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Liquid Crystalline Thermosets from Dimeric LC Epoxy Resins Cured with Primary and Tertiary Amines

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Summary: Liquid crystalline thermosets (LCTs) were prepared by curing difunctional LC dimeric epoxy monomers with imine moieties in the mesogenic core and central spacers of different length. Primary diamines or tertiary amines were used as curing agents obtaining materials with different characteristics. The results obtained were related to the mesogen structure, since dipolar moments in the mesogenic cores affect the ability to form ordered networks.

Keywords: crosslinking, epoxy resins, high performance polymers, liquid-crystalline polymers (LCP), networks

Introduction

There are two different ways to obtain liquid crystalline thermosets (LCTs). One of them is the thermal, chemical or photochemical crosslinking of high molecular LC polymers having reactive groups. This route is versatile, because many reactive groups can be crosslinked with several curing agents.[1] The second procedure, proposed by De Gennes,[2] consists of polymerizing a difunctional monomer, which reacts with a curing agent to form a tridimensional network. The advantage of this method is that monomers have a low viscosity, which facilitates processing and makes it possible to work at lower temperatures.

Epoxy networks are widely applied as engineering thermosets because they have good mechanical and thermal properties. They have been extensively used to prepare LCTs.[3] The first references to epoxy LCTs appeared in the 1986, when large industrial groups patented their results.[4] It has been described[5,6] that the best characteristics of epoxy LCTs are their high order parameter and their high birefringence. Moreover, the ordering in the liquid crystal state facilitates a rapid transition to the solid phase with little molecular movement. This means that there is a reduction in the thermal expansion coefficient and the

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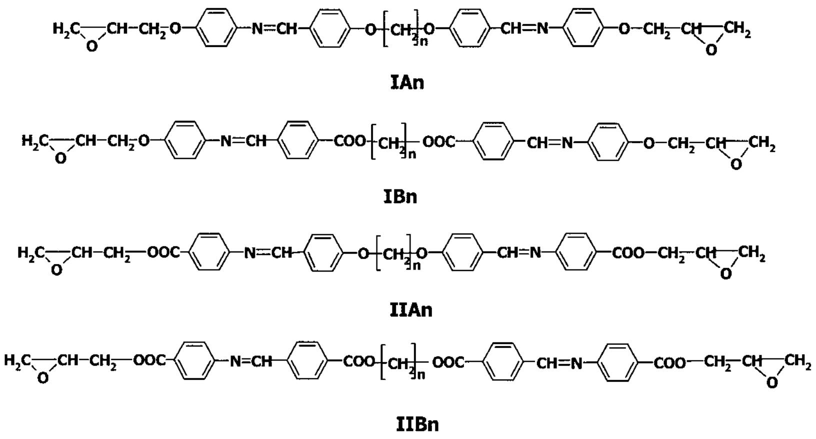
shrinkage upon curing, which are problems inherent to the technological applications of epoxy resins.

In the nematic mesophase, monomers are easier to orient because of their low viscosity. The anisotropic networks obtained by fixing nematic mesophases are interesting as structural materials or as insulation for microelectronics. They are also suitable for electro-optical applications.[7] Although smectic networks have not been studied so much, they are described to be exceptionally tough.

The monomers studied in the present work are epoxy resins with dimeric or twin architectures consisting of two calamitic mesogens and central aliphatic spacers of different lengths. This architecture is chosen to lower the melting and isotropization temperatures and to increase the mesophase stability. Thus, the crosslinking can be carried out at relatively low temperatures. The mesogenic moiety contains aromatic imine groups, with a high mesogenic character and a high thermal stability.[8] This unit is easy to synthesize from commercially available products with high yields. At the end of the mesogenic unit, ether or ester groups link the mesogen to the aliphatic spacer and the glycidylic reactive group as is shown in the following scheme.



IAn

IBn

IIAn

IIBn

Scheme 1

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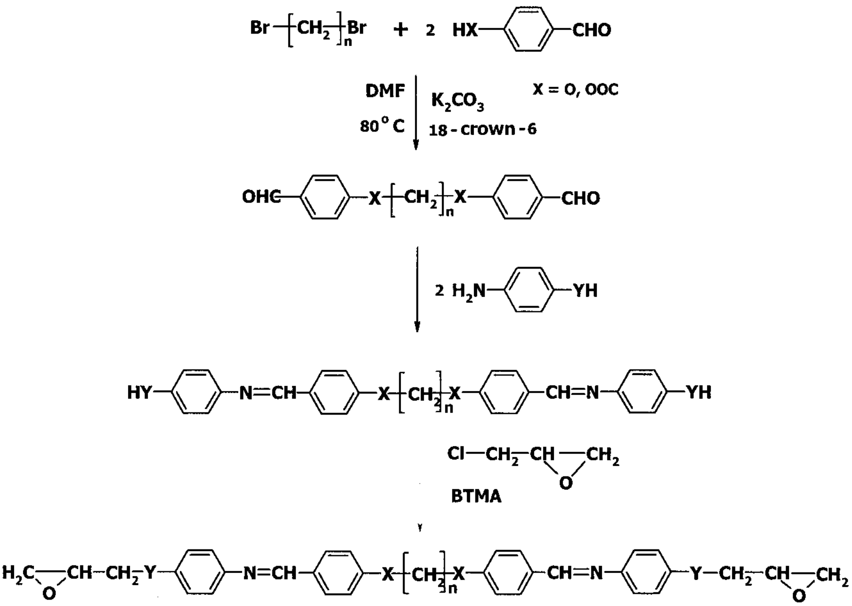
The aim of the present paper is to show how the ether or ester groups directly attached to the mesogen and the length and parity of the central spacer affect the ability to form ordered phases and the nature of these mesophases. We have also studied the influence of the structure of these monomers in the formation of LCTs by crosslinking.

Results and Discussion

The monomers were synthesized as shown in Scheme 2. The first step is the substitution of bromine atoms of a dibromoalkane by a p-formyl phenolate or benzoate in the presence of potassium carbonate and 18-crown-6. These compounds were condensed with p-aminophenol and p-aminobenzoic acid[9,10] to produce the imino compounds with high yields and purities. The reactive glycidylic groups are introduced by reacting these compounds with an excess of epiclorohydrin and a quaternary ammonium salt. The products obtained were characterized by standard methods.



Scheme 2

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Table 1 shows the mesogenic behaviour of the IB series and some structural characteristics. As we can see, monomers IB3, IB5 and IB7, which have spacers with an odd number of methylenes form smectic C mesophases while those that have an even number of methylenes form smectic A mesophases. Some of these monomers also show nematic mesophases. Generally, the smectic A range decreases and nematic mesophase stabilizes slightly as the spacer length increases. These results confirm that the spacer of the monomers has a strong odd-even effect on both the melting and isotropization temperatures and on the type of smectic mesophase formed. Both the melting and isotropization temperatures in each series of odd- and even-membered spacers decrease as the spacer length increases.

Table 1. Characteristics of dimeric epoxy compounds of the IB series.

Comp	Transition Temperatures (°C)	Mesophase ranges S/N (°C)	Half spacer length (Å) [b]	Monomer length (Å) [b] l	Layer spacing (Å) [c] d	d/l
IB3[a]	K 149 S_C 159 I	10	3.66	34.46	33.04	0.96
IB4	K 176 S_A 210 N 212 I	34/2	4.30	39.16	20.27	0.52
IB5	K 107 S_C 149 I	42	4.92	37.21	18.96	0.51
IB6	K 151 S_A 181 I	30	5.56	41.23	21.72	0.53
IB7	K 114 S_C 127 I	13	6.19	39.85	20.41	0.51
IB8	K_1 133 K_2 139 S_A 157 N 162 I	18/5	6.82	43.27	22.89	0.53
IB10[a]	K 131 S_A 138 N 145 I	7/7	8.09	44.88	21.81	0.49

a. Monotropic mesophase;
b. calculated by Cerius2;
c. determined by WAXS

The spacings of the smectic layers were evaluated by X-Ray diffraction. If we compare these results with the length of the monomer calculated by Cerius 2, the d/l ratio is around 0.5, which indicates that the even monomers are intercalated. Imrie[11] described that symmetric calamitic dimers have a strong tendency to form monolayer smectic phases. Our

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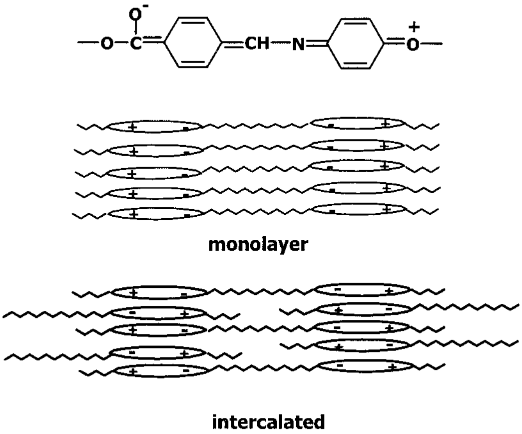
results can be explained if we consider the structural characteristics of the mesogens. So, we can formulate a resonance structure, in which the ether assumes a positive charge and the ester a negative one. Because of the polarization of the mesogenic core favourable electrostatic interactions appear, which favours an intercalated structure, as can be seen in the Scheme 3. These interactions disfavour monolayer arrangements.



Scheme 3

Odd-membered spacer monomers show smectic C phases. In this case intercalated organizations were also confirmed by the d/l ratio for monomers with spacers of 5 and 7 methylene carbons. However, a monolayer arrangement was formed in the case of monomer IB3, because the terminal chain (4.60 Å) was longer than half of the spacer. Thus, in this case, steric hindrance of the aliphatic chains is predominant over electronic interactions between mesogens.

The liquid crystalline behaviour of the other series of diglycidylic compounds is collected in Table 2. In all monomers only nematic mesophases were detected. Of the compounds with spacers of 10 or 12 methylene carbons only IIA compounds show LC behaviour. This observation, in addition to the broader mesophase range, leads to the conclusion that IIA series have a higher mesomorphic character.

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If we compare the mesomorphic characteristics of the compounds synthesized in this study, only compounds of the IB series form smectic mesophases, while the others present only nematic ones. Imrie reported that an ester linkage connecting the central spacer to the mesogen promotes smectic behaviour. Compounds in IIB series also have ester linkages in the same position, but only nematic mesophases are formed. In addition to ester groups linking the central spacer to the mesogens, it seems that the nature of both groups plays a significant role in the LC behaviour. Strong lateral interactions between mesogens facilitate smectic arrangements, since the smectic mesophases are produced by a microseparation of the phases, in which the mesogens are close in a definite region, while the alkyl chains constitute another well differentiated. The interactions between mesogens may be of electrostatic nature, because electron-donating and electron-withdrawing groups at their ends, cause high dipolar moments.

Table 2. Mesomorphic characteristics of compounds of IA, IIA and IIB series.

Comp.	Transition temp. (°C)	Mesophase range (°C)	ΔH (kJ/mol)
IA6	K 208 N 224 I	16	70 / 6
IA8	K 201 N 209 I	8	90 / 7
IA12	K 188 I	-	67
IIA3	K 142 I	-	38
IIA4	K 162 N 207 I	45	35 / 4
IIA5	K 106 N 130 I	24	21 / 1
IIA6	K 178 N 189 I	11	69 / 4
IIA8	K 114 N 164 I	50	43 / 5
IIA10	K 119 N 158 I	39	55 / 5
IIA12	K 122 N 149 I	27	55 / 5
IIB4	K 164 N 167 I	3	45 / 4
IIB6[a]	K 99 N 138 I	39	37 / 4
IIB8[a]	K 93 N 119 I	26	46 / 5

[a] Monotropic mesophase

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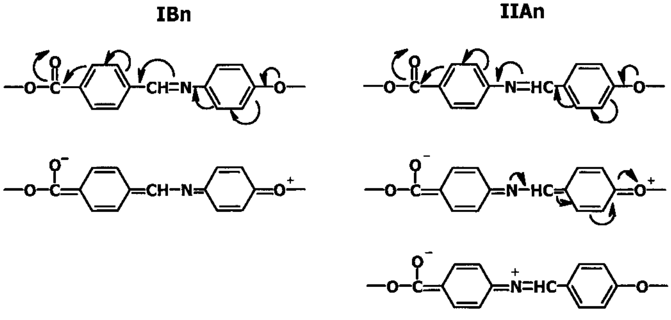
Monomers of the IA and IIB series have functional groups of the same character at the end of the mesogens and, therefore, electrostatic interactions are low. However, IB and IIA monomers have groups of different characters at the end of the mesogens, although IB monomers have a maximum dipolar moment, such is represented in Scheme 4. The relative orientation of the imine group to the final groups in the IIA series allows an additional resonant structure to be formulated. This reduces the positive charge in the ethereal oxygen. Therefore, these results confirm that dipolar moments have considerable influence on the smectogenic character of this type of dimeric compounds.



Scheme 4

To obtain LCTs, we studied the reaction of these epoxy compounds with primary aromatic diamines. In a first step, the primary amine reacts with epoxide to form linear oligomers with an extended chain that enhances the molecular anisotropy. In a second step, the secondary amine groups react to fix the anisotropic network. So, from an isotropic initial melt, ordered networks can be formed.

Shiota and Ober[12] used primary aromatic diamines to study the crosslinking of epoxy resins with dimeric architectures. They obtained smectic networks in spite of the initial mesophase. They suggested that the crosslinking sites at the end of the mesogens help to fix the spacing distances between crosslinks and favour smectic layer organizations.

Of the various primary aromatic diamines, the most suitable for getting from our epoxy monomers ordered networks were 2,4-diaminotoluene (DAT) and p-amino-acetophenone azine (NA2). It should be pointed out that NA2 was more effective than DAT at fixing

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ordered networks, although thermogravimetry always detected a weight loss, which can be due to a release of nitrogen.

We managed to fix ordered networks only when mesogens have both ether and ester linkages at the end. This confirmed the significance of the polarization of the mesogenic cores. As we can see in Table 3, in the most cases the ordering was nematic even from the isotropic melt. Smectic C organizations were locked only from monomers with long spacers. The monomers not included in the table led to isotropic networks. The mesophases fixed in the networks were identified by polarized optical microscopy and XR-diffraction.

Table 3. Isothermal curing conditions and characteristics of the LCTs obtained from mixtures of monomers IB and IIA with primary aromatic diamines.

Compound	Amine	Curing temperature (°C)	Curing time (min)	Initial mesophase	Network	Tg (°C)
IB4	DAT	160	30	I	N	-
IB5	DAT	110	57	I	N	120
IB6	DAT	150	36	I	N	-
IB8	DAT	150	47	I	Sc	-
IB10	DAT	140	70	I	N	108
IB4	NA2	170	40	N	N	-
IB5	NA2	130	120	N	N	102
IB6	NA2	180	40	N	N	-
IB8	NA2	180	70	N	S_C	-
IB10	NA2	180	120	N	S_C	-
IIA4	NA2	190	35	N	N	131
IIA5	NA2	190	40	N	N	118
IIA6	NA2	190	30	N	N	122
IIA8	NA2	190	40	N	N	110
IIA10	NA2	190	40	N	N	89

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If mesogenic epoxy resins are cured with primary aromatic diamines, a relative large proportion of amine is required, which can disturb the organization of the monomer in the mesophase. In order to achieve highly ordered structures, we have studied the catalytic crosslinking of liquid crystalline compounds with tertiary amines. In this way, curing agent remains at the beginning of the crosslinked chain and does not disturb the inner structure. Another advantage of catalytic systems is the possibility to select the appropriate proportion of catalyst, so the crosslinking process can be carried out at different temperatures and reaction rates.

The used reaction conditions and the obtained results when the curing was catalyzed by a 3%.-w/w. of 4-(N,N-dimethylamino)pyridine (DMAP) are collected in Table 4.

Table 4. Isothermal curing conditions and characteristics of the LCTs obtained from mixtures of monomers IB and IIA with 3 phr. of DMAP as curing agent.

Compound	Curing temperature (°C)	Curing time (min)	Initial state	Network	ΔH (KJ/mol)	Tg (°C)
IB4	180	26	S_A	S_C	112	-
IB5	120	240	S_C	S_C	103	-
IB6	160	32	S_A	S_C	114	-
IB7	120	300	S_C	S_C	114	-
IB8	150	140	S_A	S_C	97	-
IB10	148	50	S_A	S_C	72	-
IIA4	180	100	N	N	150	110
IIA5	120	160	N	N	100	73
IIA6	180	130	N	N	143	98
IIA8	150	180	N	N	141	86
IIA10	150	160	N	N	148	79
IIA12	145	180	N	N	163	72

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As we can see, monomers of the series IB led to smectic C-like networks. On the other hand monomers IIA led to nematic organizations in all cases. Also in this case, the behaviour of both series is different, although LCTs are obtained from all these monomers. However, when the groups linked at the end of the mesogens have identical nature only isotropic materials were always obtained. These results confirm the influence of the dipolar moments on the mesogens in the obtention of materials with different degree of order and the suitability of tertiary amine as the curing system to obtain liquid crystalline thermosets.

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