Spherical Polyimide Particles as a Novel Stationary Phase in Liquid Chromatography

Ohjiro SUMIYA1, Toshiaki TAZAWA1, Koki NAKAGAMI1, Yuki SHIRAI2, Koji MORIUCHI2, Ikuo UETA3, Yoshihiro SAITO*1

1Department of Environmental and Life Sciences, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku-cho, Toyohashi 441-8580, Japan
2Research Center, I.S.T Corporation, 5-13-13 Ichiriyama, Otsu 520-2153, Japan
3Department of Applied Chemistry, University of Yamanashi, 4-3-11 Takeda, Kofu 400-8511, Japan

Abstract
Spherical polyimide (PI) particles have been introduced as a stationary phase in liquid chromatography (LC). The PI was prepared with the starting materials of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (4,4'-oxydianiline, ODA), resulting the spherical PI (PMDA-ODA type) particles with an average diameter of about 5 μm. The synthesized PI particles were packed into a conventional blank LC column having a typical size of 4.6 mm i.d, 150 mm length, and the retention behavior for a group of polycyclic aromatic compounds (PACs) was evaluated in LC. The retention behavior was compared with that obtained on a commercially-available octadecysilica (ODS) phase. The results indicated a significantly larger retentivity of PACs on the PI stationary phase than that on typical ODS stationary phases, where the retention tendency on the PI phase for various PACs having different molecular size and shape was similar to the trend on the ODS phase. The large retention on the PI phase can be interpreted on the basis of the surface structure of the PI particles, because a number of aromatic functionalities are in the chemical structure of the polymer chain backbone.

Keywords: Stationary phase; Polyimide; Polycyclic aromatic compounds; Retention behavior; Molecular shape recognition; Liquid chromatography

1. Introduction
Polymer-based materials have been widely employed in chromatographic methods, especially for the stationary phase in liquid chromatography (LC) and also in size-exclusion chromatography (SEC) as one of the variations in LC methods [1-3]. Taking advantage of a good stability to a mobile phase of highly-acidic and highly-basic conditions, various applications have been reported. Another advantageous feature of the polymer-based phase in separation science is a simple phase structure design and the relatively easy synthesis of the phase, allowing a cost-effective development of novel stationary phases.

In terms of the use of polymer-based materials in LC, spherical particles of the various polymers and copolymers have been mainly studied as the stationary phase, although fibrous polymeric materials were also introduced as a stationary phase in gas chromatography [4-14] and LC [13-26], along with an extraction medium in sample preparation techniques for liquid samples [27-39] and gas samples [40-45]. In our previous investigation, a spherical polyimide (PI) particles have been introduced as a novel extraction medium in miniaturized sample preparation technique [45,46]. The PI was prepared with the starting materials of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (4,4'-oxydianiline, ODA). The synthesized PI (PMDA-ODA) showed a good extraction performance as the extraction medium for typical volatile
organic compounds. The results also suggest that a possibility of the PI to the application as the stationary phase in chromatography, because of a good resistance to typical organic solvents, such as dichloromethane and tetrahydrofuran (THF) along with a good stability at high-temperature conditions typically up to 300°C [45-47].

As an extension of these previous investigations, in this work, the spherical PI particles were introduced as the stationary phase in LC, where the retention behavior of the PI for a group of polycyclic aromatic compounds (PACs) was evaluated along with a comparison with that observed on a typical octadecylsilica (ODS) phase.

2. Experimental

2.1. Reagents and solvents

Polycyclic aromatic hydrocarbons (PAHs), and all polyphenyls used as the sample probes were of analytical reagent grade, and obtained from Tokyo Chemical Industry (Tokyo, Japan). All other reagents and solvents were of analytical reagent grade, and obtained from either Kishida Chemical (Osaka, Japan).

2.2. Preparation of PMDA-ODA PI particles

Polyimide particles with starting materials of PMDA and ODA were synthesized on the basis of conventional procedure as shown in Fig. 1. Details of the synthesis could be found elsewhere [46-48]. From a typical SEM image of the PI particles (Fig. 2), it can be found that the particles have a spherical shape with an average diameter of about 5 μm. The specific surface area of the particles was 60 m²/g. The synthesized PI stationary phase was packed into a conventional blank stainless-steel column of 4.6 mm i.d., 150 mm length with a slurry packing method, where dichloromethane as the slurry solvent and methanol as the driving solvent were used at a packing pressure of 40MPa.

2.3. LC measurements

For all the measurements, a LC system consisted of a PU1585 and a UV2075 (Jasco, Tokyo, Japan), a Model 7120 injector (20-µL sample loop volume) (Rheodyne, Cotati, CA, USA) was used. Chromatogram was recorded with ChromNAV Chromatography Data Handling Software (Jasco, Tokyo, Japan) running on a personal computer.
Fig. 4. Retention of various PACs on the PI and ODS phases. (a) particulate PI and (b) ODS phases. Mobile phase: dichloromethane/methanol (70/30) for PI; methanol for ODS. Other conditions are in the text.
As the mobile phase, methanol or mixtures of methanol/dichloromethane were used, and the flow-rate was set at 1.0 mL/min unless otherwise specified. UV detection wavelength was determined in the preliminary experiments for all the analytes.

As the sample probes for the analysis of the retention behavior, a group of PAHs were employed along with polyphenyl compounds including o-terphenyl, m-terphenyl and p-terphenyl. The chemical structures of these sample analytes are illustrated in Fig. 3.

3. Results and discussion

3.1. Retention behavior for aromatic compounds on the particulate PI stationary phase

For a systematic analysis of the retention behavior on the PI phase, a group of PAHs and polyphenyls having various molecular size and shape were introduced as the sample probes. This is because the molecular size can be quantitatively described by one of the molecular size descriptors, F number. The F number is proposed by Hurtubise et al. [49], which is defined as follows: 

\[ F = (\text{number of double bonds}) + (\text{number of primary and secondary carbons}) - 0.5 \times (\text{number of non-aromatic rings}) \]

and a high linear correlation between the logarithmic retention factor and F number has been confirmed for a typical monomeric ODS stationary phases in aqueous LC [50].

In Fig. 4, logarithmic retention factors for the sample analytes were plotted against the corresponding F numbers, where the plot for a typical column, having the same dimensions, packed with a commercially available ODS phase (Develosil ODS-UG-5; Nomura Chemical, Seto, Japan) was also shown. From these plots, a similar trend for the selectivity to the molecular size of the analytes can be confirmed for planer analytes, i.e. the logarithmic retention value will be increased linearly with increasing the molecular size of these planar analytes, although the magnitude of the retention factors on the PI phase was much larger than that on the ODS phase. For example, the retention factor of coronene on the ODS phase with pure methanol as the mobile phase is comparable with that on the PI phase with methanol/dichloromethane (30/70) as the mobile phase.

A good linear correlation between the logarithmic retention factor and the F number for the planar PACs on these two phases was observed in Fig. 4, although a negative deviation for non-planer analytes and a positive deviation for the analytes having "rod-like" shapes were also observed. The trend in Fig. 4a is somewhat different from that on a phenylbutyl bonded silica (PBS) phase [26]. The contribution of the aromatic functionality on the PI phase might be different from that on the PBS phase in terms of the interaction with these PACs.

3.2. Molecular shape recognition capability of the PI stationary phase for PACs

In order to further interpret the above results on the molecular shape recognition for the analytes, the selectivity for the two-dimensional shape of the analytes has been studied, where another molecular descriptor, length-to-breadth (L/B) ratio was introduced. This molecular shape parameter was proposed by Wise et al. and Kaliszsz et al., and defined as the length-to-breadth ratio of the two-dimensional molecular shape projected on a flat surface [51,52]. With this molecular shape descriptor, "rod-like" molecules and "square-like" molecules can be quantitatively classified.

<table>
<thead>
<tr>
<th>Solute Pair [L/B]</th>
<th>Selectivity</th>
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<tr>
<td></td>
<td>PI</td>
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<tr>
<td>[1.57]</td>
<td>1.59</td>
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<tr>
<td>[1.46]</td>
<td></td>
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<tr>
<td>[1.89]</td>
<td>1.51</td>
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<td>[1.72]</td>
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Table 1. Selectivity for various solute pairs having the same F number.

Mobile phase: dichloromethane/methanol (70/30) for PI; methanol for ODS. Other conditions are in the text.
Table 1 summarized the selectivities to some critical solute pairs consisted of ortho-fused PAHs having the same $F$ number, where the $F$ number of anthracene and phenanthrene is 7, and that of all other four-ring PAHs is 9. The results demonstrated a larger retention on the PI phase for the solute molecule having relatively "rod-like" shape in these solute pairs. The elution order of these analytes on the PI phase is the same as the ODS phase, although the retentivity on the PI phase is significantly larger than that on the ODS phase.

As reported previously [50,53] a slight shape selectivity to isomeric PAHs having different molecular shape, i.e. different $L/B$ value, is confirmed on the ODS phase. However, a larger selectivity for these pairs on the PI phase is obtained.

Table 2. Selectivity for solute pairs having different molecular planarities.

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<tr>
<th>Solute Pair [L/B]</th>
<th>Selectivity</th>
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<tbody>
<tr>
<td></td>
<td>PI</td>
</tr>
<tr>
<td>[1.12]</td>
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<tr>
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<td>4.50</td>
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<tr>
<td>[2.34]</td>
<td>17.8</td>
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</table>

Mobile phase: dichloromethane/methanol (70/30) for PI; methanol for ODS. Other conditions are in the text.

Another steric parameter, planarity of the analyte molecule, has been proposed by Tanaka et al. and Jinno et al., where a set of triphenylene and o-terphenyl was employed to quantitatively compare the molecular planarity recognition capability of the stationary phases in LC [54,55]. The selectivities for three solute pairs including triphenylene (planar) and o-terphenyl (non-planar) are summarized in Table 2. In terms of the molecular size on the basis of $F$ number, these four analytes have the same, i.e. $F=9$. Taking into account the difference in the mobile phase composition for these stationary phases, it can be confirmed that the PI phase has a quite large solute planarity recognition ability than a typical ODS phase, because the selectivities for these solute pairs are normally decreasing with increasing the content of less polar mobile phase component as reported previously [56].

Fig. 5. Typical chromatograms of naphthacene on the PI stationary phase at various column temperatures. Column temperature: (a) 30°C, (b) 40°C, (c) 60°C and (d) 80°C. Mobile phase: dichloromethane/methanol (70/30). Other conditions are in the text.

Fig. 6. van't Hoff plot for naphthacene (from 30°C to 100°C) on the PI stationary phase. Other conditions are the same as in Fig. 5.

3.3 Stability of the particulate PI stationary phase

Comparing with conventional ODS phases, the heat-resistance is one of the major advantages as the stationary phase in LC. The PI particles have a good resistance to typical organic solvents [45-47] along with a
good stability at a high temperature. Fig. 5 shows the chromatograms for naphthacene at various column temperatures, where a good stability to the PI stationary phase even with a high content of dichloromethane in the mobile phase solvent. The resulting van't Hoff plot is depicted in Fig. 6, suggesting a good stability of the PI particles in the above conditions. The linear plot with the correlation coefficient of more than 0.998 also demonstrates that there is no phase transition or decomposition of the PI materials at the column temperature up to 100°C. The PI phase showed a good repeatability in the high temperature conditions.

The particulate PI phase was also employed with pure water as the mobile phase. There is no significant change was found for the retention factors of all the PACs before and after using pure water as the mobile phase solvent. This is another advantageous feature of the PI stationary phase over typical conventional silica-based stationary phases such as ODS phases [46,12]. As an increased solubility of analytes can be expected at a high column temperature if the mobile phase composition is the same, the excellent resistance to severe separation conditions enables an increased throughput in preparative separations.

4. Conclusions
Particulate PI was introduced as a stationary phase in LC. On the basis of the excellent solvent resistance, the PI phase was successfully employed as the stationary phase. In this work, typical column pressure (with a size of 4.6 mm i.d., 150 mm length) of the particulate PI column was about 7.0 MPa with methanol (at a flowrate of 1.0 mL/min) as the mobile phase solvent, suggesting a practical use of this stationary phase material in a conventional LC system. Compared with a conventional ODS stationary phase, the PI phase demonstrated a significantly high retention for PACs. A good molecular shape recognition capability of the PI stationary phase can be attributed to the rigid and "rod-like" chemical structure on the polymer chain exposed on the surface of the PI particles, although a more systematic retention analysis for a variety of sample analytes must be carried out to interpret the retention mechanism in detail.

Due to a relatively large particle size distribution of the particulate PI phase, the resulting efficiency was somewhat limited for the separation of a mixture at this stage. However, the theoretical plate number will be improved on the basis of a precise particle size control in the synthesis. Another approach to the improvement of theoretical plates is a preparation of so-called "core-shell-type" particle consisted of a rigid core of a highly-crosslinked polymer and a thin shell of the PI material.

Further investigations are currently conducted in our laboratory including the retention behavior for various polar compounds that may have a specific interaction to the polar functional groups in the PI stationary phase structure. The potential applications to high temperature separations on the PI stationary phase are also studied along with the use of pure water as the mobile phase in LC.

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