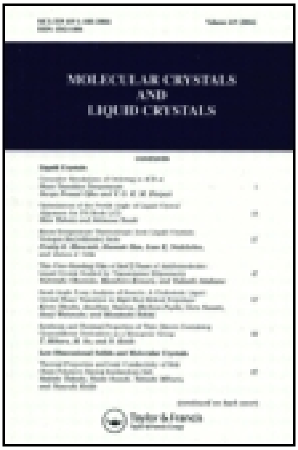

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Side-On Fixed Liquid Crystalline Polymers: New Stationary Phases for High Performance Liquid Chromatography

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Side-On Fixed Liquid Crystalline Polymers: New Stationary Phases for High Performance Liquid Chromatography

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New stationary phases are obtained by coating on a silica support liquid crystalline polysiloxanes with mesogenic side groups laterally attached to the polymer backbone through the flexible spacer. They show very good chromatographic performances in HPLC for the separation of polycyclic aromatic hydrocarbons. Solute/mesogenic group interactions are evaluated through molecular mechanics calculations and correlated to the chromatographic results.

Keywords: High Performance liquid Chromatography; side-on fixed liquid crystalline polymers

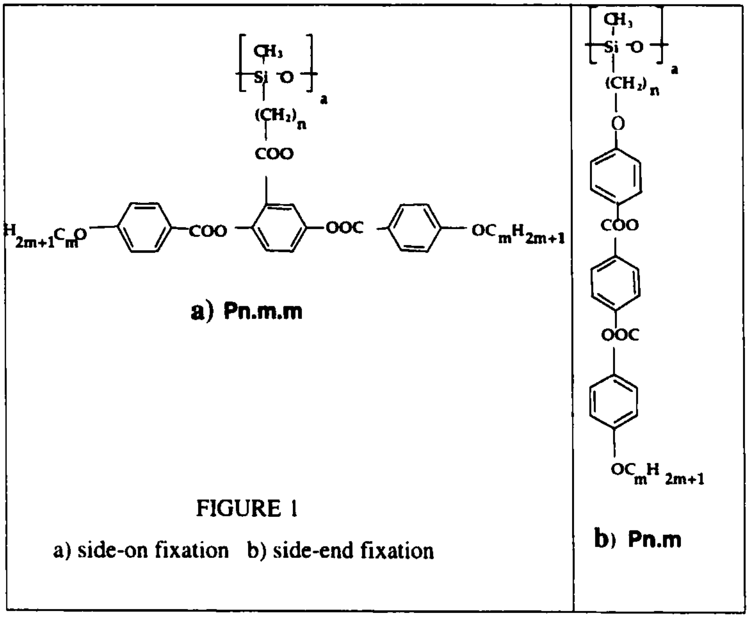
INTRODUCTION

Liquid crystalline materials were first introduced in 1963 as a stationary phase in gas chromatography separations [1] and since then numerous works have been published. The first attempts to utilize liquid crystalline substances in high performance liquid chromatography (HPLC) were carried out more recently [2]. Preparation of liquid crystalline stationary phases for HPLC involves a surface modification of a solid support such as porous silica by coating or bonding either a low molar weight (LMW) liquid crystal, or a liquid crystalline polymer (LCP). Klein and Springer prepared such LCP stationary phases using polyacrylates with side-end fixed mesogenic groups [3]. In addition, we recently showed that the LCP coatings give better chromatographic results than the direct fixation of LMW liquid crystals on the silica [4]. This work reports the chromatographic results carried on stationary phases obtained by coating "side-on fixed LCP" which corresponds to the lateral fixation of the mesogenic groups to the polymer chain through the flexible spacer.

MATERIALS

Liquid crystalline polymers

Side-on fixed LCPs have been prepared according to a procedure already described [5]. These polymers are labeled Pn.m.m, where n and m represent the spacer and the terminal chain lengths respectively.



a) Pn.m.m

b) Pn.m

FIGURE 1

a) side-on fixation b) side-end fixation

"Side-end fixed" Pn.m homologues with the same three phenyl rings as the rigid core have been also synthesized to study the influence of the type of fixation on the chromatographic results. These "side-end fixed" polymers exhibit a nematic-smectic polymorphism whilst the "side-on fixed" LCP are essentially nematic.

LCP	g		S_C		S_A		N		I
Side-on fixed P4.4.4	•	36					•	130	•
Side-on fixed P10.4.4	•	17					•	99	•
Side-end fixed P4.8	•	90	•	220	•	250	•	260	•

LCP coated stationary phases

The liquid crystalline polymers (LCP) were physically coated on the silica surface using a solution of tetrahydrofuran. The stationary phases were packed in stainless-steel tubes and chromatographic studies were done with a modular HPLC apparatus with an UV-Vis. detector set at 254 nm. Reversed-phase conditions using a methanol-water mixture (70/30) are chosen for chromatographic studies and the typical flow rate was 1 ml/min. Under these mobile phase conditions, we observed a good stability of the stationary phases. Chromatographic performances of each stationary phase were studied by using polycyclic aromatic hydrocarbons (PAH) as solutes test: isomeric PAHs such as anthracene/phenanthrene and chrysene/benz[a]anthracene allow to evaluate the shape recognition capability and triphenylene/o-terphenyl the planar/non planar discrimination possibilities.

RESULTS

Comparison between "side-end" and "side-on" fixation

To investigate the influence on the chromatographic performance of the type of fixation of the mesomorphic units on the polymer backbone, we compare longitudinal P 4.8 to lateral P4.4.4 coated stationary phases. The results from elemental analysis indicate the same concentrations in terms of mesomorphic units ([M] = 0.234, 0.236 mmol per gram of silica) were obtained for these two stationary phases.

The selectivity difference between these two classes of LCP coated stationary phases is clearly evident for the separation of the PAHs. All the PAHs isomers are completely resolved on P4.4.4 stationary phase and not on P4.8. On P4.4.4 stationary phase, the solutes are longer retained and the retention factor k' ($k' = (t_r - t_0)/t_0$), where t_r is the retention time and t_0 the dead time) increases as the solutes become more rod-like. Figure 2 illustrates with an example the main chromatographic difference between the two stationary phases, i.e. the lack of separation of the three-ring isomers on P4.8 stationary phase and the longer retention times on P4.4.4 one.

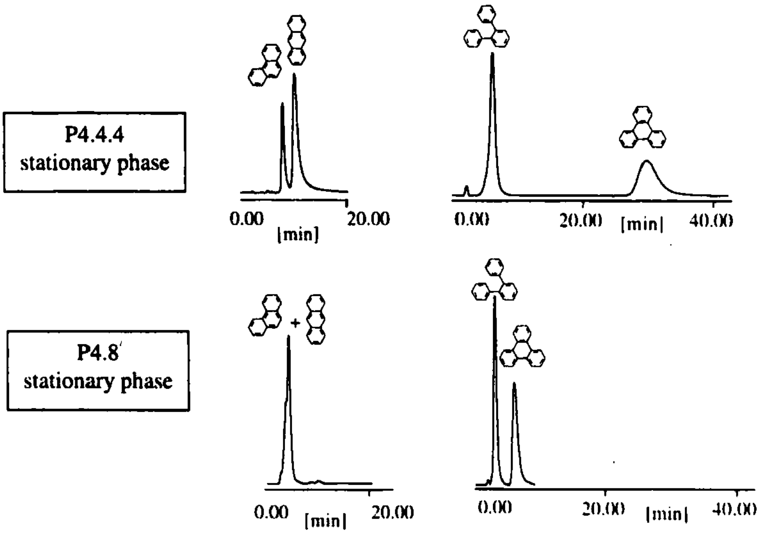


FIGURE 2 Typical chromatograms for the stationary phases prepared with either a side-on fixed LCP (P4.4.4) or its side-end fixed homologue (P4.8).

In terms of planarity recognition, the non-planar solutes are less retained on both stationary phases than the corresponding planar PAHs. The planarity recognition ability of triphenylene/o-terphenyl is significantly higher for the lateral P4.4.4 coated stationary phase (α = k'_{tri} /$k'_{o\text{-}ter}$ = 6.4) than for longitudinal P 4.8 one (α = 2.8).

Since the two LCPs bear comparable mesogenic rods, the chromatographic performances, thus, appear to be highly dependent on the architecture of the coated liquid crystalline polymer. In side-on fixed P4.4.4 nematic (or glassy nematic) state the polymer backbone is stretched in the direction of the mesogenic groups which form a jacket around it [6] . This structure gives a good access to the solutes and favors the mesogen-solute interactions, thus increasing the discrimination capability. On the opposite, the comb-like structure, resulting from longitudinally attached mesogenic pendants, does not facilitate the solute-stationary phase interaction since the PAHs cannot easily "penetrate" between the mesogenic side-chains because of the steric hindrance due to aromatic π–electrons. This results in a partial exclusion from the stationary phase.

The main conclusion is that the lateral fixation of the mesogenic units on the polymer backbone leads to the higher chromatographic performance of coated stationary phases (in terms of anisotropy as well as planarity recognition) than the axial fixation of the mesogens.

Influence of the spacer length

In the case of side-on fixed LCP coatings, the influence on the chromatographic properties of the spacer length is now evaluated. Two stationary phases are prepared with the side-on fixed LCPs with either a short spacer (P4.4.4) or a long one (P10.4.4). The elemental analysis indicates the similar mesomorphic concentration (M = 0.234 and 0.237 mmol per gram of silica). As shown in figure 3, PAHs are more retained on the stationary phase based on P10.4.4. A longer flexible spacer gives a better access to the mesogens of the stationary phase and in this sense, allows more interaction between the mesogens and the solutes, resulting in longer retention times. Better results, in terms of shape selectivity and planar/non-planar discrimination, are thus obtained for a stationary phase coated with long spacer LCP.

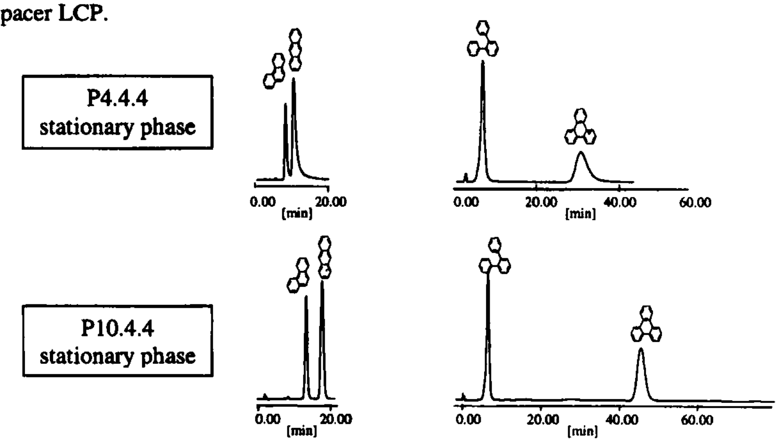


FIGURE 3 Influence of the spacer length of the side-on fixed LCPs on the chromatographic properties of the stationary phase.

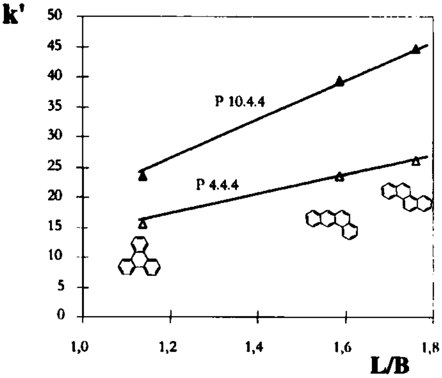


FIGURE 4 Correlation between the retention factor k' and the length-to-breadth ratio L/B for four-ring PAH isomers.

Among planar PAH isomers, solute retention on the stationary phases based on side-on fixed LCP is closely related to a shape parameter L/B defined as the length-to-breadth ratio. Rod-like molecules are retained longer than square ones and as shown in figure 4, the retention of four-ring PAH isomers linearly increases with L/B (i.e. as the shape solute becomes more rod-like).

Molecular modeling

Nevertheless, the correlation between the retention and the L/B ratio is valid only for isomeric PAHs and this molecular parameter does not correlate the retention of PAHs of different families. Thus, we attempt to connect the retention data to the mesogen/solute interactions. To this aim, we use computer simulations of molecular mechanics (MM2 force field) and molecular dynamics. We determined successively the energy of each element : E1 for an isolated mesogen and E2 for an isolated solute, and the energy E12 corresponding to the "complex" mesogen/solute. The gap of energy between the states corresponding either to isolated molecules or to molecules in interaction :

$$\Delta E_{inter.} = (E12 - E1 - E2)$$

is thus determined.

The figure 5 shows the relationship between $\Delta E_{inter.}$, a calculated parameter which represents the interaction between one solute and one mesogen, and the retention factor k', which reflects the interactions of all the molecules of solute with the whole stationary phase at a macroscopic level. This parameter $\Delta E_{inter.}$ correlate the retention factors independently of the nature of the PAHs, isomers or not , planar or non-planar and in this sense allows a general description of the retention data on a LCP based stationary phase. A more complete description of these calculations will be given elsewhere [7].

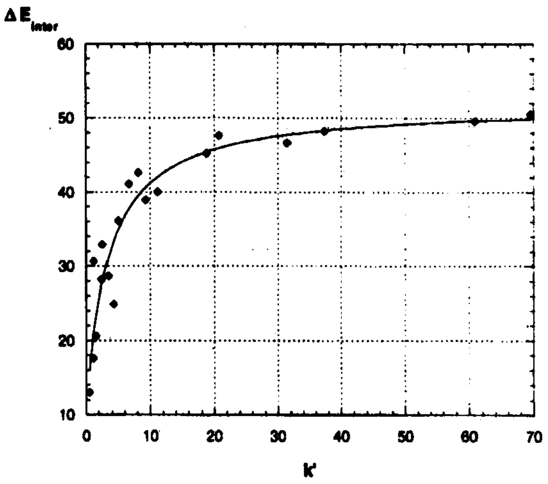


FIGURE 5 : Relationship between ΔE_{inter} and the experimental values of the retention factors k' obtained on a P10.4.4 coated stationary phase for PAHs belonging to different families.

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