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ABSTRACT: A hyperbranched aromatic poly(amide–imide) was prepared by the copolymerization of 4-(3,5-dicarboxyphenoxy)phthalic anhydride, a B′B2 type monomer, and 1,4-phenylenediamine, an A2 type monomer. The rapid reaction between the anhydride and amino group led to the formation of the dominant imide intermediate which can be regarded as a new AB′2 type of monomer. The intermediate, without isolation, was subjected to further polymerization in the presence of TPP/pyridine, as condensing agents, to give the hyperbranched poly(amide–imide), containing carboxylic acid chain ends. In comparison, the AB2 monomer was prepared separately, and the conventional self-polymerization of this monomer was also studied. The structures of the obtained polymers were characterized by FTIR and 1H NMR spectroscopy. The spectral data showed that these two polymers, prepared from two different synthetic approaches, have nearly identical structures. The degree of branching of the hyperbranched poly(amide–imide) was estimated to be 60–61%. The terminal carboxylic acid groups were modified by reaction with a variety of aromatic amines to give the corresponding amide derivatives. The nature of the chain ends was shown to have a significant effect on the solubility and Tg of the hyperbranched poly(amide–imide).

Introduction

Hyperbranched macromolecules have received considerable attention since their unique, highly branched structure is expected to exhibit some unusual physical and chemical properties.1–4 These polymers can be conveniently synthesized in a single step via a one-pot polymerization,5 yet they maintain many of the architectural features and properties found in their well-defined dendrimer counterparts,6–9 which are built up by tedious stepwise synthetic sequences.9–12 The one-step synthesis allows hyperbranched polymers to be more readily available and prepared on a large scale for potential applications. These attractive features have led to the development of novel synthetic routes for the preparation of such polymers. Most hyperbranched polymers that have been developed were synthesized by the one-step self-polycondensation of ABn type monomers. Only a few studies have concerned the preparation of hyperbranched polymers through the copolymerization method, even if that route has more flexibility in generating diverse, hyperbranched materials. Fréchet et al. have reported the synthesis of hyperbranched aliphatic polyethers by the copolymerization of A2 and B3 type monomers.13 Using this A2 + B3 strategy, hyperbranched aromatic polyamides and polyimides have been prepared by Kakimoto’s and Okamoto’s groups.14–16 Recently, Yan et al. have reported a new A2 + BB′2 approach for the synthesis of hyperbranched copoly(sulfone–amines).17

Linear polyamides and polyimides are well-known as high-performance polymeric materials.18,19 Their hyperbranched analogues have been prepared by the self-polymerization of AB2 type monomers20–25 or more recently by copolymerization methods.14–16 Aromatic poly(amide–imide) is a class of high-performance polymers which may combine the advantages of polyamides and polyimides; the resulting polymers should possess high thermal stabilities, coupled with good mechanical and chemical properties.26,27 To the best of our knowledge, there has been no report regarding the preparation of hyperbranched aromatic poly(amide–imide). In this paper, we report the synthesis of a new hyperbranched poly(amide–imide) by copolymerization of an unsymmetrical B′B2 type monomer with an A2 type monomer. In the B′B2 monomer, there are one anhydride and two carboxylic groups, while in the A2 monomer, there are two amino functionalities. The anhydride (B′) is much more reactive than the carboxylic group (B) toward the amino group in the A2 monomer. At the initial stage of the polycondensation, the rapid reaction between B′ and A groups results in the formation of the dominant imide intermediate. The intermediate can be regarded as a new AB′2 type of monomer, which contains one aminophenyl and two carboxyl functionalities. Without isolation, the AB2 intermediate was subjected to further polymerization in the presence of TPP/pyridine, as condensing agents, to give the hyperbranched poly(amide–imide).28,29 For comparison, the AB2 intermediate was prepared separately and characterized; the conventional one-step self-polymerization of this AB2 monomer was also studied.

Experimental Section

General Directions. N-Methyl-2-pyrrolidinone (NMP) and N,N-dimethylformamide (DMF) were distilled over CaH2 under reduced pressure. Pyridine was dried by distillation after being refluxed with KOH. 1,4-Phenylenediamine was recrystallized from MeOH. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. (2,3-Dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) was used as received. All other reagents and solvents were used as received from commercial sources unless otherwise stated. 1H and 13C NMR spectra were recorded on a Varian Unity 300 MHz or a Bruker-DRX 300 MHz spectrometer. IR spectra were obtained on a Nicolet 360 FT-IR spectrometer. Mass spectra were obtained on a JEOL J MS-SX 102A mass spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit, interfaced with a Waters 410 differential refractometer. Three 5 μm Waters styragel columns (300 × 7.8 mm), connected in series of decreasing order of pore size (103, 104, and 105 Å), were used with DMF as the eluent. Standard samples of PMMA were
used for calibration. Differential scanning calorimetry (DSC) was performed using a Du Pont TA 2000 instrument, with a heating/cooling rate of 20 °C min⁻¹. Samples were scanned from 30 to 400 °C and then cooled to 30 °C and scanned a second time from 30 to 400 °C. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analyses (TGA) were made on a Du Pont TGA 2950 instrument. The thermal stability of the samples was determined by measuring weight loss while heating at a rate of 20 °C min⁻¹.

**Dimethyl 5-(3,4-Dicyanophenoxoy)sophthalate (1).** A mixture of dimethyl 5-hydroxysophthalate (5.00 g, 26.9 mmol), 4-nitrophthalonitrile (4.65 g, 26.9 mmol), K₂CO₃ (5.00 g, 36.2 mmol), and DMF (20 mL) was heated at 130 °C for 4 h. After this period, the reaction mixture was cooled and poured into 200 mL of water. The precipitated crude product was collected by filtration, washed with ethyl acetate and dried to afford 1 (8.20 g, 91.4%).

**Differential Scanning Calorimetry (DSC).**

**Thermogravimetric analysis (TGA).**

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**Synthesis of Model Compound 6.** A solution of compound 3 (1.00 g, 3.05 mmol) and aniline (284 mg, 3.05 mmol) in NMP (60 mL) was heated at 150 °C under nitrogen for 12 h. The solution was then added dropwise to water (200 mL). The precipitated product was collected by filtration and purified by recrystallization from acetic acid to afford 6 (1.01 g, 82.2%).

**3D NMR (DMF-d6):**

**Thermogravimetric analysis (TGA).**

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**Synthesis of Model Compounds 7 and 8.** A solution of 5 (531 mg, 2.24 mmol), 6 (600 mg, 1.49 mmol), DBOP (570 mg, 1.49 mmol), and 3 drops of triethylamine in NMP (6.0 mL) was stirred at 25 °C under nitrogen for 12 h. The resulting solution was added dropwise to a mixture of methanol (50 mL) and water (50 mL). The precipitated product was collected by filtration and purified by column chromatography, eluting with CH₂Cl₂/CH₃OH (1:1) and recrystallization from acetic acid afforded 7 (0.31 g, 33%).

**Preparation of Polymer PAI-1.** (A) Direct polymerization of monomer 3 with 1,4-phenylenediamine: The monomer 3 (200 mg, 1.01 mmol) was added to one portion of a solution of 1,4-phenylenediamine (65.9 mg, 1.60 mmol) in NMP (2.0 mL) under nitrogen at 25 °C. Stirring was continued at 25 °C for 2 h and at 150 °C for 12 h. The solution was cooled, added pyridine (0.50 mL) and TBP (0.32 mL), 1,2 mmol), and then heated at 120 °C for 12 h. After cooling, the resulting polymer was precipitated into methanol. The polymer was washed with hot water, purified by precipitation from DMF into methanol twice, and dried under vacuum to give PAI-1 (202 mg, 83.2%). (B) A solution of compound 4 (800 mg, 1.61 mmol), TBP (1.0 mL, 3.2 mmol), and LiCl (160 mg, 3.77 mmol) in NMP/pyridine (10.0 mL, 4.1 v/v) was heated at 120 °C under nitrogen for 12 h. After cooling, the resulting polymer was precipitated into methanol. The polymer was collected, washed with hot water, purified by precipitation from DMF into methanol twice, and dried under vacuum to give PAI-2 (372 mg, 95.6%).

**Preparation of Polymer PAI-2.** A solution of 3 (100 mg, 250 μmol), aniline (85 mg, 0.91 mmol), DBOP (383 mg, 1.00 mmol), and 3 drops of triethylamine in NMP (2.0 mL) was stirred at 25 °C under nitrogen for 12 h. The resulting solution was added dropwise to methanol (100 mL) with agitation. The polymer was collected by filtration, washed with warm water, and purified by precipitation from DMF into methanol twice to give PAI-2 (114 mg, 96.0%).

**Preparation of Polymer PAI-3.** PAI-3 was prepared from PAI-1 (100 mg, 250 μmol) and 4-n-decanylaniline (233 mg, 1.00 mmol) following the same procedure as described for the preparation of PAI-2. Yield: 138 mg, 89.8%. 

**3D NMR (DMF-d6):**

**Synthesis of Model Compound 6.** A solution of compound 3 (1.00 g, 3.05 mmol) and aniline (284 mg, 3.05 mmol) in NMP (60 mL) was heated at 150 °C under nitrogen for 12 h. The solution was then added dropwise to water (200 mL). The precipitated product was collected by filtration and purified by recrystallization from acetic acid to afford 6 (1.01 g, 82.2%).

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Preparation of Polymer PAI-4. PAI-4 was prepared from PAI-1 (100 mg, 250 μmol) and compound 5 (238 mg, 1.00 mmol) following the same procedure as described for the preparation of PAI-2. Yield: 146 mg, 94.2%. 1H NMR (DMSO-d$_6$): δ 7.30–7.68 (m, 6H), 7.80–8.08 (m, 11H), 8.54 (br, 1H), 10.69 (br, 2H). IR (KBr): 1772, 1716 (C=O, amide), 1665 cm$^{-1}$ (C=O, imide).

Results and Discussion

Monomer Synthesis. Two kinds of monomers, 3 and 4, were prepared as shown in Scheme 1. Nucleophilic substitution of the nitro function of 4-nitrophthalonitrile with the phenoxide of dimethyl 5-hydroxyisophthalate in a K$_2$CO$_3$/DMF medium yielded dimethyl 5-(3,4-dicyanophenoxy)isophthalate (1). Alkaline hydrolysis of compound 1 in KOH(aq)/ethanol gave 4-(3,5-dicarboxyphenoxy)phthalic acid (2), which was subsequently dehydrated with acetic anhydride to form the B′B$_2$ type monomer 3. The condensation of 3 with 1,4-phenylenediamine followed by cyclodehydration afforded the AB$_2$ monomer 4. Monomer 3 has one phthalic anhydride and two carboxylic acid groups, while monomer 4 contains one aminophenyl and two carboxyl functionalities joined with an ether–imide linkage. The structures of the synthesized compounds were verified by 1H NMR and 13C NMR spectroscopy as well as by mass spectroscopy. Figure 1 shows the 1H NMR spectra of monomers 3 and 4, which are consistent with the assigned structures.

Polymer Synthesis. As shown in Scheme 2, the hyperbranched poly(amide–imide) PAI-1 was prepared by the direct polymerization of the B′B$_2$ monomer 3 with the A$_2$ monomer 1,4-phenylenediamine. An equimolar mixture of the monomer 3 and 1,4-phenylenediamine was reacted in NMP to form the amic acid, which was then thermally cyclized to give the AB$_2$-type intermediate in situ, with an imide linkage. It should be noted that the amino group in the AB$_2$ molecule is deactivated in comparison with the original amino groups in the A$_2$ monomer, due to the formation of the imide (amide) group in the para position of the benzene ring system. Therefore, the possibility of reaction of the former with the phthalic anhydride (B′) of a second B′B$_2$ molecule is diminished and can be neglected under the reaction conditions; the formation of the AB$_3$ intermediate is the predominant reaction at the initial stage of the copolymerization. This is supported by the fact that the AB$_2$ intermediate, which is identical to the AB$_2$-type monomer 4, can be isolated with an almost quantitative yield in the first stage of the polymerization. Without isolation, the AB$_2$ type intermediate was polymerized at 120 °C for 12 h in the presence of TPP/pyridine as condensing agents, to yield PAI-3. No gelation occurred during this polymerization. This polymer could also be synthesized by the self-polycondensation of the AB$_2$ type monomer 4. The one-step polymerization of 4 was carried out in NMP at 120 °C for 12 h using TPP/pyridine as condensing agents. The structure of PAI-1 was characterized by FTIR and 1H NMR spectroscopy. It was found that the two different synthetic approaches led to hyperbranched poly(amide–imides) with almost identical structures. In the IR spectra, the polymers exhibit characteristic carbonyl absorptions corresponding to an imide ring at 1772 (C=O asymmetric stretching) and 1716 cm$^{-1}$ (C=O symmetric stretching), in addition to the typical aromatic imide C–N stretching at 1373 cm$^{-1}$. The carbonyl absorptions of the cyclic anhydride unit at 1849 and 1783 cm$^{-1}$ in monomer 3 have disappeared. In addition, the C=O stretching of the amide group appears at 1665 cm$^{-1}$. The carbonyl stretching of the terminal carboxylic acid group at ~1700 cm$^{-1}$ is obscured by the absorption of the imide ring. The broad bands between 2500 and 3500 cm$^{-1}$ are attributed to amide N–H and acid O–H stretches. In the 1H NMR spectrum of PAI-1s, the resonance of the proton of the amide group appears at 10.69 ppm, and a broad peak at 13.51 ppm from the proton of the terminal carboxylic acid group is also observed.

The hyperbranched poly(amide–imide), PAI-1, which has a high number of terminal carboxyl groups, could not be analyzed directly by gel permeation chromatography (GPC) because the polymer adsorbed to the column, resulting in incomplete elution. This problem was overcome by the transformation of the carboxylic acids groups into amide groups. By reacting with excess aniline, PAI-1 was readily converted to the amide-terminated polymer PAI-2 (vide post). GPC analyses showed that the weight-average molecular weights (M$_w$) and polydispersities (M$_w$/M$_n$) were approximately 4.4 ×
Scheme 3

$10^4$ g/mol and 2.7, respectively, for the amide-terminated polymer of **PAI-1** prepared from the direct polymerization of the B'B$_2$ with the A$_2$ monomers. The amide derivative of **PAI-1**, prepared by the self-polycondensation of the AB$_2$ type monomer 4 under the same conditions, has similar $M_w$ and $M_n/M_w$ values: $4.1 \times 10^4$ g/mol and 2.5. These values, however, are only indicative, since the highly branched nature of **PAI-1** deviates strongly from that of linear, coillike poly(methyl methacrylate) standards. The solution viscosity of **PAI-1s** was also evaluated in DMAc at a concentration of 0.5 g/dL at 30 °C. The inherent viscosity ($\eta_{inh}$) was 0.29 and 0.28 g/dL, respectively for the hyperbranched polymers **PAI-1s** prepared by the copolymerization method and by the self-polymerization of monomer 4. The comparison of the solution viscosity reveals that there is no cross-linking taken place in the direct copolymerization. This is consistent with the observation that no gelation occurred during the copolymerization.

Degree of Branching. Hyperbranched polymers, which were formed by a sequence of condensation of AB$_2$ monomers, have an irregular dendritic structure in which three different types of subunits may be present. In this work, the hyperbranched poly(amide–imide) **PAI-1** is composed of three kinds of repeating units: the terminal units, which have two carboxylic acid groups, the linear units, which have one amide group and one carboxylic acid group, and the dendritic units, which have two amide groups and no free carboxylic acid group. The degree of branching (DB), a typical property often used to evaluate the structural irregularity of hyperbranched polymers, was defined as the sum of dendritic and terminal units vs the total number of units.$^{31,32}$ A combination of NMR spectroscopy and comparative studies on a model compound was used to quantify the different subunits present in the hyperbranched polymer and, subsequently, to determine its DB.$^{31}$

The preparation of the model compounds useful for NMR characterization is illustrated in Scheme 3. Model compounds 6, 7, and 8 resemble the terminal unit, the linear unit, and the dendritic unit, respectively. Their $^1$H NMR spectra are depicted in Figure 2. A distinct resonance for the terminal model compound, 6, appears at 8.32 ppm (H$_t$), whereas resonances of the corresponding protons for the linear and dendritic model compounds, 7 (H$_l$), and 8 (H$_d$), are observed at 8.47 and 8.55 ppm, respectively. Figure 2 also shows the $^1$H NMR spectra of the hyperbranched poly(amide–imide)s. In comparing the $^1$H NMR spectra of **PAI-1s** with those of the model compounds, one can clearly assign the resonances at 8.32, 8.47, and 8.55 ppm to the proton of the terminal, linear, and dendritic subunits in the hyperbranched polymer, respectively. On the basis of the integration of these well-resolved resonances, the relative percentages of each subunit in **PAI-1s** can be determined. It was noted that the percentage estimated for the terminal subunit is approximately equal to that for the dendritic subunit. This result is consistent with the theoretical prediction that the number of dendritic units is equal to the number of terminal units for an AB$_2$ type hyperbranched polymer possessing high molecular weight.$^{5}$ With these formulas, the DB of the poly(amide–imide) **PAI-1**, prepared by the direct polymerization of monomer 3 with 1,4-phenylenediamine, is estimated to be 61%. This value is nearly the same as the DB calculated for the **PAI-1** synthesized by the self-polycondensation of the AB$_2$ type monomer 4, which is 60%.

Chemical Modification. As predicted theoretically by Flory,$^{5}$ the direct polymerization of AB$_2$ type monomers is expected to produce a highly branched, irregular structure that contains a large number of end groups. In this study, the end groups in the resulting hyperbranched poly(amide–imide) **PAI-1** are carboxylic acids, which could be readily functionalized to yield hyperbranched polymers with a variety of functional chain ends. As shown in Scheme 4, the modification of the carboxylic end groups of **PAI-1** was carried out with different kinds of aromatic amines, in the presence of DBOP as the condensation agent, to give the corresponding amide derivatives. We chose DBOP as the activator$^{39}$ and ran the condensation reaction at room temperature to prevent transamination, which is a side reaction occurring at high temperatures. In the modi-
fication reaction, the use of excess amino reagents resulted in almost complete (> 95%) functionalization, as confirmed by the $^1$H NMR spectra of the derivative. After end-capping, the broad peak at 13.51 ppm, associated with the proton of the terminal carboxylic acid group, disappeared. For PAI-2-3, an additional resonance due to the proton of the terminal amide group appears in the region of 10.4–10.5 ppm. It is interesting to note that for PAI-4 the signals corresponding to the proton of the terminal (Ht), linear (Hl), and dendritic (Hd) subunits shown in Figure 2 coalesce at 8.54 ppm. This is attributed to the similarity of the chemical environments for the three different subunits in PAI-4. This result is consistent with the observation that, in PAI-4, the chemical shift of the proton of the terminal amide group is the same as that of the interior amide group. Thus, there is only one resonance with an integration of 2 H for the protons of the two different kinds of amides. The integration analyses of $^1$H NMR spectra of the derivatives indicate that the modification reactions proceeded almost quantitatively.

The nature of the end groups influences the physical and chemical properties of hyperbranched polymers. The glass transition temperatures ($T_g$) of poly(amide-imide)s were investigated by differential scanning calorimetry (DSC), and the results are presented in Figure 3 and Table 1. As reported, the transition from the polar function to nonpolar end groups results in a decrease in $T_g$ due to the reduction in the extent of intermolecular interactions in the polymeric molecules. The $T_g$ of PAI-1, which has polar carboxylic terminal groups, is 262 °C, while the $T_g$ value of PAI-2, which has less polar amide terminal groups, is 248 °C. A further decrease in $T_g$ to 223 °C was observed for PAI-3, due to the introduction of long, flexible n-decyl chain ends. PAI-4, which has rigid, imide chain ends, has a $T_g$ of 283 °C. Because of their highly branched structures, these poly(amide-imide)s have enhanced solubility in organic solvents and are highly soluble in polar solvents such as DMAc, NMP, and pyridine (Table 1). However, the different chain ends led to solubility differences in very polar and in relatively nonpolar solvents. PAI-1, 2, and PAI-4 are soluble in DMSO and insoluble in THF, whereas PAI-3, which possesses long n-decyl chain ends, is soluble in hot DMSO as well as in THF.

Summary
We have synthesized a hyperbranched poly(amide-imide) via the A2 + B′2 approach. The copolymerization of 4-(3,5-dicarboxyphenoxy)phthalhydride (3), a B′2 type monomer, and 1,4-phenylenediamine, an A2 type monomer, resulted in a hyperbranched poly(amide-imide) containing terminal carboxylic acid groups. No gelation occurred during the polymerization. For comparison, we also carried out the synthesis of this hyperbranched polymer via the conventional self-polymerization of N-(4-aminophenyl)-4-(3,5-dicarboxyphenoxy)phthalimide (4), an AB2 monomer. Both approaches led to hyperbranched poly(amide-imide)s with almost identical structures. The degree of branching of the polymers was approximately 60%, as determined by a combination of model compound studies and $^1$H NMR integration data. End-capping of the terminal carboxylic acid groups was accomplished by reacting with different kinds of aromatic amines. Thermal and solubility properties of the resulting polymers depend on the nature of the chain-end groups.

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References and Notes

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