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Performance and selectivity of dicyanuric-functionalized polycaprolactone as stationary phase for capillary gas chromatography

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ABSTRACT

Dicyanuric-functionalized polycaprolactone (DPCL) was explored for its separation performance in gas chromatography (GC). The statically coated DPCL capillary column (0.25 mm, i.d.) showed column efficiency of 3460 plates/m determined by naphthalene at 120 °C. McReynolds constants and Abrahamís system constants were also determined to evaluate the polarity and possible molecular interactions of the stationary phase. As a result, DPCL column exhibited excellent separation performance for diverse types of analytes with good peak shapes. Most interestingly, it shows unique amphiphilic selectivity and high-resolution capability for both apolar to polar isomers. In addition, DPCL column had good column repeatability with the RSD values below 0.06% for run-to-run, 0.09–0.40% for day-to-day and 1.7–3.6% for column-to-column, and good thermal stability up to 280 °C. The high selectivity and resolving capability demonstrate the great advantages of the DPCL stationary phase for simultaneous determination of analytes of great variety in complex samples.

1. Introduction

Polymeric materials with good film-forming ability and stability have been used as stationary phases for gas chromatography (GC). Among them, polysiloxanes and polyethylene glycol (PEG, e.g. PEG–20 M) with polyether backbone structures are most widely used and well recognized [1,2]. Developing stationary phases with high resolving capability has been the pursuit of researchers in GC to address the growing need for separation of analytes with high resemblance in complex samples, such as structural and positional isomers covering from nonpolar to polar ones. Over the past decade, the reported stationary phases for GC separation of such isomers mainly involved macrocycles [3–5], metal-organic frameworks [6–8], ionic liquids [9,10] and liquid crystals [11]. Most of them showed high selectivity for nonpolar to weakly polar isomers such as alkanes and alkyl-substituted benzenes. It is not well documented for a GC stationary phase that possesses high resolution for both apolar and polar isomers due to their large difference in polarity.

Poly(ϵ-caprolactone) (PCL) is a linear polyester with repeated hexanoate units. PCL-based macroporous biocomposites [12,13] and amphiphilic polyesters [14,15] were investigated for drug delivery and protein adsorption, respectively. PCL functionalized with dicyanuric units (DPCL, Fig. 1) showed the enhanced recognition ability of the polymer [16] through additional H-bonding interaction of cyanuric units with specific molecules [16–18]. Unlike PEG with a simple composition, DPCL is a linear polyester with amphiphilic nature, composed of repeated hexanoate units and benzoate, cyanuric and 1,2,3-triazole units. Its unique structure and physicochemical stability interested us to investigate its separation capability as GC stationary phase, especially its potential amphiphilic selectivity. Undoubtedly, a stationary phase with amphiphilic selectivity is essential for GC analysis of complex samples.

Herein, we present the investigation of DPCL stationary phase for GC separations regarding its polarity, selectivity, resolving ability and retention trend for analytes with a wide varying polarity, and their structural and positional isomers. Also, the separation ability of the DPCL stationary phase was evaluated in comparison

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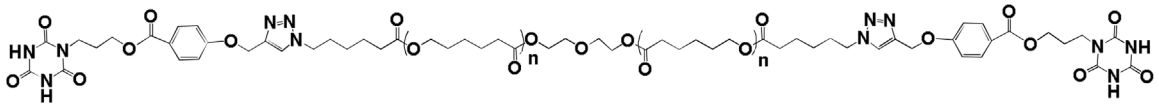

Fig 1. Structure of DPCL (n = 9.6).

with the typical polar PEG–20 M phase (using a commercial column). Moreover, column repeatability, reproducibility and thermal stability were evaluated. To the best of our knowledge, this is the first report on employing PCL-based polymers as stationary phases for chromatographic separations, showing their promising future in this field.

2. Experimental

2.1. Materials and equipment

All chemicals and reagents used in this work were at least of analytical grade and used without purification. Octane, nonane, decane, undecane, nonanal, 2,3-butanediol, 1-octanol, methyl decanoate, methyl undecanoate, 2,6-dimethylaniline, 2-ethylhexanoic acid, 2, 6-dimethylphenol, methyl dodecanoate, *o*-dichlorobenzene, *m*-dichlorobenzene, *o*-cresol, *p*-cresol, *o*-dibromobenzene, *p*-dibromobenzene, *m*-dibromobenzene, *o*-diethylbenzene, *p*-diethylbenzene, *m*-diethylbenzene, 2,2,3-trimethylbutane, 2, 3-dimethylpentane, *n*-heptane and dicyclohexylamine were purchased from J&K. Scientific. Ltd. (Beijing, China). 1-Nitropropane, 1-butanol, 2-pentanone, methyl hexanoate, methyl heptanoate, methyl octanoate, methyl nonanoate, *n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, 2-heptanone, cyclohexanone, cyclohexanol, 1-bromononane, 1,4-dibromobutane, salicylaldehyde, N-methyl-2-pyrrolidone, 1-nonanol and 1,6-dibromohexane were from Aladdin Industrial Corp. (Shanghai, China). Benzene, *p*-dichlorobenzene, *n*-butylbenzene, toluene, chlorobenzene, *o*-chlorotoluene, benzaldehyde, 1,2,4-trichlorobenzene, benzonitrile, ethyl benzoate, nitrobenzene, *o*-toluidine, benzyl alcohol, *m*-methylnitrobenzene, 2-chloroaniline, phenol, pyridine, *m*-cresol, dichloromethane, chloroform, *tert*-butanol, *sec*-butanol, isobutanol, *N,Ní*-dimethylformamide (DMF) and methanol were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All the analytes were dissolved in dichloromethane except butanol isomers that were dissolved in DMF. Fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). A commercial HP-INNOWAX capillary column with crosslinked PEG–20 M (10 m long × 0.25 mm i.d., film thickness 0.25 μm) was purchased from Agilent Technologies Co. Ltd. (Palo Alto, USA).

An Agilent 7890A gas chromatograph (Palo Alto, USA) was used, equipped with a split/splitless injector, a flame ionization detector (FID) and ChemStation software. Nitrogen (99.999%) was used as the carrier gas. The GC conditions are provided as follows: injection port at 250 °C, split ratio at 50:1, FID at 300 °C. Temperature program for each GC separation is specified in its figure caption below. In addition, the instruments used for the characterization of the synthesized DPCL product included a Shimadzu DTG-60AH thermal gravimetric analyzer (Kyoto, Japan) using the program from 30 °Cto 700 °Cat 10 °C/min under nitrogen, a Varian Unity INOVA-300 NMR spectrometer (Salt Lake City, USA) and a Bruker Autoflex Speed TOF/TOF (Bremen, Germany).

2.2. Methods

2.2.1. Synthesis and characterization of DPCL

DPCL was synthesized according to the method described in Ref. [16], by click reaction of PCL-N_3 with *p*-hydroxybenzoic acid substituted by alkynyl and cyanuric groups. Briefly, PCL-N_3 (3.03 g, 1.45 mmol) and the above derivative of *p*-hydroxybenzoic acid (2.00 g, 5.79 mmol) were dissolved in DMF (60 mL). Then, to the solution, the aqueous solution of mono-sodium L-ascorbate (2.30 g, 11.6 mmol) and $CuSO_4 \times 5H_2O$ (1.44 g, 5.79 mmol) was added and the mixture stayed at 60 °C for 24 h. After the solvent was removed by a rotary evaporator, the residue was extracted with H_2O/CH_2Cl_2. Afterwards, the organic layer was dried with anhydrous Na_2SO_4 and rotoevaporated to remove the solvent. The obtained residue was dissolved in THF and the mixture was precipitated by excessive diethyl ether. After the precipitate was dried in a vacuum oven under room temperature, the final product was obtained as a white solid (2.50 g, yield: 52%). ^{1}H NMR (300 MHz, $CDCl_3$):δ 8.98 (s, 4H), 7.97 (d, J = 8.8 Hz, 4H), 7.63 (s, 2H), 7.00 (d, J = 8.8 Hz, 4H), 5.26 (s, 4H), 4.36 (dd, J = 11.3, 6.2 Hz, 8H), 4.26–4.20 (m, 4H), 3.72–3.66 (m, 4H), 2.17–2.08 (m, 5H), 1.94 (dd, J = 14.8, 7.3 Hz, 4H). MALDI-TOF-MS: 3267.4043 (m/z).

2.2.2. Preparation of DPCL coated capillary column

Untreated fused-silica capillary tubing (10m × long, 0.25 mm, i.d.) was used to prepare the DPCL column. Prior to static coating, the capillary column was pretreated with a saturated solution of sodium chloride in methanol for its inner surface roughing [19]. Then, the column was conditioned up to 200 °Cat 10 °C/min and held at the temperature for 3 h under nitrogen atmosphere. Afterwards, the column was statically coated with the solution of DPCL stationary phase in dichloromethane (0.25%, *w/v*) at 40 °C in a water bath. One end of the capillary column was sealed by epoxy glue and the other end was connected to a vacuum system via a vacuum bottle under 200 mmHg to remove the solvent and leave a coating layer of the stationary phase behind. The solvent evacuation took about 10 h for a capillary column (10 m × 0.25 mm). Further conditioning of the coated column was performed with the temperature program: 40 °C for 30 min to 180 °C at 1 °C/min and held at the high-end temperature for 7 h under nitrogen. The coating thickness (d_f) of the DPCL capillary column can be calculated as about 0.16 μm by the empirical formula, $d_f = (d_c \times c)/400$, where d_c is the inner diameter of the capillary (mm), c is the concentration of the stationary phase solution (%, *w/v*) [20].

2.2.3. Abraham solvation parameters

The Abraham solvation parameter model is widely used for the quantification of molecular interactions between a given stationary phase and probe molecules [21–23], which is set out below 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 is the model intercept, related to the phase ratio of the as-prepared column. The solute descriptors (E, S, A, B and L) are probe-specific parameters and are available for various probe compounds in Ref. [23]. Specially, E represents the excess molar refraction calculated from the soluteís refractive index; S relates to the solute dipolarity/polarizability; A refers to the solute H-bonding acidity and B indicates the solute H-bonding basicity; L is the solute partition coefficient determined by hexadecane at 298 K. The lowercase letters (e, s, a, b and l) are defined as the system constants, representing the contributions of