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# Crosslinking of vinyl-terminated side-chain liquid crystalline polyethers using low molecular weight analogous mesogenic esters as reactive diluents

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## Abstract

We have synthesized two methyl 4'-( $\omega$ -alkenoxy)-4-biphenylcarboxylates and two methyl 6-( $\omega$ -alkenoxy)-2-naphthalenecarboxylates and used them as reactive diluents in the crosslinking of vinyl-terminated side-chain liquid-crystal polyepichlorohydrin derivatives containing analogous mesogenic moieties. The crosslinking was done with a 10 mol% of a free radical initiator system. Differential scanning calorimetry, polarized optical microscopy and X-ray diffraction measurements show that the mixtures of polymers with the reactive diluents had the same mesophases as pure polymers. We obtained liquid crystal thermosets from the biphenyl derivatives but, because of the low isotropization temperatures of the polymer–diluent mixtures, the naphthalene derivatives did not produce crosslinked anisotropic materials. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Liquid-crystalline polymers; Crosslinking; Polyethers

## 1. Introduction

We have previously reported the synthesis [1] and the crosslinking [2] of a set of liquid-crystal vinyl-terminated biphenyl and naphthalene poly(epichlorohydrin) derivatives leading to anisotropic thermosets and elastomers. This synthesis, performed by the chemical modification of poly(epichlorohydrin) with mesogenic acids, led to the structures shown in Scheme 1 with a high degree of functionalization (>90%). This degree of functionalization was determined by chlorine elemental analysis.

We used several radical initiators to crosslink these polymers through their double bonds. In this crosslinking, however, the double bonds did not completely disappear, probably because there was a high proportion of vinyl groups and because the rigidity introduced by aromatic mesogenic moieties was high. The lability of the remaining vinyl groups can negatively affect the properties of the final material, so in this paper we aim to increase the degree of crosslinking by using reactive diluents, as we have used in a previous work in non-liquid crystal polymers [3]. These

reactive diluents can act as a plasticizer that reduces the intensity of the interactions between polymeric chains and leads to a highly mobile system. Mixtures of side-chain liquid-crystal polymers and analogous monomeric compounds have been studied by several authors and these studies showed a dependence of the macroscopic elastic constants [4] and/or the phase behavior and morphology [5,6] with the content of reactive diluent.

So as not to alter the mesophase organization, the reactive diluents we chose were the methylic esters of the corresponding mesogenic acids introduced in the polymer.

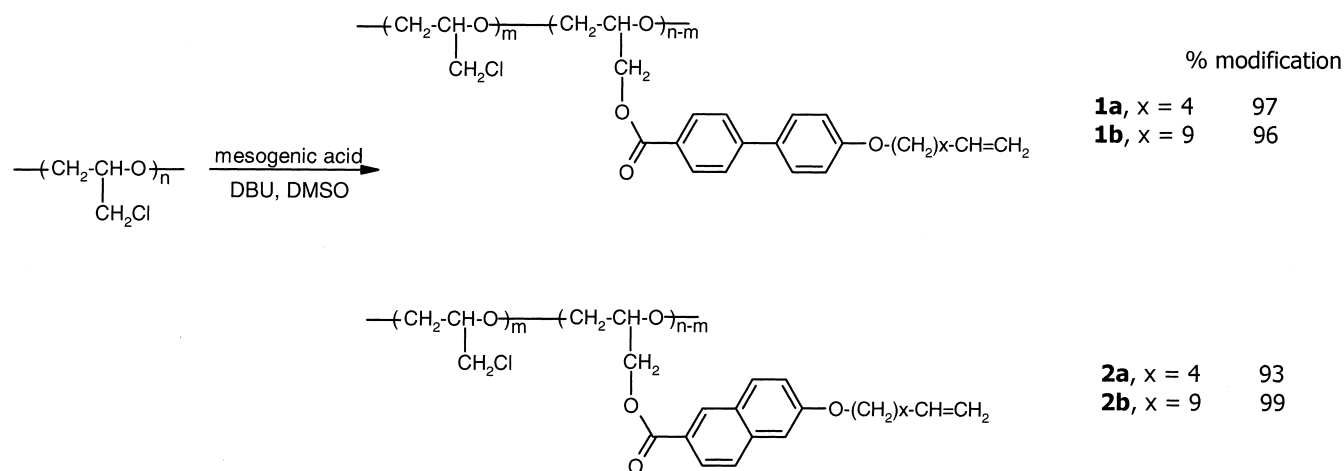
## 2. Experimental section

### 2.1. Materials

Polymers **1a** (97 mol% of double bond,  $\eta_{inh} = 0.17$  dl/g,  $\bar{M}_w = 74,000$ ), **1b** (96 mol% of double bond,  $\eta_{inh} = 0.26$  dl/g,  $\bar{M}_w = 87,000$ ), **2a** (93 mol% of double bond,  $\eta_{inh} = 0.15$  dl/g,  $\bar{M}_w = 80,000$ ) and **2b** (99 mol% of double bond,  $\eta_{inh} = 0.14$  dl/g,  $\bar{M}_w = 116,000$ ) were synthesized by chemical modification of poly(epichlorohydrin) as previously described [1]. Dicumyl peroxide (DP), lauroyl

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Scheme 1.

peroxide (LP) and 4-dimethylaminopyridine (DMAP) (Fluka) were used as received.

## 2.2. Synthesis of methylic esters

The esters **E-1a**, **E-1b**, **E-2a** and **E-2b** (Scheme 2) were obtained from the previously synthesized mesogenic acids [1]. A general procedure is as follows.

In a 100 ml round-bottomed flask, 0.02 mol of acid, 60 ml of methanol and few drops of concentrated sulphuric acid were added and then the mixture was refluxed and mechanically stirred. The reaction was followed by TLC using chloroform/methanol 10:1 as eluent. Once the reaction was completed (20–24 h), the crude was left to cool and poured onto ice. The precipitate that formed was filtered, recrystallized from methanol and dried in vacuo.

### 2.2.1. Methyl 4'-(5-hexenoxy)-4-biphenylcarboxylate (**E-1a**)

Yield: 99%. Liquid crystal transitions (°C): K 100 S<sub>B</sub> 137 I. IR (KBr, cm<sup>-1</sup>): 3069 (ν C–H alkene and aromatic), 1719 (ν C=O), 1642 (ν C=C), 1604 (ν C–C aromatic), 1390 (δ CH<sub>3</sub>), 1285 and 1192 (ν C–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 1.60 (m, 2H), 1.82 (m, 2H), 2.15 (m, 2H), 3.93 (s, 3H), 4.01 (t, 2H, J = 6.6 Hz), 4.96 (d, 1H, J<sub>cis</sub> = 10.9 Hz), 5.04 (d, 1H, J<sub>trans</sub> = 17.0 Hz), 5.84 (m, 1H), 6.98 (d, 2H, J = 8.8 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.61 (d, 2H, J = 8.2 Hz), 8.07 (d, 2H, J = 8.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ (ppm)): 25.30 (t), 28.78 (t), 33.54 (t), 52.18 (q), 67.95 (t), 114.91 (t), 114.98 (d), 126.51 (d), 128.24 (s), 128.42 (d),

130.19 (d), 132.24 (s), 138.59 (d), 145.34 (s), 159.45 (s), 167.18 (s).

### 2.2.2. Methyl 4'-(10-undecenoxy)-4-biphenylcarboxylate (**E-1b**)

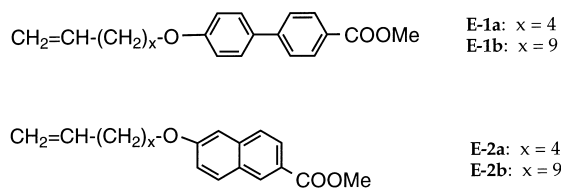
Yield: 94%. Liquid crystal transitions (°C): K 110 S<sub>E</sub> 114 S<sub>A</sub> 118 I. IR (KBr, cm<sup>-1</sup>): 3072 (ν C–H alkene and aromatic), 1719 (ν C=O), 1640 (ν C=C), 1604 (ν C–C aromatic), 1391 (δ CH<sub>3</sub>), 1285 and 1194 (ν C–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 1.31 (m, 12H), 1.80 (m, 2H), 2.04 (m, 2H), 3.93 (s, 3H), 3.99 (t, 2H, J = 6.6 Hz), 5.03 (m, 2H), 5.81 (m, 1H), 6.97 (d, 2H, J = 8.8 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.61 (d, 2H, J = 8.2 Hz), 8.07 (d, 2H, J = 8.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ (ppm)): 26.00 (t), 28.89 (t), 29.09 (t), 29.21 (t), 29.35 (t), 29.40 (t), 29.49 (t), 33.79 (t), 52.05 (q), 68.07 (t), 114.11 (t), 114.86 (d), 126.38 (d), 128.08 (s), 128.27 (d), 130.05 (d), 132.06 (s), 139.19 (d), 145.22 (s), 159.37 (s), 167.06 (s).

### 2.2.3. Methyl 6-(5-hexenoxy)-2-naphthalenecarboxylate (**E-2a**)

Yield: 35%. Mp: 49–50 °C. IR (KBr, cm<sup>-1</sup>): 3062 (ν C–H alkene and aromatic), 1717 (ν C=O), 1631 and 1615 (ν C–C aromatic), 1381 (δ CH<sub>3</sub>), 1285 and 1196 (ν C–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ (ppm)): 1.62 (m, 2H), 1.87 (m, 2H), 2.15 (m, 2H), 3.96 (s, 3H), 4.08 (m, 2H), 5.01 (m, 2H), 5.84 (m, 1H), 7.13 (s, 1H), 7.17 (m, 1H), 7.72 (d, 1H, J = 8.2 Hz), 7.82 (d, 1H, J = 8.2 Hz), 8.00 (m, 1H), 8.52 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ (ppm)): 25.29 (t), 28.53 (t), 33.39 (t), 52.08 (q), 67.84 (t), 106.23 (d), 114.82 (t), 119.86 (d), 124.97 (s), 125.81 (d), 126.74 (d), 127.72 (s), 130.81 (d), 130.82 (d), 137.15 (s), 138.43 (d), 158.97 (s), 167.42 (s).

### 2.2.4. Methyl 6-(10-undecenoxy)-2-naphthalenecarboxylate (**E-2b**)

Yield: 99%. Mp (°C): 70–71. IR (KBr, cm<sup>-1</sup>): 3073 (ν C–H alkene and aromatic), 1719 (ν C=O), 1627 and 1604 (ν C–C aromatic), 1387 (δ CH<sub>3</sub>), 1287 and 1205 (ν C–O).



Scheme 2.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 1.31 (m, 10H), 1.50 (m, 2H), 1.84 (m, 2H), 2.05 (m, 2H), 3.96 (s, 3H), 4.08 (t, 2H,  $J = 6.6$  Hz), 4.95 (d, 1H,  $J_{\text{cis}} = 10.9$  Hz), 5.05 (d, 1H,  $J_{\text{trans}} = 17.6$  Hz), 5.85 (m, 1H), 7.13 (d, 1H,  $J = 2.2$  Hz), 7.20 (dd, 1H,  $J = 8.8$  Hz,  $J = 2.2$  Hz), 7.73 (d, 1H,  $J = 8.8$  Hz), 7.82 (d, 1H,  $J = 8.8$  Hz), 8.01 (dd, 1H,  $J = 8.8$  Hz,  $J = 1.6$  Hz), 8.52 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  (ppm)): 26.05 (t), 28.89 (t), 29.12 (t), 29.25 (t), 29.36 (t), 29.41 (t), 29.50 (t), 33.79 (t), 52.04 (q), 68.07 (t), 106.26 (d), 114.12 (t), 119.88 (d), 124.98 (s), 125.81 (d), 126.73 (d), 127.72 (s), 130.77 (d), 130.78 (d), 137.17 (s), 139.16 (d), 158.04 (s), 167.36 (s).

### 2.3. Preparation of samples for DSC studies

Samples were prepared by mixing solutions in dichloromethane of polymer, analogous methyl ester (10 mol%) and eventually an initiator system, and then removing the solvent at low pressure and at room temperature. The mixtures were stored in the dark at 0–5 °C.

### 2.4. Instrumentation

DSC studies were performed on a Mettler DSC-30 thermal analyzer using samples of ca. 5 mg in covered Al pans under nitrogen atmosphere. Liquid crystal transitions, melting points and  $T_g$ s were determined from DSC curves recorded at a heating rate of 20 °C/min. FTIR spectra were recorded in KBr pellets on a Midac Prospect-IR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Varian Gemini 300 spectrometer with  $\text{CDCl}_3$  as a solvent and TMS as an internal standard. The textures of the mesophases were observed with a polarizing microscope AXIOLAB Zeiss provided with a LINKAM THMS 600 hot-stage connected to a TP-92 temperature control unit.

### 2.5. X-ray diffraction measurements

Powder X-ray diffraction measurements were performed at several temperatures on a Siemens D5000 diffractometer with  $\theta$ – $\theta$  configuration and fitted with an Anton Paar TTK temperature chamber. Cu  $K\alpha$  radiation was used and graphite was the secondary monochromator. The Bragg angle step was 0.05° and the time per step was 3 s.

Pole figures were recorded on a Siemens D5000 diffractometer equipped with a goniometer with an Open Eulerian cradle using Cu  $K\alpha$  radiation.

All samples were prepared on a  $34 \times 34 \text{ mm}^2$  thin silicon single-crystal wafer surface cut parallel to the (510) plane.

The polymer samples studied by X-ray diffraction were mechanically oriented by shearing the polymer in the mesophase at a temperature higher than  $T_g$ , and the mesophase order was maintained by suddenly reducing the temperature to room temperature.

## 3. Results and discussion

### 3.1. Synthesis and characterization of reactive diluents

As mentioned above, the chosen reactive diluents were the methylic esters of the four different mesogenic acids introduced to the polymers. They were synthesized, in almost quantitative yields, by a Fischer esterification reaction of the previously synthesized acids [1] (Scheme 2).

These products were chemically characterized by IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies. With IR spectroscopy, esterification was confirmed by the disappearance of the acid carbonyl band at  $1686 \text{ cm}^{-1}$  and the appearance of the ester carbonyl band at  $1719 \text{ cm}^{-1}$ . With NMR spectroscopy, the disappearance of the acid proton signal and the appearance of the methyl ester signals (3.96 ppm in  $^1\text{H}$  and 52 ppm in  $^{13}\text{C}$ ) were observed.

We studied the thermal behavior of these esters by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Table 1 shows the thermal transitions of esters and of their acid precursors. Only biphenylic esters behaved as liquid crystals so it seems that the formation of dimer structures through hydrogen bonds in the carboxylic acids strongly facilitates the formation of mesophases and increases their range of stability as have been described [7].

The mesophase for ester **E-1a** was recognized as smectic B because on cooling from the isotropic liquid a platelet mosaic texture formed [8] (Fig. 1a). For ester **E-1b**, on cooling from isotropic liquid, first a bâtonnet texture formed and this then developed into a focal-conic fan texture. Further cooling led to an arced paramorphic focal-conic fan texture (Fig. 1b). The mesophases were, therefore, assigned as smectic A and E, respectively [8].

We studied esters **E-1a** and **E-1b** by powder X-ray diffraction at temperatures of each mesophase. Table 2 shows the reflections and the corresponding reticular spacings, which are compatible with the recognized mesophase [9]. Particularly, the reflection at lower angles corresponds to the smectic period and is, in all cases, roughly close to the length of the ester calculated by the Cerius2 [10] molecular modeling program (Table 2). Thus, it seems that the three smectic mesophases are organized as a monolayer structure.

Table 1  
Thermal transitions (°C) of methyl esters and their acid precursors

	Methyl ester	Acid precursor
<b>E-1a</b>	K 100 $S_B$ 137 I	K 207 $S_A$ 238 N 269 I
<b>E-1b</b>	K 110 $S_E$ 114 $S_A$ 118 I	K 124 $S_E$ 162 $S_A$ 247 I
<b>E-2a</b>	K 49 I	$K_1$ 126 $K_2$ 141 N 186 I
<b>E-2b</b>	K 70 I	K 120 $S_C$ 146 N 176 I

Thermal transitions determined by DSC second heating scan. Phases were recognized by POM and X-ray diffraction. K: crystal;  $S_A$ ,  $S_B$ ,  $S_C$ ,  $S_E$ : smectic mesophases; N: nematic mesophase; I: isotropic melt.

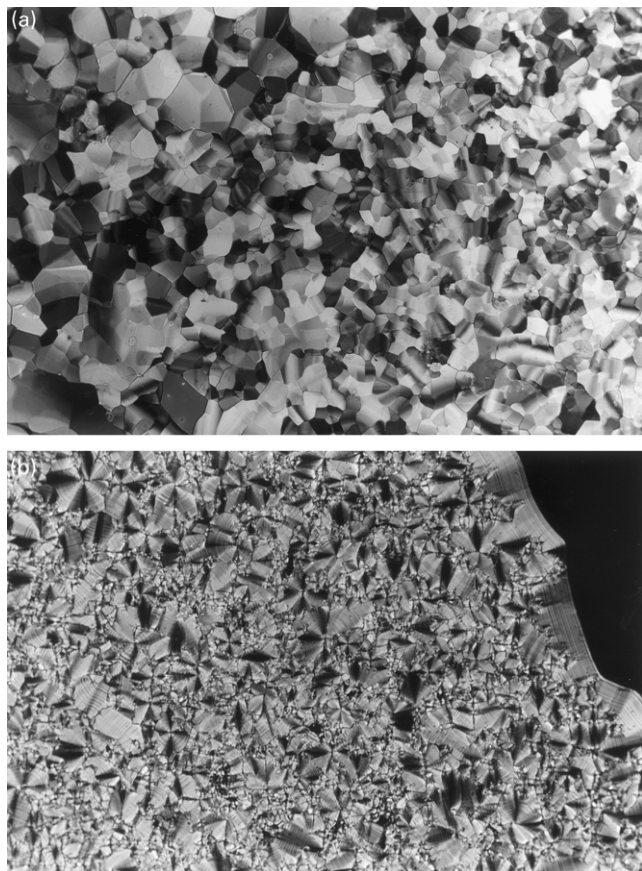


Fig. 1. 100 × magnified POM photographs of (a) platelet mosaic texture of **E-1a** at 135 °C; (b) arced focal-conic fan texture of **E-1b** at 111 °C.

### 3.2. Crosslinking study

As mentioned above, we aimed to crosslink a set of vinyl-terminated side-chain liquid-crystalline polyethers (Scheme 1) in the presence of a small amount of analogous reactive diluents. We, therefore, prepared mixtures of each polymer and a 10 mol% of their analogous methylic ester (the percentage refers to the double bond content).

First we studied the thermal behavior of these mixtures to see how the reactive diluent affected the structure and stability of the mesophases. Table 3 shows the thermal transitions and the mesophases of polymers and mixtures. The glass transition and isotropization temperatures were determined by DSC and the mesophases were recognized by

Table 3

Thermal characterization of the polymer-reactive diluent mixtures

	$T_g$ (°C)	DSC endotherms (°C)	Transition temperatures <sup>a</sup> (C)
Polymer <b>1a</b>	111	194	G 111 S <sub>A</sub> 189 I
<b>1b</b>	51	163	G 51 S <sub>A</sub> 168 I
<b>2a</b>	28	–	G 28 N 41 I
<b>2b</b>	45	60	G 45 S <sub>C</sub> 62 I
Mixture <b>1a + E-1a</b>	108	168	G 116 S <sub>A</sub> 169 I
<b>1b + E-1b</b>	48	153	G 74 S <sub>A</sub> 154 I
<b>2a + E-2a</b>	15	–	G 15 N 39 I
<b>2b + E-2b</b>	30	54	G 30 S <sub>C</sub> 55 I

<sup>a</sup> Phases were recognized by POM and X-ray diffraction. G: glassy; S<sub>C</sub>: bilayer smectic C mesophase; S<sub>A</sub>: bilayer smectic A mesophase; S<sub>A</sub>: modulated antiphase smectic A mesophase; N: nematic mesophase; I: isotropic melt.

POM and X-ray diffraction. As we can see, the mesophase structure always coincides with that of the polymer. This shows that the mesomorphic properties of diluents do not strongly affect the mesophase organization of the polymers even when the diluents have no liquid crystalline properties (naphthalene derivatives). This is probably due to the small proportion of reactive diluent used. However, because of the mobility introduced by the diluent, there was always a drop in the isotropization temperature.

When the mixtures of the biphenyl derivatives were studied by POM, the textures were the same as those developed by the corresponding polymers [1]. So, when the mixtures were cooled from the isotropic phase, bâtonnets were formed. These bâtonnets coalesced and developed a slight focal-conic texture. These observations are consistent with a smectic A or a smectic C mesophase [11]. Naphthalene derivative mixtures did not develop a texture that was good enough to be identified.

We assigned the mesophase using X-ray diffraction experiments on mechanically oriented samples. This orientation was performed by shearing the polymer–diluent mixtures at a temperature on the mesophase and suddenly cooling to room temperature to freeze the mesophase order. We studied these samples by powder X-ray diffraction and recorded pole figures [12] to see the relative orientation of the diffraction planes.

Table 4 shows the diffractions and the corresponding reticular spacings for the polymers and mixtures. In general,

Table 2

$d_{hkl}$  spacings (Å) of the liquid crystal phases of methyl esters

Ester	Mesophase	Low-angle region	High-angle region	Ester length (Å) <sup>a</sup>
<b>E-1a</b>	S <sub>B</sub>	21.7 (4.1), 10.9 (8.1), 7.2 (12.2)	4.5 (19.5), 4.1 (21.8), 3.3 (27.3)	19.8
<b>E-1b</b>	S <sub>E</sub> S <sub>A</sub>	28.9 (3.0), 14.4 (6.1), 9.5 (9.3) 28.7 (3.1), 14.3 (6.2)	4.6 (19.5), 4.5 (19.7), 4.1 (21.7) 4.3 (20.4) <sup>b</sup>	26.2

<sup>a</sup>  $2\theta$  values between brackets.

<sup>a</sup> Calculated by Cerius2 molecular modeling program.

<sup>b</sup> This diffraction is broad.

Table 4  
 $d_{hkl}$  spacings (Å) of the mesophases of the polymer-reactive diluent mixtures

		Low-angle region	High-angle region <sup>a</sup>
Polymer	<b>1a</b>	30.2 (2.9), 22.7 (3.9)	4.4 (20.0)
	<b>1b</b>	44.1 (2.0), 22.1 (4.0)	4.3 (20.5)
	<b>2a</b>	26.1 (3.4) <sup>a</sup>	4.3 (20.5)
	<b>2b</b>	37.7 (2.4), 18.7 (4.7)	4.3 (20.5)
Mixture	<b>1a + E-1a</b>	29.0 (3.0), 22.2 (4.0)	4.5 (19.7)
	<b>1b + E-1b</b>	44.2 (2.0), 22.7 (3.9)	4.4 (20.0)
	<b>2a + E-2a</b>	26.1 (3.4) <sup>a</sup>	4.3 (20.5)
	<b>2b + E-2b</b>	44.8 (1.9), 36.4 (2.4), 28.8 (3.9), 11.2 (7.7)	4.5 (19.6)

$2\theta$  values between brackets.

<sup>a</sup> These diffractions are broad.

powder X-ray diffraction patterns and pole figures coincided for polymers and the corresponding mixtures. This shows that the mesophase organization was the same. The only exception was polymer **2b**; since for the mixture, in addition to the reflection at  $2\theta = 2.4^\circ$  due to the smectic order, which was also seen in the polymer, three less intense reflections appeared in the low angle region. If we compare this with the X-ray pattern of the diluent (Fig. 2), we can see that in the mixture coexists a small amount of crystalline ester **E-2b** and thus the mixture is not completely homogeneous.

After the thermal study of the polymer–diluent mixtures, we used radical initiators [13,14,15,16] to study their crosslinking and obtain anisotropic networks. For this we

had to choose initiators that promote the crosslinking of each mixture in the mesophase. Since, as mentioned above, introducing the diluents does not strongly affect the order and stability of the mesophases, we used the same initiator systems as for the crosslinking of the pure polymers in a previous study [2]. We, therefore, chose dicumyl peroxide for biphenyl derivatives and the lauroyl peroxide–DMAP system for the naphthalene derivative **2b**.

In the crosslinking study of pure naphthalene derivative **2a** [2] it was not possible to obtain an anisotropic reticulated material, at least in a relatively short time, due to the low isotropization temperature. Since in this case the addition of the corresponding reactive ester slightly reduces this temperature, the crosslinking of the mixture of **2a** was not further studied.

For the crosslinking of the other mixtures, we first recorded a dynamic DSC scan to choose a suitable temperature to allow crosslinking in the mesophase and determine the whole enthalpy of the reaction. A fresh sample was then isothermally cured at the selected temperature and a second dynamic scan was then run to measure the residual enthalpy.

Table 5 shows the peroxide-initiated crosslinking data of the mixtures and polymers. For the mixtures of biphenyl derivatives, a complete crosslinking in the mesophase was achieved with dicumyl peroxide under slightly milder conditions than in pure polymers. Reactive diluents, therefore, seem to facilitate the reaction. As expected, cure samples were insoluble in solvents in which the polymers

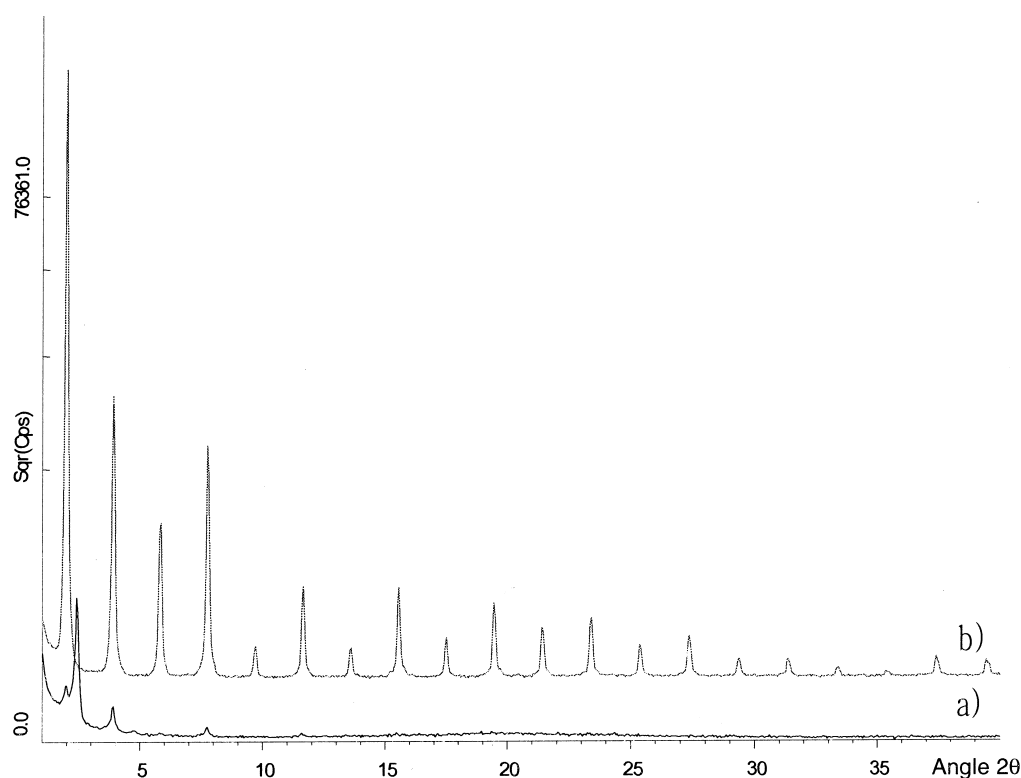


Fig. 2. Powder X-ray diffraction patterns of (a) **2b/E-2b** mixture, and (b) **E-2b** ester.

Table 5  
Isothermal DSC peroxide-initiated crosslinking of polymer-reactive diluent mixtures

		Initiator	Temperature of curing (°C)	Total crosslinking enthalpy (J/g)	Residual enthalpy (J/g)
Polymer	<b>1a</b>	PDC	175	153	0
	<b>1b</b>	PDC	145	161	16
	<b>2b</b>	PL/DMAP <sup>a</sup>	50	115	85
Mixture	<b>1a + E-1a</b>	PDC	150	130	0
	<b>1b + E-1b</b>	PDC	145	132	0
	<b>2b + E-2b</b>	PL/DMAP <sup>a</sup>	50	52	50
			50 <sup>b</sup>	52	43

The double bond–peroxide molar ratio used was 10:1. Time of curing was 2 h.

<sup>a</sup> The PL–DMAP molar ratio used was 20:1.

<sup>b</sup> Time of curing was 4 h.

were soluble. Moreover, in the second DSC dynamic scan, there was no endotherm due to the isotropization process, which indicates that an anisotropic thermoset was formed. POM studies of the cured polymer–diluent–initiator mixtures confirmed the absence of isotropization. In both cases the textures coincided with those of the uncured mixtures. IR spectra of the mixtures before and after isothermal crosslinking showed that the consumption of double bonds was not complete, as inferred by the presence of the C=C stretching band at 1642 cm<sup>-1</sup> in the spectra of the crosslinked materials.

For the crosslinking of the naphthalenic derivative **2b** mixture, an initiator with a low decomposition temperature, the lauroyl peroxide–DMAP system, was needed to set the mesophase order. This was because of its lower isotropization temperature. Although tertiary amines are described to promote the decomposition of peroxides [13], in this case only a slight degree of reticulation was achieved, probably because of the low reaction temperature selected. In fact, a longer reaction time (4 h) only slightly increases the extent of the reaction. Also, reacted mixtures were soluble in several solvents and the isotropization process was observed by both DSC and POM studies.

We obtained mechanically oriented crosslinked samples by curing after shearing and then X-ray powder diffraction patterns and pole figures were recorded. In no case did the mesophase structure seem to be changed by crosslinking, so the mesophase order was retained. Thus the formation of anisotropic thermosets from mixtures of polymers **1a** and **1b** was confirmed.

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