Development of Liquid Crystalline Order During Cure of Mesogenic Epoxy Resins

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Summary: In the present paper we describe the curing process of a new liquid crystalline epoxy monomer with 4,4'-diaminodiphenylenemethane (DDM). The characteristic of cured product is presented. Both the monomer and cured product have been characterized by IR and NMR spectroscopy, differential scanning calorimetry (DSC), polarized optical microscopy (POM), wide-angle X-ray scattering (WAXS) and dielectric relaxation spectroscopy (DRS).The curing process was analysed with the use of DSC and real-time DRS.

Keywords: anisotropic curing; curing process; liquid crystals epoxy monomers

Introduction

The liquid crystalline polymer systems, both thermotropic and lyotropic, have been extensively studied for more than forty years. Most of the systems described so far contain mesogenic groups, typical for low-molecular liquid crystals, mainly of rod-like and disc-like type. The ability of fragments of molecules to be oriented by an external field is the key feature of such polymer systems in practical applications. The possibility of aligning molecules in required direction during processing and shaping these materials allows for control and selective modification of their properties.[1-5] Another interesting group of materials constitute anisotropic polymer networks - liquid crystalline network polymers (LCNP) – for the first time were described in the turn of sixties and seventies of the last century.[6,7] This group contains usually slightly cross-linked materials, based on side- and main-chain liquid crystalline polymers or monomers (often named LC elastomers). The other group constitutes the liquid crystalline cross-linked polymers (LC thermosets) usually obtained by thermal curing of a suitable system. The monomers, typically liquid crystalline materials, contain most often aromatic mesogenic groups, although the synthesis of LCNP from non-liquid-crystalline precursors has

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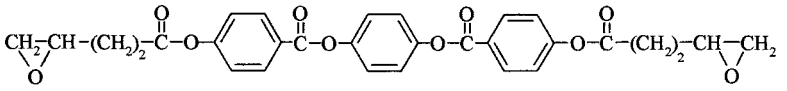
also been described.[8,9] Unlike LC elastomers, the LC thermosets are usually glassy polymers and their molecular order, if any, is frozen during curing stage.

Among LC thermosets, the cross-linked liquid-crystalline epoxy resins brought a great deal of attention. A series of syntheses of epoxy monomers with mesogenic groups have been described, from which the anisotropic polymer networks were obtained.[9,10-26] They exhibited good mechanical and electrical properties, heat and corrosion resistance and better adhesion to various substrates than had other thermosets.[27] LCNPs prepared from epoxy resins were used for embedding optical devices in the data storage systems, as the waveguides and as matrices for polymer dispersions of liquid crystals. The latter were used as filters, shutters, architectural glass, display devices etc.[28] The high degree of orientation was achieved by carrying out the curing process in an external (e.g. magnetic) field.[10,18-21]

Experimental

Synthesis

The synthesis of epoxy monomer **MU2** has been described previously.[29] The characteristic of the monomer **MU2** is summarized in Table 1.



MU2

Table 1. Transition temperatures and phase transition enthalpies for monomer **MU2**.

	C→N		N→I		N→C**	
Compound	*T* [°C]	Δ*H* [kJ/mol]	*T* [°C]	Δ*H* [kJ/mol]	*T* [°C]	Δ*H* [kJ/mol]
MU2	168	27,1	276,5*	1,00	157	-24,2

* degradation

** after heating to 200°C

C – crystal state, N – nematic phase, I- isotropic state.

Curing of LC monomer

The liquid crystalline epoxy monomer synthesized in this experiment was cured using 4,4'-diaminodiphenylmethane (DDM). The curing mixture was prepared by dissolving stoichiometric amounts of epoxy monomer and DDM in dichloromethane at room temperature. Diepoxy monomer **MU2** was treated as difunctional and the amine DDM as tetrafunctional. After evaporation of the solvent the mixture was dried in vacuum and stored at 10-15°C before use. The resulting powder was used in all further experiments. The curing proc-

ess was monitored in several different temperatures. The mixtures cured at 160°C or 180°C for 4 hrs. and post-cured at 200°C for 2 hrs. were selected for further analysis of the cured products.

Physical measurements and characterization

The textures of the curing system and cured resin were observed with a polarizing microscope Zeiss at a magnification of 80×. The temperature was controlled by means of a Linkam TMS 91 hot stage.

Differential scanning calorimetry (DSC) was performed with a Mettler Toledo DSC30 instrument under nitrogen. DSC was used for determination of phase transitions of monomers and for the study of dynamic and isothermal curing behaviour of epoxy resins synthesized in this work. Isothermal curing temperatures were 140, 160, 180, 200 and 220°C. The samples (9-10 mg) were inserted into the DSC oven equilibrated at desired temperature. The DSC analysis was utilized also for characterization of curing products.

WAXS (wide angle X-ray scattering) measurements were conducted using a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a two-dimensional detector (Siemens) with 1024×1024 pixels. A double graphite monochromator for the CuK_α radiation (λ=0.154 nm) was used. The beam diameter was about 0.5 mm and the sample to detector distance was 80 mm. The samples of cured product were prepared without or with magnetic field (1.8 T).

The frequency and temperature dependent dielectric measurements were performed using the experimental set-up of Novocontrol. The system was equipped with Alpha high-resolution dielectric analyser, the impedance analyser HP 4191A and the temperature controller Quatro version 4.0. The complex permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ was evaluated in the frequency range from 10^{-2} to 10^6 Hz. The value of AC voltage applied to the capacitor was equal to 0.5 V. For measurements between 10^6 and 10^9 Hz, a coaxial arrangement with the sample capacitor (diameter 6 mm, thickness 0.05 mm) mounted as a part of the inner conductor was used. The temperature was controlled using a nitrogen-gas cryostat and the temperature stability of the sample was better than 0.1K. The real-time analysis of isothermal curing at selected temperatures was performed by repetitive recordings of the frequency dependence of the complex permittivity during the reaction. Each frequency sweep took about 3 min. and the sweeps were initiated every 4 min. enabling accurate monitoring of the changes in dielectric response.

Application of DRS technique for monitoring the cure of thermosetting systems was reviewed by Senturia and Shephard.[30] A dielectric cure-monitoring procedure for epoxide-amine thermosets and other systems was developed by Kranbuehl et al.[31] Their results as well as other studies have confirmed that DRS was an appropriate technique for monitoring curing behaviour of polymer systems. It allowed for tracking the changes in the mobility of dipoles and ions during the reaction. It also provided indication on the reaction dynamics in various temperatures.

Results and discussion

The analysis of curing process

The dynamics of curing reaction was studied by DSC analysis of the monomer **MU2** – diamine DDM system during heating with the constant rate of 10 deg/min and also in isothermal conditions. The first endothermic peak in the dynamic curve (Figure 1) corresponded to melting of amine (88-92°C), as could be concluded from microscopic observations. The second endothermic peak was caused by a structural change in the monomer, which occurred during the first heating, as described earlier.[29] The exothermic effect caused by the initiation of the reaction between amine and diepoxy monomer appeared at the temperature of about 140°C. In this temperature the monomer existed mainly as a dispersion in melted amine. The reaction started in the temperature below the transition of monomer to liquid crystalline phase (168°C) as the monomer partially dissolved in melted amine. Further heating, as well as the exothermic effect from the progressing reaction, caused dissolution and melting of the remaining part of the monomer. Consequently, the maximum exothermic effect was observed at about 145°C. The total heat of the reaction was established to be 97.0 kJ per mole of epoxy groups, in good agreement with literature data (cf. e.g.[15]).

The isothermal DSC curves of the same system, registered at 140, 160, 180, 200 and 220°C, are shown in Figure 2. At 140°C the monomer remained dispersed in melted amine and partially reacted. The reaction rate in this temperature did not reach the maximum immediately after introduction of the sample, as it was the case in higher temperatures, and the exothermic effect remained small. After less than 8 minutes the heat flow nearly vanished and the reaction rate approached zero (for samples of weight ca. 10 mg). The heat of curing process carried out in isothermal conditions increased roughly linearly as temperature raised from 140 to 200°C. At 220°C the reaction heat reduced. Then, the curing mechanism was changed or, more likely, polymerisation was accompanied by endothermic degradation. Summarizing, the

DSC measurements were useful in selecting curing temperature. They also showed the reaction time to depend on the temperature of curing process, but the total time, required for full reaction (especially in large samples), could not safely be estimated only on the basis of these results.

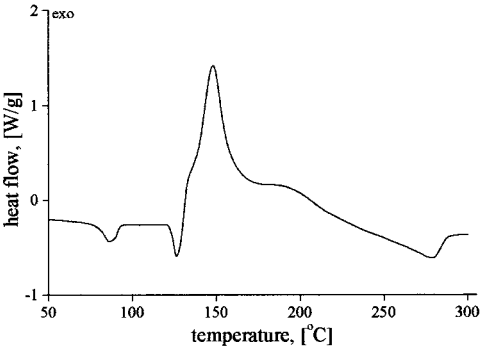


Figure 1. DSC thermogram for monomer **MU2**-DDM system recorded at heating rate 10 deg/min

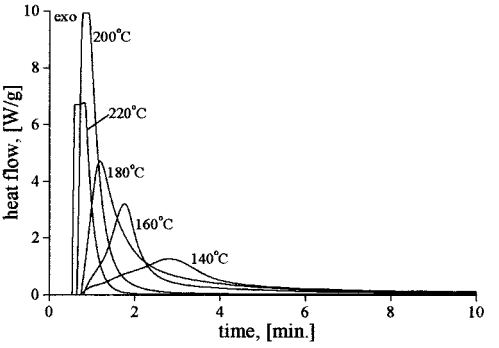


Figure 2. DSC curves for the isothermal cure of monomer **MU2** - DDM mixture

In order to investigate the curing process more closely both the optical observations and broadband dielectric spectroscopy were used. The curing experiments with large samples (~0.5 g) were carried out for four hours, at 160°C and 180°C. These conditions roughly corresponded to those in the standard curing procedure applied for commercial epoxy resins, e.g., resins used for encapsulation of integrated circuits.[32] After reaching the target temperature

the investigated mixture was a viscous liquid, which gradually hardened. The system could then be observed in a polarizing microscope as the changes in the image occurred rather slowly.

The dielectric spectroscopy measurements during the curing process were carried out at 160°C and 180°C. In this temperature range there was a very high ionic conductivity in the investigated material. The changes related to the ionic conductivity were conveniently observed by means of the real-time dielectric spectroscopy (Figure 3). The analysis of changes in the dielectric response with time revealed the maximum of relaxation peak to move initially towards lower frequencies, but after some period of time, the peak frequency stabilized and the relaxation curves became independent of time. The explanation of this behaviour was that the chemical reaction was halted or considerably slowed down possibly because of reaching a high degree of conversion. The fact that the reaction reached completion in the course of the measurements made it possible to compare the duration of the reaction in various temperatures. As seen in DRS data plot (Figure 3), the reaction rate was very high at the beginning. The peak frequency f_{max} changed significantly in about 60 minutes from the start. Between 60th and 100th minutes the reaction slowed down, but small changes in f_{max} were still visible (Figures 3 and 4a). After 100 minutes no further changes in peak frequency occurred. In contrast, at 180°C the reaction progress was so fast that just after about 16 minutes, the relaxation curves became independent of time (Figure 4a). Thus, the changes of f_{max} were difficult to observe because only a few frequency sweeps could be acquired during reaction time.

With DRS measurements one could observe the reaction progress in larger samples than in DSC experiments. As expected, the higher reaction rates were registered in high temperature, in accordance with DSC. The apparent reaction time however, was considerably different in both cases. It might have been interpreted in terms of different curing conditions (e.g. due to dimensions of sample) as well as the difficulties in detecting low reaction rates with DSC technique.

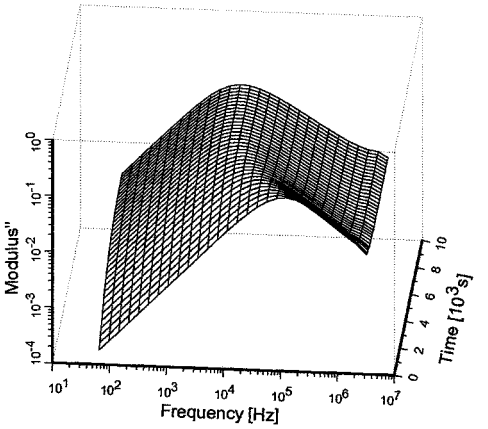
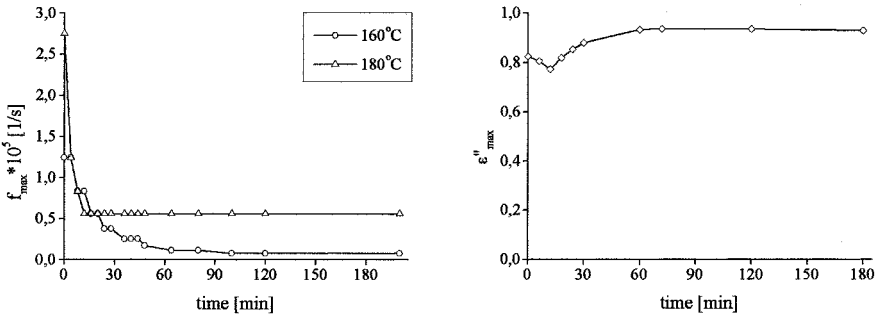


Figure 3. The dielectric response of monomer **MU2** in the course of curing at the temperature of 160°C. Data presented in the electric modulus representation



a b

Figure 4. Monitoring of the reaction progress using dielectric spectroscopy: a) frequency f_{max} of ionic conductivity peak vs. time (T=160°C and 180°C), b) amplitude of high frequency relaxation process vs. time (T=160°C).

Similar conclusions about the duration of the curing may be drawn from the analysis of dielectric relaxation in the frequency range of 10^6-10^9 Hz. In this range, at 160°C, the data plots show a peak, which is usually interpreted as the αβ-process in the monomer.[33] This peak moved towards low frequencies with time. The amplitude of the peak decreased slightly in the beginning, but after a short time it increased noticeably (Figure 4b). Following the discussion presented in [33] this observation could be explained in terms of splitting of the αβ peak into separate α and β peaks. As the β peak – according to the theoretical expectations – had low amplitude and moved towards higher frequencies, it was likely to fall beyond the frequency

range used in our experiment. This might explain why it was not visible as a separate peak in our results. The other (α) peak was expected to move towards low frequencies and its amplitude - to increase.[33] In our case this process could be more complex, since the orientation of monomer molecules might have changed during the cure, which would consequently change the contribution of both modes to the dielectric response. In addition, one of the modes became suppressed as the monomers linked together building up larger structures. That is why, in our measurements, the exact reasons for the changes in the amplitude of the high frequency peak (seen in Figure 4b) remain unclear. Although in T=160°C the frequency f_{max} of this peak changed only during initial several minutes, the progress of the reaction could be observed in the plots of amplitude and width of the relaxation peak. These values continued to change for about 60 minutes more (Figure 4b). After some time the frequency and amplitude of the high frequency process reached their limiting values and then remained unchanged. The most obvious explanation for this behaviour was that the reaction had been completed. It is noteworthy that the reaction times estimated from the measurements of high-frequency relaxation processes and the low-frequency measurements of ionic conductivity were very close to each other. It means that the dielectric relaxation spectroscopy may serve as an effective technique for monitoring the progress and duration of the reaction.

The cured product

The curing process was carried out at 160 or 180°C for 4 hrs. and followed by post curing at 200°C for 2 hrs. The product was analysed by DSC, POM, WAXS, and DRS. Conversion of epoxy groups and formation of hydroxy ones was confirmed by FTIR spectra. The bands characteristic for epoxy groups at 1248, 922, 866-855, 764 cm^{-1} disappeared almost completely. The DSC diagram for the product of curing is presented in Figure 5. The material retained its structure up to temperature of about 250°C. The endothermic peak on DSC curve was ascribed to 'melting' of a part of crystalline phase with simultaneous thermal degradation of the resin. The texture observed in polarization microscope changed at this temperature and remained fixed.

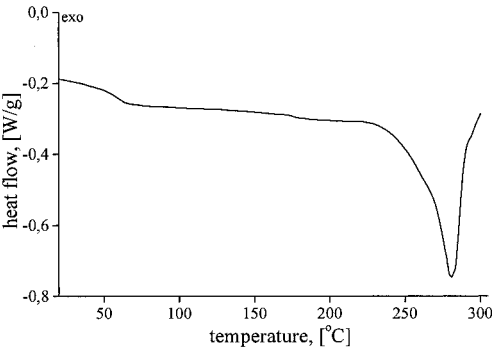
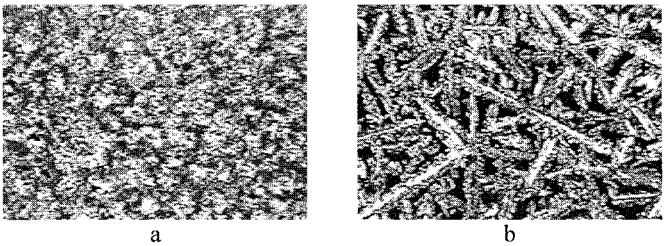


Figure 5. DSC thermogram of epoxy monomer **MU2** - DDM system cured at 180°C for 4 hrs. and post-cured at 200°C for 2 hrs.

Somewhat puzzling to us was the presence of a small peak on DSC curve at around 60°C, similar to that of glass transition. The practitioners working with bisphenol A and novolak based epoxy resins claim that T_g of cured epoxies lays close to the curing temperature. Fully cured classical epoxy resins have T_g well above 150°C.[34] Heating of the cured samples above 100°C did not change its elasticity. Probably the transformation was connected with the conformation changes of aliphatic parts in cured product.



a b

Figure 6. Optical texture of epoxy monomer **MU2** - DDM system cured at 180°C for 4 hrs. and post-cured at 200°C for 2 hrs.: a) between glass plates without ordering layer, b) between glasses covered with polyimide film with antiparralel rubbing enforcing planar orientation), magnification 80×

Polarization microscopic observations confirmed the presence of anisotropic parts in the samples. The texture of samples cured between glass plates was different depending on whether or not an ordering layer was deposited on the glass. The differences are shown in Figure 6. The texture of the product obtained with ordering layer was obviously better 'ordered' than

that obtained between ordinary glass plates. Monomer **MU2** in its liquid-crystalline state ordered completely between polyimide coated glass, but the texture of the cured product was more complex, possibly of a higher degree of order. Known are examples of nematic liquid crystalline monomers that yielded upon curing a structure typical for smectic phase.[9]

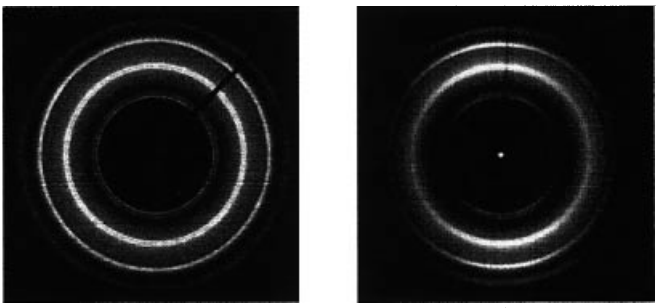


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Figure 7. WAXS images of the product of curing of epoxy monomer **MU2** by DDM (at 180°C for 4 hrs. and post-cured at 200°C for 2 hrs.: a) the product cured without a magnetic field; sharp rings indicate relatively high degree of crystallinity, but no global alignment is observed, b) the product cured in 1.8 T magnetic field. The direction of the applied field is parallel to the equator. The meridional crescents indicate that the initial alignment of the nematic molecules is partially preserved in the cured product

The X-ray analysis of the cured product was done for two samples, one of which was cured in the presence of magnetic field of about 1.8 T. The sample images are presented in Figure 7. The most prominent feature in both images is the presence of two rather strong and sharp rings, accompanied by several rings of much smaller intensity. The strongest ring, located at $2\theta \sim 18.75°$, may be identified as related to the intermolecular spacing in the direction perpendicular to the long molecular axes. A ring at similar position was also detected in the investigations of pure monomer. The presence of several rings instead of just one indicates a higher degree of molecular ordering as compared to pure monomer. The sharpness of the rings confirms that the molecules are effectively "frozen" in the structure due to the creation of cross-linking and indicates relatively high degree of crystallinity in the product. All the rings in the image recorded for the sample cured without magnetic field (Figure 7a) are uniform which is an evidence of the lack of any general orientation in the sample. In contrast, the diffraction patterns obtained for the sample cured in the presence of the magnetic field (Figure 7b) exhibit much stronger maxima in the meridional plane, than in equatorial one. It means that the initial alignment of the molecules in the nematic phase, enforced by magnetic field, has not been destroyed during the curing process and remains (at least partially) unchanged. The im-

portance of this observation comes from the fact that the mechanical performance of polymeric materials is usually much better when its molecules are well oriented.

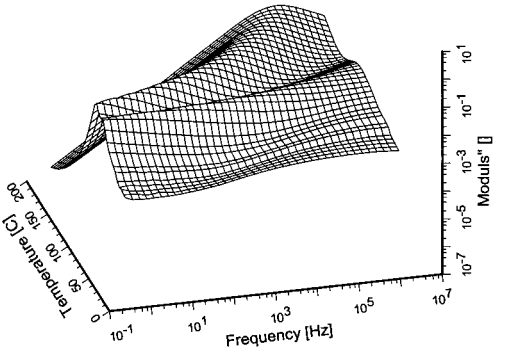

Figure 8. Dielectric response of the cured resin in a wide range of temperature. The data are presented by using the electric modulus representation.

The dielectric response of the cured product was measured in a wide range of temperature (120 - 180°C). In the electric modulus representation three relaxation peaks are visible (Figure 8). The first peak can be ascribed to the ionic conductivity and its activation energy is the same as in the case of pure monomer (E_a=1.5eV). The α-process may be identified with the dynamics of segmental motion of parts of polymeric chains. The activation energy of this process is remarkably high (E_a=3.8eV). The β-process with small activation energy (E_a=0.5eV) is also visible at the lowest temperatures, which suggests that it is a relaxation of dipolar groups located in the main chain.

Conclusions

- Convenient curing conditions of monomer **MU2** with 4,4'-diaminodiphenylmethane were established to be 160-180°C for 4 hrs. followed by post curing at 200°C for 2 hrs.
- The resulting polymer network has anisotropic structure. The WAXS images contain several sharp rings, which indicate relatively high degree of crystallinity of the product. The diffraction patterns obtained for samples cured in the presence of a magnetic field show that the initial alignment of the molecules is retained (at least partially) in the cured product.

- Dielectric measurements made for curing system and cured material in the frequency range 10^{-2} to 10^{9} Hz confirmed the data obtained by other techniques and proved to be useful in identifying high frequency relaxation processes and low frequency ionic conductivity.

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