Synthesis and Carbonization of Polyimide Nanoparticles Modified with Long Alkyl Chains Aspiring to Non-precious-metal Fuel Cell Catalysts

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Polyimide (PI) nanoparticles are known as precursors of non-precious metal cathode catalysts, which are expected to be the alternatives for platinum-based catalysts for the globalization of polymer electrolyte fuel cells. Our research group previously reported the synthesis of PI nanoparticles with diameters of approximately 60 nm by the precipitation polymerization of pyromellitic dianhydride and 1,3,5-tris(4-aminophenyl)benzene. This study focuses on the synthesis of PI nanoparticles with even smaller size by stabilizing the polymer/solvent interface. In addition to the same monomers as the previous study, dodecylamine was added to the polymerization system as an end-capping agent, and PI nanoparticles with diameters less than 50 nm have been successfully obtained.

Keywords: Polyimides, End capping, Precipitation polymerization, Non-precious-metal catalysts, Polycondensation

1. Introduction
Polyimides (PIs) exhibit excellent heat resistance, mechanical strength, chemical stability and electrical resistivity and are utilized as aerospace and electronic materials [1-4]. In terms of expanding their applicability, controlling the morphology of polyimides is an important research topic [5-9]. Especially, spherical PI nanoparticles have drawn much attention due to their potentials for next generation materials, such as catalysis, nanoreactors, nanofillers, drug delivery carriers [10-14].

In this context, our research group has been interested in morphology-controlled PIs as precursors of carbonaceous materials for non-precious-metal (NPM) catalysts, which enhances the electrochemical reduction of oxygen to water in polymer electrolyte fuel cells (PEFCs) [15-19]. PI nanoparticles can be converted into catalytically active carbon materials by the pyrolysis at a high temperature in the presence of a small amount of Fe additive. Our research group previously reported NPM cathode catalysts prepared by pyrolyzing polyimides (PI) nanoparticles with diameters of approximately 60 nm, which was prepared by the precipitation polymerization of pyromellitic dianhydride (PMDA) and 1,3,5-tris(4-aminophenyl)benzene (TAPB), and demonstrated one of the best fuel cell performances using NPM catalysts. If further smaller particle sizes of PIs could be obtained, a significant improvement will be expected in the development of NPM catalysts.

This study focuses on the preparation of PI nanoparticles with diameters smaller than 60 nm. Our previous studies have optimized the monomer concentration, polymerization temperature and the concentration of dispersant, N,N-dimethyldodecylamine for the precipitation polymerization of PIs [16]. The dispersant is likely effective to stabilize the interface of the poly(amic acid) droplet and solvent, for providing small particle sizes of the precipitating polymers. In this study, we have been motivated to stabilize the interface more extensively by introducing covalently immobilized dispersant in addition to N,N-dimethyldodecylamine, as illustrated in Fig. 1. For this purpose, dodecylamine was added into the polymerization system as an end-capping agent of the poly(amic acid) which is

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precursor of PI as shown in Scheme 1. The particle sizes of the PI particles prepared with various stoichiometric ratio of the end-capping agent were evaluated by field-emission scanning electron microscopy (FE-SEM). The particle sizes after the carbonization at 900 °C were also studied to confirm that the obtained PI nanoparticles have an appropriate thermal stability to retain the particle size even after the high temperature pyrolysis. The precipitation polymerization of PMDA and 4,4’-oxydianiline (ODA) was also studied as a control (Scheme 2).

Fig. 1. Schematic illustration for poly(amic acid) droplet dispersed in a polymerization solvent.

2. Experimental

2.1. Materials

PMDA and ODA were purchased from TCI and purified by sublimation before use. TAPB, dodecylamine, N,N-dimethyldodecylamine, and iron(III) acetylacetonate (Fe(acac)₃) were purchased from TCI or Aldrich and used as received. All other reagents were of reagent grade and used as received.

2.2. Preparation of PI nanoparticles from PMDA and TAPB

To obtain PI nanoparticles without the end-capping agent, a solution of TAPB (4 mmol, 1.41 g) in acetone (50 mL) was added to a solution of PMDA (6 mmol, 1.31 g), Fe(acac)₃ (48.3 mg) and the dispersant (0.3 mL) in acetone (50 mL). The amount Fe was set as 0.3 wt% with respect to the resulting polyimide. The mixture was stirred for 60 min at 0 °C. After evaporation of the solvent, the curing reaction was conducted by heating the poly(amic acid) at 240 °C under reduced pressure to obtain polyimide nanoparticles.

To obtain PI nanoparticles with the end-capping agent, x mmol of TAPB (x = 0.8-0.04) was replaced with 3x mmol of dodecylamine (185.35 × 3x g), and the above-mentioned procedure was conducted.

These obtained PI samples were denoted as PI-TAPB(x), where x (0.8-0) represents the amount of TAPB replaced by the end-capping agent.

2.3. Preparation of PI nanoparticles from PMDA and ODA

To obtain PI nanoparticles without the end-capping agent, a solution of ODA (6 mmol, 1.20 g) in acetone (50 mL) was added to a solution of PMDA (6 mmol, 1.31 g), Fe(acac)₃ (48.3 mg) and the dispersant (0.3 mL) in acetone (50 mL). The mixture was stirred for 60 min at 0 °C. After evaporation of the solvent, the curing reaction proceeded by heating the poly(amic acid) at 240 °C under evacuation to obtain polyimide nanoparticles.

To obtain PI nanoparticles with the end-capping agent, dodecylamine (0.84 mmol, 155.7 mg) was added to the ODA solution, and the above-mentioned procedure was conducted.

These obtained PI samples were denoted as PI-ODA(y), where y (0 or 0.84) represents the amount of the end-capping agent.

2.4. Measurements

Field emission scanning electron microscopy (FE-SEM) was conducted using an S5500 microscope (Hitachi) at 1.0 kV. Infrared (IR)
spectra were recorded on a JASCO 4100 spectrometer using the KBr pellet method. Thermogravimetric analysis (TGA) was performed with an SII TGA 7300 system at a heating rate of 10 °C min⁻¹. Raman spectroscopy was performed at 532 nm using a JASCO RMP-510 spectrometer.

3. Results and discussion

3.1. Characterization of the PI nanoparticles

The PI nanoparticles prepared with/without the end-capping agent, dodecylamine, were prepared by the synthetic route shown in Schemes 1 and 2, and characterized by FE-SEM and IR spectroscopy. The Fe complex, Fe(acac)₃, is not necessary for this polymerization reaction, but was added as a catalyst for the following carbonization procedure [21].

Figure 2 shows the Fourier-Transform (FT) IR spectra for PI-TAPB(ₓ). The adsorption peaks at 1725 cm⁻¹ and 1776 cm⁻¹ suggest the formation of an imide group [22]. The peak intensity at 2850 and 2920 cm⁻¹, which are attributed to C-H stretching vibration, increased as the charged amount of dodecylamine increased, suggesting more alkyl chains were introduced onto the terminals of the PIs. Similar phenomena were observed in the FT-IR spectra for PI-ODA(ᵧ), as shown in Fig. 3.

The FE-SEM images of PI-TAPB(ₓ) are summarized in the left-hand side of Fig. 4. The PI nanoparticles prepared without the end-capping agent, PI-TAPB(0), shows fairly uniform spheres...
with diameters over 100 nm. The samples prepared with the end-capping agent, PI-TAPB(\(x\) \((x = 0.04-0.6)\), show smaller PI spheres with diameter less than 100 nm. In contrast, PI-TAPB(0.8) with an extremely large amount of end-capping agent did not show any controlled morphology. Among them, PI-TAPB(0.28) seems to provide the smallest PI nanoparticles with a diameter less than 50 nm. As a control sample, PI nanoparticles from PMDA and ODA was also prepared in the presence of the same amount of dodecyl amine to that of PI-TAPB(0.28), and the FE-SEM image is shown in Fig. 5. Such PI-ODA(0.84) does not show any effect of dodecylamine on the particle size. This suggest that the addition of dodecyl amine is effective only when the number of the reactive sites is increased by introducing the triamine monomer, TAPB. Therefore, it is assumed that the dodecylamine is working as a covalently immobilized dispersant as illustrated in Fig. 1, and contributing to the stabilization of the interface between the poly(amic acid) droplet and solvent, for providing small particle sizes of precipitating polymers.

Fig. 5. FE-SEM images of the PI nanoparticles from PMDA and ODA before and after the carbonization at 900 °C.

3.2. Pyrolysis of the PI nanoparticles

The PI samples were analyzed by TGA to study their thermal stability and to obtain carbonized samples. Approximately 10 mg of PI sample was charged in a platinum pan, and heated up to 900 °C at a heating rate of 10 °C min\(^{-1}\). The carbonized residue was denoted as C-TAPB(\(x\)) or C-ODA(\(y\)). Such carbonized samples were further analyzed by FE-SEM and Raman spectroscopy.

The TGA curve and its differential (DTG) for PI-TAPB(0) is summarized in Fig. 6a. The pyrolysis of the polymer started at around 300 °C, and a significant weight loss due to the carbonization was observed at around 600 °C, accompanied by the final char yield of 51%. The results with PI-TAPB(0.28), which was obtained in the presence of the end-capping agent, is summarized in Fig. 6b. This TGA curve exhibits a similar trend to that of PI-TAPB(0), apart from a small DTG peak at around 500 °C. This weight loss at 500 °C is probably due to the decomposition of the alkyl chains introduced by the end-capping agent. Figure 7 shows the Raman spectra of the carbonized samples, C-TAPB(0) and C-TAPB(0.28). From both samples, strong G-bands and D-bands were observed at 1609 cm\(^{-1}\) and 1367 cm\(^{-1}\), respectively [23]. A similar measurement to obtain a Raman spectra for PI-TAPB(0.28) was also tried but did not provide any analyzable Raman signals because of a huge background due to fluorescence. The appearance of the G-band suggests that the PI samples were effectively carbonized by the heat-treatment at 900 °C, while the appearance of the D-band suggests the formation of a disordered carbon network in C-TAPB(0.28) and C-TAPB(0). No significant effect by the end-capping agent on the carbon structure was suggested in the Raman spectra.

Fig. 6. TGA curves and their differentials for (a) PI-TAPB(0) and PI-TAPB(0.28).

If one considers this series of PI nanoparticles as a precursor for carbonaceous materials in catalysis, retaining the original morphology even after the carbonization is critically important. The FE-SEM images of the PI nanoparticles after the
carbonization, C-TAPB(x), are summarized in the right-hand side in Figs. 4 and 5. Furthermore, one of the smallest samples, PI-TAPB(0.28) and C-TAPB(0.28) are compared in Fig. 8, with a higher magnification. Even after the high temperature pyrolysis, the majority of PI nanoparticles retained the original morphology as polymerized. This is presumably due to the high thermal stability of polyimides.

4. Conclusion
PIs nanoparticles with diameters of 30 nm at a minimum with good thermal stability have been successfully fabricated by the precipitation polymerization. It was found that the diameters of PIs nanoparticles can be controlled by the terminal modification with alkyl chains. This finding will advance the size control and functionalization of the PI nanoparticles. Further studies will be done by fabricating actual NPM catalysts by the multi-step pyrolysis [15] and demonstrating the catalytic activity for oxygen reduction in PEMFCs.

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