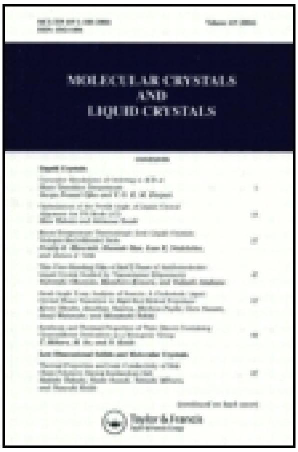

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Liquid Crystalline Epoxy Thermosets

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LIQUID CRYSTALLINE EPOXY THERMOSETS

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Abstract Rigid rod epoxy compounds can be cured in liquid crystalline structure. The so obtained networks exhibit better mechanical properties with respect to the isotropic ones. The mesogenic character of the epoxy compounds appears more crucial than the molecular geometry of the curing agent in developing liquid crystallinity. The curing temperature plays an important role in affecting the state of order of the thermosets.

INTRODUCTION

The interest of scientific community towards liquid crystalline networks has increased in the last years due to the peculiar properties exhibited by this class of materials.

In the case of poorly crosslinked networks, elastomers with outstanding optical properties can find application in non linear optics (NLO), as waveguides or polymer dispersed liquid crystals[1-3] (PDLC). In the case of higher crosslinking density, thermosets with superior mechanical properties and heat resistance can find applications in aerospace industry [4-9].

Since 1985 intense patent activity has been concentrated by industries on the synthesis of new Liquid Crystalline Epoxy Resins (LCER) [10-11].

LCER can offer a new rewarding challenge in the field of high performance resins. In fact they can potentially join the performances of epoxy with the outstanding properties of liquid crystalline polymers. Therefore a mesogenic epoxy resin can display higher mechanical properties, better chemical and heat resistance, lower viscosity during the processing. In particular, the Achille's heel of traditional epoxy resins, their intrinsic brittleness, can be strongly reduced in the case of an ordered crosslinked material.

However, the "molecular engineering" ought to take in account that the state of order of the cured material can be affected by different parameters .

They are:

- length and nature of the rigid block in the epoxy monomer;
- nature of the curing agent;
- temperature of curing.

All these variables are crucial to obtain a liquid cristalline epoxy resin.

This paper deals with the relationship between the above mentioned parameters and the physical properties of the resulting thermoset.
Our strategy is based on the synthesis of hydroxy terminated rigid rod molecules, their glycidyl termination and curing.

For this purpose, the following molecules were selected.

a) 4,4' dihydroxyacetophenone azine
b) 4,4' dihydroxy-α-methylstilbene
c) 4,4' dihydroxydiphenyl
d) 4'- hydroxyphenyl-4-hydroxybenzoate
e) 2,6- dihydroxynaphthalene
f) 2,2'-binaphtyl-6,6'-diol
g) 2-propen-1-one, 1,3-bis(4-hydroxyphenyl)
h) 4-hydroxyphenyl-4"-hydroxybiphenyl-4'-carboxylate

The molecular skeletons of the compounds are reported in figure 1.

EXPERIMENTAL

Synthesis of epoxy resins

I) Synthesis of the dihydroxy compounds

(a) 4,4' dihydroxyacetophenone azine

34g p-hydroxyacetophenone(0.25 mol), 100 ml ethanol, (95% aqueous solution), and three drops of glacial acetic acid were charged into a 500 ml, 4 neck flask equipped with magnetic strirrer, N_2 sweep, temperature probe, addition funnel and condenser. While stirring, it was heated to 60 ^{o}C . Hydrazine (35 wt.% solution in water, 12 ml) was added dropwise, for 30 minutes, and then the solution was refluxed for 2 hours. Then it was cooled, filtered and recrystallized from ethanol. m.p.=226°C (lit. 221°C [12], 222-223°C [13], 224°C [14]); yield=75%.

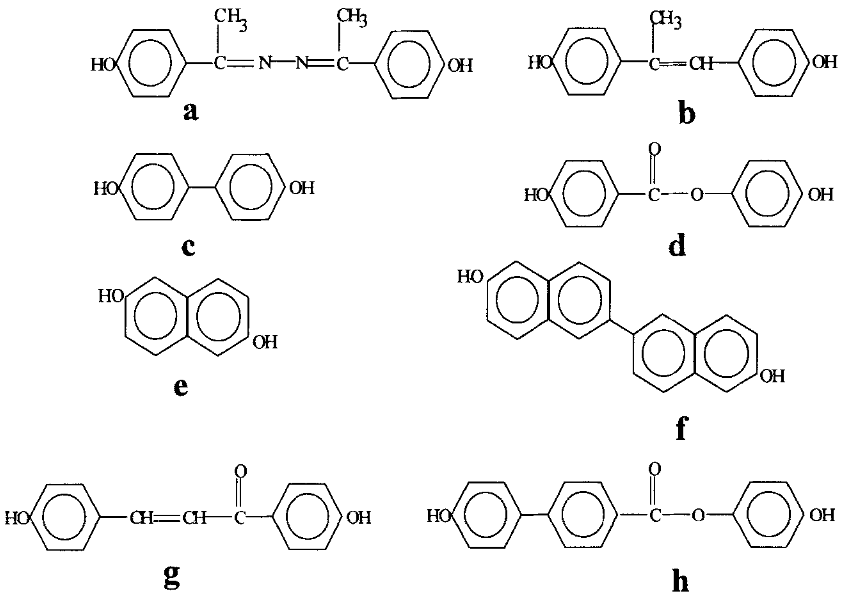


FIGURE 1 Molecular skeletons of dihydroxy compounds (a)-(h)

(b) 4,4' dihydroxy-α-methylstilbene

Chloroaceton (5.5 g, 0.059 mol) and phenol (11.4 g, 0.12 mol) were charged into a 500 ml, 4 neck flask equipped with a stirrer, temperature probe, N_2 sweep and addition funnel. While stirring, it was cooled to 8 °C. H_2SO_4 (96%, 59g) was added dropwise maintaining the temperature at 5°C. After one hour, 90% of the H_2SO_4 had been added, the temperature increased to 43°C. 100 ml of isopropyl alcohol were added. At the end of the addition of acid the mixture was added to 1 l of cold water. The water was decanted off and more (1 l) added. It was recrystallized from a water-ethanol mixture.

m.p.=182°C (lit. 182°C [15].); yield=46%

(d) 4'-hydroxyphenyl ,4-hydroxybenzoate

p-hydroxybenzoic acid (14 g, 0.1 mol) and hydroquinone (110 g, 1.0 mol) were charged into a 4 neck round flask equipped with a stirrer, condenser, temperature probe and N_2 sweep and then heated to 260°C for 2 hours. At the end

of the reaction the hot mixture was poured into 500 mL of distilled water, yielding a white solid. It was recrystallized from a 50% vol. ethanol/water mixture.
m.p.=245°C (lit. 242-245°C [16].); yield=65%.

4,4'-dihydroxydiphenyl (c) and 2,6-dihydroxynaphthalene (e) were directly purchased from Aldrich (99% purity) and used without any further purification.

(f) 2,2'-binaphthyl-6,6'-diol

30 g 2-bromo-6-methoxynaphthalene (0.127 mol), 1.54 g magnesium turnings (0.0635 mol), 80 mL anhydrous tetrahydrofuran and 0.127 g ($4.4 \cdot 10^{-4}$ mol) [bipyridyl-nickel (II)]chloride (for its synthesis, see below) were charged into a 500 mL, 3 neck flask equipped with stirrer, condenser, temperature probe and N_2 sweep. It was heated to reflux and held at reflux for 120 minutes while stirring. It was then poured into 100 mL ethanol and filtered. The resulting white solid was washed with HCl (15 vol.% aqueous solution), filtered, washed with ethanol. It was filtered again, then dried in vacuum at 90°C, yielding 6, 6'-methoxy-2,2'-binaphthyl[17](yield=75%). This last compound (5 g, 0.0159 mol) and 7.4g (0.0641 mol) pyridine hydrochloride were charged into a 250 mL, 3 neck flask equipped with stirrer, condenser, temperature probe and N_2 sweep. The mixture was heated to 270°C and held at reflux for 120 minutes. It was then poured into water and filtered, yielding a grey solid. It was recrystallized from ethanol.
m.p.=302°C (lit. 297-298°C [18].); yield 45%.

Synthesis of the catalyst [bipyridyl-nickel (II)]chloride: 2.0 g anhydrous Ni (II) chloride (0.0154 mol) and 50 mL ethanol were charged into a 250 mL, 3 neck flask equipped with magnetic stirrer and N_2 sweep. 2.89 g 2,2'-bipyridyl (0.0185 mol; 0.37 mol/L in ethanol solution) were added dropwise, and the resulting mixture was stirred at room temperature for 6 hours. The resulting green solution was charged into roto-vap, yielding a green solid which was washed with acetone, filtered and vacuum dried (yield=45%).

(g) 2-propen-1-one, 1,3-bis(4-hydroxyphenyl)

A solution of 22 g sodium hydroxide (0.55 mol) in 200 mL of water and 100 g of rectified spirit was placed in a 500 mL bold head flask provided with a mechanical stirrer. The flask was bathed in crushed ice. 58 g acetophenone (0.43 mol) were poured in, and subsequently 52 g hydroxybenzaldeide (0.43 mol) were added while stirring. The temperature was kept at 25°C and the mixture was vigorously stirred for 1 hour.The stirrer was then removed and the mixture was kept at 4°C overnight. The product was filtered with suction on a Buchner funnel, washed with cold water up to neutrality if the washing waters and then with 20 mL of ice-cold rectified spirit.

m.p.= 195°C. Elemental analysis: Carbon 74.76%, Hydrogen 5.17% (theoretical values: C 74.99%, H 5.03%); yield= 54%.

(h) 4-hydroxyphenyl-4"-hydroxybiphenyl-4'-carboxylate

5 g hydroxydiphenylcarboxilic acid (0.023 mol) and 13 g hydroquinone (0.120 mol) were charged in a flask equipped with a mechanical stirrer and a heating mantle, under N_2 sweep, and heated for 1 hour at 270°C. The mixture was poured in water and filtered. The solid was recrystallized from ethanol.

m.p.=290°C; yield=35%; Elemental analysis: Carbon 73.57%, Hydrogen 4.77% (theoretical values: C 74.51%, H 4.61%)

II) Glycidyl termination of the rigid molecules

p-(2,3-epoxypropyl)acetophenone azine (EF3)

16g (a) (0.0597 mol) and tetrahydrofuran (THF) (150 ml,) were charged into 500 ml , 4 neck flask equipped with a stirrer, condenser, temperature probe and N_2 sweep. Sodium hydride (2.87 g, 0.12 mol; 60 wt.% oil suspension) was added slowly to this solution. During the addition the temperature rose to 31°C. It was then allowed to stir at room temperature overnight. It was then filtered and the filter cake washed with tetrahydrofuran. The yellow solid was charged back into the reaction set up with 200 ml of epichlorohydrin (2.5 mol) and 0,5 g of tetrabutylammonium chloride (1.8 mmol). While stirring it was heated slowly to 90°C and kept at this temperature for two hours. It was then hot filtered and the filter cake was washed with 50 ml of epichlorohydrin.The filtrate was cooled, filtered and washed with hexane. The product was vacuum dried at 55°C. m.p.= 176°C; yield= 66%; WPE (molecular weight per epoxy group) = 194 (calc.=190)

The compound (h) was glycidyl terminated according to the following procedure: 2.1 g (0.007 mol) comp. (h), 16.1 mL epichlorohydrin (0.21 mol), 0.046 g tetrabutylammonium chloride (1.66×10^{-4} mol) were charged into a 500 mL 3 neck flask, equipped with temperature probe, magnetic stirrer and condenser. The mixture was reacted for 16 hours at 60°C. Then the system pressure was driven to 0.8 atm and 0.69 g sodium hydroxide (45 wt.% aqueous solution) were added dropwise. It was reacted at 65°C for 5 hours. The white solid obtained was dissolved with 200 mL boiling acetonitrile. The solid residue was then removed by filtrating and 100 mL methanol were added to the solution. 4-(2,3-epoxypropoxy)phenyl, 4"-(2,3-epoxypropoxy)biphenyl-4'-carboxylate (DIFHB) was obtained.

m.p.=120°C; yield=25%; WPE=211 (calc. 209)

The compounds (b), (c), (d), (e), (f), (g) were glycidyl terminated by using epichlorohydrin in the presence of sodium hydroxide according to the procedure described in the literature [19], yielding, respectively, p-(2,3-epoxypropoxy)-α-methylstilbene (DOMS), p-(2,3-epoxypropoxy)-diphenyl (DIF), p'-(2,3-epoxypropoxy)-phenyl-p-(2,3-epoxypropoxy)benzoate (PHBHQ), 2,6-(2,3-epoxypropoxy)-naphthalene (NAFT), 6,6'-Bis(2,3-epoxypropoxy)-2,2'-binaphthyl (EPBN), 2-propen-1-one, 1,3-bis[4-(2,3-epoxypropoxy)phenyl] (CHALC).

The characteristics of the epoxy terminated compounds are summarized in table 1.

Curing agents

The following curing agent were selected:

p-aminoacetophenone azine (NA2)
2,7 diamino fluorene (DAF)
1,4- diaminobutane (DB)
Diaminodiphenylsulphone (DDS)
t-1,4-diaminociclohexane (t-CN)
2,4-diaminotoluene (DAT)

TABLE 1 Characteristics of the glycidyl terminated compounds; Tn,i=nematic-isotropic phase transition temperature; m=monotropic; RRL = rigid rod length

Compound	m.p. (°C)	Tn,i (°C)	WPE	RRL (Å)	Yield (%)
EF3	176	-	194	10.3	66
DOMS	130	115, m	185	9.2	80
DIF	153	160, m	166	7.2	65
PHBHQ	113	97, m	180	8.5	40
NAFT	186	-	140	4.7	60
BINAFT	240	270	205	10.2	30
CHALC	115	-	194	9.99	25
DIFHB	120	220	211	13.5	35

NA2 was synthesized according to the following procedure: p-aminoacetophenone (27 g, 0.20 mol) and 95% ethanol (100 ml) were charged in a 3 round neck flask, equipped with a condenser, N_2 sweep, and addition funnel. Hydrazine (0.22 mol, 35% water solution, 20 ml) was added dropwise. The solution was refluxed for two hours. 900 ml of water were added and the solution neutralized with glacial acetic acid. The product was filtered and recrystallized from 95% ethanol. M.p.=167°C; yield= 41%.

DAF, DDS, BA, t-CN, DAT were purchased from Aldrich and their purity was checked by NMR.

Differential scanning calorimetry

The phase transition of the specimens and the chemical reactions were monitored with a differential scanning calorimeter (DSC) DuPont Mod. 2910. Nitrogen was used as purge gas. In dynamic experiments a heating rate of 10°C/min was adopted.

Scanning electronic microscopy

The fracture surface of the samples was analized by means of a scanning electron microscope (SEM) Hitachi mod. S-2300. Transversal sections of the samples were obtained by fracturing them in liquid nitrogen.

Optical microscopy

The textures of the monomers and cured resins were observed with an optical microscope Reichert- Jung, mod. Polyvar in transmitted light, equipped with crossed polarizers. The temperature was controlled by means of a Linkam mod.TH600 hot stage.

X ray analysis

The X-ray diffraction spectra were obtained by the photographic method using a Rigaku mod. III/D max generator. A Ni-filtered Cu-K_α radiation was used.

Mechanical properties

Fracture toughness was evaluated according to ASTM E-399 test procedure using a 1"x 1"x 1/8" compact tension specimens

Flexural properties of the cured resins were measured according to ASTM D 790.

Coefficients of thermal expansion (CTE) were evaluated by means of a thermomechanical analyzer (TMA) DuPont Mod. 2940.

The length of the rigid rod molecules was calculated after minimizing energy by means of the program Desktop Molecular Modeller.

RELATIONSHIP BETWEEN THE STATE OF ORDER OF THE CURED RESIN AND PHYSICAL PROPERTIES

In order to evaluate which properties could be affected by the liquid crystalline state, the DIF-NA2 system was chosen as a model compound and cured in two different temperature ranges. At lower temperatures the resin could be cured into a nematic structure, while at higher temperature an isotropic crosslinked material resulted. The stoichiometric mixture of DIF and NA2 powders was heated between two glass slides in the hot stage of the microscope up to 130°C. The molten components dissolved one in another and their mixture appeared completely dark under crossed polarizers, thus indicating that it was isotropic.

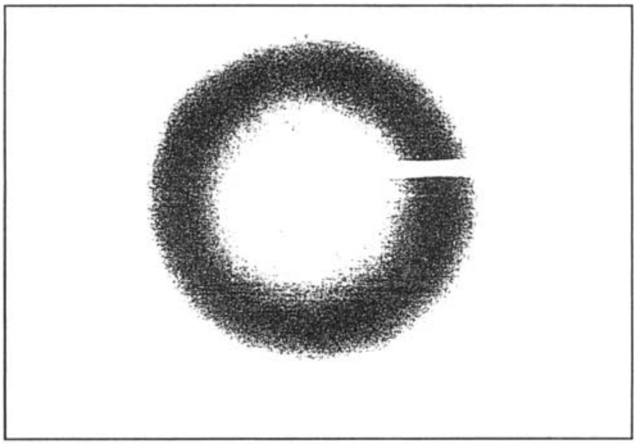
The temperature was held constant at 130°C. In the first minutes the melt remained dark and then a peculiar coloration was developed indicating formation of a liquid crystalline texture. The birefringence did not disappear with time revealing that the texture remained stable while the crosslinking reaction proceeded. No further changes could be observed upon cooling down to room temperature. Then the specimen was reheated up to its degradation temperature (about 260°C). During this whole process of reheating, the specimen had strong coloration up to its degradation.

By heating the stoichiometric mixture at the temperature of 170°C after the melting of the two components, the reaction produced a homogeneous isotropic network.

Fig.2 shows the X-ray diffraction pattern of the thermoset obtained curing DIF with NA2 at 130 °C. The sharp halo clearly indicates the nematic nature of the phase excluding any more ordered states.

The isotropic and nematic materials have the same temperature dependance of their modulus and the same glass transition temperatures of approximately 220°C. The flexural properties (Table 2) are also practically identical for both materials. The main difference in properties of nematic and isotropic samples is their fracture toughness. The nematic sample has fracture toughness of 1200 psi*in.$^{1/2}$ which is 50% higher than fracture toughness of the isotropic material (800 psi*in.$^{1/2}$). Therefore the main advantage of nematic morphology compared to isotropic morphology is the enhancement in the material toughness which takes place without any sacrifice in other mechanical properties. Just as a comparison, such a strong increase in fracture toughness can be reached by including more than 10% of a functionalized rubber in a conventional epoxy resin, with a consequent dramatic reduction of modulus and Tg [20].

FIGURE 2 X-ray diffraction spectrum of DIF-NA2 system cured at 130°C.



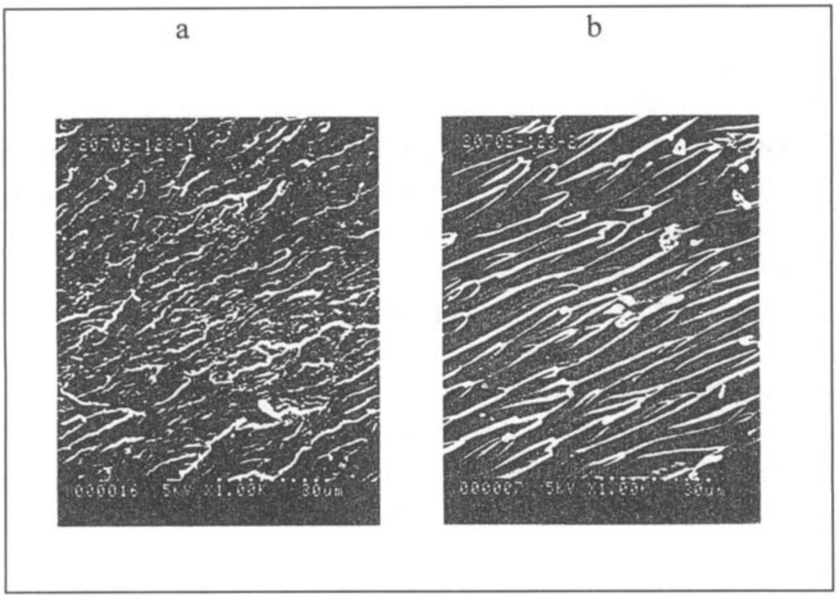
The fracture toughness increase due to nematic morphology can be explained as follows. The difference in fracture surfaces revealed by electron micrographs (fig.3) shows that nematic material has a rough fracture surface while isotropic material has a smooth, mirror-like fracture surface typical for highly crosslinked thermosets. The microstructure of the isotropic material is homogeneous with properties equivalent in all directions which results in straight, undeviating manner of crack propagation. The nematic material consists of anisotropic domains with properties, such as strength, different along and across their molecular orientations. This results in deviating the crack propagation from a straight line. This suggests that the inhomogeneity and localized anisotropy of nematic texture is the main reason for fracture toughness increase in the nematic material.

The flexural modulus of both isotropic and nematic specimens are relatively low (330 ksi). The possible explanation is that one of the major factors responsible for the elastic modulus of thermoset systems, the degree of intermolecular packing, is suppressed due to the rod-like nature of the components of the system. On the other hand, unlike the traditional flexible chain thermosets, for which lower modulus are usually associated with increase in coefficient of thermal expansion (CTE), in the case of rod-like thermoset system, CTE ($50*10^{-6}/°C$) does not increase compared to traditional high modulus thermoset materials. Therefore, the product of modulus and CTE is significantly less for rod-like thermosets than for traditional flexible chain thermosets. This makes rod-like thermosets very attractive for low stress electronics packaging applications.

TABLE 2 Physical properties of DIF-NA2 system cured in liquid crystalline (LC) or isotropic structure (ISO).

Structure	Strength Ksi	Strain %	Modulus Ksi	Tg ^{o}C	CTE $10^{-6}/^{o}C$	Kq psi* $in^{1/2}$
LC	15.8	8.0	334	230	50	1200
ISO	16.2	8.3	328	225	60	780

FIGURE 3 Fracture surface of DIF-NA2 system. a): liquid crystalline sample; b): isotropic sample.



MECHANISM OF CROSSLINKING OF THE LIQUID CRYSTALLINE PHASE

In order to evaluate the effect of the nature of the rigid block of the epoxy monomer and the role played by the curing agent on the mechanism of curing, the epoxy resins above described were separately cured with several curing agents (Table 3)

TABLE 3 Structural characteristics of the networks obtained by curing rigid rod epoxy monomers with several curing agents.

SYSTEM	Tcure (°C)	Structure	Tg (°C)
EF3-NA2	170	LC	220
DIF-NA2	130	LC	230
DOMS-DAF	107	LC	138
DIF-DAF	150	LC	219
NAFT-DAF	150	ISO	190
PHBHQ-DAF	120	LC	174
EPBN-DDS	250	LC	254
CHALC-DAT	160	ISO	122
DIFHB-DAT	150	LC	178
PHBHQ-tCN	95	LC	118
DIF-DB	180	LC	140

In all the cases but samples NAFT-DAF and CHALC-DAT the materials develop a liquid crystalline structure upon curing .

In the case of CHALC curing with DAT was performed at 160°C: during heat treatment, the epoxy molecule can be decomposed due to the crosslinking of the double bond. This reaction can increase the extent of crosslinking of the product while the liquid crystalline character of the cured resin is lost because the reaction destroys the rigid block in the epoxy monomer[19].

The mechanism of isotropic-nematic transition for the curing thermosets can be attributed to the development of weak interactions which contribute to the stabilization of the nematic phase. At a given temperature, the mixture of epoxy resin and curing agent can be in an isotropic state. Upon reaction of primary reactive hydrogen of amine groups, the effective axial ratio of the rigid blocks does not substantially change. What changes upon reaction is the molecular weight of the compound containing the mesogenic group, as shown by gel permeation cromatography experiments [5]. In fact two or more epoxy terminated rigid blocks can be linked together by the curing agent. At this extent of the curing reaction, the resulting growing prepolymer exhibits a nematic phase at the reaction temperature.

As a matter of fact, like in the case of many thermotropic polymers, the liquid crystalline structure coexists with an amorphous isotropic state, leading to a biphasic system. Also in this case a nematic phase can be surrounded by regions in which the polymer is arranged in an isotropic structure.

At this stage of the reaction the polymer is not yet crosslinked and by post-heating to higher temperature it can become isotropic again and, when cooled, it returns to the nematic state. By continuing cure in the nematic state, the development of permanent linkages due to the reaction of secondary reactive groups stabilizes the nematic phase further to the point that it cannot be destroyed by heating. The thermal characterization of the curing reaction for these systems reveals an unusual behaviour [21, 22]. The kynetic analysis of the curing reaction performed on DSC and Infra-red spectroscopy data for one of these systems confirmed a biphasic curing mechanism: in the first stage, the addition of the primary amine to the epoxy group is responsible for the increase in molecular weight; then the chain extension allows the isotropic to nematic phase transition of the growing prepolymer. Finally, the further addition of the secondary amine proceeds quickly [22].

When systems are cured at temperatures higher than the isotropization temperature of the growing prepolymer, the crosslinking takes place before the chain extension has been developed enough to stabilize the nematic structure and the system cures in the isotropic state. This is what happens when the compounds DIF and NA2 react at 150°C .

However another parameter should be considered during the cure of the thermoset in the ordered structure. This is the nematogenic character of the epoxy monomer. If the rigid block is not long enough, it will be crosslinked only in the isotropic structure. This happens in the case of NAFT. Table I reports the length of the rigid part for different epoxy compounds in the more extended conformation. While for all the other compounds the stiff blocks have a length comprised between 7 and 13.5 Å, in the case of NAFT it is too short (4.7 Å) to allow a stable nematic phase.

The curing agent seems to hold a less crucial role in developing a liquid crystalline structure network. In order to evaluate this effect different nematogenic epoxy compounds were separately cured with different curing agents having different degrees of flexibility. In all the cases the obtained network has nematic structure. This holds true if the curing agent is flexible (BA, tCN), rigid (NA2, DAF, DAT) or kinked (DDS). In every case the micro Brownian motions of the chains can allow the mesogenic groups to lie with their major axes roughly parallel, thus developing a liquid crystalline structure.

CONCLUSIONS

New epoxy resins can be cured in a liquid crystalline structure. By epoxy endcapping nematogenic dihydroxy terminated molecules it is possible to obtain a reactive substance that can subsequently be cured in a nematic state. The liquid crystalline phase develops during the first step of gelation and is subsequently maintained during the post curing.

The greatest difference between the isotropic and the liquid crystalline network regards the fracture toughness. The nematic thermoset is largely tougher than the isotropic one. The curing agent seems to be less important for the state of order of the network. A flexible, rigid or kinked curing agent can allow the rigid block to arrange in a nematic phase. The main role in the development of a liquid crystalline structure during the curing process is played by the nematogenic character of the epoxy monomer. From the practical point of view, the major difference in processing conditions which results in nematic or isotropic structure of the cured product is a "hold" at a certain temperature below the isotropization temperature of the prepolymer. The minimum hold time depends on the selected temperature. If the curing process contains such a "hold", the system develops a liquid crystalline structure which does not disappear at high temperatures.

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