Macromolecules **1992,** *25,* 133–137

Side-Chain Liquid-Crystal Epoxy Polymer Binders for Polymer-Dispersed Liquid Crystals[†]

L.-C. Chien,* C. Lin, David S. Fredley, and James W. McCargar

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

Received November 30, 1990; Revised Manuscript Received April 16, 1991

ABSTRACT: This paper describes the synthesis and characterization of mesogenic amines, 4-[ω-[(4-aminobenzoyl)oxy]alkoxy]-4′-cyanobiphenyls, 4-[ω-[(3,5-diaminobenzoyl)oxy]alkoxy]-4′-cyanobiphenyls, and 4-[ω-[(4-aminophenyl)oxy]alkoxy]-4′-cyanobiphenyls and their side-chain liquid-crystal polymers and copolymers. Most of the synthesized liquid-crystalline epoxy polymers (LCEPs) exhibit liquid-crystalline behavior. The cross-linked epoxy polymer has the highest glass transition temperature, indicating the presence of a network formation. These polymers are used in producing polymer-dispersed liquid crystals.

Introduction

The ease of orientation of nematic liquid-crystalline materials in an electric field and their resulting anisotropic optical properties make them useful in display devices.[1-3] Recently developed technology based on polymer-dispersed liquid crystals (PDLC) shows great potential for applications in light modulators and large area displays. Polymer liquid crystals have been studied for use as binders in PDLC films[4,5] in an effort to better control the alignment of the liquid crystal at the droplet wall. Also, an aligned polymer liquid-crystal binder should improve the contrast and viewing angle of a PDLC device. With both the polymer matrix and the droplets being birefringent, it is possible to index match for wide viewing angles. The aim of improving the optical properties of PDLC films has led to the investigation of liquid-crystal polymers.

Epoxy resins have been shown to be good binders for PDLC films; therefore, we have sought to introduce mesogenic side groups into a thermoplastic epoxy and thermoset. The formation of liquid-crystal epoxy polymers (LCEPs) may be achieved by using a mesogenic primary amine to cure an epoxy resin. A series of mesogenic amines, 4-[ω-[(4-aminobenzoyl)oxy]alkoxy]-4′-cyanobiphenyls and 4-[ω-[(3,5-diaminobenzoyl)oxy]alkoxy]-4′-cyanobiphenyls, were synthesized for this purpose (see Scheme I). Basically, each consists of three constituents: (1) reactive group(s), (2) spacer, and (3) mesogenic unit. This paper describes the synthesis and characterization of mesogenic amines and epoxy liquid-crystal polymers. Also described is the preparation of a PDLC film incorporating a side-chain liquid-crystal polymer.

Experimental Section

Materials. Epoxy resin (Epon 828) of Bisphenol A diglycidyl ether (BADE) with $M_n = 370$ was obtained from Shell Chemical Co. and used as received. Ethylene glycol diglycidyl ether (EGDE) from Aldrich Chemical Co. was vacuum distilled at 90 °C (0.15 mmHg) prior to use. 4-Hydroxy-4′-cyanobiphenyl was purchased from American Tokyo Kasei Chemical Co. and used as received.

Techniques. NMR spectra were recorded on a Varian FT-80 (or GE-300) instrument in deuterated chloroform with TMS as an internal standard. A Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine thermal transitions, which were read at the maximum of the endothermic or exothermic peaks. Unless otherwise specified, all heating and cooling scans were 10 °C/min. Glass transition temperatures (T_g) were read as the middle of the change in the heat capacity. Most thermal transitions were read from second or later heating scans and first or later cooling scans. A Leitz optical polarizing microscope equipped with a Mettler FP-2 hot stage and a Mettler FP-82 control unit was used to observe thermal transitions and anisotropic textures. Molecular weights were determined by gel permeation chromatography (GPC) with a Waters System 1, calibrated with polystyrene standards. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

Synthesis of Mesogenic Curing Agents. 4-[(Hydroxyoctyl)oxy]-4′-cyanobiphenyl (1b). This compound was prepared by refluxing a phenolate solution obtained by the interaction of 4-hydroxy-4′-cyanobiphenyl and potassium carbonate with ω-bromooctanol in acetone for 12 h. After the reaction was over, chloroform and water were added to the reaction mixture and the whole solution was shaken. The organic layer was separated, washed with water, and dried. The solvent was removed with a Rotavapor. The crude product was purified by flash column chromatography using a 2:1 mixture of hexane and ethyl acetate as the eluent. T_m: 104–106 °C. Yield: 60%.

The IR spectrum of this compound showed the following characteristic absorptions (cm^{-1}): 3540 (OH); 2230 (CN); 1601, 1500 (C–C aromatics); 1255, 1040 (C–O–C).

4-[[ω-[(4-Nitrobenzoyl)oxy]octyl]oxy]-4′-cyanobiphenyl (2b). Compound 2b was obtained by acylation of the alcohol **1b** with the acid chloride of nitrobenzoic acid in the presence of triethylamine and a catalytic amount of *N,N*-dimethyl-4-aminopyridine in dry tetrahydrofuran at room temperature. The reaction mixture was added to chloroform and water. The organic layer was washed several times with water and dried with $MgSO_4$. The solvent was evaporated, and the substance was then dissolved in methylene chloride and passed through a chromatographic column with silica gel, using methylene chloride as the eluent. The product was recrystallized from methanol. T_m: 113–114 °C. Yield: 70%.

The IR spectrum of the product showed the following characteristic absorptions (cm^{-1}): 2230 (CN); 1720 (C=O); 1601, 1500 (C—C aromatics); 1350 (NO); 1255, 1050 (C—O—C aromatics). ^{1}H NMR ($CDCl_3$, TMS, δ, ppm): 1.37–1.82 (m, $(CH_2)_6$, 12 H); 3.90–4.05 (t, CH_2OPh, 2 H); 4.20–4.35 (t, $O_2CO_2CH_2$, 2 H); 6.85–7.75 (m, 8 aromatic protons); 7.80–8.00 (m, 2 aromatic protons next to the ester group); 8.00–8.20 (m, 2 aromatic protons next to the nitro group).

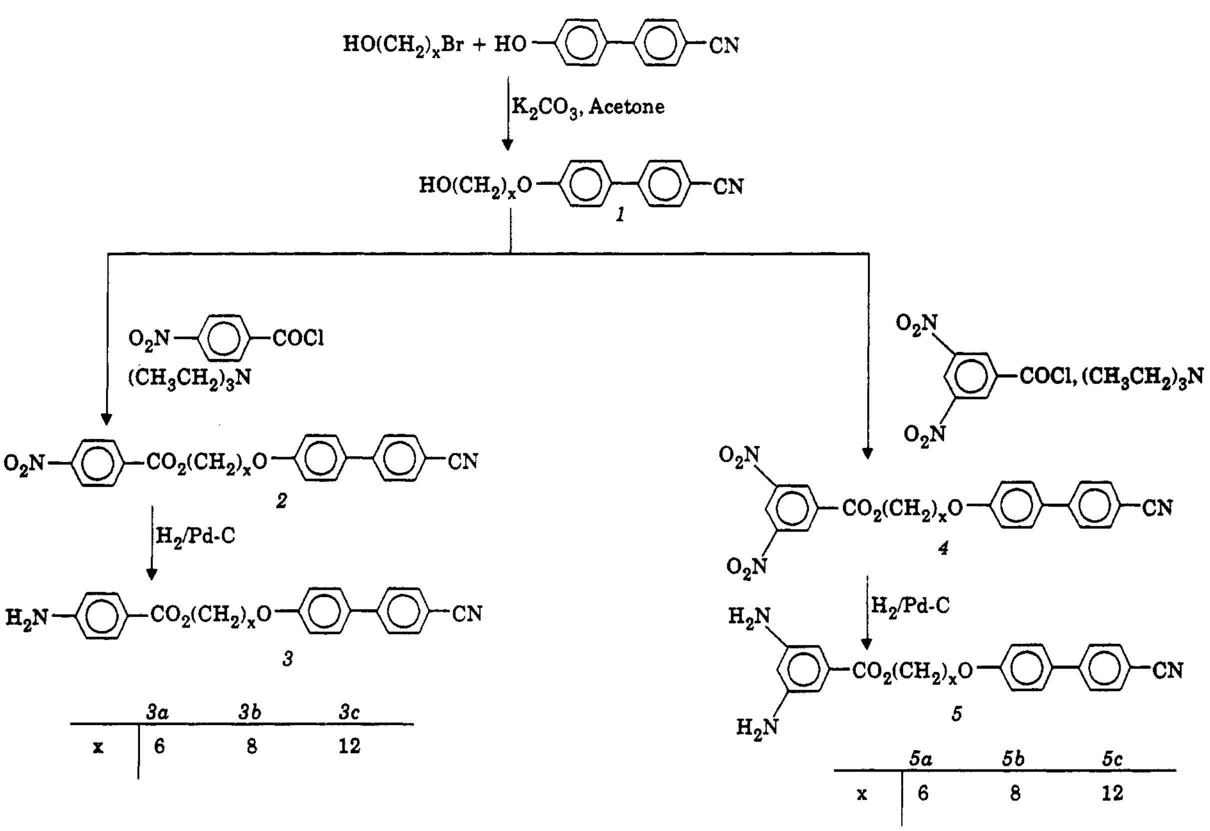
4-[[ω-[(4-Aminobenzoyl)oxy]octyl]oxy]-4′-cyanobiphenyl (3b). Compound **3b** was obtained by the reduction of the nitro group of compound **2b**. To a solution of 12 mmol of **2b** in 150 mL of ethyl acetate and 25 mL of ethanol was added 0.25 mmol of 5% Pd on charcoal. This reaction mixture was hydrogenated under 52 lb (3.6 atm) pressure at room temperature for 4 h. The reaction was monitored by TLC. After hydrogenation was complete, the catalyst was filtered off and the filtrate was evaporated to dryness to give a solid product. The crude product was recrystallized twice from a mixture of

---

[†] Presented at the 13th International Liquid Crystal Conference, Vancouver, BC, Canada, July 1990.

0024-9297/92/2225-0133$03.00/0

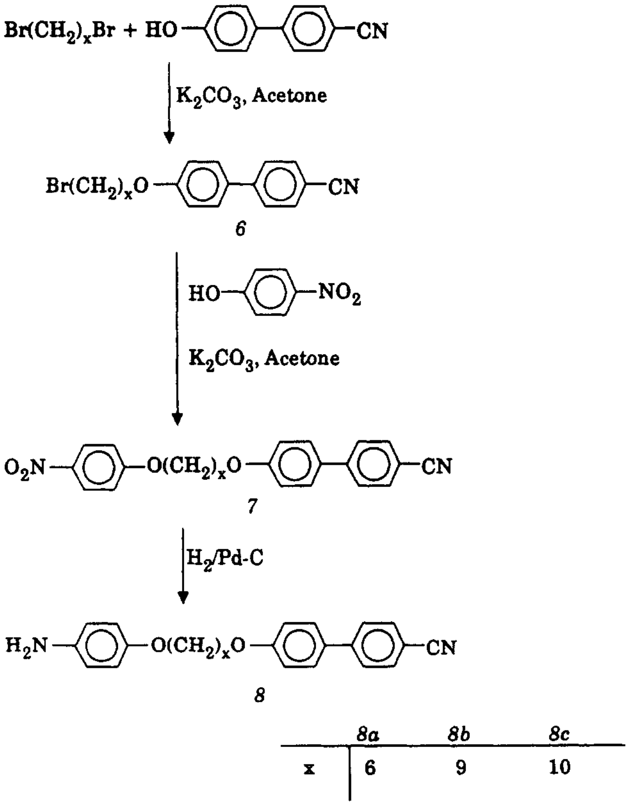
Scheme I



	3a	3b	3c
x	6	8	12

	5a	5b	5c
x	6	8	12

Scheme II



	8a	8b	8c
x	6	9	10

ethyl acetate and ethanol. T_m: 100–102 °C. Yield: 78%.

The IR spectrum of the product showed the following characteristic absorptions (cm^{-1}): 3500–3250 (NH_2); 2235 (CN); 1680 (C=O); 1601, 1500 (C—C aromatics); 1260, 1050 (C—O—C aromatics). ^1H NMR ($CDCl_3$, TMS, δ, ppm): 1.3–1.87 (m, $(CH_2)_6$, 12 H), 3.98–4.05 (t, CH_2OPh, 2 H); 4.23–4.27 (t, CO_2CH_2, 2 H); 6.62–6.64 (m, 2 aromatic protons next to amine); 6.97–7.73 (m, 8 aromatic protons of biphenyl); 7.84–7.90 (m, 2 aromatic protons next to ester).

4-(ω-Bromoalkoxy)-4′-cyanobiphenyls 6. These compounds were prepared analogous to the reported procedure.[6] The yields of such compounds[1] ranged from 59 to 66%. **6a**: IR (cm^{-1}): 2200 (CN); 1600, 1510 (C-C aromatics), 1240 (C-O-Ph). Ge-300 ^1H NMR (in $CDCl_3$, TMS, δ ppm): 1.5–1.7 (m, $(CH_2)_2$, 4 H), 1.8–2.0 (m, $(OH_2)_2$, 4 H), 3.4 (t, $BrCH_2$, 2 H), 4.0 (t, OCH_2, 2 H), 6.97 (d, OPhH, 2 H), 7.5 (d, *m*-PhH, 2 H), 7.6 (t, HPhCN, 4 H).

4-[[(4-Nitrophenyl)oxy]alkoxy]-4′-cyanobiphenyls 7. The etherifications were carried out in a manner similar to the synthesis of compound 6. The yield varied from 55 to 98%. **7a.** IR (cm^{-1}): 2210 (CN); 1610, 1500 (C-C aromatics), 1340 (C-NO_2), 1270 (C-O-Ph). GE-300 ^1H NMR (in $CDCl_3$, TMS, δ ppm): 1.5–1.7 (m, $(CH_2)_2$ 4 H), 1.8–2.0 (m, $(OH_2)_2$, 4 H), 4.0–4.1 (*m*-PhH, 4 H), 6.9–7.0 (m, OPhH, 4 H), 7.5 (D, *m*-OPhH, 2H), 7.7 (m, HPhCN, 4H), 8.2 (D, $OHPhNO_2$, 2H).

4-[ω-[(4-Aminophenyl)oxy]alkoxy]-4′-cyanobiphenyls 8. To a solution of 11 mmol of 4-[[(4-nitrophenyl)oxy]alkoxy]-4′-cyanobiphenyl in 190 mL of ethyl acetate and 20 mL of ethanol was added 0.25 mmol of 5% Pd-C. This reaction mixture was hydrogenated under 53 lb (3.8 atm) pressure for 4 h. The reaction was monitored by TLC. After hydrogenation was complete, the catalyst was filtered off and the filtrate was evaporated to dryness. The crude product was recrystallized from a mixture of ethyl acetate and ethanol. Yields range from 22 to 40%.

8a. IR (cm^{-1}): 3500–3250 (NH_2); 2210 (CN); 1601, 1500 (C-C aromatics); 1250 (C-O-Ph). GE-300 ^1H NMR ($CDCl_3$, TMS, δ ppm): 1.53–1.56 (m, $(CH_2)_2$, 4 H), 1.7–1.84 (m, $(CH_2)_2$, 4 H), 2.2 (D, NH_2, 1 H), 6.6–6.8 (m, H_2NPhH, 2 H), 7.0 (D, OPhH, 2 H), 7.5 (D, *m*-PhH, 2 H), 7.7 (m, HPhCN, 4 H).

Preparation of Polymers. All polymers were prepared by weighing equivalent amounts of the mesogenic amine and epoxy into a polymerization vessel. The reaction mixture was thoroughly purged with dry nitrogen, sealed, and placed in an oil bath at 120 °C for 24 h. After it was cooled to room temperature, the mixture was diluted with THF and precipitated into a 3:1 mixture of petroleum ether and ethyl ether. The precipitate was filtered and again dissolved in THF. The purification process was performed three times and the final precipitated polymer dried in a vacuum oven at room temperature for 3 days. A cross-

Table I
Characterizations and Properties of Mesogenic Amines 3 and 5

compd	x	elem formula		elemental analysis C	H	N	phase transitn,[a] °C
3a	6	$C_{26}H_{26}N_2O_3$	calcd:	75.34	6.32	6.76	k 122 i
			found:	75.12	6.30	6.58	
3b	8	$C_{28}H_{30}N_2O_3$	calcd:	76.99	6.83	6.32	k 101 (n 72) i
			found:	76.74	6.94	6.23	
3c	12	$C_{32}H_{38}N_2O_3$	calcd:	77.07	7.68	5.62	k 81 n 89 i
			found:	77.14	7.95	5.39	
5a	6	$C_{26}H_{27}N_2O_3$	calcd:	72.70	6.34	9.78	k 163 i
			found:	72.73	6.38	9.02	
5b	8	$C_{28}H_{31}N_3O_3$	calcd:	73.49	6.83	9.18	k 157 i
			found:	73.31	6.69	9.06	
5c	12	$C_{32}H_{39}N_3O_3$	calcd:	74.82	7.65	8.18	k 115 i
			found:	73.44	7.51	7.64	

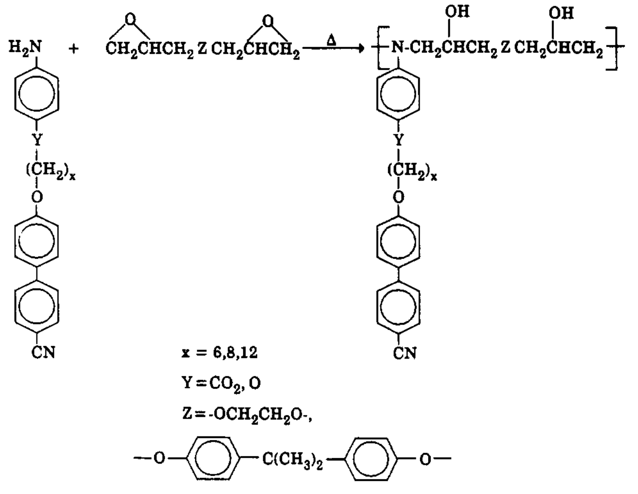
[a] K, crystal; n, nematic; i, isotropic.

Table II
Yields and Properties of Mesogenic Amines 8

compd	yield, %	TLC R_f	elem formula		elemental analysis C	H	N	phase transitn,[b] °C
8a	46	0.34	$C_{25}H_{26}N_2O_2$	calcd:	77.70	6.78	7.25	k 113 n 141 i
				found:	77.80	6.26	6.68	
8b	31	0.23	$C_{28}H_{32}N_2O_2$	calcd:	78.47	7.50	6.54	k 94 n 105 i
				found:	78.18	7.88	5.10	
8c	22	0.28	$C_{29}H_{34}N_2O_2$	calcd:	78.70	7.76	6.33	k 114 n 122 i
				found:	77.25	7.80	5.94	

[a] Silica gel; nH: EA = 2:1. [b] See footnote *a* in Table I for definitions.

Scheme III
Polymerization (1) Linear Epoxy Polymer



linked polymer was prepared by mixing stoichiometric amounts of diamine cross-linker **5b** and epoxy of BADE and curing at 160 °C for 48 h.

Solution Polymerization. Equivalent molar ratios of epoxy resin and mesogenic amine **8** were dissolved in 5–10 mL of DMF in a polymerization vessel. The reaction mixture was thoroughly purged with nitrogen. The polymerization was carried out at 80 °C for 12 h and 120 °C for 4 h. The mixture was cooled, diluted with THF, and precipitated into a mixture of petroleum ether and ethyl ether with 7:1 ratio. The polymer was filtered and dried in a vacuum oven. The yield ranged from 58 to 71%.

Copolymerization. All copolymers were prepared by solution polymerization, as described under solution polymerization, at 90 °C for 30 h.

Preparation of PDLC. A thermally induced phase separation (TIPS) process[6] was emplyed to prepare the PDLC films by mixing 50% E7 (liquid crystal from Merck) with a liquid-crystal epoxy polymer (LCEP). The mixture of low molecular weight liquid-crystal (LMWLC) and LCEP was heated above the T_m of the binder and cooled slowly at a rate of −1.0 °C/min. Droplets of LMWLC formed as the temperature decreased past the phase separation point. The resulting films scatter light and are electrically switchable.

Table III
Phase Transitions and Molecular Weights of LCEPs[a]

polymer	mesogenic amine	epoxy resin	phase transitn, °C	mol wt M_n	MWD
LCEP-1	**3a**	EGDE	g 40.0 i	2600	1.08
LCEP-2	**3a**	BADE	g 50.6 i	2300	1.04
LCEP-3	**3b**	EGDE	g 28.0 n 71 i	2200	1.05
LCEP-4	**3b**	BADE	g 61.0 i	6000	1.67
LCEP-5	**3c**	EGDE	g 31.5 n 76 i	2600	1.16
LCEP-6	**3c**	BADE	g 52.0 i	3700	1.33
LCEP-7	**5b**	BADE	g 90.0 i		

[a] M_n, number-average molecular weight; MWD, polydispersity; g, glass transition temperature; n, nematic; i, isotropic.

Results and Discussion

The mesogenic amines **3** and diamines **5** were prepared according to the synthetic routes outlined in Schemes I and II. Table I summarizes the characterization and properties of these monomers. Only **3c**, the mesogenic amine with 12 methylene groups, exhibits a short nematic mesophase range. Mesogenic amine **3b** shows monotropic mesophase on cooling. All three homologues of diamine display no mesophase.

The mesogenic amines **8** were prepared according to the synthetic routes in Scheme II. The results of the monomer synthesis are given in Table II. All the homologues show nematic schlieren textures.

The epoxy polymers were produced by condensation of commercially available epoxy resins and mesogenic amines **3** (see Scheme III). The phase behavior and the molecular weights of the resulting epoxy polymers are given in Table III. These linear epoxy polymers have low molecular weights and narrow molecular weight distribution. The liquid-crystalline phase was observed and identified as a nematic mesophase from optical microscopy and thermal analysis (Figures 1 and 2). The photomicrograph of the polymer displays a characteristic nematic texture.

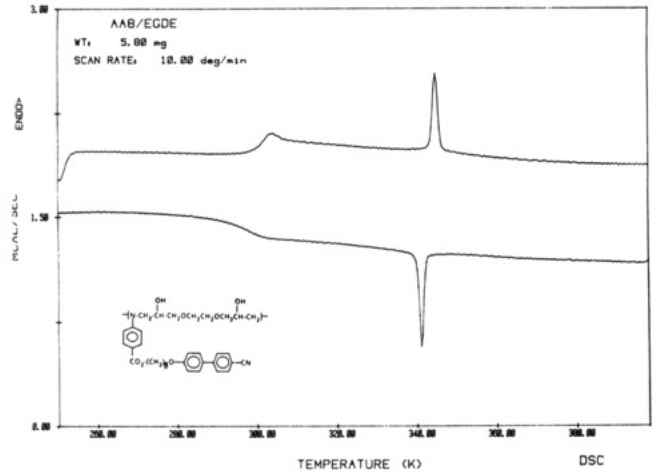


Figure 1. DSC curves of LCEP-3.

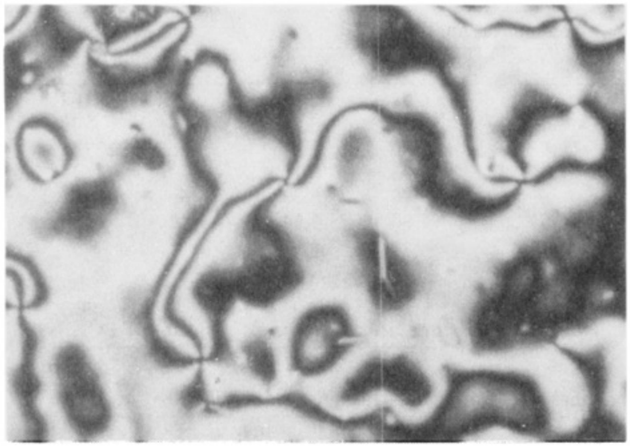


Figure 2. Optical microphotograph of LCEP-3.

Table IV
Phase Transitions and Molecular Weights of Second Series LCEPs[a]

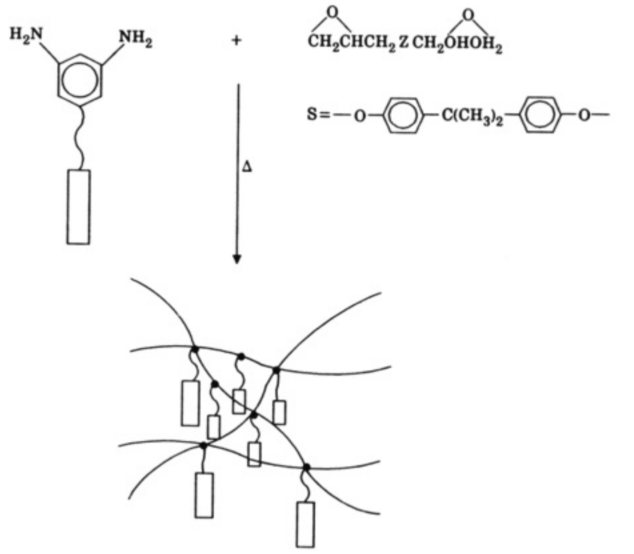
polymer	mesogenic amine	epoxy resin	phase transitn, °C	mol wt M_n	mol wt MWD
LCEP-8	**8a**	EGDE	g 29 n 87 i	4500[b]	1.38
LCEP-9	**8a**	BADE	g 37 n 105 i	15800*	3.36
LCEP-10	**8b**	EGDE	g 24 n 62 i	3000	1.61
LCEP-11	**8b**	BADE	g 35 n 67 i	3700	2.34
LCEP-12	**8c**	EGDE	g 51 k 89 n 117 i	1600	1.12
LCEP-12	**8c**	BADE	g 52 k 105 i	2300	1.36

[a] See Table III for definitions; k, crystal. [b] Melt polymerization.

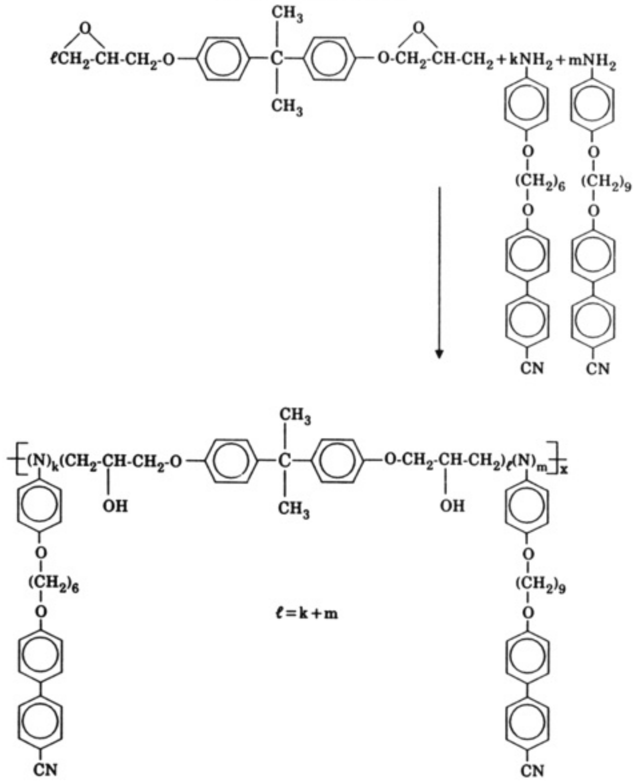
With cyanobiphenyl terminal side chains this is unusual. Siloxanes,[7,8] acrylates,[9,10] etc. with such side chains are predominantly smectic. The predominant nematic polymers may result from the hydrogen bondings that destroy the antiparallel molecular packing of the smectic phase. The Bisphenol A spacer of BADE provides too large a separation between the mesogenic side groups to observe a liquid-crystalline phase. Also, the rigidity of the Bisphenol A backbone greatly increases the glass transition temperature of the polymer. Epoxy networks prepared by mixing epoxy resins with mesogenic diamines **5** exhibit no liquid-crystalline phase. LCEP-7 prepared by mixing diamine **5b** with BADE, at the clearing temperature of **5b**, has a greatly increased T_g because of the rigidity of the backbone and the formation of a network (see Scheme IV).

The molecular weights and phase behaviors of the second series of epoxy polymers, prepared by the reaction of epoxy resins and mesogenic amines **8**, are summarized in Table IV. The molecular weights of the homopolymers ranged from 3000 to 15 800 and the polydispersities from 1.6 to 3.4, depending on the polymerizations. Melt polymerizations (LCEP-8 and -9) give higher molecular weight polymers. The liquid-crystalline to isotropic transition temperatures decrease ~25 °C to 38 °C with the increase of spacer length from six to nine methylene groups.

Scheme IV
Polymerization (2) Cross-Linked Network



Scheme V
Copolymerization



The results for the copolymers, prepared according to Scheme V, are summarized in Table V. All the copolymers exhibit liquid-crystalline behavior. There are no trends in observed transition temperatures as a function of mole percent composition for these two mesogenic amines resulting from these low molecular weight polymers.

In the preparation of PDLC films, side-chain liquid-crystal epoxy polymers with cyanobiphenyl pendants were

Table V
Phase Transitions and Molecular Weights of LCEP Copolymers[a]

polymer	*k*, mol %	*m*, mol %	phase transitn, °C	mol wt M_n	mol wt MWD
LCEP-14	75	25	g 37 n 70 i	2700	1.65
LCEP-15	50	50	g 52 n 97 i	2400	1.75
LCEP-16	25	75	g 36 n 93 i	2700	2.27

[a] See Table III for definitions.

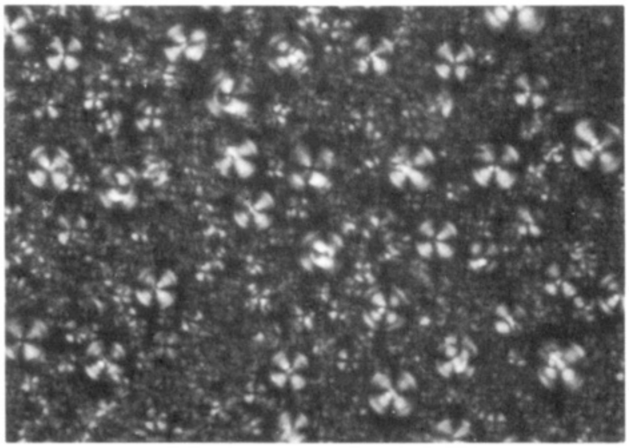


Figure 3. Optical polarizing micrograph of anisotropic LCEP-3 dispersed liquid crystals (E7) (50/50).

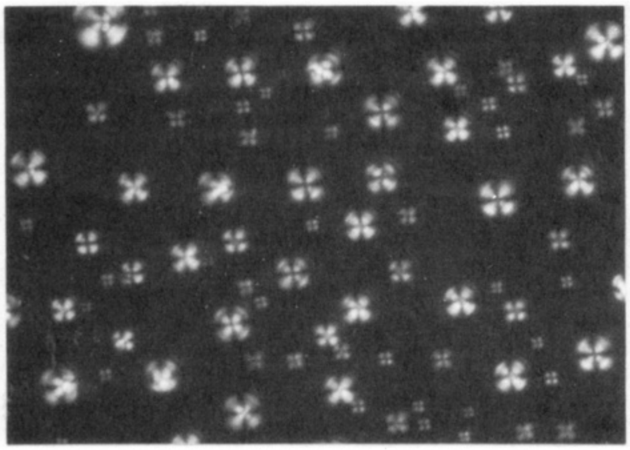


Figure 4. Typical optical polarizing micrograph of isotropic polymer dispersed liquid crystals (E7) (50/50).

used for the matrix, and a commercial cyanobiphenyl mixture, E7 (EM Chemicals), was used for the droplets. Some dispersions were prepared with droplets large enough to be examined with a microscope. These droplets ranged in diameter from 10 to 20 μm and exhibited a texture under a polarizing microscope, illustrated in Figure 3 characteristic of the radial nematic configuration.[11-13] With optically isotropic polymers as the matrix, only the droplets of low molecular weight liquid crystals exhibit birefringence (see Figure 4) under the polarizing microscope.

Conclusions

Using mesogenic amines in the curing of epoxy resins provides a new route for the preparation of liquid-crystalline polymers. The side-chain liquid-crystalline epoxy polymers synthesized by this concept display broad mesomorphic phase ranges. Epoxy copolymers, prepared by varying the composition of mesogenic curing agents, also exhibit liquid-crystalline behavior.

We believe this to be the first illustration of synthesis and application of liquid-crystalline epoxy polymers. However, the materials used in this demonstration of preparing PDLC films will need improvement for useful commercial devices. Primarily, we explored a new route to synthesize side-chain or network liquid-crystal epoxy polymers by mixing mesogenic curing agents with epoxy resins.

To prepare an anisotropic network for any electrooptical application, it will be necessary to align the mesogens to obtain a liquid-crystalline phase. The frozen aligned state can be achieved by curing such materials in an applied field.

Further electrooptic studies of these materials are in progress. We expect that the refractive indices can be better matched by replacing the isotropic matrix with an anisotropic matrix in a PDLC film. The question now to be asked is why epoxy polymers. The answer is that an epoxy system is easily formulated. An alternative formulation is to synthesize liquid-crystalline epoxy resins and cure such resins with commercial isotropic curing agents or combine both the mesogenic curing agents and liquid-crystalline epoxy resins to obtain main-chain side-chain anisotropic materials.

Improvements in the polymerization method to better control molecular weight and polydisperity are in progess. Future studies will involve molecular engineering of mesogenic amines and liquid-crystalline epoxy resins to obtain optimum systems for the PDLC technology.

Acknowledgment. We thank Dr. John L. West for helpful discussions on PDLC work. This work was supported in part by DARPA/Office of Naval Research/URI Program under Prime Grant N00014-90-J-1559.

References and Notes

(1) West, J. L. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 427.

(2) Doane, J. W.; Golemme, A.; West, J. L.; Whitehead, J. B., Jr.; Wu, B.-G. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511.

(3) Drzaic, P. S. *J. Appl. Phys.* **1986**, *60*, 2142.

(4) Doane, J. W.; West, J. L. Tamura-Lis, W.; Whitehead, J. B., Jr. *Pac. Polym. Prepr.* **1989**, *1*, 245 (first Pacific Polymer Conference).

(5) West, J. L.; Chien, L.-C.; Tamura-Lis, W. *Pac. Polym. Prepr.* **1989**, *1*, 247 (first Pacific Polymer Conference).

(6) Crivello, J. V.; Deptolla, M.; Ringsdorf, H. *Liq. Cryst.* **1988**, *3*, 235.

(7) Gemmell, P. A.; Gray, G. W.; Lacey, D. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 205.

(8) Kostromin, S. G.; Shibaev, V. P.; Plate, N. A. *Liq. Cryst.* **1987**, *2*, 195.

(9) Shibaev, V. P.; Kostromin, S. G.; Plate, N. A. *Eur. Polym. J.* **1982**, *18*, 651.

(10) Dubois, J. C.; Decobert, G.; LeBarny, P.; Esselin, S.; Friedrich, C.; Noel, C. *Mol. Cryst. Liq. Cryst.* **1986**, *137*, 349.

(11) Žumer, S.; Doane, J. W. *Phys. Rev. A* **1986**, *34*, 3373.

(12) Wu, B.-G.; Erdmann, J. H.; Doane, J. W. *Liq. Cryst.* **1989**, *5*, 1453.

(13) Ondris-Crawford, R.; Boyko, E. P.; Wagner, B. G.; Erdmann, J. H.; Žumer, S.; Doane, J. W., *J. Appl. Phys.*, in press.