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New naphthalene containing side-chain liquid crystalline polysiloxane stationary phases for high-resolution gas chromatography

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Abstract

A new side-chain liquid crystalline polysiloxane (SCLCP) having a wide liquid crystalline range of 140°C to 315°C was used as a stationary phase in capillary column gas chromatography. A series of new SCLCPs was synthesized using olefins containing 2,6-disubstituted naphthalene. The olefins were attached to a hydromethylpolysiloxane backbone by a hydrosilylation reaction using a platinum catalyst. Reproducible fused-silica capillary columns were made from the new SCLCP stationary phase. The columns have high thermal stability, efficiency and isomer specificity for the separation of isomeric compounds. The separations on the SCLCP stationary phase column and on a dimethyl (5% phenyl)polysiloxane stationary phase column are compared. The applications of capillary columns made from the new SCLCP for the separation of isomeric polychlorinated dibenzo-*p*-dioxins, polycyclic aromatic hydrocarbons and pesticides are demonstrated as examples.

Keywords: Stationary phases, GC; Liquid crystals; Polynuclear aromatic hydrocarbons; Pesticides; Polychlorinated dibenzodioxins

1. Introduction

Compounds with different boiling points and molecular masses are easily separated and analyzed using conventional stationary phases in capillary column gas chromatography (GC). The separation of compounds with similar volatilities or boiling points using capillary columns with conventional stationary phases is very difficult, because the separation is based on differences in volatilities of the sample components. The separation and analytical task becomes difficult and challenging for the compounds with close boiling points and molecular masses, especially positional and structural isomers. Very long capillary columns (>60 m) with conventional stationary phases can provide the separation of close boiling compounds if they differ in molecular masses and structures. However, the use of long capillary columns results in a longer time for the analysis, which is not practical for routine analysis and the separation of isomeric compounds are not satisfactory. Therefore, it is necessary to develop stationary phases that differ from those known and have

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advantageous properties. Liquid crystalline polysiloxanes (LCPs) are among such stationary phases.

Liquid crystalline stationary phases have shown unique selectivity for the separation of isomeric compounds of similar volatilities, the subject has been reviewed several times [1–6]. After the initial discovery of the selectivity of liquid crystalline stationary phases the main thrust was to develop liquid crystalline compounds with wide liquid crystalline temperature ranges for columns with higher operating temperatures and lower bleed in GC applications [7–13]. The correlation between the separation factor for positional isomers of disubstituted benzenes (*meta* and *para*), liquid crystalline range and structures of liquid crystalline stationary phases has been studied [14–26]. It was found that the separation factor for a particular pair of isomers depends not only on the liquid crystalline range but also on the chemical structure of the liquid crystalline stationary phase. Thus, depending on the structure of the liquid crystalline stationary phase, the selectivity for the separation of isomer pairs of different sizes and shapes varies. The correlation between the structure of the stationary phase and the separation of the isomeric compounds provides very important clues to develop specific liquid crystalline stationary phases for the separation of isomeric compounds, this correlation has prime importance in designing tailor made stationary phases.

The synthesis and applications of side-chain liquid crystalline polysiloxanes (SCLCPs) [27–37] and polyacrylates [38–40] in capillary column GC have been reported. Among the side-chain liquid crystalline polymers, mostly phenyl and biphenyl carboxylic acid esters containing side-chain polymers were developed and used as stationary phases. It would be of interest to develop SCLCPs containing a variety of substituted aromatics and to explore their properties as stationary phases in capillary GC. Thus, considering the structures, liquid crystalline ranges and thermal stability of the liquid crystalline stationary phase so far studied [27–40], it was decided to develop new SCLCPs with 2,6-disubstituted naphthalene, a fused-ring aromatic system containing side-chains, to study their properties as GC stationary phases. Initially, several 2,6-disubstituted naphthalene containing liquid crystalline olefins were synthesized. Those olefins were then attached to a polysiloxane backbone by hydrosilylation reaction. The synthetic procedures and properties of a series of olefins, and the SCLCPs from those olefins, will be published elsewhere. A new SCLCP containing disubstituted naphthalene was studied as a stationary phase in capillary column GC and the results are reported in this paper.

2. Experimental

The new SCLCP developed under the current investigation was used as a stationary phase to make fused-silica capillary columns. The columns were made using the static coating technique. In a typical procedure, the fused-silica capillary tubing of about 60 m in length, was cleaned by passing toluene (five-times the volume of the tubing) through the tubing. Then the tubing was dried by heating in a GC oven from 40°C to 300°C at a program rate of 10°C/min, with helium passing through the tubing at a flow-rate of about 3 ml/min. The stationary phase solution was prepared by dissolving a calculated amount of SCLCP in dichloromethane. A pre-treated fused-silica capillary tubing of desired length was then filled with the stationary phase solution. The filled tubing was then sealed at one end and solvent was removed by applying vacuum to the other end. The coated column was conditioned by heating from 40°C to 295°C at 4°C/min, and holding at 295°C for 5 h. The SCLCP used as the stationary phase had a wide liquid crystalline range of 140°C to 315°C. Three columns: (1) 30 m×0.25 mm I.D., 0.125 μm film, (2) 20 m×0.25 mm I.D., 0.15 μm film, (3) 10 m×0.25 mm I.D., 0.15 μm film were prepared and evaluated in the current studies. The columns made using the SCLCPs developed in this study are designated as LC-50 columns, where LC stands for liquid crystalline and 50 indicates that the backbone polysiloxane contains about 50% liquid crystal side-chains. For the comparison a ICB-5 [immobilized and chemically bonded, dimethyl (5% phenyl) polysiloxane stationary phase] column, 30 m×0.25 mm, 0.25 μm film was also prepared using the static method as described above. A mixture of polychlorinated dibenzo-*p*-dioxins (PCDDs) synthesised in our laboratory and individual standards of 2,3,7,8-substituted PCDD isomers available from commercial

sources were used to determine the selectivity of the newly developed column. The standards of polycyclic aromatic hydrocarbons (PAHs) and pesticides were used from our laboratory stock. The ions monitored for the tetra- to octachlorinated PCDDs during a GC–mass spectrometry (MS) run were M, M+2, M+4 or M+2, M+4, M+6 for each congener group. A Hewlett-Packard 5890 GC/5970 mass-selective detection (MSD) system and a HP 5880 gas chromatograph equipped with electron-capture detection (ECD) and flame ionization detection (FID) systems was used to evaluate the performance of the columns regarding efficiency, stability and the isomer specific selectivity. Liquid crystalline transition temperatures were determined using a heating stage polarizing microscope (Leitz, Germany).

3. Results and discussion

The structure of the SCLCP used as the stationary phase is shown in Fig. 1. The transition temperatures of the SCLCP were 140°C (crystalline to nematic, cn) and 315°C (nematic to isotopic, ni), which were determined by a heating stage polarizing microscope. Different batches showed minor variation in transition temperatures, however, the performance of fused-silica capillary columns made from different batches of the SCLCP was identical. Although, the SCLCP has a wide liquid crystalline range between 140 to 315°C, our extensive studies of the stability of the stationary phase shows that the columns conditioned at 295°C for 5 h can be operated between 100°C to 270°C with optimum performance for a long period of time. Extension of the lower column operating temperature from 140°C to 100°C seems to be due to cross-linking of the backbone polysiloxane chain during column conditioning.

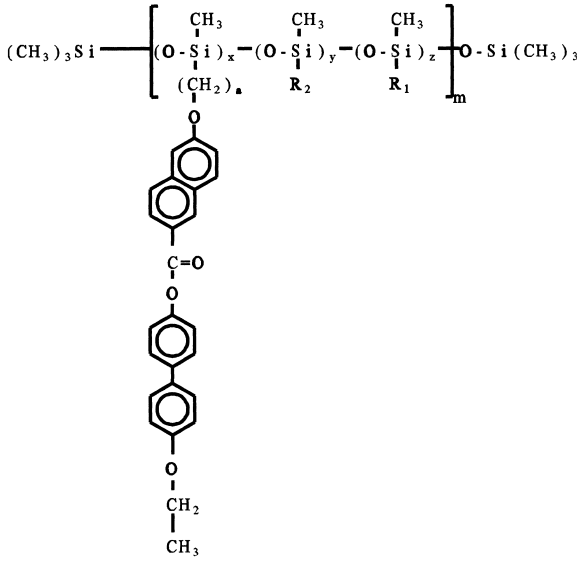

Fig. 1. Structure of a SCLCP stationary phase. Liquid crystalline phase transition temperatures: crystalline to nematic (cn), 140°C; nematic to isotropic (ni), 315°C.

Generally, columns made from liquid crystalline stationary phases have shown lower efficiencies than from those made from traditional polysiloxane stationary phases [28,30]. Capillary columns with the traditional polysiloxane stationary phases shows high efficiency when *n*-alkanes or fatty acid methyl esters were used as solutes, however, it was observed that PAHs such as triphenylene and chrysene show high efficiency on the SCLCP stationary phases. This may be due to the high polarity of the SCLCP and also due to the matrix effect of the ordered structure of the SCLCP stationary phase. The columns made using the SCLCP stationary phase under current investigation shows efficiencies up to 3600 theoretical plates per meter for triphenylene and chrysene for the columns with an internal diameter of 0.25 mm and film thickness up to 0.25 μm.

The preparation and uses of various side-chain liquid crystalline polymer stationary phases in capillary column GC have been reported [27–40]. However, lower column efficiency and higher column bleed over 240°C are the main drawbacks of these stationary phases. The reports of the use of polymeric liquid crystal stationary phases show that most of the capillary columns start bleeding above 240°C. Columns with the SCLCP developed in our studies are stable up to 295°C. We have observed a column bleed of less than 10 picoamperes (pA) at 270°C for columns up to 20 m in length (I.D. 0.25 mm) with a film thickness of 0.15 μm. It is observed that the operation of the columns above 270° (up to 295°C) is also possible. In our studies it was found that instead of using longer columns (30 m) at higher temperatures for shorter run times for less volatile sample components, it is better to use shorter columns (10 to 20 m) with smaller film thicknesses. Liquid crystal

columns have very large separation factors for the separation of isomeric compounds, so it is possible to use 10 to 20 m columns to separate compounds difficult or impossible to separate on longer (>60 m) capillary columns with conventional stationary phases. The column developed under the current investigation is operable between 40 to 310°C, however, below 100°C column efficiency is poor and above 295°C column bleed is excessive. Thus, for the optimum performance and longer life of the column it seems that the column should be used in the range of 100°C to 270°C.

A graph of separation factor vs temperature for phenanthrene (M_r 178, b.p. 324°C) and anthracene (M_r 178, b.p. 324°C) on LC-50 and ICB-5 columns is shown in Fig. 2. A higher separation factor on the LC-50 column was observed. Interestingly, a baseline separation of phenanthrene and anthracene was observed even at 230°C on the LC-50 column, where as they eluted as a single peak on the ICB-5 column.

The separation of a mixture of PAHs on the LC-50 and ICB-5 columns is shown in Fig. 3. Separation of the mixture of PAHs, especially isomeric PAHs, phenanthrene/anthracene, triphenylene/chrysene and benzo[*e*]pyrene/benzo[*a*]pyrene is fast and superior on the LC-50 column. It is appreciable that such a superb selectivity and separation is observed on a 10 m column compared to a 30 m ICB-5 column with the conventional stationary phase. Comparison of the chromatograms also shows that the SCLCP column has produced very symmetrical peaks and comparable bleed to that of the ICB-5 column, these results indicate that the LC-50 can be used for trace analysis of complex environmental samples.

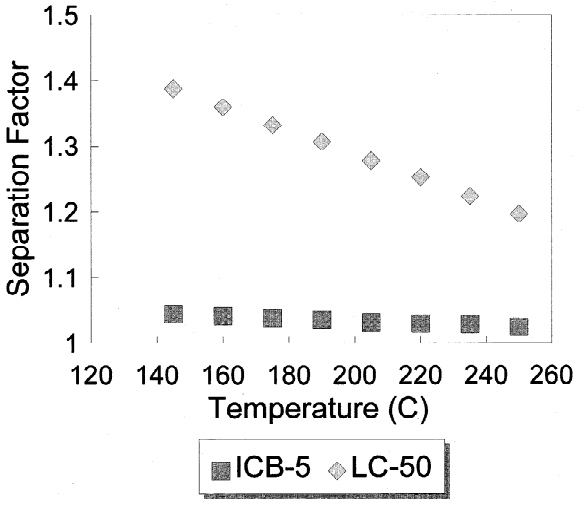

Fig. 2. A graph of separation factor (α) vs. column temperature (°C) for phenanthrene and anthracene on ICB-5 and LC-50 columns.

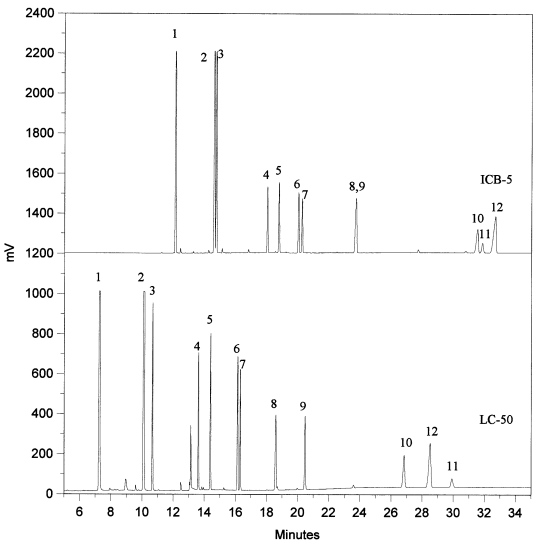

Fig. 3. Separation of a mixture of PAHs on ICB-5 and LC-50 columns. Chromatographic conditions: columns: ICB-5, 30 m× 0.25 mm, 0.25 μm film; LC-50, 10 m×0.25 mm, 0.15 μm film; temperature program: 100°C for 1 min, 100 to 240°C at 10°C/min, 240 to 275°C at 4°C/min, 275°C for 20 min. Injector: cool-on-column. Detection: FID at 320°C; carrier: helium; amount of each compound: 10 to 100 ng. Peaks: 1=fluorene, 2=phenanthrene, 3=anthracene, 4=fluoranthene, 5=pyrene, 6=1,2-benzofluorene, 7=2,3-benzofluorene, 8=triphenylene, 9=chrysene, 10=benzo[*e*]pyrene, 11=perylene, 12=benzo[*a*]pyrene.

GC–MS in the electron impact selected ion monitoring (EISIM) mode is generally used for analysis of PCDDs. The separation of PCDDs from other interfering compounds can be achieved using high-resolution (HR) GC–HR-MS and HR-GC–MS–MS techniques. However these techniques are not useful for the separation of isomers in each congener group. The separation of 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) from other TCDD isomers is very important to determine the toxicity of a particular sample. The analytical methodology could be simplified if a gas chromatographic column could sepa-

rate the interfering compounds as well as the isomers in all congener groups of dioxins and dibenzofurans. The complete separation of 2,3,7,8-TCDD from all other TCDD isomers using the newly developed capillary column by GC–MS is shown in Fig. 4A. The separation and retention time of 2,3,7,8-TCDD

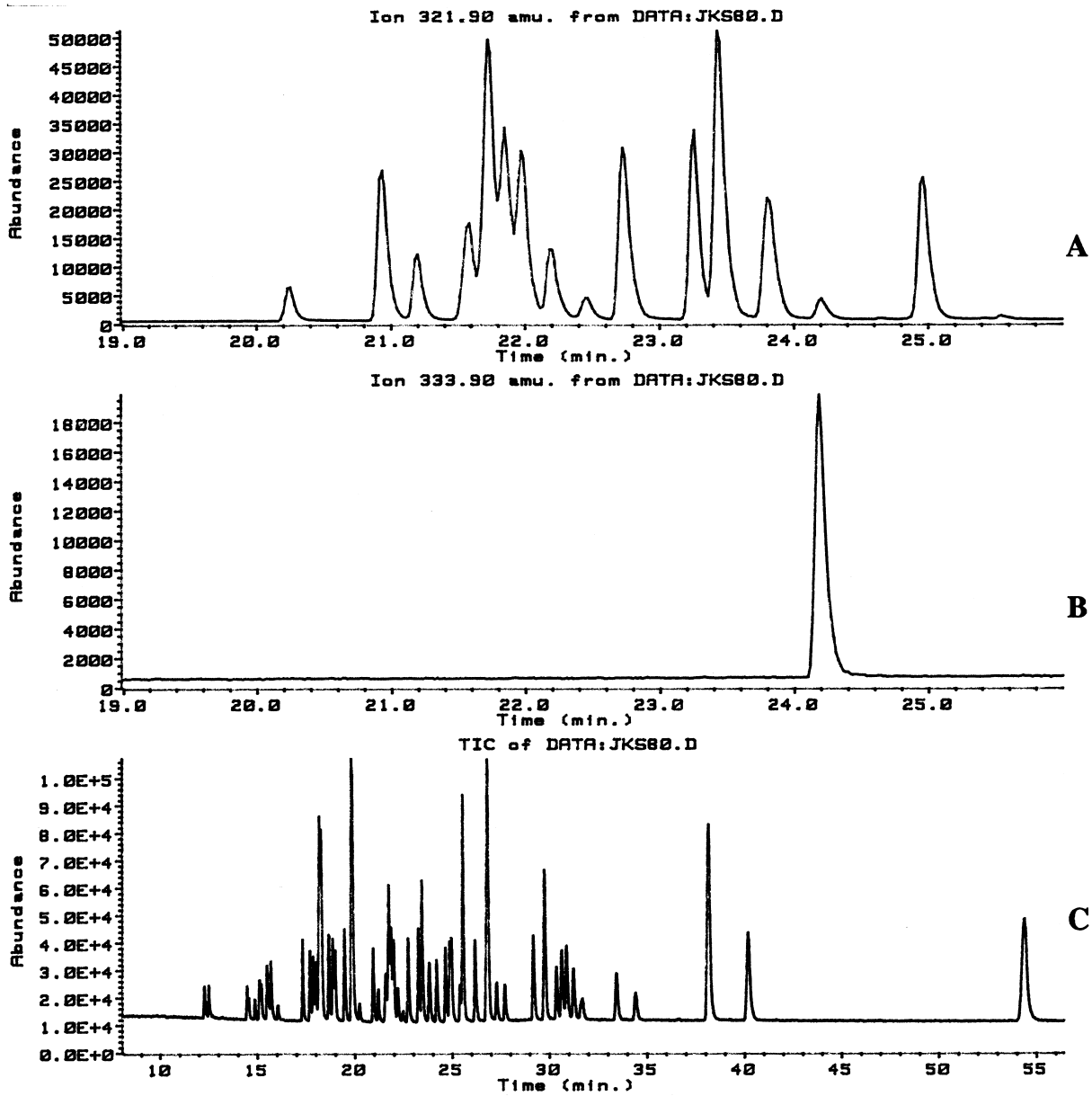

Fig. 4. Separation of 2,3,7,8-TCDD from other TCDD isomers, GC–MS/EI-SIM data. (A) Mass chromatogram of M+2 ion of T_4CDD (m/z 321.9) for a synthetic mixture of PCDDs, (B) mass chromatogram of M+2 ion of [^{13}C]TCDD (m/z 333.9) for a spiked labelled standard, (C) total ion chromatogram of a synthetic mixture of PCDDs. Chromatographic conditions: LC-50 column: 30 m×0.25 mm I.D., 0.125 μm film. Temperature program: 100°C for 1 min, 100 to 250°C at 10°C/min, 250 to 285°C at 5°C/min, 285°C for 40 min. Injector: cool-on-column. Interface at 285°C.

was confirmed from the retention time of the spiked [^{13}C]TCDD, Fig. 4B. It can be seen from Fig. 4A and Fig. 4B that 2,3,7,8-TCDD is completely separated from all other tetra-CDD isomers. The selectivity of this new column can be explained based on the mechanism of separation on liquid crystalline stationary phases. Among the isomers with similar volatilities, the linear and symmetrical isomers will be retained longer than the bulkier isomers because the linear and symmetrical isomers favour the geometry of the liquid crystal stationary phase. The 2,3,7,8-TCDD is the most symmetrical and linear of all 22 TCDD isomers and, hence, retain longer. The separation achieved using the new column and GC–MS selected ion monitoring (SIM) technique for a synthetic mixture containing mono- to octachlorodibenzo-*p*-dioxin isomers is shown in Fig. 4C. There are several advantages of the newly developed column for the analysis of environmental samples. It can be used for the analysis of the total PCDD/PCDF in addition to 2,3,7,8-TCDD in the environmental samples. The separation of 2,3,7,8-TCDD from other tetra isomers and analysis of all mono- to octachlorinated dibenzo-*p*-dioxins in a single run is a promising feature of this column.

Polychlorinated pesticides have been extensively used worldwide and are now recognized as major environmental pollutants. Their analysis in environmental samples can be performed using capillary columns in GC. However, the capillary columns with traditional stationary phases, such as dimethyl (5% phenyl)polysiloxane or dimethyl (50% phenyl) polysiloxane, are not adequate to resolve various isomeric pesticides. Comparison of elution order of a laboratory mixture of pesticides on ICB-5 and LC-50 columns is shown in Fig. 5. It is interesting to note that heptachlor, eluting as the 4th peak on ICB-5 column, elutes as the second peak on liquid crystal column. The elution order for BHC (benzene hexachloride) isomers has been changed on the liquid crystal column. Also, the change in elution order of 4,4′-DDD and 4,4-DDT on liquid crystal columns can be explained based on their structural differences. Also, it should be noticed that in addition to the separation based on structural differences, better separations are observed on a 20 m long liquid crystal column compared to a 30 m ICB-5 column. This indicates that liquid crystal columns can be used for fast analysis of complicated pesticide samples, and can provide isomer specific separations based on the structures of the compounds.

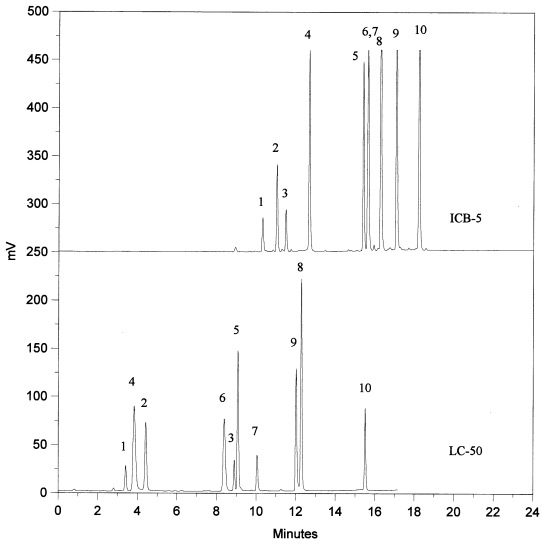

Fig. 5. Separation of a mixture of pesticides on ICB-5 and LC-50 columns. Chromatographic conditions: columns: ICB-5, 30 m× 0.25 mm, 0.25 μm film; LC-50, 20 m×0.25 mm, 0.15 μm film. Temperature program: 100°C for 1 min, 100 to 240°C at 10°C/min, 240 to 275°C at 4°C/min, 275°C for 20 min. Injector: cool-on-column, detection: ECD at 300°C; carrier: helium; amount of each compound: 5 to 10 ng. Peaks: 1=α-BHC, 2=γ-BHC, 3=δ-BHC, 4=heptachlor, 5=2,4′-DDE, 6=dieldrin, 7=2,4′-DDD, 8=4,4′-DDD, 9=4,4′-DDT, 10=methoxychlor.

4. Conclusions

A new SCLCP stationary phase containing 2,6-disubstituted naphthalene shows high thermal stability when used as a stationary phase in capillary GC. Reproducible columns can be made from the new stationary phase, which show high efficiency, thermal stability and selectivity for the separation of isomeric compounds. The new column can be used in GC and GC–MS for the separation and analysis of isomeric polychlorinated dibenzo-*p*-dioxins, PAHs and pesticides.

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References

[1] H. Kelker, E. Von Schivizhoffen, Adv. Chromatogr. 6 (1968) 247.
[2] J.P. Schroeder, in: G.W. Grey, P.A. Winsor (Eds.), Liquid Crystals and Plastic Crystals, Vol. 1, Ellis Horwood, New York, 1974, p. 365.
[3] M.S. Vigdergauz, R.V. Vigalok, G.V. Dmitrieva, Russ. Chem. Rev. 50 (1981) 498.
[4] Z. Witkiewicz, J. Chromatogr. 251 (1982) 311.
[5] J.M. Janini, Adv. Chromatogr. 17 (1982) 231.
[6] G.M. Janini, R.J. Laub, J.H. Purnell, O.S. Tyagi, in: C.B. McArdle (Ed.), Side Chain Liquid Crystalline Polysiloxanes, Chapman and Hall, New York, 1989, p. 395.
[7] J.M. Janini, K. Johnston, W.L. Zielinski Jr., Anal. Chem. 47 (1975) 670.
[8] G.M. Janini, G.M. Muschik, J.A. Schroer, W.L. Zielinski Jr., Anal. Chem. 48 (1976) 1879.
[9] G.M. Janini, G.M. Muschik, W.L. Zielinski Jr., Anal. Chem. 48 (1976) 809.
[10] G.M. Janini, G.M. Muschik, C.M. Hanlon, Mol. Cryst. Liq. Cryst. 53 (1979) 15.
[11] G. Chiavari, L. Pastorelli, G. Perrakis, Talanta 33 (1986) 979.
[12] A. Ziolek, Z. Witkiewicz, R. Dabrowski, J. Chromatogr. 294 (1984) 139.
[13] H.J. Issaq, G.M. Janini, B. Poehland, R. Shipe, G.M. Muschik, Chromatographia 14 (1981) 655.
[14] K.P. Naikwadi, D.G. Panse, B.V. Bapat, B.B. Ghatge, J. Chromatogr. 206 (1981) 361.
[15] K.P. Naikwadi, B.V. Bapat, B.B. Ghatge, Ind. J. Chem. Sec. B 20 (1981) 165.
[16] K.P. Naikwadi, D.G. Panse, B.V. Bapat, B.B. Ghatge, J. Chromatogr. 195 (1981) 309.
[17] D.G. Panse, K.P. Naikwadi, A.L. Jadhav, B.V. Bapat, B.B. Ghatge, Ind. J. Technol. 22 (1984) 112.
[18] P.P. Pawar, K.P. Naikwadi, S.M. Likhite, B.V. Bapat, B.B. Ghatge, J. Chromatogr. 245 (1982) 57.
[19] D.G. Panse, K.P. Naikwadi, B.V. Bapat, B.B. Ghatge, Ind. J. Technol. 19 (1981) 518.
[20] Z. Witkiewicz, H. Grajek, J. Szule, J. Chromatogr. 312 (1984) 141.
[21] E. Matisova, G. Kraus, A. Kraus, J. Chromatogr. 439 (1988) 381.
[22] J. Szule, Z. Witkiewicz, J. Chromatogr. 262 (1983) 141.
[23] Z. Suprynowicz, W.M. Buda, M. Mardarowicz, A. Patrykiejew, J. Chromatogr. 333 (1985) 11.
[24] H. Lamparczyk, J. High Resolut. Chromatogr., Chromatogr. Commun. 8 (1985) 90.
[25] A. Isenberg, G. Kraus, H. Zaschke, J. Chromatogr. 292 (1984) 67.
[26] A. Ziolek, Z. Witkiewicz, R. Debrowski, J. Chromatogr. 299 (1984) 159.
[27] H. Finkelmann, R.J. Laub, W.L. Roberts, C.A. Smith, in: M.W. Cook, A.J. Dennis, G.L. Fisher (Eds.), Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Battelle Press, Columbus, 1981, p. 275.
[28] R.C. Kong, M.L. Lee, Y. Tominaga, R. Pratap, M. Iwao, R.N. Castle, Anal. Chem. 54 (1982) 1802.
[29] B.A. Jones, J.S. Bradshaw, M. Nishioka, M.L. Lee, J. Org. Chem. 49 (1984) 4947.
[30] M.A. Apfel, H. Finkelmann, G.M. Janini, R.J. Laub, B.H. Luhmann, A. Price, W.L. Roberts, T.J. Shaw, C.A. Smith, Anal. Chem. 57 (1985) 651.
[31] G.M. Janini, R.J. Laub, T.J. Shaw, Macromol. Chem. Rapid Commun. 6 (1985) 57.
[32] K.E. Markides, M. Nishioka, B.J. Tarbet, J.S. Bradshaw, M.L. Lee, Anal. Chem. 57 (1985) 1296.
[33] M. Nishioka, B.A. Jones, B.J. Tarbet, J.S. Bradshaw, M.L. Lee, J. Chromatogr. 357 (1986) 79.
[34] J.S. Bradshaw, Ch. Schregenberger, K.H.C. Chang, K.E. Markides, M.L. Lee, J. Chromatogr. 358 (1986) 95.
[35] K.P. Naikwadi, A.M. McGovern, F.W. Karasek, Can. J. Chem. 65 (1987) 970.
[36] G.M. Janini, G.M. Muschik, H.J. Issaq, R.J. Laub, Anal. Chem. 60 (1988) 1119.
[37] I.D. Albrecht, K.P. Naikwadi, F.W. Karasek, J. High Resolut. Chromatogr. 14 (1991) 143.
[38] K.P. Naikwadi, A.L. Jadhav, S. Rokushika, H. Hatano, M. Ohsima, Macromol. Chem. 187 (1986) 1407.
[39] K.P. Naikwadi, A.L. Jadhav, S. Rokushika, H. Hatano, J. High Resolut. Chromatogr. Chromatogr. Commun. 8 (1985) 480–484.
[40] K.P. Naikwadi, A.L. Jadhav, S. Rokushika, H. Hatano, J. High. Resolut. Chromatogr. Chromatogr. Commun. 10 (1987) 77–81.