DEVELOPMENT OF CAPILLARY COLUMNS FOR ENVIRONMENTAL ANALYSIS

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1. Abstract

New main-chain liquid crystal polymer (MCLCP) stationary phases were developed for their use in capillary columns for gas chromatography (GC). Fused silica capillary columns with MCLCP shows superior selectivity for the separation of 2,3,7,8-substituted chlorinated dioxin isomers compared to regular columns with dimethyl or phenyl polysiloxane phases. Separations of polychlorinated dibenzo-p-dioxins and dibenzofurans on conventional columns and on columns developed in our laboratory are compared.

2. Introduction

There are two main types of thermotropic polymeric liquid crystals, main-chain and side chain liquid crystal polymers. There are several publications on use of side-chain liquid crystal polymers (SCLCP) in capillary column GC[1-5]. Side chain liquid crystal polysiloxanes have shown superb separations for structural isomers. There are very few reports on use of the MCLCP in capillary GC. This paper describes the development and use of main chain liquid crystal polymer capillary columns for environmental analysis.

3. Experimental

Two new liquid crystalline main chain polymers were synthesized. General structure of the MCPLC consists of alternate units of dimethyl siloxane and liquid crystal moiety. The method of synthesis consists of, synthesis of liquid crystalline monomer with vinyl end groups, then the reaction of liquid crystalline monomers with polysiloxane having hydride (hydrogen) end groups using platinum catalyst. Hydrosilylation reaction between those monomers then results in MCPLC. Purified MCPLC were then coated in deactivated fused

silica capillary tubing using static coating method. To prepare the column the appropriate amount of stationary phase solution was placed inside a small test-tube. This tube was then placed in the holder tube. With the column installed in the GC oven, one end of the column was placed inside the test-tube holding the stationary phase. The holder tube was sealed by means of tightening the top nut with the appropriate sized ferrule. With the control valve allowing nitrogen into the holder tube, a pressure of 15 psi was applied to the system. After several minutes, drops of stationary phase solution were formed at the free end of the column. This was an indication that the column was filled with the solution. Then, the pressure was turned off at the N_2 valve and at the tube holder. The free end was sealed using wax. To remove the solvent, the control valve was turned to the vacuum outlet. The test tube that held the remaining stationary phase was replaced with a clean test tube, and the seal of the holder tube was re-established with that end of the column inside the tube. The vacuum was turned on and the migration of the solvent plug at the end of the column was observed to ensure that the stationary phase solution did not exit the column. After all the solvent was removed by vacuum the column was conditioned using slow temperature program such as 2 C/minute from 50 C to 300 C, hold for 2 hours at 300C.

4. HRGC and HRGC-MS analytical procedures

Instruments and conditions for the analysis:

gas chromatograph:	Hewlett Packard 5890
mass selective detector:	Hewlett Packard 5970
work-station:	Hewlett Packard 59970
column:	MCLCP Column 1 and 2, 30 m, 0.25 mm i.d., df=0.1μm
injection:	on column, volume: 1 or 2 μl
carrier gas:	Helium, @5 psi head pressure
temperature programm:	150°C for 1 min, 6°C/min to 260°C, then 4°C/min to 300°C, hold for 20 min. at 300°C
ionizing voltage:	70 eV
ions monitored:	$[M+2]^+$ or $[M+4]^+$, for each congener group of tetra- to octa-CDD and -CDF

5. Results and discussion

Two new MCLCP were developed. The operating range of the columns prepared using the MCLCP is up to 300°C. It should be emphasized that previously developed SCPLC are stable up to 275°C. Stability of MCPLC could be due to the attachment of monomeric liquid crystal to siloxane at both sides increasing the strength of the backbone polysiloxane. A column (30 m X 0.25 mm, df =0.1 μm) prepared using MCPLC stationary phase shows very interesting elution patterns for PCDD isomers. Elution behaviour of 2,3,7,8-substituted tetra- and penta-chlorinated dioxin isomers is shown in **Figure 1**. The retention behaviour of 2,3,7,8-TCDD is partially according to mechanism of separation on liquid crystal

stationary phases. This retention behaviour provides clues about making tailored stationary phase with varying composition to tune the selectivity for desire separations in the shortest time. It is observed that, complete separation of OCDD from OCDF with in 30 minutes run time can be achieved using MCPLC columns. These columns also gives better separation of 2,3,7,8- substituted dioxins isomers and isomeric polycyclic aromatic hydrocarbons.

6. Conclusions

Two new main-chain polymeric liquid crystal stationary phases were developed. These stationary phases are stable up to 300°C when used in capillary columns. Selectivity for the separation of 2,3,7,8-Substituted dioxin isomers has been observed for the columns developed using new stationary phases.

References:

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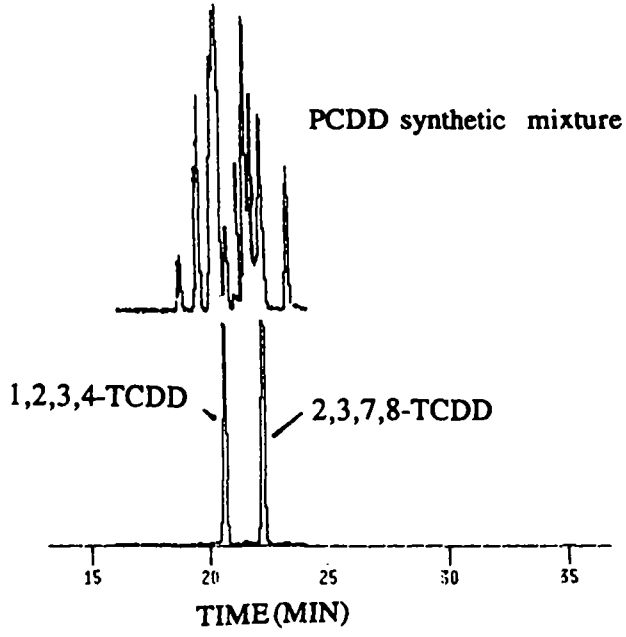
FIGURE 1.

a) Separation of 2,3,7,8-TCDD from other TCDD isomers, GC-MS/SIM data, see text for chromatographic conditions



b) Separation of 1,2,3,7,8-P5CDD from other P5CDD isomers, GC-MS/SIM data, see text for chromatographic conditions