Synthesis of TEMPO Functionalized Polyimides by A₂ + B₃ Polymerization

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1. Introduction

Polyimides are typical high performance polymers with high thermal and chemical stability and have been widely used in electric, electronic and aerospace applications. In addition, polyimides with numerous functional groups, such as acidic groups [1], are attracting much attention because they will combine high thermal stability of polyimides and various functionalities. Such functional polyimides will expand the application of polyimides to a wider range of fields.

As a novel functionality introduced into polyimides, our research group is interested in nitroxyl radicals such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). TEMPO is a stable free radical and known as an oxidation catalyst for primary alcohols [2]. It is also used as a radical scavenger in various chemical reactions. TEMPO is typically used in homogeneous systems, but the immobilization of TEMPO onto solid supports such as polystyrene [3] and silica [4] has also been developed. As polyimides are more thermally stable than polystyrene and more flexible than silica, the development of TEMPO functionalized polyimides will exhibit quite promising results.

To prepare functionalized polyimides, the A₂ + B₃ polymerization is one of the suitable methods. It has been known that hyperbranched polymers can be synthesized by a solution polymerization, especially if the polymerization and imidization are performed by one-pot method with high boiling point solvents [6]. Moreover, if one considers polyimide-based materials as solid catalysts, the particle size of polyimides will also be an important property, which can be controlled by the precipitation polymerization method [7-10].

As mentioned above, in terms of exploring novel solid catalyst materials based on dendritic polyimides, the number of terminal functional groups, porosity, and particle size are important properties. This paper describes three types of polymerizations, 1) one-pot polymerization/imidization in high boiling point solvents, 2) precipitation polymerization and 3) solution polymerization with a drop-wise feeding method, using the same A₂ and B₃ monomers, pyromellitic dianhydride (PMDA) and 1,3,5-tris(4-aminophenyl)benzene (TAPB) (Scheme 1). A slightly excess amount PMDA was used to terminate the polymer with phthalic anhydride groups, and the terminals were end-capped with 4-amino-TEMPO to obtain TEMPO functionalized polyimides. The concentration of TEMPO, porosity and morphology of the prepared polymers were characterized by electron spin resonance (ESR), N₂ adsorption and scanning electron microscopy (SEM) measurements, respectively.

2. Experimental

2.1. Materials

PMDA (TCI) was used after sublimation. TAPB (TCI) was used after recrystallization from ethanol. m-Cresol (TCI) and dimethylacetamide (DMAc, Kanto Chemical) were used after vacuum distillation over calcium hydride. 4-amino-TEMPO (TCI) and all other chemicals are
reagent grade and used as purchased unless otherwise stated.

Scheme 1. Synthesis of TEMPO functionalized polyimides.

2.2. One-pot polymerization/imidization
This polymerization/imidization was performed following an earlier work with a minor modification [6]. In a 20 mL flask, a solution of TAPB (80.8 mg, 0.23 mmol) in m-cresol (2 mL) was added to a solution of PMDA (100 mg, 0.46 mmol) in m-cresol (3 mL) and stirred under a N₂ flow at 0 °C for 2 h. After adding a catalytic amount of isoquinoline at RT, the mixture was stirred at 30 °C for 8 h, 80 °C for 4 h, 160 °C for 4 h, 200 °C for 8 h and 220 °C for 4 h. The precipitated polymer was isolated by filtration and washed with DMF, acetone and THF, and then further stirred in 300 mL of THF at RT overnight. After filtration and drying at 110 °C under vacuum, an yellowish polyimide powder (PI1) was obtained.

In a 10 mL flask, 4-amino-TEMPO (54.8 mg, 0.32 mmol) and PI1 (50 mg) were stirred in 3 mL of CHCl₃ at RT for 12 h. After filtration, the thermal imidization of the terminals was performed at 220 °C under vacuum overnight to obtain a dark brownish powder, PI1-TEMPO-H. PI1-TEMPO-Ch was obtained by performing a chemical imidization instead of the thermal imidization. The powder was stirred in a mixture of pyridine (1 mL) and acetic anhydride (1 mL) at 100 °C overnight and then filtered. After washing with acetone and drying at RT under vacuum, a dark brownish powder was obtained.

2.3. Precipitation polymerization
In a 10 mL flask, a solution of TAPB (80.8 mg, 0.23 mmol) in acetone (2.6 mL) was added in one-portian to a solution of PMDA (100 mg, 0.46 mmol) in acetone (4.2 mL) at 0 °C under vigorous stirring. After stirring for 2 h, the solvent was removed with a rotary evaporator and a thermal imidization was performed at 220 °C under vacuum for 12 h. The powder was washed with 300 mL of acetone and dried at 110 °C under vacuum to obtain a yellowish polyimide powder, (PI2).

The end-capping reaction with 4-amino-TEMPO followed by the thermal and chemical imidization was performed in the same manner as mentioned above to obtain PI2-TEMPO-H and PI2-TEMPO-Ch, respectively.

2.4. Solution polymerization
In a 30 mL flask, a solution of TAPB (72.8 mg, 0.21 mmol) in DMAc (7 mL) was added drop-wise over 30 min to a solution of PMDA (100 mg, 0.46 mmol) in DMAc (7 mL) at 0 °C. The mixture was further stirred at RT for 2 h. And then, 4-amino-TEMPO (158 mg, 0.92 mmol) was added and stirred at RT for 3 h. The solution was poured into ethyl acetate and the polymer was collected by filtration. After drying at RT under vacuum, a pinkish powder (PA3-TEMPO) was obtained. As a controlled sample, PA3 was also synthesized without reacting with 4-amino-TEMPO.

The thermal and chemical imidization of PA3-TEMPO was performed in the same manner as mentioned above to obtain PI3-TEMPO-H and PI3-TEMPO-Ch, respectively. PI3 was obtained by the chemical imidization of PA3.

2.5. Characterization
FT-IR spectra were obtained with a JASCO
4100 spectrometer by the KBr pellet method. SEM was carried out using a VE9800 spectrometer (Keyence). The N$_2$ adsorption was measured using a volumetric adsorption measurement instrument (Bel Japan, Belsorp-mini II). ESR measurement was carried out using a JES-FA100 spectrometer (JEOL) in a powder form. The TEMPO loading was estimated by integrating the ESR spectrum twice and comparing the intensity with relative to that of 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl benzoate (TEMPOB).

3. Results and discussion

3.1. One-pot polymerization/imidization

PI1 was synthesized by the one-pot polymerization/imidization of TAPB and PMDA in $m$-cresol and PI1-TEMPO-H and PI1-TEMPO-Ch were prepared by the end-capping reaction for PI1 with 4-amino-TEMPO, followed by the thermal and chemical imidizations, respectively.

![Fig. 1. SEM image of PI1-TEMPO-Ch.](image)

**Fig. 1.** SEM image of PI1-TEMPO-Ch.

![Fig. 2. N$_2$ isotherms at 77 K with the PI1 based samples.](image)

**Fig. 2.** N$_2$ isotherms at 77 K with the PI1 based samples.

Fig. 1 shows the SEM image of PI1-TEMPO-Ch. The particle size seems over 500 nm and the morphology is not uniform. Fig. 2 shows the N$_2$ isotherms with the PI1 based samples. These samples show Type I isotherms in the IUPAC classification, suggesting the presence of microspores. The BET surface areas evaluated from the N$_2$ isotherms are summarized in Table 1. All the PI1 based samples show quite high specific surface areas, which are probably due to three dimensional networks of polyimide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area / m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI1</td>
<td>659</td>
</tr>
<tr>
<td>PI1-TEMPO-H</td>
<td>593</td>
</tr>
<tr>
<td>PI1-TEMPO-Ch</td>
<td>658</td>
</tr>
</tbody>
</table>

![Table 1. Specific surface area of the PI1 based samples](image)

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3.2. FT-IR and ESR spectra

![Fig. 3. FT-IR spectra of the PI1 based samples.](image)

**Fig. 3.** FT-IR spectra of the PI1 based samples.

![Fig. 4. ESR spectra of the PI1 based samples.](image)

**Fig. 4.** ESR spectra of the PI1 based samples.

Fig. 3 shows the FT-IR spectra of the PI1 based samples. The peaks at 1776 cm$^{-1}$ (C=O stretch) and 1375 cm$^{-1}$ (C-N-C stretch) suggest the formation of polyimide. If a polymer contains numerous phthalic anhydride groups, a peak due to the C=O stretch should appear at around 1860 cm$^{-1}$, but none of these samples showed such peaks. To confirm the existence of nitrroxy radical, ESR
measurements were performed and the results are summarized in Fig 4. Compared to the reference sample, TEMOB, none of these three samples showed ESR peaks due to the free radical. It is unlikely that TEMPO group was introduced onto the terminals of PI1.

These experimental results suggest that the one-pot polymerization/imidization of PMDA and TAPB provides microporous polyimides with a high specific surface area, however the obtained polyimides did not have many terminals because of an excess growth of three dimensional network.

3.2. Precipitation polymerization

PI2 was synthesized by the precipitation polymerization of PMDA and TAPB. PI2-TEMPO-H and PI2-TEMPO-Ch were prepared by the end-capping reaction for PI2 with 4-amino-TEMPO, followed by the thermal and chemical imidization, respectively.

Fig. 5. SEM image of PI2-TEMPO-Ch.

Fig 6. N2 isotherms at 77 K with the PI2 based samples. The isotherms show very little adsorption of N2 except for the macropore region. The BET surface area was in the range of 10-26 m2 g⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI2</td>
<td>22</td>
</tr>
<tr>
<td>PI2-TEMPO-H</td>
<td>26</td>
</tr>
<tr>
<td>PI2-TEMPO-Ch</td>
<td>10</td>
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</tbody>
</table>

Table 2. Specific surface area of the PI2 based samples

Fig. 7. FT-IR spectra of the PI2 based samples.

Fig. 8. ESR spectra of the PI2 based samples.

Fig. 7 shows the FT-IR spectra of the PI2 based samples. The peaks at 1776 cm⁻¹ (C=O stretch) and 1375 cm⁻¹ (C-N-C stretch) suggest the formation of polyimide. In addition, another peak due to C=O stretch appeared at 1860 cm⁻¹, suggesting the presence of phthalic anhydride. Fig. 8 shows the ESR spectra of PI2 based samples. Compared to the reference sample, TEMOB, none of these three samples showed ESR peaks due to the free radical. It is unlikely that TEMPO groups was introduced onto the terminals of PI2.
These experimental results suggest that the precipitation polymerization provides fine nano-particles of polyimide containing considerable amounts of phthalic anhydride terminal groups but those terminals cannot be functionalized by an end-capping reaction probably because those terminals are hidden in the polymer matrix.

3.3. Solution polymerization

PA3 was synthesized by the solution polymerization of PMDA and TAPB in DMAc with a drop-wise feeding method. PA3-TEMPO was prepared by reacting PA with 4-amino-TEMPO in the same flask for the polymerization. PI3-TEMPO-H, PI3-TEMPO-Ch and PI3 were prepared by the thermal imidization of PA3-TEMPO, the chemical imidization of PA3-TEMPO and the chemical imidization of PA3, respectively.

Table 3. Specific surface area of the PI3 based samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>PA3-TEMPO</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>PI3-TEMPO-H</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>PI3-TEMPO-Ch</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Fig. 11. FT-IR spectra of the PI3 based samples.

Fig. 12. ESR spectra of the PI3 based samples.

Fig. 10 shows the SEM image of PI3-TEMPO-Ch. The observed polyimide particles are quite bulky and the morphology is not uniform. Fig. 10 and Table 3 show the N₂ isotherms and the BET surface areas of the PI3 based samples. The isotherms show little adsorption of N₂ and the BET surface areas were evaluated as less than 1 m² g⁻¹. This is probably because the morphology of the polyimides are decided at the stage of the reprecipitation.
PA3-TEPMO and PI3-TEMO-Ch clearly show ESR signals due to nitroxyl radical. The concentration of nitroxyl radical was evaluated as approximately 1.2 mmol g\(^{-1}\), based on a comparison against the reference spectrum of TEMPO-B. If one considers an ideal hyperbranched structure from the current A\(_2\) + B\(_3\) monomer and fully functionalized terminals, the theoretical value will be 1.13 mmol g\(^{-1}\). Therefore, the structure of PI3 is probably quite close to a hyperbranched structure rather than a network structure. In contrast, PI3-TEMPO-H did not show any clear ESR signal. This is probably because the TEMPO structure decomposed by the thermal imidization procedure.

These experimental results suggest that a TEMPO functionalized polyimide has been successfully synthesized by a solution polymerization of PMDA and TAPB with a drop-wise feeding method, followed by an \textit{in-situ} end-capping reaction with 4-amino-TEMPO. Further studies will be done to perform the optimization of morphology, introduction of different functionalities and catalysis utilizing this series of functionalized polyimides.

4. Conclusion

Three different polymerization methods were studied for the A\(_2\) + B\(_3\) polymerization to provide a TEMPO functionalized polyimides. The one-pot polymerization/imidization and the precipitation polymerization provided a microporous polyimide and a spherical polyimide, respectively; however, the functionalization of the terminals was difficult. In contrast, the solution polymerization with a drop-wise feeding method provided a hyperbranched polyimides and the terminals have been successfully functionalized with TEMPO by the \textit{in-situ} end-capping reaction. This polymerization and end-capping method will be applicable for the introduction of other various functionalities and might result in the development of various novel polyimide materials.

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References