Synthesis and Properties of Hyperbranched Aromatic Polyimides via Thermal Self-Polycondensation

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The thermal self-polycondensation of 4-(3,5-bis(4-aminophenoxy)phenoxy)phthalic acid, an AB2 type monomer, proceeded successfully at 140°C to form a hyperbranched poly(amic acid). The subsequent chemical imidization of the poly(amic acid) afforded hyperbranched aromatic polyimides bearing acetylamide (HBPI-Ac) or imide terminal (HBPI-Im) groups. The formation of high molecular weight polymers was confirmed by gel permeation chromatography measurements using a light scattering detector. The resulting polymers exhibited good solubility and low solution viscosity, which is typical for hyperbranched polymers. The degree of branching of HBPI-Ac was determined to be 0.48. Moreover, the 1H NMR measurement of the model phthalic acid compound at 120°C suggested that the formation of carboxyl anhydride units facilitated the amide bond formation, resulting in the hyperbranched poly(amic acid). HBPI-Im showed the temperature for a 5% weight loss at 470°C, which was much higher than that of HBPI-Ac (400°C). HBPI-Im film, coated on a glass plate, became insoluble in amide solvents after heating at 280°C for 10 min, indicating that it could be applied as a solvent-resistant and thermally stable coating in the microelectronics industry.

Keywords: hyperbranched polyimide, thermal self-polycondensation, degree of branching, thermal stability coating film

1 INTRODUCTION

Dendritic macromolecules, such as dendrimers, dendrons, and hyperbranched polymers, are a new class of materials with unique properties owing to their consecutive branching architecture.[1-6] Specifically, the hyperbranched polymers are easily synthesized by a one-step polymerization process of AB2 type monomers or A2 and B3 monomers.[7-14] Many properties of the hyperbranched polymers, such as solubility and viscosity, are similar to those of dendrimers, which, however, require several reaction and purification steps for their production. Therefore, the hyperbranched polymers are promising polymers for scale-up production and industrial applications.

Aromatic polyimides are one of the most important high-performance polymers in advanced industries such as microelectronics, aerospace, composites, fuel cells, optoelectronics, and solar cells.[15-19] Polyimide films are usually fabricated by coating the precursor polymer, the poly(amic acid), followed by heating at high temperature. Because of their rigid aromatic structure, polyimides are insoluble in solvents and infusible after the imidization process. Therefore, the development and application of soluble polyimides as coating materials in the microelectronics industry is required. The introduction of a hyperbranched structure is one method to generate rigid aromatic polymers with good solubility and high thermal stability. Hyperbranched aromatic polyimides were first reported by Moore and coworkers.[20, 21] Thermally stable hyperbranched polymers were obtained through etherification reactions of the protected AB2 type monomer at 240°C. Because of the high temperature reaction, the transesterification and molecular rearrangements were also observed for the model reaction at 240°C.[21] Kakimoto and coworkers reported the synthesis and the properties of hyperbranched polyimides through the condensation reaction of carboxy and amino groups in the presence of condensation agents.[22, 23] The obtained hyperbranched poly(amic acid) (HBPI-AA) esters were then chemically or thermally imidized to form hyperbranched polyimides. However, the use of phosphorous condensation agents raises the risk of contamination, which in turn causes severe problems in the microelectronics industry. The synthesis of hyperbranched polyimides through commercially available A2 and B3 monomers has been also reported in the literature.[24-30] Nevertheless, the reaction conditions require careful optimization in order to avoid gelation. Moreover, the resulting polymers contain partially crosslinked structures and often show high solution viscosity in contrast to hyperbranched polymers.

In this study, hyperbranched aromatic polyimides were synthesized from AB2 type monomers without the use of condensation agents. The HBPI-AA was synthesized by heating the AB2 type monomer at a relatively low temperature (140°C) without gelation. The subsequent chemical imidization afforded the hyperbranched polyimides, which were characterized by gel permeation chromatography (GPC) measurements with a light scattering detector and NMR measurements. The thermal properties, the film foaming ability, and the solubility change after heating were also discussed.
2 EXPERIMENTAL

2.1 Materials

4-Nitrophthalonitrile, 3,5-dimethoxyphenol, 4-fluoronitrobenzene, phthalic anhydride, and acetic anhydride were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan) and used as received. Dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), toluene, pyridine, and palladium on activated carbon (Pd 10%) were purchased from FUJIFILM Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used without further purification. Potassium hydroxide and potassium carbonate were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) and also used without further purification. All other chemicals and solvents were used as received, unless otherwise indicated.

2.2 Characterization

The \( ^1H \) and \( ^13C \) NMR spectra were recorded by a JEOL JNM ECX 500 NMR spectrometer (JEOL, Tokyo, Japan) using DMSO-\( d_6 \) as the solvent. The optical transparency of the polymer films was recorded on a UV–Vis spectrophotometer (Jasco V-750) in a range 200–800 nm. The molecular weight was determined by GPC measurements (Shodex LF-804 column) using DMF containing lithium bromide (0.01 mol/L) as the solvent and a laser light scattering (LS) detector (DAWN HELEOSII Plus, Wyatt Technology Co., CA, USA). The specific refractive index increment (dn/dc) at 632.8 nm was measured using a refractive index (RI) detector (Optilab rEX differential refractometer, Wyatt Technology Co.). The molecular weight and its distribution were also estimated by polystyrene standards. The same RI detector (Optilab rEX differential refractometer) was used as a concentration-sensitive detector. Thermogravimetric analysis was performed using a STA7300 analyzer (Hitachi High-Tech Science, Tokyo, Japan) over a temperature range of 50–600°C at a heating rate of 10°C/min under nitrogen atmosphere. The average thickness of the film on the glass plate was determined to be 0.87 μm by using a laser microscope VK-X200 (Keyence Co., Osaka, Japan).

2.3 Synthesis of 4-(3,5-bis-(4-aminophenoxy)phenoxy) phthalic acid (AB₂-NH₂)

4-Nitrophthalonitrile (5.0 g, 28.9 mmol), 3,5-dimethoxyphenol (4.45 g, 28.9 mmol), and anhydrous potassium carbonate (9.98 g, 72.3 mmol) in DMSO (25 mL) were added in a round-bottom flask and the mixture was stirred at room temperature for 3 h under nitrogen flow. Then, the resultant mixture was poured slowly into ice water (200 mL) and the pH was adjusted to 1 using dilute HCl (1 M) to afford a white solid, which was isolated by filtration. The product was washed well with water and dried under vacuum at 50°C to afford 4-(3,5-dimethoxyphenoxy)phthalonitrile (8.14 g, 100% yield). \( ^1H \) NMR (δ, ppm): 8.09 (1H), 7.79 (1H), 7.41 (dd, 1H), 6.45 (t, 1H), 6.36 (d, 2H), 3.74 (s, 6H).

4-(3,5-Dimethoxyphenoxy)phthalonitrile (8.10 g, 28.9 mmol) was dissolved in a mixture of ethylene glycol (142.5 mL) and water (2:1 vol/vol) in a round-bottom flask upon stirring. Potassium hydroxide (11.8 g, 211 mmol) was then added, and the mixture was refluxed at 100°C for 12 h. After cooling to room temperature, the mixture was poured into 300 mL distilled water and the pH of the solution was adjusted to 1 using dilute HCl (1 M). The resulting precipitate was collected by filtration, washed thoroughly with water, and dried under vacuum at 50°C for 12 h to afford 4-(3,5-dimethoxyphenoxy)phthalic acid as a light yellow powder in 95% yield (8.78 g). \( ^1H \) NMR (δ, ppm): 7.76 (d, 1H), 7.15–7.09 (m, 2H), 6.40 (t, 1H), 6.29 (d, 2H), 3.73 (s, 6H).

4-(3,5-Dimethoxyphenoxy)phthalic acid (5.0 g, 15.7 mmol) and dichloromethane (100 mL) were mixed in a round-bottom flask equipped with a dropping funnel. The white suspension was cooled to 0°C and boron tribromide (11.9 mL, 125.6 mmol) was added slowly over a period of 15 min upon constant stirring and the resulting mixture was stirred for 1 h at the same temperature. The mixture was then allowed to warm to room temperature and stirred for 24 h. After cooling with an ice-bath, ice water (150 mL) was added to the reaction mixture, which was stirred at 0°C for 1 h and at room temperature for 2 h. The organic phase was extracted with diethyl ether (100 mL × 3). The combined organic layers were washed with dilute HCl (0.6 M, 100 mL × 2) and dried over magnesium sulfate, and the solvent was removed under reduced pressure. Dichloromethane (300 mL) was added to the resulting yellow oily liquid, and the mixture was stirred for 12 h. The formed precipitate was isolated by filtration, washed with dichloromethane, and dried under vacuum at 50°C to yield 4-(3,5-dihydroxyphenoxy)phthalic acid (3.64 g, 80%). \( ^1H \) NMR (δ, ppm): 9.56 (s, 2H), 7.75 (d, 1H), 7.13 (dd, 1H), 7.08 (d, 1H), 6.08 (t, 1H), 5.91 (d, 2H).

4-(3,5-Dihydroxyphenoxy)phthalic acid (3.0 g, 10.3 mmol), anhydrous potassium carbonate (11.4 g, 82.5 mmol), DMSO (75 mL), and toluene (80 mL) were mixed in a round-bottom flask equipped with a nitrogen inlet, and a Dean–Stark Trap. The mixture was stirred at 100°C for 2 h and at 140°C for 1 h under nitrogen. During the heating process, an azetropic mixture of toluene-water and toluene were removed from the reaction mixture. After cooling to 100°C, toluene (40 mL) was added again to the reaction mixture and the mixture was heated at 140°C for 1 h under nitrogen flow to remove the azetropic mixture and toluene. After cooling to 100°C, 4-fluoronitrobenzene (3.05 g, 21.6 mmol) was added into the mixture and the mixture was stirred at 150°C for 3 h. The reaction mixture was concentrated until the liquid amount was reduced to one third, and then poured in ice water (500 mL). The water mixture was cooled with an ice bath and acidified to pH 1 using aq. HCl (1 M). The resulting yellow–brown precipitate was collected by filtration, washed several times with water, and dried at 60°C for 12 h under vacuum to yield pure 4-(3,5-bis-(4-nitrophenoxoy)phenoxy)phthalic acid (AB₂-NO₂) (5.31 g, 97%). \( ^1H \) NMR (δ, ppm): 8.27 (d, 4H), 7.80 (d, 1H), 7.34–7.27 (m, 6H), 6.92–6.88 (m, 3H).

Pd/C (750 mg) was added to a stirred solution of AB₂-NO₂ (2.5 g, 4.7 mmol) in a 1:1 mixture of methanol (25 mL) and THF (25 mL). The reaction mixture was stirred at room temperature under a hydrogen atmosphere (1.5 MPa). After 24 h, the mixture was filtered by celite to remove the Pd/C residue. The filtrate was concentrated and then poured into water (30 mL). The precipitate was recovered by filtration, washed with water, freeze-dried under vacuum overnight, and then dried under vacuum at 65°C overnight to afford AB₂-NH₂ (2.14 g, 95%). \( ^1H \) NMR (δ, ppm): 7.79 (d, 1H), 7.20 (s, 1H), 7.14 (dd, 1H), 6.81 (d, 4H), 6.60 (d, 4H), 6.18 (s, 3H). \( ^1H \) C NMR (δ, ppm): 168.2, 167.4, 161.3, 158.3, 156.9, 145.0, 144.9, 136.6, 131.9, 126.8, 121.1, 119.1, 117.5, 115.4, 101.1, 100.7.

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2.4 Thermal polymerization, endcapping reaction, and chemical imidization

\( \text{AB}_2\text{-NH}_2 \) (0.9 g, 1.90 mmol) was dissolved in DMAc (5.5 mL) in a dried round-bottom flask equipped with a magnetic stirrer. The mixture was degassed three times with freeze–pump–thaw cycling, and the flask was purged with nitrogen, followed by stirring at 140 °C under nitrogen for 20 h. After cooling to room temperature, the mixture was poured into methanol (60 mL) containing lithium chloride (0.1 wt %) to afford a light-brown precipitate. The formed solid was collected by filtration, washed with methanol, and dried under vacuum at 60 °C for 12 h to afford the corresponding HBPI-AA in 86% yield.

HBPI-AA (0.34 g), acetic anhydride (1.7 mL), and pyridine (1.36 mL) were dissolved in NMP (13 mL). The mixture was heated at 115°C for 24 h. After cooling to room temperature, the reaction mixture was concentrated until the liquid amount was reduced to one-fourth, and then poured into methanol (50 mL) that contained lithium chloride (0.1 wt %). The precipitate was collected by filtration, washed with methanol, and dried in a vacuum oven at 80°C overnight to afford the acetyl-terminated hyperbranched polyimide (HBPI-Ac) as a light-brown powder (93%).

HBPI-AA (0.4 g) was dissolved in NMP (4 mL), and the mixture was stirred at 0 °C for 30 min, followed by the addition of phthalic anhydride (0.637 g, 4.3 mmol). The resulting mixture was stirred in an ice bath for 1 h, warmed up to room temperature, and stirred for 3 h. The mixture was then heated at 100°C for 3 h. After cooling to room temperature, the mixture was added dropwise to methanol (50 mL) containing lithium chloride (0.1 wt %) to yield a light-brown precipitate, which was recovered by filtration, washed with methanol, and dried under vacuum at 50°C for 4 h, yielding the endcapped HBPI-AA in 93% yield.

The endcapped HBPI-AA was chemically imidized similar to HBPI-Ac to form imide-terminated hyperbranched polyimide (HBPI-Im) in 100% yield.

2.5 Film preparation

HBPI-Im was dissolved in DMF (0.2 g/mL) at room temperature. The solution was spin-coated on a flat clean glass plate (1000 rpm, 15 s). The film was dried at 100°C for 1 h, and 150°C for 1 h under atmospheric pressure, and 150°C for 1 h under vacuum. Finally, the resulting film was heated at 280°C for 10 min under air atmosphere.

3 RESULTS AND DISCUSSION

The \( \text{AB}_2\)-type monomer (\( \text{AB}_2\text{-NH}_2 \)) was synthesized from 4-nitrophthalonitrile and 3,5-dimethoxyphenol in five steps (Scheme 1). The structure of each compound was confirmed by \(^1\)H NMR measurement. In this study, \( \text{AB}_2\text{-NO}_2 \), which has already been reported as an intermediate compound,[22, 23] was isolated and catalytically hydrogenated to form \( \text{AB}_2\text{-NH}_2 \). Figure 1 shows the \(^1\)H NMR spectrum and the peak assignment of \( \text{AB}_2\text{-NH}_2 \). The \(^{13}\)C NMR spectrum also confirmed the formation of the target compound.

The thermal polycondensation of \( \text{AB}_2\text{-NH}_2 \) was carried out as shown in Scheme 2. On the basis of our previous reports, the synthesis of the hyperbranched polyimides required the use of an...
The degree of branching (DB) is one of the factors that determine the structure of the hyperbranched polymers and is calculated from the ratio of fully-reacted (dendritic), partially-reacted (linear), and non-reacted (terminal) units of the AB₃ monomer. Figure 3 shows the ¹H NMR spectra of HBPI-Ac, HBPI-Im, and the terminal model compound. The terminal model compound was synthesized from AB₂-NO₂, as shown in Scheme 3. The DB of HBPI-Ac was calculated from the peaks between 6.7 and 6.3 ppm, which were assigned to the protons connected to the aromatic rings bearing three ether bonds. Three peak types were observed for HBPI-Ac in this region, whereas HBPI-Im showed only one peak at 6.6 ppm, which was assigned to the aromatic protons of the dendritic units. The terminal model compound demonstrated peaks attributed to the aromatic protons from 6.43 to 6.32 ppm. Therefore, the central peak at 6.5 ppm in HBPI-Ac was calculated to be 0.48, which was close to the hyperbranched polyimide that was prepared using

### Table 1 Synthesis of HBPI-Ac and HBPI-Im by thermal self-polymerization and chemical imidization.

| Polymer     | Yield (%) | Mₙ⁴ | Mₚ⁴ | ηsol⁵ | DB⁶ |
|-------------|-----------|-----|-----|-------|-----|
| HBPI-Ac     | 92        | 584,700 | 240,000 | 0.26 | 0.48 |
| HBPI-Im     | 91        | 647,300 | 198,600 | 0.25 | -   |

⁴ Determined by GPC measurements with a laser light scattering. The specific refractive increments (dn/dc) were 0.2060 (mL/g) for HBPI-Ac and 0.2057 (mL/g) for HBPI-Im.

⁵ Determined by GPC measurements based on polystyrene standards.

⁶ Measured in NMP at 30°C at a concentration of 0.5 g/dL.

③ Determined by the integration ratio of ¹H NMR measurement.
condensation agents.[22, 23] Because AB$_2$-NH$_2$ contains two carboxy groups at the ortho-position, carboxylic anhydride can be formed by heating, thus facilitating the amide bond formation during thermal self-polycondensation. The $^1$H NMR spectra of AB$_2$-NO$_2$ and its anhydride were measured at 120 °C and are presented in Figure 4. The small peaks at 8.05, 7.65, and 6.85 ppm, assigned to the aromatic protons of the anhydride, appeared in the spectrum of AB$_2$-NO$_2$ after heating for 1 h, implying that the anhydride facilitated the formation of the HBPI-AA during the thermal self-polycondensation at 140°C in DMAc.

The thermal and solubility properties of the synthesized HBPIs are listed in Table 2. The glass transition temperatures were slightly higher than the reported temperature in the literature.[23] Moreover, the thermal degradation was highly dependent on the terminal groups of the HBPIs. HBPI-Im showed a 5% weight loss ($T_{d5}$) at 470°C, which was much higher than that of HBPI-Ac (400°C). Because the main chain of the HBPIs consisted of thermally stable aromatic ether and aromatic imide units, the thermal degradation was initiated at the terminal functional groups. The stable imide terminals in HBPI-Im should have contributed to the higher thermal stability. In addition, HBPIs are soluble in common polar aprotic solvents, such as NMP, DMAc, DMF, and DMSO, at room temperature owing to the hyperbranched architecture. Herein, the maximum concentration of HBPI-Im in DMAc was 21% (w/v).

The satisfying solubility of the HBPIs facilitated also the fabrication of thin films on any substrates by solution casting or spin-coating methods. The thin coating film prepared on a glass plate and its absorption spectra are shown in Figure 5. When the film was heated at 280°C for 10 min, the film became insoluble in amide solvents. This solubility change was probably affected by strong interactions such as donor-acceptor interaction. The absorption was slightly red-shifted because of the chain packing caused by the strong interaction. Thus, because of this solubility change, such films could be applied as solvent-resistant coatings.

**CONCLUSION**

The thermal polycondensation of AB$_2$-NH$_2$ successfully proceeded to form an HBPI-AA and the subsequent chemical imidization resulted in the formation of high molecular weight hyperbranched polyimides (HBPI-Ac and HBPI-Im). The resulting polymers exhibited good solubility and low solution viscosity, which is typical for hyperbranched polymers. The DB of HBPI-Ac was determined to be 0.48. The $^1$H NMR measurement...
of AB₂-NO₂ at 120°C suggested that the formation of carboxyl anhydride units facilitates the amide bond formation towards the generation of the HBPI-AA. HBPI-Im showed a 5% weight loss ($T_{\text{w5}}$) at 470°C, which was much higher than that of HBPI-Ac (400°C). Moreover, the HBPI-Im film coated on a glass plate became insoluble in amide solvents after heating at 280°C for 10 min.

Because HBPIs can be synthesized without using condensation agents, the developed process is a cost-effective method with low risk of contamination that is caused by condensation agents. Because of the good solubility, high thermal stability, and solubility change after heating, HBPIs could be potentially used for coating applications in the microelectronics industry.

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