Liquid Crystalline Epoxy Thermosets

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Epoxy resins are used in many applications because of their strength, stiffness, good thermal stability, and excellent adhesion properties. Liquid crystalline epoxy (LCE) networks are an important area of research due to their potential use in a number of applications, such as electronics, advanced composites, non-linear optics etc. The synthesis of LC epoxy resins can be carried out either by using LC epoxy prepolymers, which preserve their ordered morphology in the curing process, or by curing of some functionalized mesogenic rigid molecules using a suitable curing agent In recent years growing interest has been focused on LC thermosets (LCTs), because of their opportunities found in ordered, anisotropic network structures. This paper is a review on our proper results regarding the synthesis and characterization of some LCTs based on monomers with both naphthalene and azomethine mesogenic rigid structures in the main chain.

Keywords: epoxy, mesophase, thermoset, liquid crystal, curing

Epoxy resins are the most important thermosetting polymers, widely commercialized as a matrix for fiber-based composites, structural adhesives, surface coatings and so on [1]. However, epoxy resins have some disadvantages, such as shrinkage during cure and brittleness [2,3]. These disadvantages can be significantly improved by modification using fillers and flexibilizing agents, functionalized groups on the epoxy chains, reactive diluents, additives and curing agents [4-8].

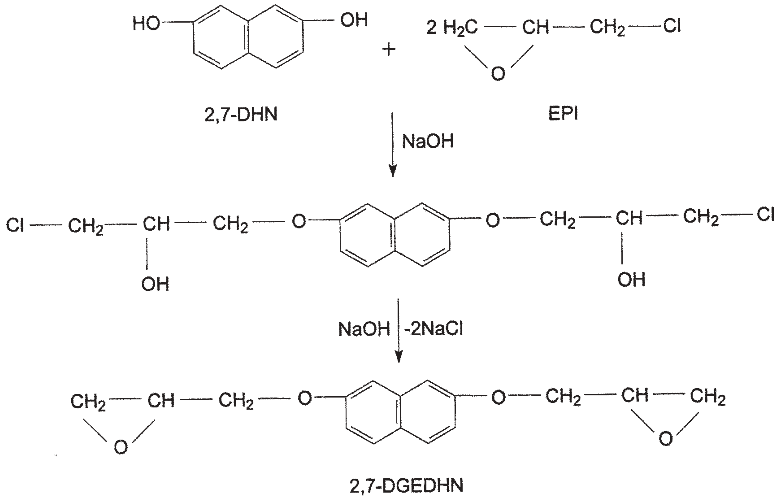
In recent years much attention has been focused on ordered polymeric networks as potential materials for electronic packaging, optoelectronics and advanced composites. These materials could be produced in systems with capacity of self-assembling, as in the case of liquid crystalline thermosets [LCTs]. The LCTs are characterized by high thermal stability, low shrinkage upon curing and low thermal expansion coefficient, respectively decreased dielectric constant [9-11].

The LC epoxies (LCEs), due to their special properties, are particularly interesting as monomers for obtaining LCTs. One way to synthesize the LCTs starting from epoxy resins is the curing of some functionalized mesogenic rigid molecules with a suitable curing agent. Introduction of the mesogenic groups into the structure of the epoxy resins leads to compounds that combine the properties which are specific to the epoxy resins with those which are characteristic to the liquid crystals [12-14]. Generally, LC epoxy resins have been prepared by using biphenyl [15-17], naphthalene [18-20] and ester groups [21,22] as aromatic rigid structures in the diepoxy compounds. Today, there is an increased interest in the synthesis of azomethine epoxy monomers, because of their mesogenic character, easy preparation and good thermal stability [23, 24].

The LC epoxy thermosets with biphenyl mesogen in the main chain have been synthesized and characterized by our group [25-29]. A review was published with subject of these kinds of thermosets [30]. The present paper is a review of our proper results obtained regarding the synthesis and the characterization of some mesogenic epoxy monomers based on naphthalene and azomethines, as well as their curing in presence of various curing agents. The synthesized thermosets were analyzed using differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide angle X-ray scattering (WAXS) techniques.

Synthesis and characterization of mesomorphe epoxy monomers

The monomer diglycidyl ether of 2,7-dihydroxy-naphthalene (2,7-DGEDHN) was synthesized starting from 2,7-dihydroxy-naphthalene (2,7-DHN), epichlorohydrine (EPI) and NaOH, used as catalyst (scheme 1) [31]



Scheme 1. Synthesis of 2,7-DJEDHN monomer

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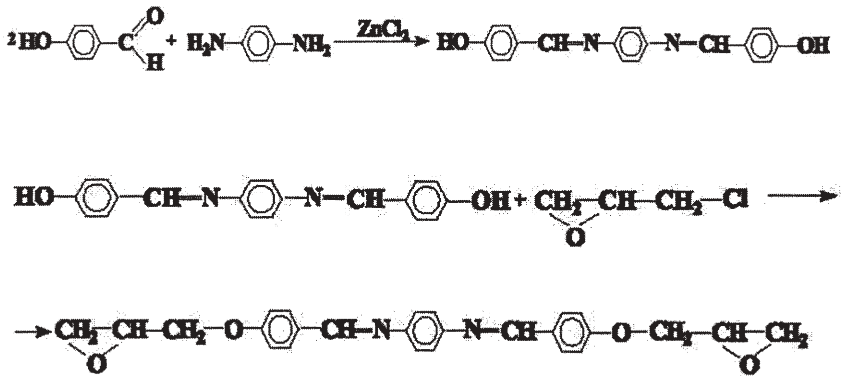


Scheme 2. Synthesis of AZ-1 epoxy monomer.

The synthesized monomer was characterized by IR and [1]H-NMR spectroscopy. The main characteristic bands, as evidenced by IR spectroscopy, were as follows: 1600 and 1500 cm^{-1} for the aromatic ring, 850, 910 and 1200 cm^{-1} for the epoxy group, 575 and 1100 cm^{-1} for the etheric bond. The [1]H-NMR spectrum is characterized by the chemical shifts of the protons from the monomer structure at δ = 2.6 -2.9 ppm (4H, dd, CH_2 of epoxy), δ = 3.1 -3.3 ppm (2H, m, CH of epoxy), δ = 3.8 -4.4 ppm (4H, m, CH_2 of glycidyl), δ = 6.8 -7.0 ppm (4H, m, aromatic ring) and δ = 7.4 – 7.5 ppm (2H, m, aromatic ring).

The LC epoxide monomer N,N´-bis[4-(2,3-epoxy-propoxy)benzylidene]-1,4-phenylenediamine (AZ-1) was obtained by reacting the previous synthesized azomethinic biphenol with an excess of EPI, in the presence of tetrabutylammonium bromide, as a catalyst (scheme 2) [32].

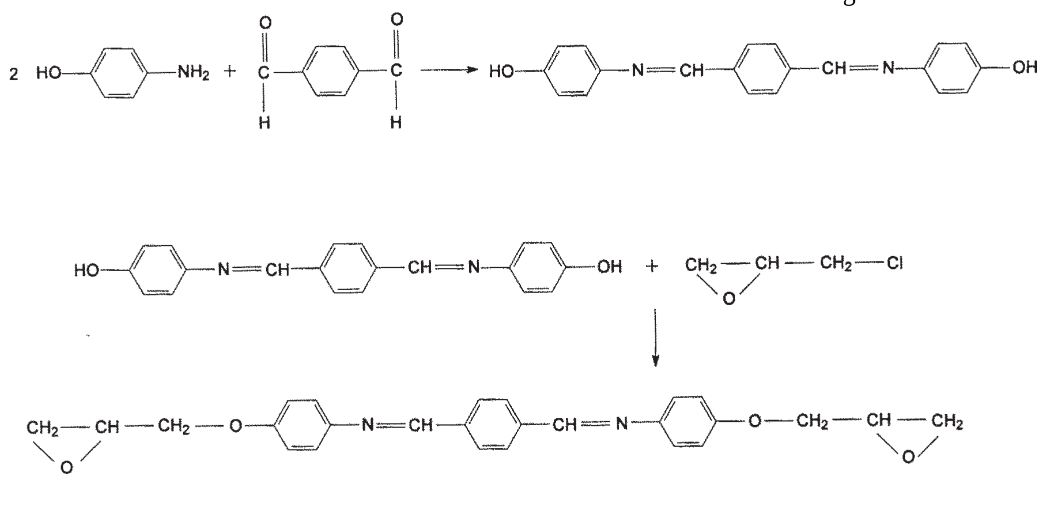
The epoxy azomethinic monomer was characterized by IR, [1]H-NMR and elemental analysis. The main absorbtion bands obtained in the IR spectroscopy (KBr, cm^{-1}}: 1612, 1500 (aromatic ring), 840, 920, 1180 (epoxy), 1615 (azomethine), 580, 1150 (ether group). The [1]H-NMR characterization (ä ppm): 2.5 – 2.8 (m, CH_2 of oxyrane ring, 4H), 3.1 – 3.3 (m, CH of oxyrane ring, 2H), 3.8 – 4.4 (m, CH_2 of epoxy, 4H), 6.6 – 7.6 (m, aromatic ring, 8H), 7.15 (s, aromatic ring, 4H) and 8.25 (s, azomethine, 2H). Elemental analysis ($C_{26}H_{24}O_4N_2$), calc: C, 72.9 %, H, 5.7 %, N, 5.9 %, found: C, 73.5 %, H, 6.2 %, N, 6.1%

.The azomethine epoxy monomer N,N´-(1,4-phenylenedimethylidene)-di-4-(2,3-epoxypropopxy)aniline (AZ-2) was obtained according to scheme 3, starting from the corresponding biphenol and EPI, in presence of benzyltrimethylammonium bromide, as catalyst [33].

AZ-2 epoxy monomer characterization: IR (cm^{-1}), 1600 (aromatic ring),. 910, 1180 and 1250 (epoxy), 1650 (azomethine), 1350 and 2875 (OH groups); [1]H - NMR (δ ppm), 2.7 -2.9 (m, CH_2 of oxyrane ring, 4H), 3.2 – 3.7 (m, CH of oxyrane ring, 2H), 3.9 – 4.2 (m, CH_2 of epoxy, 4H), 6.7 -7.2 (m, aromatic ring, 8H), 7.8 (s, aromatic ring, 4H), 8.45 (s, azomethine, 2H); elemental analysis ($C_{26}H_{24}0_4N_2$, calc ; C, 72.9 %, H, 5.7 %, N, 5.7 %, found, C, 73.8 %, H, 5.9 %, N, 6.2 %.

Samples preparation

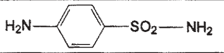
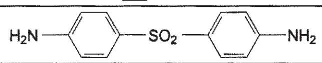
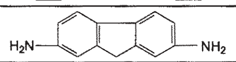
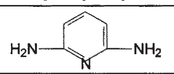
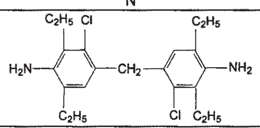
The synthesized epoxy monomers with naphthalene and azomethine mesogens in the main chain and amines (Table 1) appeared as crystalline powders. The monomers and amines were mixed in the solid state in stoichiometric ratios, without using a solvent to prevent the curing reaction to start during dissolution. The cross-linking reactions were



Scheme 3. Synthesis of AZ-2 epoxy monomer

Table 1

AMINES USED AS CURINGY AGENTS

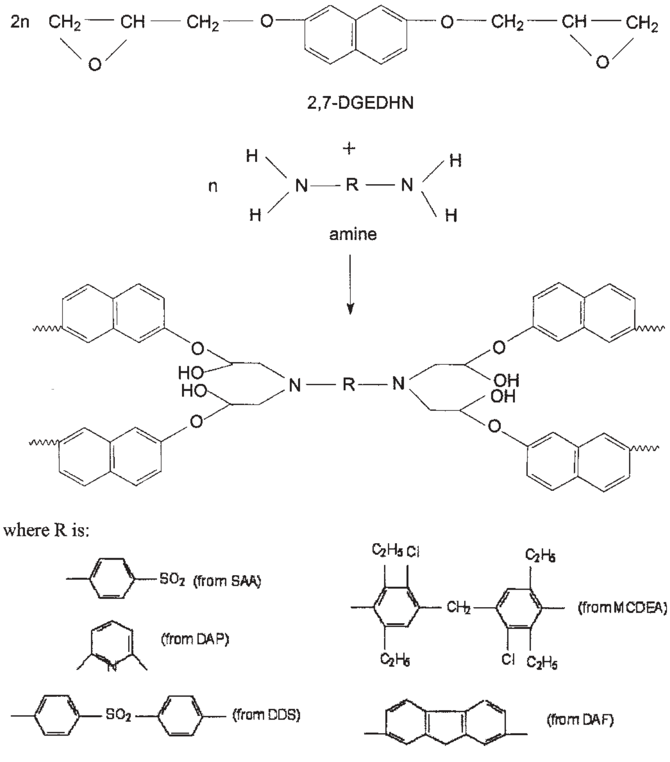
Amine	Formula	Abbreviation
Sulphanilamide		SAA
4,4'-Diamino-diphenyl-sulphone		DDS
2,7-Diamino-fluorene		DAF
Diaminopyridine		DAP
4,4'-Methylene-bis (3-chloro-2,6-diethylaniline)		MCDEA

directly performed in DSC aluminium pans, by simple heating. Samples of about 5-10 mg were sealed in the aluminium pan and heated in a static atmosphere. Calibration of DSC temperatures was carried out using an indium standard.

Epoxy thermosets with naphthalene mesogen in the main chain

2,7-DGEDHN, an isotrope monomer, can be transform from the isotropic phase into a LC polymer by curing in the presence of tetrafunctional aromatic amines [34]. The nature of the amines, used as the curing agents, is very important for the resulting state of the network order.

The phase transformation of the isotropic monomer was carried out using various amines, respectively SAA, DAP, DDS [31,34], MCDEA and DAF [34-36]. The reactions between 2,7-DGEDHN and amines are shown in scheme 4.



Scheme 4. Reactions between 2,7-DGEDHN monomer and amines

The transitions observed by DSC on the curing of 2,7-DGEDHN with SAA amine between 20 and 270^{0}C are due to the melting of the mixture components, as well as to the cross-linking reaction of the 2,7-DGEDHN monomer. The melting of the monomer takes place in the temperature range between 27 and 52^{0}C, with a peak centered at T_{peak} = 43^{0}C. In the temperature range between 117 and 255^{0}C two exothermal transitions are observed, with a centered peak at 193^{0}C. This peak indicates the cross-linking of 2,7-DGEDHN/SAA mixture.

The study of the curing reaction of 2,7-DGEDHN/SAA mixture by POM technique showed that the mesophase appears after the whole melting of the mixture components, around 170^{0}C. The texture of the Schlieren type remains stable until the end of the crosslinking reaction, without the phase transformation. X-ray diffraction technique confirmed the Schlieren texture (nematic type) of the cross-linked product. WAXS of the network (fig.1) shows the presence of a diffuse diffraction ring, with diameter of 4.5Å, characteristic to the nematic texture.

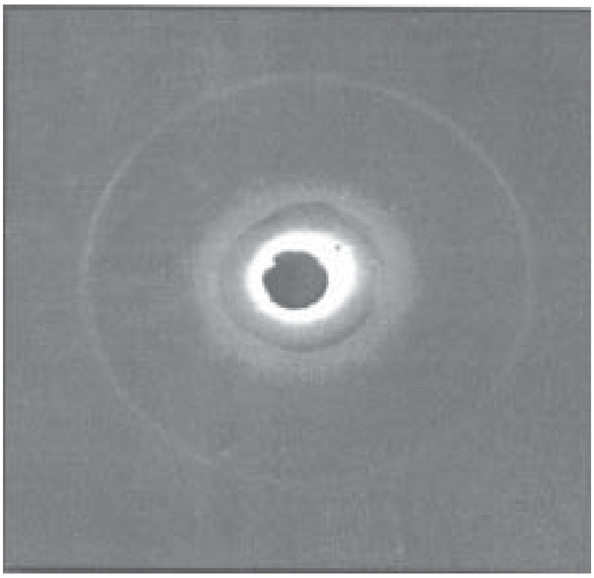


Fig.1. WAXS pattern of 2,7-DGEDHN/SAA mixture

The cross-linking reaction of 2,7-DGEDHN/DAP system takes place in the temperature range between 120 and 191^{0}C. At 150^{0}C the system presents a high density texture of smectic-like structure. The curing reaction of 2,7-DGEDHN/DDS mixture led to a network without LC properties.

The cross-linking reaction of 2,7-DGEDHN/MCDEA mixture takes place in a large interval of temperatures, between 158 and 259^{0}C. In this interval, the reactivity of the amine, used as the curing agent, is much diminished by the inductive effects of the electron donors, due to the chlorine atoms. This can be the explanation why the product obtained by the curing reaction of 2,7-DGEDHN/MCDEA mixture is without LC properties,

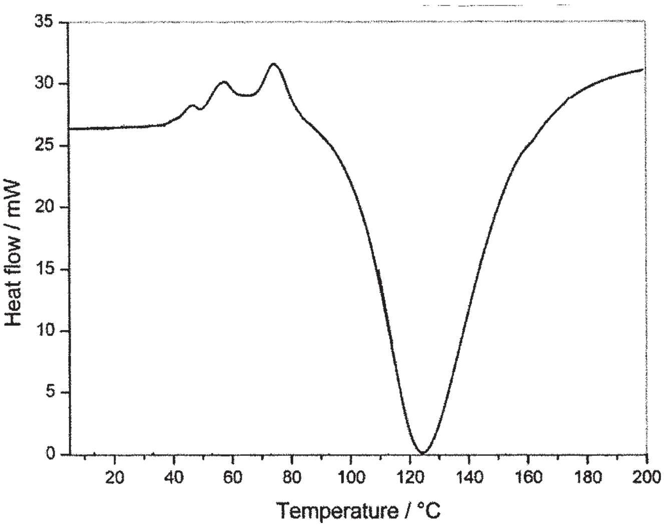
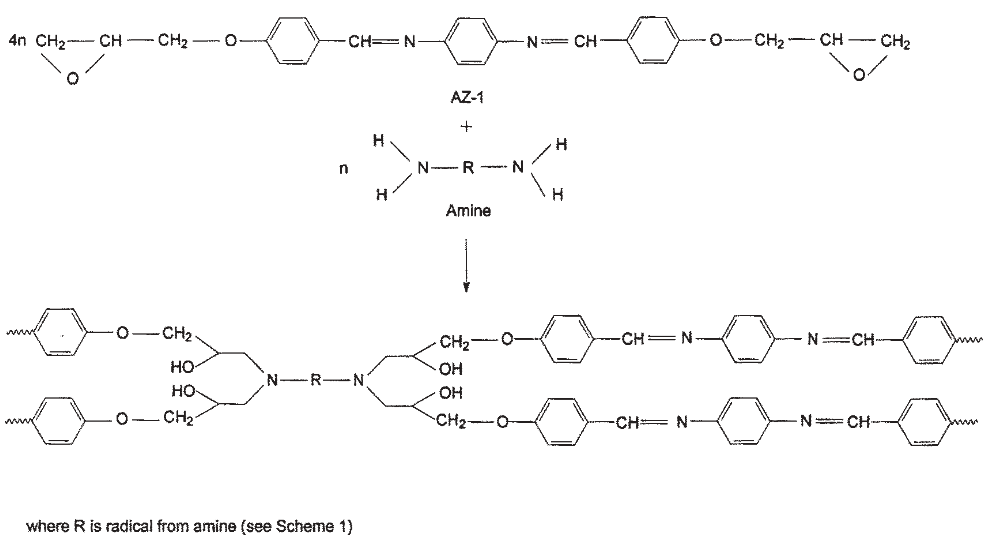


Fig.2. DSC thermogram of 2,7-DGEDHN/DAP mixture at 10^{0}C/min

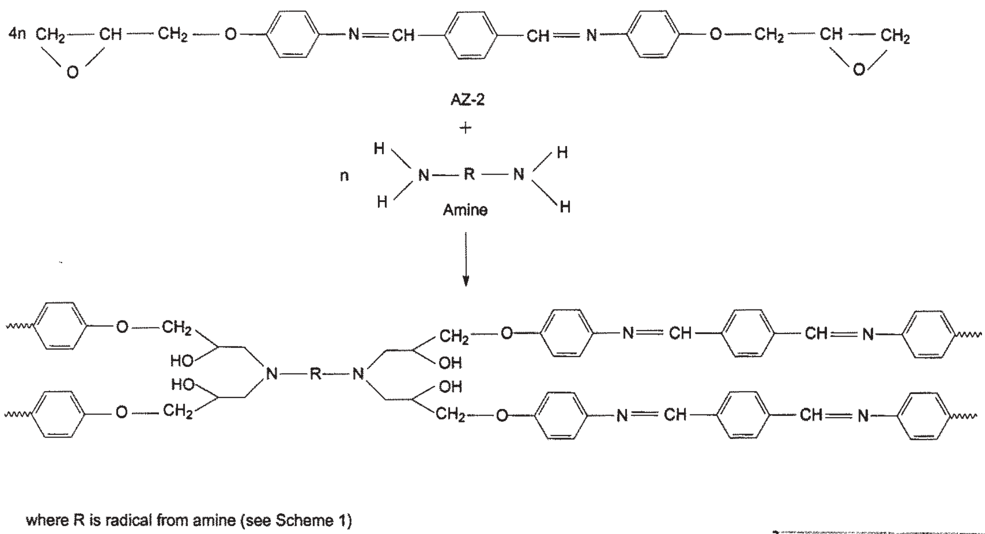
The DSC thermogram obtained by the curing reaction of 2,7-DGEDHN/DAF mixture at a heating rate of 10^{0}C/min is shown in figure 2. The thermogram starts with the melt of the epoxide between 36 and 54^{0}C, with T_{peak} = 50^{0}C, and the melt of amine at T_{peak} = 72^{0}C. The curing reaction of 2,7-DGEDHN/DAF mixture takes place between 81 and 171^{0}C. The obtained product is characterized by a texture of smectic-like structure.

Thermosets with azomethine mesogen in the main chain

Especially, the azo compounds are investigated for their potential applications in optical switching and information storage. Most of the rigid azomethine epoxies exhibit LC behaviour, much attention being given to the LC



Scheme 5. Reactions between AZ-1 monomer and amines



Scheme 6. Reactions between AZ-2 monomer and amines

azomethiner epoxy resins with flexible spacers, both in the main chain and in the side chains.

The synthesized epoxy azomethine monomers, AZ-1 and AZ-2, were cured in the presence of various aromatic amines, respectively SAA [32], MCDEA [31, 37, 38] and DDS [34, 39]. The general reactions between amines and AZ-1, respectively AZ-2 monomers, are shown in Scheme 5 and scheme 6.

The DSC thermogram obtained in dynamic conditions on the curing reaction of the AZ-1/SAA mixture is shown in figure 3. It can be noted that the mixture melts in the range between 133 and 157^{0}C. The curing reaction of AZ-1 monomer in presence of SAA amine takes place between 157 and 190^{0}C. Prior to the end of the curing reaction an endotherm centered at 188^{0}C appears. This endotherm could be attributed to the transition of the LC phase into an isotrope phase, as was observed by POM technique POM under polarized light showed that the AZ-1/SAA mixture was in the melting state at 157^{0}C. The curing reaction began above 160^{0}C, with the formation of a nematic Schlieren texture with thread-like defects (fig.4).

The DSC experiments carried out in dynamic conditions showed the presence of a number of four transitions for AZ-1/MCDEA mixture, namely: melting of amine (T_{peak} = 191^{0}C), melting of epoxy monomer (T_{peak} = 246^{0}C) and thermal degradation (T_{peak} = 290^{0}C). The curing reaction of AZ-1/MCDEA mixture carried out by DSC in isothermal conditions showed that MCDEA amine has a low reactivity. This means long times of reaction, which are favorable to

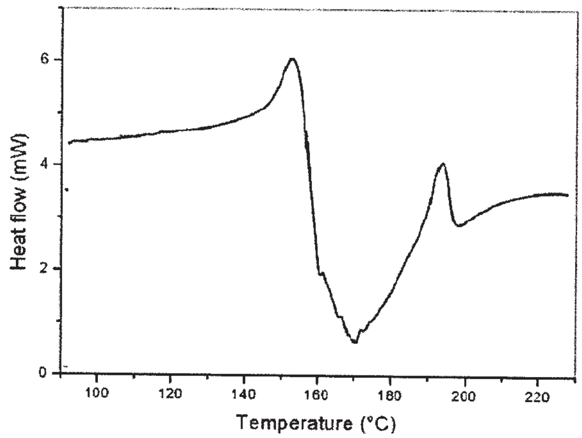


Fig..3. DSC thermogram of AZ-1/SAA mixture at 10^{0}C/min.

the formation of the macromolecular chains with ordered structures. Study of the curing reaction of AZ-1/MCDEA mixture by means of POM technique showed that the mesophase appears starting with 180^{0}C. A smectic type mesophase is formed (fig. 5a). In some time, a smectic-nematic phase transition is produced, which is indicated by the presence of the Schlieren type defects, specific to the nematic texture mesophase (fig, 5b).

The DAF amine is a very fast curing agent for AZ-1 epoxy azomethine monomer that is why the curing reaction of AZ-1/DAF mixture led to a heterogeneous structure, without LC properties.

A LCT was prepared by curing the mesogenic azomethine diepoxide AZ-2 with MCDEA amine. The cross-

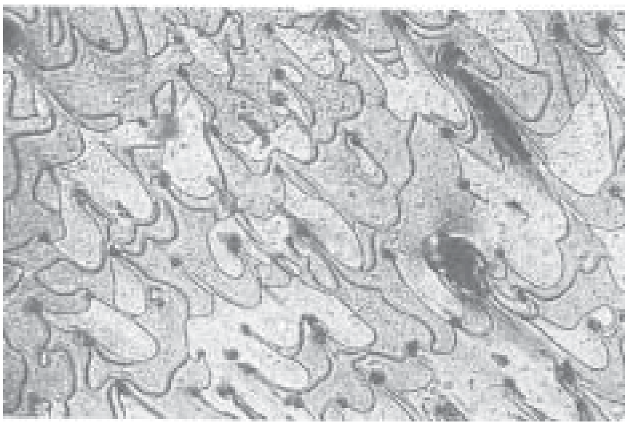


Fig.4. Schlieren texture of AZ-1/SAA cross-linking product.

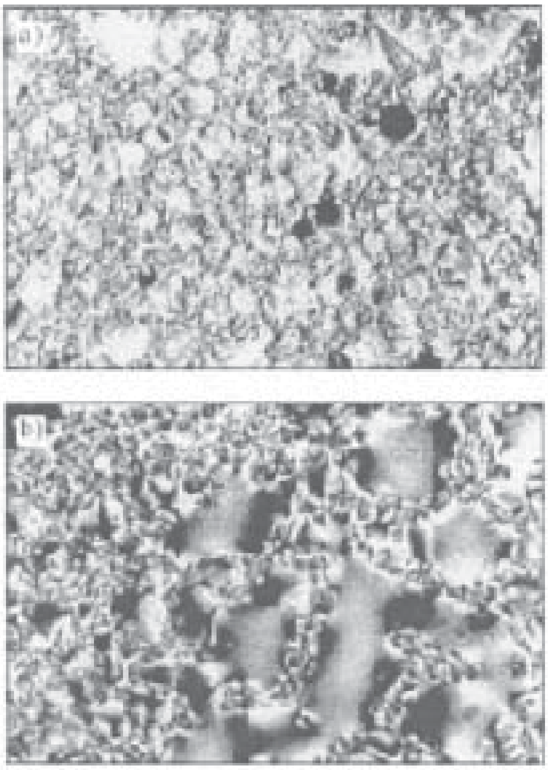


Fig.5. Smectic (a) and nematic (b) Schlieren texture of AZ-1/MCDEA cross-linked product.

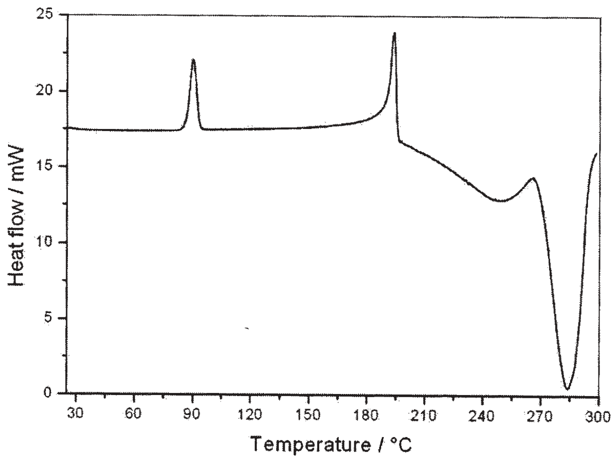


Fig.6. DSC thermogram of AZ-2/MCDEA mixture at 10^0C/min

linking reaction, the phase transitions and the thermal properties of the obtained LCT have been investigated using DSC technique. Figure 6 shows the DSC thermograms recorded on the heating of AZ-2/MCDEA mixture at 10^0C/min. A number of four transitions were observed in the

Fig.7. Texture of AZ-2/MCDEA thermoset under polarized light

temperature range between 30 and 300^0C, due to both the melting of the mixture components and to the cross-linking reaction.

Figure 6 shows that the MCDEA amine melts between 81 and 98^0C, with T_{peak} = 91^0C, while AZ-2 monomer melts between 163 and 197^0C, with T_{peak} = 194^0C. The curing reaction of AZ-2 monomer with MCDEA amine takes place in the range between 196 and 264^0C, with T_{peak} = 245^0C. A thermal degradation process starts on temperatures higher than 264^0C. POM technique evidenced the presence of a smectic B mesophase, which appeared as a result of the cross-linking reaction of AZ-2/MCDEA mixture. The cross-linking reaction in its progress is characterized in POM by appearance of the bands which are gathering under the form of “conical focals” (fig.7).

Over a certain conversion degree the passing from the smectic phase B to the smectic phase E takes place. It is well known that the E type smectic texture is one of the most ordered structures inside of the smectic type mesophases [40].

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Manuscript received: 20.03.2008