

Liquid crystalline thermosets (LCT) from diaromatic mesogenic diepoxides and aromatic diamines: synthesis and phase behaviour of model compounds and intermediate structures

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Two mesogenic monoepoxides, nematogenic 4-(2,3-epoxypropoxy)-4'-ethoxy-biphenyl (**1**) and smectic-A 4-butoxyphenyl-4-(2,3-epoxypropoxy)-benzoate (**2**) were synthesized and reacted with 4,4'-diaminobiphenyl (**3**), or 4-aminophenyl-4-aminobenzoate (**4**) to obtain model compounds for the chain extended and branched intermediates (cross-link sites) formed in the amine curing of epoxides. All epoxy/amine-adducts have higher clearing points than the original epoxide/amine mixtures, though with one exception only monotropic mesophases were observed. The order of the clearing points for a given epoxide/amine combination is symm. 2:1 > 4:1 > 1:1 ≈ 3:1 > non symm. 2:1. The type of mesophase of the adducts is that of the monoepoxide used except for the 1:1 adduct of smectic **2** and **4**, where a nematic phase was obtained. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Networks with a chemically fixed liquid crystalline organization have been studied for various reasons^{1,2}. Epoxy/amine networks are among the most intensely investigated LCTs in academic and industrial research^{3–10}. Monomers used were α -methylstilbene derived diepoxides and dimesogenic diepoxides⁶, 4-(2,3-epoxypropoxy)-phenyl-4-(2,3-epoxypropoxy)-benzoate³ and 4,4'-bis(2,3-epoxypropoxy)-biphenyl^{7,10}.

The influence of the mesogenic properties of either the epoxide or the amine on the conditions under which LCT can be obtained has not been studied to our knowledge. A number of epoxide amine reaction products of various stoichiometric ratios are formed in the course of a network built up in an amine cured epoxy resin. The mesogenic properties of these chain-extended or branched oligomers which constitute the cross-link sites in the final network, i.e. the influence of the cross-linking reaction on the mesogenic properties of the reacting mixture, has not been investigated. Knowledge of these relations will allow the selection of temperature profiles for curing by which either liquid crystalline or isotropic networks can be obtained.

A useful approach to close this gap is to study the epoxy/amine reaction with model compounds, e.g. of mesogenic monoepoxides with diamines. The other alternative, diepoxides and monoamines, is less suitable because linear polymers with pendant side groups are formed. This structure is not very likely to be present during network formation and absent in the cured networks. 4-Alkoxy-4'-hydroxy biphenyls and alkoxy-hydroxy phenyl benzoates can be easily obtained in laboratory quantities and converted to the corresponding monoepoxides. These

materials are suitable models for monomers and for model reactions of amine cured epoxies. Variation of the diamines, in addition, allows the study of the influence of the amine structure on the mesogenic properties of the epoxy/amine network.

In this paper, we describe the results obtained from the reaction of 4-(2,3-epoxypropoxy)-4'-ethoxy-biphenyl and 4-butoxyphenyl-4-(2,3-epoxypropoxy)-benzoate with 4,4'-diaminobiphenyl, and 4-aminophenyl-4-aminobenzoate.

EXPERIMENTAL

Materials

Bis-(4-hydroxy)-biphenyl and 4-aminophenyl-4-amino benzoate were gifts from the Bayer AG, 4,4'-diaminobiphenyl¹¹ was synthesized from hydrazobenzene (Fluka). Silica gel 60 (Merck) was used as stationary phase for flash chromatography.

Methods of characterization

Infrared spectra: Bruker IFS48-FTi.r. spectrometer, as films between NaCl plates. 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 DSC/30 TC 11/TC 15-system (heating rate was 10 K min⁻¹), 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 μ m, 250 \times 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

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1 ml min⁻¹. System control and data treatment was carried out with the chromatography-software EZ-Chrom V. 6.5 from Scientific Software Inc. (San Ramon). Elemental analyses were made by Beller, Göttingen.

Monomer synthesis

4-Ethoxy-4'-hydroxybiphenyl (1p). In a 1000 ml three-necked flask with a KPG-stirrer 75 g (0.403 mol) 4,4'-dihydroxy biphenyl was dissolved in 400 ml of aqueous sodium hydroxide (10 wt%). In an argon atmosphere 61.36 g (0.398 mol) diethyl sulfate was added over a period of 1 h to the stirred mixture. The precipitate formed was filtered off and treated with 400 ml of aqueous sodium hydroxide (10 wt%), the residual solid was isolated, dissolved in 5 wt% aqueous potassium hydroxide and the insoluble part was removed by filtration. The filtrate was acidified with aqueous hydrochloric acid, the precipitate collected in a Büchner funnel and dried. Yield was 50%.

¹H n.m.r. (DMSO-[D₆]), δ (ppm) 1.31 (t, 3 H), 4.03 (q, 2 H), 6.72–7.39 (m, 8 H), 9.42 (s, 1 H); ¹³C n.m.r., δ (ppm) 14.7, 63.0, 114.7, 115.7, 127.0, 127.2, 130.8, 132.8, 156.4, 157.6; T_m: 166°C; FT i.r. (cm⁻¹) 3334 (OH); elemental analysis, C₁₄H₁₄O₂ (214.26), calc. (found), C 78.5 (78.3), H 6.6 (6.5).

4-butoxyphenyl-4-hydroxybenzoate (2p). A 250 ml three-necked flask with Dean-Stark-trap, condenser and stirring bar was charged with 15.24 g (91.7 mmol) 4-butoxyphenol, 11.4 g (82.6 mmol) 4-hydroxybenzoic acid and 45 ml benzene. One drop of sulfuric acid was added as catalyst. The mixture was heated to reflux until no more water was collected. After cooling to room temperature the crude product was filtered off and recrystallized from water/acetone (v/v = 2/1). Yield was 75%.

¹H n.m.r. (DMSO-[D₆]), δ (ppm) 0.92 (t, 3 H), 1.44 (m, 2 H), 1.69 (m, 2 H), 3.95 (t, 2 H), 6.92 (m, 4 H), 7.13 (m, 2 H), 7.93 (m, 2 H), 10.49 (s, 1 H); ¹³C n.m.r., δ (ppm) 13.87, 18.93, 30.93, 67.69, 115.09, 115.73, 119.68, 122.91, 132.30, 144.20, 156.44, 162.75, 164.81; T_m: 158°C; FT i.r. (cm⁻¹) 3382 (OH), 1702 (C=O), 1608 (C=C); elemental analysis, C₁₇H₁₈O₄ (286.33), calc. (found), C 71.3 (71.1), H 6.3 (6.3).

4-(2,3-epoxypropoxy)-4'-ethoxy-biphenyl (1) and 4-butoxyphenyl-4-(2,3-epoxypropoxy)-benzoate (2). A

500 ml flask with reflux condenser and dropping funnel was charged with 0.1 mol of the phenol, 1 mol epichlorohydrine and 1.5 mol% of benzyltrimethyl ammonium bromide as a catalyst. The stirred mixture was heated to reflux for 40 min. Then 0.1 mol sodium hydroxide was added as a 15 wt% aqueous solution. The mixture was cooled to 60°C and stirred for an additional 1.5 h. Volatiles were removed under reduced pressure, the residue was stirred with methanol and water and dried in vacuo. The crude products were purified by distillation in a Kugelrohrapparatus. A 83% yield of **1** (75% of **2**) was obtained.

1: ¹H n.m.r. (CDCl₃), δ (ppm) 1.42 (t, 3 H), 2.74–2.93 (m, 2 H), 3.36 (m, 1 H), 3.93–4.28 (m, 4 H), 6.95 (m, 4 H), 7.49 (m, 4 H); ¹³C n.m.r., δ (ppm) 14.9, 44.7, 50.2, 63.5, 68.8, 114.7, 114.9, 127.7, 133.1, 134.1, 157.5, 158.1; T_m: 153°C; FT i.r. (cm⁻¹) 1608 (C=C), 914 (oxirane); elemental analysis, C₁₇H₁₈O₃ (270.14), calc. (found), C 75.5 (75.3), H 6.7 (6.7).

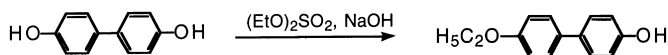
2: ¹H n.m.r. (CDCl₃), δ (ppm) 0.96 (t, 3 H), 1.47 (m, 2 H), 1.76 (m, 2 H), 2.74–2.93 (m, 2 H), 3.36 (m, 1 H), 3.97 (m, 3 H), 4.31 (m, 1 H), 6.88–7.10 (m, 6 H), 8.12 (d, 2 H); ¹³C n.m.r., δ (ppm) 13.8, 19.2, 31.3, 44.5, 49.8, 68.0, 68.8, 114.3, 115.0, 122.4, 122.5, 132.2, 144.3, 156.8, 162.6, 165.1; T_m: 94°C; FT i.r. (cm⁻¹) 1732 (C=O), 914 (oxirane); elemental analysis, C₂₀H₂₂O₅ (270.14), calc. (found), C 70.2 (69.4), H 6.5 (6.4).

Synthesis of model compounds

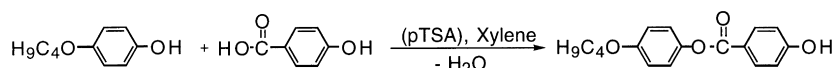
The model compounds were synthesized either in *o*-dichlorobenzene or without a solvent. The products were isolated by recrystallization, extraction or flash chromatography and characterized by n.m.r.-spectroscopy, i.r.-spectroscopy, and thermal analysis (d.s.c.). The ratio of starting materials, reaction conditions, method of isolation and the analytical properties of the model compounds are presented in Table 1.

Virtual clearing points (T_i^a)

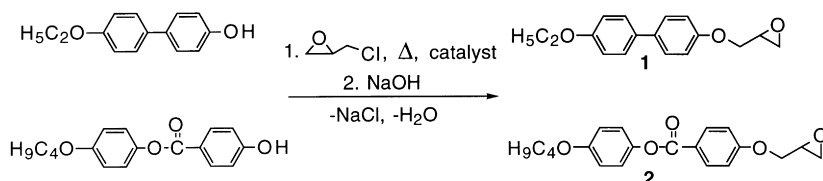
4-(2,3-Epoxypropoxy)-4'-ethoxy-biphenyl (**1**), reference methylhydroquinone-di-4-(2,3-epoxypropoxy)phenyl benzoate (T_m: 131°C, T_i: 223°C)¹⁰; model compound **134**, reference model compound **124**.



Scheme 1 Synthesis of 4-ethoxy-4'-hydroxybiphenyl (**1p**)



Scheme 2 Synthesis of 4-butoxyphenyl-4-hydroxybenzoate (**2p**)



Scheme 3 Synthesis of monoepoxides **1** and **2**

Table 1 Synthesis details and analytical properties of epoxy/amine model compounds

No.	Epoxy/amine educts (mol)	Reaction temp. (°C)	Reaction time (h)	Isolation, purification	yield (%)	¹ H-n.m.r., δ (ppm)
1₂3	2/1	150	1.75	Residue from treatment with THF	61	DMSO-[D ₆]: 1.32 (<i>t</i> , 6 H), 3.13, 3.23 (<i>m</i> , 2H), 4.04 (<i>m</i> , 10 H), 5.21 (<i>d</i> , 1.8 H), 5.58 (<i>t</i> , 1.4 H), 6.64 (<i>d</i> 4 H), 6.97 (<i>m</i> , 8 H), 7.26 (<i>d</i> , 4 H), 7.51 (<i>m</i> , 8 H)
1₄3	4/1 (DCB)	170	13.5	Residue from treatment with THF, recr. from xylene	25	DMSO-[D ₆]: 1.32 (<i>t</i> , 12 H), 3.38, 3.60, 4.03 (<i>m</i> , 28 H), 5.25 (<i>d</i> , 1.2 H), 5.40 (<i>d</i> , 1.4 H), 6.96, 7.48 (<i>m</i> , 40 H)
1₁4	1/1 (2/1)	160	0.3	Residue from treatment with THF, flash chrom. toluene/THF	17	CDCl ₃ : 1.38 (<i>t</i> , 3 H), 2.57 (<i>s</i> , 0.8 H), 3.36 (<i>m</i> , 2 H), 4.08 (<i>m</i> , 6 H), 4.26 (<i>m</i> , 1 H), 6.64–6.70 (<i>m</i> , 4 H), 6.90–7.02 (<i>m</i> , 6 H), 7.43–7.49 (<i>m</i> , 4 H), 7.97 (<i>d</i> , 2 H)
1₂4	2/1	160	0.3	Residue from treatment with THF, flash chrom. CHCl ₃ /THF	24	CDCl ₃ : 1.42 (<i>t</i> , 6 H), 3.27–4.33 (<i>m</i> , 17 H), 6.64–6.99 (<i>m</i> , 14 H), 7.42 (<i>m</i> , 8 H), 8.00 (<i>d</i> , 2 H)
1₃4	3/1	160	2	Treatment with acetone, CHCl ₃ , recr. from toluene	13	DMSO-[D ₆]: 1.32 (<i>t</i> , 9 H), 3.24–4.07 (<i>m</i> , 21 H), 5.24–5.41 (<i>m</i> , 4 H), 6.69–7.02 (<i>m</i> , 18 H), 7.45–7.54 (<i>m</i> , 12 H), 7.78–7.82 (<i>d</i> , 2 H)
1₄4	4/1	180	0.3	Residue from treatment with acetone	68	DMSO-[D ₆]: 1.28 (<i>t</i> , 12 H), 3.23–4.42 (<i>m</i> , 28 H), 5.20–5.61 (<i>m</i> , 3.11 H), 6.60–8.15 (<i>m</i> , 40 H)
2₂3	2/1	150	14.5	Residue from extr. with THF, CHCl ₃	61	DMSO-[D ₆]: 0.93 (<i>t</i> , 6 H), 1.42 (<i>m</i> , 4 H), 1.69 (<i>m</i> , 4 H), 3.17–3.25 (<i>m</i> , 4 H), 3.96 (<i>m</i> , 10 H), 5.31 (<i>s</i> , 1.21 H), 6.65 (<i>d</i> , 4 H), 6.96 (<i>d</i> , 4 H), 7.14 (<i>m</i> , 12 H), 8.05 (<i>d</i> , 4 H)
2₄3	4/1 (DCB)	150	2.5	Treatment with THF/H ₂ O isolated from org. layer	4	CDCl ₃ : 0.96 (<i>t</i> , 12 H), 1.43 (<i>m</i> , 8 H), 1.77 (<i>m</i> , 8 H), 3.60, 3.93, 4.29 (<i>m</i> , 28 H), 6.96 (<i>m</i> , 28 H), 7.44 (<i>m</i> , 4 H), 8.09 (<i>m</i> , 8 H)
2₁4	1/2 (DCB)	135	1	Treatment with EtOH/THF, flash chrom. THF/H ₂ O	35	DMSO-[D ₆]: 0.93 (<i>t</i> , 3 H), 1.43 (<i>m</i> , 2 H), 1.70 (<i>m</i> , 2 H), 3.17–3.25 (<i>m</i> , 2 H), 3.93–4.14 (<i>m</i> , 5 H), 5.31 (<i>d</i> , 1 H), 5.64 (<i>t</i> , 1 H), 6.1 (<i>s</i> , 2 H), 6.61–7.13 (<i>m</i> , 12 H), 7.74 (<i>d</i> , 2 H), 8.05 (<i>d</i> , 2 H)
2₂4	2/1	150	4.5	Residue from treatment with acetone	10	DMSO-[D ₆]: 0.93 (<i>t</i> , 6 H), 1.43 (<i>m</i> , 4 H), 1.69 (<i>m</i> , 4 H), 3.25 (<i>m</i> , 4 H), 4.05 (<i>m</i> , 10 H), 5.29, 5.37 (<i>m</i> , 2 H), 5.64 (<i>t</i> , 1 H), 6.65 (<i>m</i> , 4 H), 6.93 (<i>m</i> , 6 H), 7.31 (<i>m</i> , 8 H), 7.78 (<i>d</i> , 2 H), 8.05 (<i>d</i> , 4 H)
2₄4	4/1 (DCB)	150	21	Treatment with THF/H ₂ O isolated from org. layer after extr. with ether	8	CDCl ₃ : 0.91 (<i>t</i> , 12 H), 1.44 (<i>m</i> , 8 H), 1.75 (<i>m</i> , 8 H), 3.70, 3.91, 4.04 (<i>m</i> , 32 H), 6.85, 6.91 (<i>m</i> , 30 H), 8.08 (<i>m</i> , 10 H)

RESULTS AND DISCUSSION

Synthesis of monomers

4-(2,3-Epoxypropoxy)-4'-ethoxy-biphenyl (**1**) and 4-butoxyphenyl-4-(2,3-epoxypropoxy)-benzoate (**2**) were chosen as monoepoxides, because alkoxy groups are similar to the glycidyl moieties of the corresponding diepoxides. The phenols were synthesized as shown in *Schemes 1* and *2*. 4-Ethoxy-4'-hydroxybiphenyl (**1p**) was obtained from dihydroxy biphenyl and diethyl sulfate, while 4-butoxyphenyl-4-hydroxybenzoate (**2p**) was made by azeotropic esterification from 4-butoxyphenol and 4-hydroxybenzoic acid. This straightforward synthesis gave **2p** in 75% yield avoiding the tedious and less yield efficient five-step synthesis reported in the literature¹². The phenols were purified by recrystallization and characterized by i.r., n.m.r.-spectroscopy, and elemental analysis.

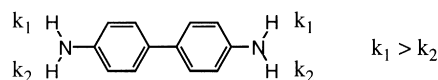
Epoxides **1** and **2** were obtained from the phenols by reaction with a tenfold excess of epichlorohydrine using benzyltrimethylammonium bromide as catalyst and conversion of the chlorohydrines into the epoxides with sodium hydroxide (*Scheme 3*). They were purified by recrystallization or short path distillation and characterized in the usual way.

The diamines used in this study were 4,4'-diaminobiphenyl (**3**), which was synthesized from hydrazobenzene¹¹ and 4-aminophenyl-4-aminobenzoate (**4**) which was a gift from Bayer.

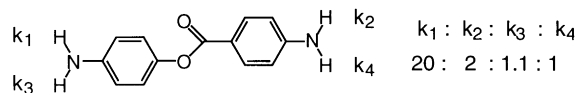
Synthesis of epoxy/amine addition model compounds

The reaction of a diepoxide with an aromatic diamine proceeds in steps. The first addition of an epoxide giving a secondary amine is faster than the second addition leading to a *tert* amine¹³. A symmetrical diamine with no steric or electronic interaction of the amino groups will form a 1:1

addition product, a symmetrical 2:1 addition product, one 3:1, and one 4:1 addition product.



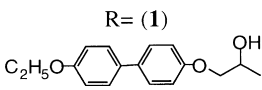
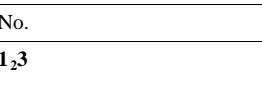





In non symmetrical diamines like **4**, the reactivities of the amino groups are unequal already for the first addition step. Kirchmeyer *et al.* studied the reaction of isomeric aminophenyl aminobenzoates with 2,3-epoxypropoxy benzene and reported the following order of reactivity of the amine hydrogens¹⁴. k_1 is 10 times the size of k_2 and 20 times larger than k_3 and k_4 . Hence, it is reasonable to expect one 1:1 adduct, two 2:1 adducts—a symmetrical N,N' -adduct and the non symmetrical N,N -adduct, one 3:1 and the 4:1 epoxy/amine adduct.

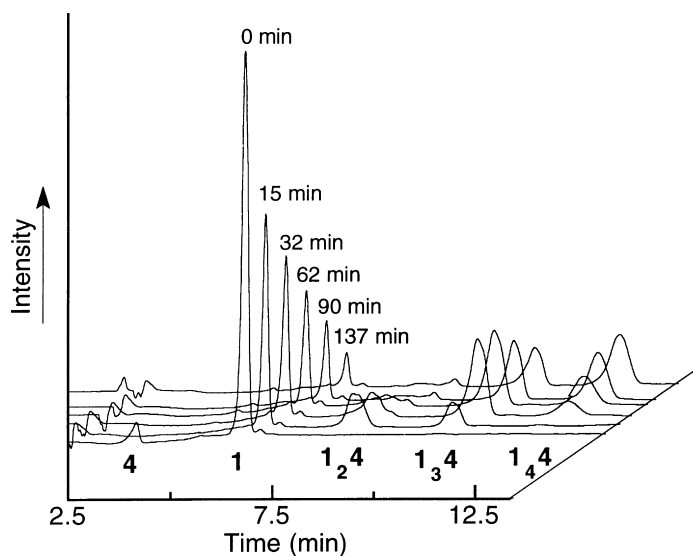


The structures of the model compounds one can expect from the two cases discussed are shown in *Table 2*. As a numbering system for the model compounds the number of the epoxide together with the stoichiometric coefficient followed by the number of the diamine will be used. Thus, **1₃4** means the 3:1 adduct of epoxide **1** and diamine **4**.

The model compounds were synthesized either in *o*-dichlorobenzene or without a solvent. The solvent

Table 2 Structures and thermal properties of epoxy/amine model compounds

No.	Phase transitions/°C	Structure	Phase transitions/°C	No.
1₂3	T_m 258 i		T_m 221 (s T_i 195)	2₂3
1₄3	T_m 200 i		T_m 171 (s T_i 166)	2₄3
1₁4	T_m 187 (n T_i 141)		T_m 182 (n T_i 145)	2₁4
1₂4	T_m 129 (n T_i 104)		—	—
—	—		T_m 239 (s T_i 211)	2₂4
1₃4	T_m 212 (n T_i^a 139)		—	—
1₄4	T_m 249 i		T_m 130 s T_i 162	2₄4

^aObtained from extrapolation**Figure 1** H.p.l.c.-chromatograms of a 4:1 reaction mixture of **1** and **4**, reaction at 170°C

proved to be useful, if one of the adducts crystallized from the reaction mixture. The ratio epoxide/amine was varied according to the compound to be obtained. Reactions were monitored by high-performance liquid chromatography; they were stopped after the concentration of the desired product had reached a maximum. Peak assignment first was made on the basis of the relative reaction rates, as discussed earlier, and verified by injection of isolated model compounds.

In *Figure 1* the h.p.l.c.-chromatograms of a 4:1 reaction

mixture of **1** and **4** are plotted at different times (stages) of curing. **1₁4** has the same elution volume as **1** and the symmetric and non symmetrical **1₂4** adducts cannot be distinguished. The amine has completely disappeared after 15 min, while 60% of **1** have reacted during that period. **1₂4** has maximum concentration at this time which implies that the concentration of **1₁4** is already declining. **1₂3** reaches maximum concentration after 45 min, while the concentration of **1₄3** is steadily increasing. Even after 2.5 h, a significant amount of the epoxide (**1**) is still left.

With diaminobiphenyl (**3**) and both **1** and **2**, the symmetric 2:1 and the 4:1 addition products could be isolated. The 2:1 adducts (**1₂3**, **2₂3**) were synthesized without solvent, the 4:1 products (**1₄3**, **2₄3**) in *o*-dichlorobenzene, because the intermediate 2:1-adducts precipitated from the melt. 1:1- and 3:1- adducts were not detected in a concentration that allowed their isolation. From the reaction of 4,4'-diaminophenyl benzoate (**4**) with 4-(2,3-epoxypropoxy)-4'-ethoxybiphenyl (**1**) the 1:1 (**1₁4**), the non symmetrical 2:1 (**1₂4**), the 3:1 (**1₃4**) and the 4:1-adduct (**1₄4**) could be isolated. With **2** the 1:1 (**2₁4**), the symmetric 2:1 (**2₂4**) and 4:1 products (**2₄4**) were obtained.

The products were isolated on the basis of their difference in solubility by recrystallization, extraction or flash chromatography and characterized by n.m.r.-spectroscopy and d.s.c.. The ratio of starting materials, reaction conditions, the method of isolation and the analytical properties of the model compounds are summarized in *Table 1*.

Identification of the amino groups in **3** and **4** that had reacted with the epoxide was possible on the basis of the n.m.r.-spectra. The results obtained with **4** are in agreement with the reaction rates published¹³. *Figure 2* shows the n.m.r.-spectrum of **4**, *Figure 3* that of the 1:1 adduct **2₁4**. The aromatic protons can be distinguished and allow the determination of the amine/epoxide ratio. The two amino groups give rise to two singlets; one of them has no change in chemical shift after addition of one epoxide (a in *Figures 2 and 3*), the other (f) signal is a triplet with an intensity decreased by 50%. This confirms the amine/epoxide ratio and allows to identify the amino group that has reacted, in this case the amino group which is attached to the phenoxy ring.

Mesogenic properties of epoxy/amine addition compounds

The mesophase behaviour of the monomers and model compounds was studied by polarized light microscopy and

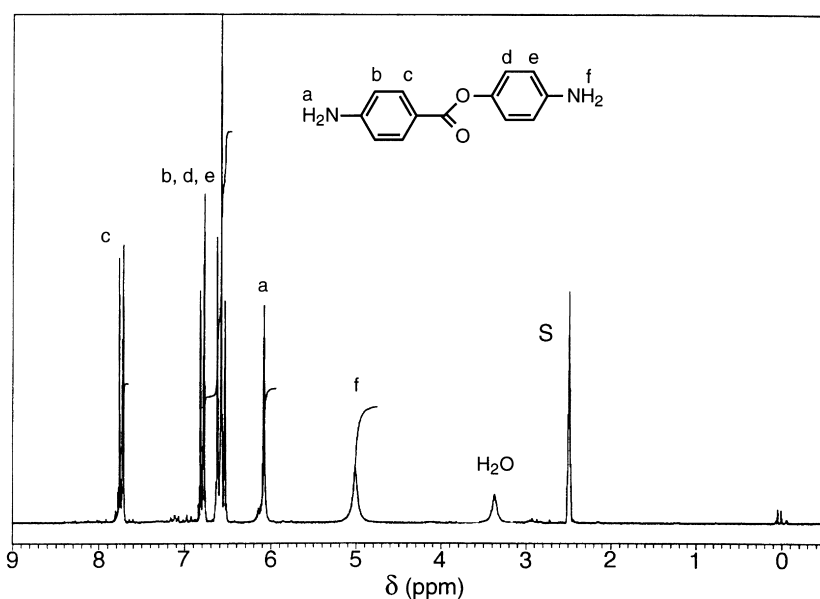


Figure 2 ¹H n.m.r.-spectrum of 4-aminophenyl-4-amino benzoate (**4**) (DMSO-[D₆])

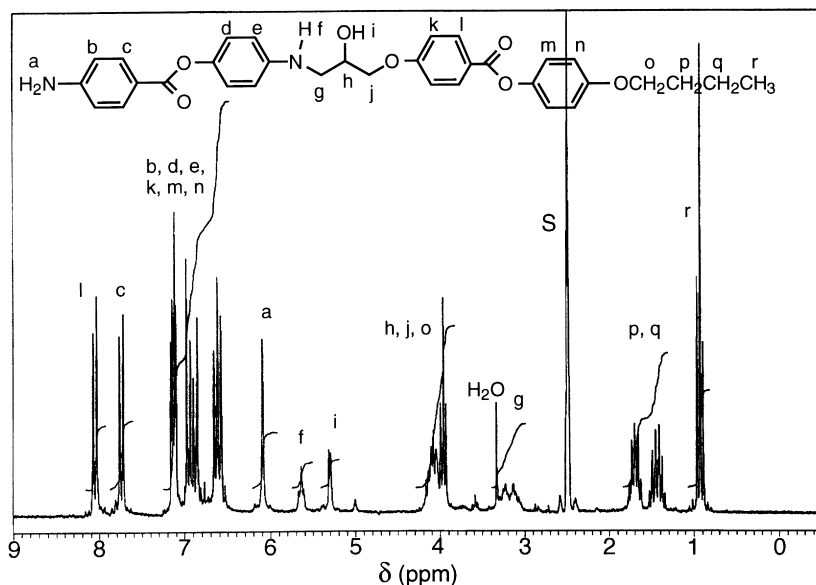
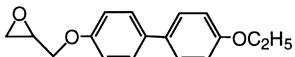
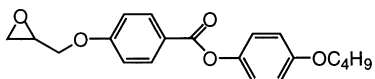
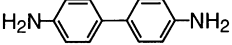
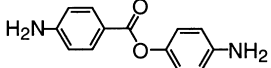
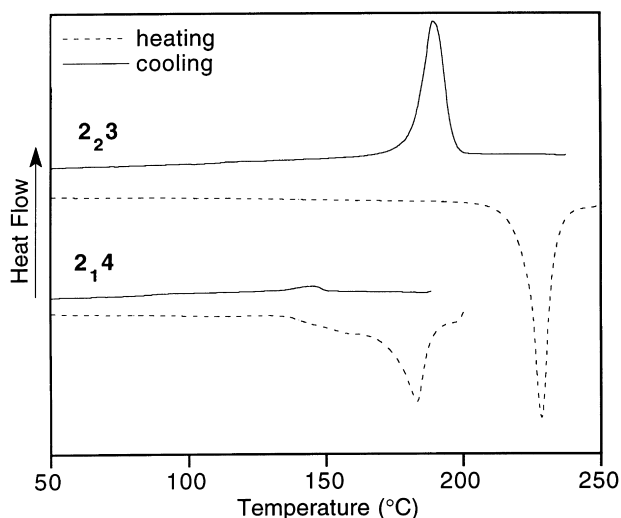


Figure 3 ¹H n.m.r.-spectrum of model compound **2₁4** (DMSO-[D₆])

Table 3 Structures and thermal transitions of monoepoxides and diamines 1–4

1		T_m 153°C (n T_i^a 82°C)
2		T_m 94°C (s T_i 92°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)

^aObtained from extrapolation**Figure 4** D.s.c.-traces of model compounds **2₂3** and **2₁4**

differential scanning calorimetry (d.s.c.). The mesophases were identified on the basis of the textures exhibited between crossed polarizers in the microscope. Clearing points of the monotropic mesophases could not be detected from d.s.c. in most cases because of recrystallization.

The thermal transitions of the monoepoxides and diamines are given in *Table 3*. Epoxide **1** has a nematic mesophase which, owing to the high melting point (153°C) and the high tendency to crystallize, could be determined only from mixtures with methylhydroquinone-di-4-(2,3-epoxypropoxy)phenyl benzoate (T_m : 131°C, T_i : 223°C)¹⁰. The virtual clearing point was found to be at 82°C. **2** has a much lower melting point (94°C) and a monotropic smectic phase with a clearing point of 92°C. The virtual clearing points of the diamines **3** and **4** have been reported in a previous paper¹⁰. Though they are probably not very precise they give a qualitative impression of the mesogenic potential of the diamines.

The thermal properties of the model compounds are included in *Table 2*. In agreement with the properties of the epoxides compounds made from **1** have higher melting points than similar compounds with **2** as epoxide. The biphenyl unit, in addition, has a higher tendency to crystallize than the phenyl benzoate moiety which shows from the fact that compounds made from **1** cannot be supercooled to the same extent as those containing **2**. This is also demonstrated by the d.s.c.-traces of **2₂3** and **2₁4** which are shown in *Figure 4*.

Model compounds from diaminobiphenyl (**3**) and **1** (**1₂3** and **1₄3**) do not form a liquid crystalline phase. Their melting points (258°C and 200°C) are about 30°C higher than those of the corresponding compounds from **2** and **3** (**2₂3**, **2₄3**), which melt at 221°C and 171°C, respectively. The latter have a monotropic smectic phase. It is noteworthy that the 2:1 adducts have higher melting and clearing points than the 4:1 adducts. The smectic phase of **2₂3** is shown in *Figure 5*.

With 4-aminophenyl-4'-amino benzoate (**4**), which has a higher virtual clearing point than **3**, both epoxides gave adducts with monotropic liquid crystal behaviour. The 1:1 reaction product **1₁4** has a clearing point of 141°C. The clearing point of the nonsymmetrical 2:1 compound **1₂4** is lower (104°C) than that of **1₁4**, while that of **1₃4** increases again to 139°C. The 4:1 adduct **1₄4** melts too high (249°C) to detect a clearing point. All model compounds **1_n4** have a nematic phase.

In the **2_n4** series the 1:1 adduct **2₁4**, the symmetric 2:1 (**2₂4**), and the 4:1 adduct **2₄4** could be isolated. **2₁4** has a

**Figure 5** Smectic texture of model compound **2₂3** (193°C, 150 ×)

monotropic nematic phase with a clearing point at 145°C, while the symmetrically substituted compounds **2₂4** and **2₄4** have a smectic mesophase. **2₄4** has a remarkably low melting point and, hence, is the only epoxy/amine compound in this paper forming an enantiotropic mesophase. The clearing point of **2₂4** is almost 70°C higher than that of **2₁4**, while the 4:1 adduct has a lower isotropization temperature than **2₂4**. This can be understood from the aspect ratio of the model compounds. The remarkable increase of **2₁4** with respect to the monomer mixture (estimated clearing point approximately 60°C) indicates that it should be possible to obtain liquid crystal thermosets from the corresponding diepoxide if a suitable reaction temperature is chosen.

Though we have not been able to isolate all possible adducts of each combination the results obtained can be generalized in the following way: reaction of a mesogenic epoxide with a suitable amine results in an increase of the clearing point with respect to that of the epoxide and in a stronger increase with respect to that of the epoxide/amine mixture. The symmetry of the adducts and their aspect ratio determine the extent of this increase. The order of the clearing temperatures for a given epoxide/amine combination is $\text{symm. } 2:1 > 4:1 > 1:1 \approx 3:1 > \text{nonsymm. } 2:1 \gg \text{monomer mixture}$. The diamines used do not have to be mesogenic themselves, because liquid crystal thermosets have been obtained also from 4-(2,3-epoxypropoxy)-phenyl-4-(2,3-epoxypropoxy)-benzoate, the diepoxide which corresponds to **2**, and 4,4'-diaminodiphenylmethane¹⁵.

Another important factor are the melting points of the intermediates formed. As the melting points of the intermediates roughly parallel the clearing points crystallization of oligomers from the curing mixture can occur¹⁰ depending on the solubility and concentration of the intermediates. Miscibility and eutectic behaviour of intermediates, therefore, is another requirement that needs to be fulfilled if liquid crystal thermosets are to be obtained.

CONCLUSIONS

The study of the reaction of 4-(2,3-epoxypropoxy)-4'-ethoxy-biphenyl (**1**) and of 4-butoxyphenyl-4-(2,3-epoxypropoxy)-benzoate (**2**) with 4,4'-diaminobiphenyl (**3**), and 4-aminophenyl-4-aminobenzoate (**4**) has shown that model

compounds are very useful for the understanding and for modelling of the formation of a liquid crystal thermoset. The order of clearing temperatures for a given epoxide/amine: $2:1 > 4:1 > 1:1 \approx 3:1 > \text{nonsymm. } 2:1 \gg \text{monomer mixture}$ shows that chain extending and cross-linking reactions increase the clearing points of the reacting system. They also show that the phase behaviour in epoxy/amine thermosets is determined by that of the epoxide used.

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