %), wide angle X-ray diffraction, and melt viscosity have been reported in chapter III[7].

IV. RESULTS AND DISCUSSION

A. $^2$H-NMR spectra measured continuously during the polymerization reaction.

The $^2$H-NMR measurements were conducted in two separate experiments. In the first the orientational order of the epoxide, deuterated in the central aromatic ring was monitored during the copolymerization reaction with the non-deuterated amine. In the second experiment the behaviour of the deuterated amine was investigated. Both experiments were carried out at 120 °C, inside the NMR probe, under exactly the same conditions. In the following we assume that the quadrupolar splitting (Δ) as a function of the polymerization time is directly proportional to the orientational order of the long molecular axis with respect to the director, an assumption which is proved to be justified later in the text.

EXPERIMENT 1:

Figure 2 shows the $^2$H-NMR spectra of the deuterated epoxide measured as a function of time at 120 °C which is the temperature just above the eutectic melting point. The monitoring of the reaction at higher temperatures becomes increasingly difficult because of the high reaction rates. Ignoring for the moment the dipolar fine structure, the first spectrum in figure 2 consists of a sharp doublet, indicating that the four deuterons
Figure 2. $^2$H-NMR spectra of the deuterated diepoxide measured as a function of copolymerization reaction time at 120 °C with the protonated diamine.
are equivalent on the NMR time scale because of, for example, 180° rotational jumps of the central ring (see figure 3). This type of motion seems to be common for phenyl groups, indeed this mechanism has also been suggested to operate in, for example, low molecular weight LC-systems\textsuperscript{20,21} and side chain LC-polymers\textsuperscript{22,23}.

![Figure 3. Structural formula of the diepoxide I deuterated in the central aromatic ring](image)

The quadrupolar splittings determined directly from the spectra, are shown in figure 4. At the start of the reaction $\Delta$ increases linearly with time until the rate is drastically reduced at 13 minutes. Under the polarization microscope a clear nematic (N) to smectic (S) transition (N→S) was observed around the same reaction time at 120 °C\textsuperscript{7}. The transition found in the NMR experiment could then be attributed to the formation of the smectic phase. From figure 4 it follows that the molecular order in the nematic phase is very sensitive to the degree of the polymerization and although the reaction seems to proceed continuously into the smectic phase (see figure 5), the dependency in the smectic phase on the chemical conversion is much less pronounced. Evidently the molecular order in the smectic phase has already reached a high value so that it becomes rather insensitive to the further reaction.

We now consider the dipolar structure which can clearly be observed at least up to the N→S transition. The form of a \textsuperscript{2}H-NMR spectrum for two equivalent deuterons with quadrupolar and direct dipolar interactions is predicted to consists of a quadrupolar doublet with each line split into three components, with relative intensities of 2, 3 and 1 and with frequencies relative to the centre of gravity of +(3/2)D, -(1/2)D, and -(3/2)D\textsuperscript{20}. The computer simulation of such a three component peak has revealed that the observed line shape in figure 2 can be reproduced to a good approximation by varying just the ratio L/D, where L is the linewidth. In figure 6, the linewidth of a member of the quadrupolar doublet, measured directly from the spectra (figure 2), is plotted as a function of polymerization time at 120 °C. The line broadening could be the result of various mechanisms,
Figure 4. Time dependence of the quadrupolar splittings (Δ) as determined from figure 2. The increase in scattering of the data points is connected with the extensive line broadening during the polymerization reaction.

Figure 5. Conversion of the epoxy groups (α) measured up to the gel point as a function of the polymerization time at 120 °C.

operating either simultaneously or not in these reactive systems\textsuperscript{19}. In the first place L broadens due to the increase of the degree of ordering. However, the contribution of this effect seems to be small, because in the nematic phase, where S is rapidly increasing, L is almost constant.
Figure 6. Linewidth of the $^2$H-NMR spectra measured directly from figure 2 as a function of time.

Also the correlation times for different type of motions, like rotation and reorientation of the long molecular axis, are expected to increase as a function of the degree of the polymerization, which is reflected in the increase of the viscosity of the system\textsuperscript{12). Figure 7 shows the variation of complex viscosity ($\eta^*$) as a function of reaction time at 120 °C. Of course the rheological behaviour of liquid crystals is quite complicated and $\eta^*$ is not sufficient to represent fully the viscosity of the system. In the present case $\eta^*$ is believed to give a value representative for the degree of the conversion. By comparing figure 6 with figure 7 it becomes clear that both L and $\eta^*$ start to increase in the vicinity of the $N\rightarrow S$ transition until they level off after about 40 minutes.

It would be interesting to examine how in the present case the $^2$H-NMR spectra are affected by the process of gelation. Frequency dependent rheological measurements have shown that the system, at 120 °C, starts to gel at 27±1 minutes (see chapter V)\textsuperscript{24). This corresponds well with the time where the material becomes insoluble in DMSO. Furthermore, the conversion of the epoxy groups at the gel point (55±3 %) agreed with the
value predicted by a statistical approach for a isotropic epoxy-amine mixture; depending on the relative reactivity of the secondary \(K_2\) to the primary \(K_1\) amine hydrogens, the gelation occurs between 50 % \(K_2/K_1\rightarrow0\) and 61.8 % \(K_2/K_1\rightarrow\infty\)\(^{25}\). Dynamic mechanical measurements have also shown that at 120 °C the material does not transfer to the glassy state for at least 2 hours of reaction time (see chapter III and V)\(^{7,24}\), because the glass transition temperature is still below the curing temperature\(^{26}\).

The influence of the crosslinking reaction on the chain mobility and chain conformation are the most important issues when considering the possible effect of gelation on the observed \(^2\text{H}-\text{NMR}\) spectra. Beltzung et al.\(^{27}\) demonstrated with the aid of small-angle neutron scattering that the chain dimensions did not change as a result of the crosslinking reaction in a melt of poly(dimethyl siloxane) chains. In the case of \(^2\text{H}-\text{NMR}\) experiments performed on flexible poly(propylene oxide-\text{d}_6) elastomers some increase of the linewidth upon the crosslinking reaction was observed, which was attributed to the incompletely averaging of the quadrupolar interactions once the chain mobility is restricted by anchoring the chain ends (by a covalent reaction)\(^{28}\). In the present case, as can be seen in figure 6, \(L\) is rather insensitive to the process of crosslinking. Apparently the macroscopic phenomenon of gelation is hardly detectable by \(^2\text{H}-\text{NMR}\) which is probing the system on a molecular level.
The line broadening can also be the result of disturbances of the director alignment during the polymerization reaction\textsuperscript{19}. In figure 8 the $^2$H-NMR spectra at the beginning and the end of the reaction at 120 °C are compared. After 99 minutes the spectrum is asymmetrically broadened, which indicates that this mechanism, operating simultaneously with the previous one, is responsible for the observed line shapes as well.

![Figure 8. $^2$H-NMR spectra taken from figure 2 after 2.5 and 99 minutes of reaction time.](image)

From the measured values of the quadrupolar splittings we can determine the order parameter of the long molecular axis ($z$), provided that the molecular geometry and in particular the angle between the phenyl para axis and $z$ ($\alpha$) is known. An estimate of this angle can be obtained from the ratio of the dipolar interaction of the two neighbouring deuterons and their quadrupolar splitting ($R = D/\Delta$)\textsuperscript{16,20}. In figure 9 the values of $R$ in the nematic and the beginning of the smectic phase is plotted as a function of time at 120 °C. $D$ is determined from figure 4, assuming that the distance between the two maxima on each member of quadrupolar doublet equals 2D. The reported values could be an overestimation by as much as 10%.

As can be seen in figure 9 the values of $R$ are nearly constant, indicating that $D$ and $\Delta$ are probing the degree of orientation to the same extent. As stated before, the four deuterons in figure 3 are equivalent, owing to rapid 180° rotational jumps of the central ring about the para axis. This motion modulates the orientation of the CD bond relative to $z$ from 60°+$\alpha$
to 60° - α, and so according to equations 2 and 3, the ratio R can be written as 16,20):

$$R = \frac{D}{\Delta} = \frac{d(3\cos^2\alpha - 1)}{q\frac{1}{2}[3\cos^2(60^\circ + \alpha) - 1 + 3\cos^2(60^\circ - \alpha) - 1]}$$

where \( q = \frac{3e^2qQ}{2h} \)  \hspace{1cm} (4)

Solving equation 4, using the data given in figure 9, an angle of 15° is calculated for the first 15 minutes of reaction. This is in good agreement with the value of 16° which was obtained from molecular modeling of a LC-diacyrate compound with the same mesogenic group 29). The values of S, shown in figure 10a, were determined using α=15°. In order to evaluate the accuracy of these results, it would be worthwhile to compare the calculated values of S just at the start of the reaction with the values reported in the literature for similar mesogenic groups at the same reduced temperature T*/T_1. The comparison becomes somewhat difficult because in our case T_1, as a function of the degree of the polymerization, is continuously shifting towards higher temperatures 7,24). Nevertheless, very fast DSC scans have shown that T_1 of the unreacted mixture is about 180 °C. Other investigators
using various techniques\textsuperscript{12,30} for similar systems found a value of around 0.7, at $T^* = 0.87$, which is much smaller than the values reported in the beginning of figure 10a. Also the calculated values at the end of reaction are, of course, unrealistically high. By taking into account that the values of D could be overestimated by 10\%, an angle of $13^\circ$ is calculated. With the aid of the same procedure, Luz and co-workers\textsuperscript{16,20} determined an angle of 8-12\% for a series of two and three ring compounds.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure10.png}
\caption{Values of $S$ calculated from the data in figure 4 taking $\alpha = 15^\circ$ (a) and $\alpha = 13^\circ$ (b)}
\end{figure}

The data reported in figure 10b, using $\alpha = 13^\circ$, seems to be much more reasonable. However, although it is obvious that the degree of order is high, it remains quite difficult to determine the absolute values of $S$ because of the lack of knowledge of the molecular geometry. The situation is aggravated by the fact that the curve $(3\cos^2\varphi - 1)/2$ is very steep around $\varphi = 60^\circ$, which is roughly the angle between the CD bond and z. This means, according to equation 3, that a small deviation from the actual value in this region will have a large effect on the calculated $S$\textsuperscript{31}.

\section*{EXPERIMENT 2:}

Figure 11 displays the measured $^2$H-NMR spectra of the diamine, deuterated in the aromatic part (see figure 12), as a function of polymerization time at 120 °C. At the beginning of the reaction two sharp doublets are measured, corresponding to the $^2$H-NMR spectrum of the
Figure 11. $^2$H-NMR spectra of the deuterated diamine measured as a function of copolymerization time at 120 °C with the protonated diepoxide. As can be seen, some reaction has occurred during preparing of the polymerization mixture and filling the NMR tube. One can also recognize some similarities with figure 2 (i.e., A levels off also in this experiment in the vicinity of the $N\rightarrow S$ transition).
unreacted diamine. It is believed that the presence of the amine groups have perturbed the molecular geometry, resulting in two sets of non-equivalent deuterons. Also, the value of the quadrupolar constant could be affected by the presence of the amine groups\textsuperscript{10}. However, the observed difference between the two doublets corresponds to a variation in $\varphi$ of no more than $1^\circ$, indicating that the perturbing effect of the amine groups on the geometry is probably the dominating factor.

![Structural formula of the diamine II deuterated in the aromatic part.](image)

Because the two doublets have the same intensity and considering the molecular symmetry of the compound, the signals correspond either to the four inner deuterons (D\textsubscript{1}) or to the four outer ones (D\textsubscript{2}). Without specific deuteriation, it seems rather an impossible task to give an exact assignment to the signals, but this is not important for our discussion. From figure 11 it is obvious that the peaks corresponding to the unreacted amines decrease in intensity as a function of time and that somewhat similar double doublets appear with larger quadrupolar splittings. However, the intensities

![2H-NMR spectrum taken from figure 11 after 8 minutes of polymerization time. In this figure the various peaks can be identified as coming from unreacted amine (A\textsubscript{1}, A\textsubscript{2}), epoxyamine dimers (D\textsubscript{1}, D\textsubscript{2}), and higher molecular weight compounds (P\textsubscript{1}, P\textsubscript{2}).](image)
of the two larger doublets are not equal implying that these signals cannot be attributed to the same species. In fact, a more careful analysis indicates that during the reaction the $^2$H-NMR spectra consist of a maximum of three double doublets, corresponding to unreacted amine (A), epoxy-amine dimers (D), and higher molecular weight compounds (P). Although some of the peaks overlap, the various components can still be recognized in figure 13, showing the $^2$H-NMR spectrum measured after 8 minutes of polymerization time. In this figure the numbers 1 and 2 correspond to the inner and outer doublets, respectively. According to this interpretation, the intensities of the peaks $A_1$ and $P_2$ correspond directly to the amount of respectively unreacted amines and higher molecular weight compounds. The difference between the intensities of $P_2$ and $P_1 + D_2$, peaks, is taken as a measure of the concentration of dimers formed during the polymerization reaction. The relative concentration of all the compounds are displayed in figure 14 for the first 15 minutes of reaction time. The intensity for each compound is normalized relative to its highest value. The concentration of diamine and higher molecular weight species is decreasing and increasing respectively, during the polymerization. The concentration of the dimers increases up to the first 5 minutes of reaction, and then starts to decrease until it almost disappears after 15 minutes. The course of the polymerization, as depicted here, corresponds to a step-addition reaction.

![Graph showing the variation in normalized intensity over time for different compounds during polymerization](image)

Figure 14. Variation in the relative concentration of various compounds during the polymerization reaction. The data were extracted from figure 11.
With the aid of GPC it is also possible to monitor the reaction in a quasi real-time manner, determining the relative concentrations of various compounds formed (see figure 15). The peaks assigned with letters A, E, D, and P, correspond to the diamine, diepoxide, epoxy-amine dimers, and higher molecular weight species, respectively. The assignments in figure 15 are made inspite of the slight deviation of the measured molecular weight from the actual values owing to experimental artefacts.

![Figure 15. The composition of the polymerization mixture during the first 16 minutes of reaction time at 120 °C (measured with a interval of 2 minutes). The peaks marked with the letters A, E, D and P correspond to the amine monomers, epoxy monomers, epoxy-amine dimers and higher molecular weight compounds respectively.](image)

Except for the epoxide monomers, a comparison can be made between the relative variations of these peaks and those of the corresponding signals in the $^2$H-NMR experiment 2. Parts a-c of figure 16 show that there is good agreement between the relative concentration of the compounds A, D and P as determined by NMR and GPC experiments. This proves that the interpretation of $^2$H-NMR spectra in figure 11 is correct. For the dimers (figure 16b) the agreement is somewhat less satisfactory, because of the assumptions made concerning the peak intensities in the $^2$H-NMR and GPC experiments.
Figure 16. Comparison between the variation of the relative concentration of various compounds as determined by GPC and $^2$H-NMR; (a) unreacted amine monomers; (b) epoxy-amine dimers; (c) higher molecular weight compounds.
As can be seen in figure 15 the peak corresponding to the higher molecular weight compounds is rather broad. This could be the reason why the components of higher molecular weight cannot be observed separately in figure 11. The possibility also exists that after a certain degree of polymerization the system becomes, as far as the orientational order is concerned, rather insensitive to further polymerization. Figure 17 also displays the theoretical values of $M_n$ calculated using

$$ M_n = \frac{n_A M_A + n_E M_E}{1 - 2n_E \alpha_E} \quad (5) $$

Where $M_A (M_E)$ is the molecular weight of the diamine (diepoxide), $n_A (n_E)$ is the molar ratio of the diamine (diepoxide), and $\alpha_E$ is the conversion of the epoxy groups. As $M_n$ is only sensitive to the number of the bonds formed, the reasonable agreement between the experimental and theoretical values indicates that only the reaction between the epoxy and amine groups contributes to the polymerization and consequently no side reactions occur.
In figure 18 the values of S are plotted as a function of time for unreacted amine, dimer and higher molecular weight compounds. For the calculation of S in all cases the values of $\Delta$ for the larger splittings are taken with $\varphi=60^\circ$. This gave the best agreement between S of the free amines at the start of the reaction and the corresponding values for the similar two-ring dye molecules in low molecular weight LC-mixtures$^{32,33}$ at the same $T^\star$. Nevertheless, in this case also the same limitations apply as explained in the previous section.

As can be seen in figure 18 the order increases on going from unreacted amines to epoxy-amine dimers and higher molecular weight compounds. In this regard the nature of the spacer part, connecting the mesogenic groups, could play an important role. A distinct odd-even effect, concerning the orientational order, has already been shown to exist in LC-dimers consisting of a flexible core, linking two rigid groups$^{34}$. Similar effects were observed in main-chain LC polymers comprising a rigid mesogenic core and a flexible spacer in a repeating unit$^{35}$. In all these
studies relatively simple aliphatic chains were used as the flexible part, whereas in our case the nature of the spacer is quite complex. Also the

\[ S \]

\[ \Delta (\text{kHz}) \]

0 20 40 60 80 100

\( \Delta \) (kHz)

\( S \)

Time (min)

\[ \Delta \] (kHz)

Monomer

Dimer

Polymer

Figure 18. Values of the order parameter \( S \) calculated for the deuterated aromatic part of the amine; also the corresponding values of \( \Delta \) are displayed.

mesogenic groups connected by the spacer are not similar. Therefore, a direct comparison between the LC-dimers (polymers) from the literature and the present system is not possible. It seems worthwhile to study systematically the effect of the spacer length on, for example, the relative variation of the orientational order during the polymerization reaction. The influence of the spacer length was shown to be small on the orientational order of the networks, prepared by photoinitiated polymerization of low molecular weight LC-diacylates\(^{30}\).

The slope (P) of the curves in figure 18 is a measure of the sensitivity of the order of the deuterated amines for the degree of the polymerization. In the nematic phase P for the unreacted amine is 0.47 kHz/min, which is somewhat lower than the value for the higher molecular weight compounds (0.57 kHz/min). In both cases these values are about twice as large as the P determined from figure 4 for the deuterated epoxide also in the nematic phase (0.24 kHz/min). Evidently the order of the epoxide monomeric unit is
less sensitive to the degree of polymerization because of the action of the spacer segment, which decouples the mesogenic part from the reaction site. In view of the inaccuracy connected with the absolute values of \( S \), no comments can be given on the level of ordering of the amine as compared with that of the epoxide.

**B. Birefringence and wide angle X-ray diffraction measurements**

Figure 19 displays the variation of \( \Delta n \) during the polymerization reaction carried out isothermally at various isothermal temperatures. As \( \Delta n \) is directly proportional to \( S^{36} \), the ratio of \( \Delta n \) at the start and the end of the reaction at 120 °C should correspond to the relative increase of \( \Delta \) measured in \( ^2\text{H}-\text{NMR} \) experiment 1 and 2. The agreement between the two techniques seems to be quite good; \( \Delta n \) has increased by a factor of 1.65 as compared with an increase of \( \Delta \) by 1.73. The latter is calculated from \( ^2\text{H}-\text{NMR} \) experiments 1 and 2 by taking into account the molar ratio of the two compounds. Consequently the assumption made earlier, that the measured \( \Delta \) during the polymerization is directly proportional to the orientational order of the long molecular axis, is indeed reasonable.

![Figure 19. Change of birefringence (Δn) as a function of time at different cure temperatures.](image)

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Microscopic observations, between crossed polarizers, have revealed that the mixture is transformed into a smectic phase also at cure temperatures up to 150 °C. At higher temperatures the mixture remained nematic during the polymerization reaction. The variation of \( \Delta n \) seems to be influenced only slightly by the N→S transition in contrast with \(^2\)H-NMR experiments 1 and 2 where this transition could clearly be observed. Figure 20 shows that there is a very good agreement between the time that the \( \Delta n \) values start to level off at various cure temperatures and the point of gelation determined by solubility experiments in DMSO. This means that in this system the orientational order increases during the chain extension process up to the point where it becomes fixed by the action of the crosslinks.

![Figure 20. Point of gelation, estimated from the solubility experiments in DMSO and \( \Delta n \) measurements, as a function of cure temperature.](image)

The increase of the orientational order as a function of the degree of polymerization has also been observed in several oligomeric and polymeric systems\(^{37,38}\). Clearly this is connected with the increase of the mesogenic potential of the monomers as a result of the chain extension; the nematic to isotropic transition temperature (\( T_i \)) increases as a function of the degree of the polymerization and so the reduced temperature (\( T^*=T/T_i \)) decreases.
and the order increases. However, this does not always have to be the case, as in comparable systems, where the reaction center was located in the middle of the LC molecule, the mesogenic potential of the monomers actually decreased\textsuperscript{39}. Some theoretical work concerning the influence of gelation on the state of order predicts that crosslinking in the nematic and isotropic phase should respectively raise and lower $T_{I}\textsuperscript{40,41}$. This seems to be in contradiction with the present results, which demonstrate that the role of the crosslinking process is simply to freeze in the order. The discrepancy in the results is probably caused by the fact that these theories are developed for networks which consist of chains having a Gaussian character. It is more reasonable to approximate the present network as a system consisting of stiff rods.

At 120 °C and at 140 °C $\Delta n$ reaches the same plateau value whereas at 160 °C it levels off at a somewhat lower value. This suggests that at cure temperatures up to 140 °C a maximum level of order is achieved. However, this does not necessarily mean that $S$ at these temperatures approaches the limiting value of 1. The possibility exists that the maximum achievable level of orientational order is limited by geometrical constraints. Indeed the order parameter of an added dye guest was only about 0.8 after 1 hour of reaction time at 120 °C\textsuperscript{7}. However this value could have been somewhat higher if the dye molecules were chemically attached to the network. In the case of the photoinitiated crosslinking of mesogenic diacrylates, $\Delta n$ decreased during the polymerization reaction at temperatures just above the melting point and increased at higher cure temperatures\textsuperscript{2}. From these observations it is concluded that some of the order is lost when the monomer is polymerized at the highest initial state of order. Comparison with the present system is difficult because acrylates polymerize in a different manner. For example, it is known that gelation for these systems already occurs at a very low degree of conversion\textsuperscript{30}.

Figure 21a shows the X-ray diffraction pattern (measured at RT) of the $^2$H-NMR sample obtained by the reaction at 120 °C. The X-ray and microscopic studies of the same (non-oriented) material pointed to the existence of a $S_A$ structure (see chapter III)\textsuperscript{7}. As can be seen in figure 21a the wide-angle crescents are located in a direction perpendicular to the magnetic field, indicating that the mesogenic groups are oriented in the direction of the field as assumed in the analysis of the NMR data. Also some weak reflections, the origin of which is a point of discussion, can be
observed on the equator. Figure 21b displays the X-ray pattern of the same material as in figure 21a, with the exception that the network has undergone a thermal treatment (10 °C/min to 200 °C) in the absence of a magnetic field. The macroscopic order of the material has hardly been altered even though most of the post-curing process took place while the system remained in the rubbery region; the maximum in tan δ occurs at 95 °C after 1 hour of reaction at 120 °C and it shifts by almost 30 °C after the thermal treatment\(^7\). Similar behaviour concerning the state of order was observed with the aid of temperature dependent \(\Delta n\) measurements\(^7\). The high stability of the ordered state can be attributed to the action of the crosslinks, which have locked in the macroscopic order and prevented a multi-domain structure. It is noteworthy that the variation of \(\Delta\) in both \(^2\)H-NMR experiments was quite reversible after cooling to RT and heating back to 120 °C.

Figure 21. Wide angle X-ray diffraction pattern taken after 1 hour at 120 °C (a) and after the material has undergone an additional postcuring treatment in the absence of the magnetic field (b). Both measurements were carried out at RT.
V. CONCLUSIONS

The orientational order of both reacting monomeric units in our LC epoxy-amine system increased during the chain extension step and became irreversibly fixed upon cross-linking. The gel point could hardly be detected by $^2$H-NMR. Birefringence measurements, on the other hand, were more responsive to the macroscopic process of gelation; the point where $\Delta n$ started to level off, during the isothermal polymerization, corresponded well to the onset of gelation. Owing to the effect of the spacer segment, the orientational order of the diepoxide was influenced to a lesser extent by the copolymerization reaction than the orientational order of the diamine. During isothermal polymerization, at 120 and 140 °C, the maximum level of orientation is achieved. However, this does not necessarily mean that the degree of order of the networks equals 1. The order of the networks hardly changes upon subsequent cooling and heating in the absence of the magnetic field.

The network formation in the ordered state seems to proceed in a statistical manner, as both the position of the gel point on the conversion scale and the increase of the number average molecular weight, agree well with the theoretical predictions.

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Chapter V- Liquid Crystalline Epoxide Thermosets: Dynamic mechanical and thermal properties

Abstract: Dynamic mechanical and thermal properties of a liquid crystalline (LC) diepoxide crosslinked with three different aromatic diamines were studied. For one epoxy-amine mixture, the position of the gel point was determined with the aid of frequency dependent rheological measurements. The value of the critical relaxation exponent was 0.5. The gel point was also determined by solubility experiments. There was a clear agreement between the two methods. The degree of conversion of the epoxy groups at the gel point (55% ±3) corresponded well with the value predicted by the statistical theory for network formation in isotropic stoichiometric epoxy-amine mixtures. Mechanical measurements were carried out on macroscopically ordered networks in the direction of orientation. In highly ordered networks, prepared from the LC diepoxide and a rigid aromatic diamine, the value of rubber modulus deviated from the predictions of rubber elasticity theory by a factor of 30 times higher. In networks, with the same high level of macroscopic orientation, prepared from the LC diepoxide and a relatively more flexible diamine, the deviation from the classical theory was much less (factor 1.7). In the rubbery region, the value of Young's elastic modulus decreased as a function of temperature which seems to be connected to the decrease of the order. This is confirmed by a theory, presented by T. Odijk, concerning the polymer nematic gels under tension (see appendix). The thermal expansion coefficient of the macroscopically ordered networks was highly anisotropic. It was indeed possible to combine the good mechanical and thermal properties of conventional epoxy polymer networks with the special features that LC polymers offer.

I. INTRODUCTION

Epoxy networks are widely applied as engineering thermosets, because of their good mechanical and thermal properties. Recently it has been recognized that these properties could be greatly enhanced if liquid crystalline (LC) like structures are incorporated into the epoxy networks.

It is common knowledge that LC main chain polymers show a high modulus and a very low thermal expansion in the direction of the macroscopic orientation. In the direction transverse to the orientation of the chains, however, the properties are rather poor. These differences can be reduced by the introduction of crosslinks between the chains which improves the dimensional stability of these ordered systems.

Although there have been several attempts, it has not yet been possible to produce epoxy networks with both high crosslink density and high macroscopic order. The basic idea has been, in nearly all these studies, to polymerize and crosslink low molecular weight mesogenic monomers in the mesophase which leads then to the fixation of the LC order. It seems

*) Based on: Jahromi, S., Kuipers, W.A.G., Norder, B., Mijs, W.J., Macromolecules. Accepted
almost trivial to state, but the existence of the macroscopic order is essential, when highly anisotropic bulk properties are desired. This point has not always been appreciated in the current literature\textsuperscript{7,8}.

In chapter II, we described the synthesis and LC properties of a series of mesogenic diepoxide compounds\textsuperscript{9}. It was shown that highly macroscopically ordered networks can be prepared by photoinitiated chain polymerization of these monomers in the LC phase. The reaction, however, proceeds in quite an uncontrolled manner; the network formation continues in the dark for a long time. This makes control of, for example mechanical properties, which are directly related to the degree of conversion, very difficult. Alternatively we showed, for the first time, that highly crosslinked epoxy networks with a high macroscopic order can also be produced by copolymerization with aromatic diamines (see chapter III)\textsuperscript{10}. This step growth polymerization proceeds in a much more controllable fashion\textsuperscript{11}. Also, the chemical reactions involved are rather specific.

From these investigations it followed that LC diepoxide (I) was the best monomer for producing ordered networks by copolymerization with aromatic diamines partly because of its broad nematic range:

\[
\begin{align*}
\text{crystal} & \xrightarrow{124 \degree C} \text{nematic} \quad \xrightarrow{186 \degree C} \text{isotropic}
\end{align*}
\]

Further studies showed that, owing to the action of the short spacer segment, which decouples the reaction center from the mesogenic part, the orientational order of the diepoxide is less sensitive to the degree of polymerization in comparison with that of the diamine A-1 (see table 1 and chapter IV)\textsuperscript{12}. In addition, comparison of the reactivity of the epoxy group in compound I with that of compounds where the epoxy groups are connected to the mesogenic group without the short spacer segment (indicated in structure I) revealed that the presence of a spacer also lowers the reactivity of the epoxy groups: upon melting there is sufficient time to orient the reactive LC mixture macroscopically, before a substantial amount of reaction takes place\textsuperscript{13}. This is probably related to the activating effect of the aromatic group which diminishes upon insertion of the spacer segment.
Also, addition of the spacer lowers the melting point of the diepoxide by almost 62 °C, so that the reaction can be carried out at moderate temperatures. Indeed the copolymerization of spacerless epichlorohydrine-bisphenol based low molecular weight LC diepoxide compounds with aromatic diamines, as was carried out by Barclay et al.⁵, resulted, even under the influence of a very strong magnetic field (13.5 T), in networks with a very low degree of macroscopic orientation. The local level of orientation, on the other hand, was high in view of the fact that the mixture transformed from the nematic phase to the higher order smectic phase during the polymerization. Consequently the authors rightly concluded that, as result of the high reaction rates, the polydomain structure became fixed before the macroscopic orientation could be fully achieved. This situation is aggravated by the fact that the LC order can also increase the rate of the polymerization (see chapter II)⁹,¹³.

Recently Mallon and Adams studied the copolymerization of a LC diepoxide, containing a spacer segment between the epoxy group and the mesogenic part, with aromatic diamines⁸. Although the mesogenic parts were the same, the LC diepoxide synthesized by Mallon and Adams differs from our compound in one essential respect: in contrast to compound I, there is no oxygen atom present in the position β to the epoxy group. In our investigations on photoinitiated polymerization, we demonstrated that replacement of a methylene group by an oxygen atom, in the position β to the epoxy group, leads to an increase of the reactivity, resulting in densely crosslinked networks which maintain their orientation up to 300 °C⁹. Similar observations were made when the polymerization was carried out with aromatic diamines¹³. Mallon and Adams reported that even after prolonged curing the networks, prepared from stoichiometric ratio of the LC diepoxide and a certain aromatic diamine, displayed smectic to nematic and even in some cases LC to isotropic transitions. This behaviour is characteristic for networks with a low crosslink density. Furthermore, the networks prepared by Mallon and Adams were inhomogeneous since the regions of isotropic, nematic and smectic phases were all coexisting during the polymerization reaction. As phase separation is a kinetically controlled process, it can be argued that, because of the low polymerization rates, the system is prone to become inhomogeneous during the polymerization. Also, it is our experience that the initial mixing process of the two reactive compounds plays an important role in producing well defined networks. The networks prepared by copolymerization of the diepoxide I with aromatic
diamines were all homogeneous and showed no thermal transitions after a short period of curing (see chapter III).\textsuperscript{10}

Summarising, we can state that the LC diepoxide I is a suitable compound for producing ordered networks by copolymerization with aromatic diamines because it has a broad nematic range and the reactivity of the epoxy groups is low enough in order to orient the system macroscopically but also high enough to produce networks with a high crosslink density.

When considering the properties of ordered networks, there are two topics that are of prime importance. In the first place, of course, the state of order of these systems and possible change of the level of orientation as a function of the degree of polymerization and crosslinking should be investigated. In chapter IV, we monitored the copolymerization reaction in real time with the aid of deuterium nuclear magnetic resonance (\textsuperscript{2}H-NMR) in combination with birefringence measurements\textsuperscript{12}. The main conclusion from these investigations was that the orientational order increased during the chain extension process and it became irreversibly fixed as a result of the crosslinking reaction.

The second point of interest, which is also the subject of the present chapter, is the elastic behaviour of ordered networks. The rigid character of the monomers and the ordered structure are the two main factors which distinguish the networks, discussed in this paper, from conventional crosslinked polymers. We will examine the mechanical properties of macroscopically oriented networks, from I and different aromatic diamines, in terms of both rigidity and order. Also, rheological measurements (position of the gel point) as a function of reaction time and analyses of the anisotropic thermal expansion coefficient of ordered networks are described and discussed.
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a) These values are determined from the second heating rate at $T = T_g + 50^\circ C$
b) These values are calculated using the equation 2 with $\rho = 1.2 \text{ g.cm}^{-3}$ and $T = T_g + 50^\circ C$

Table 1. Structure and characteristics of the various crosslinking agents. The experimental ($E_r,\text{exp}$) and theoretical ($E_r,\text{theo}$) values of the Young’s elastic rubber modulus for different, fully cured, systems are also compared.
II. EXPERIMENTAL

The synthesis of the diepoxide compound I has been described in chapter II\(^9\): Epoxy value= 3.48 equivalent/kg (theoretical value: 3.63) 4,4'-diaminobiphenyl (A-1) was supplied by RPL (Leuven, Belgium), 4,4'-diaminodiphenyl-methane (A-2) by Aldrich Chemicals Co. and Epikure 1061 (A-3) by Shell Resins (USA) (see table 1). These diamine compounds were used without further purification (purity > 98 %). All the physical measurements were carried out on stoichiometric mixtures of diepoxide I with the appropriate diamine. The polymerization mixtures were prepared as described in chapter IV\(^{12}\). In the text they are referred to according to the codes given to the diamine compounds.

The conversion of epoxy groups (\(\alpha\)) up to the gel point was determined by \(^1\)H-NMR (Varian VXR 400 S). The reaction mixtures, cured for various times at 120 °C, were dissolved in dimethylsulfoxide (DMSO). The conversion was calculated from the decrease in the intensity of the epoxy ring protons at 2.77 ppm relative to the intensity of the aromatic part at 8.09 ppm (relative accuracy of 5 %). The conversion beyond the gel point was determined by potentiometric titration of the remaining epoxy groups; \(\alpha = 87 \% \pm 3 \%\) after 1 hour at 120 °C (system A-1) and 96 \% ± 3 \% for all systems that have undergone the thermal treatment up to 200 °C.

Rheological measurements were performed with the aid of Rheometrics RMS-800 dynamic mechanical spectrometer using parallel-plates (8 mm in diameter) geometry. During the frequency-dependent measurements, the strain amplitude was varied inversely with reaction time in order to obtain proper torque signals. The measurements were performed on the reaction mixture A-1, which is a favourable system because it is free of complicating factors occurring during cure like vitrification. The system does not transfer to the glassy state due to the fact that the cure temperature (i.e. \(T_{\text{cure}}=120 \, ^\circ\text{C}\)) is close to the glass transition temperature of the fully reacted system (see table 2).

The macroscopically oriented samples were prepared by conducting the polymerization in the NMR probe (Varian VXR 400) at the required temperature (± 1 °C) in the presence of a magnetic field (9.4 T). It was shown previously that under such conditions the macroscopic alignment is indeed almost complete\(^{12}\).
Mechanical behaviour from the glassy state to the 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 on macroscopically oriented rectangular specimen (20 \(\times\) 3 \(\times\) 1.5 mm) in the three point bending mode. The measurements were carried out in the direction of the macroscopic orientation from 30 to 200 °C at a heating rate of 5 °C/min and a fixed frequency of 1 Hz.

Anisotropic thermal behaviour of the macroscopically ordered rectangular samples (4 \(\times\) 3 \(\times\) 3 mm) was determined using a Perkin-Elmer DMA-7 which had also the possibility to operate in the thermo mechanical mode, measuring the linear displacement as a function of temperature. The measurements were carried out between 30 and 200 °C (5 °C/min) under a constant force of 10 mN. The experimental conditions for differential scanning calorimetry (DSC) and birefringence (\(\Delta n\)) measurements have been reported chapter III\(^{10}\).

III. RESULTS AND DISCUSSION

A. Rheological behaviour of a liquid crystalline epoxy-amine mixture in the vicinity of the gel point.

In recent years it has been demonstrated for various chemically\(^{14-19}\) and physically\(^{20,21}\) crosslinked isotropic systems that the position of the gel point can be accurately determined by frequency dependent dynamic mechanical measurements. A brief description of this method is as follows.

At the start of the reaction the system behaves as a viscoelastic liquid; \(G'(\omega) \sim \omega^2\) and \(G''(\omega) \sim \omega\) where \(G'\) and \(G''\) are the storage and loss modulus respectively and \(\omega\) is the angular frequency\(^{22}\). As the reaction proceeds small clusters are formed which are often supposed to behave as mechanically self similar regions; the same properties are found at each length scale. It has been shown by Cates\(^{23}\) and Muthukumar\(^{24}\) that the dynamic mechanical properties of these self similar regions follow a frequency dependent power law. At high frequencies, probing the small length scales, the system exhibits gel like behaviour whereas at low frequencies liquid like behaviour is observed. At the gel point the frequency dependency of \(G'\) and \(G''\) is represented by a power law over the entire range of frequencies:
where \( n \) is the critical viscoelastic exponent which is expected to be characteristic for the system.

It should be pointed out that measurement of \( G' \) and \( G'' \) does not fully describe the rheological behaviour of these liquid crystal polymers which, in general, is quite complex\(^{25-27} \). Additional complications may arise from the rigid character of the starting materials and the polydomain structure of the medium. Attempts were made to perform the rheological measurements in the macroscopically ordered state. Although it was possible to induce homeotropic orientation under the influence of surface active agents, unfortunately the monodomain structure became disturbed as a result of the deformation applied during the measurements. The question is whether, in spite these complexities, the method is still applicable to the present system.

For the investigation of network formation in an ordered state we have used in most of our studies the diamine 4,4'-diaminobiphenyl (A-1, see table 1) as the crosslinking agent, because, as was found earlier (see chapter III\(^{10} \)) it forms an eutectic mixture with the diepoxydine 1. Figure 1 shows a DSC trace of a stoichiometric mixture of the diepoxydine 1 and diamine A-1. The mixture is an eutectic with melting point of 115.9 °C, above which a nematic phase is formed.

![DSC trace](image-url)

Figure 1. DSC trace of a stoichiometric mixture of diepoxydine 1 and diamine A-1.
Figure 2 shows the evolution of $G'$ and $G''$ at 15 Hz during the isothermal reaction at 120 °C, which is just above the eutectic melting point. At this temperature the reaction can be easily monitored, since it is still relatively slow. As can be seen in figure 2, both $G'$ and $G''$ start to increase at around 12 min. This coincides well with the time at which the mixture transforms from the nematic into the higher viscous smectic phase (see chapter III and IV)\textsuperscript{10,12}. At 27 min the $G'$ and $G''$ curves cross and then they start to level off. Before this crossover point, viscous properties are dominating ($G''>G'$) while thereafter the elastic behaviour is predominant ($G''<G'$).

![Graph](image)

*Figure 2. Evolution of the storage ($G'$) and loss ($G''$) modulus as a function of the reaction time at 120 °C for the mixture A-1 (frequency= 15 Hz).*

As mentioned above, in order to determine exactly the position of the gel point, frequency dependent measurements of the moduli are required. Figure 3 shows the result of such measurements where $G'$ and $G''$ are plotted against the frequency at various reaction times. With our experimental set up, it was not possible to measure the values of $G'$ and $G''$ instantaneously at different frequencies. The results, reported in figure 3, are obtained by interpolation of the experimental data measured at different times during one frequency cycle. At the gel point (27 ±1 min) which is defined by a similar power law exponent for $G'$ and $G''$, the value of the two moduli are equal. This is in agreement with $n$ equalling 0.5 as derived from figure 3. This is consistent with the value determined for most of stoichiometrically balanced gels\textsuperscript{28}. Somewhat higher values, however, are found for a series of stoichiometric isotropic epoxy-amine mixtures\textsuperscript{29,30}. This is not surprising since it known that the exponent $n$ does not have a
universal value, as is suggested by several theories describing the dynamic behaviour near the gel point\(^{29,30}\), but depends on various parameters like material structure and stoichiometry\(^{31}\).

![Graph showing dynamic mechanical properties](image)

*Figure 3. Dynamic mechanical properties of system A-1 as a function of the frequency plotted at different reaction times near the gel point \(T_{\text{cure}} = 120 \, ^{\circ}\text{C}\). The storage \(G'\) and loss \(G''\) moduli are obtained by interpolation of the experimental data at different times.*

Solubility experiments during the isothermal reaction at 120 °C have shown that the material becomes partly insoluble in DMSO at 27±1 min. This corresponds well with the gel point, determined by the analyses of \(G'\) and \(G''\) above.

We were also interested to examine whether the chemical conversion of the epoxy groups \((\alpha)\) at the gel point corresponds with the theoretical value predicted by a statistical approach for a stoichiometrically balanced isotropic epoxy-amine mixture. Depending of the relative reactivity of the secondary \((K_2)\) to the primary \((K_1)\) amine hydrogen atoms the gelation occurs between 50 % \((K_2/K_1 \to 0)\) and 61.8 %\((K_2/K_1 \to \infty)\)\(^{32}\). Figure 4 shows \(\alpha\) measured up to the gel point as a function of polymerization time at 120 °C. The good agreement between the experimentally determined \((\alpha = 55\pm3 \%)\) and the theoretical value of \(\alpha\) at the gel point indicates that network formation in these ordered epoxy-amine mixtures also seems to proceed in a statistical manner.
Figure 4. Conversion of the epoxy groups ($\alpha$) measured up to the gel point as a function of the polymerization time at 120 °C.

B. Viscoelastic response and thermal behaviour of macroscopically ordered networks.

Figure 5 shows the dynamic mechanical properties of system A-1 cured isothermally at various temperatures under the influence of the magnetic field. The behaviour of ordered networks, especially in the rubbery state, is rather peculiar. First the very high value of the rubber modulus is considered. We will continue to use the term rubber for this state despite its high value of the Young's elastic modulus. In table 1 the experimental value of the rubber elastic modulus ($E'_{r,\text{exp}}$) is compared with the theoretical value ($E'_{r,\text{theo}}$) determined with the aid of the simplest form of the classical rubber elasticity equation\textsuperscript{33}):

$$E'_{\text{rubber}} = \phi \frac{3\rho RT}{M_c}$$  \hspace{1cm} (2)

where $\rho$ is the density of the network at $T$, $R$ is the gas constant, $\phi$ is the front factor which allows for effects of several theoretical approximations. For a phantom network, in which the chains freely penetrate each other, with fully suppressed fluctuations of crosslinks displaced affinely with
strain, $\phi$ equals to one$^{34}$). $M_c$ is the average molecular weight between crosslinks which can be calculated using equation 3.

$$M_c = \frac{m_a + 2m_c}{3}$$  \hspace{1cm} (3)

Where $m_a$ and $m_c$ are the molecular weights of the diamine and diepoxide, respectively.

![Figure 5. Dynamic mechanical response of the fully cured, macroscopically ordered A-1 system, measured in the direction of the orientation at 1 Hz. The data are shown for different cure temperatures.](image)

There are basically two main factors which can be responsible for the large difference between the experimental and theoretical value of the rubber modulus (see table 1). In the theory of rubber elasticity, it is assumed, in analogy with the behaviour of ideal gasses that the retractive stress of a rubber is caused by a reduction of entropy rather than by a change in enthalpy$^{34}$. In this approach the distribution of the end-to-end distances of a single polymer chain is expressed as a Gaussian function. In principle this can only be expected to hold true for long flexible chains. In the present case the distances between the crosslink junctions are too short and especially too rigid to behave as Gaussian chains. In the literature there are several examples where it has been shown that, in the case of epoxy-amine networks, the deviation from ideal behaviour increases with concentration of rigid segments$^{35-37}$. In all these studies, however, the networks have not been examined for their possible LC like structural order.
Several attempts have been made recently to describe the deformation behaviour of networks comprising rigid rod segments. On the basis of the nature of the crosslink points, distinction has been made between networks where the rods are rigidly connected at the junction points and networks where the rods are freely jointed. In the first case, assuming the rods cannot freely rotate around the crosslink points, the deformation behaviour is purely enthalpic; owing to the rigid character of the chains, no conformational changes occur under stress and deformation of the network can only be accomplished by the bending of the rods. In the second case, because of the flexible nature of the network at the crosslink points, there is still a contribution of entropy to the elastic modulus; the network deforms entropically. Due to the presence of the spacer segments, it is believed that our system resembles more the entropic model, although the deformation of the mesogenic groups could also play a role.

In the case of the "entropic networks" produced by rigid rods, it was shown, in a qualitative manner, that surprisingly the elastic behaviour for small deformations is the same as for networks comprising flexible chains. At large deformations, however, there is a fast increase of the free energy because of the inextensibility and rigidity of the elements. Similar results were found from some earlier theoretical descriptions of non-Gaussian networks. It must be noted that in all these studies, the system was assumed to be isotropic and complicating factors such as LC ordering have not been included.

Apart from rigidity of the starting materials, the long range orientational order is the second factor which distinguishes the present networks from conventional systems. Warner et al. have considered the deformation behaviour of nematic networks, in continuation of the original work of de Gennes. This theory, however, is derived for networks build up of Gaussian chains and it is basically a modification of the classical theory of rubber elasticity.

In figure 5 it can be seen that the value of the rubber modulus is independent of Tcure. It was shown chapter IV with the aid of 2H-NMR that the networks cured, at 120 °C have, an order parameter S ≥ 0.9 where S equals to the second order Legendre polynomial. Furthermore, it was demonstrated that the networks prepared at Tcure up to 160 °C, have roughly the same Δn value (= 0.15 at 50 °C above Tg). Assuming that Δn =
S, we conclude that the level of orientation for all the networks cured isothermally up to 160 °C is equal which is reflected in the same value of the rubber modulus.

In the glassy state, the elastic modulus seems to depend somewhat on \( T_{\text{cure}} \). The interpretation of these results in terms of the molecular structure is, however, very difficult, because in the glassy state the mechanical properties are mainly governed by Van-der-Waals interactions and are not directly related to the network topology and chemical structure\(^{47}\). The glass transition relaxation for the networks cured at 160 °C occurs somewhat earlier, on the temperature scale, as compared with those cured at 120 and 140 °C (see table 2). Furthermore there seem to be some differences in the amplitude and width of the tan \( \delta \) peaks. This is an indication of a difference in the homogeneity of macromolecular chain motions associated with the glass transition. These observations could be related to the fact that the networks cured at 120 and 140 °C have a smectic structure (probably smectic A) whereas those cured at 160 °C and above exhibit a nematic structure (see chapters III and IV)\(^{10,12}\). But, we will show that other factors, like differences in cure kinetics which can ultimately result in different local network structure, could also play an important role.

The insensitivity of the final macroscopic order on \( T_{\text{cure}} \) is also evident from the anisotropic coefficients of thermal expansion (CTE) of the networks (see figure 6a). As can be seen in table 2, the CTE values are highly anisotropic and rather independent of \( T_{\text{cure}} \). This anisotropic behaviour is characteristic of highly oriented polymers\(^{48}\) and has also been observed for networks prepared from LC diacrylates\(^{49,50}\). However, although several attempts have been reported before \(^5,8\), this is the first time that such behaviour is observed for ordered and highly crosslinked epoxy-amine networks providing a combination of good mechanical and thermal properties of conventional epoxy networks\(^{51}\) with the anisotropic behaviour connected with the high macroscopic order.

To examine further the effect of both order and rigidity on the mechanical behaviour of the networks, we have altered systematically the molecular structure of the crosslinker. First the influence of introducing one flexibilizing unit (methyl group) in the diamine is studied (see 4,4'-diaminodiphenylmethane; A-2 in table 1).
Figure 6. Linear displacement measured parallel (||) with and perpendicular (⊥) to the direction of macroscopic orientation for A-1 (a) and A-2 (b) systems (T_{cure} = 120 °C).

Table 2. Values of coefficient of thermal expansion (CTE) measured parallel with (||) and perpendicular (⊥) to the direction of the macroscopic orientation for different systems measured in the glassy (50-90 °C) and rubbery (140-190 °C) regions. The values of the glass transition temperatures (Tg) are also shown.

<table>
<thead>
<tr>
<th>Code</th>
<th>T_{cure}(°C)</th>
<th>CTE (°C)^a)</th>
<th></th>
<th></th>
<th>Tg (°C)^b</th>
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<td></td>
<td>rubber</td>
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<tr>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>119.9</td>
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</table>

a) Determined from the second heating scan.
b) Tg is taken as the maximum of tan δ peak. These values are in good agreement with those determined from the thermal expansion measurements.
Figure 7 shows a DSC trace of a stoichiometric mixture of the diepoxide I and diamine A-2. It is evident that, at this ratio, the two compounds do not form a eutectic mixture. Microscopic observations between crossed polarizers revealed that, immediately after the second melting point, an isotropic fluid was formed. Obviously the LC phase has been destabilized by the introduction of the flexibilizing unit. However, as the reaction proceeded, the nematic to isotropic transition shifted to higher temperatures (see chapters III and IV\(^{10,12}\)) and within one minute the mixture transformed into a nematic phase which became irreversibly fixed upon further polymerization. Similar behaviour was observed at higher \(T_{\text{cure}}\) up to 200 °C, although the time at which the mixture transformed into a LC phase increased somewhat with \(T_{\text{cure}}\).

![Graph showing DSC trace](image)

*Figure 7. DSC trace of a stoichiometric mixture of diepoxide I and diamine A-2.*

Figure 8 shows the dynamic mechanical properties of the macroscopically oriented A-2 networks cured isothermally at various temperatures under the influence of the magnetic field. Also, in this case the values of the elastic modulus seem to be rather insensitive to \(T_{\text{cure}}\). Again, this is in accordance with the observation that the values of \(\Delta n\) (= 0.09 at 50 °C above \(T_g\)) and CTE do not significantly depend on \(T_{\text{cure}}\) (see table 2).

The present data reveal that the systems A-1 and A-2 show roughly the same anisotropic thermal behaviour (see figure 6 and Table 2) which means, according to ref. 50, that the macroscopic order for both networks is the same. Consequently, the lower values of \(\Delta n\) for system A-2 in comparison with system A-1 is probably not caused by the lower level of
orientation, but it is connected with differences in molecular polarizability\textsuperscript{52}).

\[ E' (\text{Pa}) \]
\[ T \]
\[ 60 \quad 80 \quad 100 \quad 120 \quad 140 \quad 160 \quad 180 \quad 200 \]
\[ 120 ^\circ C \]
\[ 130 ^\circ C \]
\[ 150 ^\circ C \]

Figure 8. Dynamic mechanical response of the fully cured, macroscopically ordered A-2 system, measured in the direction of the orientation at 1 Hz. The data are shown for different cure temperatures.

From table 1 it is obvious that, even though both A-1 and A-2 networks have the same high level of macroscopic orientation, the value of the rubber modulus for system A-2 agrees much better with the theoretical prediction than the value of system A-1. This might suggest that, in the present networks, the rigidity of the segments is playing a more important role in causing a deviation from classical theory than the ordered structure. On the other hand, for system A-1, the value of the Young’s elastic modulus, measured on the macroscopically isotropic network is $E' = 3G' = 6 \times 10^7$ Pa assuming the Poisson ratio is 0.5 (see figure 2). This, in turn, implies that the macroscopic order is the main cause of deviation from the classical behaviour. It should be pointed out that the random domain orientation can cause elastic strains and complicate the interpretation of the results\textsuperscript{53}). Clearly, on the basis of these investigations it is difficult to decide what the main cause of deviation is from the classical rubbery behaviour. Furthermore, one may wonder whether it is justified to make a direct distinction between the effect of both factors, because of the possible coupling of the influence of the rigidity and order on the elastic properties.

As mentioned earlier, for system A-2 at all cure temperatures, there was no change in LC morphology; the nematic structure became fixed as a result of the polymerization reaction. Thus, the differences in the
homogeneity of the macromolecular chain motions at the glass transition, as can be seen in figure 8, can not be attributed to the modifications in the LC morphology. Some alterations in the network structure is expected to result from the variations in cure kinetics due to the different cure temperatures.

The next interesting point that should be considered is the behaviour of the rubber modulus of these ordered networks as a function of temperature. As can be seen in figures 5 and 8, in all cases the rubber modulus is decreasing as a function of the temperature. Similar behaviour was observed for crosslinked LC main chain polymers\textsuperscript{54,55}. The comparision with our system is, however, difficult, mainly because of two reasons: 1- The crosslink densities were, in contrast with our networks, quite low 2- The mechanical measurements were carried out, in contrast with the present experiments, on non-oriented, macroscopically isotropic systems. As mentioned earlier, this can seriously hamper the interpretation of the results.

For isotropic "enthalpic networks", it was shown experimentally by Aharoni and Edwards\textsuperscript{56}) that the value of the modulus was independent of temperature. This was later theoretically verified by Jones and Marques\textsuperscript{39}). The theoretical predictions concerning the temperature dependence of modulus for isotropic "entropic networks" constituted of rigid rods is not straightforward because of the complex nature of equation of the free energy in ref. 40. Assuming that all the terms on the right hand side of this equation are temperature independent, the modulus should increase with a slope equal to kT. Thus, the temperature behaviour of the modulus, for systems discussed here, does not agree with the predictions of either of the two models (see figure 5 and 8). As can be seen in figure 9, the decrease of the rubber modulus, for both A-1 and A-2 networks, seems to be connected to the decrease of order as a function of the temperature, assuming again that Δn ∝ S. Also for the networks prepared at higher T\textsubscript{cure}, we found that a good correlation exists between the relative decrease of the modulus and order as a function of the temperature, provided that the results are only compared in the rubbery region. The temperature dependence of the modulus in the glassy state for highly oriented polymers has recently been discussed elsewhere by Bronnikov et al.\textsuperscript{57}). The behaviour of the rubber elastic modulus for these ordered networks as a function of the temperature is reminiscent of the stress-optical behaviour of the Gaussian networks.
where it is shown that $\Delta n$ is directly proportional to the applied stress$^{42}$. In the appendix to this paper a theory is presented, by T. Odijk concerning nematic gels under tension, where it is shown that the rubber modulus could indeed decrease as a function of the temperature because of the decrease of order.

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**Figure 9.** Normalized values of the Young elastic modulus ($E'$) and birefringence ($\Delta n$) measured as a function of the temperature in the rubbery region for macroscopically ordered systems A-1 (a) and A-2 (b). $T_{cure}=120$ °C.
In the systems A-1 and A-2, because of the high crosslink density, it was possible to investigate the temperature dependence of the modulus only within a limited range of orientational order. The rubber modulus is expected to reach a plateau value around $S = 0$; around the hypothetical LC to isotropic transition. In this regard, it would be interesting to study the temperature dependence of modulus and order in a moderately crosslinked LC polymers where a nematic to isotropic transition can still be observed\textsuperscript{53,54}.

Some attempts were made to study the behaviour of the present systems in the isotropic phase. However, in order to prepare isotropic networks the polymerization reaction should be conducted at $T \geq 200 \, ^\circ C$, for both A-1 and A-2 systems. It proved to be difficult to prepare well characterized samples at these high temperatures. Complications may also arise from the fact that the chemical reactions at such elevated temperatures will probably suffer from side reactions like etherification\textsuperscript{11}.

Alternatively, we studied the diamine A-3, which contains two flexibilizing units, as the crosslinking agent (see table 2). Owing to this flexible nature, the mixture A-3 transformed to a isotropic phase upon melting and remained so during the network formation (see figure 10). As can be seen in table 1, there is a good agreement between the theoretical and experimental value of the rubber modulus which gradually increase with temperature (see figure 11).

![Figure 10. DSC trace of a stoichiometric mixture of diepoxide 1 and diamine A-3.](image-url)
The reasonable agreement found for system A-3, between the simplest form of the rubber elasticity theory and the experiments is rather surprising, because even though the segments between the crosslink points are more flexible, especially in comparison with system A-1, as mentioned above they are still too short and too rigid to expect a behaviour as Gaussian chains. Similar results are found in the literature, where it is shown that, even in the case of some highly crosslinked epoxy-amine networks, the classical theory of rubber elasticity is able to predict reasonably the value of the rubber moduli\(^{58-60}\). These findings could be brought in qualitative agreement with the theories of non-Gaussian networks, assuming that the present experiments are carried out in the range of strains (i.e., < 0.25 %) where the networks exhibit still a behaviour similar to the Gaussian networks. The crossover point which separates the Gaussian from the non-Gaussian regime, is expected to shift to lower values of strain as the rigidity of the segments increases. Therefore, it might be argued that in the case of the A-1 system the monomers are probably so stiff that even with strain values as low as 0.25 % the classical Gaussian theory fails to predict the value of the rubber modulus.

![Figure 11. Dynamic mechanical response of the fully cured A-3 system, measured at 1 Hz.](image)

From the above discussion it may become obvious that there is an urgent need for a theory which describes the deformation behaviour of rigid rod networks in a quantitative manner. However, in setting up such an theory, one seems to encounter many great mathematical and physical obstacles, partly because the assumptions, like affine deformation, which made the case of the Gaussian networks relatively simple, are no longer
valid for non-Gaussian systems\textsuperscript{40,61}. The situation is in our systems even more aggravated by the presence of long range orientational order.

As it is shown in figure 11, tan δ shows, for system A-3, a maximum at approximately 120 °C, which is comparable with the value found for the systems A-1 and A-2 (see table 2). Some differences in the Tg’s were to be expected in accordance with the rigidity of the monomers\textsuperscript{47,62}. However, the comparision of the Tg’s becomes difficult, owing to the fact that the LC ordering might also affect the process of glass transition\textsuperscript{63}.

IV. CONCLUSIONS

The network formation in the LC epoxy-amine mixtures investigated, proceeds in a statistical manner in view of the fact that the position of the gel point, on the conversion scale, agrees well with the theoretical predictions, made originally for isotropic systems.

There are two factors that can cause deviations from the classical rubber like behaviour, namely the rigid character of the starting materials and the existence of the orientational order. It proved to be difficult to determine which factor is playing a more important role. However, one should be careful with making a direct distinction between the contribution of the two effects. It is more plausible to consider the influence of both rigidity and order as a whole on the elastic properties. The decrease of the rubber modulus as a function of temperature is connected, as theoretically verified (see appendix), to the decrease of order.

It was shown that the thermal behaviour of the macroscopically ordered epoxy-amine networks is highly anisotropic. In some cases, in the direction of the orientation, the coefficient of thermal expansion was almost zero below Tg, and even negative above Tg. These anisotropic properties are a direct consequence of the high macroscopic order of these networks (see chapter IV)\textsuperscript{12}.
APPENDIX
Polymer Nematic Gel Under Tension

In the limit of strong nematic order, the Hamiltonian $H$ for a nematic semiflexible chain of length $L$ under a tension $f$ is given by the sum of a bending energy and a background nematic potential (see equation VIII.19 of ref. 64) and a tensile potential (see equation 12 of ref. 65)

$$H/k_B T = \frac{1}{2} P \int_0^L \left( \frac{d\vec{\theta}}{ds} \right)^2 ds + \frac{\Gamma_n}{2P} \int_0^L \vec{\theta}^2 ds + \frac{f}{2k_B T} \int_0^L \vec{\theta}^2 ds \quad (A1)$$

Here, $k_B$ is Boltzmann's constant, $T$ is the temperature, $P$ is the persistence length, $\Gamma_n$ is a nematic coupling constant, and $\vec{\theta}(s) = (\theta_x, \theta_y)$ represents the (small) angles of the tangent vector of the chain at contour point $s$ with respect to the director. The external tension is exerted parallel to the director. The statistical properties of the confined chain are readily analyzed with the help of a Gaussian trial function $\exp\left[-\frac{1}{2} \alpha \theta^2\right]$ (see ref. 64; $\alpha = \text{variational parameter; } \alpha \gg 1; \quad \langle \theta^2 \rangle = \frac{2}{\alpha}$). The total free energy is

$$F_{\text{tot}}/k_B T = \frac{L\alpha}{4P} + \frac{L\Gamma_n}{\alpha P} + \frac{Lf}{\alpha k_B T} \quad (A2)$$

valid when $L > \lambda = P/\alpha$ where $\lambda$ is deflection length (see figure 12).

The first term is a free energy of confinement. Minimization of equation A2 yields

$$\alpha = \left( \frac{\alpha_0^2 + \frac{4fP}{k_B T}}{k_B T} \right)^{\frac{1}{2}} \quad (A3)$$

*) A Contribution of:

T. Odijk
Department of Polymer Technology; Faculty of Chemical Engineering and Materials Science, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands

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With $\Gamma_n \equiv \frac{1}{4} \alpha_o^2$ (assumed independent of $f$ at this level of approximation) or

$$\langle \theta^2 \rangle = \left( \frac{1}{4} \alpha_o^2 + \frac{4P}{k_BT} \right)^{1/2} \tag{A4}$$

As it should, equation A4 reduces to equation VIII.22 of ref. 64 as $f$ tends to zero, or to equations 14 and 15 of ref. 65 as $\Gamma_n$ goes to zero.

![Diagram](https://via.placeholder.com/150)

*Figure 12. The nematic gel with deflection length \(\lambda = P/\alpha (\lambda \ll P)\).*

Finally, the deformational behaviour of the chain is derived from the mean extension

$$R \equiv L \langle \cos \theta \rangle = L \left[ 1 - \frac{1}{2} \langle \theta^2 \rangle \right] = L \left[ 1 - \left( \alpha_o^2 + \frac{4P}{k_BT} \right)^{1/2} \right] \tag{A5}$$

$$R(f = 0) = L(1 - \alpha_o^{-1})$$

Hence, at small tensions we have

$$\delta R = R - R(f = 0) \equiv \frac{2LPf}{\alpha_o k_BT} \tag{A7}$$

or
\[ f \equiv \frac{\alpha_0^3 k_B T \delta R}{2LP} \] (A8)

which is to be compared to the equivalent expression for a flexible Gaussian chain

\[ f = \frac{3k_B T \delta R}{2LP} \] (A9)

We conclude that the front factor in equation 2 is connected with the order parameter

\[ S = 1 - \frac{3}{\alpha_0} \] (A10)

via

\[ \phi \propto \alpha_0^3 \] (A11)

Therefore, on the one hand the modulus increases with temperature because of entropic effects, yet it decreases with increasing T since S and \(\alpha_0\) decrease. Our whole derivation is qualitative in view of the approximations employed.

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CHAPTER VI- Possible Application of Liquid Crystalline Epoxide Thermosets as Encapsulation Materials for Integrated Circuits

At the present time, more than 80% of all semiconductor devices are encapsulated by epoxy molding materials\textsuperscript{1}. These plastic packages are to provide protection from the surrounding environment, for example against moisture (see figure 1).

![Diagram of an integrated circuit](image_url)

*Figure 1. Internal structure of a typical integrated circuit.*

The current trend in the production of integrated circuits (ICs) is to increase the integration density and at the same time decrease the size of the plastic packages. This imposes continuously new demands on the physical properties of the encapsulating materials. One of the major drawbacks of the current materials is their relatively high coefficient of thermal expansion (CTE) in comparison with that of the silicon chip, for example (see Table 1). The thermal stress, caused by mismatch of the expansion coefficient, leads to the occurrence of cracks in the package and passivation layers. The thermal stress ($\sigma$), thus generated, can be estimated by the following equation\textsuperscript{1}:

$$\sigma = k \left[ (\alpha_g - \alpha_c) E_g (T_g - T_i) + (\alpha_r - \alpha_c) E_r (T_r - T_g) \right]$$  \hspace{2cm} (1)$$

where $k$ is a constant $\alpha_g$ and $\alpha_r$ are the CTE of the network in the glassy and rubbery state, respectively. $\alpha_c$ is the CTE of the chip. $E_g$ and $E_r$ are the
Young's modulus in the glassy and rubbery state, respectively. Tg is the glass transition temperature of the plastic package. From equation (1) it follows that by lowering the CTE and elastic modulus of the molding compound, it is possible to reduce the thermal stress. The elastic modulus can be decreased by dispersing rubber particles, as flexibilizers into the encapsulating materials\(^2,3\) and the CTE can be lowered by addition of fillers (e.g. quartz).

**Table 1.** Coefficients of thermal expansion (CTE) for several materials used in the conventional IC's. Typical CTE values for ordered epoxy-amine networks are also reported.

<table>
<thead>
<tr>
<th>Materials</th>
<th>CTE ((/°C).10^{-6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chip (Silicon)</td>
<td>3-4</td>
</tr>
<tr>
<td>Lead frame (Alloy 42)</td>
<td>4.5-5.8</td>
</tr>
<tr>
<td>Epoxy (Conventional)</td>
<td>15-35</td>
</tr>
<tr>
<td>Epoxy (Ordered)</td>
<td>-3-0.3</td>
</tr>
</tbody>
</table>

Although these methods have been successful so far, further addition of flexibilizers and fillers is expected to cause problems; thermal stability and moisture resistance of the package decreases with the addition of rubber particles. Presence of large amount of fillers can lead, during the transfer molding process, to the destruction of wire bonds. Also, fillers (e.g. silica) are the prime source of \(\alpha\)-rays which can decrease markedly the quality of the chip. Owing to these difficulties, other approaches must be taken into the consideration.

As was shown in chapter V, the ordered epoxy networks prepared by copolymerization of LC diepoxide I (see chapter V) with several aromatic diamines have anisotropic thermal expansion coefficients (see table 1 and figure 2). Attempts were made to modify the CTE values by altering the polymerization temperature. The order parameter, however, increased in all cases as a function of the degree of polymerization and levelled off at the same value at all cure temperatures. Consequently, no noticeable change in the CTE values could be achieved. Some variations in the thermal expansion behaviour was observed between the networks cured with different aromatic diamines. As can be seen in table 1 the CTE values of the ordered epoxy networks, below \(T_g\) \((\approx 120 \degree C)\), are comparable with the CTE values of the chip. Above \(T_g\), the ordered networks start to contract resulting in highly negative CTE values. This behaviour is, of course, not desirable because the opposite situation is now expected to occur; the
thermal stress will be caused not by the high expansion of the plastic package, but by the contraction of it. By modifying the molecular structure of the starting monomers, it should be possible to increase the $T_g$ up to the highest operation temperature of IC’s, i.e., 160-200 °C.

The other point of concern is that the networks produced by us have low CTE values only in one direction whereas it is well known that, in order to considerably reduce the thermal stress, the thermal expansion should be comparable with that of the silicon in two directions, on the surface of the chip.

![Figure 2. Linear displacement measured parallel (||) with and perpendicular (⊥) to the direction of macroscopic orientation for a typical ordered epoxy-amine network.](image)

It is common knowledge from the low molecular weight liquid crystals that a nematic phase can be converted into a cholesteric phase, in which the molecules adopt a helical configuration, just by adding a small amount of chiral substance.\(^4\) It was shown by Broer and Mol that starting the crosslinking reaction in a cholesteric phase results in helically ordered networks in which a low thermal expansion is observed in two directions.\(^5\) Similar behaviour is expected for ordered epoxy-amine networks doped with a small amount of chiral molecules.

The question is now whether it is feasible, from a commercial point of view, to replace the conventional encapsulating materials by the much more expensive LC epoxy-amine compounds. Moreover, in order to achieve anisotropic macroscopic properties an external field should be applied during the polymerization reaction. The macroscopic orientation could be
achieved, in principle, during the filling of the mold, as a result of the flow aligning mechanism. However, the rheology of liquid crystals is quite complicated and other approaches, like application of a small strength magnetic field on the mold are perhaps more practicable but they require a complete modification of the conventional transfer molding process.

An alternative route would be to apply the cholesteric ordered epoxy-amine network as a thin film at the interfaces where the thermal stress is originated (e.g. between the chip and package). In this way, the thermal stress can be also eliminated systematically at other interfaces like the chip and the lead frame; epoxy-amine networks are generally excellent adhesives which can be used to mount the chip on the lead frame. In this approach, the macroscopic orientation can be achieved with the aid of the well known surface treatment techniques, like rubbed polyimide (see chapter III). A thin polyimide film should be applied on the chip and subsequently cured and rubbed in one direction. This process is not expected to cause any problems because low thermal expansion polyimides are already being applied as stress relief films, in a similar way, in a large number of semiconductor devices\textsuperscript{6).} After application of the ordered epoxy-amine monomers as a thin film on the polyimide layer and curing, the chip can be encapsulated by the conventional materials.

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Summary

Epoxy networks are frequently applied as engineering plastics, because of their good mechanical and thermal properties. In this thesis, we have incorporated liquid crystalline (LC) like structures into the epoxy networks. As a result, these networks have highly anisotropic physical properties, like the coefficient of thermal expansion. Owing to their relatively simple and "clean" chemistry, conventional epoxy networks are also widely used as model compounds to study network formation in non-LC systems. Therefore, LC epoxy monomers were used as the starting materials in order to study network formation in an ordered state.

The basic idea for producing highly ordered and highly crosslinked materials was to orient low molecular weight (LMW) LC monomers uniaxially in the mesophase and subsequently freeze-in the orientation by polymerization and crosslinking.

In chapter II, the synthesis is presented of a series of LMW LC diepoxides. The influence of the molecular structure on the LC properties and the rate of the photoinitiated polymerization was studied. The oxygen atom, positioned β to the epoxy group in the spacer part of the molecule, destabilized the nematic phase and increased the rate of the polymerization. The rate of the photoinitiated polymerization was also increased by the LC-like molecular arrangement. Highly ordered networks could be produced by photoinitiated polymerization in the mesophase of LMW LC diepoxides. It was shown that the polymerization continued in the dark for a long time. In some cases, it was necessary to subject the networks to a thermal postcuring step in order to produce networks with a high orientational stability.

In chapter III, we showed that a more convenient way of producing ordered networks, especially for bulk applications, is by copolymerization of the LC diepoxides with aromatic diamines. A series of aromatic diamines were synthesised and their polymerization reaction with a certain LC diepoxide was studied with the aid of differential scanning calorimetry. By selecting a crosslinker with an appropriate melting point, it was possible to obtain an eutectic LC epoxy-amine mixture. With the help of dichroism and birefringence (Δn) measurements, it was demonstrated, for the first time,
that epoxy-amine networks can indeed be produced which possess both a high crosslink density and a high macroscopic order.

In chapter IV, we monitored, in real time, the orientational order of a certain LC diepoxy-amine mixture, as a function of the polymerization time by deuterium magnetic resonance (2H-NMR) and Δn measurements. The polymerization of selectively deuterated reacting monomers, was carried out, quite uniquely, in the NMR probe at 120 °C, i.e., just above the eutectic melting point (115.9 °C). In this way the orientational order could be determined separately for each monomer on a molecular level as a function of the polymerization time. The interpretation of the NMR spectra was backed by the results obtained from gel permeation chromatography. The main conclusion from these investigations was that the orientational order increased during the chain extension process and became fixed as a result of the crosslinking reaction. It was shown that the order parameter of the amine monomer was more sensitive to the degree of polymerization than that of the diepoxide. This can be attributed to the action of the spacer segment which decouples, in the case of the diepoxide monomer, the reaction center from the mesogenic part. During the polymerization reaction, the point where Δn started to level off corresponded well with the point of gelation as determined by the solubility experiments.

In chapter V, we studied the dynamic mechanical properties of a series of LC epoxy-amine systems, both during the polymerization and at the end of the reaction, i.e., on fully cured macroscopically ordered networks. The position of the gel point was determined with the aid of frequency dependent rheological measurements and there was a good agreement with the results obtained from solubility and Δn measurements. This is quite interesting since it means that the position of the gel point determined by a static technique (Δn) agrees well with that obtained from the dynamic measurements. These results provide additional evidence for the value of the frequency dependent rheological technique to study gelation in non-LC systems.

The network formation in these LC epoxy-amine mixtures proceeds in a statistical manner since both the conversion of the epoxy groups at the gel point and the increase of the number average molecular weight as a function of the polymerization reaction time (see chapter IV) agree well with the theoretical predictions, made originally for isotropic systems.
The rigid character of the starting materials and the ordered structure, are the two factors which distinguish the present systems from the conventional networks. It is probably not feasible to consider the effect of both factors on the mechanical properties separately. Interestingly, in the rubbery region the value of the Young's elastic modulus, in contrast with the classical behaviour, decreased as a function of temperature. As theoretically verified, this is connected with the decrease of order.

The fact the networks possess a very high macroscopic order, as was shown in chapter IV, was once more confirmed by the highly anisotropic values of the coefficient of the thermal expansion (CTE). In some cases, in the direction of the orientation, CTE values were almost zero below Tg, and even negative above Tg. It was, indeed possible to combine the good mechanical and thermal properties of the conventional epoxy polymer networks with the special features that LC polymers offer. Owing to these outstanding properties, it is proposed, in chapter VI, that these materials could be used, in principle, for encapsulation of semiconductor devices.
Samenvatting

Polymeer netwerken op basis van epoxy harsen worden veelvuldig toegepast als "engineering plastics" vanwege hun goede mechanische en thermische eigenschappen. In het onderzoek beschreven in dit proefschrift, is vloeibaar kristallijne (VK) ordening in de epoxynetwerken geïntroduceerd. Daardoor bezitten deze netwerken hoog anisotrope fysische eigenschappen, zoals de coëfficiënt van de thermische expansie. Het feit dat netwerkvorming van epoxy verbindingen, vooral met amines, over het algemeen, volgens een relatief simpel reactieschema verloopt, heeft er toe geleid dat deze materialen regelmatig als modelsystemen gebruikt worden om de netwerkvorming in conventionele (isotrope) systemen te onderzoeken. Daarom zijn VK epoxy verbindingen gebruikt als model-systemen om de netwerkvorming in een anisotrope fase te bestuderen. Het basisprincipe voor het produceren van hoog vernette en hoog geordende netwerken is om laag moleculaire (LM) VK monomeren uniaxiaal te orienteren in de mesofase en vervolgens deze ordening in te vriezen door polymerisatie.

In hoofdstuk II, wordt de synthese beschreven van een serie LM-VK diepoxide. De invloed van de moleculaire structuur op de VK eigenschappen en de met licht geïnduceerde (foto) polymerisatiesnelheid is onderzocht. Het zuurstof atoom, in de positie β t.o.v de epoxy groep in het spacer gedeelte van het molecuul, verstoort de nematische fase en verhoogt de polymerisatiesnelheid. De fotopolymerisatiesnelheid wordt ook verhoogd door de VK ordening. Hoog geordende netwerken werden geproduceerd door fotopolymerisatie van LM VK epoxide in de mesofase. De keten-polymerisatiereactie bleek gedurende lange tijd in het donker door te gaan. Daarom was , in sommige gevallen, postcuren noodzakelijk om netwerken te maken met een hoge stabilititeit van ordening als functie van temperatuur.

In hoofdstuk III is aangetoond dat er een betere manier is om, vooral in bulk, hoog geordende en hoog verknoopte netwerken te produceren door copolymerizatie van de VK epoxide met aromatische amines. Een serie aromatische amines werd gesynthetiseerd en de copolymerisatie-reactie met een bepaald VK diepoxide werd onderzocht m.b.v "differential scanning calorimetry". Door de structuur van de diamine te veranderen en daarmee het smeltpunt, was de mogelijk om een eutectisch VK epoxy-amine mengsel te verkrijgen. M.b.v dichroïsme en dubbelbreking (Δn) metingen werd voor de
te verkrijgen. M.b.v dichroïsme en dubbelbreking (Δn) metingen werd voor de eerste keer gedemonstreerd dat het inderdaad mogelijk is om epoxy-amine netwerken te maken met een hoge macroscopische ordening en een hoge vernettingsgraad.

In hoofdstuk IV, wordt beschreven hoe de verandering van de mate van ordening, voor een bepaalde VK epoxy-amine mengsel als functie van polymerisatiertijd (graad), werd gevolgd m.b.v “deuterium nuclear magnetic resonance” (²H-NMR) en Δn metingen. De polymerisatie, van selectief gedeutereerde monomeren, werd uitgevoerd in de NMR probe bij 120 °C, d.i., net boven het eutectische smelt punt (115.9 °C). Op deze manier, was het mogelijk om de verandering van de ordening als functie van de polymerisatiegraad, apart voor elke monmeer, te volgen. Deze toepassing van ²H-NMR, voor in de tijd opgeloste bestudering van de ordening tijdens de polymerisatie, is uniek. De interpretatie van de ²H-NMR spectra werden ondersteund m.b.v de resultaten verkregen uit andere technieken, zoals gel permeatie chromatografie. De hoofdconclusie uit dit onderzoek was de volgende: de ordening nam tijdens de ketenverlenging toe en werd irreversibel vastgelegd door de vernettingsreactie. Aangetoond werd dat de orde parameter van het amine gevoeliger was voor de polymerisatiegraad dan die van het diepoxide. Dit kan worden toegeschreven aan de werking van het spacer gedeelte van het epoxy molecuul waardoor het centrum van de reactie ontkoppeld wordt van de mesogene groep. Tijdens de isotherme polymerisatieractie, het punt waarbij Δn begon af te vlakken, kwam goed overeen met het gelpunt, bepaald m.b.v oplosbaarheidsmetingen.

In hoofdstuk V, worden de dynamisch mechanische eigenschappen beschreven van de VK epoxy-amine systemen zowel tijdens de netwerkvorming als aan het eind van de reactie, d.w.z., van volledig omgezette, macroscopisch georiënteerde, netwerken. Het gelpunt is bepaald m.b.v. frequentie afhankelijke rheologische metingen. De overeenkomst met de resultaten verkregen uit de oplosbaarheid en Δn metingen was vrij goed. Dit is een interessante observatie, want het betekent dat het gelpunt bepaald door een statische methode (Δn) overeen komt met dat bepaald m.b.v. dynamische metingen. Deze resultaten zorgen voor een extra bewijs dat de frequentie afhankelijke rheologische metingen inderdaad een goede methode is om gelering i.h.a. te bestuderen.
De netwerkvorming in de VK epoxy-amine mengsels, die bestudeerd is door ons, verloopt op een statistische manier gezien het feit dat de conversie van de epoxygroepen bij het gelpunt en de toename van het aantal gemiddelde molecuul gewicht tijdens de polymerisatie (zie hfd. IV) overeen komt met de theoretische voorspellingen die oorspronkelijk bedoeld zijn voor isotrope systemen. Het rigide karakter van de monomeren en de geordende structuren zijn de twee factoren die deze epoxy-amine netwerken onderscheiden van de conventionele gecrosslinkte polymeren. Een direct onderscheid tussen het effect van beide factoren op de mechanische eigenschappen is waarschijnlijk niet geoorloofd.

Het feit dat de epoxy-amine netwerken, geproduceerd door ons, een heel hoge macroscopische ordening bezitten, zoals aangetoond in hoofdstuk IV, is nogmaals bevestigd door de zeer anisotrope coëfficienten van de thermische expansie (CTE). In sommige gevallen, zijn onder Tg in de richting van de macroscopische orientatie, de waarden van de CTE bijna nul, en boven Tg zelfs negatief. Het is inderdaad mogelijk om de goede mechanische en thermische eigenschappen van de conventionele epoxy-amine netwerken te combineren met de zeer goede eigenschappen van de VK polymeren. In hoofdstuk VI, is voorgesteld dat deze materialen, in principe, toegepast kunnen worden voor omhulling van chips, vooral vanwege hun zeer lage CTE.
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Biography

I was born in March 1966 in Teheran-Iran. After receiving my high school diploma, I came to Holland and started to study chemistry in 1985 at the University of Amsterdam. During my undergraduate research, I worked on the morphology of acrylate dispersions under the supervision of Prof. dr. J. W. Verhoeven. I started my PhD course in 1989 at the Polymer department of Delft University of Technology. From November 1994, I will be working at the DSM research center (Geleen, The Netherlands) in the group of Polymer Networks.