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Curing reaction of azomethine epoxy liquid crystals

Summary — The aromatic epoxy *N,N*-bis[4-(2,3-epoxy propoxy)benzylidene]-1,4-phenylenediamine (AZ-1) with mesogenic properties was synthesized and cured in the presence of 4,4′-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA) or 2,7-diaminofluorene (DAF) as the curing agents. The curing reactions were studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide-angle X-ray scattering. The product obtained in the curing reaction of AZ-1/MCDEA mixture shows a texture of smectic-like structure. The curing reaction of AZ-1/DAF mixture led to a heterogeneous structure, without liquid crystalline properties.

Key words: azomethine epoxy monomer, curing, mesogenic properties, liquid crystal.

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Streszczenie — Zsyntetyzowano aromatyczną epoksydową *N,N′*-bis[4-(2,3-epoksypropoksy)benzylideno]-1,4-fenylenodiaminę (AZ-1, Schemat A) wykazującą właściwości mezogeniczne, którą następnie utwardzano w obecności 4,4′-metyleno-bis(3-chloro-2,6-dietyloaniliny) (MCDEA) lub 2,7-diaminofluorenu (DAF) (schemat B). Reakcję utwardzania badano metodą skaningowej kalorymetrii różnicowej (DSC) (rys. 1, 4 i 5), szerokokątowego rozpraszania promieni rentgenowskich (WAXS) (rys. 3) i za pomocą polaryzacyjnego mikroskopu optycznego (POM) (rys. 2). Produkt otrzymany w wyniku utwardzania mieszaniny AZ-1/MCDEA charakteryzuje się teksturą odpowiadającą fazie smektycznej. Utwardzanie mieszaniny AZ-1/DAF prowadzi do otrzymania struktury heterogenicznej, która nie wykazuje właściwości ciekłokrystalicznych.

Słowa kluczowe: azometynowy monomer epoksydowy, utwardzanie, właściwości mezogeniczne, ciekły kryształ.

Epoxy resins are the most important thermosetting polymers, widely commercialized as structural adhesives, surface coatings, matrices for fiber-based composites and so on [1]. Also, advanced materials starting from epoxy resins have been prepared [2—6].

In recent years there has been increased interest in ordered polymeric networks as potential materials for electronic packaging, optoelectronics and advanced composites. A lot of attention has been given to the epoxy liquid crystalline thermosets (LCTs), due to their high chemical resistance, very good mechanical and thermal properties, as well as good electrical insulation. These make LCTs suitable for advanced applications, such as microelectrical packings, matrices for composites and nonlinear optics, respectively [7, 8].

The LCTs are characterized by high thermal stability, low shrinkage upon curing, low thermal expansion coefficient and low dielectric constant [9]. The liquid crystalline (LC) epoxides, 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. LC epoxy resins containing aromatic rigid rod-structures, such as biphenyl [10—14], naphthalene [15—18], esters [19, 20] or σ-methylstilbene [21, 22] are the monomers that have been the most frequently studied to obtain LCTs.

In the last few years a lot of attention was given to LC azomethine epoxy monomers, because of their mesogenic character, easy preparation and good thermal stability [23—26].

In a previous paper [27] we investigated the synthesis and the curing reaction of LC epoxy azomethine *N,N′*-bis[4-(2,3-epoxypropoxy)benzylidene]-1,4-phenylenediamine (AZ-1). The monomer was cured in the nematic phase by means of sulfanilamide (SAA), used as a curing agent. It was noted that Schlieren nematic-like texture of the studied monomer was preserved also after the curing process.

The aim of this paper is to extend the study on the curing reaction of AZ-1 monomer in the presence of other aromatic amines, namely 4-4′-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA) and 2,7-diaminofluorene (DAF), used as the curing agents. The phase transition of the azomethine monomer and the thermotropic properties of the networks obtained as a result of the curing reaction were monitored by differential scan-

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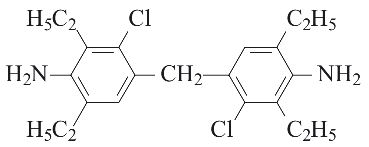
ning calorimetry (DSC), polarized optical microscopy (POM) and wide-angle X-ray scattering (WAXS) techniques.

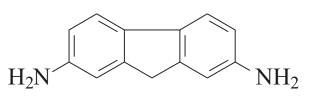
EXPERIMENTAL

Materials

The AZ-1 monomer with three aromatic rings linked by azomethine central groups was obtained as previously reported [26, 27], starting from corresponding biphenol in reaction with epichlorohydrin (EPI) (Scheme A). The 4-hydroxybenzaldehyde (4-HB), 1,4-phenylenediamine (1,4-PhD), EPI and amine curing agents *i.e.* MCDEA [formula (I)] and DAF [formula (II)] were chemically pure reagents (Aldrich) and were used without further purification.



(I)



(II)

Curing reaction of monomer

The curing reaction was carried out by mechanical mixing of AZ-1 monomer with aromatic amine in stoichiometric ratio of 2:1, then heating the mixture in the differential scanning calorimeter pan.

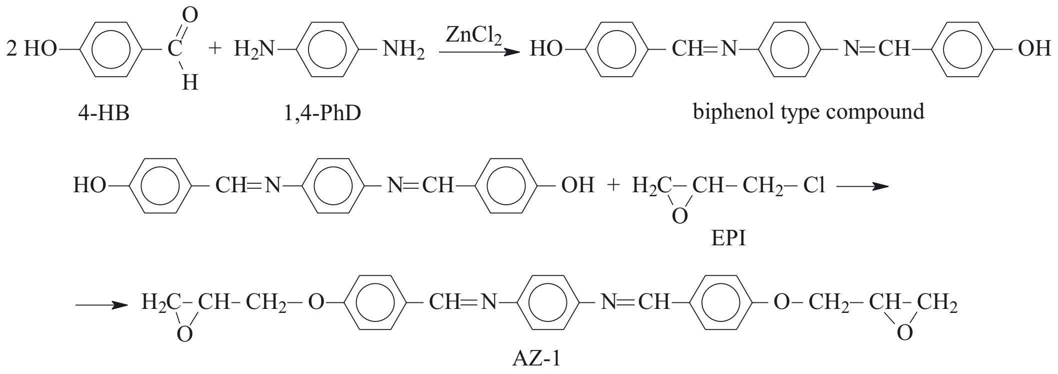
Method of testing

The curing reaction of AZ-1 monomer with amines was monitored by DSC, POM and WAXS techniques.

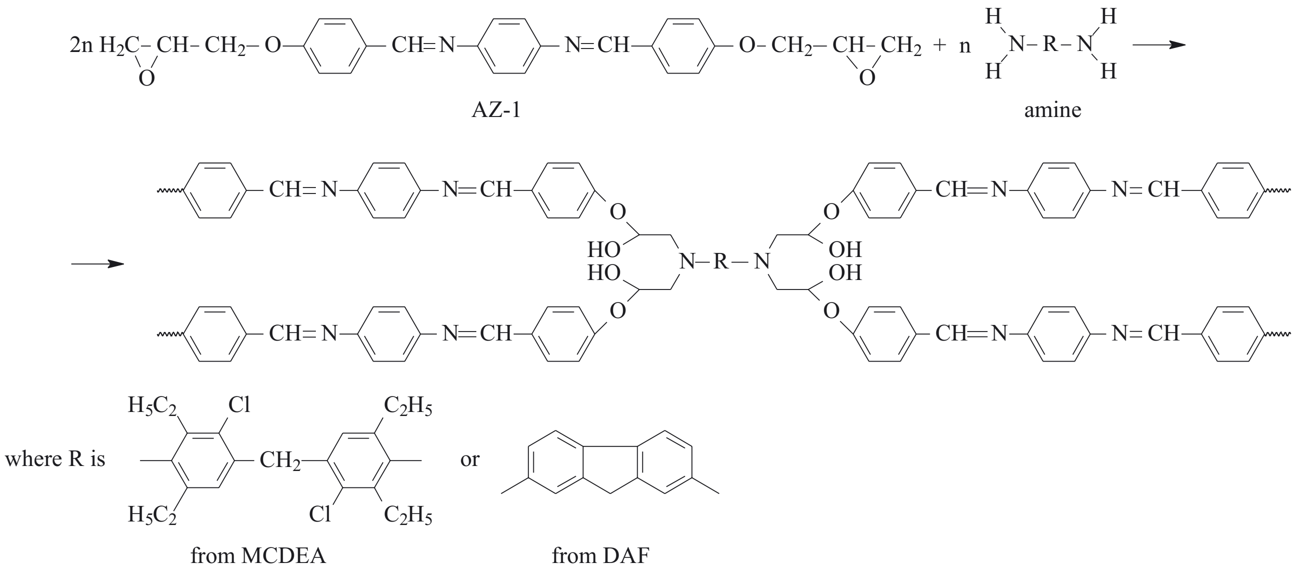
The thermotropic properties of the synthesized cross-linked resins were studied using a Perkin-Elmer DSC-7 differential scanning calorimeter.

The texture of the cured resins was observed using a Reichert Jung optical microscope under crossed polarizers, equipped with hot stage Linkam THMS 600.

The WAXS analyses were performed using a Philips Electronics PW 1830 generator provided with a copper



Scheme A. Synthesis of AZ-1 epoxy azomethine monomer



Scheme B. Curing reaction between AZ-1 and amine (MCDEA or DAF) anticathode tube having a nickel filter. The generator was operated at 45 kV and 30 mA.

RESULTS AND DISCUSSION

Analyses by DSC, POM and WAXS showed that AZ-1 monomer presents a nematic-like texture.

The phase transformation of AZ-1 monomer was carried out in the presence of two aromatic diamines, respective MCDEA and DAF, used as the curing agents. The reactions of AZ-1 with amines are schematically shown in Scheme B.

Curing reaction of AZ-1/MCDEA mixture

The DSC experiments carried out in dynamic conditions (Fig. 1) showed four transitions for AZ-1/MCDEA mixture, namely: melting of amine (T_{peak} = 191 °C, ΔH_m = 252 J/g), melting of epoxy monomer (T_{peak} = 189 °C, ΔH_m = 52.7 J/g), crosslinking reaction (T_{peak} = 246 °C, ΔH_{cr} = 231 J/g) and thermal degradation (T_{peak} = 290 °C).

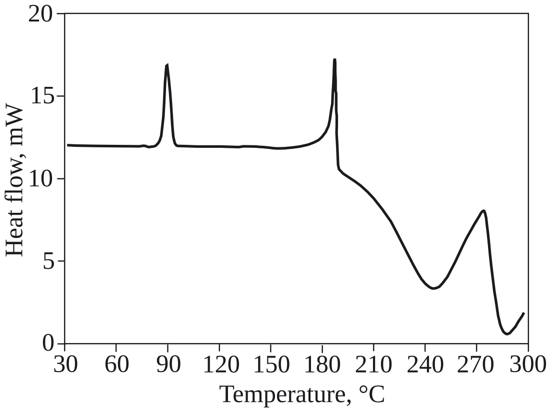


Fig. 1. DSC thermogram of AZ-1/MCDEA mixture; heating rate 10 °C/min

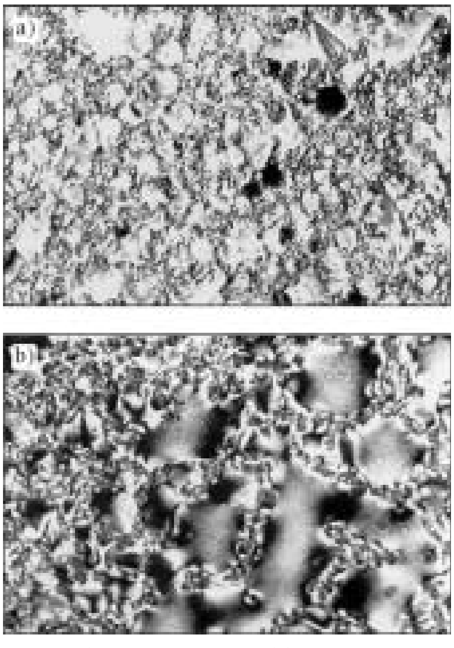


Fig. 2. Smectic (a) and nematic Schlieren texture (b) of crosslinked product of AZ-1/MCDEA mixture

The curing reaction of AZ-1/MCDEA mixture studied by DSC in isothermal conditions showed that MCDEA amine has a low reactivity. This means long time of reaction, which promote the formation of macromolecular chains with ordered structures.

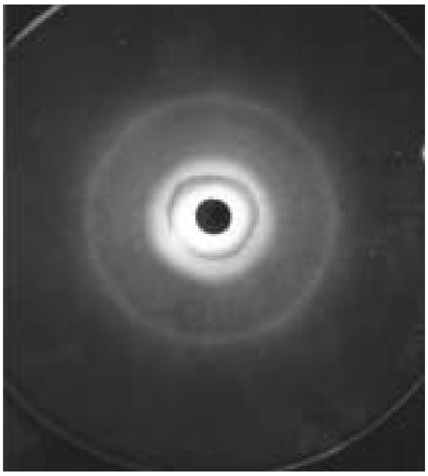


Fig 3. WAXS pattern of AZ-1/MCDEA mixture

Study of the curing reaction of AZ-1/MCDEA mixture by means of POM technique showed that the mesophase appears starting at 180 °C. A smectic-like mesophase is formed (Fig. 2a). In some time, a smectic-nematic phase transition is produced, which is indicated by the presence of defects of Schlieren type, specyfic to the nematic mesophase (Fig. 2b).

The presence of smectic-nematic mesophase was confirmed by WAXS method. The WAXS pattern of AZ-1/MCDEA mixture obtained at 180 °C is shown in Fig 3. The LC epoxy thermoset shows a layered structure with intermolecular correlation within the layers of 3.67 Å (smectic) and 4.29 Å (nematic).

Curing reaction of AZ-1/DAF mixture

The DSC trace obtained for the curing reaction of AZ-1/DAF mixture in dynamic conditions between 25 and 250 °C is shown in Fig. 4.

The melting of the mixture takes place between 113 and 139 °C, with a peak centered at T_{peak} = 135 °C and enthalpy ΔH_m = 10.6 J/g. The chemical reaction between AZ-1 monomer and DAF amine starts at 139 °C and finished at 217 °C, being accompanied with high enthalpy value (280 J/g). The DSC measurement carried out in isothermal conditions showed that the reaction between these two components of mixture was very fast (Fig. 5). At temperature of 135 °C, after 2 min time of curing a high degree of crosslinking was reacted.

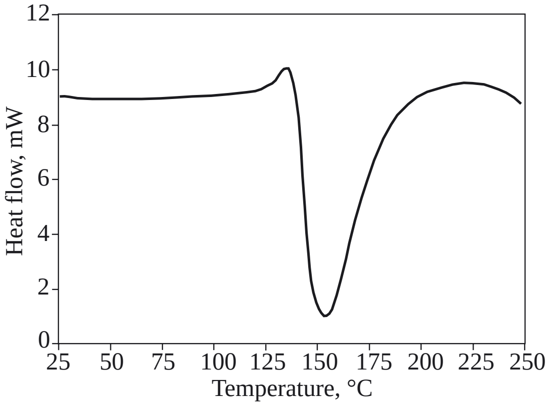


Fig 4. DSC thermogram of AZ-1/DAF mixture; heating rate 10 °C/min

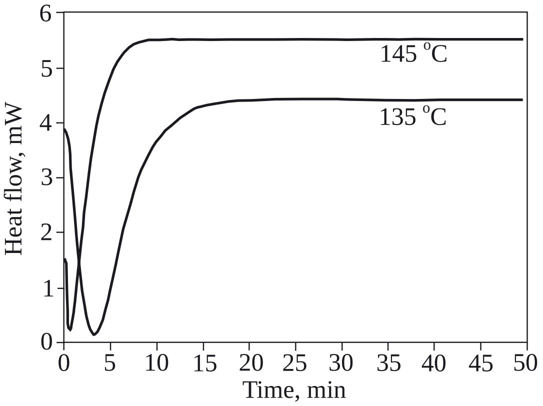


Fig 5. DSC thermogram of AZ-1/DAF mixture heated in isothermal conditions

The POM experiments carried out while heating of AZ-1/DAF mixture showed the partial melting of amine and its incomplete reaction with epoxy. Conclusion is that DAF amine is a very fast curing agent for AZ-1 epoxy azomethine monomer. Finally, a heterogeneous structure is obtained for AZ-1/DAF mixture in curring reaction.

CONCLUSIONS

Epoxy azomethine monomer *N,N′*-bis[4-(2,3-epoxypropoxy)benzylidene]-1,4-phenylenediamine (AZ-1) has mesogenic properties. The nematic-like texture of AZ-1 monomer was indicated by DSC, POM and WAXS techniques [27]. Its Schlieren type texture is preserved after the curing reaction in the presence of sulfanilamide (SAA). The curing reaction of AZ-1 monomer with MCDEA amine, used as the curing agent, led to a texture of smectic-like structure. In the presence of DAF amine AZ-1 monomer, formed by curing a heterogeneous structure, without LC properties. In DSC experiments of the investigated systems the second heating has not shown any residual release. This behavior means that the studied reactions were completed.

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