

Synthesis and Characterization of Dendronized Aromatic Polyamides with Bromomethyl Groups in the Periphery

Yanru Miao, Guoliang Wu, Li Zhou, Wei Xu, Xinnian Xia, Weijian Xu

Institute of Polymer Science and Engineering, State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

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ABSTRACT: This paper focused on the synthesis of novel functionalized dendronized aromatic polyamides, which contained a polyamide backbone and polyamide dendrons decorated with bromomethyl groups, by the macromonomer route. The new activating procedure of the synthesis of dendrons and macromonomers using thionyl chloride as an activating agent eliminated the protection/deprotection procedure and reduced side reactions. The structures of the dendrons, macromonomers, and polyamides were

confirmed by FTIR, ^1H NMR, ^{13}C NMR, and elemental analysis. The properties of the resulting dendronized polyamides, which were compared with that of the linear polyamide (LP), were studied using GPC, XRD, TGA, DSC, inherent viscosity measurement, and solubility experiment. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 397–405, 2008

Key words: bromomethyl; thionyl chloride; synthesis; polyamides; macromonomers

INTRODUCTION

Dendronized polymers, consisting of polymers with pendant dendron side chains, are attributed to comb polymers.^{1,2} With increasing generation of the dendrons, the structure of these polymers would change from random coil conformation into cylindrical conformation, which is due to the steric repulsion between the dendrons of dendronized polymers.^{1,3} This new class of polymers was first described by Tomalia in 1987.⁴ Because of insufficient analytical techniques and much attention on spherical dendrimers, these polymers became interesting a few years later.³ They have been used as catalysts,⁵ poly-initiators,⁶ light harvesting,⁷ conducting materials,⁸ and nanoscopic building blocks⁹ because of their nanoscale size, rigidity, and functionality. Three main synthetic routes to them are the graft-to, the graft-from, and the macromonomer route. The macromonomer route has been used most frequently among three routes, because the resulting polymers with a perfect coverage of the side chains could be obtained by this route.

Although the dendronized polymers have developed remarkably, there are many aspects to be improved such as chain length control and surface decoration. A few attempts have already been undertaken for both, but it may take a few more years to solve these, specifically concerning length

control.¹⁰ Fortunately, the reports on the synthesis of functionalized dendronized polymers have been ever increasing, but the essential three steps need be carried out involving: (1) synthesis of monomers with protected functional groups in the periphery, (2) polymerization of the monomers, and complete deprotection and (3) derivatization of the deprotected polymer with the desired groups.^{9,11–13} However, the protection and deprotection procedure has two disadvantages: (1) the condition of the protection and deprotection procedure was critical because the protection was required for compatibility with the polymerization conditions and the resulting deprotected polymer needed to be soluble, and (2) the procedure of the protection and deprotection was complex.

In recent years, a number of dendritic polyamides have been synthesized with easy methods.^{14–18} However, only a few of the dendronized polyamides were reported. Dendronized polymers with a polyamide backbone have been synthesized by Schlüter,^{19–22} dendronized polymers with polyamide dendrons have been reported by Li et al.,^{23,24} and only one dendronized polymer with both a polyamide backbone and polyamide dendrons has been synthesized by Liu et al.²⁵ by far.

Thionyl chloride is well known as an activating agent for the preparation of amides as well as acid chlorides from carboxylic acids.²⁶ The authors have previously reported that thionyl chloride is effective for the synthesis of polyamide.²⁷ The activating procedure with thionyl chloride for the synthesis of polyamide dendrimers was reported successfully,²⁸

Correspondence to: W. Xu (weijxu_59@sohu.com).

but the purification of thionyl chloride was too tedious and the molar ratio of thionyl chloride to the carboxyl group of different dendrons was difficult to confirm. To avoid these problems, our group adopted an optimized method with thionyl chloride.²⁵ Although the method had more advantages than those methods reported in the previous literature, the excessive thionyl chloride in *N*-methyl-2-pyrrolidone (NMP) was difficult to be removed absolutely and acid chlorides reacted with NMP at 90°C because acid chlorides reacted with NMP above room temperature. To avoid all these problems, in this article, the best procedure with thionyl chloride as an activating agent was introduced. On the other hand, in this article, SOCl₂ had no influence on the bromomethyl groups and the reaction could be conducted below room temperature, so that the approach of protection and deprotection could be avoided.

In this article, we reported novel dendronized polyamides by the macromonomer route with a polyamide backbone and polyamide dendrons decorated with bromomethyl groups. The syntheses of the dendrons, macromonomers, and the polyamides were all easy and did not need the protection/deprotection procedures using the new activation process as described above with thionyl chloride as the condensing reagent. The dendronized polyamides may be used as initiators for atom transfer radical polymerization (ATRP) in moderate condition to synthesize 'hairy' functional derivatives. Otherwise, these polyamides could also be applied in other fields by converting easily bromomethyl groups into other groups.

EXPERIMENTAL

Instruments

Infrared (IR) spectra were performed with a WQF-410 Fourier transform infrared spectrometer (Beijing, China). ¹H and ¹³C NMR were obtained using an Inova 400 spectrometer (Palo Alto, CA). Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Netzsch STA 449C (Netzsch, Germany) at a heating rate of 10°C/min under nitrogen atmosphere. Inherent viscosity was measured in *N,N*-dimethylformamide (DMF; 0.5 g/dL) at 25°C with a suspended level Ubbelohde viscometer. Gel permeation chromatography (GPC) analysis was conducted on an Alltech (Altech Associate, Deerfield, IL) model 626 high-performance liquid chromatography (HPLC) pump with PL HFIP gel columns, equipped with a UVIS-201 detector, using polystyrene standards. DMF containing 0.01 mol/L lithium bromide (LiBr) was used as an eluent and

the flow rate was 1.0 mL/min. X-ray diffraction analysis (XRD) was conducted on a Bruker (Madison, WI) D8 Advance diffractometer with Cu Kα1 radiation.

Materials

3,5-Diaminobenzoic acid (**2**, 98%) was purchased from ABCR GmbH (Karlsruhe, Germany). 5-Aminoisophthalic acid (**5**, 95%), isophthalic acid (99%), and bromomethyl bromide (**1**) were purchased from Alfa Aesar. *N*-methyl-2-pyrrolidone (NMP), SOCl₂, 4,4'-oxydianiline (4,4'-ODA, **8**), DMF, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), methanol, ethyl ether, sulfuric acid (96%), LiBr, lithium chloride (LiCl), acetone, and hydrochloric acid (HCl, 36%) were all analytical-grade and were purchased from Sinopharm Chemical Reagent, (Beijing, China). NMP was purified by distillation over P₂O₅ under reduced pressure, the other agents were used as received without further purification.

G1 dendron (**3**)

In a flask equipped with a magnetic stirrer and nitrogen-inlet and -outlet tubes, **2** (3.04 g, 20 mmol) and NMP (25 mL) were added under nitrogen atmosphere. The solution was cooled with -15 to -20°C saturated brine-ice bath for 0.5 h after **2** was dissolved in NMP completely at room temperature and then **1** (12.12 g, 60 mmol) was added dropwise under nitrogen. After stirring for another 1 h at that temperature, the reaction mixture was allowed to react for 8 h at 0°C and 2 h at room temperature. The reaction mixture was poured into HCl/water (1/25 v/v) and then the precipitate was collected. The crude product was redissolved in DMF and the resulting solution was reprecipitated with water. The precipitate was collected by filtration and washed with water and then dried in vacuum at 70°C. The yield was 91%.

IR (KBr, cm⁻¹): 1685 (carboxyl C=O), 1655, 1560 (amide C=O), 1610, 1444 (aromatic), 685(C-Br). ¹H NMR (DMSO-d₆, ppm): 4.06(s, 4H, CH₂), 7.96(d, 2H, ArH), 8.19(q, 1H, ArH), 10.64(s, 2H, CONH). ¹³C NMR (DMSO-d₆, ppm): 43.95, 115.11, 116.09, 131.59, 139.19, 165.05, 166.90. Anal. Calcd. for C₁₁H₁₀O₄N₂Br₂: C, 33.50; H, 2.54; N, 7.11. Found: C, 33.23; H, 2.92; N, 6.99.

G2 dendron (**4**)

3 and **2** were dried in vacuum at 100°C for 2 h before being used. **3**(3.94 g, 10 mmol) and SOCl₂ (20 mL) were added into the flask and stirred for 4 h at 80°C, then the solution was distilled under reduced pressure for 1 h at 70°C to remove the excessive thionyl chloride completely. After the flask was cooled

to 0°C, NMP (10 mL) was added to the flask under nitrogen. The resulting mixture was stirred at 0°C until it turned to be a homogeneous solution and then a solution of 0.48 equiv. of **2** (0.73 g, 4.8 mmol) with respect to **3** in NMP (10 mL) was added. The reaction was kept at 0°C for 30 min and at room temperature for 20 h and then the reaction mixture was poured into HCl/water (1/25 v/v) to precipitate the product. The precipitate was isolated by filtration, washed with water and methanol, and dried in vacuum at 70°C. The yield was 95%.

IR (KBr, cm^{-1}): 1685 (carboxyl C=O), 1685, 1558 (amide C=O), 1608, 1454 (aromatic), 679 (C—Br). ^1H NMR (DMSO- d_6 , ppm): 4.29(m, 8H, CH₂), 7.86(d, 4H, ArH), 8.13(d, 2H, ArH), 8.20(t, 2H, ArH), 8.56(d, 1H, ArH), 10.63(s, 4H, CONH), 10.64(s, 2H, CONH). ^{13}C NMR (DMSO- d_6 , ppm): 43.57, 113.52, 114.32, 116.67, 116.90, 131.42, 136.41, 138.94, 139.54, 165.03, 165.76, 167.08. Anal. Calcd. for $\text{C}_{29}\text{H}_{24}\text{O}_8\text{N}_6\text{Br}_4$: C, 38.50; H, 2.65; N, 9.29. Found: C, 38.30; H, 2.48; N, 9.17.

G1 macromonomer (6)

3 and **5** were dried in vacuum at 80°C for 2 h before being used. The activation procedure of **3** (1.97 g, 5 mmol) here was the same as that of **3** for the synthesis of **4**. Then, a solution of 0.96 equiv. of **5** (0.92 g, 4.8 mmol) with respect to **3** in NMP (10 mL) was added to the reaction mixture. The reaction was allowed to react for 1 h at 0°C and for 20 h at room temperature. The reaction mixture was poured into HCl/water (1/25 v/v) to precipitate the product. The precipitate was collected by filtration and washed with water and methanol, and then dried in vacuum at 70°C. The yield was 91%.

IR (KBr, cm^{-1}): 1689 (carboxyl C=O), 1689, 1560 (amide C=O), 1608, 1450 (aromatic), 671 (C—Br). ^1H NMR (DMSO- d_6 , ppm): 4.32(s, 4H, CH₂), 7.89(d, 2H, ArH), 8.21(s, 1H, ArH), 8.24(s, 1H, ArH), 8.65(d, 2H, ArH), 10.64(s, 2H, CONH), 10.78(s, 1H, CONH). ^{13}C NMR (DMSO- d_6 , ppm): 43.56, 113.37, 114.29, 124.71, 125.08, 131.70, 136.04, 138.84, 139.80, 165.06, 165.88, 166.52. Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_7\text{N}_3\text{Br}_2$: C, 40.93; H, 2.69; N, 7.54. Found: C, 40.62; H, 2.95; N, 7.41.

G2 macromonomer (7)

4 and **5** were dried in vacuum at 80°C for 2 h before being used. The activation procedure of **4** (2.71 g, 3 mmol) was similar to that of **3**, but the time of activation was prolonged to 8 h. Then, a solution of 0.96 equiv. of **5** (0.55 g, 2.89 mmol) with respect to **4** in NMP (10 mL) was added to the reaction mixture. The reaction was kept at 0°C for 1 h and at room temperature for 22 h. The reaction mixture was poured into HCl/water (1/25 v/v) to precipitate the

product. The precipitate was collected by filtration and washed with water and methanol, and then dried in vacuum at 70°C. The yield was 93%.

IR (KBr, cm^{-1}): 1680 (carboxyl C=O), 1680, 1552 (amide C=O), 1606, 1452 (aromatic), 681 (C—Br). ^1H NMR(DMSO- d_6 , ppm): 4.32(s, 8H,CH₂), 7.90(d, 4H,ArH), 8.07(d, 2H,ArH), 8.20(s, 2H,ArH), 8.24(s, 1H,ArH), 8.49(s, 1H,ArH), 8.69(d, 2H,ArH), 10.63(t, 4H,CONH), 10.68(s, 2H,CONH), 10.77(s, 1H,CONH), ^{13}C NMR (DMSO- d_6 , ppm): 43.56, 113.18, 114.29, 115.52, 115.78, 124.63, 125.03, 131.72, 135.60, 136.42, 138.99, 139.43, 139.90, 165.01, 165.81, 166.10, 166.52. Anal. Calcd. for $\text{C}_{37}\text{H}_{29}\text{O}_{11}\text{N}_7\text{Br}_4$: C, 41.61; H, 2.72; N, 9.18. Found: C, 41.29; H, 2.94; N, 9.03.

Linear polyamide (LP)

The activation procedure of isophthalic acid (3.32 g, 20 mmol) was similar to that of **3**, but the time of activation was prolonged to 8 h. Then, a solution of **8** (4.00 g, 20 mmol) in NMP (10 mL) was added. The reaction was kept at 0°C for 0.5 h and at room temperature for 24 h and then the reaction mixture was poured into HCl/water (1/10 v/v) to precipitate and then the precipitate was collected by filtration. The crude product was dipped into HCl/water (1/5 v/v) again and the precipitate was filtered, washed with water, and methanol. The resulting polyamides were dried at 80°C in vacuum. The yield was 89%.

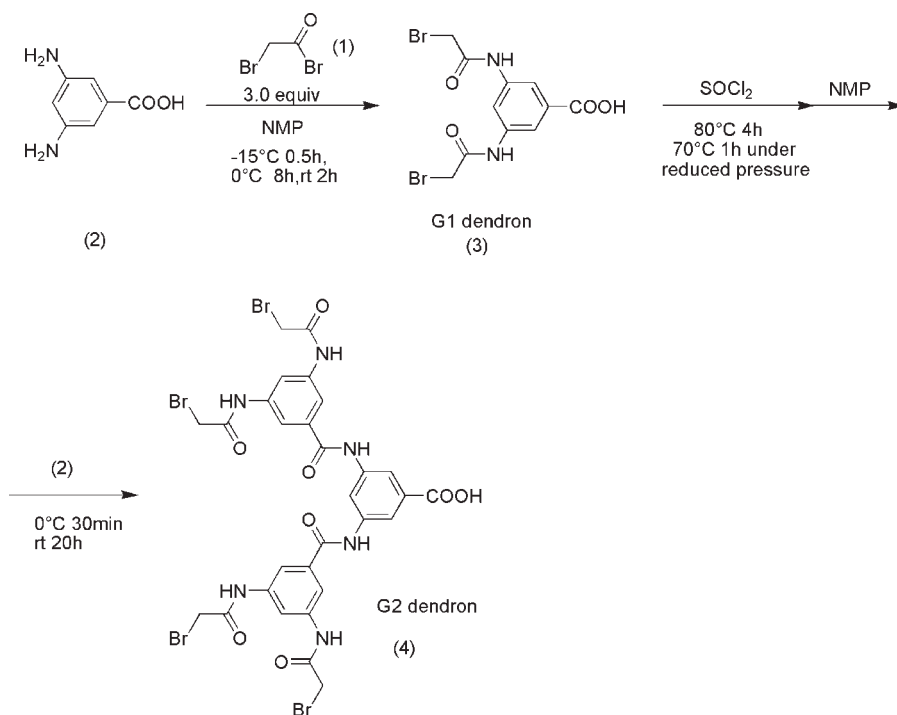
IR (KBr, cm^{-1}): 1665, 1542 (amide C=O), 1601, 1500, 1452 (aromatic), 1227 (oxyphenylene). Anal. Calcd. for $(\text{C}_{20}\text{H}_{14}\text{O}_3\text{N}_2)_n$: C, 72.73; H, 4.24; N, 8.48. Found: C, 72.31; H, 4.58; N, 8.37.

General polycondensation procedure

The activation procedure of macromonomers (2 mmol) was similar to that of **3**, but the time of activation was prolonged to 24 h. Then a solution of 0.7 equiv. of **8** (0.28 g, 1.4 mmol) with respect to macromonomers in NMP (10 mL) was added. The reaction was kept at 0°C for 2 h and at room temperature for 24 h and then the reaction mixture was poured into HCl/water (1/10 v/v) to precipitate and then the precipitate was collected by filtration. The crude product was dipped into HCl/water (1/5 v/v) again and the precipitate was filtered, washed with water, acetone, ethyl ether, and methanol. The resulting polyamides were dried at 70°C in vacuum.

G1 functionalized dendronized polyamide (Fdp_{g1},9)

The yield was 87%. IR (KBr, cm^{-1}): 1662, 1541 (amide C=O), 1601, 1498, 1448 (aromatic), 1227 (oxyphenylene), 679 (C—Br). ^1H NMR (DMSO- d_6 , ppm): 4.30(d, 4H,CH₂), 7.06(d, 4H,ArH), 7.79(d, 4H,ArH),



Scheme 1 Synthesis of dendrons.

7.92(m, 2H,ArH), 8.18(s, 1H,ArH), 8.28(s, 1H,ArH), 8.49(q, 2H,ArH), 10.54(s, 2H,CONH), 10.63(s, 2H,CONH), 10.80(s, 1H,CONH). ¹³C NMR (DMSO-d₆, ppm): 43.54, 113.30, 114.26, 118.72, 122.02, 131.46, 134.60, 135.94, 136.12, 138.96, 139.44, 139.58, 164.90, 165.02, 165.86, 166.75. Anal. Calcd. for (C₃₁H₂₃O₆N₅Br₂)_n: C, 51.60; H, 3.19; N, 9.71. Found: C, 51.39; H, 3.38; N, 9.58.

G2 functionalized dendronized polyamide (Fdpg2,10)

The yield was 85%. IR (KBr, cm⁻¹): 1676, 1543 (amide C=O), 1603, 1500, 1450 (aromatic), 1227 (oxyphenylene), 681 (C—Br). ¹H NMR (DMSO-d₆, ppm): 4.28(d, 8H,CH₂), 7.11(t, 4H,ArH), 7.35(d, 4H,ArH), 7.90(m, 4H,ArH), 8.07(d, 2H,ArH), 8.20(d, 2H,ArH), 8.23(s, 1H,ArH), 8.50(d, 1H,ArH), 8.68(t, 2H,ArH), 10.62(s, 2H,CONH), 10.66(t, 4H,CONH), 10.68(s, 2H,CONH), 10.77(d, 1H,CONH). ¹³C NMR (DMSO-d₆, ppm): 43.55, 113.18, 114.29, 115.52, 118.82, 119.63, 122.27, 124.82, 125.01, 131.71, 135.70, 136.40, 138.94, 139.42, 165.02, 165.81, 166.51. Anal. Calcd. for (C₄₉H₃₇O₁₀N₉Br₄)_n: C, 47.77; H, 3.01; N, 10.24. Found: C, 47.46; H, 3.43; N, 10.12.

RESULTS AND DISCUSSION

Synthesis of dendrons

The convergent synthesis of polyamide dendrons using thionyl chloride was carried out by a two-step

method involving (1) activation of carboxylic group with thionyl chloride and (2) condensation with an unprotected AB₂ building block, which should contain one carboxylic and two amino groups. Here, we selected 3,5-diaminobenzoic acid as an unprotected AB₂ building block.

In this article, an innovation was the adoption of a new activating process with thionyl chloride. We adopted a method in which dendrons were kept in thionyl chloride for activation at 80°C after which excessive thionyl chloride was distilled under reduced pressure at 70°C and removed completely, and then NMP was added after the activated dendrons was cooled to 0°C. The process avoided the complex purification of thionyl chloride, and the difficult confirmation of the molar ratio of thionyl chloride to the carboxyl group of different dendrons and decreased side reactions. In addition, SOCl₂ had no influence on the bromomethyl groups even at 80°C and the reaction could occur below room temperature to avoid the side reaction between the bromomethyl groups and the amino group or carboxyl group at high temperature, so that the dendrons do not need to be protected and deprotected. The synthesis of G1 and G2 dendrons is shown in Scheme 1. The AB₂ building block 2 was reacted with bromomethyl bromide to give the G1 dendron in a 91% yield after reprecipitation in water. The G2 dendron was synthesized by the two-step procedure as described earlier and was purified simply by washing with water and methanol to remove the parent dendron. The

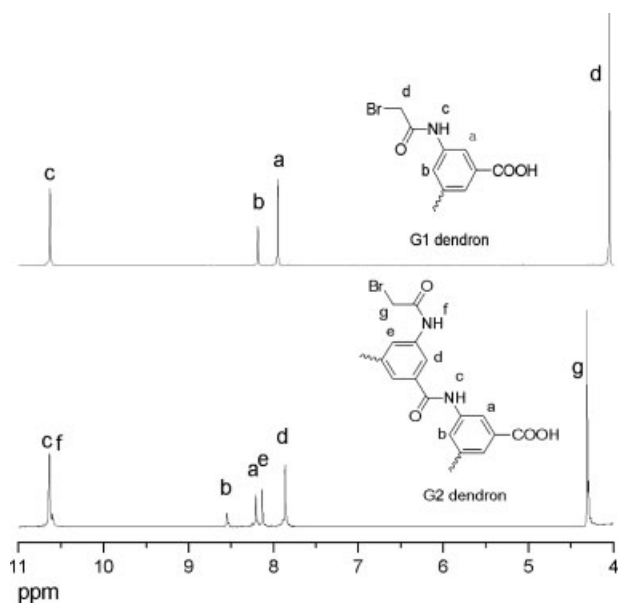


Figure 1 ^1H NMR spectra of dendrons.

reaction time was prolonged correspondingly depending on the generation of dendron.

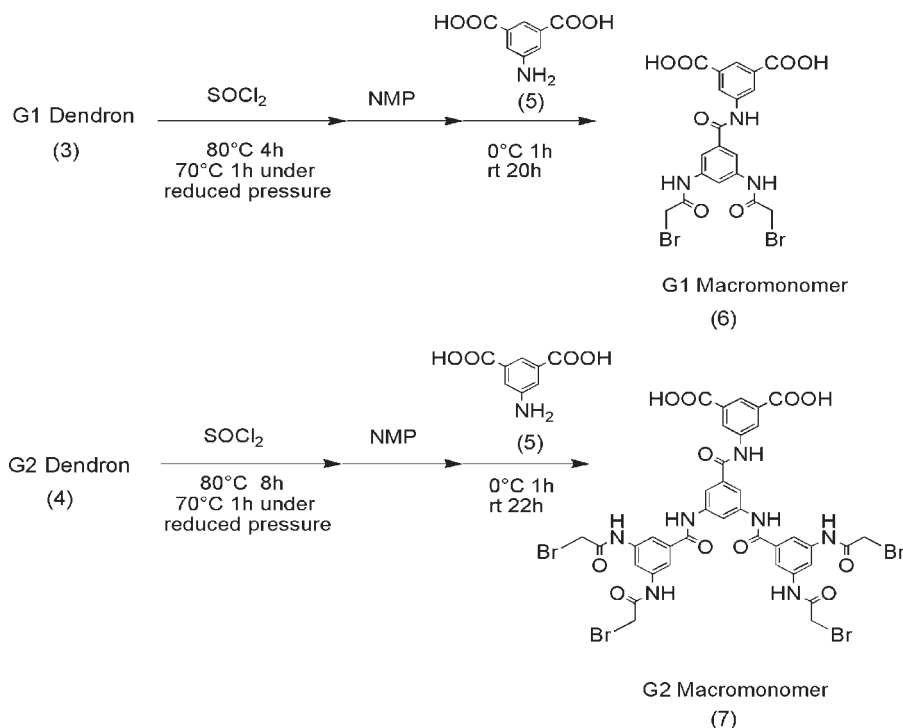
The structures of G1 and G2 dendrons were characterized by IR, NMR, and elemental analysis. The IR spectra of G1 and G2 dendrons showed strong absorptions at 1685 and 1655–1685 cm^{-1} , characteristic of the carbonyl stretching of carboxyl groups and amide groups, respectively. There were also absorptions in the IR spectra of G1 and G2 dendrons at

679–685 cm^{-1} attributed to the C–Br stretching, and the ^1H NMR spectra of both dendrons showed signals to methylene protons at 4.06–4.29 ppm, which indicated that SOCl_2 had really no influence on the bromomethyl groups even at 80°C. Meanwhile, ^1H NMR spectra of both dendrons also showed signals to aromatic protons and amide protons at 10.63–10.64 and 7.86–8.56 ppm, respectively, as shown in Figure 1. In addition, elemental analysis in each dendron was in very good agreement with the theoretical value. So, these data indicated that the dendrons were synthesized successfully.

Synthesis of macromonomers

The macromonomers were synthesized from corresponding dendrons and 5-aminoisophthalic acid according to the same two-step procedure as used in the synthesis of G2 dendron. The synthesis of G1 and G2 macromonomers is shown in Scheme 2. Because 5-aminoisophthalic acid contains one amino and two carboxylic acid groups, each macromonomer poses two carboxylic acid groups, which is suitable for polycondensation.

The structures of the macromonomers were characterized by IR, NMR, and elemental analysis. The IR spectra of the macromonomers showed strong absorptions at 1680–1689 and 1552–1560 cm^{-1} , characteristic of the carbonyl stretching of carboxyl groups and amide groups, respectively. It also displayed absorptions at 671–681 cm^{-1} , characteristic of



Scheme 2 Synthesis of macromonomers.

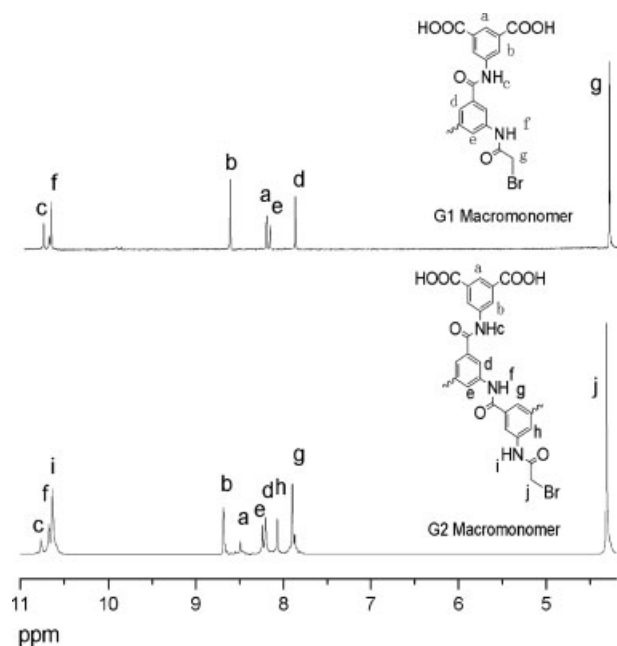


Figure 2 ^1H NMR spectra of macromonomers.

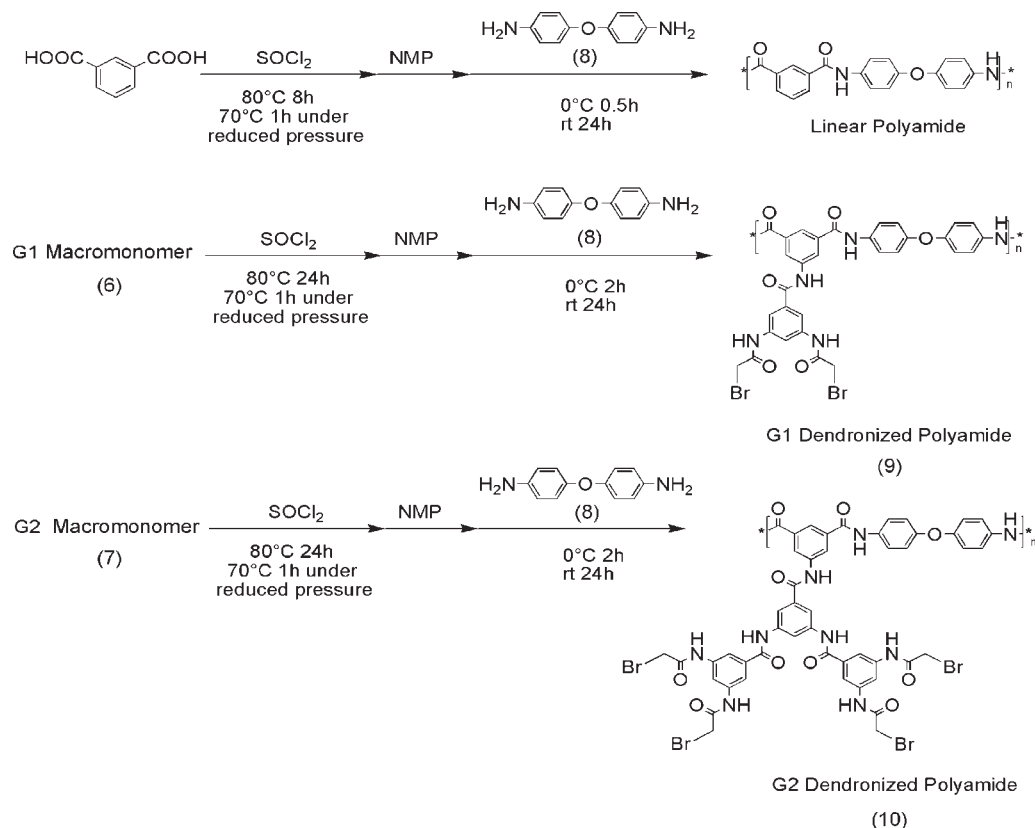
the C—Br stretching. ^1H NMR spectra of both macromonomers showed signals corresponding to methylene protons, amide protons, and aromatic protons at 4.32, 7.89–8.69, and 10.64–10.78 ppm, respectively,

as shown in Figure 2. The proportion of protons of the ^1H NMR grams was in very good agreement with that of the desired macromonomers, and elemental analysis in each macromonomer accorded with the theoretical value, and so these indicated the satisfactory formation of the desired macromonomers.

Synthesis of polyamides

These polyamides were synthesized from the considerable monomers and 4,4'-oxydianiline (ODA) with thionyl chloride as condensation agent as shown in Scheme 3.

Triphenyl phosphite/pyridine, diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (DBOP), thionyl chloride, and *N,N'*-carbonyl diimidazole (CDI) are efficient condensation agents for the syntheses of polyamides. In this article, we selected thionyl chloride as the condensation agent in that the protection and deprotection procedures needn't be used. The bromomethyl groups in the periphery of macromonomers were active and ready to react with the amino groups of ODA at high temperature when the polycondensation was carried out using triphenyl phosphite/pyridine and CDI as condensation agents. If triphenyl phosphite/pyridine and CDI were selected as condensation agents, the protection



Scheme 3 Synthesis of polyamides.

and deprotection procedures need be used. But the condensation reaction occurred below room temperature to avoid side reactions using thionyl chloride. DBOP is too expensive to be suitable for synthetic use. So, thionyl chloride was the most suitable condensation agent.

Because of the higher steric hindrance of macromonomers, the carboxylic group in macromonomers could not converse to acid chloride completely. Liu et al. have proved that 60–70% of similar macromonomers converted to acid chloride.²⁵ The stoichiometric ratio of ODA to acid chloride is very important for high molecule weight of dendronized polyamides, and so 0.7 equiv. of ODA with respect to macromonomers was added.

The structures of the polyamides were also confirmed by IR, NMR, and elemental analysis. The IR spectra of linear polyamide displayed strong absorption peaks at 1665 and 1542 cm^{-1} , characteristic of the carbonyl stretching of amide groups, which indicated that the linear polyamide was synthesized. The IR spectra of both the dendronized polyamides showed a new strong absorption peak at 1227 cm^{-1} attributed to symmetric vibrations of the aromatic ether groups, which primarily indicated the success of the synthesis. The peaks at 1662, 1541, and 679 cm^{-1} for FDPG1 or those at 1676, 1543, and 681 cm^{-1} for FDPG2 were attributed to the amide carbonyl groups and the C–Br stretching, but there was no peak at about 1700 cm^{-1} belonging to the carboxylic group, which it indicated that both the polyamides are with amino end groups. As shown in Figure 3, the ^1H NMR spectra of the functionalized dendronized polyamides indicated that all

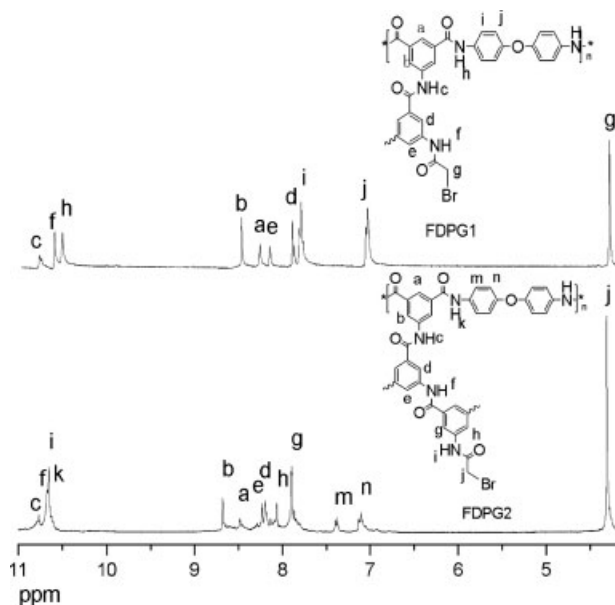


Figure 3 ^1H NMR spectra of functionalized dendronized polyamides.

TABLE I
Inherent Viscosity and Molecular Weights of the Resulting Polyamides

Sample	Inherent viscosity	M_w	M_w/M_n
LP			
FDPG1	0.59	103009	2.38
FDPG2	0.09	50061	2.74

amide and aromatic protons in the spectra of the macromonomers could be found in that of the corresponding polymers. In addition, two new peaks were observed at 7.06 and 7.79 ppm for FDPG1 or 7.11 and 7.35 ppm for FDPG2, which indicated the incorporation of the 4,4'-ODA unit. But in the ^{13}C NMR spectra of FDPG2, the peaks of aromatic protons in backbone were not found mostly, and so the bulkiness of G2 dendron resulted in the shielding effect. Otherwise, elemental analysis in each polyamide was in very good agreement with the theoretical value. So, the structures of the polyamides accorded with the desired polymers and the syntheses were feasible and successful.

Properties of polyamides

The molecular weights of the polyamides were measured by GPC with DMF as the eluent, calibrated with polystyrene standards, as shown in Table I. The data for LP was not completed because of the bad solubility of LP in DMF. The data showed that the weight average molecular weights (M_w) for FDPG1 and FDPG2 were found up to 103,009 and 50,061 with polydispersities (M_w/M_n) of 2.38 and 2.74, respectively. As far as FDPG2 was concerned, the molecular weight was relatively lower compared with FDPG1 possibly because of bulkiness of G2 macromonomer.

The inherent viscosities of the polyamides are also shown in Table I. The data for LP was also not completed because of the same reason. The data showed that the inherent viscosities of the dendronized polyamides were low, and they fell with increasing generation of the polyamides possibly due to the shielding affect of the dendrons.²⁹ Pertinent research on the relationship between the molecular weights of dendronized polymers and their inherent viscosities has not been reported.

The solubility behavior of the polyamides is shown in Table II. The solubility of the functionalized dendronized polyamides was much better than that of LP. These dendronized polyamides were both easily soluble in aprotic polar solvents such as DMF, DMAc, DMSO, NMP, and sulfuric acid, but LP was soluble only in sulfuric acid and partially soluble in NMP with lithium salt. The highly soluble

TABLE II
Solubility of the Resulting Polyamides

Solvent	LP	FDPG1	FDPG2
DMF	–	+	+
DMF/LiCl ^a	–	+	+
DMAC	–	+	+
DMSO	–	+	+
NMP	–	+	+
NMP/LiCl ^a	+	+	+
Sulfuric acid	+	+	+

+, soluble; – insoluble.

^a The concentration of LiCl was 5% (w/w).

nature of these dendronized polyamides was attributed to the presence of highly branched dendrons and the bromomethyl groups in the periphery. Because side dendrons destroyed the hydrogen bonds among the polyamide backbone and the bromomethyl groups enhanced the interactions between the polymer molecules and polar solvents, the solubility of the functionalized dendronized polyamides was improved remarkably.

The structure of the dendronized polyamides was characterized by XRD, which is shown in Figure 4. From the XRD patterns, we can see that there was no peak at a small-angle region, but there were amorphous peaks in a wide-angle region for both the polyamides. The XRD patterns for the polyamides were similar, and just the 2θ of the amorphous peak for FDPG1 was 22.76°C and that for FDPG2 was 25.08°C. As reported in the previous literature, a sharp peak at a small angle indicated the formation of columnar mesophases,³⁰ and so the polyamides could not form columnar object due to no peak at a small-angle region. This phenomenon may be attributed to the smallness of the side dendrons. Because of the highly branched dendrons in

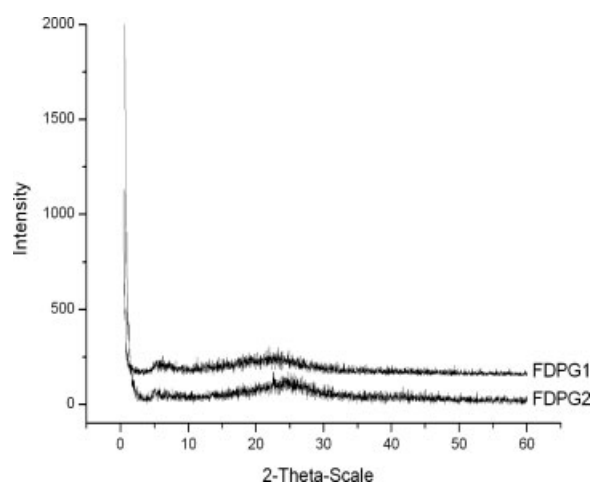


Figure 4 XRD diffractogram of functionalized dendronized polyamides.

TABLE III
Thermal Properties of the Resulting Polyamides

Sample	T_g (°C)	$T_{5\%}$ (°C) ^a	$T_{10\%}$ (°C) ^a	$T_{50\%}$ (°C) ^a
LP	264	477		
FDPG1	227	194	294	525
FDPG2	136	142	220	485

^a The temperatures of 5, 10, and 50% weight loss.

the periphery, both the polyamides presented an amorphous structure.

The thermal properties of the polyamides were investigated using DSC and TGA, with the data presented in Table III. The glass transition temperatures (T_g s) of the polyamides were measured from the second heating DSC run and taken as the turning of the transition. T_g s for LP, FDPG1, and FDPG2 were 264, 227, and 136°C, respectively, declining acutely with increasing generation of the side dendrons. For different generations of the dendronized polymer, the change of T_g was related to the degree of polymerization (DP) of the polymer.³¹ A shorter chain length (or lower DP) possibly increased the segmental mobility of the dendronized polymer and reduced the fraction of a less mobile polymer core, which resulted in the falling of T_g of the dendronized polymer. Because the molecular weight for FDPG1 was much higher than that for FDPG2 and the molecular weight of G2 macromonomer was higher than that of G1 macromonomer, that is, DP of the FDPG2 was much lower. In addition, the change of T_g was mostly related to Fox-Flory relationship. Side-branched dendrons of the dendronized polyamides decreased the intermolecular interactions, which will improve the motion of the polymer chains, and the G2 dendrons decreased more largely. So, T_g for the FDPG2 was much lower than that for FDPG1. Because of the presence of branched dendrons, T_g s of the functionalized dendronized polyamides were lower than the T_g of LP.

The TGA curves of the polyamides are depicted in Figure 5, and the concerned data is shown in Table III. The 5% weight loss temperatures ($T_{5\%}$'s) were for FDPG1 and FDPG2 were 194 and 142°C, respectively, which were lower than that of LP, which was 477°C. This phenomenon was attributed to the existence of the bromomethyl groups in the periphery of the dendronized polyamides. At high temperature, the bromomethyl groups react with amino groups, which were at the double end of the dendronized polyamides. Otherwise, the polymer chain of FDPG2 was shorter than that of FDPG1 due to the lower molecular weights of FDPG2, which resulted in the relatively higher proportion of amino groups, and so the reaction easily occurred between the bromomethyl groups and amino groups for FDPG2. There-

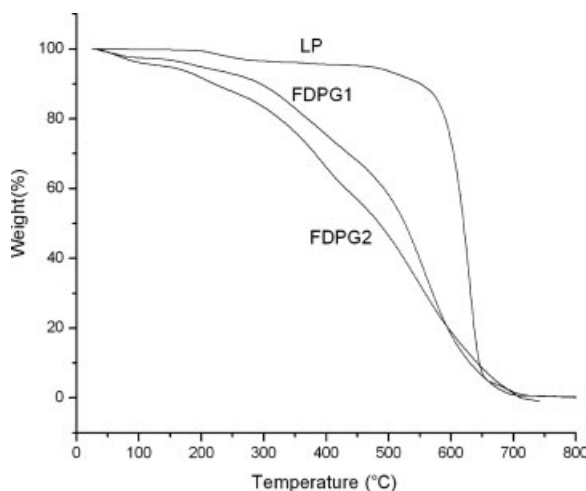


Figure 5 TGA thermograms of polyamides.

fore, the 5% weight loss temperature for FDPG2 was much lower than that of FDPG1. Because of the same reason, the 10% weight loss temperatures ($T_{10\%/s}$) were 294°C for FDPG1 and 220°C for FDPG2, respectively. But the 50% weight loss temperatures ($T_{50\%/s}$) were up to 525°C for FDPG1 and 485°C for FDPG2, and it might be attributed to the formation of the new products, which were obtained through the reaction of the bromomethyl groups in the periphery and the amino groups at the end of the resulting polyamides.

CONCLUSIONS

In this study, novel dendronized polyamides with considerable active bromomethyl groups in the periphery have been synthesized successfully. The new activation procedure using SOCl_2 , no protection/deprotection procedures, and the macromonomer route made the syntheses easier. The molecular weights for the dendronized polyamides were high and the molecular weight for FDPG2 was lower than that for FDPG1 because of the bulkiness of G2 macromonomer. The inherent viscosities of the dendronized polyamides were low and those for FDPG1 and FDPG2 were 0.59 and 0.09, respectively. The solubility of the dendronized polyamides was improved remarkably, and they all dissolved in DMF, DMAc, DMSO, NMP, and sulfuric acid. The dendronized polyamides showed an amorphous structure because of the highly branched dendrons. T_g s for FDPG1 and FDPG2 were lower than that of LP, and the thermal property of the dendronized polyamides was poorer than that of LP.

Because of a large number of active bromomethyl groups in the periphery, the functionalized dendronized polyamides will have a good application foreground. They could be used as initiators for ATRP

to synthesize 'hairy' functional derivatives and could be applied in many fields by converting bromomethyl groups into other desired groups. Now, we are synthesizing 'hairy' functional derivatives using the resulting polyamides and the polyamides with the chloromethyl groups²⁵ in the periphery as initiators and will compare the different points by the two classes of the initiators.

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