Scientific paper

# An Amphiphilic Star-Shaped Polymer (Star-PEG-PCL<sub>2</sub>) used as a Stationary Phase for GC

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#### Abstract

A star-shaped polymer (Star-PEG-PCL<sub>2</sub>) was synthesized to with PCL and PEG, and used as a stationary phase for gas chromatography. The statically coated Star-PEG-PCL<sub>2</sub> column exhibited an efficiency of 2260 plates/m determined by naphthalene at 120 °C and moderate polarity. The Star-PEG-PCL<sub>2</sub> column showed high resolution performance for isomers of a wide ranging polarity, including methylnaphthalenes, halogenated benzenes, nitrobenzene, phenols, and anilines, and displayed dual-nature selectivity for a mixture of 17 analytes. Also, the Star-PEG-PCL<sub>2</sub> column exhibited good separation performance and column inertness for Grob test mixture and a series of *cis-/trans*-isomers. In addition, it exhibited advantageous separation performance over the commercial HP-35 and PEG-20M columns for chloroaniline and bromoaniline isomers through its unique three-dimensional framework. In conclusion, it has good potential as a new stationary phase for separating a variety of analytes because of its special structure and excellent separation performance.

Keywords: Stationary phase; capillary gas chromatography; star-shaped polymer; separation performance

#### 1. Introduction

Capillary gas chromatography (GC) has been widely used in petrochemical, pharmaceutical, environmental, biochemistry, food and other fields, while the stationary phase is the key of GC analysis because the separation performance and retention behavior of a capillary GC column mostly depend on the chromatographic features of its stationary phase. <sup>1-4</sup> Currently, polymers, <sup>5-8</sup> macrocyclics, <sup>9-12</sup> ionic liquids, <sup>13,14</sup> metal-organic frameworks (MOFs), <sup>15,16</sup> and covalent organic frameworks (COFs)<sup>17,18</sup> have been reported as stationary phases for GC separations. It is worth noting that polymers are the most popular chromatographic stationary phases because of their excellent physicochemical properties such as good film-forming properties, chemical stability and easy modification.

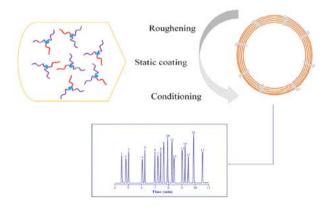
Poly(ethylene)glycol (PEG) is widely used in the fields of medicine, cosmetics, plastics and biology because of its non-toxic, non-volatile and hydrophilic properties.<sup>19</sup> It is well known that PEG is one of the commonly used

stationary phases in GC, which is suitable for the separation of polar analytes. With the development of PEG-based materials, the researchers found that the selectivity of the stationary phase could be improved by PEG-derivatization. Peg-22 Poly( $\varepsilon$ -caprolactone) (PCL) has the advantages of biocompatibility, biodegradability and good film-forming ability, and is easily soluble in common organic solvents such as aromatic compounds, ketones and polar solvents. It is a hydrophobic and flexible polymer with five nonpolar methylene groups and one polar ester group in the structurally repeating unit, which can be a selector in chromatographic separations.

Star-shaped polymer is a kind of polymer with characteristic shape, which is a star shape with linear chain as the core and three or more than three branched chains as the arms. Moreover, it is the simplest branched polymer and can be obtained by two polymerization approaches: core-first and arm-first.<sup>27</sup> For the application of GC stationary phase, compared with linear polymers, the star-shaped

polymer has unique 3D network structure, which can increase the interaction areas between the stationary phase and analytes, play the role of 3D molecular recognition interactions of the stationary phase, and then improve the selectivity and chromatographic separation performance of the stationary phase. Based on these features, star-shaped polymer is a promising candidate for GC stationary phase.<sup>28</sup>

Herein, the star-shaped polymer (Star-PEG-PCL<sub>2</sub>) was synthesized and characterized, and coated on the inner wall of capillary column (Scheme 1). Subsequently, we investigated the separation performance of the Star-PEG-PCL<sub>2</sub>. Firstly, we measured its column efficiency through the Golay curve and obtained its polarity by McReynolds constants. Secondly, we investigated the chromatographic retention behavior of the Star-PEG-PCL<sub>2</sub> column with the Grob test mixture, a mixture of 17 analytes of various polarities, and challenging halogenated anilines as analytes.



**Scheme 1.** The Star-PEG-PCL<sub>2</sub> capillary column for GC separation.

Additionally, we also explored its separation performance for a variety of positional and *cis-/trans*-isomers with different polarities. To our knowledge, this is the first report on the use of Star-PEG-PCL<sub>2</sub> as a GC stationary phase.

## 2. Experimental

#### 2. 1. Materials and Methods

N,N'-Dicyclohexylcarbodiimide (DCC) was phurchased from Heowns Biochemical Technology Co., Ltd. (Tianjin, China). 4-Dimethylaminopyridine (DMAP) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). Succinic anhydride, triethylamine (TEA), 2-amino-1,3-propanediol (serinol), poly(ethylene glycol) methyl ether (Mn.2000), tin(II) 2-ethylhexanoate, 6-hexanolactone and N-hydroxysuccinimide (NHS) were phurchased from Sun Chemical Technology Co., Ltd. (Shanghai, China). The analytical samples and standards were abtained from Energy Chemical and used without further purification. All the analytes in this work were analytical grade and dissolved in dichloromethane (DCM). Fused-silica capillary column (0.25 mm i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd (Hebei, China). The HP-35  $(15 \text{ m} \times 0.25 \text{ mm i.d.}, 0.25 \text{ }\mu\text{m} \text{ film thickness})$  and PEG-20M  $(15 \text{ m} \times 0.25 \text{ mm i.d.}, 0.25 \text{ } \mu\text{m} \text{ film thickness})$  capillary commercial columns were purchased from Agilent Technologies Co., Ltd. (Palo Alto, Califonia, USA) for comparison.

The synthesized polymers were characterized by FT-IR and <sup>1</sup>H NMR. The IR spectra were obtained by a Tensor II FT-IR spectrometer (Bruker, Karlsruhe, Germany) and the <sup>1</sup>H NMR were recorded on a Bruker Biospin 400 MHz instrument (Bruker Biospin, Rheinstetten, Germany).

Scheme 2. The synthesis of Star-PEG-PCL2.

Thermal gravimetric analysis (TGA) was done on a DTG-60AH instrument (Shimadzu, Japan).

GC separations were performed on an Agilent 7890A system (Palo Alto, USA) with a flame ionization detector (FID). All the GC separations were performed under the following conditions: nitrogen of high purity (99.999%) as carrier gas, injection port at 300 °C, split injection mode at a split ratio of 100: 1 and FID detector at 300 °C. The specific temperature program and flow rate of carrier gas are indicated in the caption of each figure.

# 2. 2. Synthesis

Synthesis route is shown in Scheme 2. The synthesis according to the method in the reference.<sup>29</sup>

#### 2. 2. 1. Synthesis of the mPEG-serinol

Firstly, the carboxylated mPEG and mPEG-NHS were synthesized following the procedure described in reference. And then, mPEG-NHS (0.720 g, 0.334 mmol) and serinol (0.222 g, 2.338 mmol) were added into DMSO (15 mL). The mixture was stirred at room temperature for 36 h. After the reaction, the deionized water was added into the crude product, and extracted with DCM. The organic phase was concentrated in vacuo and the product was precipitated with cold diethyl ether. The solid was filtered and dried in vacuo at 40 °C (48.89% yield). m. p. 46.9-54.1 °C;  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.65 (s, H<sub>b</sub>), 3.38 (s, H<sub>a</sub>), 2.62 (s, H<sub>c</sub>, H<sub>d</sub> and H<sub>e</sub>). IR (KBr, cm<sup>-1</sup>): 1060.34 (C-O-C), 1087.18 (C-O-C), 1728.76 (C=O), 2849.42 (CH<sub>2</sub>), 2891.68 (CH<sub>2</sub>), 2926.83 (CH<sub>3</sub>), 3322.35 (OH).

#### 2. 2. 2. Synthesis of the Star-PEG-PCL<sub>2</sub>

The mPEG-serinol (0.479 g, 0.224 mmol), PCL (1.437 g, 12.590 mmol) and  $Sn(Oct)_2$  (0.012 g, 0.0311 mmol) were added to a round-bottom flask and stirred at 120 °C for 18 h. After the reaction, the mixture was slowly cooled down at room temperature. Then, the reaction mixture was added into cold diethyl ether and stirred to obtain white solid, then the solid was filtered and dried in vacuo at 40 °C (39.23% yield). m. p. 49.9–56.4 °C; ¹H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.23 (t, J = 5.2 Hz, H<sub>e</sub> and H<sub>f</sub>), 4.06 (t, J = 6.8 Hz, H<sub>I</sub>), 3.65 (s, H<sub>b</sub>), 3.38 (s, H<sub>a</sub>), 2.63 (s, H<sub>c</sub> and H<sub>d</sub>), 2.31 (t, J = 7.6 Hz, H<sub>g</sub>), 1.67–1.63 (m, H<sub>i</sub> and H<sub>k</sub>), 1.44–1.33 (m, H<sub>i</sub>). IR (KBr, cm<sup>-1</sup>): 1062.95 (C-O-C), 1104.39

(C-O-C), 1720.77 (C=O), 2862.56 (CH<sub>2</sub>), 2891.11 (CH<sub>2</sub>), 2944.04 (CH<sub>3</sub>).

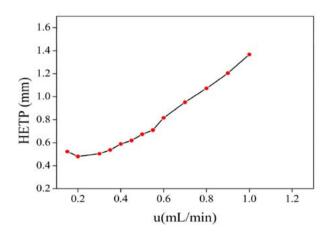
# 2. 3. Fabrication of the Star-PEG-PCL<sub>2</sub> Capillary Column

The capillary column was made by static coating method. After rinsing, the inner surface of the capillary column was roughened with saturated sodium chloride methanol solution. Then, the column was filled with coating solution (Star-PEG-PCL<sub>2</sub> dissolved in DCM). At last, after the solvent was evaporated, the column was conditioned by temperature program. The specific process is refered to in the previous literature of our research group. <sup>30,31</sup>

#### 3. Results and Discussion

# 3. 1. Column Efficiency and McReynolds Constants of Star-PEG-PCL<sub>2</sub> Stationary Phase and Capillary Column

The column efficiency of Star-PEG-PCL $_2$  stationary phase was determined through plotting the height equivalent to a theoretical plate (HETP) of naphthalene at 120 °C. According to the measured data, the Golay curve in Fig.1 was drawn, and the results showed that the measured minimum HETP was 0.44 mm, corresponding to a column efficiency of 2260 plates/m at flow rate of 0.3 mL/min.



**Fig. 1** Golay curve of the Star-PEG-PCL<sub>2</sub> column.

Table 1. McReynolds constants of the Star-PEG-PCL2, HP-35 and PEG-20M columns

Stationary phase	X'	Y'	Z'	U'	S'	General polarity	Average
Star-PEG-PCL2	194	379	251	409	342	1575	315
HP-35	96	149	142	226	176	790	158
PEG-20M	303	520	351	557	484	2215	443

X', benzene; Y', 1-butanol; Z', 2-pentanone; U', 1-nitropropane; S', pyridine. Temperature: 120 °C.

Moreover, the polarity of the stationary phase was characterized by McReynolds constants, and its measurement was determined by the five probe solutes of benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine. <sup>32,33</sup> Table 1 shows that the average value of Star-PEG-PCL<sub>2</sub> stationary phase was 315, indicating its moderate polarity. Also, the polarity of the Star-PEG-PCL<sub>2</sub> column is between that of the HP-35 and PEG-20M columns, in particular the lower polarity than that of the PEG-20M stationary phase may be due to the introduction of two PCL chains as polymer arms.

# 3. 2. Separation Performance and Retention Behaviours

In order to explore the separation performance of Star-PEG-PCL $_2$  stationary phase, the Grob test mixture, a

mixture of 17 analytes, positional and *cis-/trans*-isomers were used as the analytes.

#### 3. 2. 1. Grob Test Mixture

Grob test mixture is a commonly used diagnostic reagent for GC stationary phase evaluation, which can evaluate the separation performance of the stationary phase and the inertness of the chromatographic column. Fig. 2 revealed the separation performance of Star-PEG-PCL<sub>2</sub>, PCL-PEG-PCL, HP-35 and PEG-20M columns. PCL-PEG-PCL stationary phase has a linear structure, which has been reported by our group.<sup>30</sup> As shown, the Star-PEG-PCL<sub>2</sub> column can separate almost all analytes except 2,6-dimethylphenol/2-ethylhexanoic acid (peaks 9/10) and dicyclohexylamine/methyl dodecanoate (peaks 11/12), showing its excellent resolving capability for the

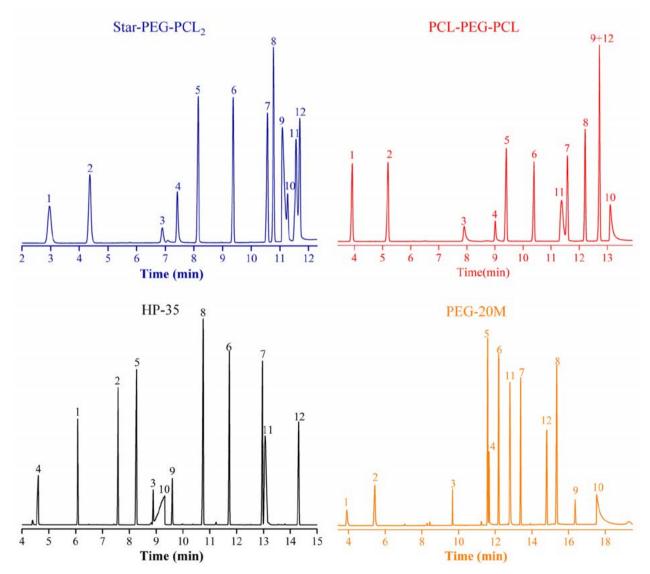
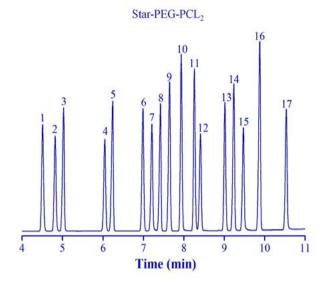
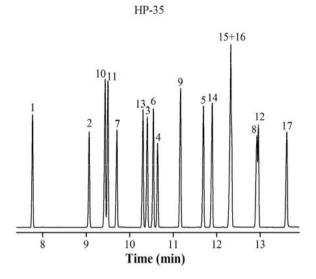
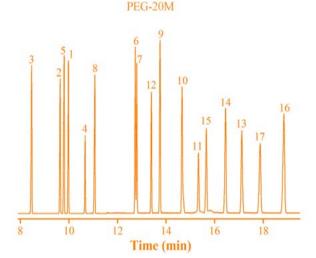


Fig. 2 Separations of Grob test mixture on the Star-PEG-PCL<sub>2</sub>, PCL-PEG-PCL, HP-35, and PEG-20M columns. Peaks: (1) *n*-decane, (2) *n*-undecane, (3) nonanal, (4) 2,3-butanediol, (5) 1-octanol, (6) methyl decanoate, (7) methyl undecanoate, (8) 2,6-xylidine, (9) 2,6-dimethylphenol, (10) 2-ethylhexanoic acid, (11) dicyclohexylamine, (12) methyl laurate. Oven program: 40 °C (1min) to 160 °C at 10 °C/min. Flow rate at 0.6 mL/min.







**Fig. 3** Separations of the mixture of 17 analytes on the Star-PEG-PCL<sub>2</sub>, HP-35 and PEG-20M capillary columns. Peaks: (1) 1,3-dichlorobenzene, (2) methyl octanoate, (3) *n*-tridecane, (4) 1-bromononane, (5) *n*-tetradecane, (6) 1,2,4-trichlorobenzene, (7) 1-nanol, (8) *n*-pentadecane, (9) 1,2,3-trichlorobenzene, (10) *o*-toluidine (11) *m*-toluidine, (12) methyl undecanoate, (13) 2-chloroaniline, (14) *m*-chloronitrobenzene, (15) 1-undecanol, (16) *o*-chloronitrobenzene, (17) 1-dodecanol. Oven program: 40 °C (1min) to 160 °C at 10 °C/min. Flow rate at 0.6 mL/min. Capillary column length: Star-PEG-PCL<sub>2</sub>, HP-35, PEG-20M are respectively 10 m, 15 m, and

complex mixture. Regarding the retention behavior, the Star-PEG-PCL<sub>2</sub> column exhibited distinct elution order compared to other comparative columns. Star PEG-PCL<sub>2</sub> stationary phase had strong retention for polar analytes such as 2,3-butanediol and 2-ethylhexanoic acid (peaks 4 and 10) due to its PEG-group, and its retention behavior was similar to that of PCL-PEG-PCL and PEG-20M stationary phases. Specifically, weakly polar analytes including dicyclohexylamine and methyl laurate (peaks 11 and 12) exhibited prolonged retention times on the Star PEG-PCL<sub>2</sub> stationary phase, similar to the polysiloxane HP-35 stationary phase. This may be due to the star-shaped structure of Star-PEG-PCL2, which had stereo recognition interaction with analytes, and the dispersion interaction between them was enhanced. In addition, all the components had good chromatographic peak shapes on the Star-PEG-PCL<sub>2</sub> column, including 2-ethylhexanoic acid and dicyclohexylamine which are easy to tail in chromatographic analysis. The above results showed that the Star-PEG-PCL<sub>2</sub> column had good chromatographic separation performance and column inertness which originated from its unique chemical structure and properties.

#### 3. 2. 2. A Mixture of 17 Analytes

To further investigate the separation performance and retention behavior of Star-PEG-PCL<sub>2</sub> column, a mixture of 17 analytes containing different types, including n-alkanes, anilines, halogenated benzenes, alcohols, and esters, was used as the analytes. The HP-35 and PEG-20M columns were employed for reference. As shown in Fig. 3, the Star-PEG-PCL<sub>2</sub> column presented excellent chromatographic separation performance over the HP-35 and PEG-20M columns. It can be observed from Fig. 3 that the mixture of 17 analytes was baseline separated (R > 1.5), while some components of them were overlapped or co-eluted on the two commercial columns, *i.e.*, n-pentadecane/methyl undecanoate (peaks 8/12), o-toluidine/m-toluidine (peaks 10/11) and 1-undecanol/o-chloronitrobenzene (peaks 15/16) on HP-35 column, 1,2,4-trichlorobenzene/1-nanol

(peaks 6/7) on PEG-20M column. For some pairs of the analytes, such as methyl octanoate/*n*-tridecane, 1-bromononane/*n*-tetradecane, 1-nanol/*n*-pentadecane, *m*-toluidine/methyl undecanoate, *m*-chloronitrobenzene/1-unde-

canol, *o*-chloronitrobenzene/1-dodecanol (peaks 2/3, 4/5, 7/8, 11/12, 14/15, 16/17), the elution order on the Star-PEG-PCL<sub>2</sub> column was consistent with that on the HP-35 column with weaker polarity, and was opposite to that on

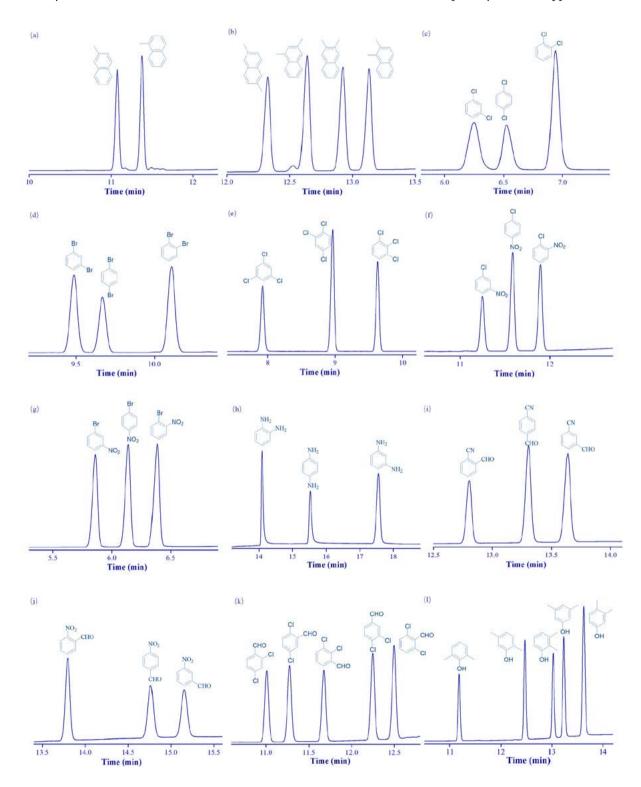


Fig. 4 GC separation of (a) methylnaphthalene, (b) dimethylnaphthalene, (c) dichlorobenzene, (d) dibromobenzene, (e) trichlorobenzene, (f) chloronitrobenzene, (g) bromonitrobenzene, (h) phenylenediamine, (i) cyanobenzaldehyde, (j) nitrobenzaldehyde, (k) dichlorobenzaldehyde, and (l) dimethylphenol isomers on Star-PEG-PCL<sub>2</sub> column. Temperature program: 40 °C for 1 min to 160 °C at 10 °C/min, flow rate at 0.6 mL/min.

the PEG-20M column with stronger polarity. This may be due to the Star-PEG-PCL<sub>2</sub> containing two PCL blocks where the apolar methylene (-CH<sub>2</sub>-) units had stronger dispersion interactions with the weakly polar analytes (peaks 3, 5, 8, 12, 15, 17). Besides, for some other pairs of analytes, such as *n*-tetradecane/1,2,4-trichlorobenzene, *n*-pentadecane/1,2,3-trichlorobenzene, methyl undecanoate/2-chloroaniline (peaks 5/6, 8/9, 12/13), the elution order on the Star-PEG-PCL<sub>2</sub> column was consistent with that on the PEG-20M column, and was opposite to that on the HP-35 column. Using Star-PEG-PCL<sub>2</sub> stationary phase

allowed for prolonged retention time for some polar components (peaks 6, 9, 13), indicating stronger H-bonding and dipole-dipole interactions between them through the PEG chains. The above results demonstrated that Star-PEG-PCL<sub>2</sub> was suitable for the separation of analytes with a wide range of polarity and had dual-nature selectivity.

#### 3. 2. 3. Positional Isomers

Isomers often exist as by-products during synthesis, which are close in nature and structure. Separation capa-

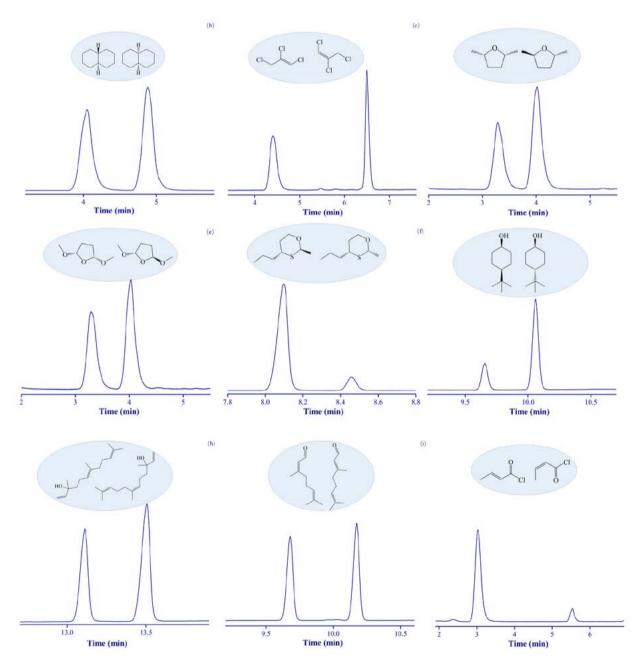


Fig. 5 Chromatogram of cis-/trans-isomers of (a) decahydronaphthalene, (b) 1,2,3-trichloropropene, (c) 2,5-dimethyltetrahydrofuran, (d) 2,5-dimethoxytetrahydrofuran, (e) 2-methyl-4-propyl-1,3-oxathiane, (f) 4-tert-butylcyclohexanol, (g) nerolidol, (h) citral, and (i) crotonyl chloride on the Star-PEG-PCL<sub>2</sub> column. Oven program: 40 °C (1 min) to 160 °C at 10 °C/min. Flow rate at 0.6 mL/min.

bility for isomers is also an indicator to evaluate the performance of a stationary phase. Therefore, dozens of positional isomer mixtures were selected to investigate the capability of the Star-PEG-PCL2 column. Fig. 4 illustrates the resolving capacity of Star-PEG-PCL2 stationary phase for 12 positional isomers from non-polar to polar, exhibiting that Star-PEG-PCL2 stationary phase achieved baseline resolution and good peak shapes. Methylnaphthalene and dimethylnaphthalene (Fig. 4a-b) were well separated on the Star-PEG-PCL2 column, and the dispersion interaction between them played an important role. The observations of Fig. 4c-g reaveled high distinguishing ability of dichlorobenzene, dibromobenzene, trichlorobenzene, chloronitrobenzene, and bromonitrobenzene on the Star-PEG-PCL<sub>2</sub> column. Especially, m/p-dichlorobenzene whose boiling point difference is less than 1 °C were completely separated, suggesting there may be C-H... $\pi$  interaction and halogen bonds between the analytes and the Star-PEG-PCL<sub>2</sub> stationary phase. The outstanding separation performance of Star-PEG-PCL2 colum for phenylenediamine (Fig. 4h) can be descibed with the existence of H-bonding interaction. In GC analyses, the peaks of benzaldehydes and phenols are prone to tail but the indicating analytes in Fig. 4i-l (cyanobenzaldehyde, nitrobenzaldehyde, dichlorobenzaldehyde and dimethylphenol isomer) displayed sharp and symmetrical peak shapes on the Star-PEG-PCL<sub>2</sub> column, revealing the Star-PEG-PCL<sub>2</sub> column had good column inertness and appropriate H-bonding interaction with the analytes.

#### 3. 2. 4. Cis-/trans-isomers

Cis-/trans-isomers were used to further determine the distinguishing performance of Star-PEG-PCL<sub>2</sub> column, and the analytes included decahydronaphthalene, 1,2,3-trichloropropene, 2,5-dimethyltetrahydrofuran, 2,5dimethoxytetrahydrofuran, 2-methyl-4-propyl-1,3-oxathiane, 4-tert-butylcyclohexanol, nerolidol, citral, and crotonyl chloride. As can be clearly seen from Fig. 5, analytes with highly similar structures could be completely resolved. This is perhaps derived from the unique structure of the stationary phase as previously stated, which endows the 3D molecular recognition and multiple molecular interactions involving van der Waals, H-bonding, dipole-dipole, C-H... $\pi$ , halogen bonds, and dispersion interactions with solutes. Accordingly, the combination of the above-mentioned interactions can be capable of improving separation capability.

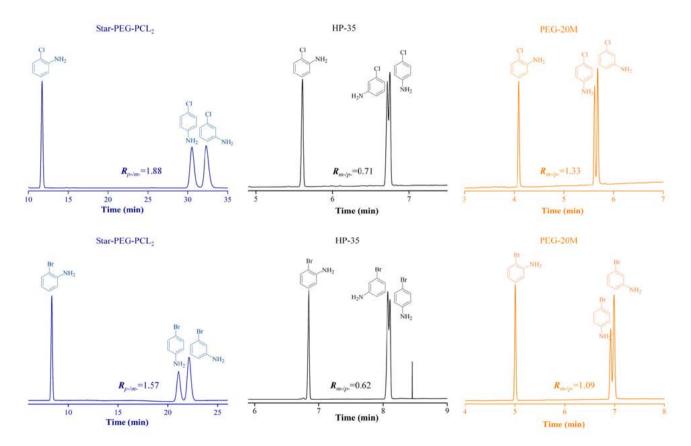


Fig. 6 Separations of the chloroaniline and bromoaniline isomers on the Star-PEG-PCL<sub>2</sub>, HP-35, and PEG-20M columns. Temperature program on Star-PEG-PCL<sub>2</sub> capillary column for chloroaniline and bromoaniline: keep 100 °C and 120 °C, respectively. Temperature program on HP-35 capillary columns: 40 °C (1 min) to 160 °C at 10 °C/min. Temperature program on PEG-20M capillary column: 160 °C (1 min) to 220 °C at 10 °C/min. Flow rate of all at 0.6 mL/min.

#### 3. 2. 5. Halogenated Aromatic Amines

The high toxicity and carcinogenicity of aromatic amines pose a great threat to humans and the environment, so the separation of aromatic amine isomers is extremely important.<sup>34–36</sup> The separation of aromatic amines is a challenge in the field of GC analysis. Fig. 6 showed the separation performance of Star-PEG-PCL2, HP-35 and PEG-20M columns for chloroaniline and bromoaniline isomers. The Star-PEG-PCL<sub>2</sub> column attained the baseline separation of all the analytes and the isomers (R > 1.5) in contrast to the overlapping peaks that took place on the commercial columns such as the co-eluting peaks including m/p-chloroaniline (R = 0.71) and m/p-bromoaniline (R = 0.62) on the HP-35 column, and m/p-chloroaniline (R = 1.33) and m/p-bromoaniline (R = 1.09) on PEG-20M column, despite of these critical pairs of isomers having high similarity in their structure and physicochemical properties, including boiling points and dipolar moment (Table 2). The higher resolution of Star-PEG-PCL<sub>2</sub> column compared with the weakly polar HP-35 and polar PEG-20M columns, can be attributed to the unique architecture with branched chains that endow Star-PEG-PCL2 more abundant and stronger retention interactions including dipole-dipole and H-bonding interactions with the isomers of different conformation.

umn exhibited good separation performance for Grob test mixture and a mixture of 17 analytes containing different types. Moreover, the Star-PEG-PCL<sub>2</sub> column exhibited high resolving capability for a series of positional and *cis-/trans*-isomers with different polarities. Remarkably, the chloroaniline and bromoaniline isomers were completely separated by the Star-PEG-PCL<sub>2</sub> column, and the resolution was better than the two commercial columns. In addition, we found that the Star-PEG-PCL<sub>2</sub> stationary phase has dual-nature selectivity and high distinguishing capability for different analytes. This work shows that star-shaped materials have great potential as a new type of GC stationary phase.

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Table 2. Structure and	l properties o	f the ana	lytes in Fig. 6
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Compound	CAS	Structure	<b>Boiling point</b>	Dipole	
o-chloroaniline	95-51-2	NH <sub>2</sub>	209 °C	1.77 Debye	
<i>m</i> -chloroaniline	108-42-9	H <sub>2</sub> N CI	230 °C	2.82 Debye	
<i>p</i> -chloroaniline	106-47-8	CI NH2	232 °C	3.20 Debye	
o-bromoaniline	615-36-1	$NH_2$ $Br$	229 °C	1.73 Debye	
<i>m</i> -bromoaniline	591-19-5	H <sub>2</sub> N Br	251 °C	2.86 Debye	
<i>p</i> -bromoaniline	106-40-1	NH <sub>2</sub>	250 °C	3.27 Debye	

#### 4. Conclusion

Here we present a star-shaped polymer Star-PEG-PCL<sub>2</sub> as a GC stationary phase for the first time. Star-PEG-PCL<sub>2</sub> column was composed of one PEG chain and two PCL chains, with star-shaped structure and amphiphilic nature. The results showed that the Star-PEG-PCL<sub>2</sub> col-

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### **Povzetek**

V tem prispevku smo iz PCL in PEG sintetizirali zvezdasti polimer Star-PEG-PCL<sub>2</sub> in ga uporabili kot stacionarno fazo za plinsko kromatografijo. Statično prevlečena kolona Star-PEG-PCL<sub>2</sub> ima učinkovitost 2260 teoretskih prekatov/meter za naftalen pri 120 °C in je zmerno polarna. Pokazala je visoko ločljivost za izomere v širokem območju polarnosti, vključno z metilnaftaleni, halogeniranimi benzeni, nitrobenzenom, fenoli in anilini, ter izkazala dva tipa selektivnosti za zmes 17 analitov. Prav tako je izkazala dobro ločbo in inertnost za Grobovo testno mešanico ter serijo *cis-/trans*-izomerov. Dodatno je zaradi svojega edinstvenega tridimenzionalnega ogrodja pokazala prednosti pri ločbi kloroanilinov in bromoanilinov v primerjavi s komercialnima kolonama HP-35 in PEG-20M. Star-PEG-PCL<sub>2</sub> polimer ima dober potencial kot nova stacionarna faza za ločbo različnih analitov zaradi svoje posebne strukture in odličnih separacijskih lastnosti.



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