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Facile preparation of an alternating copolymer-based high molecular shape-selective organic phase for reversed-phase liquid chromatography

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ABSTRACT

The synthesis of a new alternating copolymer-grafted silica phase is described for the separation of shape-constrained isomers of polycyclic aromatic hydrocarbons (PAHs) and tocopherols in reversed-phase high-performance liquid chromatography (RP-HPLC). Telomerization of the monomers (octadecyl acrylate and *N*-methylmaleimide) was carried out with a silane coupling agent; 3-mercaptopropyltrimethoxysilane (MPS), and the telomer (T) was grafted onto porous silica surface to prepare the alternating copolymer-grafted silica phase (Sil-*alt*-T). The new hybrid material was characterized by elemental analyses, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, and solid-state ¹³C and ²⁹Si cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy. The results of ¹³C CP/MAS NMR demonstrated that the alkyl chains of the grafted polymers in Sil-*alt*-T remained disordered, amorphous, and mobile represented by *gauche* conformational form. Separation abilities and molecular-shape selectivities of the prepared organic phase were evaluated by the separation of PAHs isomers and Standard Reference Material 869b, Column Selectivity Test Mixture for Liquid Chromatography, respectively and compared with commercially available octadecylsilylated silica (ODS) and C₃₀ columns as well as previously reported alternating copolymer-based column. The effectiveness of this phase is also demonstrated by the separation of tocopherol isomers. Oriented functional groups along the polymer main chains and cavity formations are investigated to be the driving force for better separation with multiple-interactions with the solutes. One of the advantages of the Sil-*alt*-T phase to that of the previously reported phase is the synthesis of the telomer first and then immobilized onto silica surface. In this case, the telomer was characterized easily with simple spectroscopic techniques and the molecular mass and polydispersity index of the telomer were determined by size exclusion chromatography (SEC) before grafting onto silica surface. Moreover, both of the monomers were commercially available. Therefore, the technique of preparation was very facile and better separation was achieved with the Sil-*alt*-T phase compared to the ODS, C₃₀ and other previously reported alternating copolymer-based columns.

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1. Introduction

Surface grafting of polymers or chemical binding of polymers onto the silica or inorganic particles surface is of great interest for the design of new functional inorganic/organic hybrid materials. Organic modification of inorganic materials such as silicas and/or silicates, not only permits a precise control of surface properties for specific applications, but also can affect their bulk properties [1,2]. Additionally, incorporation of copolymers with various monomers having different chemical and/or physical properties in the same

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structure can enhance properties of the hybrid materials synergistically [3,4]. One of the extensively applied fields of these hybrid materials are the use as packing materials for high-performance liquid chromatography (HPLC). Alternating copolymer-based stationary phases are gaining attention for their high molecular-shape selectivity in RP-HPLC [5–9]. Alternating copolymer can be spontaneously obtained by the copolymerization of an electron-rich (donor type) monomer and an electron-deficient (acceptor type) monomer through the formation of charge transfer complexes (CTCs) [10–12]. Alternating copolymerization mediated by electron donor-acceptor interactions remains a popular approach for achieving special materials with different functionalities in a wide range of scientific fields including nanotechnology [13] and drug delivery [14]. Furthermore, the *N*-substituted maleimides are valuable as comonomers for radical copolymerization in order to improve the properties of commodity polymers [15,16]. The specialty of the alternating copolymer containing *N*-substituted maleimide repeating units is that they are semiflexible polymers due to the steric hindrance and the restricted rotation along the main chain [17,18].

On the other hand, the separation of certain class of isomers is important in the field of environment, food, agriculture, and pharmaceuticals. Usually, the geometrical isomers have very similar polarity and molecular-shape and therefore, their separation is very difficult. However, their separation is essential as the individual isomer has different properties. Octadecylsilylated silica phases (ODSs or C₁₈) have been used in most reversed-phase liquid chromatographic applications. Depending on the bonding chemistry, ODS phases are mainly divided into two types (monomeric and polymeric). In general, polymeric ODS shows better molecular-shape selectivity than monomeric ODS. However, the selectivity in ODS column varies with the phase type [19], substrate properties [20], phase density [21], and alkyl chain length of the bonded phase. Ultimately, in alkyl chain-based stationary phases molecular-shape selectivity increase with increasing alkyl chain ordering [22]. Long-chain isomeric solutes such as carotenoids [23], tocopherols [24], and fatty acids [25] are not always adequately separated on ODS columns. Therefore, longer alkyl chain phases (e.g., C₃₀) have been developed for the separation of tocopherols and carotenoids [23,24]. We also reported about the separation of carotenoids and tocopherols with alternating copolymer (from octadecyl acrylate and *N*-octadecylmaleimide)-grafted silica phase (Sil-poly(ODA-*alt*-OMI)), prepared by “grafting from” method [9]. In that case, we could not use “grafting to” method because in that case too low grafting density was achieved to be used as stationary phase due to the steric hindrance of the bulky monomers. Therefore, we used “grafting from” method, which has a limitation because we could not characterize the copolymer by the NMR technique as the polymerization was carried from the initiator-grafted silica surface. Another limitation for the preparation of previous phase was troublesome synthesis of the comonomer (OMI).

In this work, we designed and synthesized a new alternating copolymer-based stationary phase with octadecyl acrylate (ODA) and *N*-methaylmaleimide (MMI) for multiple carbonyl- π interactions with the analytes (Fig. 1). Here, we used “grafting to” method so that the copolymer could be characterized well before grafting onto silica. Moreover, none of the monomers needed to be synthesized therefore, the technique was very facile. Since the alternating copolymers are semi-flexible and comparatively rigid, multiple-interactions are expected with the solutes along the polymer main chain. Furthermore, one monomer contain long alkyl chain and another without alkyl chain made the copolymer suitable to enclose the analytes to their void spaces (cavities). Consequently, very high molecular-shape selectivity was observed for the separation of polycyclic aromatic hydrocarbons (PAHs). The Sil-*alt*-T phase was also able to separate the isomers of tocopherol. Chromatographic

results were also compared with commercial polymeric ODS, C₃₀ and previously reported alternating copolymer-grafted silica (Sil-poly(ODA-*alt*-OMI)) [9] columns.

2. Experimental

2.1. Materials and methods

Poly(octadecyl acrylate-*alt*-*N*-methylmaleimide)-grafted silica (Sil-*alt*-T) stationary phase was synthesized, characterized, and packed into a stainless steel column (150 × 4.6 mm i.d.) by slurry packing technique. A YMC silica (YMC SIL-120-S5 having diameter 5 μ m, pore size 12 nm, and surface area 300 m² g⁻¹) obtained from Kyoto (Japan) was used for surface modification. In contrast, we used commercial polymeric ODS column (Shodex, C18P 4D, column size 250 mm × 4.6 mm I.D., a 5 μ m particle size, a 10 nm pore size, and surface area 320 m² g⁻¹) containing 17.5% C obtained from Shodex (Tokyo, Japan) and C₃₀ column (150 mm × 4.6 mm I.D., Develosil, a 5 μ m particle size, a 13 nm pore size, and surface area 297 m² g⁻¹ containing 17.8% C) purchased from Nomura Chemical Co. Ltd. (Japan) for the comparison of chromatographic results. *N*-Methylmaleimide (MMI) was purchased from TCI (Tokyo, Japan). Octadecyl acrylate (ODA) was obtained from Tokyo Kasei Kogyo (Tokyo, Japan) and used after removing polymerization inhibitor. 3-Mercaptopropyltrimethoxysilane (MPS) was purchased from Azmax (Chiba, Japan). HPLC grade methanol was obtained from Wako (Osaka, Japan). All of the PAHs samples were commercially available and used without further purification. The tocopherol isomers were obtained from Calbiochem (Darmstadt, Germany). Standard Reference Material (SRM) 869b, Column Selectivity Test Mixture for Liquid Chromatography, was obtained from the Standard Reference Materials Program (NIST, Gaithersburg, MD, USA). SRM 869b contains benzo[*a*]pyrene (BaP), phenanthro[3,4-*c*]phenanthrene (PhPh), and 1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN).

2.2. Solid-state ¹³C and ²⁹Si NMR spectroscopy

Solid-state ¹³C cross-polarization magic angle spinning (CP/MAS) NMR spectra were measured at different temperatures (20–50 °C) using a line-broadening factor of 5 (lb=5) in a Varian Unity^{nova} AS400 NMR instrument. The sample was tightly filled in Varian 7 mm VT CP/MAS sample tube. Other vital parameters were as follows: spectral width, sw=50,000 Hz; proton pulse width, pw90=11.6 μ s; contact time for cross polarization, contact=5 ms; delay before acquisition, d1=2s, numbers of transients were 20,000 (for assigning relevant peaks) and 1000 (for variable temperature experiments). High power proton decoupling of 63 db with fine attenuation of dipole *r*=2500 was used only during detection periods. ²⁹Si CP/MAS NMR spectra were collected with the same instrument. Representative samples of 200–250 mg were spun at 3500 Hz using 7 mm double bearing ZrO₂ rotors as reported earlier [9].

2.3. FT-IR, DRIFT, ¹H NMR spectroscopy, and SEC

FT-IR measurements were carried out on a JASCO (Japan) FT/IR-4100 plus instrument in KBr. For DRIFT measurement accessory DR PRO410-M (JASCO, Japan) was used. ¹H NMR spectra were recorded on a JEOL JNM-LA400 (Japan) instrument. Size exclusion chromatography (SEC) was carried out with THF as a mobile phase at a flow rate of 0.5 ml min⁻¹. The chromatographic system included a JASCO 1580 pump (JASCO, Japan) and OMNISEC REVEAL (Malvern, England). For SEC column, GPC KF-803 (Shodex, Japan) was used.

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