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Liquid crystalline epoxy thermoset with azomethine mesogen

Summary — This work is a continuation of our earlier investigations on the liquid crystalline epoxy resins containing azomethine as mesogen group. The present study concerns the curing reaction of an azomethine epoxy monomer, namely, *N,N´*-(1,4-phenylenedimethylidyne)-di-4-(2,3-epoxypropoxy) aniline (AZ-2) in the presence of 2-amino-biphenyl (2-ABPh), used as a curing agent. The crosslinking reaction, the phase transitions and the thermal properties of the synthesized thermoset were monitored by differential scanning calorimetry (DSC), polarized optical microscopy and wide-angle X-ray scattering (WAXS). The main thermal transitions observed by DSC in dynamic conditions are due to both melting of the mixture components and the crosslinking reaction. The reaction of AZ-2 monomer with 2-ABPh takes place in the temperature range from 184 to 278 ^{o}C, and the process is accompanied with homopolymerization of the epoxy groups. The microscopic technique revealed the appearance of a smectic type mesophase, the result being confirmed by WAXS measurements.

Key words: epoxy resins, azomethine mesogen, curing, liquid crystal, smectic mesophase.

CIEKŁOKRYSTALICZNE TERMOUTWARDZALNE MATERIAŁY EPOKSYDOWE Z AZOMETINOWĄ GRUPĄ MEZOGENICZNĄ

Streszczenie — Artykuł przedstawia pracę stanowiącą kontynuację wcześniejszych badań nad ciekłokrystalicznymi żywicami epoksydowymi zawierającymi azometinowe grupy mezogeniczne. Obecne badania obejmowały proces utwardzania epoksydowego monomeru azometynowego, mianowicie *N,N*-(1,4-fenylenodimetylidyno)-di-4-(2,3-epoksypropoksy)aniliny (AZ-2) w obecności 2-amino-bifenylu (2-ABPh) jak czynnika utwardzającego. Reakcję sieciowania, przejścia fazowe i właściwości termiczne syntetyzowanych materiałów termoutwardzalnych oceniano za pomocą metod DSC w warunkach dynamicznych (rys. 1) i izotermicznych (rys. 2), WAXS (rys. 4) oraz polaryzacyjnej mikroskopii optycznej (rys. 3). Główne przejścia termiczne obserwowane na krzywych DSC (w warunkach dynamicznych) wynikają z procesu topnienia obu składników mieszaniny, a także z reakcji sieciowania. Sieciowanie AZ-2 z 2-ABPh następuje w przedziale temp. 184—278 ^{o}C z jednoczesną homopolimeryzacją przebiegającą kosztem grup epoksydowych. Metodą mikroskopową wykazano smektyczny charakter mezofazy, co potwierdzono również techniką WAXS.

Słowa kluczowe: żywice epoksydowe, azometynowe ugrupowanie mezogeniczne, sieciowanie, struktura ciekłokrystaliczna, mezofaza smektyczna.

In the material science one of the present trends consists in generation of ordered polymeric structures for applications in advanced technological fields, including optical data storage, non-linear optics, electronic packaging, insulating layers and high performance composites. Numerous studies were carried out on the polymers with ordered structures. These structures can be obtained in the systems with self-assembling ability, as in the case of liquid crystals [1—5].

Epoxy resins are the most important thermosetting polymers, widely commercialized as matrices for fiber-based composites, structural adhesives, surface coatings and so on [6]. Accordingly, advanced materials have been prepared starting from epoxy resins [7—10].

In recent years there has been increased interest in epoxy liquid crystalline thermosets (ELCT), due to their high chemical resistance, very good mechanical and thermal properties, as well as good electrical insulation [11—14]. The ELCT are characterized by high thermal stability, low shrinkage upon curing, low thermal expansion coefficient and low dielectric constant. Generally, ELCT can be obtained starting from epoxy resins containing aromatic rigid rod structures, such as biphenyl, naphthalene, α-methylstylbene and some esters [15—18]. Presently, a great attention is given to azomethine epoxy resins, due to their mesogenic character, easy preparation and good thermal stability [19—21]

In a previous paper [22] we presented the synthesis and the characterization of a triad diepoxide with azomethine linked unsubstituted aromatic rings, namely *N,N´*-(1,4-phenylenedimethylidine)-di-4-(2,3-epoxy propoxy) aniline (AZ-2). When cured with 4,4´-methylene-bis-(3-chloro-2,6-diethylaniline) (MCDEA) the AZ-2 monomer developed a thermoset with an ordered liquid crystal smectic type texture.

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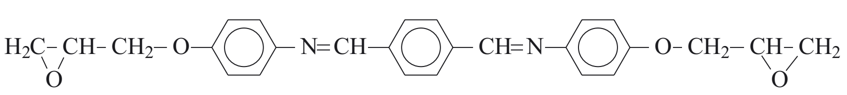
The aim of this work is to extend the study on the curing reaction of AZ-2 monomer in the presence of other aromatic amine, namely 2-amino-biphenyl (2-ABPh). The curing reaction of AZ-2 monomer in the presence of 2-ABPh as a curing agent was monitored by differential scanning calorimetry (DSC), polarized optical microscopy and wide-angle X-ray scattering (WAXS) techniques.

EXPERIMENTAL

Materials

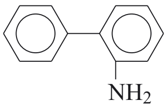
The chemical structures both of AZ-2 monomer and 2-ABPh amine are as follows [formula (I) and formula (II)].

The AZ-2 monomer with three aromatic rings linked by azomethine central groups was obtained as previously reported [22], starting from corresponding biphenol in the reaction with epichlorohydrin (EPI) [Scheme A].



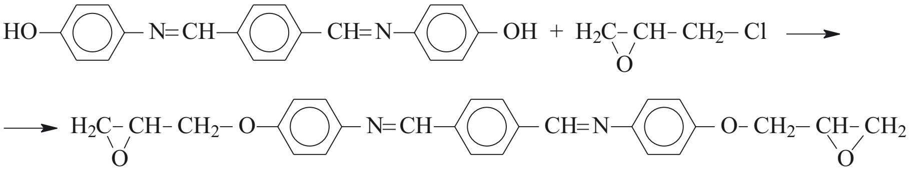
(I)

AZ-2 (smectic)

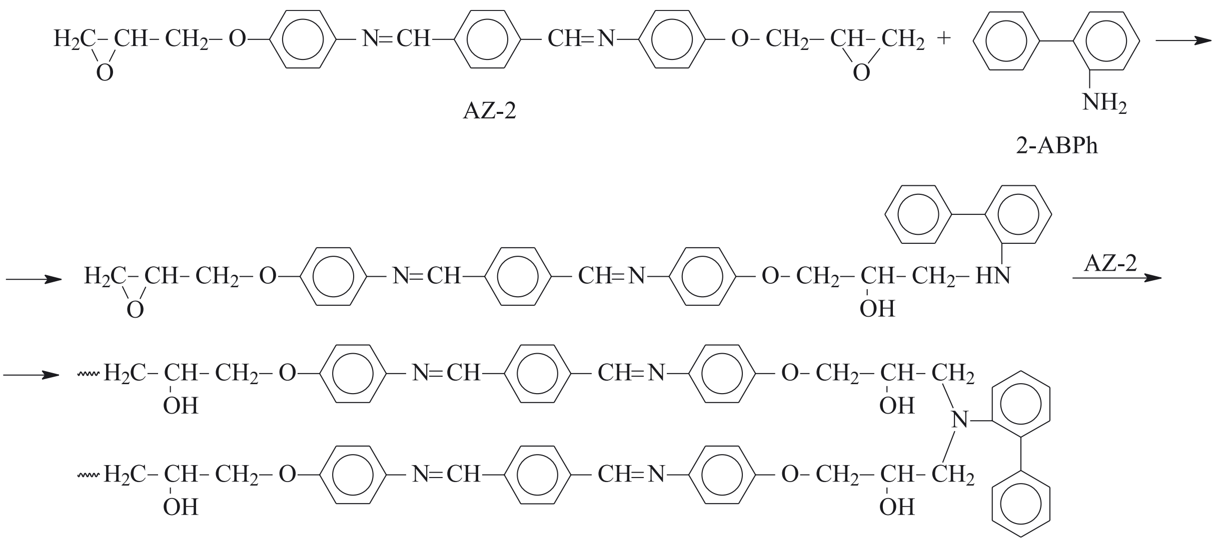


(II)

2-ABPh (isotrope)



Scheme A: Synthesis of AZ-2 epoxy azomethine monomer



Scheme B: Curing reaction of ZA-2 with 2ABPh

Terephthalaldehyde and *p*-aminophenol (for synthesis of corresponding biphenol) as well as EPI and 2-ABPh were chemically pure reagents (Aldrich), and were used without further purification.

Curing reaction of AZ-2 monomer

Both AZ-2 monomer and 2-ABPh amine, as crystalline powders, were mixed in stoichiometric ratio of 2:1, then the mixture was heated in the differential scanning calorimeter pan.

Method of testing

— The thermotropic properties of the synthesized thermoset were studied using a Perkin-Elmer differential scanning calorimeter.

— The texture 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 at 45 kV and 30 mA.

RESULTS AND DISCUSSION

The reaction of AZ-2 diepoxy monomer with 2-ABPh curing agent is schematically shown in Scheme B. The DSC thermogram obtained during this reaction conducted in dynamic conditions (10 °C/min) is shown in Fig. 1.

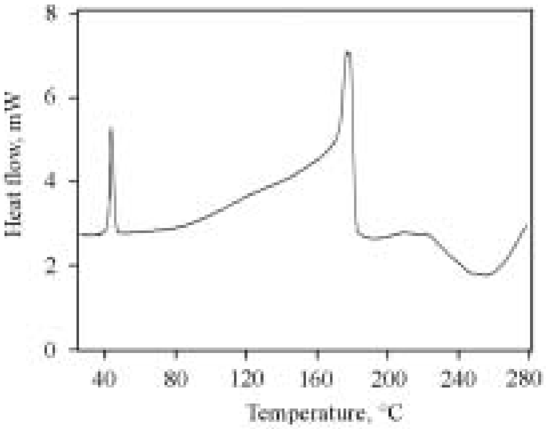


Fig. 1. DSC curve of AZ-2/2-ABPh mixture in dynamic conditions (10 °C/min)

The main thermal transitions observed in the temperature range from 25 to 280 °C are due to both the melting of the mixture components and the crosslinking reaction. Figure 1 indicates that amine melts between 41 and 55 °C, with T_{peak} = 50 °C and a melting reaction enthalpy ΔH_m = 9.06 J/g. Diepoxy monomer melts in the range 161—182 °C, with T_{peak} = 181 °C and ΔH_m = 18.9 J/g. The curing reaction of AZ-2 monomer in the presence of 2-ABPh amine starts at temp. 184 °C and the presence of a double peak is observed in DSC thermogram. The curing reaction takes place at temperature below 250 °C, being followed by homopolymerization of the epoxy groups at higher temperatures.

The curing reaction of AZ-2/2-ABPh mixture studied by DSC in isothermal conditions showed that 2-ABPh compound had a high reactivity with AZ-2 monomer. The DSC curves recorded using three various temperatures (Fig. 2) showed the presence of the multiple peaks and short times for curing reaction to be finished, decreasing with increase in measurement temperature. Thus, for the temperature 165 °C the reaction reached the highest conversion after 2.5 minutes, for 170 °C the curing reaction needed no more than 1.1 minutes.

More information on the curing reaction of the studied mixture were obtained using polarized optical microscopy technique. At temperature 185 °C the mixture was in totally molten state, with well defined bire-

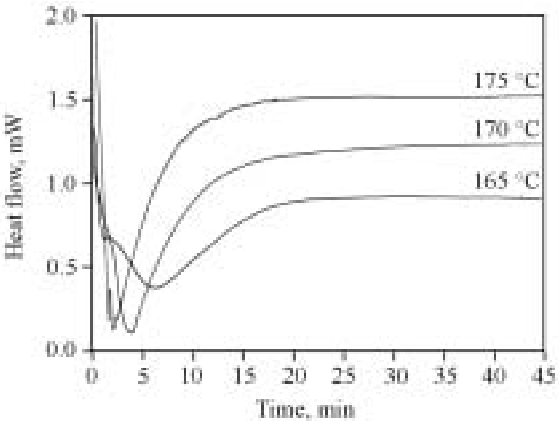


Fig. 2. DSC curves of AZ-2/2-ABPh mixture at isothermal conditions in three different temperatures

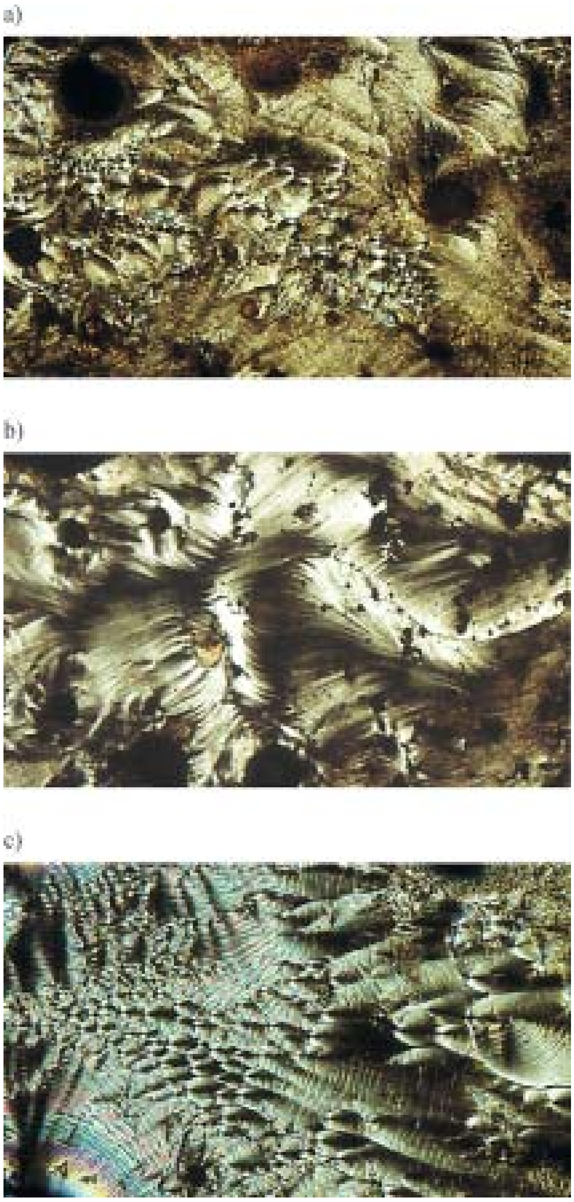


Fig. 3. Changes of texture of AZ-2/2-ABPh thermoset under polarized light with the progress of curing at temp. 170 °C (a→b→c)

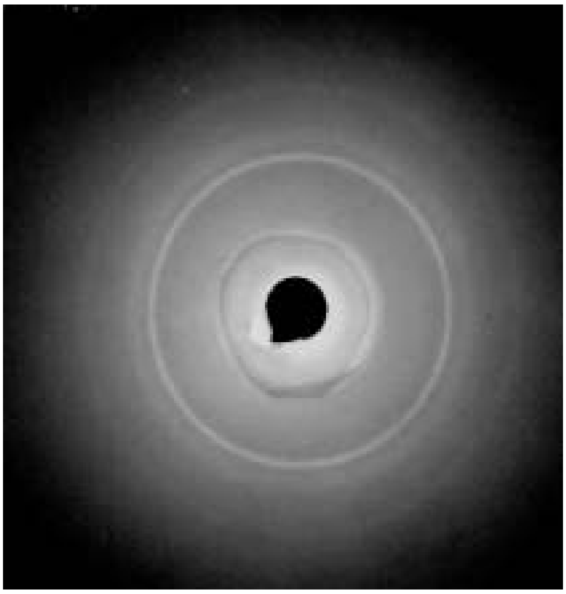


Fig. 4. Wide-angle X-ray diffraction pattern of AZ-2/2-ABPh thermoset

fringent zones, which corresponded to a texture of high density of Schlieren type. When the curing reaction was carried out in the isothermal conditions at 170 °C the AZ-2/2-ABPh mixture formed a smectic mesophase of S_A type, being characterized by the presence of many ellipses, which were statistically distributed in the polymer texture (Fig. 3a). The crosslinking reaction in its progress is characterized by appearance of the bands, which are gathering under the form of "conical focals" (Fig. 3b). Over a certain conversion degree a new phase transition took place, when a striated texture was obtained (Fig. 3c). This kind of texture could be attributed to S_B and/or S_E smectic texture. These two kinds of textures were formed together with S_A type texture. The obtained textures show a very low thermal stability at temperature higher than 170 °C. The instability of the smectic like-texture with increasing temperature is due to the absence of the connection liaisons between the polymeric chains, formed as a result of the curing reaction. As a general conclusion, the microscopic data showed that it was difficult to affirm with a high precision which kind of texture was obtained during the curing reaction of AZ-2 monomer in the presence of 2-ABPh amine.

The smectic type texture of the obtained ELCT was confirmed by X-ray diffraction. The WAXS pattern of the AZ-2/2-ABPh curing product obtained at 170 °C, for time 2 h, is shown in Fig. 4. The ELCT has a layered structure network with d-spacing among mesogens of 4.37 Å (strong), 3.85 Å (weak) or 3.01 Å (very weak).

CONCLUSIONS

The mesogenic AZ-2 monomer shows liquid crystalline properties. Its smectic-like structure was preserved during the curing reaction with 2-ABPh amine, used as the curing agent. The AZ-2/2-ABPh mixture, when cured, led to a smectic mesophase with a high ordered structure.

The curing reaction, studied by DSC, polarized optical microscopy and WAXS techniques, showed that this process was accompanied with the reaction of the residual oxirane groups homopolymerization.

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