Synthesis, characterization and liquid chromatographic behaviours of a new chemically bonded liquid crystal

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Abstract

A new bonded liquid crystal stationary phase ($2OC_{12}$) for high-performance liquid chromatography was studied. It resulted from coupling of LiChrospher Si 100 NH_2 and a mesogenic carboxylic acid, 4-(4-(4-(3,4-didoceyloxy-styrenyl)phenyl-diazenyl)phenyloxy-methylene) benzoic acid (ILC). ILC was characterized with proton NMR and differential scanning calorimetry, while $2OC_{12}$ was characterized by solid state ^{13}C NMR and elemental analysis. $2OC_{12}$ surface area was determined by the BET method. The chromatographic behaviour of $2OC_{12}$ was investigated under both normal- and reversed-phase conditions. The plots of ln k against $1/T$ showed transition temperatures at 325 and 337 K. Polyaromatic hydrocarbons (PAHs) were separated using hexane, isooctane or hexane-chloroform. Above the transition temperatures, the bonded material exhibited a liquid crystal-like behaviour: (i) the plate number N was always highest possible, and (ii) the more retained the solute the more elongated it was (anthracene is eluted after phenanthrene, chrysene before tetracene, pentacene after dibenzo-a,h-anthracene). Using acetonitrile/water (60/40), reversed-phase data of aromatic hydrocarbons are similar (highest values of N, better resolution below than during the transitions).
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1. Introduction

The use of liquid crystals as stationary phases in gas–liquid chromatography was first reported by Kelker [1,2] and Dewar and Shröeder [3]. Liquid crystals as stationary phases in gas chromatography have been intensively used because of their unique selectivity [4–9]. These interesting solvent properties are due to the rod-like shape and the ordered arrangement of their molecules.

Comparatively, liquid crystals have been less used as stationary phase in liquid chromatography, essentially due to the relative difficulty of chemically bonding the liquid crystal to the silica surface. Physically coating a liquid crystal on a solid support has been reported [10,11]. Rapid loss of the stationary phase resulted due to the solubility of the liquid crystal in the mobile phase. Important work on the chemical bonding of liquid crystals using an organochlorosilane pathway or a liquid crystal type

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ILC

4-{ 4-[4-(3,4-didodecyloxy-styrenyl) phenyl-diazenyl] phenyloxy-methylene} benzoic acid
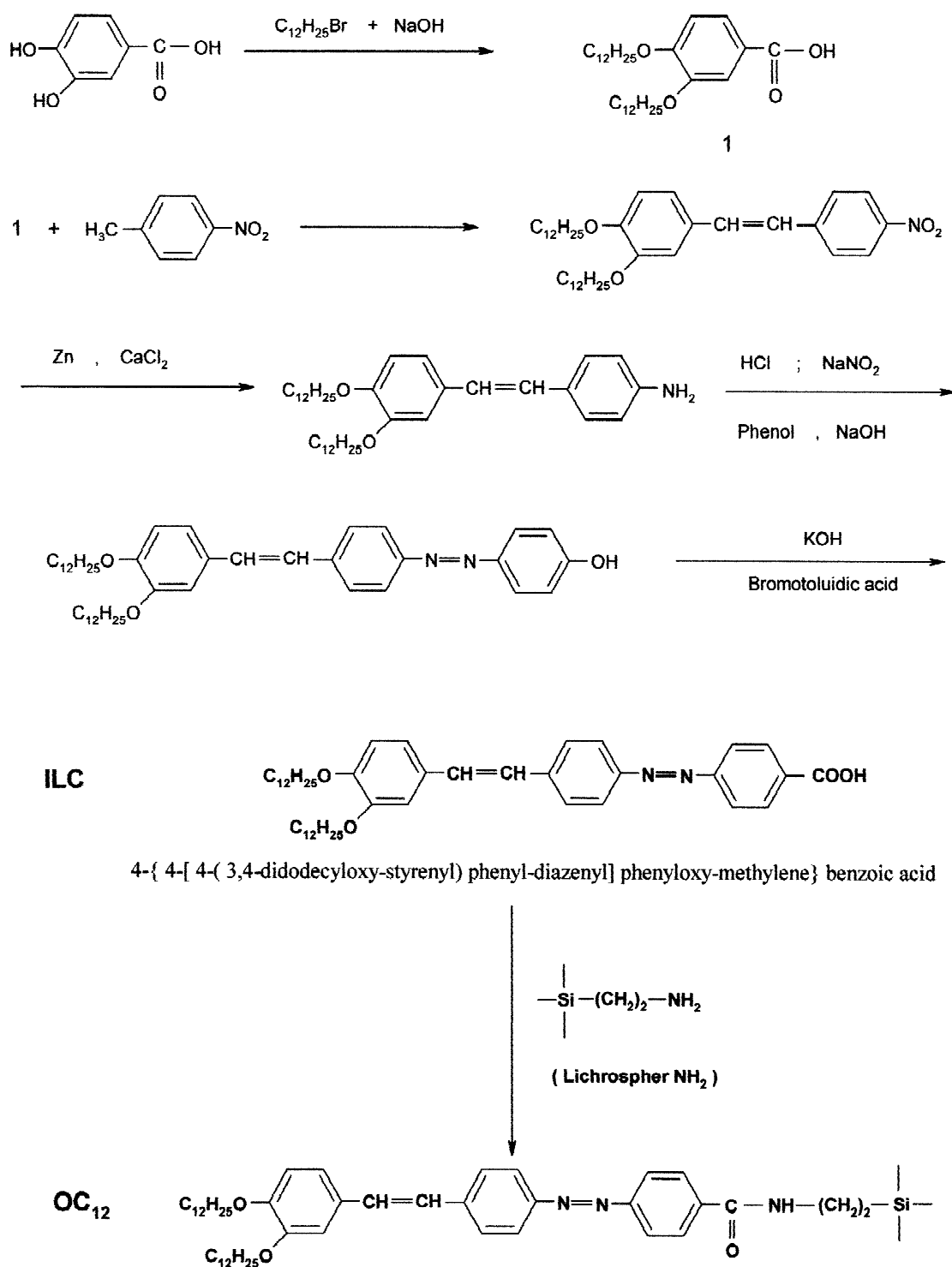
(Lichrospher NH₂)

OC₁₂

Fig. 1. Synthesis scheme of initial liquid crystal (ILC) and bonded liquid crystal stationary phases (2OC₁₂).

Table 1
Proton NMR chemical shifts of ILC

Proton position	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
δ (ppm)	5.45	8.2	7.6	5.2	6.7	7.65	7.9	7.2
Proton position	*i*	*j*	*k*	*l*	*m*	*n*	*o*	*p*
δ (ppm)	4.12	4.12	7.15	6.88	7.08	3.9	1.4	0.9

stationary phase silica hydride surface was reported by Pesek et al. [12–20]. Recently, Felix et al. laterally bonded polymeric liquid crystals to silica gel using smaller pores and particle sizes, thus increasing the interface [21–25]. Amidification reaction between aminopropylsilica and the nematic liquid crystal molecules bearing a terminal carboxylic group is a convenient way of bonding. This method was developed in our laboratory [26,27] and the resulting stationary phase exhibited interesting separation properties using normal- or reversed-phases. Delaurent et al. [28] used the same method to bond cholesteryl chloroformate on aminopropyl silica.

In this work, we report the synthesis of a new bonded liquid crystal stationary phase called $2OC_{12}$ based on amidification between commercial aminopropylsilica and nematic liquid crystals bearing a terminal carboxylic group 4-(4-(4-(3,4-didoceyloxy-styrenyl)phenyl-diazenyl)phenyloxy-methylene) benzoic acid (ILC). Formula and names of ILC and $2OC_{12}$ are given in Fig. 1.

Characterization by different techniques (differential scanning calorimetry, BET measurement, solid state NMR) and preliminary chromatographic results are reported.

2. Experimental

2.1. Reagents

All reagents used in the different syntheses were purchased from Acros (Noisy-Le-Grand, France). LiChrospher Si 100 NH_2, 5-μm particle size, was obtained from Merck (Darmstad, Germany). Hexane, isooctane, and chloroform (chromatographic grades) and standards were from Fluka (Buchs, Switzerland).

2.2. Apparatus

Elementary analysis was conducted at the 'Service de microanalyse, CNRS' (Gif sur Yvette, France). Proton NMR experiments were conducted on a Bruker AM 250 spectrometer, ^{13}C cross polarizing magic angle spinning NMR on a Bruker MSL 200 spectrometer, and differential scanning calorimetry of ILC on a DSC Mettler FP85.

The HPLC system included a Waters chromatograph ALC/GPC 244 with a 6000A pump, 7125 Rheodyne injector, and UV 975 Jasco detector operating at 254 nm. Two 15×0.4-cm columns were home packed with $2OC_{12}$ using the slurry technique. Mobile phases used were hexane, hexane-chloroform or isooctane in the normal-phase, and acetonitrile/water in the reversed-phase. Flow rate was fixed to 1 ml min^{-1}.

Thermal and chromatographic properties of $2OC_{12}$ were determined by varying column temperature using a controlled temperature water bath. Specific areas of $2OC_{12}$ were determined by the nitrogen BET method on a Micromeritics Accusorb 200.

2.3. ILC and $2OC_{12}$ scheme synthesis

A scheme of the ILC synthesis is given in Fig. 1.

Table 2
Temperature transitions (determined by DSC)

Transition	Solid→nematic	Nematic→liquid
Temperature °C	265 °C	295 °C

$2OC_{12}$ was synthetized by amidification between ILC derivative and LiChrospher NH_2 (Fig. 1).

3. Results and discussion

3.1. ILC and $2OC_{12}$ characterization

Proton NMR chemical shifts of ILC are given in Table 1. The chemical shift located at 5.45 ppm confirms the acidic character of ILC. Transition temperatures of ILC determined by DSC are given in Table 2 showing a small nematic range at high temperature. The chemical shifts of cross polarizing magic angle spinning solid state ^{13}C NMR spectra of $2OC_{12}$ are listed in Table 3.

Elemental analysis (Table 4) suggests that 1.44/ 3.8=37.9% of the NH_2 groups present in amino-propylsilica are bonded. In previous works [26,27], the bonding ratios obtained were lower when the bonded liquid crystal had a long lateral dodecyloxy substituent.

Specific areas of LiChrospher Si 100 NH_2 (331 m^2 g^{-1}) and $2OC_{12}$ (315 m^2 g^{-1}) determined by the BET method are almost equivalent (Table 4) and no real change in the specific area is obtained by bonding the liquid crystal.

Table 4
BET and elemental analysis of LiChrospher Si 100 NH_2 and $2OC_{12}$

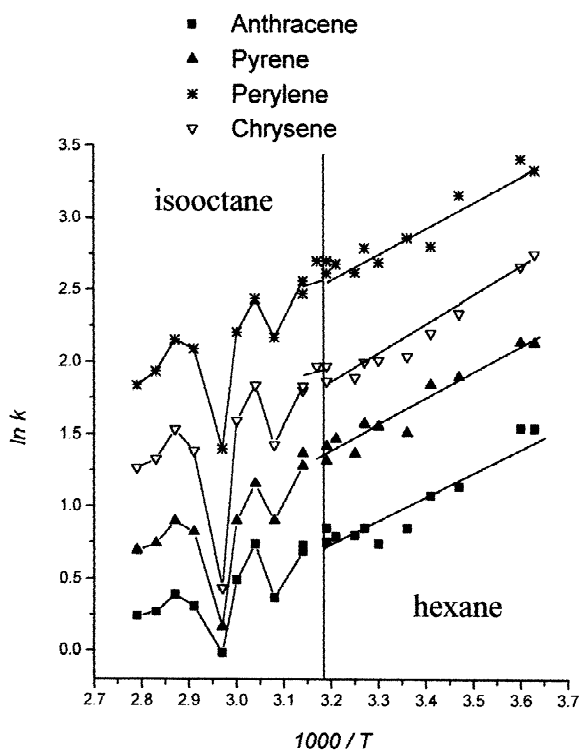|	LiChrospher Si 100 NH_2	$2OC_{12}$
Specific area (N_2), m^2 g^{-1}	331	315
Carbon, %	3.2	15.8
Free SiOH, μmol m^{-2}	8	8
Bonded SiOH, μmol m^{-2}	3.8	3.8
Bonded aminopropyl, μmol m^{-2}		1.44

Fig. 2. Variation of ln k with the reciprocal absolute temperature in the normal-phase using polyaromatic hydrocarbons as solutes.

Table 3
Chemical shifts of $2OC_{12}$ cross polarizing magic angle spinning solid state ^{13}C NMR

C position	a	b	c	d	e	f	g	h
δ (ppm)	21	32	70	133	115	188	47	7

Table 5
Plate numbers N of $2OC_{12}$ column below (289 K), during (336 K) and above (358 K) the transitions using normal or reversed-phases

Solute	Normal phase			Reversed phase	
	289 K	336 K	358 K	289 K	336 K
Phenanthrene	6100	3300	13 300		
Anthracene	7300	3600	13 800		
Fluoranthene	4500	2900	8800		
Pyrene	7200	3700	10 100		
Chrysene	6900	3500	8500		
Benzo-a-fluorene	6500	2800	9100		
Benzo-b-fluorene	6800	3100	9500		
o-Xylene				10 700	5100
p-Xylene				10 500	4900
m-Xylene				11 200	5400
o-Diethylbenzene				9800	5800
p-Diethylbenzene				9700	5200
m-Diethylbenzene				9500	4800

3.2. Chromatographic properties of $2OC_{12}$

3.2.1. Normal-phase conditions

Using hexane as mobile phase, the retention factors k of the polyaromatic hydrocarbons (PAHs) were measured by varying column temperature. In Fig. 2, $\ln k$ were plotted against $1/T$ (reciprocal absolute temperature) for four polyaromatic hydrocarbons. All the curves seem to be linear within $1/T$ in the temperature range studied (278–313 K). It was impossible to work at higher temperature with hexane as mobile phase. To extend the temperature range, the same study was carried out using iso-

octane. The corresponding $\ln k$ curves are also given in Fig. 2. Some remarks can be made.

Two transitions were found as shown in Fig. 2. They were located at 325 and 337 K. The first, located at 325 K, is the lowest. At this temperature, some of chain $OC_{12}H_{25}$ probably began to move. The motion of the second $OC_{12}H_{25}$ occurred at a higher temperature and corresponds to the more intensive second transition (337 K) as shown in Fig. 2. The same phenomenon was observed in previous work [26,27]. Two transitions were found when the bonded liquid crystal had a lateral dodecyloxy substituent. Because of the dodecyloxy lateral posi-

Table 6
Resolutions and selectivities between some solutes above and below transition temperatures

Solutes		Normal phase			Reversed phase	
		289 K	336 K	358 K	289 K	336 K
Anthracene/phenanthrene	R	1.1	0	1.9		
	α	0.90	1	1.2		
Tetracene/chrysene	R	1.2	0	1.9		
	α	0.9	1	1.35		
Pentacene/dibenzo-a,h-anthracene	R	1.5	0.2	2		
	α	0.80	0.9	1.25		
p-Xylene/*m*-xylene	R				0.8	0
	α				0.85	0.95
p-Diethylbenzene/*m*-diethylbenzene	R				0.75	0.1
	α				0.75	0.9

tion, the difference between the transition temperatures was greater.

Above the transitions, $2OC_{12}$ bonded phase exhibited a liquid crystal-like behaviour. The plate number N was always highest above the transition temperature range shown in Table 5. This behaviour was nearly identical to that observed in the comparison of the nematic and solid or liquid phase gas chromatographic performances [4,5].

Isomer elution order was another characteristic of liquid crystals. For example, anthracene is more elongated than phenanthrene and eluted before phenanthrene below the transitions. The elution order was reversed above the transitions as shown by the selectivity results in Table 6. In this table, the same remark can be made about the selectivities of the pairs chrysene/tetracene, and pentacene/dibenzo-a,h-anthracene. Above the transition, the more retained solute was the more elongated solute, tetracene was more retained than chrysene, and dibenzo-a,h-anthracene was eluted after pentacene.

Resolutions given in Table 6 confirm the liquid crystal-like behaviour above the transition temperatures. Indeed, the highest values correspond to the liquid crystal-like temperature range.

With isooctane or hexane, the retention factors of the heavy PAHs exceeded 10. A small amount of chloroform in the mobile phase allows elution of the studied PAHs in 20 min. Fig. 3 shows the chromatogram of the considered compounds below, during and above the transitions. Total resolution of the 15 PAHs studied is obtained only above the transition temperatures.

3.2.2. Reversed-phase conditions

Using acetonitrile/water (60/40), different aromatic hydrocarbons were chromatographed at different temperatures and their retention factors measured.

Because of the volatility of acetonitrile, the temperature was varied between 235 and 336 K. The first and second transition temperatures can be seen in Fig. 4. As in the normal-phase, they were located at 325 and 337 K. Reversed-phase data shown in Tables 5 and 6 are similar to the corresponding normal-phase data if we consider the temperatures located below and during the transitions (highest values of N, better resolution below than during the
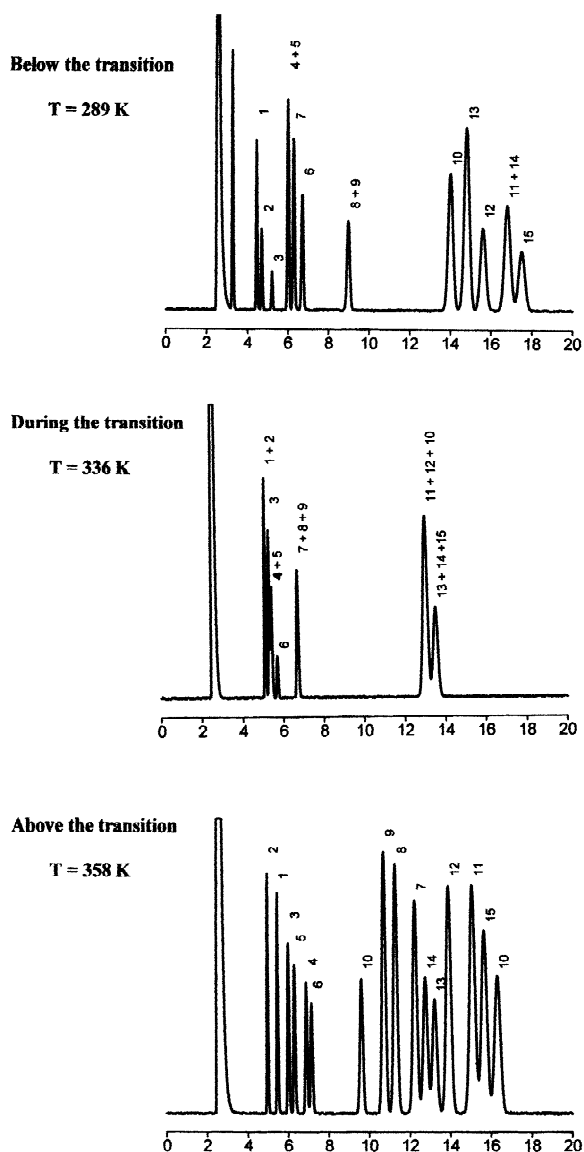

Fig. 3. Separation of some polyaromatic hydrocarbons below (289 K), during (336 K) and above (358 K) the transitions. Mobile phase: isooctane/chloroforme (97.5/2.5). 1 = Anthracene; 2 = phenanthrene; 3 = fluoranthene; 4 = benzo-a-fluorene; 5 = benzo-b-fluorene; 6 = pyrene; 7 = tetracene; 8 = 1,2-benzanthracene; 9 = chrysene; 10 = triphenylene; 11 = perylene; 12 = benzo-a-pyrene; 13 = pentacene; 14 = dibenzo-a,h-anthracene; 15 = dibenzo-a,c-anthracene.

transitions). Furthermore, the elongated isomer was eluted first below the transitions; the para isomer of xylenes or diethylbenzenes had smaller retention
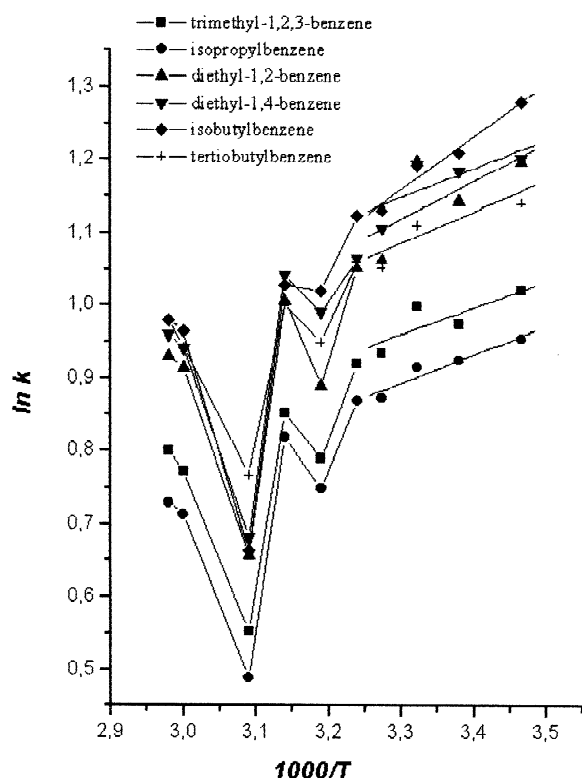
Fig. 4. Variation of ln k with the reciprocal absolute temperature in the reversed-phase.

times than the corresponding meta isomer. Probably, if the experiments were possible, the elution order would be inverted above the transition because of the crystal-like behaviour of the bonded phase. Fig. 5 shows the chromatogram of some of the considered aromatic hydrocarbon compounds obtained below and during the transitions.

4. Conclusions

The new bonded liquid crystal stationary phase for high-performance liquid chromatography presented in this work exhibits two transition temperatures at 337 and 325 K.

Under normal-phase conditions, with isooctane and hexane as mobile phase, the two transitions are clearly shown using polyaromatics as solutes. They probably correspond to movement of the $OC_{12}H_{25}$ chains present in the bonded substituent. The bonded
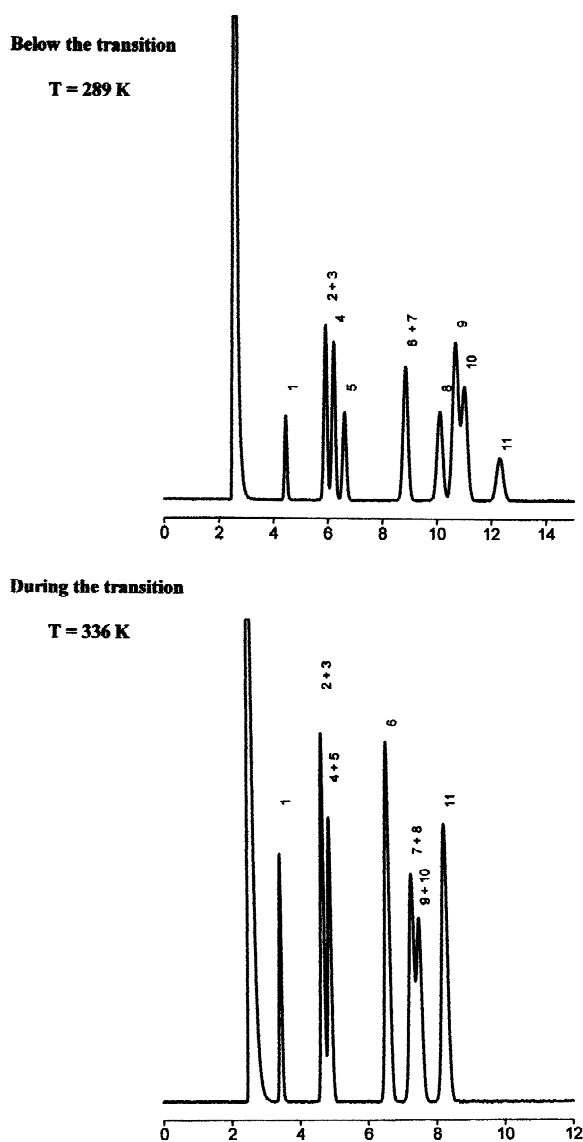
Fig. 5. Separation of some aromatic hydrocarbons below (289 K) and during (336 K) the transitions. Mobile phase: acetonitrile/ water (60/40). 1 = Toluene; 2 = o-xylene; 3 = ethylbenzene; 4 = m-xylene; 5 = p-xylene; 6 = isopropylbenzene; 7 = ethyl-4-toluene; 8 = trimethyl-1,3,5-benzene; 9 = diethyl-1,3-benzene; 10 = diethyl-1,4-benzene; 11 = hexamethylbenzene.

material exhibits a liquid crystal-like behaviour. The more elongated isomers are more retained. Thus, phenanthrene elutes before anthracene above the transitions. A number of polyaromatic hydrocarbons including the following pairs, anthracene and phen-

anthrene, chrysene and tetracene, and pentacene and dibenzo-a,h-anthracene, are separated. A small amount of chloroform in isooctane allowed separation of all the studied PAHs.

Under reversed-phase conditions, because of the volatility of acetonitrile, it was not possible to study the temperature range located above the transition or to observe the liquid crystal-like behaviour of the bonded material.

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