



Poly(butylene terephthalate) based novel achiral stationary phase investigated under supercritical fluid chromatography conditions

Kanji Nagai, Tohru Shibata*, Satoshi Shinkura, Atsushi Ohnishi

DAICEL Corporation, CPI Company, Life Science Development Center, Innovation Park, 1239, Shinzaike, Aboshi-ku, Himeji, Hyogo, 671-1283, Japan



ARTICLE INFO

Article history:

Received 26 January 2018

Received in revised form 13 March 2018

Accepted 15 March 2018

Available online 17 March 2018

Keywords:

Supercritical fluid chromatography

Stationary phase

Polymer

Ligand

Poly(butylene terephthalate), PBT

Selector

ABSTRACT

Poly(butylene terephthalate) based novel stationary phase (SP), composed of planar aromatic phenyl group together with ester group monomer units, was designed for supercritical fluid chromatography (SFC) use. As expected from its structure, this phase shows planarity recognition of isomeric aromatics and closely similar compounds. Interestingly, for most analytes, the retention behavior of this SP is significantly distinct from that of the 2-ethylpyridine based SPs which is among the most well-known SFC dedicated phases. Although the poly(butylene terephthalate) is coated on silica gel, the performance of the column did not change by using extended range modifiers such as THF, dichloromethane or ethyl acetate and column robustness was confirmed by cycle durability testing.

© 2018 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Supercritical fluid chromatography (SFC) is implemented today as routine technique in many laboratories and arises strong scientific and practical interest [1]. SFC uses pressurized carbon dioxide (CO₂) with miscible polar organic solvents (modifier) as a mobile phase and has become a powerful separation technique complementary to conventional high performance liquid chromatography (HPLC) and gas chromatography (GC) [2–10]. In the early developments of the technique, SFC was strongly driven by the enantioseparation field benefitting from the already existing chiral stationary phases (CSPs), particularly at preparative scale in pharmaceutical industry [11–18]. Recently, SFC expanded also in the achiral separation field, using achiral phases, but even applying the CSPs as powerful tools in separation of closely related sample impurities or molecules [19,20].

The mobile phase in SFC has low viscosity and high diffusivity, which makes it particularly adapted for fast flow analysis. Furthermore, SFC is regarded as an environmentally friendly separation technique because it uses nontoxic recycled CO₂ and the total amount of organic solvents is smaller than in conventional HPLC. This high throughput chromatographic performance, as well as

“green” aspect, make SFC very attractive for numerous applications [21–31].

The retention and separation characteristics in SFC mainly depend on a combination between mobile phase and stationary phase (SP) [6,32–34]. The chemical diversity of the currently available SPs has been significantly extended, benefiting from the large variety of commercially available HPLC SPs (e.g. reverse phase, normal phase, and/or HILIC) that can be also used in SFC mode. Besides this trend, some column manufacturers and research groups have originally developed SFC dedicated stationary phases. One well-known SP designed specifically for achiral SFC separation is the 2-ethylpyridine (2-EP) bonded silica phase. This 2-EP SP offers good peak shapes, especially for basic compounds, even without any additives [35].

Other novel achiral SPs dedicated to SFC have been developed [36–40], however, most of them consisted of a low-molecular-weight ligand, coated or covalently attached onto a solid support (e.g. silica gel). In contrast, only few polymeric type phases have been described so far for applications in the achiral SFC separation field. Such polymeric phases are expected to interact through multiple concerted mechanisms with the analytes [40].

Another view point is what kind of major interaction should be embedded in a SP. While SPs with a variety of interaction types are needed of course, what are those relatively unmet? The design of new phases may have to start by defining which are the interaction types needed and combined to make an efficient SP, but also which interaction mechanisms are relatively unmet in the already

* Corresponding author.

E-mail address: tr.shibata@jp.daicel.com (T. Shibata).

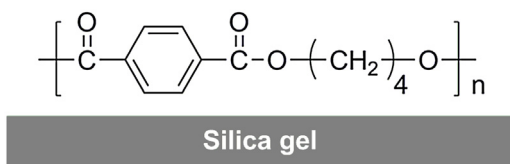


Fig. 1. Structure of poly(butylene terephthalate) or PBT-based selector of the column DCpak PBT.

existing SPs. In this light, the systematic analysis of interactions in a variety of commercially available SPs under SFC conditions, as investigated by West et al., would represent a very suggestive information [41–43]. According to their diagrams, hydrogen-bonding and van der Waals interactions are more densely covered by already existing phases, whereas dipolar and aromatic (π) interactions are less represented [43].

Based on the above consideration, when looking for innovative phases, we focused on a polymer with a dipolar group with/without an aromatic group in or close to its main chain. Among many polymers evaluated, poly(butylene terephthalate), well known as PBT, was chosen as a novel selector considering its molecular recognition ability and peak efficiency [44]. Its insolubility in most solvents and remarkable chemical stability were also positive merits supporting the selector choice for column commercial launch (Fig. 1).

In the present study, some features and applications of this SP under SFC conditions are described.

2. Experimental

2.1. Chemicals

The modifier used in this study was Japanese Industrial Standard special grade methanol (MeOH) obtained from Nacalai Tesque Inc. (Kyoto, Japan). Carbon dioxide of industrial grade (over 99.5%) was purchased from Tatsumi Industry Co., Ltd. (Hyogo, Japan).

o-Terphenyl, *m*-terphenyl, *p*-terphenyl, 3,4-dihydrocoumarin, coumarin, 6-methylcoumarin, 7-methylcoumarin, dimethyl phthalate, dimethyl isophthalate, dimethyl terephthalate, triphenylene, *cis*-stilbene, *trans*-stilbene, 2-methylbenzophenone, 3-methylbenzophenone, 4-methylbenzophenone, 2'-hydroxyflavanone, 3'-hydroxyflavanone, 4'-hydroxyflavanone, theobromine, phenanthrene, and pyrene were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). 1,3,5-Tri-*tert*-butylbenzene, 2-acetylanthracene, 9-acetylanthracene, 2-acetylphenanthrene, 3-acetylphenanthrene, 9-acetylphenanthrene, and paraxanthine were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Naphthacene was purchased from Nacalai Tesque Inc. 2-Propanol (IPA), chrysene, estrone, estradiol, estriol, caffeine, theophylline, tetrahydrofuran (THF), dichloromethane, and ethyl acetate were purchased from Wako Pure Chemical Industries (Osaka, Japan). *n*-Hexane (nHex) was purchased from Kanto Chemical Co. (Tokyo, Japan).

2.2. Instrumentation and chromatographic conditions

DCpak PBT column (initially launched as DCpak SFC-A), sized 150 mm \times 4.6 mm (i.d.), was supplied from DAICEL Corporation (Tokyo, Japan), which is composed of PBT-coated 5 μ m silica particle. A 2-ethylpyridine (2-EP) column of 5 μ m particle, sized 150 mm \times 4.6 mm (i.d.), was purchased from Waters Corporation (Milford, MA, USA). The SFC instrument used in this study is Nexera-UC supplied by Shimadzu Corporation (Kyoto, Japan) equipped with a CO₂ pump, a modifier pump, a vacuum degasser, a column oven, a multiple wavelength UV detector, and automated back

pressure regulator (ABPR), unless otherwise noted. Lab Solutions software (V 5.89) was used for system control and data acquisition.

Total flow rate was fixed at 3.0 mL/min, column temperature was set at 40 °C, and the automated backpressure regulator (ABPR) was set to 15.0 MPa, unless otherwise noted. Other conditions, such as modifier, sample concentration, injection volume, and detection wavelength are described in the figures.

The Thar SFC instrument supplied by Waters Corporation was used for Section 3.3 dealing with the orthogonal selectivity of the two columns and Section 3.4 dealing with the modifier effect.

2.3. Data analysis

Relative retention factor (k) was calculated with the equation below.

$$k = (V/V_0) - 1, \quad (1)$$

where V is the elution volume of an analyte and V_0 is the column void volume. V_0 was estimated by injecting 1,3,5-tri-*tert*-butylbenzene as a non-retained marker conducted as an independent analysis of each sample injection.

2.4. Dipole moment calculations

Dipole moment calculations were conducted using semi-empirical molecular orbital method with PM6 implemented in SCIGESS software (version 2.3, Fujitsu Ltd., Tokyo, Japan) [45].

3. Results and discussion

3.1. Planarity recognition

Based on its structural features, the new PBT selector composed of non-polar aromatic phenyl group together with ester group units was expected to interact with aromatic compounds. In order to confirm this point, terphenyl isomers (**1–3**) are investigated, which are regarded as molecular planarity indicators in HPLC [46,47] and SFC [48]. Compound **1** deviates from planarity due to the strong steric repulsion of two phenyl rings located in *ortho*-position, and this steric hindrance diminishes for **2** and **3** (in this sequential order). Fig. 2 shows the SFC chromatograms of **1–3** by using the PBT-based column (Fig. 2A), compared to the 2-EP SP (Fig. 2B) under isocratic conditions. The stronger the planarity character of the analyte, the longer retention was observed on the new column. In contrast, no resolution between **2** and **3** was achieved on the 2-EP column (Fig. 2B). This planarity recognition may be attributed to planar and rigid PBT backbone.

3.2. Molecular shape recognition

Fig. 3 shows the chromatograms of coumarin (**5**), its dihydro form (**4**), and methyl substituted form (**6** and **7**). Compound **4** eluted faster than **5**, probably because dihydro **4** has less π -electrons than **5**, resulting in a weaker interaction between analyte and SP. The PBT-derived selector can recognize the minor difference of methyl group position (**6** and **7**), whereas on the 2-EP column, coumarin **5** and its methyl substituted ones eluted almost at the same time.

Fig. 4A and B shows the SFC chromatograms of three plasticizers, dimethyl phthalate (**8**), dimethyl isophthalate (**9**), and dimethyl terephthalate (**10**) on both columns. By using the DCpak column, **8** eluted first, followed by **9** and **10** (Fig. 4A). Dipole moment of **8**, **9**, and **10** is 2.98, 1.60, and 0.01, respectively, which is calculated by using SCIGESS software. Thus, the smaller polarization of the sample, the longer the retention time tends to be. On the 2-EP column, the elution order is totally inverse (i.e. **10** eluted first,

Download English Version:

<https://daneshyari.com/en/article/7608302>

Download Persian Version:

<https://daneshyari.com/article/7608302>

[Daneshyari.com](https://daneshyari.com)