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Notes

Retention Behavior on Aminoethyl-modified Poly(*p*-phenylene terephthalamide) Fiber Stationary Phases in Gas Chromatography

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Surface derivatization of Kevlar, poly(*p*-phenylene terephthalamide), fiber has been studied along with the evaluation of the surface characteristics of the chemically-modified fiber as the stationary phase in packed-capillary gas chromatography (GC). Several experimental parameters in the derivatization reaction have been optimized, and the retention behavior of the surface-derivatized fibrous stationary phase has been investigated using various standard solutes, such as alkanes, alcohols and alkylbenzenes. By introducing aminoethyl functional groups onto the surface of the fibrous material, a specific selectivity for polar solutes has been observed.

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Introduction

Due to wide versatility as a modern separation technique, gas chromatography (GC) is one of the most common methods for the analysis of volatile compounds, and a variety of the stationary phases have been developed during the past several decades.[1] In contrast to successful applications and subsequent commercialization of polymer-coated columns, reports concerning the use of fibrous polymer-packed stationary phases, however, were somewhat limited, except for characterizing the surface of the fibers in inverse GC (IGC).[2,3] The IGC method is mainly based on systematic observations of a specific interaction between the surface of fibers packed into the column and the standard solutes injected as probes.[3] Therefore, it is quite natural that a synthetic fiber can be employed as a novel stationary phase in GC, if the fiber shows both thermal stability and resistance to the gaseous chemical species through the column during the typical separation process at elevated temperature in the GC system.

Recently, several heat-resistant synthetic fibers have been introduced as novel stationary phase materials in packed capillary GC.[4-7] A bundle of fine filaments was longitudinally packed into a short capillary of either fused-silica or stainless steel, and employed as a column for GC separation. Polymer-coating onto packed-filaments has also been studied, where typical polydimethylsiloxane-based materials that are often employed in conventional open-tubular GC column were introduced as a coating material.[5-9] The results clearly demonstrated the contribution of a fibrous support and the polymer-coating thereon to the retention behavior of the analytes; and also, a possibility has been found for a novel usage of fine fibrous polymers as a support material that can be combined with newly synthesized coating materials designed for particular separation problems.

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In our previous work,[10] a chemical modification of poly(*p*-phenylene terephthalamide) (PPTA) fiber as a GC stationary phase was investigated. The results showed the retentivity and selectivity enhancement for non-polar analytes on a fibrous stationary phase having non-polar functional groups, although a significant improvement for the separation of polar compounds was not obtained. As an extension of the previous investigation, a novel fibrous PPTA material derivatized with an aminoethyl group was studied in this work, and the selectivity for several polar analytes was evaluated. The retention factors for various sample probes has been compared with that observed on the parent fiber-packed GC columns.

Experimental

Materials and methods

Fibrous material, Kevlar 29 (the diameter of the filament: *ca*. 12.5 μm), was provided by Du Pont-Toray (Tokyo, Japan). The fiber was washed with acetone and water repeatedly, and dried at 120°C before use. Dimethylsulfoxide (DMSO) was purchased from Kishida Chemical (Tokyo, Japan), and was distilled over calcium hydride in a vacuum prior to use. Sodium hydride (in oil, 60%), 2-bromoethylamine hydrobromide, and all other chemicals were obtained from either Tokyo Chemical Industries (Tokyo, Japan) or Kanto Chemicals (Tokyo, Japan).

The chemically modified filaments were packed into the fused-silica capillary and employed as a stationary phase in GC. The column was prepared by longitudinally packing about 130 filaments of reacted or untreated fibers into a fused-silica capillary (0.32 mm i.d., 0.5 m length). The packing procedure was the same as reported previously.[5,6] A HP 6890N Gas Chromatograph (Yokogawa Analytical Systems, Tokyo, Japan) with a split/splitless injection port and a flame ionization detector (FID) was used for all GC measurements. As the carrier gas, N_2 was used, and N_2 gas and air (for FID) were supplied from the respective gas cylinders through the cartridge packed with a molecular sieve. All of the injections were made

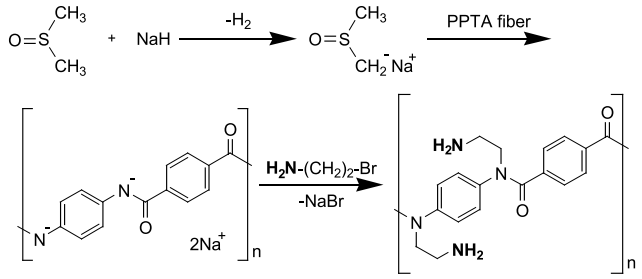

Fig. 1 Reaction scheme of poly(*p*-phenylene terephthalamide) (PPTA) fiber.

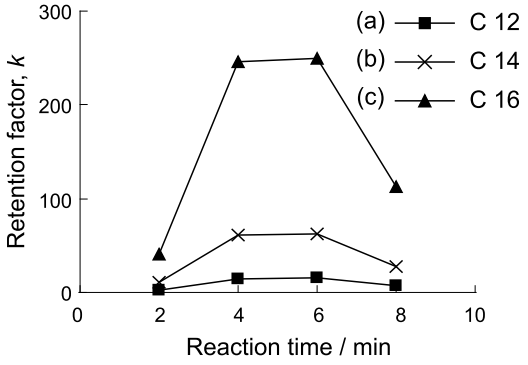

Fig. 2 Effect of the reaction time on the retention factors of alkanes on an aminoethyl-modified fibrous stationary phase. Sample: (a) $C_{12}H_{26}$, (b) $C_{14}H_{30}$, (c) $C_{16}H_{34}$. Chromatographic conditions: column temperature, isothermal at 110°C; column head pressure, 50 kPa; injector and detector temperature, 200 and 250°C, respectively; split ratio, 50:1; injection volume, 1 μL.

by split mode with a typical ratio of 50:1. The typical injection volume was 1 μL for all liquid sample probes, unless otherwise specified.

The other separation conditions, such as the carrier gas flow rate, the column head pressure, and the column temperature were determined by the results of preliminary experiments for each sample. For dead-time measurements, the peak of methane was used. All GC measurements were done at least three times, and the relative standard deviations (RSDs) for the retention time were less than 1.5%. The data collection was made with Borwin Chromatography Data Handling Software (Jasco, Tokyo, Japan) running on a personal computer.

Surface derivatization of PPTA fiber

Surface derivatization was conducted by a similar scheme as reported previously.[10] The reaction scheme is illustrated in Fig. 1.

Under a nitrogen atmosphere, sodium hydride was reacted with an excess amount of DMSO and stirred at 30°C for 20 min. Then, the solution was heated to 70°C and the reaction between sodium hydride and DMSO was proceeded for 1 h. Upon immersing the bundle of the PPTA filaments (about 130 filaments; 1.0 m length) into the solution, the metalation reaction was initiated at 30°C and continued for 10 min. The metalation reaction was confirmed by the change of the fiber color to be red from a gold color.[10,11] Next, the fiber bundle was reacted with a halogenated compound, R-$(CH_2)_2$-X, as can be seen in Fig. 1, at the same temperature for 2 h. During this step, it was confirmed that the color of the fiber surface turned back to the original golden yellow, suggesting both deactivation of the amide anion and the end of the substitution reaction. Finally, those filaments were taken out from the reaction bath, and were cleaned with acetone and water repeatedly, and then dried at 120°C for 2 h. A successful chemical modification of the filaments was confirmed by an increase in the retention factors of several standard solutes.

Table 1 Retention data for alkanes on aminoethyl-modified and untreated fiber-packed columns

Fiber	Retention factor			Selectivity	
	Dodecane	Tetradecane	Hexadecane		
	k_1	k_2	k_3	k_2/k_1	k_3/k_2
Untreated (PPTA)	1.7	4.4	16.6	2.57	3.80
Aminoethyl-modified	15.0	61.0	246	4.07	4.04

Reaction time for modification reaction, 4 h.
Column temperature, isothermal at 110°C; column head pressure, 50 kPa; injector and detector temperature, 200 and 250°C, respectively; split ratio, 50:1; injection volume, 1 μL.

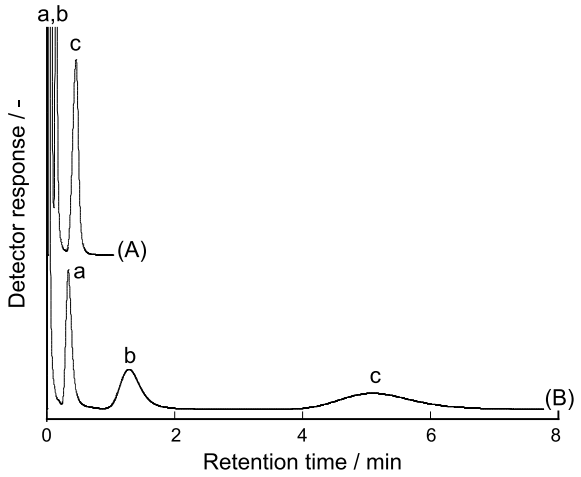

Fig. 3 Separation of three alkanes with the fiber-packed capillary columns. Packed fiber: (A) untreated, (B) aminoethyl-modified. Samples: (a) $C_{12}H_{26}$, (b) $C_{14}H_{30}$, (c) $C_{16}H_{34}$. Other conditions are the same as in Fig. 2.

Results and Discussion

Optimization of derivatization conditions

In order to confirm the surface modification of PPTA fiber with a substrate having a polar functional group, the retention of several sample probes on the fused-silica capillary column packed with the surface-modified fibrous material was evaluated. Compared to the parent PPTA fiber, the derivatized fibrous stationary phase retained all of the alkanes longer, suggesting a successful introduction of the functional groups to the PPTA fiber surface. Although the retention mechanism for the increased retention of alkanes on the derivatized fibrous stationary phase having a polar functional group should be

Table 2 Retention data for alcohols and alkylbenzenes on aminoethyl-modified and untreated fiber-packed columns

Fiber	Retention factor			Selectivity		Retention factor			Selectivity	
	Hexanol	Octanol	Decanol			Butylbenzene	Hexylbenzene	Octylbenzene		
	k_1	k_2	k_3	k_2/k_1	k_3/k_2	k_4	k_5	k_6	k_5/k_4	k_6/k_5
Untreated (PPTA)	1.4	5.3	23.8	3.70	4.48	2.4	8.5	38.7	3.61	4.56
Aminoethyl-modified	8.3	49.0	252	5.92	5.13	15.9	79.5	407	5.01	5.12

Reaction time for modification reaction, 4 h. Column temperature, isothermal at 80°C; column head pressure, 50 kPa; injector and detector temperature, 200 and 250°C, respectively; split ratio, 50:1; injection volume, 1 μL.

studied more, the above results clearly indicated that the reaction scheme in Fig. 1 could be applicable to a surface derivatization of the PPTA fiber, as found in previous publications[10] dealing with the derivatization by non-polar functional groups.

Upon a successful confirmation of the surface derivatization with aminoethyl functionality, the reaction time for derivatization with the halogenated compound, the final step in Fig. 1, was optimized. When changing the reaction time, the retentivity for three alkanes was monitored in GC, while all other conditions were maintained to be the same. An optimum reaction time of about 4 – 6 h was observed for the derivatization reaction, where the retentivity for the sample solutes was maximized, as shown in Fig. 2. The decrease in the retention factor for a reaction time of more than 8 h could be interpreted as a partial dissolution of the PPTA fiber surface into the DMSO solution. Based on the above results, it was considered that a reaction for 4 h was appropriate in the derivatized reaction.

Retention behavior of surface-derivatized stationary phases

The retention data for alkanes are summarized in Table 1, where aminoethyl derivatized fibrous stationary phases were synthesized under the optimized reaction conditions described above, and the same number of filaments were packed longitudinally into the fused-silica capillary of the same dimension. In contrast to the similar selectivity for alkanes, the retentivity on an aminoethyl-modified PPTA fiber was significantly enhanced, suggesting the successful introduction of a relatively large number of surface functional groups.

Typical chromatograms for the separation of three alkanes are depicted in Fig. 3, and the retention data for hexanol, octanol and decanol are summarized in Table 2, along with that for three alkylbenzenes. These results show a good agreement with the trend described above. The surface characterization of the derivatized fibrous stationary phase should be further studied in detail; however, the obtained results demonstrated the satisfactory retentivity of aminoethyl-derivatized fiber as a novel stationary phase in packed-capillary GC.

By introducing the amino functionality onto the surface of the PPTA fiber, an enhanced retentivity to non- and slightly polar sample solutes, such as alkanes and alkylbenzenes, has been confirmed. At the same time, however, a specific selectivity to polar analytes was also observed, as shown in Table 3, where the retention factors for several polar sample probes on the original PPTA fiber and the aminoethyl-modified PPTA fiber are summarized. For a comparison, the retention data measured on another fibrous material are also tabulated in Table 3. This fibrous stationary phase material was prepared by the reaction of the reactive intermediate with water, instead of alkyl halide, and the resulting chemical structure is assumed to be a similar structure to the parent PPTA, although a partial cleavage of the amide bond and the subsequent generation of a polar functional group could be expected during this reaction.

Table 3 Retention factors for polar probes on various fibrous stationary phases

Probe	Retention factor		
	Untreated	Aminoethyl modified	Water treatment
Acetonitrile	0.17	43.3	6.02
Pyrrolidine	1.72	120	29.9
Piperidine	2.21	111	45.9
Acetone	0.07	5.49	0.96
Ethyl acetate	0.24	14.6	3.66
Methanol	0.17	38.8	8.20
Ethanol	0.22	32.5	6.06
Propanol	0.57	120	19.2

Column temperature, isothermal at 35°C; column head pressure, 6 kPa; injector and detector temperature, 105 and 150°C, respectively; split ratio, 200:1; injection volume, 20 μL of the head space gas of the sample vial.

Taking into account the retentivity difference between the parent PPTA and the reference fibrous material prepared with the reactive intermediate and water, it is clearly confirmed that the aminoethyl-modified fibrous stationary phase has a significantly larger retentivity toward a polar solutes probably, due to introducing the aminoethyl functionality to the structure. Although the specific selectivity of these analytes should be further studied in detail, including the molecular shape and other physicochemical nature, the retention data in Table 3 could suggest a possibility of the aminoethyl-derivatized fiber as a novel stationary phase in GC separations.

Conclusions

The surface derivatization of PPTA fiber was studied with the derivatization reagent having a polar amino group; the results demonstrated that aminoethyl bromide is one of the successful derivatization approaches to PPTA fiber. A successful modification with aminoethyl bromide was confirmed along with an improved retentivity as the stationary phase to aliphatic and aromatic compounds, and a specific selectivity to polar analytes in GC. A certain selectivity improvement could be expected on the surface-derivatized filaments as the stationary phase, and the derivatized fibrous materials could be further applied as a support material for a novel GC stationary phase by introducing other functionalities and/or coating materials with the aminoethyl-group as the anchor. This two-step modification process will enable the development a novel stationary phase that could not be easily introduced to open-tubular columns.

The results also suggest that the surface-derivatized fibrous materials could be applied to the extraction medium in solid-phase extraction, and thus allowing miniaturization of the sample preparation process. These studies are currently underway in our laboratory in addition to applications to a novel extraction/trap medium designed as an interface in the LC-GC separation system. The future possibility of the short fiber-packed column has also been studied as a novel interface between two GC columns including particle-packed capillary columns.[12]

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