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High-resolution separation performance of poly(caprolactone)diol for challenging isomers of xylenes, phenols and anilines by capillary gas chromatography

Jianlin Peng, Yan Zhang, Xiaohong Yang, Meiling Qi *

Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials and School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, China

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ABSTRACT

Efficient separation of xylenes, phenols and anilines is a big issue in chemical and petroleum industries. This work presents the first example of employing poly (caprolactone) diol (PCL-Diol) as stationary phase for high-resolution gas chromatographic (GC) separations of these tough isomer mixtures. It showed medium polarity and stronger H-bonding basicity than H-bonding acidity. Impressively, PCL-Diol column exhibited extremely high resolving capability for the isomer mixtures of xylenes, cresols/xylenols, and toluidines/xylidines with good peak shapes. Moreover, it exhibited preferential retention for analytes of a linear alkyl chain, suggesting its shape fitting selectivity for specific analytes. In addition, its separation performance has good repeatability with RSD values on retention times below 0.01% for run to run ($n = 6$), 0.67–0.80% for day to day ($n = 4$) and 3.2–4.4% for column to column ($n = 4$) repeatability, respectively. Furthermore, it was applied for the determination of isomer impurities in real samples, showing good potential for practical use. This work demonstrates the advantageous high-resolution separation performance for challenging isomers and shows its promising future of PCL-Diol-based materials in separation science.

1. Introduction

High-resolution separation of positional isomers is of significant importance in chemical industry and environmental analysis. Capillary gas chromatography (GC) is one of the most efficient methods for isomer separations and diverse types of GC stationary phases have been explored over the past decade [1–8]. However, efficient separation of those challenging positional isomer mixtures, such as xylenes, cresols and xylenols, and toluidines and xylidines, is still a big issue. Currently, almost all the reported stationary phases only achieved good separation for some of the mixtures. It is quite demanding for one stationary phase to achieve good resolution for all of them since these isomers vary greatly in their chemical nature and polarity. Clearly, finding such a stationary phase with high selectivity for these isomers is a tough work but is valuable and urgently needed in practical use.

Exploration of highly selective stationary phases has been the pursuit of researchers in chromatography over the years. *o*-/*m*-/*p*-Xylenes together with ethylbenzene, the so-called C8 aromatic compounds, are important raw materials for chemical industry [9,10], and are also widely present as environmental pollutants, often monitored as BTEX (benzene, toluene, ethylbenzene and xylenes) [11,12]. Thus, their high resolution is vital for product purity control and environmental monitoring. However, their efficient separation, particularly the critical pair *p*-/*m*-xylene, is still a big issue [1,8,11]. So far, few GC stationary phases can well resolve them, such as polyethylene glycol (PEG) [11], MIL-101 [1], MAF-6 [5], and TFT [8]. Similar issues also exist for separations of positional isomers of phenols and anilines, particularly for cresols, xylenols, toluidines and xylidines, which are widely used in pharmaceutical and dye industries and wide present in the environment [13–16]. Determination of these weak organic acids or bases often requires derivatization prior to GC analysis owing to their liability to peak tailing that may deteriorate their resolution [14–16]. Undoubtedly, exploring new stationary phases with high selectivity and column inertness would favour their direct determination of these acidic/basic analytes. The aforementioned critical isomers vary from neutral, acidic to basic nature, it would be difficult but valuable to find one stationary phase to achieve good resolution for all of them.

* Corresponding author.
E-mail addresses: mlqi@bit.edu.cn, mlqi2013@163.com (M. Qi).

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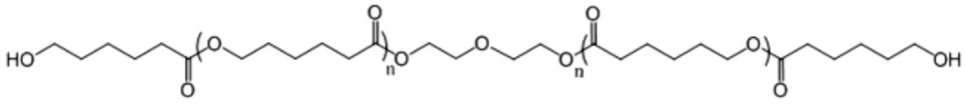

Fig. 1. Structure of PCL-Diol.

PEG as a classical polar stationary phase, composed of repetition of ether chains, exhibits excellent separation performance for a variety of analytes in diverse samples [17,18]. Inspired by this, we found the potential of poly(caprolactone)diol (PCL-Diol, Fig. 1) as a stationary phase for GC separations on the basis of its chemical structure and properties. Unlike the polyether of PEG, PCL-Diol consists of repetition of hexanoate units with terminal hydroxyl groups, suggesting its amphiphilic nature. This feature may offer advantageous separation performance for analytes of wide ranging polarity. In addition, it has good solubility in dichloromethane and thermal stability. The above features render PCL-Diol a promising candidate as GC stationary phase. However, no report is available on employing PCL-Diol as stationary phase in capillary GC up to date. Currently, PCL-Diol was investigated for its thermodynamic properties [19] and its utilization in self-assembly and hydrogel polymers [20–23].

Herein, we report the investigation of PCL-Diol as a new type of stationary phases for capillary GC separations. In this work, the PCL-Diol capillary column was evaluated for its column efficiency, general and average polarities, and Abraham solvation system constants. On this basis, its selectivity and resolving capability were explored by the tough Grob test mixture, and the challenging isomer mixtures of xylenes, phenols, anilines and dichlorobenzenes. Additionally, column repeatability and thermal stability were examined. Furthermore, we applied the PCL-Diol column for the determination of isomer impurities in real samples from commercial vendors. As demonstrated in this work, PCL-Diol column exhibits high resolving capability towards the indicated isomers from nonpolar to polar nature and from acid to base, and shows promising future for practical applications.

2. Experimental

2.1. Materials and equipment

All chemicals and reagents in this work were at least of analytical grade and used without purification. Poly(caprolactone)diol (PCL-Diol) was purchased from J&K. Scientific. Ltd. (Beijing, China) with average M. W. 2000 and used as received. Decane, undecane, nonanal, 2,3-butanediol, 1-octanol, methyl decanoate, dicyclohexylamine, methyl undecanoate, *o*-cresol, *o*-dichlorobenzene, *p*-dichlorobenzene, *m*-dichlorobenzene, 2,3-xylidine, 2,4-xylidine, 2,6-xylidine, *p*-cresol, 2,5-xylidine, 3,4-xylidine, 3,5-xylidine, 2,3-xylenol, 2,5-xylenol, 2-ethylhexanoic acid, 3,4-xylenol, 3,5-xylenol, methyl dodecanoate and 2,6-xylenol were purchased from J&K. Scientific. Ltd. (Beijing, China). 1-Nitropropane, 1-butanol and 2-pentanone were purchased from Aladdin Industrial Corp. (Shanghai, China). Benzene, toluene, ethylbenzene, *o*-toluidine, *m*-toluidine, *p*-toluidine, aniline, phenol, pyridine, *m*-cresol, *o*-xylene, *p*-xylene, *m*-xylene, dichloromethane, chloroform and methanol were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All the test solutes were dissolved in dichloromethane. Fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). A HP-INNOWAX capillary column (10 m long × 0.25 mm i.d., film thickness 0.25 μm) was purchased from Agilent Technologies Co. Ltd. (Palo Alto, USA).

GC separations were performed on an Agilent 7890A gas chromatograph (Palo Alto, USA), equipped with a split/splitless injector and a flame ionization detector (FID). Data analysis was performed using ChemStation software. Nitrogen (99.999%) was used as the carrier gas. GC conditions for separations are provided as follows unless otherwise specified: injection port at 250 °C, injection volume of 0.1 μL, flow rate of 1 mL/min, split ratio of 50:1, FID at 300 °C. The temperature programs for the separations are listed in the figure captions individually. Thermal gravimetric analysis of PCL-Diol was determined by a DTG-60AH thermal gravimetric analyzer (Kyoto, Japan).

2.2. Preparation of PCL-Diol capillary column

Before static coating, a fused-silica capillary column (10 m long, 0.25 mm, i.d.) was subjected to a saturated solution of sodium chloride in methanol and kept for 45 min to deposite NaCl microcystals on the inner wall of the capillary column for its roughing [24]. After removing the solution, the column was conditioned up to 200 °C at 10 °C/min and held for 3 h under nitrogen. Afterwards, the column was statically coated with PCL-Diol solution in dichloromethane (0.25%, *w*/*v*) at 40 °C with one end of the column sealed and the other end connected to vacuum system to slowly evaporate the solvent and leave a uniform coating of stationary phase behind. Then, the column was conditioned from 40 °C (30 min) to 180 °C at 1 °C/min and held at 180 °C for 7 h under nitrogen. The obtained column had a coating thickness of about 0.16 μm calculated by the empirical formula, $d_f = (d_c \times c)/400$, where d_c is the capillary inner diameter (μm), *c* is the concentration of the stationary phase (%, *w*/*v*).

2.3. Determination of Abraham solvation system constants

The solvation parameter model presented by Abraham, is set out below in the common form for GC with the logarithm of retention factor (log *k*) as the dependent variable:

$$\log k = c + eE + sS + aA + bB + lL$$

In the equation, *k* is the retention factor of a solute on the given stationary phase at a setting temperature; *c* relates to the phase ratio of the column and the value obtained from the model intercept. The capital letters of *E*, *S*, *A*, *B* and *L* are solute descriptors. Individually, *E* means the excess molar refraction calculated from the solute's refractive index; *S* represents the solute dipolarity/polarizability; *A* and *B* relate to the solute H-bonding acidity and H-bonding basicity, respectively; *L* is the solute gas/hexadecane partition coefficient determined at 298 K on hexadecane. The lowercase letters of *e*, *s*, *a*, *b* and *l* are defined as system constants, indicating the individual molecular interactions of a stationary phase with diverse solutes in their separation process. As defined, *e* is the capability of the stationary phase for π-π and n-π interactions, *s* represents the ability of the stationary phase for dipole-type interactions; *a* and *b* relate to the H-bonding basicity and acidity of the stationary phase, respectively; and *l* is the overall dispersive-type interaction and cavity formation of the stationary phase. In this study, 47 solutes of different types were selected to characterize the system constants (*e*, *s*, *a*, *b*, *l*) of the PCL-Diol stationary phase at 70 °C, 90 °C and 110 °C, respectively. The system constants at each temperature were calculated by multiple linear regression analysis on the basis of the determined *k* values of the solutes and their descriptor values

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