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Liquid-crystalline behaviour of 4-(ω-aminoalkyloxy)-4′-cyanobiphenyls and their side chain epoxy polymers

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Liquid-crystalline side chain polymers were obtained from the ring-opening reaction of epoxy resin with mesogenic amines, 4-(ω-aminoalkyloxy)-4′-cyanobiphenyl. The amines with the alkyl group ranging from five to nine methylene units were synthesized, and were found to exhibit an enantiotropic nematic phase. Polymerization of these amines with ethylene glycol diglycidyl ether at 100°C yielded the polymers of low glass transition and melting temperatures. The mesomorphic properties of the amines and the resulting epoxy polymers are reported.

1. Introduction

Liquid-crystalline side chain epoxy polymers are of great interest because of their electro-optical properties which are suitable for displays and light shutter applications [1]. These materials, when used as an anisotropic matrix in a polymer dispersed liquid crystal film, offer an advantage over the conventional film made with isotropic polymers in terms of greater clarity because the principal refractive indices of these liquid-crystalline polymers match those of the low molecular weight liquid crystal in the dispersed droplets [2].

An approach to design liquid-crystalline epoxy polymers has been reported in an earlier work whereby curing epoxy resins with mesogenic amines afforded side chain polymers, most of which were found to exhibit liquid-crystalline behaviour [3]. In a continuing effort to prepare other liquid-crystalline side chain epoxy polymers, with the prime interest being in formulating better indices binders for polymer dispersed liquid crystal films, we have synthesized a new series of epoxy polymers from the condensation of an epoxy resin, ethylene glycol diglycidyl ether (EGDE) and mesogenic amines, 4-(ω-aminoalkoxy)-4′-cyanobiphenyl. In this paper, we report the preparation and study of the mesomorphic properties of these materials.

2. Experimental

2.1. *Materials*

Epoxy resins of Bisphenol-A diglycidyl ether (Epon 828) and *trans*-1,4-dimethyleneoxycyclohexyl diglycidyl ether (MK 107) were obtained from Shell Chemical Co. and used as received. Ethylene glycol diglycidyl ether (EGDE) from Aldrich

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Chemical Company was vacuum distilled at 90°C (0·15 mm Hg) prior to use. 4-Hydroxy-4′-cyanobiphenyl was purchased from American Tokyo Kasei Chemical Co. and used as received.

2.2. *Techniques*

A Varian FT-200 was used to obtain the NMR spectra, with $CDCl_3$ as solvent and TMS as internal standard. A Perkin–Elmer DSC-2 equipped with TADS 3600 was used to determine thermal transitions at heating/cooling scan rate of $10°C\,min^{-1}$ for the amines, and $20°C\,min^{-1}$ for the polymers. Anisotropic textures were observed under the Leitz optical polarizing microscope equipped with a hot stage and a control unit. Molecular weights were determined by gel-permeation chromatography with a Water System 1, calibrated with polystyrene standards. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

2.3. *Synthesis of amines*

The 4-(ω-aminoalkyloxy)-4′-cyanobiphenyl **3** was prepared according to the synthetic route shown in figure 1. The phenolate solution obtained by the interaction of 4-hydroxy-4′-cyanobiphenyl and potassium carbonate was treated with the dibromo-

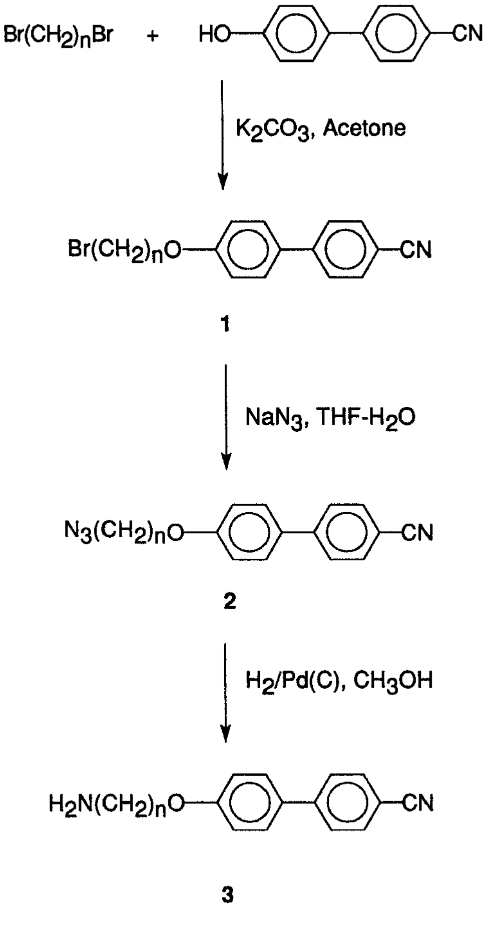

Figure 1. Synthesis of 4-(ω-aminoalkoxy)-4′-cyanobiphenyl (**3**).

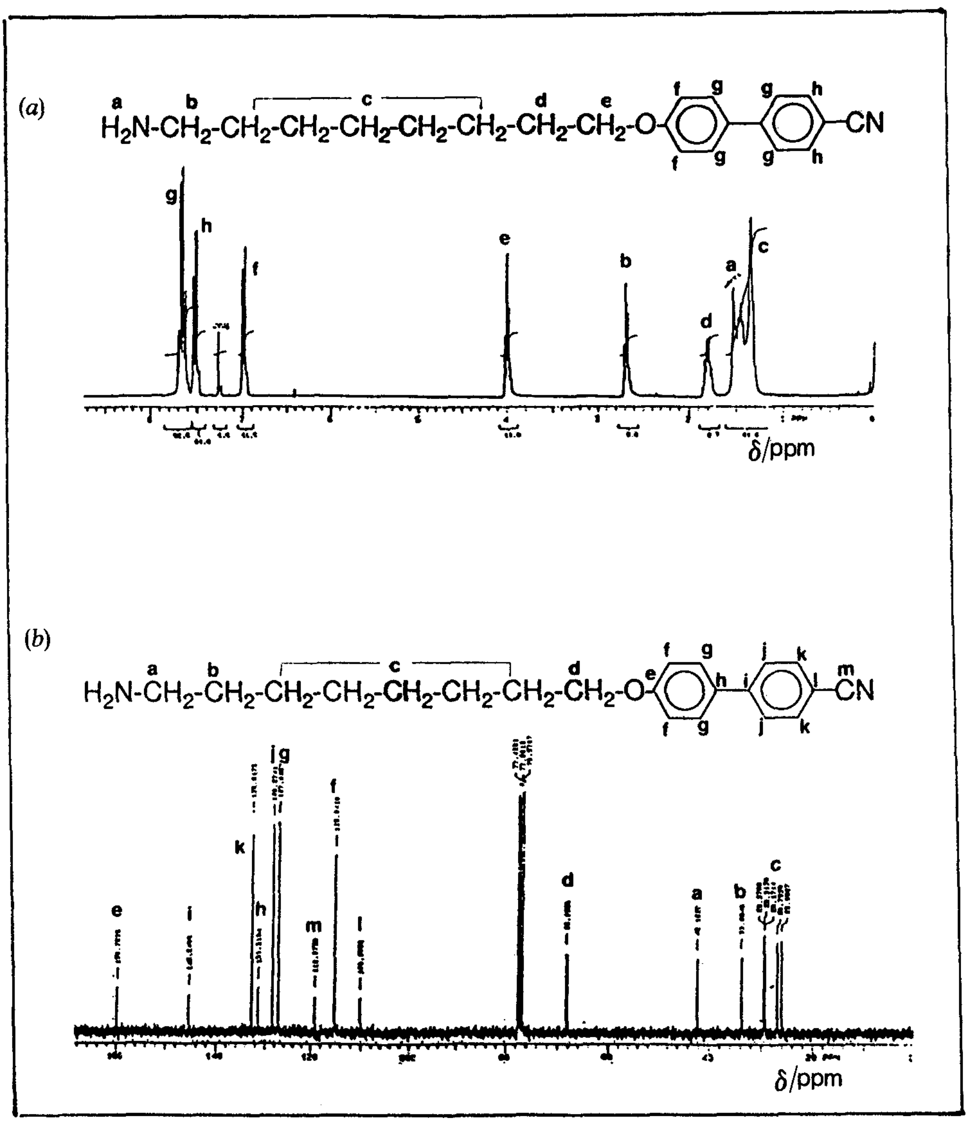

Figure 2. (*a*) ^{1}H NMR and (*b*) ^{13}C NMR spectra of 4-(ω-aminooctyloxy)-4′-cyanobiphenyl (**3d**).

alkane to give the 4-(ω-bromoalkyloxy)-4′-cyanobiphenyl **1**[4]. Compound **1** in THF was reacted with sodium azide in water, in the presence of a phase-transfer catalyst, tetrabutylammonium bromide to give the 4-(ω-azidoalkoxy)-4′-cyanobiphenyl **2**. Catalytic hydrogenation of **2** yielded the primary amine **3**. The crude samples were purified using silica gel chromatography and recrystallization from toluene. Calculated for $C_{20}H_{24}N_2O$(3c): C, 77·92 per cent; H, 7·79 per cent; N, 9·02 per cent. Found: C, 77·83 per cent; H, 7·79 per cent; N, 8·76 per cent. Structure analyses of compounds from IR and NMR spectra were satisfactory. Sample spectra are shown in figure 2.

2.4. *Synthesis of polymers*

The epoxy polymer was prepared by a ring-opening reaction shown in figure 3. Equivalent amounts of the amine and EGDE were charged into a polymerization

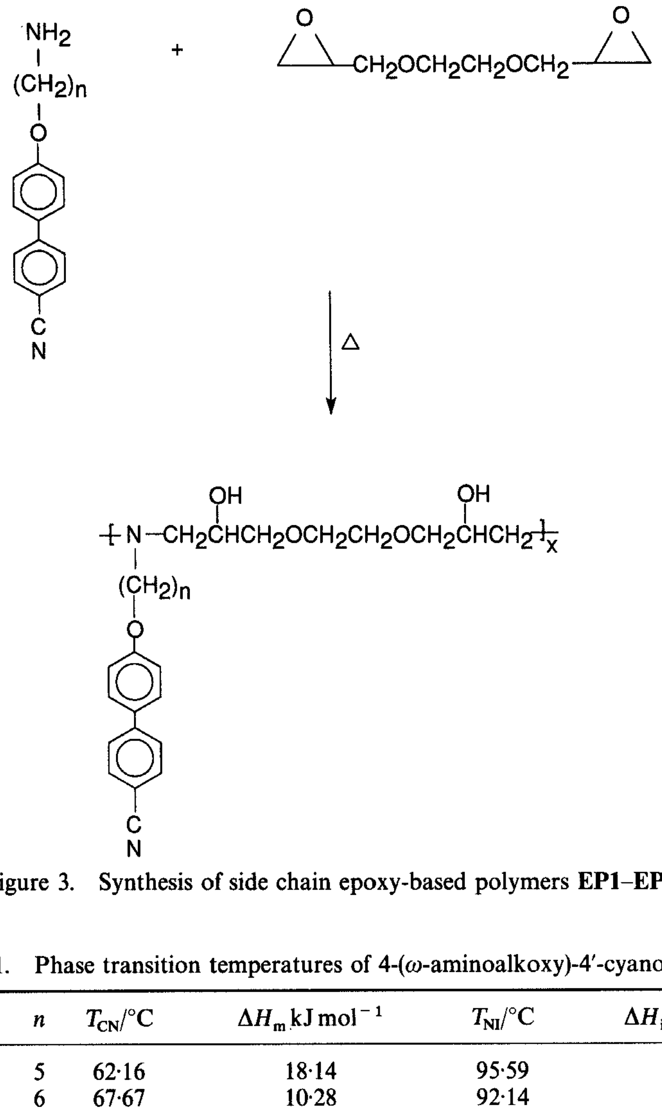

Figure 3. Synthesis of side chain epoxy-based polymers **EP1–EP5**.

Table 1. Phase transition temperatures of 4-(ω-aminoalkoxy)-4′-cyanobiphenyl.

Amines (**3**)	n	T_{CN}/°C	ΔH_m kJ mol^{-1}	T_{NI}/°C	ΔH_i/kJ mol^{-1}
a	5	62·16	18·14	95·59	0·55
b	6	67·67	10·28	92·14	0·19
c	7	69·02	21·17	87·99	0·76
d	8	73·48	26·15	86·08	0·74
e	9	75·89	33·46	83·18	0·83

vessel purged with dry nitrogen, sealed and heated in an oil bath at 60°C for 4 h and at 100°C for 16 h. The polymers were purified three times by precipitation from a THF solution into a 1 : 1 mixture of petroleum ether and ethyl ether. The same procedure was done using the mesogenic amine **3c** and the other epoxy resins: MK 107 and EPON 828. The resulting polymers were compared with that of EGDE.

3. Results and discussion

3.1. *Mesomorphic properties of amines*

By combined differential scanning calorimetry (DSC) and the polarizing microscopic studies, the prepared amines were found to exhibit an enantiotropic nematic

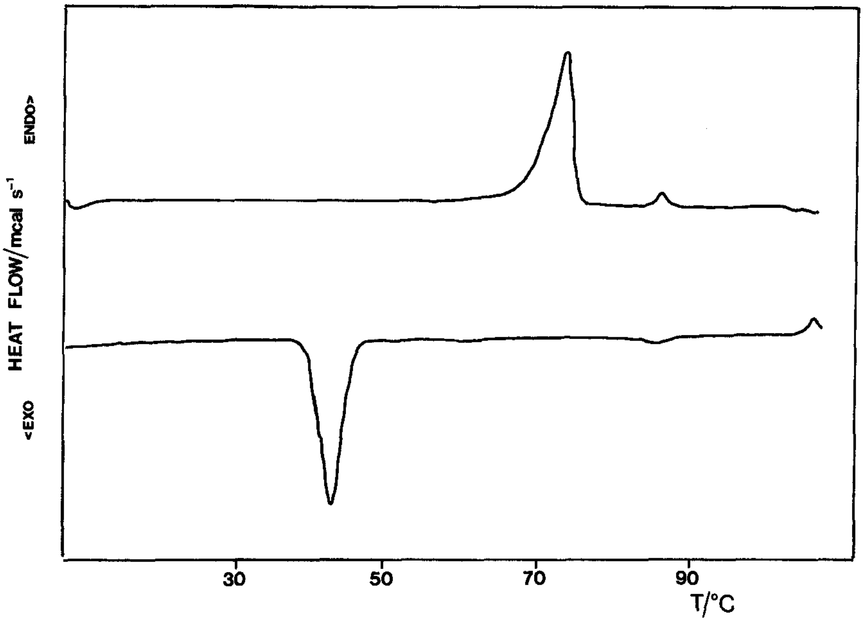

Figure 4. Differential scanning calorimetry heating/cooling scans of 4-(ω-aminooctyloxy)-4′-cyanobiphenyl (**3d**).

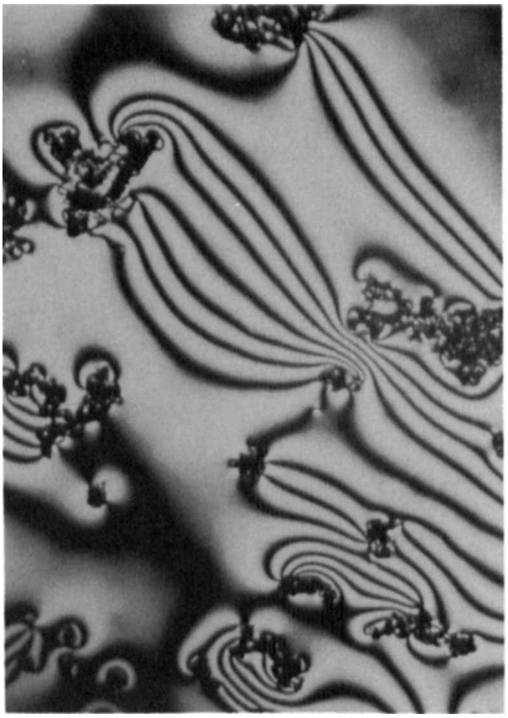

Figure 5. Photomicrograph of 4-(ω-aminooctyloxy)-4′-cyanobiphenyl (**3d**).

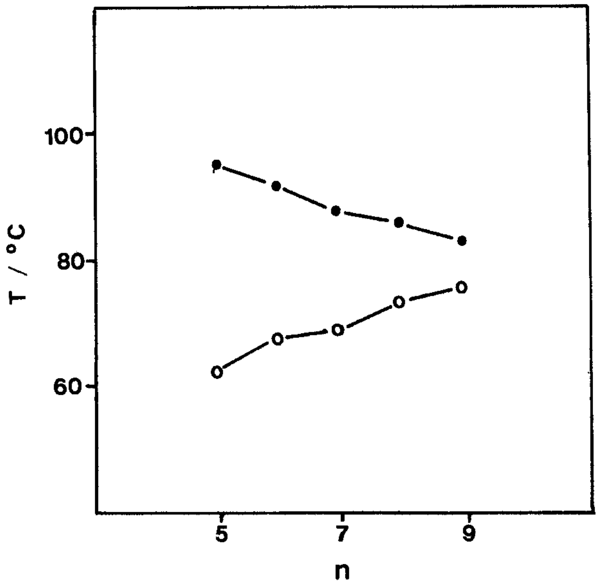

Figure 6. Effect of alkyl chain length *n*, on the transition temperatures of 4-(ω-aminoalkyloxy)-4′-cyanobiphenyl (3). ○,T_{CN}; ●,T_{NI}.

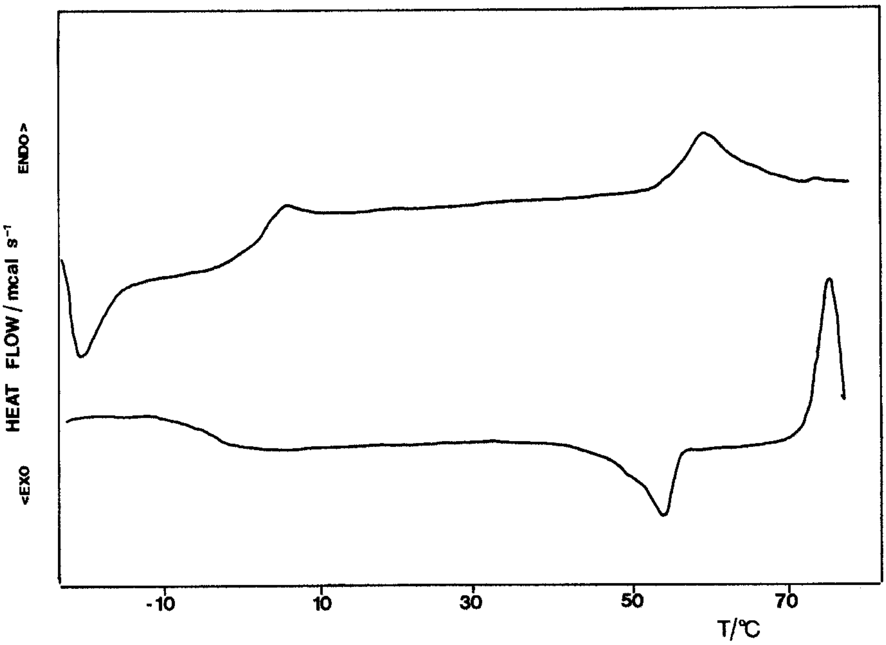

Figure 7. Differential scanning calorimetry heating/cooling scans of side chain epoxy polymer **EP4**.

mesophase. Thermal properties of these compounds based on the second DSC heating are given in table 1. The heating and cooling curves for the **3d** amine are shown in figure 4. A typical nematic texture as observed between cross-polarizers is shown in figure 5.

A plot of the transition temperatures as a function of the chain length *n* (see figure 6) shows a decrease in the nematic–isotropic temperature (T_{NI}) and an increase in the crystal–nematic temperature (T_{CN}) as the chain length increases. The pattern of behaviour shown by these curves compares closely to that of 4'-*n*-alkyloxybiphenyl-4-carboxylic acids and 4-*n*-alkyloxy-4'-cyanobiphenyls cited by Gray [5, 6], where he explained the fall of T_{NI} values with increasing *n* as due to the weakening of the terminal intermolecular attraction as the separation of the polarizable aromatic centres is being increased, and as due to reduction in entropy packing due to steric intermolecular repulsions in the longer chain species. The T_{CN} curve reflects the increasing tendency to be nematic of the shorter chain amines. As the spacer length increases, the occurrence of the nematic mesophase shifts to higher temperatures. The appearance of the smetic phase was not detected in the longer chain amines. This may be partly due to the antiparallel ordering in the cyano-containing amines which could increase the effective molecular length, thus enhancing the nematic order and weakening the smectic behaviour [6, 7].

3.2. *Liquid-crystalline behaviour of epoxy polymers*

The linear epoxy polymers obtained from the reaction of the mesogenic amines and the epoxy resin EGDE, exhibit the nematic phase. The DSC curves obtained have broad peaks which were expected of the polydispersed polymers whose molecular weight distributions range from 1·4 to 1·8 (see table 2). The heating and cooling curves of the prepared polymer, EP4, are shown in figure 7. The transition temperatures are listed in table 2. The glass transition process was identified from the endothermic step in the DSC trace, and the glass transition temperature, T_g, was estimated to be the temperature at which the DSC curve is halfway between the extrapolated tangents to the baselines above and below the glass transition region.

The observed nematic texture may imply significant structural similarity of the polymers with the low molecular weight amines. Their oligomeric nature poses no steric hindrance to the packing of the mesogens and causes the orientation of the pendant mesogenic groups to be less dependent on the behaviour of the main chain. Hence, the texture of the epoxy polymers is dictated mainly by the interaction of the amine moiety, and the mesophases of the polymers behaves like the mesophase of the low molecular weight amines, differing only with respect to the significantly higher viscosity of the polymers. Figure 8 shows the typical nematic texture exhibited by these polymers.

Table 2. Molecular weights and transition temperatures of side chain epoxy polymers from ethyleneglycol diglycidyl ether.

Polymer	Monomer	$\bar{M}_n$	*MWD*	T_g/°C	T_{NI}/°C
EP1	**3a**	1600	1·6	16·3	21·3
EP2	**3b**	1300	1·5	10·6	30·6
EP3	**3c**	3500	1·8	1·3	36·5
EP4	**3d**	1900	1·4	2·6	59·2
EP5	**3e**	2800	1·6	2·9	35·1

M_n = number average molecular weight; *MWD* = molecular weight distribution.

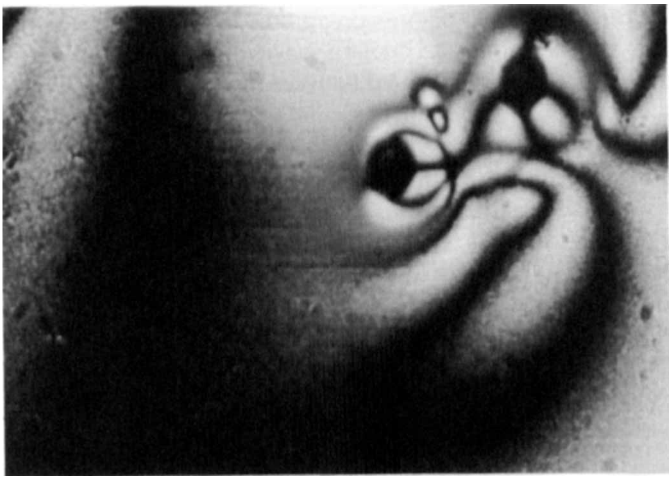

Figure 8. Photomicrograph of epoxy polymer **EP1**.

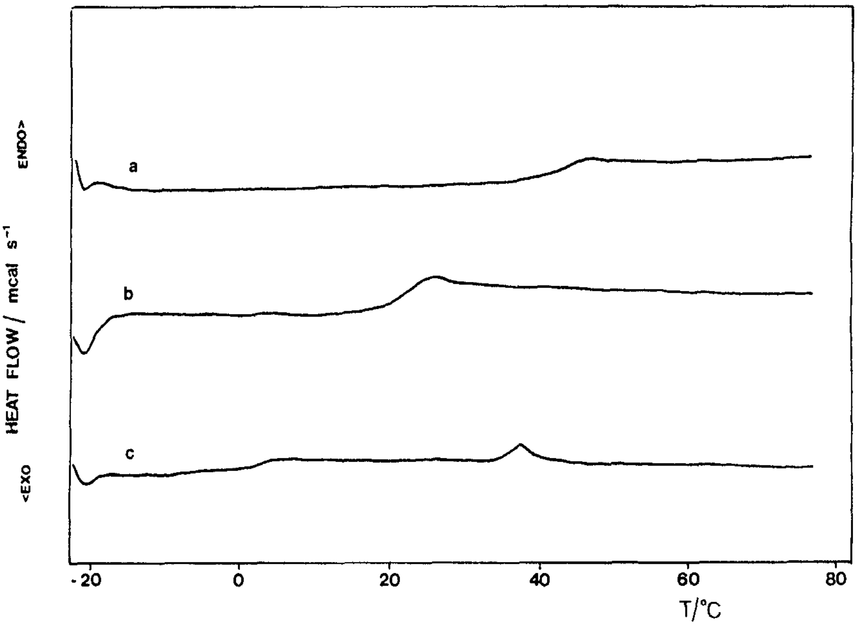

Figure 9. Differential scanning calorimetry heating scans of epoxy polymers from (*a*) EPON 828, (*b*) MK 107 and (*c*) EGDE.

The T_g values listed in table 2 decrease with increasing spacer length, revealing the plasticizing effect of the spacer on the polymers, and then level off. This observed levelling off may have been due to similar molecular masses regardless of spacer length [8].

Although both the polymers and the amines exhibit the same mesomorphism, the thermal stability of the nematic phase of the polymer as determined by the T_{NI}, is seen to be much lower than that of the amines. The T_{NI} values listed in table 2 generally increase with the spacer length. The influence of the nature of the polymer backbone on liquid-crystallinity and transition temperatures of the epoxy polymers is shown by the DSC heating curves (see figure 9) of the polymers obtained from the reaction of the same mesogenic amine **3c** with three different resins: EGDE, MK 107 and EPON 828. The glass transition increases with increasing rigidity of the backbone. The amine-EGDE polymer showed the lowest T_g reflecting the flexibility of the EGDE backbone, as compared to that of the MK 107 and EPON 828. Only the epoxy polymer from the amine-EGDE interaction showed liquid-crystallinity. In the cases of MK 107 and EPON 828 polymers, the mesogenic side groups are geometrically prohibited to assume close parallel packing required for a liquid-crystalline phase.

4. Conclusion

We have synthesized a series of amine-containing liquid crystals with cyanobiphenyl as the mesogen. All the synthesized mesogenic amines exhibit the enantiotropic nematic phase. These reactive liquid crystals were used to produce epoxy polymers by mixing with epoxy resins. The reported method provides a facile synthesis of side chain liquid-crystalline epoxy polymers. These materials may serve as an alternative formulation as binders in preparing polymer dispersed liquid-crystalline films, but optimum conditions in the polymerization process may be further explored to achieve better control of molecular weights.

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