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JOURNAL OF  
CHROMATOGRAPHY A

Journal of Chromatography A, 677 (1994) 197–200

### Short Communication

## Highly selective liquid crystalline polysiloxane stationary phase for gas chromatographic separation of isomers

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First received 29 December 1993; revised manuscript received 22 March 1994)

### Abstract

The gas chromatographic isomeric selectivity (for *p*- and *m*-xylene) of six mesogenic monomers and polysiloxanes having various side-chains, degrees of polymerization and linking ester groups (–OOC– and –COO–) were investigated. The results indicate that the polymeric stationary phases had higher isomeric selectivities. The highest selectivity coefficient for *p*- and *m*-xylene,  $\alpha = 1.21$ , was obtained at 65°C for the polymeric stationary phase [4-octyloxy(4-allyloxyphenyl benzoate)]polymethylhydrogensiloxane (POBAP-20) with an optimized film thickness of 0.63  $\mu\text{m}$ .

### 1. Introduction

Generally, liquid crystals are the most selective stationary phases for the gas chromatographic separation of isomers. The bonding of polysiloxanes with liquid crystalline compounds produces substances with interesting characteristics as stationary phases. Among liquid crystalline polymers, in this particular case mesogenic polysiloxane, are many substances useful as selective stationary phases for the separation of compounds additionally according to their molecular shape [1]. Capillary columns prepared from such polymers are generally more thermostable and often more efficient than columns coated with monomeric phases. By the selection of polysiloxane chains, namely of the correct composition and *n*-alkyl chain length,

and by the connection of the mesomorphic molecules to the polysiloxane backbone, liquid crystals can be obtained that are isotropic at temperatures exceeding 300°C. The melting points of these mesogenic polysiloxane (MEPSIL)-type phases are in the range 90–140°C [2]. This limits their application in the gas chromatographic separation to the substances that have relatively low boiling points.

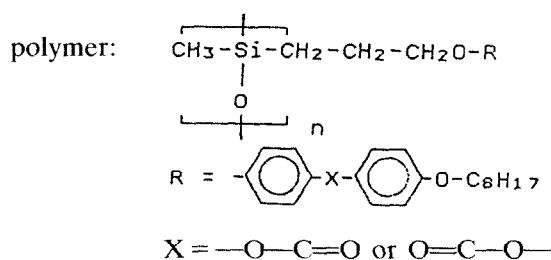
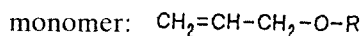
In previous work [3] the retention behaviour of MEPSIL with different lateral chains was studied. Relatively high selectivity for *p*- and *m*-xylene was observed in the smectic range of these stationary phases. Jin et al. [4] reported very high selectivity for *p*- and *m*-xylene measured on similar liquid crystalline polysiloxane phases. Based on these results, we focused our interest on selectivity studies with this type of polymeric liquid crystals. For this purpose, we synthesized monomers and polymers having dif-

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ferent side-chains, degrees of polymerization and linking ester functional groups ( $-\text{OOC}-$  and  $-\text{COO}-$ ) [3], and then investigated the gas chromatographic behaviour of these compounds with respect to their selectivity for the separation of isomers.

## 2. Experimental

The retention properties of six synthesized liquid crystalline stationary phases coated on glass capillary columns (columns 1–6 in Table 1) with different structures were studied:



The basic characteristics of phase transitions of the monomer [4-octyloxy(4-allyloxyphenyl benzoate)] (No. 1) and their polymers obtained by reaction with polymethylhydrogensiloxane (Nos. 2 and 3) and the monomer [4-allyloxy(4-octyloxyphenyl benzoate)] (No. 4) and their polymers (Nos. 5 and 6) are presented in Table

1. The phase transition temperatures were measured using a light-polarized microscopy and a DSC-7 calorimeter (Perkin-Elmer) (data were obtained from M. Müller, Halle University, Germany). These values are in a good agreement with gas chromatographic measurements. The film thickness of the stationary phases, coated on glass capillary columns (30 m  $\times$  0.31 mm I.D.) by the static method described by Grob et al. [5], were 0.31, 0.47, 0.63 and 1.00  $\mu\text{m}$ , respectively. The measurements were carried out with a Carlo Erba GI 452 gas chromatograph equipped with a flame ionization detector. Hydrogen was used as the carrier gas with a velocity of 27 cm/s. The efficiencies of the prepared glass capillary columns were within the limits published in a review [6] for other MEPSIL liquid crystalline phases.

## 3. Results and discussion

The selectivity coefficients  $\alpha$  for *p*- and *m*-xylene of the six liquid crystalline phases coated on capillary columns were measured at several temperatures. The measurements were carried out in the mesogenic, crystalline and glassy states with heating and cooling of the columns.

Fig. 1 shows dependence of  $\alpha$  on temperature with column heating for monomeric and polymeric MEPSIL columns with a stationary phases film thickness of 0.31  $\mu\text{m}$ . The curves indicate that the selectivity of polymeric phases is higher

Table 1

Phase transitions of the investigated monomeric and polymeric liquid crystalline stationary phases

No.	$n^a$	Name	Middle group	Monomer <sup>b</sup>	Polymer <sup>b</sup>
1	—	OBAP	$-\text{OOC}-$	Cr65(S <sub>A</sub> 60)N87Is	
2	20	POBAP	$-\text{OOC}-$		Cr55CL134Is
3	36	POBAP	$-\text{OOC}-$		Cr67S <sub>B</sub> 82S <sub>A</sub> 156Is
4	—	ABOP	$-\text{COO}-$	Cr63N85Is	
5	20	PABOP	$-\text{COO}-$		Cr35CL98Is
6	36	PABOP	$-\text{COO}-$		G28S89N111Is

<sup>a</sup>  $n$  = Average degree of polymerization.

<sup>b</sup> Abbreviations: Cr = crystalline; G = glassy; S<sub>A</sub>, S<sub>B</sub> = smectic A and B; N = nematic; Is = isotropic liquid; CL = crystalline liquid state; the numbers are transition temperatures in  $^{\circ}\text{C}$ .

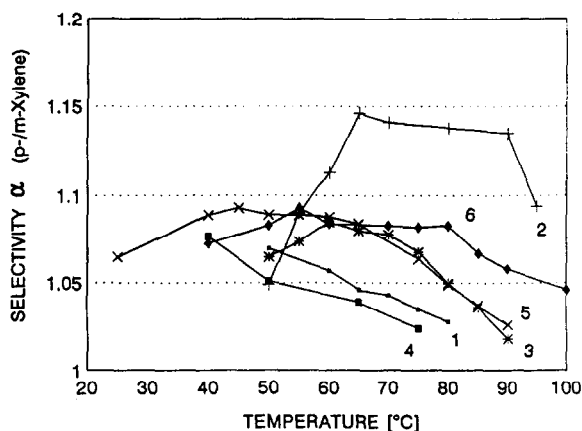


Fig. 1. Temperature dependence of selectivity coefficient of the investigated liquid crystalline stationary phases with film thicknesses  $0.31 \mu\text{m}$  in the column heating mode. 1 = OBAP; 2 = POBAP-20; 3 = POBAP-36; 4 = ABOP; 5 = PABOP-20; 6 = PABOP-36.

than that of monomeric phases. This result is contrary to the idea that the selectivity of liquid crystal polysiloxane stationary phases increases with increasing content of the mesogenic substituent in the polymeric molecule [7]. Moreover, the length of the Si chains (size of the molecule) influences the selectivity coefficient in different ways. For example, in the POBAP phase the  $\alpha$  values for the polymer with  $n = 20$  are generally higher than for the polymer with  $n = 36$ . Conversely, for the PABOP phases the polymer with  $n = 36$  has a slightly higher selectivity than the polymer with  $n = 20$  at temperatures exceeding  $75^\circ\text{C}$ , whereas at lower temperatures both polymers have similar  $\alpha$  values. From the dependences in Fig. 1, it is evident that the highest selectivity coefficients were obtained in columns with a POBAP-20 stationary phase and with a film thickness of  $0.31 \mu\text{m}$  at  $65^\circ\text{C}$  ( $\alpha = 1.15$ ). A similar dependence of the  $\alpha$  values on temperature was found also in measurements with cooling POBAP-20 capillary columns.

The column selectivity also depends on the film thickness of the liquid crystalline stationary phase [8]. In capillary columns maximum selectivity is obtained when an optimum film thickness of stationary phase is applied. Fig. 2 demonstrates the dependence of the  $\alpha$  values on the

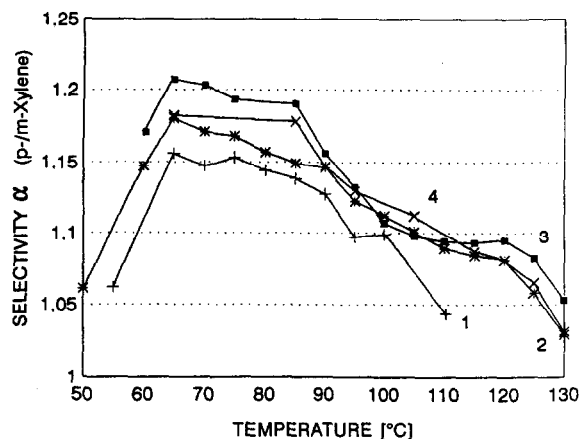


Fig. 2. Temperature dependence of selectivity coefficient on film thickness of POBAP-20 in the column cooling mode: 1 =  $0.31 \mu\text{m}$ ; 2 =  $0.47 \mu\text{m}$ ; 3 =  $0.63 \mu\text{m}$ ; 4 =  $1.00 \mu\text{m}$ .

film thickness of POBAP-20 stationary phase in the column cooling mode. It appears that in the interesting temperature range  $60\text{--}90^\circ\text{C}$ , with increasing stationary phase film thickness from  $0.31$  to  $0.63 \mu\text{m}$  the  $\alpha$  value increase, but for a film thickness of  $1.0 \mu\text{m}$  the selectivity coefficient is slightly lower. The highest value,  $\alpha = 1.21$  for *p*- and *m*-xylene, was found on a POBAP-20 capillary column with a film thickness of  $0.63 \mu\text{m}$  at  $65^\circ\text{C}$ .

A very high  $\alpha$  value of 1.33 for *p*- and *m*-xylene at  $70^\circ\text{C}$  has been reported [4] for a similar liquid crystalline stationary phase to PABOP-20 (degree of polymerization  $n = 19$ ). However, the authors subsequently reported that their experimental measurements were misinterpreted [9].

Values of selectivity coefficients for *p*- and *m*-xylene measured on liquid crystalline stationary phases were compiled by Mazur and Witkiewicz [6]. They reported the highest measured selectivity coefficient  $\alpha = 1.19$  at  $40^\circ\text{C}$  [10]. Comparison of these data with our measurements shows that the stationary phase POBAP-20 has the highest selectivity coefficient for *p*- and *m*-xylene. Possible explanations for the high selectivity of POBAP-20 might include a favourable ratio of the mesogenic group, degree of polymerization, structure of lateral chains, packing of

the molecules and/or the film thickness of the MEPSIL phase in capillary columns. A computer program is in preparation to evaluate possible correlations between the molecular structure of liquid crystals and their isomeric selectivity.

### Acknowledgements

The authors are indebted to Dr. B. Krücke for preparing the liquid crystalline compounds, M. Müller for the phase transition data and Dr. A. Kraus for suggestions regarding the manuscript (all from Halle University).

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