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New dimeric LC-epoxyimine monomers with oxyethylene central spacers. Crosslinking study

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Abstract

We have studied how substituting alkylene by oxyethylene spacers influences the mesomorphic behavior of LC-dimeric epoxy resins with imine groups in the mesogens. This structural variation has been shown to diminish the mesomorphic characteristics of the dimeric epoxy resins containing oxyethylene spacers. These compounds only show mesomorphic behavior when the mesogens are polarized by the presence of an ester and an ether group at their ends. When the ester group is located in the inner position, smectic mesophases have been observed. Depending on the parity of the central spacer, these smectic mesophases are of type A or C. Moreover, when the ether group is in the inner position only monotropic nematic mesophases are formed.

By curing these compounds with primary or tertiary amines, the monotropic character and the low isotropization temperatures of compounds with the ether group in the central position prevent an ordered network from becoming fixed.

However, LC-epoxy resins with ester groups in the inner position lead to the fixation of homogeneous smectic-C like networks only when the spacer was diethylene oxide.

Keywords: Liquid-crystalline polymers; Epoxy resins; Liquid-crystalline thermosets

1. Introduction

Liquid-crystalline polymers (LC-polymers) with mesogens in the main chain present some variations in their mesomorphic behavior when alkyl chains are substituted by oxyethylene spacers [1]. The bond length and bond angles of the oxyethylene spacers are similar to those of the homologous alkylene but there is an energetic preference for *gauche* rather than *trans* conformation for the carbon–carbon segments in the oxyethylene units [2]. The number of *gauche* conformers increases at the transition temperature from the solid state to the liquid-crystalline mesophase. The degrees of freedom of the mesogenic units also increase, enabling them to align properly and form smectic layers. Moreover, when oxyethylene spacers are inserted between mesogens, the chain more flexible improve their solubility [3].

Liquid-crystalline compounds with dimeric architecture has been studied as model compounds for main-chain LC-polymers [4]. These type of LC-polymers present some differences in the physical and mesomorphic characteristics when alkylene spacers are substituted by the homologous oxyethylene. Thus, similar differences could be expected in dimeric compounds containing oxyethylene spacers [5]. It has been shown that dimers containing long oxyethylene spacers still exhibit liquid crystallinity [6].

In previous studies [7,8], we have investigated how the polarization of the mesogenic group and the presence of ether or ester groups that link the mesogen to the central spacer influence the mesomorphic characteristics of a series of dimeric-LC epoxy resins with imine groups in the mesogens. Our results led us to conclude that, if smectic mesophases are to be formed, the mesogen must have a considerably polar character and an ester group must link it to the central spacer. Also, both factors influence the formation of LCTs with different degrees of order.

In this study, we were interested in finding out how the substitution of alkylene by oxyethylene chains of different lengths in the central spacer influences the mesomorphic characteristics of these monomers and their ability to form ordered networks. Although some studies with similar aims

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have been made on reactive [9] and non-reactive [6,10] dimeric compounds, up to now no systematic study has been published about LC-epoxy resins and their transformation into ordered networks.

2. Experimental part

2.1. Materials

4-Aminobenzoic acid, 4-hydroxybenzaldehyde, 4-formylbenzoic acid, 4-aminophenol, and benzyltrimethylammonium chloride (BTMA) from Fluka, bis(2-chloroethyl)ether, 1,2-bis(2-chloroethoxy)ethane, 18-crown-6, acetophenone and hydrazine from Aldrich and epichlorohydrin (Scharlau) were used as received. All solvents were purified by standard procedures. The curing agents 2,4-diaminotoluene (DAT) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) were purchased from Aldrich and used without further purification.

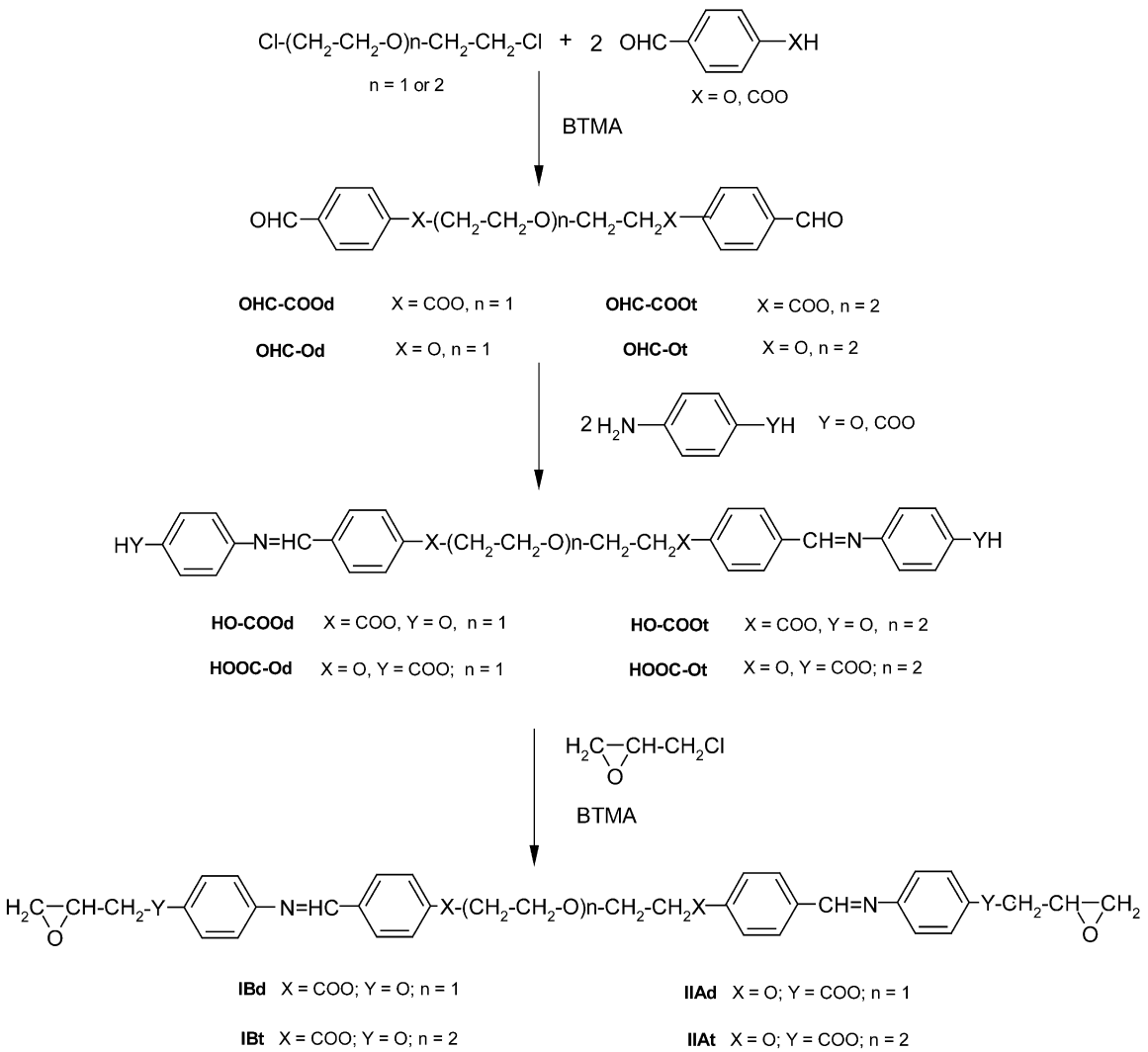
2.2. Instrumentation

NMR spectra were obtained using a Varian Gemini 300 spectrometer working at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C with deutherochloroform ($CDCl_3$) and deutherated dimethylsulphoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as internal standard.

Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer using N_2 as the purge gas at a scan rate of 10 °C/min. Thermogravimetric analyses were carried out on a Mettler TGA/SDTA 851e system under a nitrogen atmosphere at a heating rate of 10 °C/min up to 600 °C.

The textures of the mesophases were observed between crossed polarizers with an optical microscope (AXIOLAB Zeiss) equipped with a LINKAM THMS 600 hot-stage connected to a TP-92 temperature control unit.

Powder X-ray diffraction measurements were taken at different temperatures on a Siemens D5000 diffractometer with $\theta-\theta$ configuration, fitted with an Anton Parr TTK



Scheme 1.

temperature chamber. Cu Kα radiation was used, and graphite was the secondary monochromator. The Bragg angle step was 0.05° and the time per step was 3 s. X-ray experiments were performed on crosslinked samples at room temperature. Pole figures were recorded on a Siemens D5000 diffractometer equipped with a goniometer, which had an open Eulerian cradle that used Cu Kα radiation.

2.3. Molecular geometry calculations

We used the commercially available software CERIUS2 by Molecular Simulations Inc. to estimate the molecular geometry of the monomers [11]. The system energy was then relaxed by molecular mechanics minimization using the Universal Force Fields (UFF) force field provided by CERIUS2. When the chains were completely relaxed the distances between the corresponding atoms were measured.

2.4. Synthesis of p-aminoacetophenone azine (NA2)

The synthetic procedure was carried out from 4-amino-acetophenone and hydrazine hydrochloride as previously reported [12].

2.5. Synthesis of dialdehydes (Scheme 1)

A mixture of 1 mmol of the corresponding etherdichloride, 2.4 mmol of *p*-substituted benzaldehyde, 0.05 mmol of benzyltrimethylammonium chloride (BTMA) and 6 mmol of Na_2CO_3 in 50 ml of *N*,*N*-dimethylformamide (DMF) was purged with argon for 5 min and then heated at 120 °C. The reaction was monitored by TLC (toluene/acetone 9:1). After heating for 6 h, the solution was poured over a water–ice mixture, filtered and washed with water. The solid obtained was dissolved in dichloromethane and washed three times with 10% (w/w) NaOH solution. The organic layer was dried over $MgSO_4$, and dichloromethane was evaporated in vacuo to obtain the product.

2.5.1. Bis[2-(4-formylphenoxy)ethyl]ether (OHC-Od)

Mp: 142–144 °C; yield: 79%. ^{1}H NMR ($CDCl_3$, δ): 10.08 (s, 2H), 8.14 (d, 4H), 7.91 (d, 4H), 4.53 (t, 4H), 3.88 (t, 4H). ^{13}C NMR ($CDCl_3$, δ): 190.76 (d), 163.63 (s), 131.90 (d), 130.02 (s), 114.77 (d), 69.66 (t), 67.65 (t).

2.5.2. 1,2-Bis[2-(4-formylphenoxy)ethoxy]ethane (OHC-Ot)

Mp: 71–73 °C; yield 78%. ^{1}H NMR ($CDCl_3$, δ): 9.91 (s, 2H), 7.82 (d, 4H), 7.01 (d, 4H), 4.22 (t, 4H), 3.90 (t, 4H), 3.73 (s, 4H). ^{13}C NMR ($CDCl_3$, δ): 190.73 (d), 163.68 (s), 131.84 (d), 129.91 (s), 114.74 (d), 70.80 (t), 69.41 (t), 67.60 (t).

2.5.3. Bis[2-(4-formylbenzoyloxy)ethyl]ether (OHC-COOd)

Mp: 66–69 °C; yield: 75%. ^{1}H NMR ($CDCl_3$, δ): 10.09 (s, 2H), 8.15 (d, 4H), 7.88 (d, 4H), 4.53 (t, 4H), 3.89 (t, 4H). ^{13}C NMR ($CDCl_3$, δ): 191.57 (d), 165.42 (s), 139.14 (s), 134.84 (s), 130.20 (d), 129.43 (d), 68.97 (t), 64.37 (t).

2.5.4. 1,2-Bis[2-(4-formybenzoyloxy)ethoxy]ethane (OHC-COOt)

Mp: 78–80 °C; yield: 83%. ^{1}H NMR ($CDCl_3$, δ): 10.09 (s, 2H), 8.18 (d, 4H), 7.93 (d, 4H), 4.51 (t, 4H), 3.87 (t, 4H), 3.74 (s, 4H). ^{13}C NMR ($CDCl_3$, δ): 191.62 (d), 165.44 (s), 139.09 (s), 134.90 (s), 130.21 (d), 129.44 (d), 70.65 (t), 69.07 (t), 64.52 (t).

2.6. Synthesis of diimino-diphenols (Scheme 1)

A mixture of 1 mmol of the corresponding dialdehyde and 2.4 mmol of 4-aminophenol in 100 ml of ethanol was refluxed in argon atmosphere in a three-necked flask equipped with a magnetic stirrer. The reaction was followed by TLC (toluene/acetone 3:1) until the initial product disappeared and the reaction was complete (ca. 5 h). After cooling, the white solid was filtered and washed several times with methanol and ethylic ether. The solid obtained was pure enough to be used in the subsequent step without further purification.

2.6.1. Bis(2-{4-[(4-hydroxyphenylimino)methyl]benzoyl oxy}ethyl)ether (HO-COOd)

Mp: 188–189 °C; yield: 74%. ^{1}H NMR (DMSO-d_6, 100 °C, δ): 9.65 (s, 2H), 8.65 (s, 2H), 7.99 (d, 4H), 7.92 (d, 4H), 7.21 (d, 4H), 6.78 (d, 4H), 4.44 (t, 4H), 3.84 (t, 4H). ^{13}C NMR (DMSO-d_6, 100 °C, δ): 165.35 (s), 156.91 (s), 155.75 (d), 141.97 (s), 140.54 (s), 131.07 (s), 129.56 (d), 128.32 (d), 122.93 (d), 115.79 (d), 68.17 (t), 64.03 (t).

2.6.2. 1,2-Bis({4-[(4-hydroxyphenylimino)methyl]benzoyl oxy}ethoxy)ethane (HO-COOt)

Mp: 180–182 °C; yield: 89%. ^{1}H NMR (DMSO-d_6, 100 °C, δ): 9.64 (s, 2H), 8.67 (s, 2H), 8.00 (d, 4H), 7.97 (d, 4H), 7.22 (d, 4H), 6.79 (d, 4H), 4.38 (t, 4H), 3.75 (t, 4H), 3.61 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 °C, δ): 165.36 (s), 156.90 (s), 155.79 (d), 142.01 (s), 140.56 (s), 131.11 (s), 129.59 (d), 128.34 (d), 122.91 (d), 115.80 (d), 69.91 (t), 68.34 (t), 64.25 (t).

2.7. Synthesis of diimino-diacids (Scheme 1)

A mixture of 1 mmol of the corresponding dialdehyde and 2.4 mmol of 4-aminoacids in 25 ml of DMF and 75 ml of toluene was refluxed in argon atmosphere in a three-necked flask equipped with a Dean–Stark separator and magnetic stirrer. The reaction was followed by TLC (toluene/acetone 3:1) until the initial product disappeared and the reaction was complete (ca. 3 days). Toluene was distilled off at reduced pressure, and the solution was poured into methanol. The solid obtained was filtered and washed several times with methanol and ethylic ether. The solid obtained was pure enough to be used in the subsequent step without further purification.

2.7.1. Bis(2-{4-[(4-carboxyphenylimino)methyl]phenoxy} ethyl)ether (HOOC-Od)

Transitions (°C): K 293 N 312 I; yield: 95%. ^{1}H NMR (DMSO-d_6, 100 °C, δ): 12.83 (s, 2H), 8.53 (s, 2H), 7.96 (d, 4H), 7.88 (d, 4H), 7.26 (d, 4H), 7.10 (d, 4H), 4.21 (t, 4H), 3.85 (t, 4H). ^{13}C NMR (DMSO-d_6, 100 °C, δ): 167.11 (s), 161.62 (s), 161.50 (d), 155.80 (s), 130.87 (d), 130.63 (d), 128.69 (s), 127.55 (s), 121.03 (d), 114.98 (d), 68.97 (t), 67.69 (t).

2.7.2. 1,2-Bis({4-[(4-carboxyphenylimino)methyl]phenoxy} ethoxy)ethane (HOOC-Ot)

Transitions (°C): K_1 207 K_2 285 S_A 302 I; yield: 85%. ^{1}H NMR (DMSO-d_6, 100 °C, δ): 12.67 (s, 2H), 8.52 (s, 2H), 7.96 (d, 4H), 7.88 (d, 4H), 7.26 (d, 4H), 7.07 (d, 4H), 4.77 (t, 4H), 3.78 (t, 4H), 3.63 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 °C, δ): 167.00 (s), 161.47 (s), 161.28 (d), 155.68 (s), 130.76 (d), 130.52 (d), 128.62 (s), 127.54 (s), 120.88 (d), 114.77 (d), 69.94 (t), 68.80 (t), 67.41 (t).

2.8. Synthesis of diglycidylic compounds (Scheme 1)

A mixture of epichlorohydrin (50 mmol) and the corresponding diimino-diphenol or diimino-diacid (1 mmol) was heated at reflux and solid benzyltrimethylammonium chloride (0.1 mmol) was added in one batch. The reaction was followed by TLC (toluene/acetone 3:1 as eluent) using a specific developer of terminal epoxy groups [13]. The reaction finished in about 1 h. The homogeneous solution was then cooled to room temperature and the solid obtained was filtered off, washed with hexane and recrystallized from toluene.

*2.8.1. Bis(2-{4-[(2,3-epoxypropoxy)phenyliminomethyliden] benzoyloxy}ethyl) ether (**IBd**)*

Transitions (°C): K 121 S_C 166 I; yield: 83%. ^{1}H NMR ($CDCl_3$, δ): 8.48 (s, 2H), 8.09 (d, 4H), 7.88 (d, 4H), 7.20 (d, 4H), 6.90 (d, 4H), 4.54 (t, 4H), 4.25 (dd, 2H), 3.95 (dd, 2H), 3.91 (t, 4H), 3.39 (m, 2H), 2.93 (t, 2H), 2.79 (t, 2H). ^{13}C NMR ($CDCl_3$, δ): 165.98 (s), 157.48 (s), 156.93 (d), 144.52 (s), 140.19 (s), 131.73 (s), 129.95 (d), 128.32 (d), 122.38 (d), 115.07 (d), 68.98 (t), 68.93 (t), 64.01 (t), 50.07 (d), 44.61 (t). Elem. Anal. % calcd for $C_{38}H_{36}N_2O_9$ (664.7): C, 68.66%; H, 5.46%; N, 4.21%. Found: C, 68.57%; H, 5.58%; N, 4.19%.

*2.8.2. 1,2-Bis({4-[(2,3-epoxypropoxy)phenyliminomethyl iden]benzoyloxy} ethoxy)ethane (**IBt**)*

Transitions (°C): K 82 S_A 142 I; yield: 78%, ^{1}H NMR ($CDCl_3$, δ): 8.49 (s, 2H), 8.12 (d, 4H), 7.91 (d, 4H), 7.25 (d, 4H), 6.94 (d, 4H), 4.50 (t, 4H), 4.26 (dd, 2H), 3.95 (dd, 2H), 3.87 (t, 4H), 3.75 (s, 4H), 3.38 (m, 2H), 2.92 (t, 2H), 2.78 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 166.98 (s), 157.50 (s), 156.98 (d), 144.60 (s), 140.20 (s), 131.84 (s), 129.97 (d), 128.31 (d), 122.37 (d), 115.11 (d), 70.68 (t), 69.17 (t), 68.92 (t), 64.25 (t), 50.05 (d), 44.61 (t). Elem. Anal. % calcd for $C_{40}H_{40}N_2O_{10}$ (708.8): C, 67.79%; H, 5.69%; N, 3.95%. Found: C, 67.79%; H, 5.79%; N, 3.93%.

*2.8.3. Bis{2-[4-(2,3-epoxypropoxybenzoyliminomethyl idene)phenoxy]ethyl} ether (**IIAd**)*

Transitions (°C): K 57 N 86 I; yield: 75%. ^{1}H NMR ($CDCl_3$, δ): 8.35 (s, 2H), 8.08 (d, 4H), 7.84 (d, 4H), 7.18 (d, 4H), 7.00 (d, 4H), 4.66 (dd, 2H), 4.23 (t, 4H), 4.16 (dd, 2H), 3.98 (t, 4H), 3.35 (m, 2H), 2.90 (t, 2H), 2.74 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 165.97 (s), 161.74 (s), 160.87 (d), 156.72 (s), 130.99 (d), 130.79 (d), 128.93 (s), 126.40 (s), 120.73 (d), 114.83 (d), 69.79 (t), 67.56 (t), 65.31 (t), 49.49 (d), 44.68 (t). Elem. Anal. % calcd for $C_{38}H_{36}N_2O_9$ (664.7): C, 68.66%; H, 5.46%; N, 4.21%. Found: C, 68.53%; H, 5.64%; N, 4.21%.

*2.8.4. 1,2-Bis{4-[(2,3-epoxypropoxybenzoyliminomethyl idene)phenoxy] ethoxy}ethane (**IIAt**)*

Transitions (°C): K 53 N 94 I; yield: 71%. ^{1}H NMR ($CDCl_3$, δ): 8.34 (s, 2H), 8.08 (d, 4H), 7.84 (d, 4H), 7.19 (d, 4H), 7.00 (d, 4H), 4.66 (dd, 2H), 4.20 (t, 4H), 4.17 (dd, 2H), 3.91 (t, 4H), 3.77 (s, 4H), 3.35 (m, 2H), 2.91 (t, 2H), 2.75 (dd, 2H). ^{13}C NMR ($CDCl_3$, δ): 166.00 (s), 161.82 (s), 160.88 (d), 156.73 (s), 130.00 (d), 130.79 (d), 128.88 (s), 126.40 (s), 120.74 (d), 114.83 (d), 70.89 (t), 69.60 (t), 67.54 (t), 65.32 (t), 49.50 (d), 44.70 (t). Elem. Anal. % calcd for $C_{40}H_{40}N_2O_{10}$ (708.8): C, 67.79%; H, 5.69%; N, 3.95%. Found: C, 67.92%; H, 5.76%; N, 4.02%.

2.9. Preparation of the samples for curing

2,4-Diaminotoluene (DAT), 4-aminoacetophenone azine (NA2) and 4-(*N*,*N*-dimethylaminopyridine) (DMAP) were used as the curing agents to crosslink the monomers synthesized. Stoichiometric mixtures of the monomers and the corresponding aromatic primary diamine were dissolved in dichloromethane at room temperature. When DMAP was used, 3 phr of catalyst was added to the corresponding monomer and the mixture was dissolved in dichloromethane at room temperature. The solvent was evaporated in vacuo.

3. Results and discussion

3.1. Synthesis and characterization of monomers

To study the effect of substituting alkylene by oxyethylene spacers, we synthesized new dimeric epoxy resins that were structurally analogous to the series synthesized previously by us [14,15]. The new monomers contain two imine mesogens and a central oxyethylene spacer of different length (see Scheme 1). The parity of the spacers is also different, because the **IBd** and **IIAd** monomers are homologous to pentamethylene while **IBt** and **IIAt** are analogous to octamethylene derivatives. Both the central spacer and the reactive glycidylic group are linked to the mesogens by ether or ester groups. However, mesomorphic behavior can be observed only when the groups at the end of the mesogens are different. This is because the polarization

of the mesogenic unit affects the LC-character of dimeric compounds [7,8]. Dimers with the same groups at the end of the mesogens are non-mesomorphic, so they have not been included in Section 2.

Scheme 1 shows the synthetic route followed to obtain the LC-epoxy dimers. It starts from commercially available products and uses well known procedures. In the first step, dialdehydes were prepared by nucleophylic substitution of the chlorine in the dichlorooxyethylenes by 4-hydroxybenzaldehyde or 4-formylbenzoic acid in the presence of sodium carbonate and benzyltrimethylammonium chloride (BTMA) as catalyst. In contrast to the results of synthesizing the homologous alkylene, the use of a crown ether as catalyst instead of BTMA did not give good results. The condensation reaction between the dialdehydes and 4-aminophenol was conducted in ethanol at reflux; when 4-aminobenzoic acid was used, however, the reaction could only be completed with the azeotropic elimination of water in DMF as solvent. Diglycidylic compounds were synthesized by reacting the corresponding diimino-diphenol or diimino-diacid with an excess of epichlorohydrin in the presence of BTMA. The diglycidylic products were recrystallized from toluene. The structural identification was made by means of spectroscopic techniques and their purity was confirmed by elemental analysis. Fig. 1 shows the ^{1}H NMR spectrum of compound **IBt**, in which the typical singlet due to the imine proton and the five splitted signals of the glycidylic group can be observed.

The LC-behavior of the synthesized dimeric compounds was studied by DSC, POM and WAXS. The phase transition for the monomers is shown in Table 1. First of all, we can observe that monomer **IBt** has a glassy nature, which is interesting because it combines the typical properties of polymers with those of low molar mass compounds, such as effective purification methods, well defined properties and an easier orientation of the mesophase than in polymers [16]. It should be pointed out that of all the dimeric compounds we have studied, compound **IBt** is the only one that has a T_g transition in its pure state. As can be seen in the same table, monomers **IBd** and **IBt** form smectic C and smectic A mesophases, respectively. The type of the smectic mesophase may be related to the parity of the spacer. The analogous compounds with alkylene spacers behaved in a similar way: the even-membered compounds formed smectic A mesophases while the odd-membered ones formed smectic C mesophases [14]. The molecular shape of the odd-membered spacers obstructs an orthogonal smectic A organization and favours a tilted smectic C mesophase. In contrast, the shape of even-membered dimers favors an orthogonal organization.

Smectic A and smectic C mesophases can be organized in one of two main arrangements. In one, the spacers and the terminal chains are added randomly, which means that the molecules are intercalated. In the other, the spacers and the terminal chains are separated to form a monolayer. Entropically, the intercalated random arrangement should be the most favorable. Experimentally, they can be distinguished, since the ratio between the layer spacing (d) and the calculated length of the monomer (l) in the first one must be around 0.5, while in the second it must be around 1. We used the CERIUS 2 molecular modeling program [11] to calculate the monomer lengths and for monomer **IBd** we obtained a value of 36.99 Å and for monomer **IBt** a value of 42.79 Å. We used WAXS to determine the spacings between the layers. For monomers **IBd** and **IBt** the values were 20.33 and 22.26 Å, respectively. From these values, ratios (d/l) of around 0.5 were determined for both monomers, which indicated the

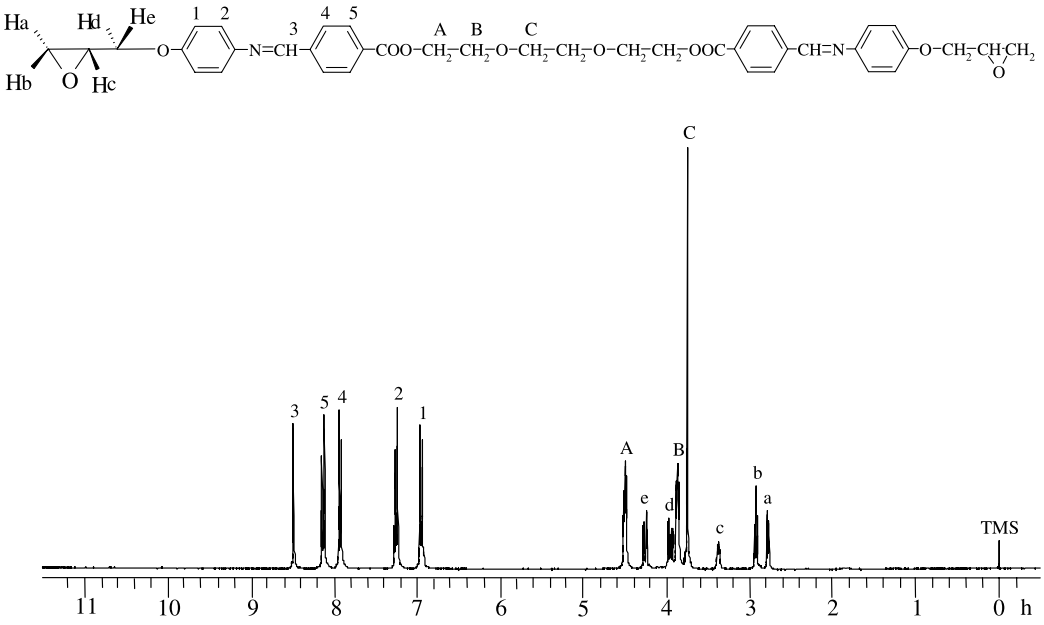


Fig. 1. ^{1}H NMR spectrum of 1,2-bis({4-[(2,3-epoxypropoxy)phenyliminomethyliden]benzoyloxy} ethoxy)ethane (**IBt**) in $CDCl_3$ (δ in ppm).

Table 1
Identified mesophases and thermal parameters from monomers **IB** and **IIA** determined by DSC and TGA

Monomer	Transitions[a] (°C)	Mesophase range[a] (°C)	ΔH[a] (kJ/mol)	T_{onset}[b] (°C)	T_{max}[b] (°C)	Char yield at 600 °C[b] (%)
IBd	K 121 S_C 166 I	45	17/13	284	325	56
IBt	G 82 S_A 142 I	60	–/13	286	354	52
IIAd	K 57 N* 86 I	29	30/1	281	334	43
IIAt	K 53 N* 94 I	41	17/1	280	350	42

*Monotropic mesophase, K: crystalline state, G: glassy state, N: Nematic mesophase, S_A: Smectic A mesophase, I: Isotropic state.
[a] Determined by DSC.
[b] Determined by TGA in N_2 atmosphere.

intercalated character of these smectic mesophases. The polarization of the mesogenic core provides favorable electrostatic interaction and, therefore, favors the intercalated arrangement and disfavors the monolayer arrangement [14].

In contrast to the monomers discussed above, **IIAd** and **IIAt** compounds form monotropic nematic mesophases which can be only observed on cooling. Thus, the substitution of alkylene by oxyethylene chains in the central spacer deteriorate the mesomorphic characteristics of this type of monomers in comparison with the methylene homologous **IIA5** and **IIA8** that showed enantiotropic nematic mesophases. In the present case, nematic mesophases are formed because of the absence of ester groups linking the mesogens to the central spacer or to a lower polarization of the mesogenic unit, as we discussed in a previous paper for their methylene analogous [15,7]. Moreover, there is a considerable decrease in transition temperatures when alkylene spacers are substituted by oxyethylene ones, specially for the longest spacer. Thus, monomer **IIA5** has a K–N transition at 106 °C and an N–I transition at 130 °C, and **IIA8** has K–N at 114 °C and N–I at 164 °C. Creed et al. [5] rationalized the decrease in the isotropization temperatures by changing ethylene by oxyethylene spacers in the basis of the more easily disordered mesogens due to their lower rotational barriers of C–O bond. However, the transition temperatures of the **IB** monomers do not vary in the same way. The oxyethylene spacers make the transition temperatures for monomer **IBd** higher than those of **IB5** (K–S_C 107 °C and S_C–I 149 °C), while **IBt** cannot be compared with **IB8**, since the latter have a K–S_A transition at 139 °C, a S_A–N at 157 °C and an N–I transition at 162 °C. From these results it seems that the flexibility of oxyethylene chains is not the only factor that affects the values of transition temperatures. It also seems that the insertion of oxyethylene spacers mainly affects the stabilization of nematic mesophases, since the **IBt** monomer does not present this type of mesophase and monomers **IIAd** and **IIAt** form only monotropic nematic mesophases.

As far as the mesophase range is concerned, it can be concluded that the longer the spacer is, the broader the range. This agrees with the published data, in which dimeric compounds with very long spacers, and as many as 34 oxyethylene units, still exhibit smectic mesophases [6]. These authors suggested that the occurrence of the liquid crystalline phase in case of such a long spacer could be connected with microphase separation and a helical organization of a poly(ethylene oxide) chain, that cannot be adopted in our case due to the shorter oxyethylene spacer.

Fig. 2 shows the POM photographs obtained in the mesophase range for monomers **IBd**, **IBt** and **IIAd**, with typical textures corresponding to smectic C, smectic A and nematic mesophases, which were further confirmed by WAXS.

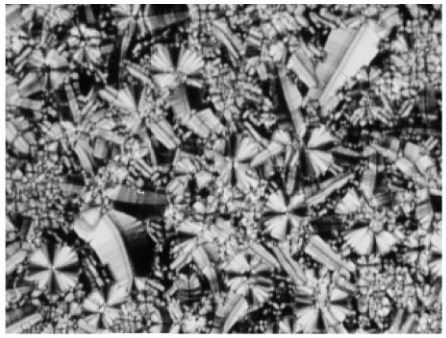
The thermogravimetric data in Table 1 show onset decomposition temperatures of around 280 °C and maximum decomposition rate temperatures in the range of 325–350 °C. There were no significant differences with their methylene analogues.

3.2. Crosslinking study

We had previously studied the crosslinking of different series of dimeric LC-epoxy resins which had methylene spacers with primary and tertiary amines. In several cases they led to LCTs with different degrees of order [14,15,17]. So we used these curing agents to prepare LCTs from the monomers described above and studied the reactions by DSC and POM.

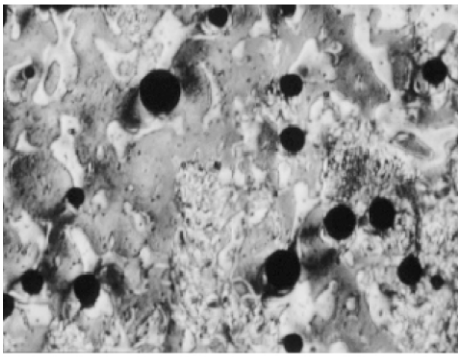
For the curing with aromatic primary diamines, stoichiometric mixtures of the corresponding diglycidyl compound and one of the selected diamines, DAT or NA2, were prepared as described in Section 2. In previous papers [7,15] we showed that NA2 was more able to obtain ordered networks, although it always leads to a loss in weight because of the presence of an azine group in the structure.

Table 2 shows the reaction conditions and the results of curing monomers **IBd** and **IBt** with DAT and NA2. From the data, we must point out that the addition of amines as curing agents to the monomer changes their mesomorphic behavior due to the great distortion produced by the amine. So, monomer **IBd** with a smectic C mesophase in its pure state became isotropic or nematic depending on the amine added (DAT or NA2, respectively) while monomer **IBt** with smectic A mesophase when pure formed isotropic mixtures in both cases. The monotropic character of the nematic mesophases and specially the low isotropization tempera-



a)

b)



c)

Fig. 2. 100× magnified POM photographs of (a) smectic C (**IBd**), (b) smectic A (**IBt**) and (c) nematic (**IIAd**) obtained by POM in the mesophase range of each compound.

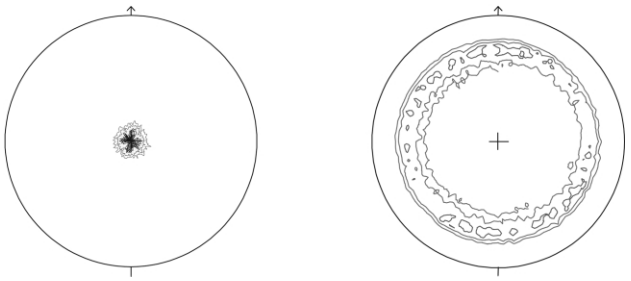


Fig. 3. Pole figures showing a smectic C organization of the LCT obtained by curing monomer **IBd** with DAT.

ture of monomers **IIAd** and **IIAt** prevented the formation of LCTs by curing. This confirms that the mesomorphic characteristics of monomers studied in this paper with oxyethylene units are worse than those of their alkylene homologues, which can be converted into nematic thermosets by curing in similar conditions.

As can be seen in the table, LCTs could only be prepared from monomer **IBd**, that could be converted into smectic C-like network by curing with DAT and into nematic by curing with NA2. These results differ from those obtained by curing the analogous alkylene compounds **IB5** and **IB8**, which formed nematic and smectic C-like networks, respectively, with both DAT and NA2 as curing agent. From these results it seems that the longer the oxyethylene spacer, the more difficult it is for LCTs to form. Fig. 3 shows the pole figures obtained for the LCT prepared by curing monomer **IBd** with DAT, in which the maximum of the diffractions at low and high angles are not orthogonal, but form an angle of about 30°. WAXS measurements gave a spacing layer of 40.01 Å. This distance is longer than the length of the monomer, which reflect the presence of the amine between the monomers. Moreover, from these values a fixed monolayer smectic C organization in the network can be assumed.

Table 2 also shows the thermogravimetric data about the thermosets obtained. The use of NA2 to form the network leads to a decrease in the initial degradation temperature, which can be attributed to the nitrogen release due to the presence of an azine group in the structure.

Catalytic crosslinking with tertiary amines was also studied. The advantage of catalytic systems is that they

Table 2
Curing conditions and thermal parameters determined by DSC and TGA and initial and final order in the materials obtained by curing monomers **IB** with stoichiometric proportions of DAT and NA2

Monomer	Amine	T_{curing} (°C)	Time (min)	Initial state	Final state	ΔH^a (kJ/mol)	T_g (°C)[a]	T_{onset}[b] (°C)	T_{max}[b] (°C)	Char yield at 600 °C[b] (%)
IBd	DAT	140	80	I	S_C	93	78	271	327	56
IBt	DAT	140	120	I	I	107	–	273	338	55
IBd	NA2	140	130	N	N	126	–	240	347	59
IBt	NA2	160	150	I	I	115	119	240	364	56

[a] Determined by DSC.
[b] Determined by TGA in N_2 atmosphere.

Table 3
Curing conditions and thermal parameters determined by DSC and TGA and initial and final order in the materials obtained by curing monomers **IB** with 3 phr of DMAP as catalyst

Monomer	T_{curing} (°C)	Time (min)	Initial state	Final state	ΔH^a (kJ/mol)	T_g (°C)[a]	$T_{onset}{}^b$ (°C)	$T_{max}{}^b$ (°C)	Char yield at 600 °C[b] (%)
IBd	140	300	S_C	S_C	112	99	274	373	60
IBt	120	300	S_A	S_C–I	119	84	267	367	59

[a] Determined by DSC.
[b] Determined by TGA in N_2 atmosphere.

require a small proportion of the curing agent, that does not produce an appreciable distortion in the ordered mesogens in the mesophase, because the curing agent generally remain attached to the initial chain unit of the polymer, which is not part of the inner structure of the network. Another advantage is that the proportion of the catalyst can be selected so that the crosslinking process can be carried out at different temperatures and reaction rates. Previous experiments using DMAP showed that the best proportion of catalyst was 3 phr. Table 3 shows the curing conditions and the results. The little proportion of tertiary amine added did not produce any appreciable distortion in the order of the melt and so the mixtures had the same mesophases that the monomers in their pure state. With this curing system, smectic C-like networks were obtained, although monomer **IBt** produced an inhomogeneous material with isotropic regions. It should be noted that the curing needed to complete the crosslinking process took longer. As in the curing with primary amines this curing system did not allow LCTs to form from monomers **IIAd** and **IIAt**, because of their monotropic character. Fig. 4 shows a photograph of a typical smectic C texture obtained by curing the monomer **IBd** with 3 phr of DMAP.

The spacing layer of the fixed smectic C organization for **IBd** was determined by WAXS and resulted in 39.81 Å, shorter than that obtained with DAT. This value confirm a monolayer arrangement of the smectic network and the lower distortion produced by tertiary amines.

The thermogravimetric data in Table 3 are comparable to the LCT data obtained by curing with DAT.

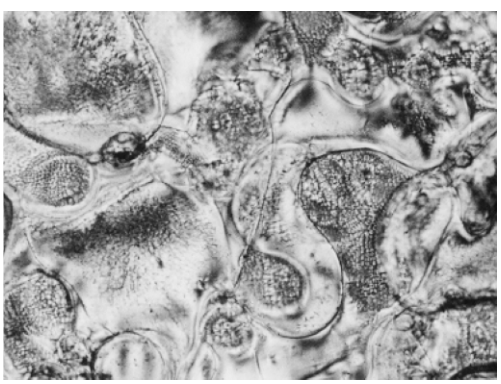


Fig. 4. 100× magnified POM photograph of a typical smectic C texture obtained by curing **IBd** with 3 phr of DMAP.

4. Conclusion

This study indicates that the substitution of alkylene spacers by oxyethylene ones leads to worse mesomorphic characteristics. Firstly, monomers with unpolarized mesogens, which have groups of the same electronic character at their ends, formed nematic mesophases when the spacers were alkylene but did not form mesophases when they were oxyethylene. Secondly, **IIA** monomers with oxyethylene spacers formed monotropic nematic mesophases, while analogous alkylene monomers formed enantiotropic nematic mesophases. Finally, it is more difficult to fix mesophases in the thermosetting materials using monomers with oxyethylene spacers, specially for the longest. Moreover, the monotropic character of **IIA** monomers means that neither of the curing systems studied could fix the ordered networks.

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