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Enhancement of Thermal Stability and Selectivity by Introducing Aminotriazine Comonomer to Poly(Octadecyl Acrylate)-Grafted Silica as Chromatography Matrix

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Abstract: This paper introduces a poly(octadecyl acrylate) (pODA)-based organic phase on silica, which is assisted by 2-vinyl-4,6-diamino-1,3,5-triazine (AT), for a chromatography stationary phase. The ODA-AT copolymer grafting onto silica surface was characterized by elemental analysis, FT-IR spectroscopy, scanning electron microscopy, thermo gravimetric analysis and differential scanning calorimeter (DSC). An endothermic peak top of the copolymer-grafted silica was increased to 46 °C from 38 °C, which was a peak top of pODA homopolymer. For high performance liquid chromatography (HPLC) application, the molecular selectivity increased with an increase in the AT contents of the ODA-AT copolymer as organic phase. The co-existence of an aminotriazine moiety in the copolymer promoted side-chain ordering of the poly(octadecyl) moiety, thus enhancing molecular planarity selectivity for PAHs in reversed-phase liquid chromatography.

Keywords: organic-inorganic hybrid; molecular shape selectivity; crystalline-to-isotropic phase transition; HPLC

1. Introduction

Surface modification of materials by polymers is an effective technique to improve the material properties and incorporate the functions of the polymer [1–3]. Surface modification with a copolymer system is another important issue for the preparation of materials with tailor-made properties that are composed of two different monomers having diverse chemical and/or physical properties [4–6]. Inorganic carrier particles with polymeric/copolymeric phases on their surface have long been used as the stationary phase for HPLC [7–11] because such tailor-made surface properties directly influence the retention and separation efficiency. However, molecular ordering of copolymeric phases results in supramolecular functionality. A simple example of poly(octadecyl acrylate) and its copolymer systems has been reported in this regard [12]. Poly(octadecyl acrylate) copolymers grafted onto a porous silica surface exhibit an ordered-to-disordered phase transition in the octadecyl side chains, similar to lipid bilayer membrane systems [13,14], as well as extremely high selectivity for the shape recognition of geometrical isomers.

In this paper, we introduce the versatility of 2-vinyl-4,6-diamino-1,3,5-triazine (AT) as a co-monomer component in a polymeric phase on silica (Figure 1). AT is known to be effective for improving the thermal stability of polymers [15] and increasing the strength of hydrogels [16,17]; in addition, it can adsorb DNA through hydrogen bonding interactions [18–21]. This is the first report demonstrating an increase in the thermal stability of copolymer systems composed of octadecyl acrylate (ODA) and AT due to the co-existence of AT, and the induction of selectivity enhancement for molecular planarity against polyaromatic hydrocarbons in HPLC applications.

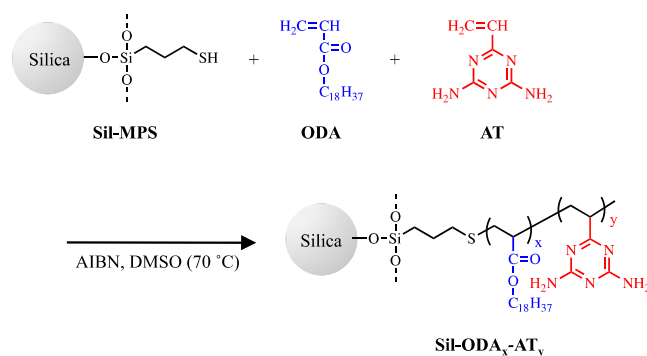


Figure 1. Reaction scheme for poly(octadecyl acrylate-co-2-vinyl-4,6-diamino-1,3,5-triazine)-grafted silica Sil-ODA_x-AT_y from 3-mercaptopropylated silica (Sil-MPS). ODA: octadecyl acrylate; AT: 2-vinyl-4,6-diamino-1,3,5-triazine.

2. Materials and Methods

ODA, AT, and 3-mercaptopropyltrimethoxysilane (MPS) were purchased from TCI (Tokyo, Japan). ODA and AT were used after removing the polymerization inhibitors. 2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Nacalai tesque (Kyoto, Japan) and recrystallized from methanol. HPLC-grade solvents were used in the chromatographic separations.

Copolymers (ODA_x-AT_y) were introduced onto porous silica via a “grafted-from” method [22] based on 3-mercaptopropylated silica (Sil-MPS). The typical procedure is as follows. Sil-MPS was prepared by using porous silica particles diameter 5 µm, pore size 12 nm, and surface area 300 m² g^{−1}, (YMC CO., LTD., Kyoto, Japan) and MPS according to a previously reported method [23]. Sil-MPS was mixed with given amounts of ODA, AT, and AIBN as a radical initiator in DMSO, and then, the mixture was gently stirred at 70 °C for 6 h. The reaction mixture was filtered and sufficiently washed with DMSO, chloroform, and methanol. The prepared stationary phases characterized using diffuse reflectance infrared Fourier transform (DRIFT). The measurements were conducted with JASCO FT/IR-4100 (Tokyo, Japan) and DRIFT measurement accessory DR PRO410-M (JASCO CO., Tokyo, Japan). Elemental analyses were carried out on a Yanaco CHN Corder MT-6 Apparatus (Yanaco Analytical Science Inc., Kyoto, Japan). The amount of copolymer loaded on silica was determined by thermogravimetric analysis (TGA) and elemental analysis (EA). TGA was performed on a Seiko Exstar 6000 TG/DTA 6200 thermal analyzer (Seiko Instruments Inc., Chiba, Japan) in air from 100 to 800 °C and a heating rate of 10 °C/min.

For comparison of the chromatographic results, ODA polymer-grafted silica (Sil-ODA₁₀) without AT [13,24] was also prepared. The orientation of copolymer side chain on silica surface was evaluated by differential scanning calorimetry (DSC) in methanol suspension. DSC analysis of Sil-ODA₁₀-AT₁ and Sil-ODA₅-AT₅ were carried out using DSC6200 and EXTRA6000 (Seiko Instruments Inc., Chiba, Japan). The sample (about 20 mg) was added in 50 µL methanol taken in a silver pan and another silver pan was used as a reference and DSC was measured between 10 and 70 °C at heating and cooling rate of 2 °C/min.

The obtained surface-modified silicas were packed into stainless-steel columns for use in HPLC. The chromatographic system consisted of a Gulliver PU-1580 intelligent HPLC pump with a Rheodyne

sample injector (JASCO CO., Tokyo, Japan). A JASCO multi-wavelength UV detector MD 1510 plus was used. The column temperature was maintained by using a column jacket having a heating and cooling system. Data were acquired using a JASCO ChromNAV (Ver. 1.17) system. Chromatography-grade methanol was used for the mobile phase. The retention factor (k) was determined by the relationship $(t_R - t_0)/t_0$, where t_R and t_0 are the retention times of the samples and methanol, respectively. The separation factor (α) was expressed as the ratio of the retention factors. The flow rate of the mobile phase was 1.0 mL/min for all analyses.

3. Results and Discussion

3.1. Characterization of Grafted Copolymers on Silica Surface

To estimate the amount of organic loading onto the silica particles, the resultant composites were subjected to EA and TGA measurements. Table 1 summarizes the results. An increase in the nitrogen content (with the C/N ratio) was observed upon increasing the initial molar ratio of the AT component in the copolymerization, indicating the introduction of the AT component. However, as shown in Figure 2, the silica surface was thoroughly covered with the polymer with an increase in the AT ratio, which decreased retentivity in the reversed-phase HPLC (RP-HPLC) mode, especially for Sil-AT₁₀ produced without the ODA component. Therefore, further investigation was carried out using Sil-ODA₁₀-AT₁ and Sil-ODA₅-AT₅.

Table 1 includes the results of weight loss between 100 and 800 °C, as observed by TGA (Figure S1). The loaded amounts for Sil-ODA₁₀-AT₁ and Sil-ODA₅-AT₅ were determined to 21.4 and 23.4 wt %, respectively, which are sufficient for HPLC applications.

Table 1. Fundamental characterization of the prepared silica composites.

Silica Composites	Molar Ratio		C (%)	EA N (%)	C/N	TGA	
	x	y				Loss (%)	Polymer (%)
Sil-MPS	-	-	03.81	0	-	11.3	-
Sil-ODA ₁₀ -AT ₁	10	1	21.75	00.64	33.98	32.7	21.4
Sil-ODA ₅ -AT ₅	5	5	19.55	04.09	04.78	34.7	23.4
Sil-AT ₁₀	0	10	20.68	23.11	00.89	28.4	17.1

The values of x and y correspond to the initial molar ratios of ODA and AT in the copolymerization process, respectively, and the obtained polymer-grafted silicas are abbreviated as Sil-ODA _{x} -AT _{y} .

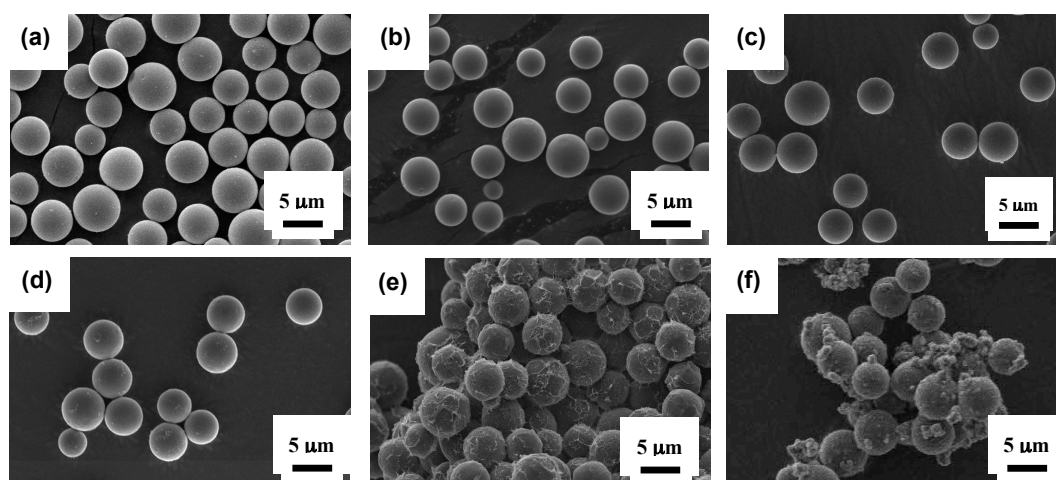


Figure 2. SEM images of the material silica (a), Sil-MPS (b), Sil-ODA₁₀ (c), Sil-ODA₁₀-AT₁ (d), Sil-ODA₅-AT₅ (e), and Sil-AT₁₀ (f).

3.2. Evaluation of Side-Chain Orientation in Grafted Polymeric Phase

The DSC thermogram of poly(octadecyl acrylate) (pODA) exhibited a sharp endothermic peak having a peak top at 48 °C, at the heating rate of 2 °C min^{−1}. This peak was attributed to a crystalline-to-isotropic phase transition based on the octadecyl moiety [25]. Figure 3 indicates that the peak-top temperature decreases from 48 °C to 38 °C, with peak shape broadening. This was due to perturbation from the silanol moiety of the base silica.

However, when a AT unit as a copolymer component was introduced into pODA, the peak-top temperatures increased from 44 °C to 46 °C with an increase in the molar ratio of AT for Sil-ODA₁₀-AT₁ to Sil-ODA₅-AT₅. These results indicated that the molecular ordering (crystallinity) of the ODA side chains is promoted by the co-existence of AT. It is presumed that pODA forms a homopolymeric block and that a AT unit interacts with ODA through hydrogen bonding interactions, in addition to interacting with a silanol moiety of the base silica. As a result, the pODA moiety becomes free from perturbations due to the silanol group. As a confirmation of this speculation, the diffuse reflectance infrared fourier transform (DRIFT) spectra exhibited distinct shifts for the carbonyl group: 1739 and 1733 in Sil-ODA₅-AT₅ and Sil-ODA₁₀-AT₁, respectively (Figure S2).

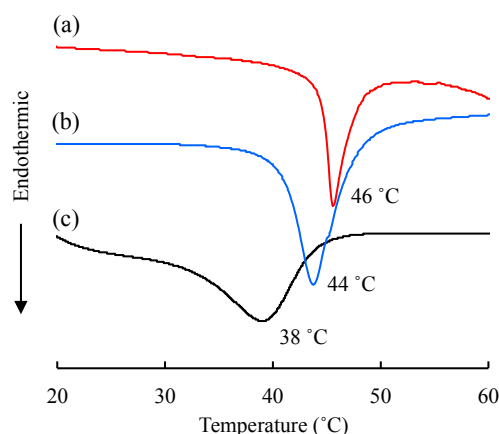


Figure 3. DSC thermograms of (a) Sil-ODA₅-AT₅, (b) Sil-ODA₁₀-AT₁, and (c) Sil-ODA₁₀.

3.3. HPLC

The liquid chromatographic performance was evaluated using polycyclic aromatic hydrocarbons (PAHs; terphenyl isomers, stilbene isomers, triphenylene, benz[*a*]anthracene, naphthacene, Figure S3) as the elutes in RP-HPLC mode. Table 2 summarizes the retention factor (*k*) and selectivity (α) for various PAHs. The PAHs used were broadly separated into two categories: planar compounds having different molecular lengths; and non-planar, twisted compounds [26–28]. The retention order of planar PAHs such as triphenylene, benzo[*a*]naphthalene, and naphthalene agreed with the log *P* order of the PAHs in all the columns. This trend is similar to that observed simple hydrophobized silicas such as ODS, thus indicating that the RP-HPLC mode was included in these columns. However, there is no significant increase in the α value among these planar PAHs, while the *k* value depended on the AT content. For example, the *k* value of naphthacene increased from 6.34 in Sil-ODA₁₀ to 12.5 in Sil-ODA₁₀-AT₁, but decreased to 4.38 in Sil-ODA₅-AT₅. This was probably due to the ODA contents, which were calculated to be 22.4 wt %, and 15.7 wt % in Sil-ODA₁₀-AT₁ and Sil-ODA₅-AT₅, respectively.

However, a significant increase in selectivity was observed between *o*-terphenyl and triphenylene (Figure S4). As shown in Table 2, the selectivity increased from 2.84 to 3.83 and then to 5.01 with an increase in the AT contents. A similar increase in selectivity was also observed between *cis*- and *trans*-stilbenes. *o*-Terphenyl and *cis*-stilbene can be categorized as non-planar compounds, but triphenylene and *trans*-stilbene are planar. Therefore, the molecular planarity selectivity increases with increasing AT content.

Table 2. Retention factors (k) and separation factors (α) for various polycyclic aromatic hydrocarbons (PAHs) with pure ODA and AT-containing ODA phases.

PAHs as Elutes		Sil-ODA ₅ -AT ₅		Sil-ODA ₁₀ -AT ₁		Sil-ODA ₁₀	
		k	α	k	α	k	α
<i>o</i> -Terphenyl	Non-planar	0.39	1	1.30	1	0.97	1
<i>m</i> -Terphenyl	Non-planar	0.88	2.27	2.47	1.90	1.48	1.52
<i>p</i> -Terphenyl	Non-planar	1.34	3.48	3.76	2.89	1.77	1.83
Triphenylene	Planar	1.93	5.01	4.98	3.83	2.76	2.84
<i>cis</i> -Stilbene	Non-planar	0.11	1	1.01	1	0.80	1
<i>trans</i> -Stilbene	Planar	0.24	2.26	1.64	1.62	1.15	1.43
Triphenylene	Planar	1.93	1	4.98	1	2.76	1
Benzo[α]anthracene	Planar	2.42	1.25	6.16	1.24	3.39	1.23
Naphthacene	Planar	4.38	2.27	12.5	2.51	6.34	2.30

Temperature: 30 °C, Mobile phase: MeOH-H₂O (90:10). The separation factors are calculated based on the retention factors of *o*-terphenyl, *cis*-stilbene, and triphenylene.

The selectivity increase for molecular planarity can be confirmed by investigating the temperature dependence. Figure 4 shows the temperature dependence of the selectivity for *o*-terphenyl and triphenylene. At all measured temperatures, the higher the AT content, the better was the selectivity. The selectivity of all phase was increased with decrease of temperature. The selectivity of Sil-ODA₁₀ was enhanced below 40 °C, which was closed to the phase transition temperature, 38 °C (Figure 3). On the other hand, for Sil-ODA₁₀-AT₁ and Sil-ODA₅-AT₅, the enhancement of their selectivities was observed in the higher range than 40 °C. This suggests due to higher phase transition temperature (44 and 46 °C, respectively, Figure 3) than Sil-ODA₁₀. Therefore, it was concluded that the co-existence of AT promotes the molecular ordering of the long-chain alkyl groups in ODA; consequently, the molecular planarity selectivity can be enhanced by an increase in the molecular ordering.

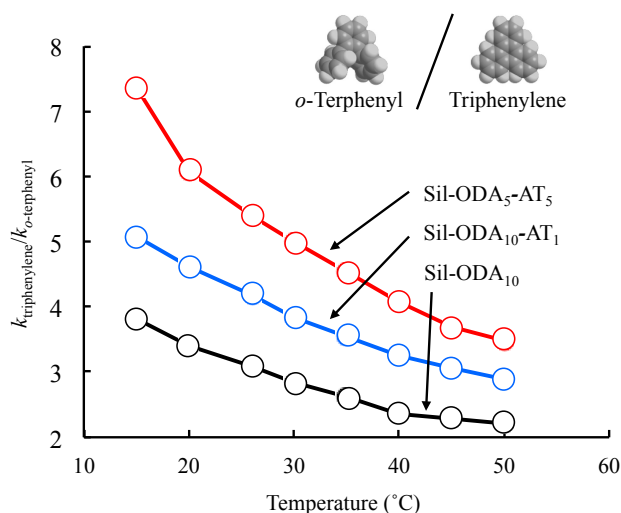


Figure 4. Temperature-dependent selectivity (α , $k_{\text{triphenylene}}/k_{\text{o-terphenyl}}$) with Sil-ODA_x-AT_y. Mobile phase: methanol-water (90:10), flow rate: 1.0 mL min^{−1}, UV detection: 275 nm.

4. Conclusions

We have demonstrated the positive effects of AT in a copolymer component for ODA. The most attractive effect is the increased thermal stability of the molecular ordering of ODA, which indicates an elevation of the phase transition temperature. Therefore, the concept of using AT as a co-monomer with ODA is a powerful way to enhance the crystalline properties of the ODA polymer. The obtained ODA-AT-copolymer-grafted porous silica can be used as a chromatographic stationary phase, as well

as an adsorbent and in applications where the thermal stability of the organic phase is important. This effective approach will encourage analysts and material scientists to synthesize new materials with better performance for research and industrial applications.

Supplementary Materials: The following are available online at www.mdpi.com/2297-8739/5/1/15/s1, Figure S1: TGA curves of Sil-MPS, Sil-AT₁₀, Sil-ODA₁₀-AT₁, and Sil-ODA₅-AT₅, Figure S2: DRIFT spectra of Sil-MPS, Sil-ODA₅-AT₅, and Sil-ODA₁₀-AT₁, Figure S3: Structures of the studied PAHs. Figure S4: Chromatograms for the separation of *o*-terphenyl, **1**, *m*-terphenyl, **2**, and triphenylene, **3**, on Sil-ODA₁₀-AT₁, Sil-ODA₅-AT₅ and Sil-ODA₁₀, respectively. Column temperature: 30 °C, Mobile phase: MeOH-H₂O (90:10). Flow rate: 1.0 mL min^{−1}.

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Conflicts of Interest: The authors declare no conflict of interest.

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