



Preparation and evaluation of a polar embedded diphenylethene bonded stationary phase for High Performance Liquid Chromatography

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ABSTRACT

A new polar embedded diphenylethene bonded stationary phase (click DIP) was prepared via click chemistry and evaluated. This new material was characterized by FT-IR spectroscopy, elemental analysis and thermal gravimetric analysis. Alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs) were separated in reverse-phase mode. Van't Hoff plot and linear solvation energy relationships model were used to investigate the separation mechanism and properties of the new column, the result shows that hydrophobic and π - π interaction are important for it to retain solutes. The packed column was employed to separate high polar solutes like carboxylic acids and nucleobase. Moreover, three isomers of terphenyl and medicine solutes including five sulfonamides and four local anaesthetics were successfully separated, much better performed than conventional C18 column. These results proved that this new stationary phase may possess great potential in environmental and pharmaceutical analysis.

1. Introduction

HPLC has become one of the most important tools to separate, identify and quantify components in a mixture for its high efficiency, speediness and easy accessibility, widely used in environmental monitoring [1], pharmaceutical analysis [2], natural product analysis [3] and etc. RP-HPLC proved to be the most widespread and efficient mode for HPLC, on account of its high column efficiency [4], satisfactory reproducibility [5] and MS compatibility [6]. However, there are still some drawbacks for silica-based RP-HPLC column like C18, such as weak retention for highly-polar compounds [7] and peak tailing for basic solutes [8], which certainly limit its application in some areas.

In the last few decades, lots of efforts have been devoted to modifying RP-HPLC to improve the usability [9, 10]. Polar embedded stationary phase turned out to be a promising method, which introduces a polar and hydrophilic group into conventional RP-HPLC stationary phase (C8, C18 and C30) [11–13]. Columns of this form employ polar groups like amides [14], imidazolium [15], close to silica surface. Gerard P. O'Sullivan et al reviewed the history of polar embedded and polar endcapped stationary phase for HPLC, and pointed out the reasons why polar embedded attracted so much attention [16]. A polar embedded C30 stationary phase prepared through easy catalytic reaction showed great performance and excellent shape selectivity in separating polar aromatic compounds [13]. Furthermore, polar

embedded stationary phases show great potential for wide-ranged application. An amide-based stationary phase was evaluated in a supercritical fluid chromatography system, and provided baseline separation of drug-like solutes while compared columns did not [17]. Polar embedded stationary phase technology is not limited in reversed phase chromatography any more, as it was when first applied. A novel imidazolium-embedded stationary phase reported by Shijia Liu show mixed modes of hydrophilic interaction and reversed-phase under different conditions [18]. An imidazolium-embedded iodoacetamide-functionalized stationary phase, prepared by surface radical chain-transfer polymerization, proved flexible selectivity and different retention property for different operation modes and different solutes, showing great potential for separating complex samples under mixed-mode [19].

Click chemistry, since presented by Sharpless in 2001 [19], has become a powerful tool for prepared stationary phase for HPLC. Zhimou Guo modified silica with ethylene glycol via azide-alkyne click chemistry, the new stationary phase shows good separation efficiency and different selectivity compared to C18 column and has potential for two-dimensional separation application [20]. Jie Wei et al. click cysteine onto silica, this zwitterionic stationary phase, compared to commercially available columns, show much better performance to separate aminoglycosides with similar structure [21].

Most of the reported polar embedded reverse-phase stationary

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phases focus on modifying alkyl chain with polar group, few works employ functional molecular containing conjugate structure and the investigation of retention property could be furthered. So in this work, diphenylethene modified with methacrylamide was employed as functional molecular and then clicked to mercapto-silica, considering that this structure may provide different selectivity and better retention for solutes with a conjugate structure. The new stationary phase was characterized by FT-IR spectroscopy, elemental analysis and thermal gravimetric analysis. The separation mode and main interaction of this new column were investigated by separating alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs). Thermodynamic investigation Van't Hoff plot and linear solvation energy relationships model were taken to clarify the retention property of the new stationary phase. And the column was applied to separating polar and medical solutes.

2. Experimental

2.1. Chemicals and materials

5 μm Spherical silica (pore size: 120 \AA , surface area: 170 $\text{m}^2 \text{g}^{-1}$) was purchased from Thermo fisher scientific corporation (Shanghai China). (3-Mercaptopropyl) trimethoxysilane was obtained from Aladdin (Shanghai, China). Sodium methylate of analytical grade was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China). Alkylbenzenes and PAHs reference substances were purchased from shanghai Macklin biochemical Co., Ltd. Acetonitrile and methanol of HPLC grade was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Double distilled water was prepared by SZ-93A automatic double pure water distillatory. All solvents used as mobile phase was filtered by 200 nm Micro-aperture filter membrane before using. Other reagents of analytical grade were obtained from different commercial sources.

2.2. Instrument and apparatus

All the chromatographic analyses were performed on an Agilent 1100 series system equipped with a G1311A quaternary pump, a G1379A on-line degasser, a G1316A column oven, a G1315B DAD detector and a 7725i manual injector with a sample loop of 20 μL . Elemental analysis was measured on Elementar vario micro select (Elementar, German). FT-IR spectra were recorded on Tensor 27 (Bruker, German). Thermal gravimetric analysis (TGA) was taken on

SDT-Q600 thermal gravity analyzer (TA Instrument, American). Roman spectra were obtained on inVia10400 (Renishaw, England).

Column packing was taken on a RPL-ZD10 packing machine (Dalian Replete Science and Technology Co., Ltd) under the pressure of 40 MPa. The columns used for comparison including Luna C8(2) (5 μm , 100 \AA , 250 \times 4.6 mm), Luna C18(2) (5 μm , 100 \AA , 250 \times 4.6 mm) were provided by Guangzhou FLM Scientific Instrument Co., Ltd.

2.3. Preparation of the new stationary phase – click DIP

2.3.1. Synthesis of (E)-N-(4-styrylphenyl) methacrylamide

(E)-1-nitro-4-styrylbenzene was derived from benzyl bromide and 4-nitrobenzaldehyde through a Horner – Wadsworth – Emmons reaction according to published works [22], the nitro group was reduced to amino groups by Fe/NH₄Cl in 85% ethanol, following amidation with methacryloyl chloride, using triethylamine as acid binding agent. Yellow solid was obtained, and the yield after three steps can reach 80.9%.

2.3.2. Preparation of the (E)-1,2-diphenylethene-bonded stationary phase

5.0 g silica gel was firstly activated by 100 mL boiling 4 M HCl for 12 h, and then washed to neutral by distilled water and ethanol, dried under vacuum overnight at 60 $^{\circ}\text{C}$. Secondly, activated silica gel and 5.0 g (3-mercaptopropyl) trimethoxysilane were added to 50 mL anhydrous toluene, the mixture was stirred and refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was centrifuged and washed with toluene, ethanol, water and ethanol respectively to remove the unreacted (3-mercaptopropyl) trimethoxysilane, and then dried under vacuum at 60 $^{\circ}\text{C}$ overnight to afford SH-silica.

Lastly, (E)-N-(4-styrylphenyl) methacrylamide was bonded to silica via thiol-ene click reaction, Fig. 1. 2.5 g (E)-N-(4-styrylphenyl) methacrylamide and 4.8 g SH-silica was dispersed in 40 mL THF in 100 mL single-neck round-bottom flask, after three minutes' ultrasound treatment, 100 mg AIBN was added and the mixture was purged with nitrogen and react in 65 $^{\circ}\text{C}$ oil bath for 48 h. The mixture was centrifuged and washed with THF, ethanol, water and ethanol respectively to remove the unreacted reagents, and then dried under vacuum at 60 $^{\circ}\text{C}$ overnight to afford (E)-1,2-diphenylethene-bonded silica, named as click DIP. The modified silica was slurry-packed into a stainless steel column (4.6 mm i.d. \times 250 mm length) using methanol/isopropanol (9/1) as slurry and methanol as propulsion solvent.

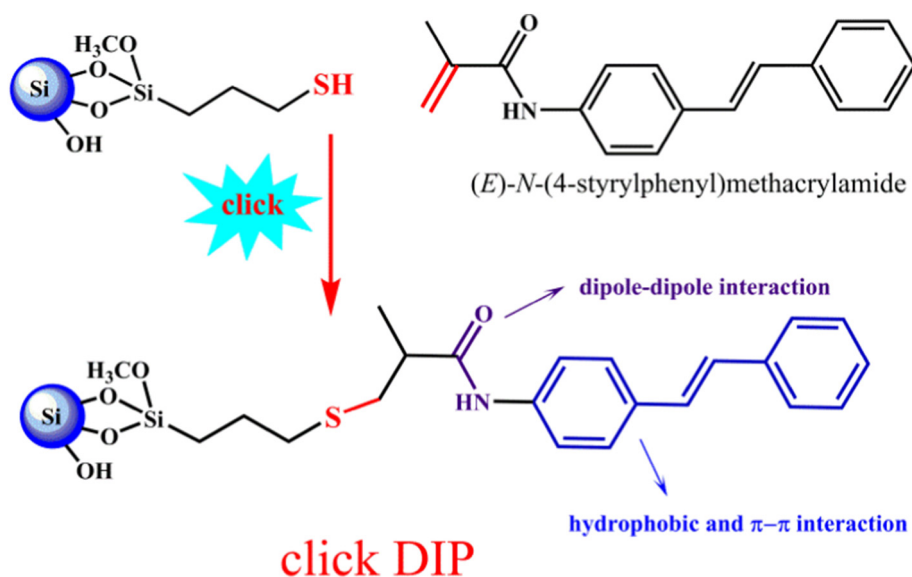


Fig. 1. Preparation route of polar embedded diphenylethene bonded stationary phase (click DIP).

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