JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 11, November 2007, p. 3628 - 3632

# Advanced ordered material based on liquid crystalline azomethine diepoxide

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A liquid crystalline thermoset (LCT) was prepared by curing a mesogenic azomethine diepoxide, N,N′-(1,4-phenylenedimethylidyne)-di-4-(2,3-epoxypropoxy) aniline (AZ-2), with 4,4′-methylene-bis-(3-chloro-2,6-diethylaniline) (MCDEA). The cross-linking reaction, the phase transition and the thermal properties of the LCT have been investigated by differential scanning calorimetry (DSC). The polarized optical microscopy (POM) reveals the formation of an ordered E smectic structure during curing. This structure has been confirmed by wide-angle-X-ray scattering (WAXS) study.

(Received September 10, 2007; accepted November 1, 2007)

*Keywords*: Epoxy, Liquid crystalline thermoset, Azomethine, Curing

## 1. Introduction

In material science one of the present trends is towards building new materials with unusual mechanical and chemical properties and with many potential applications in various domains of the performance technologies. These materials could be produced in systems with capacity of self-assembling, as in the case of liquid crystalline thermosets (LCTs).

The LC epoxy resins are the monomers that have been most frequently studied to obtain LCTs [1-7]. One way to obtain epoxy LCTs is the curing reaction of some functionalized potentially mesogenic rigid molecules with a suitable curing agent. Introduction of the mesogenic groups into the structure of the epoxy resins leads to the compounds that combine the properties, which are specific to the epoxy resins with those which are characteristic to the LC state [8-11].

Epoxy resins containing aromatic rigid rod structures, such as biphenyl, naphthalene, α-methylstylbene and esters are the compounds that have been the most frequently studied to obtain LCTs [12-19]. Recently, epoxy resins containing azo groups in their structures have been synthesized as a new class of high performance polymers [20, 21]. Especially, the azo compounds are investigated for their potential applications in optical switching and information storage. Most of rigid rod azomethine epoxies exhibit LC behaviour. Much attention was given to the LC azomethine epoxy resins with flexible spacers, both in the main chain and as a side chain [22-24].

Only few papers have so far been published on synthesis and curing reaction of LC monomers with azo groups in the central mesogenic core, without flexible spacer in the main chain [25, 26].This study presents data regarding the synthesis and the characterization of an azomethine epoxy monomer, respective N,N′-(1,4-phenylenedimethylidyne)-di-4-(2,3-epoxypropoxy) aniline (AZ-2). On curing with 4,4′-methylene-bis-(3-chloro-2,6-diethylaniline) (MCDEA) the AZ-2 monomer develops a thermoset with an ordered LC smectic texture. These kinds of materials are very interesting for advanced structural applications (e.g. matrix for nanocomposites, microelectronics packaging and nonlinear optics).

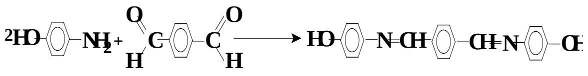
## 2. Experimental

### 2.1. Materials

The diepoxide monomer consisting of a rigid triad aromatic imine, as a central mesogenic unit, was obtained starting from the corresponding bisphenol and epichlorohydrin (EPI).

### 2.1.1. Bisphenol synthesis

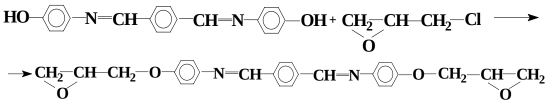
Global reaction of the bisphenol synthesis is shown in Scheme 1. Into 300 mL of dry ethanol were dissolved terephthalaldehyde (0.1mol), 4-aminophenol (0.2 mol) and a catalytic amount of 4-toluenesulfonic acid. The mixture was refluxed for 3h with stirring. After cooling at room temperature the product was separated by precipitation over a water-ice mixture, filtered, washed with distilled water and dried under vacuum. The final product was recystallized from toluene.



*Scheme 1. Synthesis of azomethinic bisphenol.*

### 2.1.2. AZ-2 monomer synthesis

A mixture of bisphenol (0.15 mol) and EPI (4.5 mol) in excess was heated at 105°C, in presence of benzyltrimethylammonium bromide (0.005 mol), as catalyst,.. Reaction is shown in Scheme 2. Into the mixture was dropwise introduced NaOH as a 45 wt % aqueous solution and the mixture was refluxed for 2h. The excess of EPI was removed by distillation in vacuum. After cooling at room temperature the crude product was separated by precipitation, filtered, washed with water several times and dried under vacuum. It was then recrystallized from toluene.



*Scheme 2. Synthesis of AZ-2 monomer.*

### 2.1.3. AZ-2/MCDEA mixture preparation

The MCDEA curing agent (Lonza) was used without further purification. MCDEA has a molar mass of 380.5 and a melting temperature of 90.5°C (isotropic liquid).

The AZ-2/MCDEA mixtures were prepared by mixing in a stoichiometric ratio the two components in the solid powder phase. C The curing reaction was carried out by heating the mixture in the differential scanning calorimeter pan.

### 2.2 Characterization

Both the synthesized bisphenol and AZ-2 monomer were first characterized by using the infrared (IR) and the nuclear magnetic resonance ($^1$H-NMR) spectrophotometric techniques. The IR spectra were recorded on an M 80 Specord spectrophotometer using KBr pellets. The $^1$H-NMR spectra were obtained using a JEOL-JNMC 60 HL apparatus, the spectra being recorded at 30°C from DMSO + TMS.

The monomer characterization and its curing reaction in presence of MCDEA amine was monitored by means of differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide-angle-X-ray scattering (WAXS).

The phase transition and the thermotropic properties, both of the monomer and of the synthesized thermoset, were studied using a Perkin-Elmer DSC-7 Tin and indium were used to calibrate the DSC apparatus.

The texture of the microphases was analyzed with an optical microscope (Reichert Jung) in transmitted light. The microscope was equipped with cross polarizers and with a hot stage Linkam, model TH 600.

The WAXS diffraction patterns of the synthesized thermoset were obtained on a Philips PW 1830 generator, at 45 kV and 30 mA. The exposure time of the Kodak DEF-5 films was about 1.5h

## 3. Results and discussion

### 3.1. Bisphenol and AZ-2 monomer characterization

The synthesized bisphenol was characterized by IR and $^1$H-NMR spectroscopy. Figure 1 shows the $^1$H-NMR spectrum of the bisphenol, while Table 1 lists some of the bisphenol structural characteristics, yield of reaction and the melting temperature (Tm).

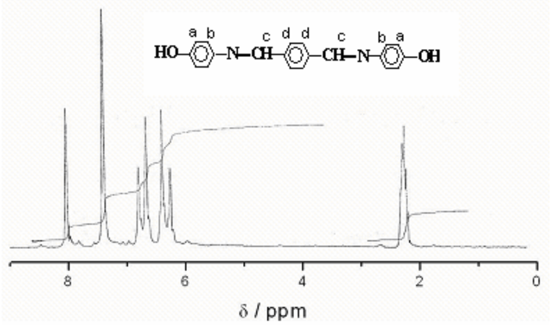


*Fig.1. $^1$H-NMR spectrum of bisphenol.*

*Table 1. Spectroscopic characterization of bisphenol.*

| Yield % | $T_m$ (°C) | $^1$H-NMR (ppm) | IR (KBr) (cm$^{-1}$) |
|---|---|---|---|
| 83 | 273 | 6.8-7.3 (m, $H_{a,b}$, 8H)<br>7.8 (s, $H_d$, 4H)<br>8.3 (s, $H_c$, 2H) | 1470, 1590 (aromatic)<br>1650 (C=N)<br>1230, 3400-3250 (OH) |

The epoxy-terminated monomer bearing azomethine group as mesogen in the central core was synthesized by reaction between the corresponding bisphenol and EPI (Scheme 2). Figure 2 shows the $^1$H-NMR spectrum of the azomethine diepoxide monomer.

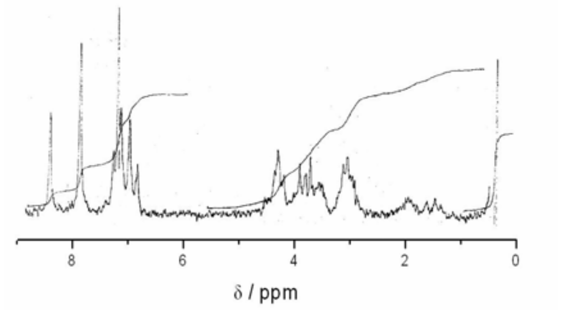


*Fig.2. $^1$H-NMR spectrum of AZ-2 monomer.*

AZ-2 monomer characterization: yield, 82%; Tm, 197°C; IR (cm$^{-1}$), 1600 (aromatic), 910, 1180 and 1250 (epoxy), 1650 (azomethine), 1350 and 2875 (OH group); $^1$H-NMR (δ, ppm), 2.7-2.9 (m, $CH_2$ of oxirane ring, 4H), 3.2-3.7 (m, CH of oxirane ring, 2H), 3.9-4.2 (m, $CH_2$ of epoxy, 4H), 6.7-7.2 (m, aromatic, 8H), 7.8 (s, aromatic, 4H), 8.45 (s, azomethine, 2H); elemental analysis ($C_{26}H_{24}O_4N_2$), calc: C, 72.9 %, H, 5.7 %, N, 5.7 %, found: C, 73.8 %, H, 5.9 %, N, 6.2 %.

The synthesized AZ-2 monomer shows LC properties. A smectic-like structure was identified in melting state, using DSC, POM and X-ray techniques.

The DSC thermogram recorded for AZ-2 monomer at $10^oC$/min heating rate (Fig. 3) shows three endothermic effects: (1) the monomer melting in the temperature range between 174 and 202°C, with a peak centered at $T_{peak}$= 197°C, and an enthalpy $\Delta H_m$= 66 J/g; (2) the smectic (s)- nematic (n) transition in the temperature range between 223 and 231°C, with $T_{s-n}$ = 229°C, and $\Delta H_{s-n}$ = 2.2 J/g ; (3) the nematic – isotrope (i) transition in the temperature range between 246 and 262°C, with $T_{n-i}$ =256°C and $\Delta H_{n-i}$ = 1.9 J/g.

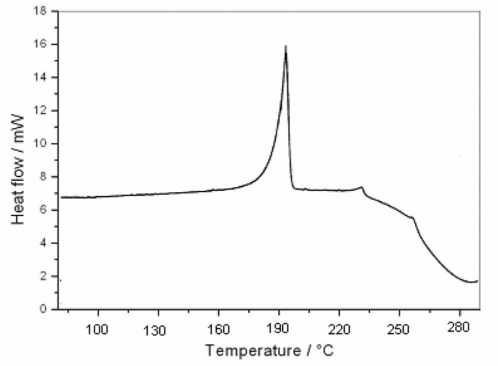


*Fig.3. DSC trace of AZ-2 monomer in dynamic conditions ($10^0C$/min).*

On cooling, the DSC curve recorded at 10 °C/min (Fig. 4) shows three exothermal peaks, with specification as follows: (1) the isotrope – nematic transition between 259 and 245°C, with $T_{i-n}$ = 248°C and $\Delta H_{i-n}$ =1.5 J/g; (2) the nematic – smectic transition between 176°C and 164°C, with $T_{n-s}$ = 167°C and $\Delta H_{n-s}$ = 6 J/g; (3) the smectic mesophase – crystal solid transition between 114 and 106°C, with $T_{s-cryst}$ = 109°C and $\Delta H_{s-cryst}$ = 2.0 J/g.

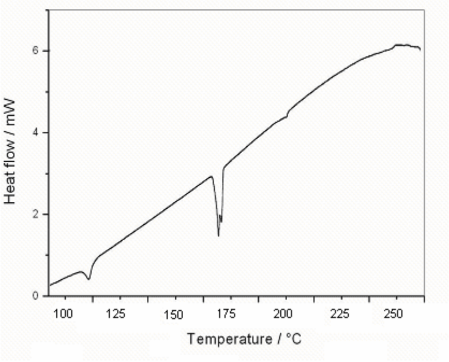


*Fig.4. DSC trace of AZ-2 monomer on cooling ($10^0C$/min).*

The DSC transitions of AZ-2 monomer were confirmed by POM technique. The POM evidenced that AZ-2 monomer develops a smectic-like texture (Fig. 5) after melting (200°C). The smectic mesophase is stable up to 220°C (Fig. 5), then passes into a nematic mesophase at 230°C, and becomes an isotrope liquid at 251°C.

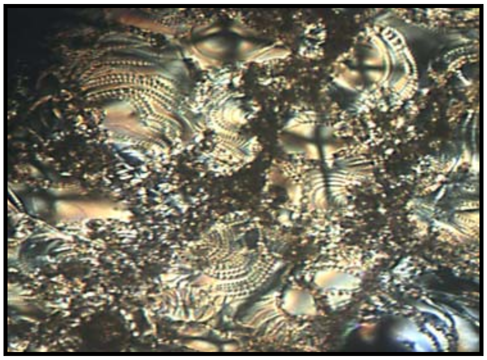


*Fig. 5. Smectic texture of AZ-2 monomer at $210^0C$, obtained under polarized light.*

The WAXS study of the AZ-2 monomer confirms the presence of nematic - smectic transition during the cooling process. Fig. 6 shows the X-ray diffraction pattern of AZ-2 monomer obtained at room temperature. It can be observed a sharp inner ring with a Bragg interplanar distance of 4.34 Å. This distance is characteristic to the smectic mesophase [21].

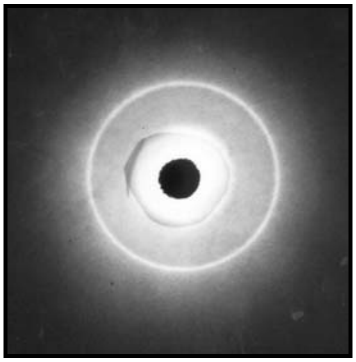
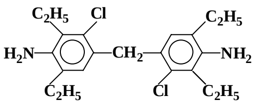


*Fig. 6. Wide-angle X-ray diffraction pattern 0f AZ-2 monomer.*

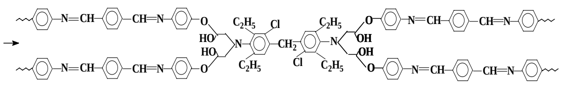
### 3.2. Curing of AZ-2/MCDEA mixture

The structure of the isotrope curing agent (MCDEA) is shown in Scheme 3



*Scheme 3. MCDEA chemical structure.*

The chemical structure of the obtained AZ-2/MCDEA thermoset is shown in Scheme 4.



*Scheme 4. Chemical structure of the thermoset obtained by the curing reaction of AZ-2 monomer with MCDEA amine.*

The study of the curing reaction was carried out by DSC, both in dynamic and in isothermal conditions. Figure 7 shows the DSC thermogram recorded on the heating of AZ-2/MCDEA mixture with 10°C/min. A number of four transitions were observed in the temperature range between 30 and 300°C, due to both the melting of the mixture components and to the cross-linking reaction.

The mixture components melt at various temperatures. Figure 7 shows that MCDEA amine melts between 81 and $98^0$C, with $T_{peak}$=$91^0$C and $\Delta H$ = 22.9 J/g. The AZ-2 monomer melts between 163 and $197^0$C, with $T_{peak}$= $194^0$C and $\Delta H$ =57.7 J/g. The curing reaction of AZ-2 monomer with MCDEA amine takes place in the range between 196 and 264°C with $T_{peak}$ =245°C and $\Delta H_{cur}$ = 87.9 J/g. A thermal degradation process starts at temperatures higher than 264°C.

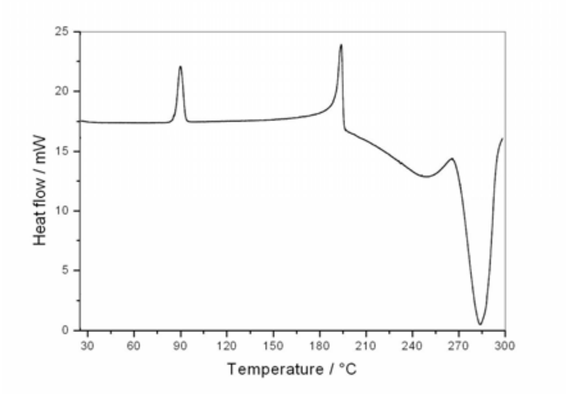


*Fig. 7. DSC trace of AZ-2/MCDEA mixture in dynamic condition ( 10°C/min).*

The curing reaction studied by DSC in isothermal conditions shows that MCDEA amine has a low reactivity. Thus, for the temperature 170°C the reaction reaches the highest conversion after about 150 minutes, for the temperature 180°C the corresponding time is around 125 minutes, while for the temperature 190°C the curing reaction needs no more than 60 minutes (Fig. 8).

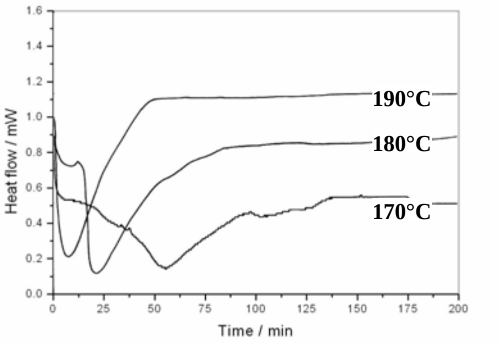


*Fig. 8. DSC thermograms of AZ-2/MCDEA mixture in isothermal conditions.*

POM technique evidences 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 is characterized by appearance of the bands which are gathering under the form of "conical focals" (Fig. 9). Over a certain conversion degree the passing from the smectic phase B to the smectic phase E takes place. This transformation is visible in POM by modification of the bands, which appear as orthorhombic structures, with dissimilar orientations.

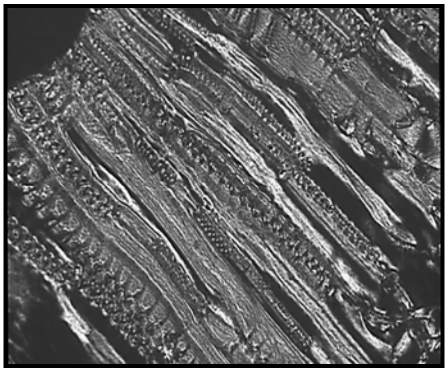


*Fig. 9. Texture of AZ-2/MCDEA thermoset under polarized light.*

It is well known that the smectic mesophase of E type is one of the most ordered structure inside of the smectic mesophases [27].

The WAXS analyses confirm the results obtained by POM technique. The X-ray pattern obtained at wide angles and shown in Fig. 10 presents the intermolecular distances between molecules of 3.19 (weak), 3.89 (strong) and 4.34 Å (very strong).

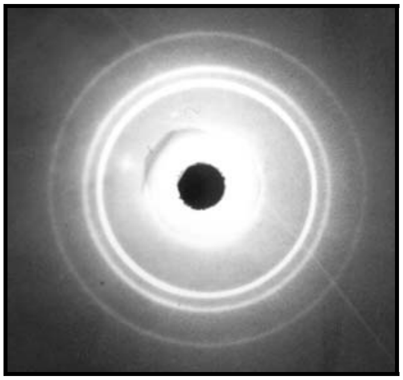


*Fig. 10. Wide-angle X-ray diffraction pattern of AZ-2/MCDEA thermoset.*

## 4. Conclusions

The mesogenic azomethine diepoxide N,N′-(1,4-phenylenedimethylidyne)-di-4-(2,3-epoxypropoxy) aniline was synthesized and characterized by IR, $^1$H-NMR, DSC, POM and WAXS techniques. The synthesized monomer shows LC properties. Its LC structure is preserved and after the curing reaction with MCDEA amine, used as the curing agent.

The curing of AZ-2/MCDEA mixture leads to a high ordered E smectic mesophase. On curing, the low reactivity of MCDEA amine allows longer reaction times and this leads to an ordered arrangement of the macromolecular chains.

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