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The synthesis of epoxy monomers with mesogenic groups

RAPID COMMUNICATION

Summary — A two-step synthesis was developed to prepare new types of diepoxy and diolefinic liquid crystalline (LC) monomers. The synthesis involved (i) esterification of 4-hydroxyphenyl-4-hydroxybenzoate or 4',4'-biphenol (**I**) with 4-pentenoic acid (**II**); (ii) epoxidation of the resulting diolefins with *m*-chloroperoxybenzoic acid. The structure of the resulting products was confirmed in terms of FTIR and ^{1}H NMR spectra. A hot-stage polarizing microscope showed mesophases to occur in the monomers **2b**, **3a** and **3b** (*cf.* scheme of reaction 1), but not in the product of esterification of **I** with **II**. Differential scanning calorimetry and thermooptical analysis were used to determine (crystal to mesomorphic (LC), and LC to isotropic) phase transition temperatures (Table 1, Fig. 1).

Key words: mesogenic groups, liquid crystalline epoxy monomers, esterification, epoxidation.

The first reports predicting the properties of liquid-crystalline polymer networks (LCPN) were published in the late 1960s and early 1970s [1, 2]. The LCPNs prepared since then indeed revealed certain unique properties such as excellent shape memory, high capacity in accommodating mechanical energy [3], different light polarization at varying deformations [4], and piezo- and pyroelectric properties [5]. All these properties predestine LCPNs as high-tech materials for various branches of electronics, aviation and space industry, as coatings of very high impact resistance [6] or as self-reinforcing composite materials [7].

Amongst various anisotropic polymer networks, the epoxy resins obtained from liquid-crystalline monomers constitute an interesting group. They have a very high mechanical strength including the resistance against brittle crack as well as a high chemical thermal stability. These LCPNs can be used as a supporting material in composites applied for optical purposes, data storage systems and as wave-guides. The epoxy resins of this type are also used as the matrices for the polymer dispersed liquid crystals (PDLC); micron-sized droplets of a liquid-crystalline substance are suspended in a transparent matrix. PDLC are used as wave-guides, filters, shutters, architectural glasses, displays, windows, *etc.* [8].

The liquid crystalline epoxy networks are obtained mainly by cross-linking the epoxy resin capable of generating a mesophase. They usually have a relatively low viscosity. The monomers are synthesized by reacting (i) mesogenic phenols having two hydroxyl groups with epichlorohydrin [7, 9, 10—13], (ii) mesogenic acids or acid halides with glycidyl alcohols [14], or (iii) by epoxidation of appropriate diolefins [15—19]. The methods (i) and (ii) most often lead to mixtures of products containing substantial proportions of oligomeric homologs, similarly as in the synthesis of classical epoxy resins [7, 11, 12, 14]. Method (iii), although requiring a multistage synthesis, allows to purify the final product containing high proportions of individual species. A high degree of orientation of the mesogenic groups in the resins provides the cross-linking carried out in a magnetic or electric field or on a substrate providing a mechanical orientation along a selected direction [8].

In this work, we present a method of synthesis of new types of diepoxy and diolefinic liquid crystalline monomers.

EXPERIMENTAL

Instrumentation

The structure of products was confirmed by ^{1}H NMR and FTIR spectroscopy, by using a Tesla BS 587 A 80 Hz spectrometer and a PARAGON 1000 FTIR spectrometer, respectively. Thermal studies were carried out by diffe-

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rential scanning calorimetry (DSC). Measurements were carried out a rate of 10°C/min in a 990-TA Instruments 2100 calorimeter (Du Pont) by using the TA Instruments Universal V2,6 D software. Thermooptical analysis (TOA) was performed with a polarizing microscope equipped with a Mettler FP-82 measuring cell.

The changes in birefringence of the sample with temperature were measured by monitoring the changes in relative transmission of polarized light, I_T/I_0, where I_T is the transmission of the sample placed between crossed polarizes at given temperature and I_0 is the transmission of a sample at room temperature.

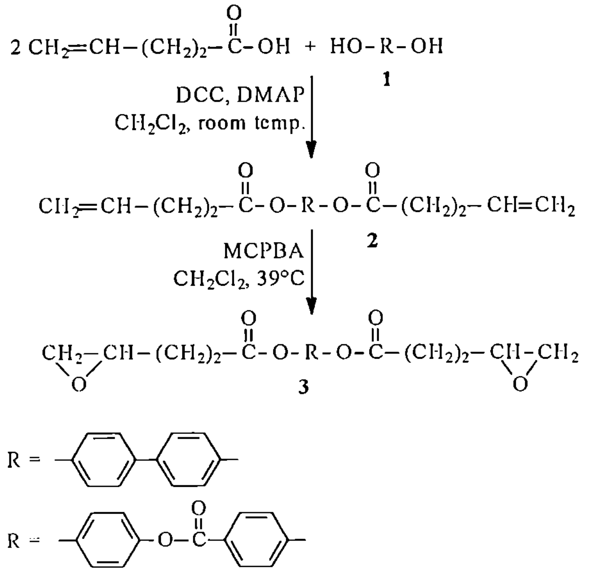
The texture of mesophases was observed by using an Ł-211 polarizing microscope equipped with a hot stage. Pictures were registered by a VHS Panasonic video camera, model NV-R50E, connected to an ASSUS 266 MHz graphic card in a computer.

Starting materials

All the chemicals used were analytical-grade commercial products (Aldrich, Fluka, Merck) and were used without further purification.

Synthesis

4-Hydroxyphenyl-4-hydroxybenzoate used in the synthesis was obtained by esterification of 4-hydroxybenzoic acid with hydroquinone by applying a procedure similar to that described in [20]. 4-Pentenoic acid was obtained in the so-called malonic synthesis described, *e.g.*, by Bochwic [21]:



Esterification

To 0.1 mol (1.86 g) of 4,4'-biphenol or 4-hydroxyphenyl-4-hydroxybenzoate (2.3 g), 0.02 mol (2.0 g) of 4-pentenoic acid in 100 cm^3 of dry dichloromethane, 0.022 mol (4.54 g) of *N,N*-dicyclohexylcarbodiimide (DCC), and a catalytic amount (8 · 10^{-4} mol, 0.0977 g) of 4-dimethylaminopyridine (DMAP) were added. The reaction mixture was stirred for 24 h, then *N,N*-dicyclohexylurea (DHU) was filtered off and, after removal of the solvent, crude product was crystallized from methanol (**2a**) or isopropanol (**2b**). Yields 67% of **2a**, 54% of **2b**.

2a: ^{1}H NMR (CDCl$_3$), δ (ppm), 2.5 (8H, m, (CH$_2$)$_2$), 5.05 (4H, m, =CH$_2$), 5.85 (2H, m, CH), 7.15 (4H, d, aromatic), 7.6 (4H, d, aromatic).

FTIR (KBr), ν (cm^{-1}), 3083, 1601—1448, 1007 (aromatic), 3000—2855, 1419—1373 (CH$_2$), 1643 (C=C$_{aliph}$), 1754, 1745 (C=O), 1218, 1169—1151 (C-O).

2b: ^{1}H NMR (CDCl$_3$), δ (ppm), 2.5 (8H, m, (CH$_2$)$_2$), 5.05 (4H, m, =CH$_2$), 5.85 (2H, m, CH), 7.2 (6H, m, aromatic), 8.15 (2H, d, aromatic).

FTIR (KBr), ν (cm^{-1}), 3109—3082, 1605—1448, 1018 (aromatic), 3001—2856, 1415—1373 (CH$_2$), 1643 (C=C$_{aliph}$), 1746, 1732 (C=O), 1287—1189, 1081, 1166 (C-O).

Epoxidation

Under continuous stirring, 5.42 g (0.022 mol, 70%) of *m*-chloroperoxybenzoic acid (MCPBA) was added to a solution of 0.01 mol of the diolefin (3.5 g of **2a** or 3.94 g of **2b**) in 80 cm^3 of dichloromethane. The mixture was refluxed for 48 h. After cooling and subsequent filtration, the mixture was washed with 80 cm^3 of aqueous 5% Na$_2$SO$_3$, 80 cm^3 of aqueous 5% NaHCO$_3$, and 50 cm^3 of aqueous 30% NaCl. The dichloromethane layer was dried over MgSO$_4$ and evaporated. Recrystallization from methanol (**3a**) or isopropanol (**3b**) yielded the final products.

Yields: 57% of **3a**, epoxy number (EN) = 0.520 (calc. 0.524), 63% of **3b** EN = 0.463 (calc. 0.469).

3a: ^{1}H NMR (CDCl$_3$), δ (ppm), 1.9 (4H, m, CH$_2$), 2.55 (4H, m, CH$_2$), 2.7 (4H, m, CH$_2$ of epoxy), 3.0 (2H, m, CH of epoxy), 7.1 (4H, d, aromatic), 7.5 (4H, d, aromatic).

FTIR (KBr), ν (cm^{-1}), 3083, 1601—1443, 1006 (aromatic), 3000—2855, 1419—1373 (CH$_2$), 1752 (C=O), 1207, 1169—1141 (C-O), 839 (epoxide).

3b: ^{1}H NMR (CDCl$_3$), δ (ppm), 1.9 (4H, m, CH$_2$), 2.55 (4H, m, CH$_2$), 2.75 (4H, m, CH$_2$ of epoxy), 3.0 (2H, m, CH of epoxy), 7.2 (6H, m, aromatic), 8.2 (2H, d, aromatic).

FTIR (KBr), ν (cm^{-1}), 3110—3071, 1603—1440, 1016 (aromatic), 2996—2929, 1414—1373 (CH$_2$), 1756, 1732 (C=O), 1276—1183, 1163—1143, 1075 (C-O), 854—841 (epoxide).

The texture of the products was observed in a polarizing microscope equipped with a hot stage. The observations confirmed the appearance of mesophases in **2b**, **3a**, and **3b** both upon heating and cooling. No mesophase was observed in the product of esterification of 4,4'-biphenol with 4-pentenoic acid. The exact phase transition temperatures were determined by DSC and TOA. Illustrative results for just one monomer, **3b**, are shown in Fig. 1 (DSC) and 2 (TOA). The ratio of the intensity of transmitted light I_T at a given temperature to that at room temperature, I_0, is plotted against temperature. The temperature of transition from the crystalline to mesomorphic (liquid crystalline) T_m and from the me-

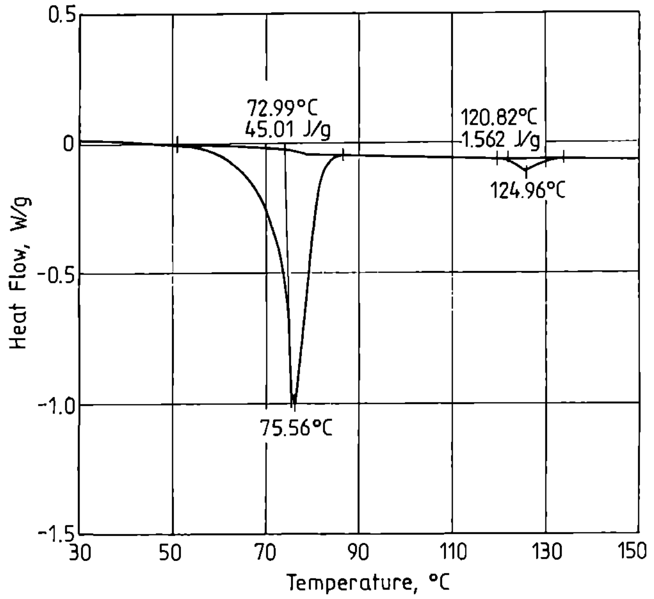


Fig. 1. The DSC thermogram recorded for monomer 3b; transitions temperatures from solid to liquid crystalline and from liquid crystalline to isotropic state are indicated

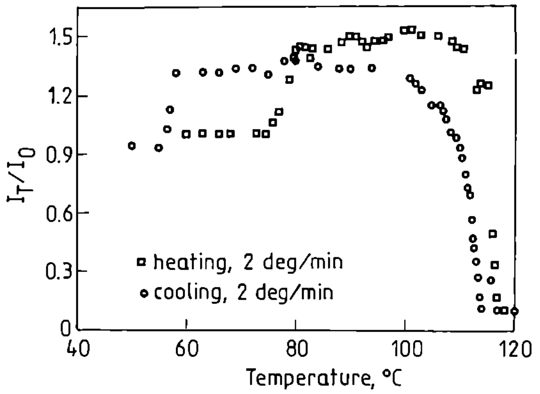


Fig. 2. Relative light transmission I_T/I_0 under crossed polarizers plotted against temperature (TOA plot) for monomer 3b

Table 1. Phase transition temperatures for liquid crystalline divinyl and epoxy monomers synthesized in this work; T_m — melting temperature (including transition from solid to liquid-crystalline state), T_i — isotropization temperature

Monomer	T_m at heating (T_m at cooling), °C	T_i at heating (T_i at cooling), °C
2a*)	—	125 (123.5)
2b	82.5 (73.5)	116.5 (113.5)
3a	102.5 (101.5)	113.0 (112.5)
3b	78.0 (57.0)	115.5 (111.5)

*) No mesophase observed.

somorphic to isotropic state T_i is well seen in the plot. Slight differences in the transition temperatures were found to occur depending on whether the measurements were made in the heating or the cooling mode. The phase transition temperatures determined by the two methods are listed in Table 1.

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