Syntheses and Properties of Hyperbranched Aromatic Polyimides with Various End-groups

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A hyperbranched poly(amic acid methyl ester) precursor was prepared from self-polycondensation of an AB₂ type monomer (1) in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) as a condensing agent. End-capping reactions of free amine end groups of the precursor with acetyl, n-heptanoyl chloride, 4-methylphthalic anhydride and 3,5-bis(4-nitrophenoxy)diphenyl ether-3',4'-dicarboxylic anhydride (10) were carried out. By chemical imidization of these precursors in the presence of acetic anhydride and pyridine, hyperbranched aromatic polyimides, which were soluble in NMP, DMF, DMSO and THF, were successfully prepared. By gel permeation chromatography (GPC) measurement, weight-average molecular weights (Mₐ) of hyperbranched aromatic polyimides were found to be 50000-98000. From IR and ¹H-NMR analyses, it was found that both end-capping and subsequent chemical imidization reactions proceeded quantitatively. The degree of branching (DB) of hyperbranched aromatic polyimides was 0.49 for 4, and 1.0 for 9. By thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements of the hyperbranched aromatic polyimides, 5 wt% thermal loss temperatures (T₅) were observed to be above 370 °C, and Tₕ values were 189, 138, 186 and 174 °C for polyimides 4, 5, 7 and 9, respectively. The densities of the transparent films of the hyperbranched polyimides having acetoamide end-groups were found to be less than 1.35, which were lower than those of their linear analogues. The film, prepared from the hyperbranched polyimide with 4-methylphthalimide end-groups (7), had lower dielectric constant, birefringence, and shorter cut-off wavelength than the film of poly(4,4'-oxydiphenylene pyromellitimide).

Keywords: hyperbranched aromatic polyimide, precursor, various end-groups

1. Introduction

Aromatic polyimides are well known as important high performance polymers. Numerous researches on the syntheses and applications of aromatic polyimides have been reported over the last few decades owing to their outstanding properties with high thermal stability. Most commercialized aromatic polyimides are produced through a two-step method. The method is composed of the preparation of poly(amic acid)s as soluble precursors and the subsequent cyclization to form insoluble polyimides. Poly(amic acid)s in solution are usually unstable in storage for long period because hydrolytic cleavage reaction readily takes place. To improve the stability, poly(amic acid ester) derivatives have been studied. Poly(amic acid ester)s can afford solutions with higher concentration compared with parent poly(amic acid)s because of lower solution viscosity. The lower viscosity often gives advantage to make thicker polyimide films.

Recently, dendritic macromolecules have attracted considerable attention due to new physical and chemical properties caused by their unique structures. These dendritic macromolecules which possess many functional end-groups and branching points are mainly classified into dendrimers and hyperbranched polymers.¹⁵ Although dendrimers are monodispersive with well-defined and perfectly branched structures, their preparations require stepwise reactions involving protection and deprotection with further purification. On the other hand, hyperbranched polymers are polydispersed macromolecules with irregular and randomly branched structures, which can be
produced on a large scale by the one-step polymerization of AB, monomers. As compared to their linear analogues, hyperbranched polymers possess good solubility in organic solvents and lower viscosity. In addition, introduction of various functional groups into hyperbranched structures can be easily achieved by chemical modification of end-groups. Hyperbranched polymers have been produced mainly by condensation reactions. In the case of hyperbranched polymers with heterocyclic structures, the syntheses of hyperbranched poly(phenylquinoxaline)s, poly(ether-imide)s, and polycarbazoles were already reported to date. These heterocyclic hyperbranched polymers, prepared by one-step method from AB, type monomers containing heterocyclic structures, had high thermal stability and good solubility. More recently, we reported the first successful two-step preparation of hyperbranched polyimides, in which the imide heterocyclic ring was formed from hyperbranched poly(amic acid methyl ester) precursor. The precursor was prepared by direct self-polycondensation of an AB, type monomer in the presence of (2,3-dihydro-2-thioxo-3-benzoazolyl)phosphonic acid diphenyl ester (DBOP) as a condensing agent. Even if the hyperbranched polyimides exhibit limited solubility in organic solvents, the processability might be improved by utilizing the precursors without chemical modification of end-groups. In addition, for future blend materials which comprise of linear and hyperbranched polyimides, the two-step preparation via precursors would result in better compatibility than the one-step one.

In this paper, we review the syntheses and properties of hyperbranched aromatic polyimides with various end-groups.

2. Results and Discussion

2.1. Polymer syntheses

An AB, type monomer 1 was prepared according to the previous report. From the 1H-NMR spectrum of 1, the ratio of the two isomers for para-, meta-methyl ester substitution was 1 : 3.8.

As reported previously, the direct self-
polycondensation of 1 was carried out in the presence of DBOP\textsuperscript{11} as a condensing agent (step a in Scheme 1). End-capped precursors 2, 3, 6, and 8 were prepared by subsequent chemical modification of free amine end-groups with acetyl, \(n\)-heptanoyl chloride, 4-methylphthalic anhydride, and 3,5-bis(4-nitrophenoxy)diphenyl ether-3',4'-dicarboxylic anhydride (10). As shown in Table 1, resulting precursors had high \(M_n\) values with moderate inherent viscosity (\(\eta_{inh}\)) values, which was characteristic of conventional hyperbranched polymers. In the \(^1H\)-NMR spectrum of 8 (spectrum B in Figure 1), two peaks for amide protons were clearly detected at 10.08 and 10.04 ppm, which were assigned to an amide proton arisen from self-polycondensation and that from end-capping reaction, respectively. The integration ratio of peaks H\(_3\) (triphenoxy-substituted aromatic protons in main chain) to H\(_4\) (those in end-groups) to H\(_5\) (aromatic protons located in both ortho positions to the nitro groups) were calculated to be 3:3:4. This ratio was in good agreement with the ratio estimated from the quantitative end-capped product. From IR analyses, both the formation of amide linkages (1665 cm\(^{-1}\)) and the presence of nitro groups (1345 cm\(^{-1}\)) were confirmed. Resulting polymers 4, 5, 7, and 9 possessed \(M_n\) of 50000 (\(M_n/M_w\) of 1.6) with \(\eta_{inh}\) of 0.18 dL/g, 75000 (2.6) with 0.19 dL/g, 91000 (2.6) with 0.13 dL/g, and 98000 (2.6) with 0.13 dL/g (Table 1). As compared with \(^1H\)-NMR spectrum of 8, the disappearance of amide and methyl ester protons was observed in the spectrum of 9 (spectrum C in Figure 1). In the IR spectrum of 9, two characteristic imide peaks appeared at 1723 and 1781 cm\(^{-1}\), while the characteristic amide peak at 1665 cm\(^{-1}\) had disappeared. The spectroscopic data indicated that polymer 9 had the fully imidized structure. It was also confirmed that other polymers 4, 5, and 7 had been fully imidized.\textsuperscript{10}

The degree of branching (DB) of hyperbranched polymer, which has been widely used to assess hyperbranched polymer structure, was defined as the ratio of the sum of dendritic and terminal units over the sum of units (linear, dendritic, and terminal units).\textsuperscript{12} As shown in the previous report,\textsuperscript{10} DB of the hyperbranched aromatic polyimide 4 was 0.47, which agreed well with the value (0.50) estimated from statistical consideration. On the other hand, DB of polyimide 9, with branching end-groups, could be determined by \(^1H\)-NMR analysis using model compound \textsuperscript{11}\textsuperscript{13}. \(^1H\)-NMR spectrum of 9 (spectrum C in Figure 1) showed two kinds of peaks for triphenoxy-substituted aromatic protons, H\(_6\) (6.56 ppm) and H\(_7\) (6.78 ppm), with the integration ratio of 1 to 1. In spectrum A of 11, peaks H\(_1\) at 6.62 ppm and H\(_2\) at 6.83 ppm can be models for dendritic and terminal units. By comparison between spectra A and C, peaks H\(_6\) and H\(_7\) can be assigned to the dendritic and terminal units in 9, respectively. In addition, any peaks assigned to the linear unit were not observed in the spectrum of 9. Therefore, DB value of 9 was determined to be 1.0. During the end-capping reaction, one linear unit should be transformed to one dendritic plus one terminal unit, and one terminal unit to one dendritic plus two terminal units. Since quantitative conversions of both end-capping and imidization reactions had out by thermal and chemical methods. In all cases, thermal imidization of precursors gave insoluble products.\textsuperscript{10} On the other hand, chemical imidization of precursors in the presence of acetic anhydride and pyridine (step c in Scheme 1) afforded powdery products in almost quantitative yields, which were soluble in NMP, DMF, and DMSO. Imidization reactions of precursors were carried

![Fig. 1. \(^1H\)-NMR spectra of (A) model compound 11, (B) polymers 8 and (C) 9 in DMSO-\(d_6\) at 100 °C.](image-url)
been achieved, polyimide 9 must be composed of only dendritic and terminal units with the ratio of 1 to 1, theoretically. This consideration also supported the formation of the hyperbranched aromatic polyimide with DB of 1.0. However, it must be noted that this polyimide 9, prepared from self-polycondensation of 1, did not have a regular architecture similar to that of dendrimers.

Relationship between $M_w$ and intrinsic viscosity $[\eta]$ for polymer 4 was investigated. A shape factor, $\alpha$, which was defined by Mark-Houwink equation ($[\eta] = KM^{\alpha}$) was calculated to be 0.30 from the slope drawn by the least-squares method. The fact that the $\alpha$ value was obviously lower than 0.5 indicated that polymer 4 had highly branching structures.

2.2 Polymer properties

Thermal properties and solubility of the resulting polymers are summarized in Table 1. In thermogravimetric (TG) curves of all precursors, thermal imidizations were completed below 250 °C. In the curve of 8, the weight loss attributed to the removal of nitro groups was detected at above 250 °C. 5 wt% thermal loss temperatures ($T_5$) were observed at 425, 405, 455 and 370 °C for polyimides 4, 5, 7 and 9, respectively. DSC thermograms on second heating showed glass transition temperatures ($T_g$) for 4, 5, 7 and 9 at 189, 138, 186 and 174 °C, respectively. Polymer 5 with n-hexyl group had a much lower $T_g$ value than others. As for 9, it was assumed that introduction of more ether linkages into end-groups afforded the lower $T_g$ than those of 4 and 5. In most cases, resulting polymers exhibited good solubility in NMP, DMF, and DMSO. Precursors 3 and 8, polyimides 5, 7 and 9 were soluble even in THF. Polyimide 4 was soluble at a concentration of 400 mg/mL in NMP at 100 °C.

Transparent yellow films could be obtained by casting from NMP or DMF solutions of hyperbranched polymers onto glass plates, followed by heating. Films prepared from precursor 2 (1.329 g/cm³) and polyimide 4 (1.332 g/cm³) with acetoamide end-groups had close density values. In addition, it was found that hyperbranched polymer films had noticeably lower density values than those of their linear analogues. This result suggests that hyperbranched polymers inherently have structures with much loose packing than linear ones.

The film of 7 with 4-methylphthalimide end-groups had a dielectric constant of 2.94, which was lower than that of the poly(4,4'-oxydiphenylene pyromellitimide) (ODA-PMDA) film (3.33). Although there were not so much differences in the refractive index between 7 (1.661) and the ODA-PMDA polyimide (1.691), birefringence of 7 (0.006) was observed to be noticeably lower in comparison with that of the ODA-PMDA polyimide (0.053). The result implies that polymer 7 has more isotropic structures than the ODA-PMDA polyimide. It is well known that for

| Table 1. Preparation and Properties of Precursors and Polyimides |
|------------------|------------------|------------------|------------------|------------------|
| Polymer | Yield (%)a | $M_w$ ($M_M/M_M$)b | $\eta_{inh}$ (dL/g)c | $T_g^\ast / T_g^\ast$ (°C) | Solubilityd |
| 2 | 82 | 112000 (2.5)$c$ | 0.27 | - | ++ / ++ / - |
| 3 | 97 | 100000 (3.0) | 0.21 | - | ++ / ++ / ++ |
| 4 | 78 | 50000 (1.6)$c$ | 0.21 | 425/189 | ++ / ++ / - |
| 5 | 79 | 75000 (2.6) | 0.19 | 405/138 | ++ / ++ / ++ |
| 6 | 83 | - | 0.18 | - | ++ / ++ / - |
| 7 | 89 | 91000 (2.6) | 0.13 | 455/186 | ++ / + / ++ |
| 8 | 98 | - | 0.13 | - | ++ / ++ / ++ |
| 9 | 93 | 98000 (2.6) | 0.13 | 370/174 | ++ / ++ / ++ |

a After reprecipitation in methanol containing 0.1 wt% lithium chloride. b Determined by GPC measurements in DMF containing lithium bromide (0.01 mol/L) as an eluent using PS standards. c With a laser light scattering detector, the specific refractive increments (dn/dc) at 630 nm were 0.152 mL/g for 2, and 0.168 mL/g for 4. d Measured at a concentration of 0.5 g/dL in NMP at 30 °C. e $T_g$ (5 wt% loss temperature) was determined by TG at a heating rate of 10 °C/min in nitrogen. f Determined by DSC at a heating rate of 10 °C/min in nitrogen on second heating. g (++) ; soluble at room temperature, (+) ; soluble on heating, (-) ; insoluble.
chains aggregate and form highly oriented structures during thermal treatment. We assume that less aggregation and orientation of polymer chains take place in the film of 7. From UV-vis spectra of both polyimide films, it was observed that polymer 7 had a shorter cut-off wavelength than the ODA-PMDA polyimide. The looser packing between imide rings might result in a less charge transfer effect.

3. Conclusion

Hyperbranched aromatic polyimides having various end-groups were successfully prepared via poly(amic acid methyl ester) precursors. The resulting hyperbranched polyimides had high molecular weight. DB value of hyperbranched polyimide with acetoamide end-groups was 0.49, which was close to the value estimated statistically. On the other hand, polyimide with the value of 1.0 was successfully prepared by using the branched end-capping reagent. To change end-group structures could control thermal properties and solubility of polymers. Films prepared from hyperbranched polymers with acetoamide end-groups had lower densities than their linear analogues. The hyperbranched polyimide film with 4-methylphthalimide end-groups possessed lower dielectric constant, birefringence, and shorter cut-off wavelength than the film of poly(4,4'-oxydiphenylene pyromellitimide). These results imply looser packing structures of hyperbranched polymers.

4. Experimental Section

4.1 Chemicals

N-Methyl-2-pyrolidinone (NMP), N,N-dimethylformamide (DMF), and pyridine were distilled from calcium hydride under reduced pressure. Acetic anhydride and acetyl chloride were used after distillation in the presence of magnesium and phosphorus pentachloride, respectively. Other solvents and reagents were used as-received.

4.2 Measurements

$^1$H and $^{13}$C NMR spectra were recorded on a Jeol JNM-AL 300 (300 MHz) spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermal analysis were performed with a Seiko DSC 6200 and TG/DTA 6200, respectively. Gel permeation chromatography (GPC) was performed with a JASCO HPLC 880 PU fitted with polystyrene-divinylbenzene columns (two Shodex KD 806 M and 802) and a Shodex RI-71 refractive index detector in DMF containing 0.01 mol/L of lithium bromide as an eluent. The absolute molecular weights were determined by laser light scattering measurements using a mini DAWN apparatus (Wyatt Technology Co.) and a Shimadzu RID-6A refractive index detector. Specific refractive increments ($dn/dc$) of polymers were measured in DMF at 690 nm by using Optilab 903 apparatus (Wyatt Technology Co.). Density of the cast films was measured by the sink-float method in the mixture of tetrachloromethane and toluene at 30 °C. Dielectric constant was measured with ITO-Al-Polyimide-Al device at 23 °C under 100 kHz. Optical measurements were done with prism coupling method using He-Ne laser.

4.3 Monomer Preparation

4.3.1 Preparation of 3,5-bis(4-amino-phenoxy)diphenyl ether-3',4'-dicarboxylic acid monomethyl ester (AB$_2$ monomer, 1) An isomeric mixture of 3,5-bis(4-aminophenoxy)diphenyl ether-3',4'-dicarboxylic acid monomethyl ester 1 was obtained as a brown powdery product; 39% total yield starting from 3,5-dimethoxyphenol; IR (KBr) 1721 cm$^{-1}$ (carboxyl, ester group); $^1$H-NMR (DMSO-d$_6$) δ 7.79-7.82 (d, 0.79H, Ar-H), 7.67-7.69 (d, 0.21H, Ar-H), 7.26-7.37 (m, 6H, Ar-H), 7.11-7.20 (m, 2H, Ar-H), 6.75-6.80 (m, 4H, Ar-H), 6.54-6.58 (m, 4H, Ar-H), 6.13-6.19 (m, 3H, Ar-H), 3.77 (br, 3H, methyl ester) ppm; Elemental Analysis (Calcd for C$_{27}$H$_{22}$N$_2$O$_7$ C: 66.66, H: 4.56, N: 5.76) Found C: 66.12, H: 4.56, N: 5.61.

4.4 Polymer Preparation

4.4.1 Preparation of 1 and subsequent end-capping reaction A typical experiment (preparation of polymer 2) is shown as follows. To a 50-ml three-necked flask fitted with gas inlet and outlet tubes, 0.603 g (1.24 mmol) of 1, 0.568 g (1.48 mmol) of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP), 0.17 ml (1.24 mmol) of triethylamine and 2.25 ml of NMP were added through nitrogen. After stirring the polymerization mixture for 3 h, the NMP (6 ml) solution of 2.80 ml (39.4 mmol, 32 equiv.) of acetyl chloride was added dropwise to the mixture in ice-water bath. After addition, the reaction
mixture was maintained for 0.5 h in ice-water bath and for 3 h at room temperature, and diluted with 20 ml of NMP. The resulting solution was poured into 2000 ml of 0.1 wt%-LiCl/CH3OH to precipitate. The resulting precipitated polymer was collected by filtration, and dissolved in DMF. After reprecipitation, the product (polymer 2) was filtered, and dried at room temperature under vacuum, giving 0.519 g ; 82 % yield ; weight-average molecular weight : \( M_w = 112000 \), polydispersity index : \( M_w / M_n = 2.5 \); inherent viscosity : \( \eta_{inh} = 0.27 \) dL/g ; \(^1\)H-NMR (DMSO-\(d_6\), 100 °C) \( \delta \) 10.10 (s, 1H, amide-H), 9.60 (s, 1H, amide-H), 7.00-7.67 (m, 11H, Ar-H), 6.35-6.41 (m, 3H, Ar-H), 3.75 (br, 3H, methyl ester), 2.00 (s, 3H, acetyl) ppm ; IR (KBr) 1671 (amide), 1727 cm\(^{-1}\) (ester group).

4.4.2 Chemical imidization A typical experiment (preparation of polymer 4) is shown as follows. To a 50-ml three-necked flask through nitrogen, 0.300 g of 2, 0.72 ml of acetic anhydride, 0.48 ml of pyridine and 6 ml of DMSO were added. The reaction mixture was stirred for 24 h at 100 °C, and diluted with 20 ml of DMSO. The resulting solution was poured into 1800 ml of 0.1 wt%-LiCl/CH3OH to precipitate. The resulting precipitated polymer was collected by filtration, and dissolved in DMF. After reprecipitation, the product (polymer 4) was filtered, washed with hot 0.1 wt%-LiCl/CH3OH, and dried overnight at 120 °C under vacuum, giving 0.221 g ; 78 % yield ; \( M_w = 50000 \), \( M_w / M_n = 1.6 \); \( \eta_{inh} = 0.21 \) dL/g ; 5 wt% loss temperature : \( T_g = 425 °C \); glass transition temperature : \( T_g = 189 °C \); \(^1\)H-NMR (DMSO-\(d_6\), 100 °C) \( \delta \) 9.60 (s, 1H, amide-H), 7.00-7.88 (m, 11H, Ar-H), 6.40-6.60 (m, 3H, Ar-H), 2.00 (s, 3H, acetyl) ppm ; IR (KBr) 1670 (amide), 1720, 1780 cm\(^{-1}\) (imide group).

4.5 Preparation of Model Compound 11

11 was obtained as a brown powdery product ; Yield 90 % ; \(^1\)H-NMR (DMSO-\(d_6\), 100 °C) \( \delta \) 8.20-8.26 (d, 8H, Ar-H), 7.91-7.94 (d+d, 3H, Ar-H), 7.51-7.56 (m, 6H, Ar-H), 7.44-7.47 (d, 4H, Ar-H), 7.24-7.33 (m, 14H, Ar-H), 7.01-7.04 (d, 2H, Ar-H), 6.83 (s, 6H, Ar-H), 6.62 (s, 3H, Ar-H), 3.81 (s, 3H, methoxy) ppm ; IR (KBr) 1345 (nitro), 1721, 1779 cm\(^{-1}\) (imide group); Elemental Analysis (Caled for \(C_{36}H_{30}N_2O_4\) C : 65.77, H : 3.18, N : 6.32) Found C : 65.77, H : 3.43, N : 6.35.

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References

13. Experimental detail on the preparation of model compound 11 is described in an article entitled “Preparation of Hyperbranched Aromatic Polymide without Linear Units by End-capping Reaction” by K. Yamanaka, M. Jikei, and M. Kakimoto, Macromolecules in press.