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Laterally attached liquid crystalline polymers as stationary phases in reversed-phase high-performance liquid chromatography

II. Optimization of the molecular parameter of the polymer

F. Gritti^{a,b}, G. Félix^{a,*}, M.F. Achard^b, F. Hardouin^b

^a*E.N.S.C.P.B. Université Bordeaux I, Avenue Pey-Berland, B.P. 108, 33405 Talence, France*

^b*C.R.P.P.-CNRS, Université Bordeaux I, Avenue du Dr. Schweitzer, 33608 Pessac, France*

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Abstract

Stationary phases obtained by coating side-chain liquid crystalline polymers (LCPs) with the mesogenic rod like units laterally attached to a polysiloxane backbone via a flexible spacer have been already reported. These phases show excellent planarity and shape recognition for polynuclear aromatic hydrocarbon (PAH) solutes in reversed-phase liquid chromatography. Optimization of these stationary phases in terms of molecular parameters of the polymer is here described. Fifteen stationary phases have been prepared varying different parameters such as the spacer length, the aliphatic tail length, and the proportion of laterally attached mesogenic units along the polymer chain. The results show that the combination of a long spacer and long terminal chains, which generates a smectic phase in the polymer bulk, leads to the best chromatographic performances towards planarity and shape recognition for PAH solutes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; Molecular shape recognition; Liquid crystalline polymers; Polynuclear aromatic hydrocarbons

1. Introduction

The use of low-molecular-mass (low- M_r) liquid crystal as stationary phase was first reported in the 1960s by Kelker [1] in gas chromatography (GC), and numerous applications have since been found using the planarity and shape recognition ability of these new stationary phases (for example see Ref. [2]). Due to increased capillary column efficiency and upper thermal stability over low- M_r liquid

crystal, liquid crystalline polymers (LCPs) were then applied to GC for the first time by Finkelman et al. [3].

Unlike the large number of publications dealing with liquid crystalline materials in GC, they are still seldom used as stationary phases in high-performance liquid chromatography (HPLC) [4–13]. This is mainly explained by the requirement to bond the liquid crystalline molecules to the solid silica support, due to their high solubility in normal mobile phase solvent conditions. Low- M_r liquid crystals have been fixed onto silica via the organochlorosilane pathway [4–8]. A more recent bonding method via the formation of a hydride intermediate

*Corresponding author. Tel.: +33-5-5684-6561; fax: +33-5-5796-2239.

on silica (Si–OH→Si–H) and hydrosilylation has also been successful [9,10]. Some authors also prepared bonded liquid crystal stationary phases from aminopropylsilica [11,12]. The first example of a chemically bonded LCP has been recently reported [13,14]. Nevertheless, chemical bonding of LCPs on the silica surface is not as imperative as for low- M_r liquid crystals and it is possible to use coated LCP stationary phases under reversed mobile phase conditions for which the polymer is completely insoluble achieving a long column lifetime [13–18]. In addition LCPs are of advantage in HPLC because an ordering structure into silica pores appears more probable when the mesogenic units are regularly attached to a polymer backbone rather than fixed onto randomly imposed silanophilic reactive sites [13,17,18].

The first LCP stationary phases were prepared using side chain polyacrylates, with the mesogenic rod-like units longitudinally attached to the polymer backbone (“side-end” fixation SE-LCP) [15,16]. Nevertheless, as previously shown [13,17,18], the shape selectivity is highly dependent on the type of fixation of the mesogenic units on the polymer chain and a lateral fixation (“side-on fixation” SO-LCP) leads to considerably higher chromatographic performances than the longitudinal one.

In this study, several liquid crystalline polymers with the mesogenic side groups laterally attached to a polysiloxane backbone via a flexible spacer (SO-LCPs) have been synthesized. The influence of the molecular parameters of the LCPs on the chromatographic performance is discussed. Non liquid crystalline, nematic and smectic polymers are successively tested and compared. A more detailed analysis has been investigated in each case by varying the spacer arm and aliphatic tail length. Dilution rates of the mesogenic unit along the polysiloxane chain have been also studied.

2. Experimental

2.1. Chemicals

Polyhydrogenosiloxane (PHMS 67) and polyhydrogenomethyl(dimethyl)siloxane were purchased

from ABCR (Karlsruhe, Germany). Silica gel (Kromasil, 5 μm , 200 Å pore size) with a specific surface of 220 m^2/g was a gift from Akzo Nobel (Bohus, Sweden). HPLC-grade methanol (purchased from ICS Nationale, St. Medard-en-Jalles, France) was used to prepare the mobile phase. Water was doubly distilled. All the polynuclear aromatic hydrocarbons (PAHs) used as test compounds were purchased from Aldrich (l'Isle d'Abeau Chesnes, France). Shape recognition (L/B) and planarity structures are shown in Fig. 1.

2.2. Apparatus

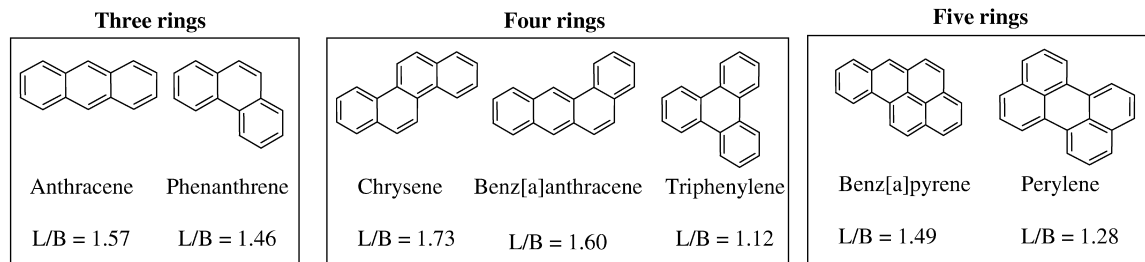
HPLC was carried out using a modular HPLC apparatus equipped with a Rheodyne 7725 injector (assembled with a 20- μl sample loop), a PU-980 Model gradient pump, a UV-975 UV-Vis detector, a LG-980-02 ternary gradient unit mobile phase mixer and a DG-980-50 three-line degasser from Jasco. Reversed-phase conditions using a mixture of methanol–water (80:20, v/v) were chosen for all chromatographic measurements at a flow of 1 ml/min.

2.3. Liquid crystalline polymers (SO-LCPs)

The LCPs used in this work belong to the family of the side chain liquid crystalline polymers where the mesogenic rod-like units are laterally attached to a flexible polysiloxane backbone via a flexible spacer. The mesogenic groups are three-phenyl rings, of benzoate type with terminal alkoxy chains. They are labeled $Mn.m.m$ where n and m are the number of carbons of the lateral alkyl ester spacer arm and alkoxy terminal chains, respectively. The synthetic method of the mesogenic compounds $Mn.m.m$ has been described previously [19].

The polysiloxanes are prepared through a classical hydrosilylation reaction [20,21] between the vinyl groups of the spacer arm of the $Mn.m.m$ precursors and the Si–H functions either of a PHMS 67 chain or of polyhydrogenomethyl(dimethyl)siloxane [22,23] giving homopolysiloxanes and copolysiloxanes, respectively. The resulting polymers have the following general formula:

Shape recognition



Planarity

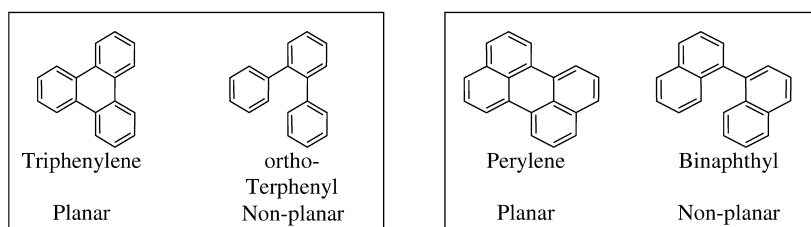
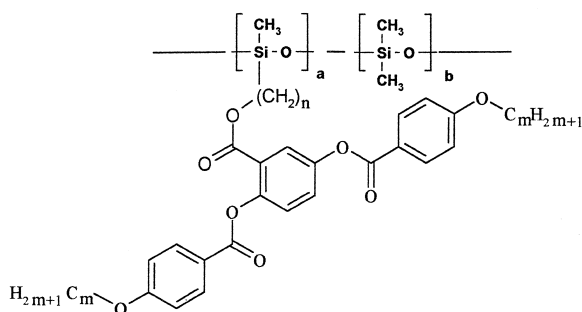


Fig. 1. PAHs used for chromatographic studies.



These LCPs are named $Pn.m.m$ $X\%$. The $X = 100a/(a+b)$ value corresponds to the fraction of silicon atoms linked to the $Mn.m.m$ unit along the polysiloxane chain. Thus, with respect to this convention, homopolymers are characterized by an X value of 100 and copolymers by $0 < X < 100$. The spacer arm n contains either four or 10 methylene groups. The terminal chain length was varied from $m=0$ to $m=12$. Twelve homopolymers and three copolymers have been synthesized.

Two variants of this general formula have been prepared – either by replacing the central phenyl ring

by a naphthalene one, giving the PN10.8.8 homopolymer – or by keeping only the central phenyl ring with the terminal chains, giving the P10.2.2_{one ring}.

All these polymers were identified by ^1H nuclear magnetic resonance (NMR) spectroscopy on a Bruker 200 MHz spectrometer. The mesomorphic properties were characterized by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC7 apparatus and by optical microscopy (Table 1).

2.4. Preparation of LCP-coated stationary phases

The silica gel was dried at 180°C under 0.01 Torr over 24 h before use (1 Torr = 133.3222 Pa). Silica was added to a tetrahydrofuran (THF) solution of polymer. A homogeneous suspension was obtained by vigorous stirring and THF was progressively removed under a slight vacuum (water pump) at room temperature. Efforts were made to prepare stationary phases with the same concentration of repetitive unit per gram of silica. This concentration was checked and calculated from carbon elemental analysis as described previously [13,17]. The coated

Table 1
Phase transition temperatures of liquid crystalline homopolymers and copolymers

Homopolymer	Transition temperatures ^c (°C)
P10.2.2 _{one ring} ^a	g I
P10.0.0 ^b	g 12 I
P4.4.4 ^b	g 36 N 130 I
P4.8.8 ^b	g 24 N 93 I
P4.12.12 ^b	g 27 N 87 I
P10.2.2 ^b	g 21 N 109 I
P10.4.4 ^b	g 17 N 99 I
P10.6.6 ^b	g 15 Sc 34 N 96 I
P10.8.8 ^b	g 13 Sc 54 N 93 I
P10.10.10 ^b	g 10 Sc 62 N 88 I
P10.12.12 ^b	g 8 Sc 63 N 81 I
PN10.8.8 ^a	g 54 Sc 80 N 120 I
Diluted copolymers	
P10.4.4, 31% ^a	g 16 N 95 I
P10.4.4, 47% ^a	g 13 N 87 I
P10.4.4, 81% ^a	g 14 N 70 I

^a From Ref. [13].

^b From Ref. [24].

^c g: glassy; Sc: smectic C; N: nematic; I: isotropic.

silica was finally dried under 0.01 Torr at room temperature.

2.5. Column packing

Each stationary phase was packed in a stainless steel column (150×4.6 mm I.D.) using a Haskel pneumatic amplification pump. The packing was carried out under a pressure of 400 bar with methanol as the pressure fluid and a mixture of methanol–cyclohexanol (25:5, v/v) as the suspension medium fluid.

3. Results and discussion

Before comparing the properties of the stationary phases versus the molecular parameters of the polymer used, we first study the influence of the polymer loading on the chromatographic performance.

3.1. Influence of the polymer loading

Concentrations of mesomorphic units on silica [M]

are calculated from elemental analysis, as follows:

$$[M] \text{ (mmol/g)} = \frac{\% C}{12N_c - M_r \% C}$$

$$[M] \text{ (}\mu\text{mol/m}^2\text{)} = S_p \cdot [M] \text{ (mmol/g)}$$

where % C is the percentage of carbon contained in the considered stationary phase, N_c is the number of carbons in one repetitive unit; M_r , the molecular mass of the repetitive unit in g/mol; S_p , the specific surface of silica in m^2/g . Despite our efforts to obtain identical mesogenic group concentration for each column, non negligible differences have sometimes been observed (Table 2).

To appreciate the quantitative influence of the loading, four columns with different loading in mesogenic groups (99, 180, 237 and 309 $\mu\text{mol/g}$ silica) were tested using the same P10.4.4 nematic LCP. As shown in Fig. 2 and Table 3, while retention factors continually increased with more heavily loaded phases, selectivities become constant. The optimal separation required a minimal interaction sites that was evaluated at 0.7 $\mu\text{mol/m}^2$ (i.e., 155 $\mu\text{mol/g}$). Beyond, selectivities were kept unchanged. Indeed, at low-level coating α is affected both by the LCP and the free underlying silica. As the amount of LCP is increased the solutes see only the polymeric phase and the selectivities will remain constant beyond. As a consequence, it was not necessary to

Table 2
Characterization of the stationary phases

Polymer-coated stationary phases	% C, elemental analysis	[M]/g silica ($\mu\text{mol/g}$)
P10.2.2 _{one ring}	7.52	323
P10.0.0	8.22	243
P4.4.4	6.65	181
P4.8.8	10.51	246
P4.12.12	10.91	215
P10.2.2	8.58	189
P10.4.4	9.77	238
P10.6.6	9.25	202
P10.8.8	10.99	226
P10.10.10	11.08	210
P10.12.12	10.91	191
PN10.8.8	10.61	199
P10.4.4, 30%	11.54	266
P10.4.4, 47%	10.03	234
P10.4.4, 81%	12.86	327

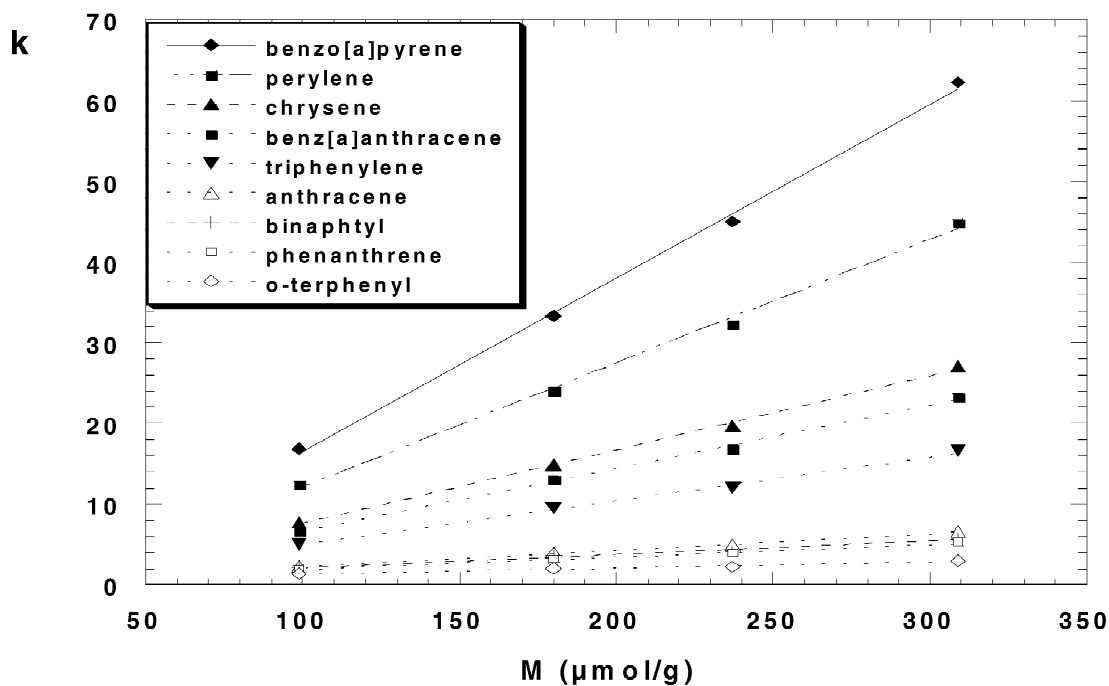


Fig. 2. Retention factor k versus the polymer loading for different PAH solutes.

Table 3
Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for different loadings with the P10.4.4-coated stationary phases

	Stationary phase: P10.4.4 coated on silica											
	Loading ($\mu\text{mol/g}$)											
	99			180			237			309		
	k	α	N	k	α	N	k	α	N	k	α	N
Phenanthrene	1.95			3.24			3.90			5.25		
Anthracene	2.31	1.18	839	4.00	1.23	994	4.94	1.27	478	6.65	1.27	687
<i>o</i> -Terphenyl	1.31	3.83		2.02	4.70		2.22	5.40		2.95	5.62	
Triphenylene	5.02			9.49			11.98			16.58		
Chrysene	7.70	1.32	1594	14.94	1.57	3167	19.71	1.41	1829	27.06	1.40	1377
Benz[<i>a</i>]anthracene	6.66	1.16		12.98	1.15		16.89	1.17		23.30	1.16	
Benzo[<i>a</i>]pyrene	16.89		1871	33.34		3566	45.02		1928	62.27		1414
Perylene	12.46	1.35		24.42	1.37		32.31	1.39		44.88	1.39	
Binaphthyl	2.07	6.02	756	3.58	6.82	2128	4.11	7.86	936	5.74	7.82	953

heavily load the silica surface all the more because column efficiency then decreases. That is why we aimed at working with columns characterized by a stationary phase density of 220 $\mu\text{mol/g}$ corresponding to a surface density of 1 $\mu\text{mol/m}^2$. Despite discrepancies between the experimental surface density and this value, it had been possible to compare the chromatographic performances between each column by normalizing the retention time to a hypothetical column having a 220 $\mu\text{mol/g}$ charge loading. Thus, the peaks were only shifted by a multiplying factor without affecting the selectivities. Thus, we compared columns with respect to the normalized retention factor calculated for a same mesogenic unit concentration per gram of silica. We were allowed to do so because selectivities were not modified as the coated polymer loading varied: $k \approx a_{\text{solute}} \times [\text{M}]$ (k : retention factor, a_{solute} : constant depending of the solute, $[\text{M}]$ polymer loading in $\mu\text{mol/g}$).

Concerning the column efficiency or the number (N_{eff}) of theoretical plates per meter of the columns calculated as follows:

$$N_{\text{eff}} = 5.54 \cdot \left(\frac{t_R}{\delta} \right)^2$$

(where t_R and δ are the retention time and the half-peak width, respectively) a seemingly strange behavior of N_{eff} is seen for all solutes. At low loading the LCP does not cover the silica support completely and therefore, the solutes have several different interaction sites on the stationary phase (the LCP as well as the silica) that result in broadened peaks. As the amount of LCP is increased the extra sites of silica are covered resulting in narrower peaks. As the amount of LCP is increased further, resistance to mass transfer issues are becoming important again resulting in broadened peaks.

Finally, having a level coating between 200 and 250 $\mu\text{mol/g}$ seemed to be a good compromise between the selectivity and the efficiency.

3.2. Influence of the molecular parameters of the polymer

We will discuss here the chromatographic modifications developed by slight progressive chemical changes carried out on the polymer and particularly

on the mesogenic unit. Indeed, the mesomorphic properties of the polymer are strongly correlated with the molecular parameters such as spacer length, aliphatic tail length and “dilution” (Table 1).

3.2.1. Non liquid crystalline polymers

Two non liquid crystalline polymers (P10.2.2_{one ring} and P10.0.0) were used. They are not liquid crystal materials because M10.2.2_{one ring} is not a rod-like molecule (since it has only a single phenyl ring) and M10.0.0, although rod-like in shape, has no terminal chains that are well known to stabilize liquid crystalline phases. Chromatographic results are summarized in Table 4. Retention times obtained with P10.2.2_{one ring} were the same as for the P10.0.0-coated stationary phase. The presence of only a single phenyl ring is equalized by the higher concentration of the mesogenic group (323 against 243 $\mu\text{mol/g}$ of silica). For the both columns, no shape recognition was observed for each set of isomeric PAH (three, four and five aromatic rings). Nevertheless, a good planarity separation occurred on these phases testing the couples triphenylene/*ortho*-terphenyl and perylene/binaphthyl. It was interesting to notice that the chemical nature of the side group (one single phenyl ring or three) had no influence on PAH separations. The most important factor appears to be the non liquid crystalline character of the polymer coated onto silica gel. The retention mechanism might be simply regarded as hydrophobic and π – π interactions without any shape parameter solute's effect (as the length-to-breath ratio L/B). These results confirm that no polymer ordering structure should be present at the silica surface as well as in the pure polymer phase.

3.2.2. Nematic liquid crystalline polymers

Five nematic liquid crystalline polymers were studied. Three have an n value of 4 (spacer arm length) and the two last possess a spacer arm with 10 carbons.

3.2.2.1. Influence of the terminal chain length m on chromatographic results

The P4. $m.m$ polymers, with a four-carbon spacer arm, only generate nematic liquid crystalline phases when m increases from 4 to 12. For $n=10$, the m

Table 4
Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for the two non liquid crystalline polymer coated on silica

	Stationary phase							
	P10.0.0 coated on silica				P10.2.2 _{one ring} coated on silica			
	Loading ($\mu\text{mol/g}$)							
	243		220		323		220	
	k	α	N	k	k	α	N	k
Phenanthrene	3.86			3.72	3.36			2.63
		1.04				1.03		
Anthracene	4.02		367	3.82	3.46		575	2.74
<i>o</i> -Terphenyl	3.35			3.22	2.92			2.28
		3.16				3.41		
Triphenylene	10.59			10.98	9.94		1.00	7.21
		1.00				1.00		
Chrysene	10.59		1754	10.98	9.94		1549	7.21
		1.00				1.00		
Benz[<i>a</i>]anthracene	10.59			10.98	9.94			7.21
Benzo[<i>a</i>]pyrene	20.79		1824	23.19	21.00		2201	14.16
		1.00				1.00		
Perylene	20.79			23.19	21.00			14.16
		3.30				3.31		
Binaphthyl	6.30		2299	7.02	6.36		1912	4.29

range was reduced to 1 to 4 because a stable smectic C mesophase appeared (Table 1).

Firstly, for each stationary phase, all solutes were separated on nematic liquid crystalline polymers. Both the planarity recognition and the shape recognition became obvious: a good correlation between the retention factor and the classical L/B ratio is represented in Fig. 3. Secondly, the selectivities did not vary largely when the aliphatic chain length increased (Tables 5 and 6). The only variations had been correlated to the retention factor k (normalized to a same concentration value of mesogenic unit per gram of silica) which similarly increased for all solutes. Thus, for example, for a normalized loading of 220 $\mu\text{mol/g}$, retention factor would be of 20.3, 27.8 and 35.6 for benzo[*a*]pyrene solutes on P4.4.4-, P4.8.8- and P4.12.12-coated stationary phases, respectively. A greater hydrophobicity (generated by longer aliphatic tails) of P4.12.12 over P4.8.8 and P4.4.4 phases could interpret this retention increase phenomenon. Similar behavior was observed for the P10.2.2 and P10.4.4 phases (Table 6).

3.2.2.2. Influence of the spacer arm length n

To investigate the influence of n , P4.4.4- and P10.4.4-coated stationary phases have been compared. The lengthening of the spacer arm (which uncouples the ordering tendency of the mesogenic units and the disorder motion of the polysiloxane backbone) led to chromatographic improvements regarding selectivities and column efficiencies (Tables 5 and 6). As an explanation, a better ordering structure might be allowed on silica with P10.4.4 because the mesogenic unit was “less linked” to the disordered polysiloxane chain and so is more susceptible to develop an organized structure.

3.2.2.3. Influence of the proportion of mesogenic units attached to the polysiloxane backbone

As shown in Table 1, the clearing temperatures of the copolymers decrease when decreasing the proportion of mesogenic side groups. Nevertheless the nematic phase is preserved even for low content of mesogenic units ($X=30\%$).

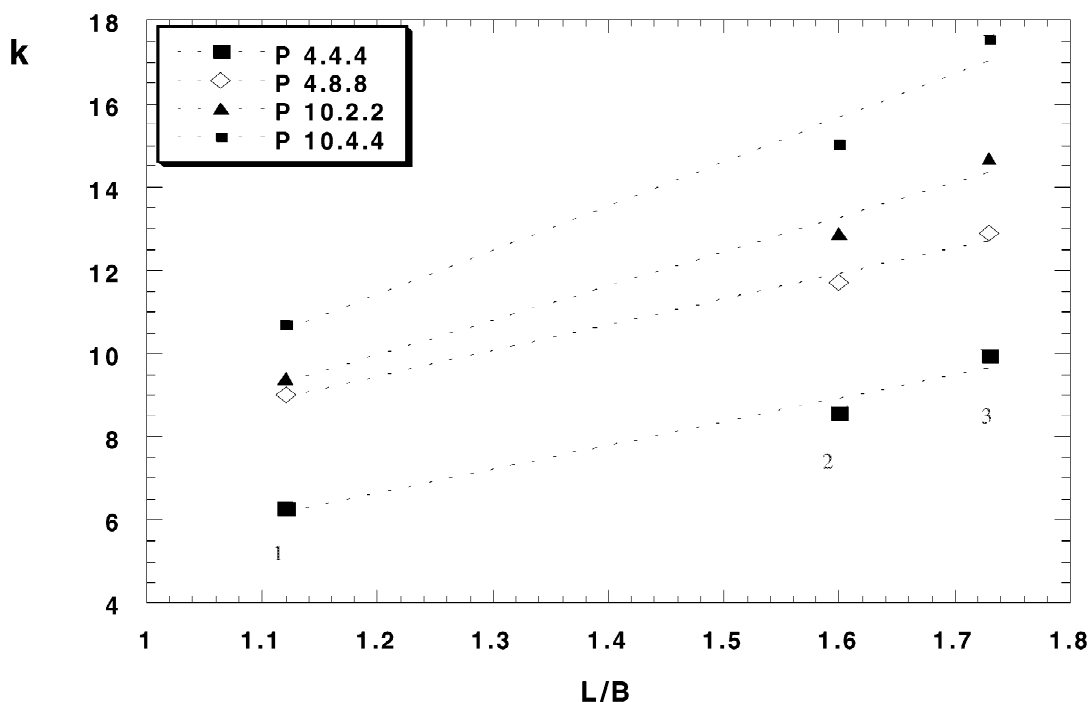


Fig. 3. Evolution of the normalized retention factor k versus the length-to-breath ratio L/B for four LCP stationary phases. 1: Triphenylene (1.12); 2: benzo[*a*]anthracene (1.60); 3: chrysene (1.73).

The stationary phases based on three P10.4.4 ($X\%$) copolymers were compared to the stationary phase prepared with P10.4.4 homopolymer (Table 7). Despite efforts made to obtain the same concentration of mesogenic groups per gram of silica, 266, 234 and 327 $\mu\text{mol/g}$ were deduced from carbon elemental analysis, respectively. When retention times were normalized to the same concentration of 220 $\mu\text{mol/g}$, it became clear that the four stationary phases behaved quite identically. However, it was important to notice that selectivities slightly decreased when the proportion of mesogenic units was lower. Conversely, column efficiencies were increased with “dilution” except for P10.4.4 (81%) certainly because its higher concentration in mesogenic units generates higher resistance to mass transfer in the stationary phase. Thus, it appears quite better to use copolysiloxanes because not only the selectivities were kept at a good level compared to the homopolysiloxanes, but above all, the column efficiencies were improved.

3.2.3. Smectic liquid crystalline polymers

For long spacer and long aliphatic tails, the occurrence of a smectic C phase is observed in those laterally attached LCPs [24].

3.2.3.1. Influence of the terminal chain length m

Five smectic liquid crystalline polymers have been obtained by lengthening the aliphatic tails from 6 to 12 carbons. As shown in Table 1, they successively generate by heating a smectic C and nematic mesophases. It is interesting to notice that the lengthening of the aliphatic chains stabilized the smectic phase and that increasing m , increased the smectic stability range over the nematic [23,24].

Chromatographic results are summarized in Table 8. Better shape selectivities occurred with smectic liquid crystalline polymers in a shorter time.

For example, shape discriminations with respect to anthracene/phenanthrene, chrysene/triphenylene and benzo[*a*]pyrene/perylene were higher on the

Table 5
Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for three nematic-coated stationary phases

	Stationary phase											
	P4.4.4 coated on silica				P4.8.8 coated on silica				P4.12.12 coated on silica			
	Loading ($\mu\text{mol/g}$)											
	181		220		246		220		215		220	
	k	α	N	k	k	α	N	k	k	α	N	k
Phenanthrene	2.10			2.55	3.58			3.20	3.81			3.90
		1.20				1.18				1.19		
Anthracene	2.53		358	3.08	4.22		858	3.77	4.54		697	4.65
<i>o</i> -Terphenyl	1.40			1.70	2.49			2.23	2.63			2.69
		3.69				4.05				3.99		
Triphenylene	5.16			6.27	10.07			9.00	10.51			10.75
		1.58				1.43				1.48		
Chrysene	8.18		945	9.94	14.42		3024	12.90	15.58		2193	15.94
		1.16				1.10				1.10		
Benz[<i>a</i>]anthracene	7.06			8.58	13.08			11.70	14.14			14.47
Benzo[<i>a</i>]pyrene	16.73		970	20.33	31.10		3376	27.81	34.59		2742	35.39
		1.30				1.28				1.32		
Perylene	12.90			15.68	24.34			21.77	26.23			26.84
		5.84				5.26				5.37		
Binaphthyl	2.21		844	2.69	4.62		1861	4.13	4.88		1657	4.99

Table 6
Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for two nematic polymer-coated stationary phases ($n = 10$)

	Stationary phase							
	P10.2.2-coated silica				P10.4.4-coated silica			
	Loading ($\mu\text{mol/g}$)							
	189		220		238		220	
	k	α	N	k	k	α	N	k
Phenanthrene	2.75			3.20	3.79			3.50
		1.25				1.26		
Anthracene	3.45		708	4.02	4.79		990	4.43
<i>o</i> -Terphenyl	1.74			2.03	2.17			2.01
		4.64				5.34		
Triphenylene	8.09			9.41	11.58			10.70
		1.56				1.64		
Chrysene	12.62		514	14.69	18.99		3041	17.55
		1.14				1.17		
Benz[<i>a</i>]anthracene	11.06			12.87	16.26			15.03
Benzo[<i>a</i>]pyrene	27.98		593	32.57	43.41		3113	40.12
		1.30				1.39		
Perylene	21.50			25.03	31.12			28.77
		7.44				7.67		
Binaphthyl	2.89		335	3.36	4.06		1722	3.75

Table 7

Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for diluted copolymer-coated stationary phases

	Stationary phase															
	P10.4.4 (100%) coated on silica				P10.4.4 (81%) coated on silica				P10.4.4 (47%) coated on silica				P10.4.4 (30%) coated on silica			
	Loading ($\mu\text{mol/g}$)															
	238		220		327		220		234		220		266		220	
	k	α	N	k	α	N	k	α	N	k	α	N	k	α	N	k
Phenanthrene	3.79			3.50	4.82		3.24	4.03		3.79	4.26					3.52
		1.26				1.28			1.22					1.21		
Anthracene	4.79		990	4.43	6.18		792	4.16	4.90		941	4.61	5.15		1311	4.26
<i>o</i> -Terphenyl	2.17			2.01	2.78		1.87	2.78		2.61	3.23					2.67
		5.34				5.40			4.17					3.64		
Triphenylene	11.58			10.70	14.99		10.08	11.62		10.92	11.78					9.74
		1.64				1.67			1.53					1.51		
Chrysene	18.99		3041	17.55	25.06		1937	16.86	17.75		3044	16.69	17.74		4129	14.67
		1.17				1.17			1.13					1.12		
Benz[<i>a</i>]anthracene	16.26			15.03	21.44		14.42	15.70		14.76	15.82					13.08
Benzo[<i>a</i>]pyrene	43.41		3113	40.12	57.26		1876	38.52	39.41		3378	37.05	38.22		4308	31.6
		1.39				1.42			1.37					1.37		
Perylene	31.12			28.77	40.40		27.18	28.70		26.98	27.90					23.07
		7.67				7.73			5.91					5.14		
Binaphthyl	4.06		1722	3.75	5.22		1296	3.51	4.86		2211	4.57	5.43		2438	4.49

Table 8

Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for smectic polymer-coated stationary phases

	Stationary phase															
	P10.6.6 coated on silica				P10.8.8 coated on silica				P10.10.10 coated on silica				P10.12.12 coated on silica			
	Loading ($\mu\text{mol/g}$)															
	202		220		226		220		210		220		191		220	
	k	α	N	k	α	N	k	α	N	k	α	N	k	α	N	k
Phenanthrene	3.44			3.75	3.24		3.15	2.63		2.76	2.66					3.06
		1.31				1.29			1.31					1.31		
Anthracene	4.50		323	4.90	4.18		566	4.07	3.46		396	3.62	3.47		595	4.00
<i>o</i> -Terphenyl	1.90			2.07	1.83		1.78	1.51		1.58	1.57					1.75
		5.37				4.91			4.37					4.24		
Triphenylene	10.22			11.13	8.99		8.75	6.60		6.91	6.66					7.67
		1.85				1.87			2.06					2.02		
Chrysene	18.95		661	20.64	16.83		1122	16.38	13.64		981	14.29	13.38		2170	15.41
		1.20				1.21			1.25					1.24		
Benz[<i>a</i>]anthracene	15.78			17.19	13.96		13.59	10.90		11.42	10.80					12.44
Benzo[<i>a</i>]pyrene	41.14		834	44.81	38.70		1072	37.67	31.21		1009	32.70	30.74		2543	35.41
		1.48				1.59			1.73					1.70		
Perylene	27.72			30.20	24.34		23.69	18.02		18.88	18.12					20.87
		9.19				7.66			7.63					7.50		
Binaphthyl	3.02		618	3.29	3.18		983	3.10	2.36		798	2.47	2.42		1186	2.79

P10.10.10 smectic polymer-coated silica ($\alpha=1.31$, 2.06 and 1.73, respectively) than on the P10.4.4 nematic polymer-coated stationary phase ($\alpha=1.26$, 1.64 and 1.39). So, in this case, the lengthening of aliphatic tail leading to a mesomorphism change of the polymer (purely nematic to smectic C–nematic) plays an important role in PAH separation.

A second point was interesting to note for the smectic P10.*m.m* polymer set: the longer the terminal chains, the higher the shape selectivity. Planarity recognition towards triphenylene/*o*-terphenyl and perylene/binaphthyl decreased because the nearly square shape planar solutes such as triphenylene and perylene were less retained on a “more ordered silica surface” probably induced by a more stable smectic phase of the polymer whereas their non planar homologous are eluted identically. These phenomena would also explain the shape selectivity increase because the retention diminution was less sensitive on long-shaped solutes than on square-like solutes.

Furthermore, when temperature ranges of the smectic phase were comparable (P10.10.10 and P10.12.12), selectivities were not changed and retention times increased due to the higher hydrophobicity of the P10.12.12 polymer over the P10.10.10 one. We recognized here the effect of the aliphatic tail lengthening already observed with P4.12.12 and P4.8.8 over P4.4.4 or with P10.4.4 and P10.2.2. In the same way, P10.12.12 polymer-coated

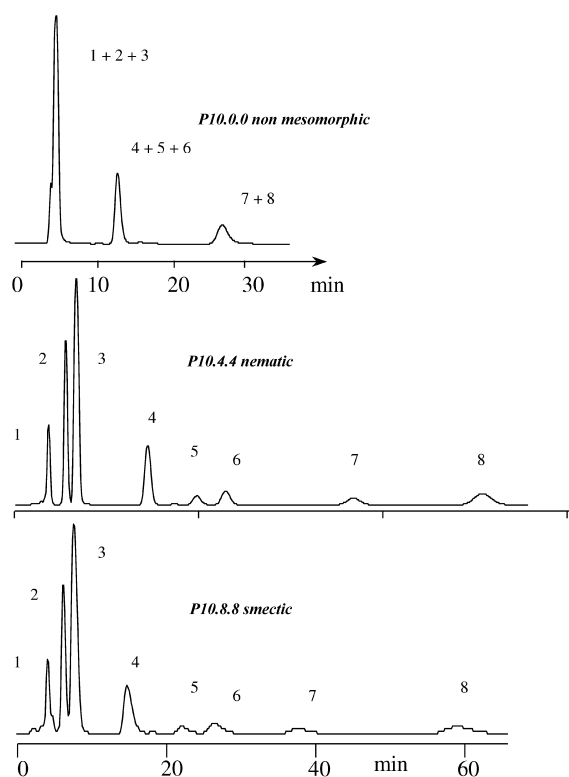


Fig. 4. Separation of PAH solutes on stationary phases based upon non mesomorphic (P10.0.0), nematic (P10.4.4) and smectic (P10.8.8) polymers. 1: *o*-Terphenyl, 2: phenanthrene, 3: anthracene, 4: triphenylene, 5: benz[*a*]anthracene, 6: chrysene, 7: perylene, 8: benzo[*a*]pyrene.

Table 9

Retention factors (k), selectivities (α) and theoretical plate numbers (N) obtained for two smectic polymers with different central cores

	Stationary phase							
	P10.8.8 coated on silica				PN10.8.8 coated on silica			
	226		220	k	199		220	k
k	α	N	k		α	N		
Phenanthrene	3.24			3.15	2.70			2.98
Anthracene	4.18	1.29	566	4.07	3.31		306	3.66
<i>o</i> -Terphenyl	1.83			1.78	1.82			2.01
Triphenylene	8.99	4.91		8.75	6.93	3.82		7.66
Chrysene	16.83	1.87	1122	16.38	11.74	1.70	566	12.98
Benz[<i>a</i>]anthracene	13.96	1.21		13.59	10.26	1.15		11.34
Benzo[<i>a</i>]pyrene	38.70		1072	37.67	25.82		584	28.54
Perylene	24.34	1.59		23.69	17.33	1.49		19.16
Binaphthyl	3.18	7.66	983	3.10	3.01	5.76	538	3.33

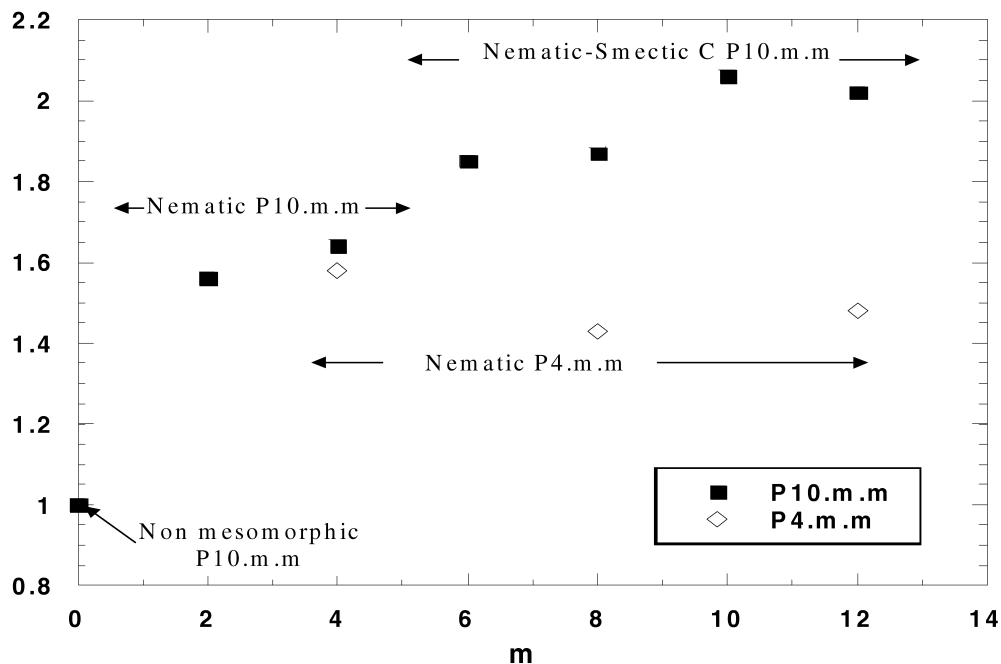
α chrysene/triphenylene

Fig. 5. Selectivity obtained for chrysene/triphenylene on P4.m.m and P10.m.m stationary phases versus the terminal tails length m .

silica gave better columns efficiencies than the P10.10.10 polymer-based column.

3.2.3.2. Influence of the nature of the aromatic core

We decided here to modify the chemical nature of the aromatic core by substituting the central phenyl ring for a naphthyl group [13]. The new polymer was called PN10.8.8 and compared with the P10.8.8 one (Table 9). Results clearly showed that separations performed on the PN10.8.8 polymer-coated silica were weaker than on the P10.8.8 stationary phase and may be due to a less long-shaped mesogenic core.

All these results are summarized in Figs. 4 and 5. First of all, the use of a mesomorphic polymer, compared to a non liquid crystalline one, generated a complete resolution of shape isomers (Fig. 4). The column efficiencies remained quite low, probably the result of the polymeric nature of the stationary phases: anyhow, the resolution of these polymeric phases is higher than this of the relevant bonded mesogenic molecules [17]. Secondly, shape recogni-

tion of PAHs appeared to be highly sensitive to the molecular parameters of the laterally attached liquid crystalline polymer: long spacer arm ($n=10$) and long aliphatic tails ($m=6-12$) were both required to obtain better selectivities (Fig. 5) because they certainly favor a more ordered structure onto the silica surface. LCPs generating stable smectic phase were all the more attractive because they were more selective in a reduced time experiment. At this step, the question of the influence of a “nematic” or “smectic” local order at the silica surface is raised. Additional experiments are currently in progress in order to appreciate the intrinsic role of the nature of the anisotropic order on the chromatographic performance.

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