Vinyl-Terminated Side-Chain Liquid-Crystalline Poly(epichlorohydrin) Derivatives Containing Biphenyl and Naphthalene Mesogenic Moieties

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ABSTRACT: Poly(epichlorohydrin) (PECH) was modified to a considerable extent with mesogenic acids, namely 4′-(*ω*-alkenoxy)-4-biphenylcarboxylic acids and 6-(*ω*-alkenoxy)-2-naphthalenecarboxylic acids, which leads to side chain liquid crystalline polymers which can be cross-linked through their terminal double bonds in a further step. Cleavage and cross-linking side reactions, which have been reported elsewhere, were observed. The polymers were characterized by NMR, IR, SEC-MALLS, viscosimetry, elemental analysis, DSC, and TGA. The thermal stability of the modified polymers was higher than that of the starting PECH. The mesophases were identified by DSC, light-polarized optical microscopy, and X-ray diffraction. The biphenyl derivatives show smectic A mesophases consisting of a bilayer or partial bilayer structure, which is modulated for the 4′-(5-hexenoxy)-4-biphenylcarboxylic acid derivatives ($S_{\tilde{A}}$). The 6-(5-hexenoxy)-2-naphthalenecarboxylic acid and the 6-(10-undecenoxy)-2-naphthalenecarboxylic acid derivatives show nematic and smectic C mesophases, respectively.

Introduction

Side-chain liquid-crystalline polymers (SCLCP's), which combine liquid-crystalline behavior and polymeric properties, have been the subject of intensive research over the last 20 years, due to their wide range of applications as high-performance materials.[1]

When these polymers are properly functionalized, they can lead, through cross-linking reactions, to either liquid-crystalline elastomers[2−5] or liquid-crystalline thermosets,[6,7] depending on the degree of cross-linking. The former have interesting optical properties, since they are capable of showing the orientation of the liquid-crystalline domains through mechanical stress. The latter are expected to have better mechanical properties in the direction transverse to the orientation direction.

Liquid-crystalline polymeric networks can be obtained either by photocrosslinking,[8] thermal cross-linking[9] or by a stoichiometric chemical reaction between the liquid-crystalline polymer and suitable cross-linking agents.[2,3]

Many studies into the synthesis and characterization of SCLCP's have been based on the need to insert a flexible spacer between the polymeric backbone and the mesogenic side group to decouple the motions of the main chain and side groups in the liquid-crystalline state.[10] However, when the main chain is a polyether, the flexibility of the polymer skeleton allows liquid crystalline behavior even when the spacer is short.[11] These polyethers can be synthesized either by ring-opening polymerization of mesogen-containing cyclic ethers[12−15] or by chemical modification of a preformed polyether such as poly(epychlorohydrin) (PECH).[16−18]

On the basis of our previous work on the synthesis and cross-linking of PECH[19−21] and poly(epybromohydrin) derivatives,[22] this study attempts to synthesize side-chain liquid-crystalline polyethers by nucleophilic substitution of PECH with carboxylic acids which contain biphenyl and naphthalene units as mesogens. These polymers also contain vinyl moieties which can act as cross-linkable functional groups in a further step. Preliminary results have shown the cross-link capability of these materials with, for example, peroxide-type radical initiators. However, the need to carry this cross-link on the mesophase involves a more wide work to be performed, which will be the topic of a forthcoming paper. The structure of the acids used is shown in Scheme 1.

Experimental Section

Materials. The solvents were purified by distillation prior to use, except for synthesis grade (Fluka-Chemie AG) dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP), which were used without previous purification.

Synthesis grade (Fluka-Chemie AG) 6-bromo-1-hexene, 10-undecen-1-ol, 4-phenylphenol, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), and tosyl chloride, synthesis grade (Aldrich-Chemie) 6-bromo-2-naphthol and 18-crown-6, synthesis grade (Acros) triphenylcarbenium hexafluorophosphate, Aldrich-Chemie triphenylcarbenium hexachloroantimoniate and Purum (Panreac) inorganic reagents were used without further purification. Epychlorohydrin (ECH: Fluka-Chemie AG) was dried over calcium hydride and distilled prior to use.

High molecular weight poly(epichlorohydrin) (PECH, η_{inh} = 2.44 dL/g, $\bar{M}_w$ = 968 000) was supplied by Aldrich-Chemie. Two low molecular weight PECH's were synthesized through triphenylcarbenium hexafluorophosphate (PECH-I) and triphenylcarbenium hexachloroantimoniate (PECH-II) promoted cationic polymerization of ECH.[23] Thus, 20 mL (256 mmol) of ECH was cooled to −5 °C under nitrogen, and then 2.56 mmol of the initiator was dissolved in dichoromethane and added. The mixture was stirred at room temperature for 4 days. The crude polymer was purified by reprecipitating several times from dichloromethane into methanol, and finally dried in

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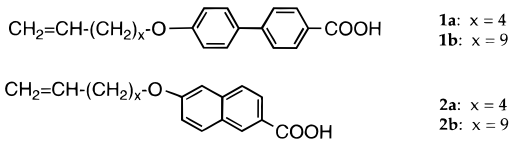
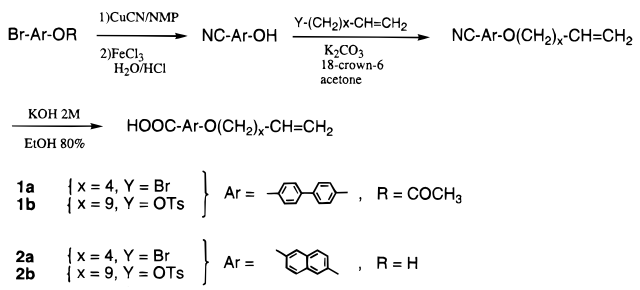
Scheme 1



Scheme 2



vacuo. (PECH-I, $\eta_{inh} = 0.11$ dL/g, $\bar{M}_w = 22\,600$; PECH-II, $\eta_{inh} = 0.01$ dL/g, $\bar{M}_w = 10\,400$). The ^{13}C NMR (DMSO-d_6) spectra of these polymers show that there are some enchainment irregularities (head-to-head and tail-to-tail).[24]

10-Undecen-1-yl tosylate and 4-acetoxy-4′-bromobiphenyl were synthesized according to published procedures from 10-undecen-1-ol[25] and 4-phenylphenol[26] respectively.

Synthesis of Mesogenic Acids. A general procedure for the synthesis of mesogenic acids is as follows (Scheme 2).

Synthesis of the Hydroxynitrile. A 81 mmol sample of the bromo derivative (23.5 g of 4-acetoxy-4′-bromobiphenyl or 18.1 g of 6-bromo-2-naphthol), 112 mmol (10.0 g) of copper(I) cyanide and 70 mL of NMP were placed in a 500 mL round-bottomed flask. The mixture was heated at 200 °C and magnetically stirred for 6 h under argon. After cooling, the reaction crude was poured into a mixture of 112 mmol (31.7 g) of iron(III) trichloride, 8 mL of concentrated hydrochloric acid, and 47 mL of water and then stirred at 70 °C for 20 min. The resulting mixture was extracted several times with diethyl ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate, and then ether was removed under vacuum and the solid obtained was recrystallized from 1:4 methanol−chloroform (biphenyl derivative) or from water (naphthalene derivative).

Synthesis of the Unsaturated Acid. A 81 mmol sample of hydroxynitrile (15.8 g of 4′-hydroxy-4-biphenylcarbonitrile or 13.7 g of 6-hydroxy-2-naphthalenecarbonitrile), 97 mmol of the alkenyl derivative (15.8 g of 6-bromo-1-hexene or 31.1 g of 10-undecen-1-yl tosylate), 4.0 mmol (1.1 g) of 18-crown-6, 243 mmol (33.6 g) of potassium carbonate, and 500 mL of acetone were placed in an 1 L round-bottomed flask. The mixture was refluxed and magnetically stirred, and the evolution of the reaction was followed by TLC (chloroform−methanol 10:1). After the reaction had finished (20−24 h), the reaction crude was left to cool, the salts were filtered off, and acetone was eliminated at lower pressure. In this way, a yellowish oil was obtained which was refluxed with 200 mL of 2 M KOH in ethanol. This reaction was followed by TLC (chloroform−methanol 10:1). After the reaction had finished (4−6 h), the ethanol was eliminated under vacuum. From the resulting solid, the free acid was obtained after stirring with diluted hydrochloric acid for several hours, filtering off, washing with water, and drying under vacuum at 50 °C. The crude acid was recrystallized from 1:3 toluene−heptane (naphthalene derivatives) or from acetone (biphenyl derivatives).

The characterization data are as follows.

4′-(5-Hexenoxy)-4-biphenylcarboxylic acid (1a). Overall yield: 81%. Liquid crystal transitions: 207, 238, 269 °C. IR (KBr, cm^{-1}): 3075 (C−H alkene and aromatic), 2938 and 2869 (C−H aliphatic), 1678 (C═O), 1640 (C═C), 1601 (C−C aromatic), 1195 (C−O). ^{1}H NMR (DMSO-d_6, 300 MHz, δ (ppm)): 1.6 (m, 2H), 1.8 (m, 2H), 2.2 (m, 2H), 4.0 (t, 2H, $J = 7$ Hz), 4.9 (dd, 1H, $J = 16$ Hz, $J = 2$ Hz), 5.1 (dd, 1H, $J = 24$ Hz, $J = 2$ Hz), 5.8 (m, 1H), 7.0 (d, 2H, $J = 9$ Hz), 7.6 (m, 4H), 7.9 (d, 2H, $J = 9$ Hz), 12.9 (s, 1H). ^{13}C NMR (DMSO-d_6, 75.4 MHz, δ (ppm)): 24.7 (t), 28.2 (t), 32.9 (t), 67.4 (t), 115.1 (t), 115.7 (d), 126.3 (d), 128.3 (d), 129.0 (d), 130.2 (s), 131.3 (s), 138.8 (d), 144.2 (s), 159.2 (s), 167.5 (s).

4′-(10-Undecenoxy)-4-biphenylcarboxylic acid (1b). Overall yield: 71%. Liquid crystal transitions: 124, 162, 247 °C. IR (KBr, cm^{-1}): 3079 (C−H alkene and aromatic), 2924 and 2853 (C−H aliphatic), 1687 (C═O), 1643 (C═C), 1604 (C−C aromatic), 1195 (C−O). ^{1}H NMR (DMSO-d_6, 300 MHz, δ (ppm)): 1.3 (m, 12H), 1.8 (m, 2H), 2.1 (m, 2H), 4.0 (t, 2H, $J = 7$ Hz), 4.9 (dd, 1H, $J = 15$ Hz, $J = 2$ Hz), 5.0 (dd, 1H, $J = 21$ Hz, $J = 2$ Hz), 5.8 (m, 1H), 7.0 (d, 2H, $J = 8$ Hz), 7.6 (m, 4H), 7.9 (d, 2H, $J = 8$ Hz), 12.9 (s, 1H). ^{13}C NMR (DMSO-d_6, 75.4 MHz, δ (ppm)): 25.5 (t), 28.2 (t), 28.5 (t), 28.6 (t), 28.7 (t), 28.8 (t), 28.9 (t), 33.2 (t), 67.6 (t), 114.7 (t), 115.1 (d), 126.2 (d), 128.2 (d), 129.0 (d), 130.1 (s), 131.2 (s), 139.0 (d), 144.2 (s), 159.2 (s), 167.4 (s).

6-(5-Hexenoxy)-2-naphthalenecarboxylic acid (2a). Overall yield: 89%. Thermal transitions: 126, 141, 186 °C. IR (KBr, cm^{-1}): 3070 (C−H alkene and aromatic), 2934 and 2865 (C−H aliphatic), 1682 (C═O), 1623 (C−C aromatic naphthalene), 1208 (C−O). ^{1}H NMR (DMSO-d_6, 300 MHz, δ (ppm)): 1.5 (m, 2H), 1.7 (m, 2H), 2.0 (m, 2H), 4.1 (t, 2H, $J = 6$ Hz), 4.9 (dd, 1H, $J = 16$ Hz, $J = 2$ Hz), 5.0 (dd, 1H, $J = 24$ Hz, $J = 2$ Hz), 5.8 (m, 1H), 7.2 (dd, 1H, $J = 9$ Hz, $J = 2$ Hz), 7.4 (d, 1H, $J = 2$ Hz), 7.8 (dd, 1H, $J = 9$ Hz, $J = 2$ Hz), 7.9 (d, 1H, $J = 9$ Hz), 8.0 (d, 1H, $J = 9$ Hz), 8.5 (d, 1H, $J = 2$ Hz), 12.9 (s, 1H). ^{13}C NMR (DMSO-d_6, 75.4 MHz, δ (ppm)): 24.7 (t), 28.0 (t), 32.8 (t), 67.6 (t), 106.7 (d), 115.1 (t), 119.8 (d), 125.8 (s), 125.9 (d), 127.0 (d), 127.6 (s), 130.6 (d), 131.1 (d), 136.9 (s), 138.7 (d), 158.7 (s), 167.8 (s).

6-(10-Undecenoxy)-2-naphthalenecarboxylic acid (2b). Overall yield: 92%. Liquid crystal transitions: 120, 146, 176 °C. IR (KBr, cm^{-1}): 3075 (C−H alkene and aromatic), 2937 and 2850 (C−H aliphatic), 1682 (C═O), 1640 (C═C), 1623 (C−C aromatic naphthalene), 1209 (C−O). ^{1}H NMR (DMSO-d_6, 300 MHz, δ (ppm)): 1.3 (m, 12H), 1.7 (m, 2H), 2.0 (m, 2H), 4.0 (t, 2H, $J = 6$ Hz), 4.9 (dd, 1H, $J = 11$ Hz, $J = 2$ Hz), 5.0 (dd, 1H, $J = 21$ Hz, $J = 2$ Hz), 5.7 (m, 1H), 7.2 (dd, 1H, $J = 9$ Hz, $J = 2$ Hz), 7.3 (d, 1H, $J = 2$ Hz), 7.8 (d, 1H, $J = 9$ Hz), 7.9 (dd, 1H, $J = 9$ Hz, $J = 2$ Hz), 8.0 (d, 1H, $J = 9$ Hz), 8.5 (d, 1H, $J = 2$ Hz), 12.9 (s, 1H). ^{13}C NMR (DMSO-d_6, 75.4 MHz, δ(ppm)): 25.5 (t), 28.3 (t), 28.5 (t), 28.6 (t), 28.7 (t), 28.8 (t), 28.9 (t), 33.2 (t), 67.7 (t), 106.6 (d), 114.7 (t), 119.7 (d), 125.8 (s), 125.9 (d), 127.0 (d), 127.6 (s), 130.6 (d), 131.0 (d), 136.9 (s), 139.0 (d), 158.7 (s), 167.8 (s).

Chemical Modification Reactions. A general procedure for modifying PECH with mesogenic acids **1a**, **1b**, **2a**, and **2b** is as follows.

In a 100 mL round-bottomed flask, 10 mmol (0.92 g) of PECH was dissolved in 60−70 mL of DMSO, and then 12 or 15 mmol of the corresponding acid and the same amount of DBU were added. The reaction mixture was stirred at several temperatures and reaction times in the dark, and then the modified polymer was precipitated by adding water. The crude polymer was purified by reprecipitating several times from tetrahydrofuran (THF) or dichlorometane into methanol and dried in vacuo at 60 °C. ^{1}H ($CDCl_3$, 300 MHz, δ (ppm)) and ^{13}C ($CDCl_3$, 75.4 MHz, δ (ppm)) NMR data are shown in Tables 1 and 2. IR data (KBr, cm^{-1}) are as follows.

PECH Modified with 4′-(5-Hexenoxy)-4-biphenylcarboxylic acid (1a): 3078 (C−H alkene and aromatic), 1720 (C═O), 1642 (C═C), 1607 (C−C aromatic).

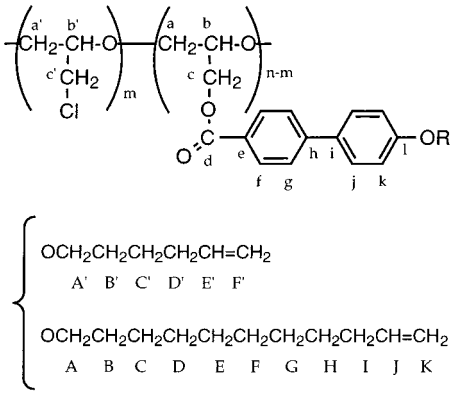
PECH Modified with 4′-(10-Undecenoxy)-4-biphenylcarboxylic acid (1b): 3075 (C−H alkene and aromatic), 1716 (C═O), 1642 (C═C), 1607 (C−C aromatic).

PECH Modified with 6-(5-Hexenoxy)-2-naphthalenecarboxylic acid (2a): 3069 (C−H alkene and aromatic), 1713 (C═O), 1627 (C−C aromatic naphthalene).

PECH Modified with 6-(10-Undecenoxy)-2-naphthalenecarboxylic acid (2b): 3069 (C−H alkene and aromatic), 1713 (C═O), 1627 (C−C aromatic naphthalene).

Instrumentation. Liquid crystal transitions and T_g's were determined on a Mettler DSC-30 thermal analyzer using

Table 1. ^{1}H and ^{13}C NMR Spectroscopic Data for the Polymers Containing 4′-(Alkenoxy)-4-biphenylcarboxylate Groups



^{1}H NMR data		^{13}C NMR data	
resonances	assignment	resonances	assignment
1.2−1.4	C, D, E, F, G, H	25.2	C′
1.5	C′	25.9	C
1.7	B′	28.6	B′
1.8	B	28.7−29.4	B, D, E, F, G, H
2.0	I	33.3	D′
2.1	D′	33.7	I
3.4−4.0	a, b, a′, b′, c′, A, A′	43.5	c′
4.2−4.6	c	64.1	c
4.9	F′, K	67.6	A, A′
5.8	E′, J	69.7−69.8	a, a′
6.7−6.8	k	77.7	b
7.3−7.4	g, j	78.9	b′
7.8−7.9	f	114.2	K
		114.7−114.8	F′, k
		126.3	g
		127.9−128.3	e
		128.2−130.2	j
		130.1−130.7	f
		131.9−132.0	i
		138.5−139.2	E′, J
		145.0	h
		159.3−159.5	l
		166.2	d

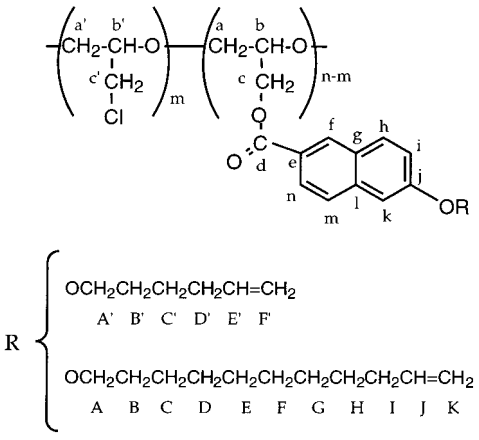
samples of ca. 5 mg in covered Al pans under a nitrogen atmosphere and at a heating rate of 20 °C/min. Thermogravimetric analyses were carried out with a Perkin-Elmer TGA-7 system under a nitrogen atmosphere at a heating rate of 10 °C/min up to 800 °C. IR spectra were recorded on a Midac Prospect-IR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained using a Varian Gemini 300 spectrometer with $CDCl_3$ or DMSO-d_6 as solvents and TMS as internal standard. Elemental analyses were performed using a Carlo Erba 1106 device. The chlorine content was determined by Schöninger's method, which involves the combustion of a sample on a platinum wire in a closed vessel. Inherent viscosities (η_{inh}) were measured in NMP-solutions (ca. 2 g/L) at 30 °C on a Schott-Geräte AVS 310 viscosimeter.

Weight-average molecular weights were determined on a SEC-MALLS system, made up of an HPLC WATERS 510-GPC pump, a Shodex K-800P precolumn, three serial columns (Shodex K-80 M, PLgel 3μ MIXED-E, and PLgel 5μ MIXED-D from Polymer Laboratories), a light-scattering detector (Mini-DAWN, Wyatt Technology), and a refractive index detector (Shimadzu RID-6A) using THF (MALLINCRODT ChromAR HPLC) as eluent. The data were processed with the ASTRette 1.2 program for Macintosh (Wyatt Technology).

The textures of the mesophases were observed with a polarizing microscope (AXIOLAB Zeiss) equipped with a LINKAM THMS 600 hot-stage connected to a TP-92 temperature control unit.

X-ray Diffraction Measurements. Powder X-ray diffraction measurements were performed at different temperatures on a Siemens D5000 diffractometer with $\theta-\theta$ configuration

Table 2. ^{1}H and ^{13}C NMR Spectroscopic Data for the Polymers Containing 6-(alkenoxy)-2-naphthalenecarboxylate Groups



^{1}H NMR data		^{13}C NMR data	
resonances	assignment	resonances	assignment
1.2−1.4	C, D, E, F, G, H	25.1	C′
1.5	C′	25.9	C
1.7	B′	28.4	B′
1.8	B	28.6−29.4	B, D, E, F, G, H
2.0	I	33.3	D′
2.1	D′	33.7	I
3.4−4.0	a, b, a′, b′, c′, A, A′	43.6	c′
4.2−4.6	c	63.9−64.0	c
5.0	F′, K	67.6−67.9	A, A′
5.8	E′, J	69.6−70.0	a, a′
6.8−6.9	i	77.7	b
7.0−7.1	k	78.9	b′
7.4	m	106.2	k
7.5	h	114.2−114.8	F′, K
7.8	n	119.6−119.8	i
8.4	f	124.7	e
		125.7	h
		126.7−126.8	m
		127.6	g
		130.8−130.9	f, n
		137.1−137.2	l
		138.5−139.2	E′, J
		158.9−159.0	j
		166.5	d

and fitted with an Anton Paar TTK temperature chamber. Cu Kα radiation was used, and graphite was the secondary monochromator. The Bragg angle step was 0.05° and the time per step 3 s.

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

The polymer samples studied by X-ray diffraction were oriented by shearing the polymer on the mesophase, and the mesophase order was maintained by suddenly reducing the temperature below T_g.

Results and Discussion

The acids **1a**, **1b**, **2a**, and **2b** were synthesized in all cases in several steps (Scheme 2), and the overall yields were fairly good (71−92%). As can be seen, the vinyl-terminated aliphatic chain was introduced by a nucleophilic substitution reaction of the phenolic group on a bromide or tosylate derivative, whereas the carboxyl group was introduced by cyanation and alkaline hydrolysis of the nitrile group incorporated.

Differential scanning calorimetry (DSC), light-polarized optical microscopy (POM), and X-ray diffraction studies proved that all these acids behave like liquid

Table 3. Thermal Properties of Synthesized Monomers[a]

monomer	thermal transitions in °C
1a	K 207 S_A 238 N 269 I
1b	K 124 S_E 162 S_A 247 I
2a	K_1 126 K_2 141 N 186 I
2b	K 120 S_C 146 N 176 I

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

crystals, and for most of them two different mesophases were recognized (Table 3). All these compounds have already been reported in the literature,[27−29] although only the liquid crystal transitions of acid **1a** have been described.[29]

Nematic mesophases were recognized because nematic liquids come from the isotropic liquids in the form of droplets which after further cooling grow and coalesce to form large domains. The smectic A and C mesophases develop a focal conic texture after annealing for several hours at a suitable temperature. Monomers **1a** and **2b** led to transient stripes in the form of a myelinic texture (Figure 1a) when the samples were slowly cooled from the nematic mesophase, which agrees with the abovementioned smectic A or C phases. On the other hand, cooling of monomer **1b** from the isotropic liquid gave to formation of bâtonnets, which also indicated a smectic A or C mesophase.

Monomer **1a** also develops a polygonal texture (see Figure 1b), which indicates that this mesophase is a smectic A. Monomer **1b** develops a smectic E phase when it cools from the other smectic state as an arced fan-shaped texture (see Figure 1c). Thus, its smectic phase at higher temperatures should be a smectic A. Monomer **2b** was seen to have a smectic C phase since its focal-conic texture seems to be broken and a sanded texture was also observed.[30,31]

X-ray diffraction patterns were recorded at several temperatures and were all in accordance with POM observations. Table 4 shows the d_{hkl} spacings and the corresponding 2θ values for each mesophase. As can be seen, the smectic A and C mesophases were recognized because of the appearance of a single sharp reflection in the low-angle region. For the smectic E mesophase, in addition to the smectic reflection, several fine reflections in the high-angle region appear. Moreover, monomer **2a** was seen to have a second crystal phase, since its X-ray pattern has many sharp reflections.

PECH was chemically modified with the mesogenic acids synthesized by using DMSO as a solvent and a bulky base, such as DBU, to enhance the nucleophilicity of the acid.[19,32] Several reaction conditions, namely reaction time, temperature, and acid/polymer ratio, were tested in order to reach the maximum degree of modification. Moreover, since the molecular weight of the starting PECH, and hence that of the modified polymers, may influence the development of the mesophases, we used three PECH of different molecular weight as starting material, namely a commercial high molecular weight polymer ($\bar{M}_w$ = 968 000) and two low molecular weight samples of $\bar{M}_w$ = 22 600 and $\bar{M}_w$ = 10 400, which have been synthesized by cationic polymerization using triphenylcarbenium hexafluorophosphate and triphenylcarbenium hexachloroantimoniate as catalysts,[23] respectively.

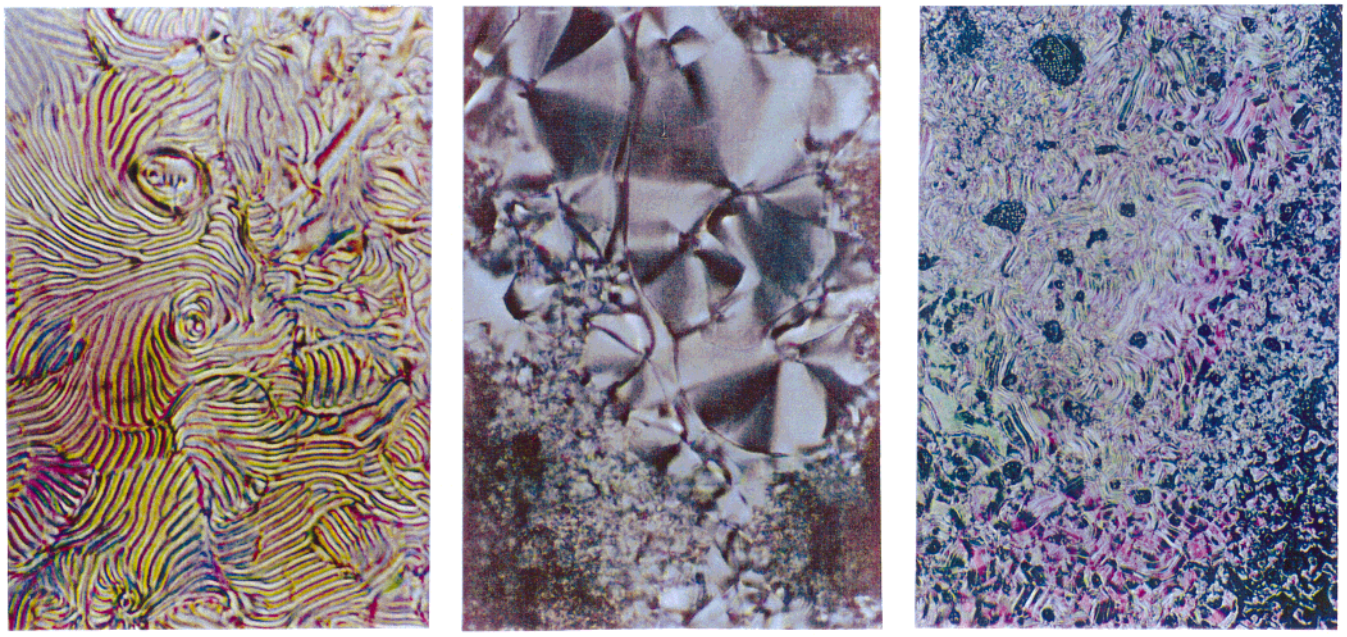
Table 5 shows the results of chemically modifying high molecular weight PECH. As can be seen, for the monomers with the shorter aliphatic chain, degrees of modification were high (>90%) when the reaction was carried out with an acid/polymer molar ratio of 1.5 at 90 °C during 2 days. For monomers **1b** and **2b**, which have a longer aliphatic chain, degrees of modification were slightly lower, and longer reaction times led to cross-linked materials, probably through double-bond polymerization reactions.[33]

The $\bar{M}_w$ values obtained indicate that the polymeric main chain degraded quite considerably during the reaction. Several papers[17,34−36] have reported that this process is an important side reaction when PECH is chemically modified through nucleophilic substitution reactions. On the other hand, although at first sight it may seem meaningless to compare viscosity values because the hydrodynamic volumes of the polymers should be considerably different, the viscosity values of all the modified polymers were much lower than virgin PECH, which suggests that the cleavage side reaction takes place.

Table 6 shows the results of chemically modifying low molecular weight PECH's. As can be seen, the degrees of modification were higher than 90% when the reaction took place at 90 °C for 4 days and with an acid/polymer molar ratio of 1.5. In these conditions, all products were soluble, which indicates that they are not cross-linked. The $\bar{M}_w$ values obtained seem to indicate that no strong degradation took place unlike for the high molecular weight PECH derivatives. However, it must be kept on mind that double bonds polymerization reactions, leading to branching, can also occur, and that each side reaction, cleavage or branching, can take place in a different extent depending of the molecular weight of the polymer, due to the different local concentration of the reactive sites.

The structure of the polymers synthesized was confirmed by IR and ^{1}H and ^{13}C NMR spectroscopy. Of the IR bands, the C═O (ester) at ca. 1715 cm^{-1}, the C═C at 1642 cm^{-1}, the naphthalene aromatic C−C at 1627 cm^{-1} and the biphenyl aromatic C−C at 1607 cm^{-1} are the most important. Tables 1 and 2 show the assigments of all the NMR signals. These assignments were made by empirical calculations, comparison with the spectra of starting PECH and mesogenic acids and, in the case of naphthalene derivatives, with the help of the two-dimensional ^{1}H−^{13}C correlated NMR spectrum of monomer **2a**. What is more, by integration of the ^{1}H NMR signals, the degree of modification could be estimated. In all cases, this agreed with the values determined by chlorine elemental analysis.

The polymers were thermally characterized by DSC and thermogravimetrical analysis (TGA). The DSC data are summarized in Tables 7 and 8 for high and low molecular weight PECH derivatives, respectively. As can be seen, all T_g values are higher than the T_g of starting PECH, and as a general trend, they increase with the degree of modification. This observation is in agreement with the introduction of stiff aromatic moieties in the polymeric matrix. In all DSC curves a large exotherm appears between 330 and 450 °C, which can be attributable to the thermal degradation and the thermally initiated cross-linking through double bonds. The TGA curves showed that the thermal stability of the polymers increases with the degree of modification, as is illustrated in Figure 2 for the low molecular weight PECH **1a** derivatives (experiments 11−13). This may be because of the subsequent lower extent of the thermal



a b c

Figure 1. 100× magnified POM photographs: (a) mylelinic texture of monomer **2b** at 140 °C; (b) polygonal texture of the smectic A mesophase of monomer **1a** at 213 °C; (c) arced fan-shaped texture of the smectic E mesophase of monomer **1b** at 159 °C. All the textures were formed upon cooling from an isotropic melt.

Table 4. d_{hkl} Spacings (Å) of the Liquid Crystal Mesophases in the Acids[a]

acid	mesophase	low-angle region	high-angle region
1a	S_A	28.7 (3.1)	4.6 (19.1)[b]
	N		4.6 (19.1)[b]
1b	S_E	33.5 (2.6), 19.6 (4.5), 17.3 (5.1)	9.7 (9.1), 7.7 (11.5), 6.4 (13.8), 4.9 (18.2), 4.5 (19.6)
	S_A	35.8 (2.5), 17.7 (5.0)	4.8 (18.4)[b]
2a	N		4.5 (19.6)[b]
2b	S_C	33.9 (2.6)	4.5 (19.5)[b]
	N		4.6 (19.2)[b]

[a] 2θ values between brackets. [b] These diffractions are wide.

Table 5. Substitution Reactions of High Molecular Weight PECH with Vinyl-Terminated Mesogenic Acids

expt	meso-genic acid	acid/ ECH unit	temp (°C)	reacn time (days)	deg of substn[a] (mol %)	yield (%)	inherent viscosity (dL/g)	$\bar{M}_w$
1	**1a**	1.5	90	2	92	84	0.29	16 000
2	**1a**	1.2	90	1	77	57	0.43	41 000
3	**1a**	1.2	60	7	72	73	0.21	29 000
4	**1b**	1.5	90	2	80	93	0.14	18 000
5	**1b**	1.2	90	1	61	98	0.16	17 000
6	**1b**	1.5	90	4	80	80	cross-linked	
7	**2a**	1.5	90	2	98	93	0.45	94 000
8	**2b**	1.5	90	2	71	94	0.21	55 000
9	**2b**	1.5	90	4	75	71	cross-linked	
10	**2b**	1.5	90	7	99	76	cross-linked	
PECH							2.44	968 000

[a] Determined by chlorine elemental analysis.

dehydrochlorination reaction[37] and the higher extent of the thermally initiated cross-linking.

Identification of the Mesophases. In the DSC curves of some polymers an endotherm appears at temperatures between the T_g and the degradation, which could be caused either by fusion processes or by liquid crystal transitions. The values of these endotherms are summarized in Tables 7 and 8. POM observations indicate that these endotherms actually correspond to isotropization processes, since between T_g and these temperatures the polymers showed a liquid crystal behavior. Likewise, isotropization temperatures were observed by POM for the polymers with no DSC endotherm. As can be seen, the isotropization temperatures of biphenyl derivatives are higher than those for naphthalene derivatives. This is probably because they have greater symmetry and are therefore more easily packed.

The polymers obtained in experiments 6, 9, and 10, despite their cross-linked character, also developed mesophases. However, POM observations showed that not all regions isotropize, probably due to the sample being nonhomogeneously cross-linked.

When the polymers containing biphenyl moieties were cooled from the isotropic phase, bâtonnets were seen to form. These bâtonnets coalesce and build up a focal-conic texture after several hours of annealing at a suitable temperature. Such observations are consistent with a smectic A or a smectic C mesophase.[31]

Table 6. Substitution Reactions of Low Molecular Weight PECH's with Vinyl-Terminated Mesogenic Acids[a]

expt	meso-genic acid	acid/ polym molar ratio	reacn time (days)	deg of substn[b] (mol %)	yield (%)	inherent viscosity (dL/g)	$\bar{M}_w$
11	**1a**	1.5	2	84	77	0.06	66 200
12	**1a**	1.2	2	81	70	0.11	49 000
13	**1a**	1.5	4	97	89	0.17	74 000
14	**1b**	1.5	4	96	89	0.26	87 000
15	**2a**	1.5	2	91	45	0.09	79 000
16	**2a**	1.5	4	93	47	0.15	80 000
17	**2b**	1.5	2	89	86	0.16	45 000
18	**2b**	1.5	4	99	83	0.14	116 000
PECH-I						0.11	22 600
PECH-II						0.01	10 400

[a] All the modifications were carried out at 90 °C. In experiments 13, 14, 15, 16, and 18 the starting material was PECH-I. In experiments 11, 12, and 17 it was PECH-II. [b] Determined by chlorine elemental analysis.

Table 7. Thermal Characterization of the High Molecular Weight PECH Modified with Vinyl-Terminated Mesogenic Acids

expt	mesogenic acid	deg of substn[a] (mol %)	T_g (°C)	DSC endotherms (°C)	transition temps[b] (°C)
1	**1a**	92	89	178	G 89 $S_{\tilde{A}}$ 181 I
2	**1a**	77	68	149	G 68 $S_{\tilde{A}}$ 155 I
3	**1a**	72	58	...	G 58 $S_{\tilde{A}}$ 125 I
4	**1b**	80	39	151	G 39 S_{Ad} 159 I
5	**1b**	61	34	149	G 34 S_{Ad} 152 I
6	**1b**	80	43	177	G 43 S_{Ad} 180 I
7	**2a**	98	30	...	G 30 N 91 I
8	**2b**	71	26	...	G 26 S_C 55 I
9	**2b**	75	30	61	G 30 S_C 59 I
10	**2b**	99	41	74	G 41 S_C 78 I
PECH			−25		

[a] Determined by chlorine analysis. [b] Phases were recognized by POM and X-ray diffraction. Key: G, glassy; S_C, S_{Ad}, and $S_{\tilde{A}}$, smectic mesophases; N, nematic mesophase; I, isotropic melt.

In the acid **2a** derivatives a homeotropic texture was recognized, since the field of view remained uniformly dark when crossed polarizers were used, but a flash-like brightness was produced instantly when the glass cover of the preparation was touched. This texture is in accordance with a nematic or a smectic A mesophase.[30] The acid **2b** derivatives did not develop a texture good enough to be identified after a long period of annealing.

X-ray diffraction studies made it possible to identify the different mesophases. As can be seen in Table 9, the X-ray diffraction patterns of biphenyl derivatives show a broad diffraction located at high Bragg angles and two sharp diffractions at low 2θ values, which is in agreement with a smectic mesophase.[38] For the **1b** polymeric derivatives (experiments 4, 6, and 14) the more intense diffraction is the one located at lower angles. Likewise, the d_{hkl} spacings corresponding to the sharp reflections indicated that the one at ∼3.8° is a high-order smectic reflection. Pole figures recorded at 2θ values of the smectic and the broad reflection showed

Table 8. Thermal Characterization of the Low Molecular Weight PECH's modified with Vinyl-Terminated Mesogenic Acids[a]

expt	mesogenic acid	deg of substn[b] (mol %)	T_g (°C)	DSC endotherms (°C)	transition temps[c] (°C)
11	**1a**	84	96	150	G 96 $S_{\tilde{A}}$ 156 I
12	**1a**	81	92	143	G 92 $S_{\tilde{A}}$ 143 I
13	**1a**	97	111	194	G 111 $S_{\tilde{A}}$ 189 I
14	**1b**	96	51	163	G 51 S_{Ad} 168 I
15	**2a**	91	27	...	G 28 N 39 I
16	**2a**	93	28	...	G 24 N 41 I
17	**2b**	89	39	61	G 39 S_C 61 I
18	**2b**	99	45	60	G 45 S_C 62 I
PECH-I			−31		
PECH-II			−26		

[a] In experiments 13, 14, 15, 16, and 18 the starting material was PECH-I. In experiments 11, 12, and 17 it was PECH-II. [b] Determined by chlorine analysis. [c] Phases were recognized by POM and X-ray diffraction. G: glassy, S_C, S_{Ad}, $S_{\tilde{A}}$:smectic mesophases, N: nematic mesophase, I: isotropic melt.

Table 9. d_{hkl} Spacings (Å) of the Liquid Crystal Mesophases in the Polyethers[a]

polymer	expt	low-angle region	high-angle region[b]
high molecular weight polymers	3	29.1 (3.03), 23.5 (3.57)	4.3 (20.5)
	4	46.9 (1.88), 23.6 (3.73)	4.2 (21.0)
	6	46.3 (1.91), 23.4 (3.77)	4.3 (20.5)
	7	27.5[b] (3.21)	4.3 (20.5)
	8	39.4 (2.24), 19.5 (4.52)	4.4 (20.0)
	10	36.1 (2.45), 18.4 (4.80)	4.3 (20.5)
low molecular weight polymers	11	30.2 (2.92), 22.7 (3.89)	4.4 (20.0)
	14	44.1 (1.98), 22.1 (3.97)	4.3 (20.5)
	15	26.1[b] (3.39)	4.3 (20.5)
	17	39.6 (2.23), 20.0 (4.41)	4.3 (20.5)
	18	37.1 (2.38), 18.7 (4.70)	4.3 (20.5)

[a] 2θ values between brackets. [b] These diffractions are wide.

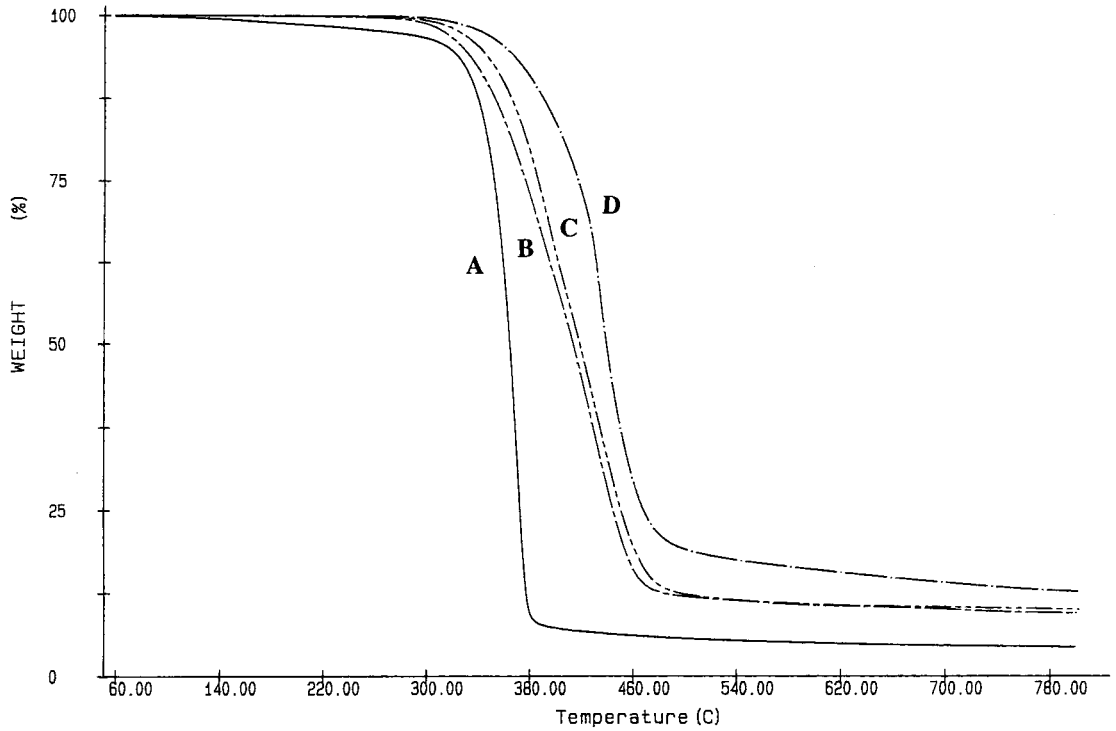


Figure 2. TGA plots of low molecular weight PECH's **1a** derivatives recorded at 10 °C/min. Degree of modification: (A) starting PECH; (B) 81%; (C) 84%; (D) 97%.

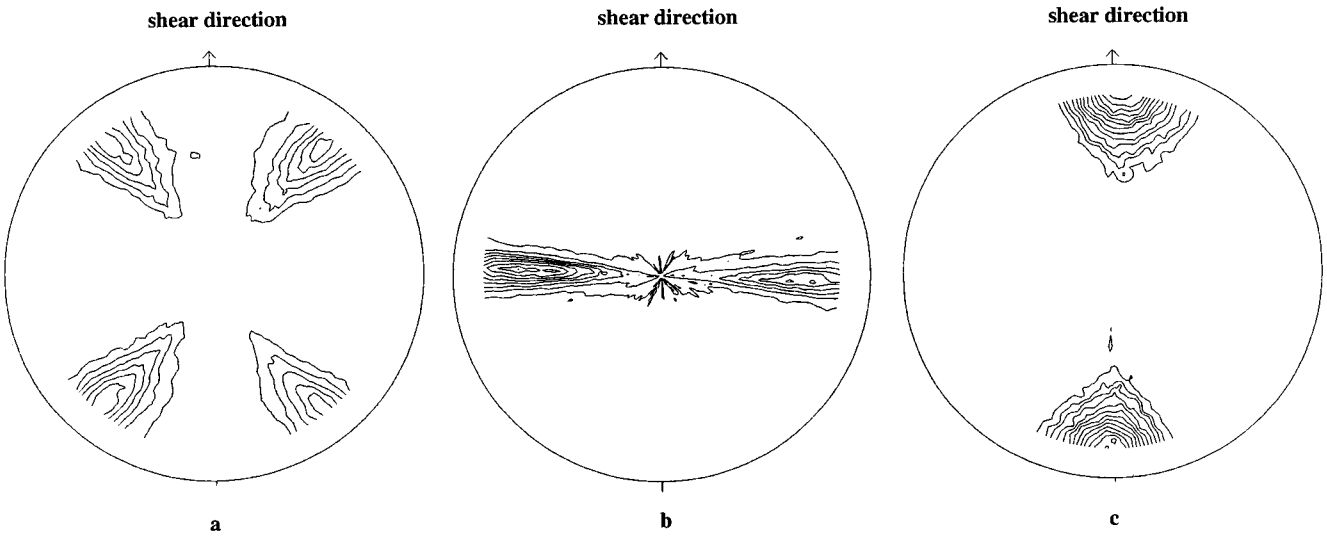


Figure 3. Pole figures recorded at (a) 2.92° , (b) 3.89°, and (c) 20° 2θ values for the low molecular weight PECH **1a** derivative (experiment 11) oriented by shearing.

that this mesophase was a smectic A, since the maxima of these reflections proved to be perpendicular to each other.

For the **1a** polymeric derivatives (experiments 3 and 11) the most intense reflection is the one located at ~3.7° and not the one at lower 2θ values. Moreover, in view of the d_{hkl} spacing values only one of the sharp diffractions can be assigned to the smectic order. Figure 3 shows, for one of these polymers (experiment 11), the pole figures recorded at all three diffraction angles. As can be seen, the diffraction at 3.89° and the broad reflection (20°) are perpendicular to each other. Therefore, the former is a smectic reflection. What is more, the pole figure recorded at 2.92° has the maximum diffraction intensity in the direction (011). All this suggests a frustrated smectic phase, particularly a modulated antiphase $S_{\tilde{A}}$. The molecular organization in this phase can be described as a local antiparallel ordering on a two-dimensional centered lattice (unit cell parameters: b = 40.4 Å; c = 45.4 Å); that is, the structure consists of a bilayer or partial bilayer in which the local orientation varies periodically along a direction which is perpendicular to the layer's normal.[39] Since this lattice is centered, the (001) reflection should be a systematic absence, and therefore the observed smectic reflection (3.89°) should be indexed to the (002) diffraction.

As can be seen in Table 9, the d_{hkl} spacings corresponding to the diffracting plane (002) are very close for both types of biphenyl derivative. This seems to indicate that this value is roughly equal to the mesogen length, that is, the length of the aliphatic lateral chain seems not to affect the smectic period. Thus, the **1b** polymeric derivatives must be organized in a smectic A_d mesophase.[38]

The **2a** polymeric derivatives (experiments 7 and 15) led to X-ray diffraction patterns which had two broad reflections at angles ~3.3 and 20.5°. This indicated that these polymers show a nematic order. However, the **2b** polymeric derivatives (experiments 8, 10, 17, and 18) showed a smectic C mesophase, since there are two smectic reflections between 2.2 and 4.8 and a broad reflection at ~20° in their X-ray diffraction patterns, with the smectic reflection maxima being nonperpendicular to the broad reflection.

To sum up, the biphenyl derivatives lead to smectic A mesophases of the bilayer type, which are modulated when the aliphatic side chain is short. The shape of the naphthalene moiety seems not to be prone to organize in an orthogonal order. In accordance with this, the observed mesophases are nematic and smectic C for the short and long aliphatic chain derivatives, respectively.

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