

'Liquid crystalline' thermosets (LCT) from diaromatic diepoxides and aromatic diamines

Werner Mormann* and Markus Bröcher

Universität Siegen, Fachbereich 8, Laboratorium für Makromolekulare Chemie,
 Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany
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Two diaromatic diepoxides 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**) and 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**) have been synthesized and their mesogenic properties have been studied. **1** and **2** were reacted with 4,4'-diaminobiphenyl (**3**), 4-aminophenyl-4-amino benzoate (**4**), 4,4'-diaminodiphenylmethane (**5**), and 2,4-diaminotoluene (**6**) to investigate the formation of anisotropic networks and to prove the results obtained with model compounds. The influence of the mesogenic properties of epoxides and diamines, the type of oligomers formed, curing temperature, vitrification and annealing at constant conversion on the formation of a liquid crystalline network was studied. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In the foregoing paper we reported the results of a study of adducts from mesogenic monoepoxides and diamines as model compounds for the chain extended and branched intermediates (cross-link sites) formed in the amine curing of epoxides¹. All epoxy/amine-adducts had higher clearing points than the original epoxy/amine mixtures, though with one exception only monotropic mesophases were observed. The order of the clearing points for a given epoxide/amine combination was $\text{symm. } 2:1 > 4:1 > 1:1 \approx 3:1 > \text{unsymm. } 2:1$. The high melting points of several of the adducts, however, indicated that eutectoid behavior and miscibility of different oligomers formed in the initial states of the reaction are necessary for the appearance of a liquid crystalline phase.

The results from the study with model compounds led us to understand the phase behaviour reported on amine cured 4,4'-bis(2,3-epoxypropoxy)biphenyl². To further prove the utility of the model approach and its applicability to monomers with similar structural features we chose 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**) and 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**) as diepoxides. They were cured with different diamines to investigate the conditions under which liquid crystal thermosets can be obtained and to correlate these with the structure of the intermediates formed in the curing process.

In this paper we describe the results obtained in the reaction of 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**) and 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**) with 4,4'-diaminobiphenyl (**3**), 4-aminophenyl-4-amino benzoate (**4**), 4,4'-diaminodiphenylmethane (**5**), and 2,4-diaminotoluene (**6**).

EXPERIMENTAL

Materials

4-Aminophenyl-4-aminobenzoate (**4**) and 4,4'-diaminodiphenylmethane (**5**) were a gift from Bayer, 2,4-diaminotoluene (**6**) was purchased from Aldrich, 4,4'-diaminobiphenyl (**3**)³ was synthesized from hydrazobenzene (Fluka). 4-Hydroxyphenyl-4-hydroxybenzoate was synthesized from hydroquinone and 4-hydroxybenzoic acid⁴.

Methods of characterization

Infrared spectra: Bruker IFS48-FTi.r. spectrometer as films between NaCl plates. High temperature FTi.r. measurements: Bruker hot stage with a Eurotherm A599 processing unit; n.m.r. spectra: Bruker AC-200 using DMSO-[D₆] or deuteriochloroform with TMS as internal standard. Polarized light microscopy: Nikon Optiphot 2 polarizing microscope, Mettler FP 82 hot stage, FP 80 processing unit and Nikon F-601 M camera; d.s.c.: Mettler DSC30 TC 11/TC 15-system (heating rate was 10 K/min), nitrogen as purge gas; h.p.l.c.: gradient system with two Waters M45 pumps, dynamic ERC mixing unit, a Rp Kromasil C 18 column (10 μm, 250 × 4 mm) from MZ-Analysentechnik (Mainz), and a Pye Unicam UV-detector PU 4021 (260–275 nm). Tetrahydrofuran and water were used as mobile phase, delay volume was 2.76 ml, and dead volume was 1.76 ml. The flow rate was 1 ml/min. System control and data treatment were carried out with the chromatography-software EZ-Chrom V. 6.5 from Scientific Software Inc. (San Ramon). Elemental analyses were made by Beller, Göttingen.

Synthesis of 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**)⁵

A 500 ml two-necked-flask was charged with 36.31 g (0.157 mol) of the bisphenol, 290 g (3.14 mol) epichlorohydrin and 0.74 g (3.22 mmol) benzyltrimethyl

* To whom correspondence should be addressed

ammonium bromide. While stirring the mixture was refluxed for 120 min. Then 12.56 g (0.314 mol) sodium hydroxide were added as a 15 wt% aqueous solution. The mixture was allowed to cool to 60°C and stirred for 1.5 h. The volatiles were removed *in vacuo* and the residue was stirred with methanol and water and dried *in vacuo* (83%).

¹H n.m.r. (CDCl₃), δ (ppm) 2.83–3.42 (3 m, 6H), 3.98, 4.24 (2 dd, ³J = 11.7 Hz, ²J = 6.7 Hz, ²J = 3.3 Hz, 4H), 6.91, 7.13, 8.18 (m, 8H); ¹³C n.m.r., δ (ppm) 144.5, 44.6, 49.9, 50.1 (oxirane), 68.9, 69.3 (methylene-C), 114.4, 115.4, 122.6, 132.2 (tert. C), 122.4, 144.9, 156.2, 162.7 (quart. C), 165.0 (C=O); T_m: 119°C; FT i.r. (cm⁻¹) 1732 (C=O), 1512 (CH₂), 911 (oxirane).

Preparation of samples for the study of thermoset networks

The diamine and the diepoxide were dissolved in anhydrous dioxane in a molar ratio of 2:1 (total content of solids approximately 2 wt %). These mixtures were freeze dried and the resulting powder was used for microscopy and thermal analysis. Investigation of the curing reaction with isothermal differential scanning calorimetry was made without waiting for temperature equilibration in the d.s.c. cell.

RESULTS AND DISCUSSION

Monomers

4-(2,3-Epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**) was synthesized from 4-hydroxyphenyl-4-hydroxybenzoate and epichlorohydrine according to a modified literature procedure⁵. The synthesis of 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**) has been described in a previous paper⁵. The diepoxides were characterized by i.r., n.m.r.-spectroscopy, and elemental analysis; h.p.l.c. proved them to be free from oligomers.

The diamines used in this study were 4,4'-diamino-biphenyl (**3**), 4-aminophenyl-4-aminobenzoate (**4**), 4,4'-diaminodiphenylmethane (**5**) and 2,4-diaminotoluene (**6**). **3** was synthesized from hydrazobenzene³, **4** and **5** were a gift from Bayer while **6** is commercially available. The structural formulae and the thermal properties of all monomers used are shown in Table 1.

Investigation of the mesophase behavior of the diepoxides by thermal analysis and polarized light microscopy proved a monotropic nematic phase for both. **1** melts at 119°C with an isotropization temperature of 92°C while **2** has a melting point of 130°C and a clearing point only 2°C lower at 128°C. For comparison virtual clearing points are also given for the diamines used in this study². They give an estimate of the mesogenic potential of the diamines. **3** and **4** have virtual clearing points of approximately 20 and 50°C respectively while the values of **5** and **6** (in the range of -150°C) just indicate that these diamines have no tendency to form a liquid crystal phase.

Networks from 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**)

Amine cured epoxy thermosets were made from **1** with the diamines **3**, **4**, **5** and **6**. Mixtures of diepoxide and diamines were prepared by dissolving the epoxide and the appropriate amine in a molar ratio (epoxide/amine) of 2:1 in 1,4-dioxane (total solids content approximately 2%) and freeze drying to obtain homogeneous mixing on a molecular level. These mixtures were cured with a heating rate of 10 K/min and isothermally at different temperatures. Curing was followed by d.s.c., polarized light microscopy, and in some cases by infrared spectroscopy. The epoxy resins are named by the number of the epoxide followed by that of the diamine. If required for clarity the curing temperature is also given.

The dynamic d.s.c.-scans of the systems **1/3** to **1/6** are

Table 1 Thermal properties of monomers **1**–**6**

No.	Structural formula	Thermal properties	
1		T _m 119°C	(n T _i 92°C)
2		T _m 130°C	(n T _i 128°C)
3		T _m 127°C	(n T _i ^a 16.5°C)
4		T _m 187°C	(n T _i ^a 53.5°C)
5		T _m 90°C	(n T _i ^a ≈ -150°C)
6		T _m 99°C	(n T _i ^a ≈ -150°C)

^a Obtained from extrapolation

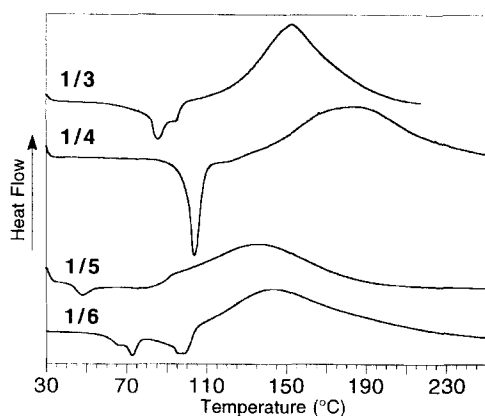


Figure 1 D.s.c.-traces of **1** cured with amines **3**, **4**, **5**, and **6**

given in Figure 1. They show first that the mixtures of **1** with the amines **3**, **5**, or **6** give multiple melting points of an amine rich and an epoxide rich phase. **1/4** has a single melting point probably because of the structural similarity of epoxide and amine. The exothermal curing reaction starts above the higher melting endotherm of the mixtures. Microscopic observation, however, proved that the reaction begins already above the first endotherm leaving crystalline material if the mixture has not been heated to a completely molten state. Isothermal curing, therefore, was performed above 120 or 130°C to ensure a homogeneous melt. The results of the dynamic and isothermal cure of the different combinations of **1** and the diamines **3–6** are summarized in Table 2.

In the series **1/n** only **1/3** gave an LCT on isothermal curing up to 180°C curing temperature. This mixture also gave an LCT upon heating at 10 K/min. The other diamines gave isotropic thermosets in both heating modes.

The reaction enthalpies per mol oxirane vary from 73 to 97 kJ/mol. This broad range is due to a superposition of the reaction exotherm and the melting endotherm. Vitrification occurs in the series **1/3** bringing the reaction to an end. Increasing the temperature will restart the reaction which is documented by an exotherm in a dynamic d.s.c. scan of an isothermally cured sample. The glass transition temperatures of fully cured thermosets from **1** and the different amines could not be detected from d.s.c.

Isothermal d.s.c.-traces of **1/3** are shown in Figure 2. There is an additional increase in heat evolution after a certain time corresponding to an increase in reaction rate. The time after which this occurs corresponds well to

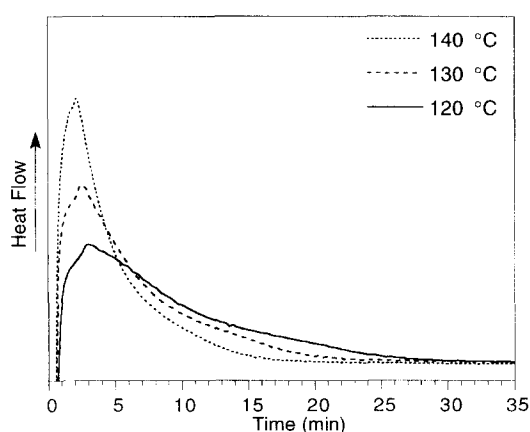


Figure 2 D.s.c.-traces of **1/3** from isothermal curing at different temperatures

the isotropic–nematic transition of the melt under the microscope. Obviously the higher order in the nematic phase with respect to the isotropic melt brings the reacting groups in a more favorable position which accelerates the addition of the oxirane to the amine. Conversion at the isotropic–nematic transitions has been calculated for the different temperatures from d.s.c. It increases with temperature from 8% at 120°C to 14% at 130°C and 19% at 140°C. This is to be expected as the clearing point increases with conversion¹ which has to be higher at higher temperature.

In isothermal curing experiments starting from an isotropic phase LCT are formed when the clearing point of the mixture reaches and exceeds the curing temperature. A different approach is to cure at a lower temperature until the liquid crystal phase is formed and to complete curing by increasing the temperature at a rate such that no isotropization occurs. This method was applied for the curing of **1** with the diamines **4–6**. The temperature programs and the results are summarized in Table 3.

The minimum curing temperature is determined by crystallization of monomers or oligomers from the reaction mixture. From Table 3, it follows that the mesogenic properties of the diamine also play an important role. Thus with **1/4** LCT are obtained at 90°C, while 65°C is required for **1/5** and **1/6**. In the latter case crystallization together with the appearance of a nematic phase at this temperature prevents formation of a homogeneous LCT.

Phase separation also occurs with **1/4** on curing at 90°C, this time, however, two liquid crystal phases are formed.

Table 2 Curing of 4-(2,3-epoxypropoxy)phenyl-4'-(2,3-epoxypropoxy)-benzoate (**1**) with diamines **3–6**

Epoxide/amine	T_{cure} (°C)	Conv. i/n (%)	t_{max} (min)	ΔH (kJ/mol)	$\Delta H_{\text{res.}}$ (kJ/mol)	T_g (°C)	Network properties
1/3	(T_{max}) 153	—	—	81	—	—	i → n LCT
	120	8	3.12	83	9	140	i → n LCT
	130	14	2.50	83	8	152	i → n LCT
	140	19	2.19	83	2	157	i → n LCT
	< 180	—	—	—	—	—	i → n LCT
1/4	(T_{max}) 184	—	—	97	—	154	i
	> 130	—	—	—	—	—	i
1/5	(T_{max}) 137	—	—	73	—	147	i
	> 120	—	—	—	—	—	i
1/6	(T_{max}) 145	—	—	82	—	—	i
	> 130	—	1.59	69	10	139	i

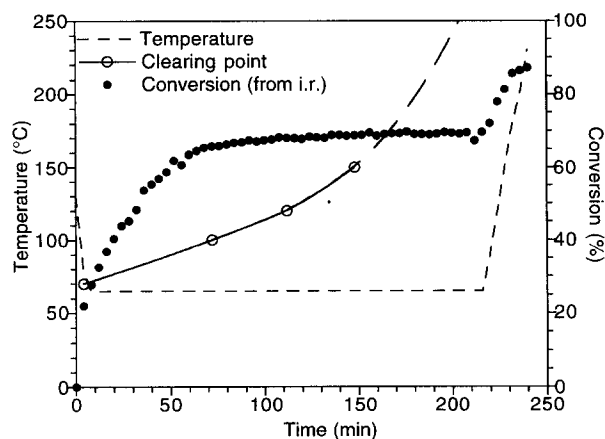
Conv. i/n: conversion at isotropic–nematic phase transition; T_{max} : from dynamic scan (heating rate 10 K/min); $\Delta H_{\text{res.}}$: additional heat of reaction from second heating to 280°C

Table 3 Curing of **1** with diamines **4–6** by using special temperature cycles

Epoxide/ amine	T (°C)	t (min)	Phase behavior	Morphology
1/4	130	0.5	i	Homogeneous melt;
	90	60	$i \rightarrow n$	Phase separation in the nematic state;
	150	15	n	No clearing till decomposition
1/5	130	0.5	i	Homogeneous melt;
	65	210	$i \rightarrow n$	cf. Table 4
	280 ^a		n	cf. Table 4
1/6	110	2	i	Homogeneous melt;
	65		$n + \text{cryst.}$	Nematic phase + crystallization during reaction

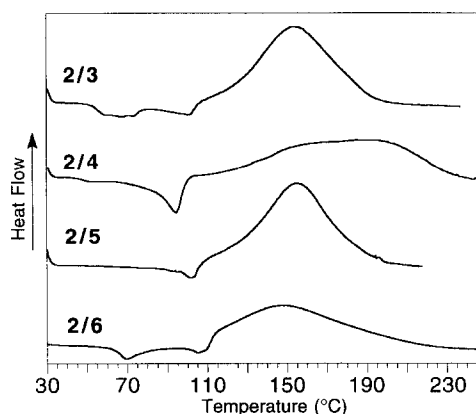
^a Dynamic heating at 10 K/min**Table 4** Curing conditions, conversion, and phase behavior during isothermal reaction of **1/5** at 65°C

Epoxide/amine	$t_{\text{iso, 65°C/min}}$	ΔH^a (kJ/mol)	Conversion (%) d.s.c. (i.r.)	T_g^b (T_g^a) (°C)	T_i^a (°C)
1/5	0	—	— (22)	—	70
	70	23.45	68 (66)	149 (74)	100
	100	23.57	68 (67)	150 (81)	120
	150	22.08	69 (69)	149 (84)	150
	210	24.50	66 (69)	145 (86)	> 330 dec.

^a From first heating after isothermal curing^b Fully cured sample, T_g from second heating after isothermal curing**Figure 3** Cure temperature, conversion and clearing point of **1/5** as a function of time

Nematic droplets and spots appear first, surrounded by isotropic domains, which later also become nematic. On heating, nematic domains which have been formed first have a higher clearing point and can be less easily sheared than those formed in a later stage of curing. A two-phase nematic morphology is finally obtained. These results are in agreement with observations reported by Kirchmeyer *et al.*⁷. It is the subject of an ongoing investigation whether this morphology or just the presence of a liquid crystal phase is responsible for the increased fracture toughness of a LCT as compared to an isotropic thermoset with identical chemical composition.

Combination **1/5** was cured at 65°C and the clearing point of the mixture was measured as a function of time and conversion. Conversion was obtained from residual heat in a dynamic d.s.c.-scan and from i.r.-spectroscopy. The results are shown in Table 4 and Figure 3. After melting at 130°C and cooling to 65°C, a nematic phase appears, the clearing

**Figure 4** D.s.c.-traces of **2** cured with amines **3, 4, 5, and 6**

point increases to 100°C in 70 min while conversion goes from 22 to 66%. Vitrification takes place and conversion goes to 69% during the next 80 min while the clearing point increases to 150°C in this period. After three and a half hours of isothermal curing, no isotropic phase can be obtained on heating. This can be explained with a further increase of the clearing point as a result of annealing; another reason is that the fast reaction taking place as temperature exceeds vitrification temperature chemically fixes the mesophase before isotropization can occur. The great stabilization of a mesophase during network built up, however, was achieved to a large extent at constant conversion.

Networks from 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**)

Network formation from **2** and diamines **3–6** was studied essentially in the same way as described above for **1**. Homogeneous melts could be obtained only above 135°C, due to the higher melting point of **2**. The dynamic

Table 5 Curing of 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**) with diamines **3–6**

Epoxide/amine	T_{cure} (°C)	Conv. i/n (%)	t_{max} (min)	ΔH^a (kJ/mol)	ΔH_{res} (kJ/mol)	T_g^a (°C)	T_g^b (°C)	Network properties
2/3	(T_{max}) 154	—	—	88	—	—	—	i → n LCT
	135	11	3.25	87	8	154	204	i → n LCT
	140	10	2.24	85	6	180	178	i → n LCT
	160	—	1.25	85	2	195	—	i → n LCT
	< 170	—	—	—	—	—	—	i → n LCT
2/4	(T_{max}) 194	—	—	80	—	—	—	i → n LCT
	140	—	1.65	76	10	162	200	i → n LCT
	150	—	1.22	78	7	166	193	i → n/i
	160	—	0.77	81	5	181	196	i
	130–145	—	—	—	—	—	—	i → n LCT
	145–160	—	—	—	—	—	—	i → n/i
	> 160	—	—	—	—	—	—	i
2/5	(T_{max}) 155	—	—	92	—	—	—	i
	> 100	—	—	—	—	—	—	i
2/6	(T_{max}) 148	—	—	69	—	—	—	i
	> 130	—	1.72	61	10	161	—	i

T_{max} : from dynamic scan; Conv. i/n: conversion at isotropic–nematic phase transition

^a From first heating after isothermal curing

^b Fully cured sample. T_g from second heating after isothermal curing

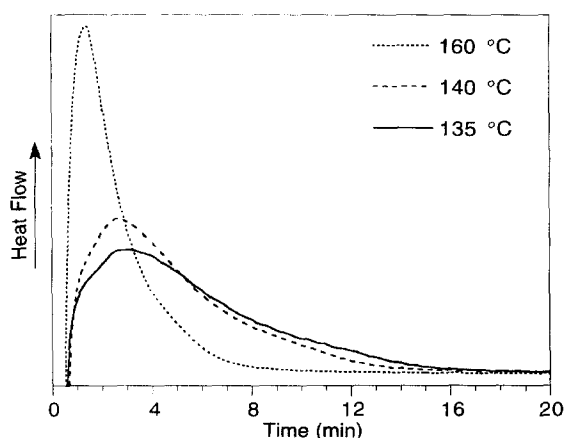


Figure 5 D.s.c.-traces of **2/3** from isothermal curing at different temperatures

d.s.c.-scans of the combinations **2/3** to **2/6** are shown in *Figure 4*. They are similar to those of the **1**-series with a shift of the melting endotherms towards higher temperature. These results together with those of the isothermal curing experiments obtained from thermal analysis and polarized light microscopy are reported in *Table 5*. In this series the final glass transition temperatures of **2/3** and **2/4** could be detected in the d.s.c., and are approximately 200°C for both. The reaction enthalpies are comparable to the series with **1** as epoxide.

LCT were obtained in dynamic curing from **2/3** and **2/4**. This seems to be due to the higher clearing point of **2** in comparison with **1**. Both combinations also gave LCT on isothermal curing above 135°C, while **2/5** and **2/6** again resulted in isotropic networks in both curing modes. The isothermal d.s.c.-scans of **2/3** are shown in *Figure 5*.

An interesting feature is the upper temperature limit of the range in which LCT are formed. This is lower for **2** (<170°C for **2/3**) than with **1** (<180°C for **1/3**); it is lower than 160°C for **2/4** while no LCT were obtained in dynamic or isothermal curing in **1/4**. Above these temperatures,

biphasic nematic–isotropic networks are formed while at even higher temperatures isotropic thermosets are obtained. This difference in mesophase stability must be due to different oligomer distributions with both epoxides probably resulting from a difference in reactivity of the two glycidyl groups. Reaction of the azomethine moiety with the oxirane ring should not be responsible as no such products were found in the reaction of phenyl glycidyl ether and benzylidene aniline.

Experiments to obtain LCT from **2/5** and **2/6** on curing at lower temperatures as described for **1/5** failed because crystallization from the melt occurred already at 95°C.

The results reported above can be generalized as follows: The mesogenic properties of epoxide and amine govern those of the intermediates formed and the mesophase of the final thermoset. The structure of these intermediates and the distribution of different intermediates in the reaction mixture are even more important. Chain extension to linear oligomers is favoured with diamines having two equally reactive amino groups (**3**). This leads to better mesophase stabilization because of the aspect ratio and, in addition, because of the polymer effect, i.e. increase of isotropization temperature with increasing degree of polymerization. This explains why LCT from **3** are accessible over a wider temperature range than from **4**. A pronounced kinetic effect on the stability of a mesophase (clearing point) has been observed with **1/4** on isothermal curing. Conversion is almost constant due to vitrification, while the clearing point increases by more than 100°C during this annealing process. After a certain period of time no isotropization occurs, as the mixture is heated, because the crosslinking reaction and irreversible chemical trapping of the mesophase proceeds faster than isotropization.

CONCLUSIONS

The curing of 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate (**1**) and 4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline (**2**) with four different diamines has been studied. Nematic LCT were obtained

with mesogenic aromatic diamines 4,4'-diaminobiphenyl (**3**) and 4-aminophenyl-4-aminobenzoate (**4**) while no mesophase formation occurred with 4,4'-diaminodiphenylmethane (**5**), and 2,4-diaminotoluene (**6**). Curing of a supercooled melt at a temperature where a mesophase is formed before crosslinking proceeds to an extent where formation of a mesophase is no longer possible, could be used to obtain LCT from **1/5**. Thus it is possible to make a nematic and an isotropic thermoset with identical chemical composition. A two-phase morphology was formed from the system **1/4**, which will be investigated for its capability in increasing fracture toughness.

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