Facile Synthesis of Dendronized Polyamides with Chloromethyl Groups in the Periphery and Some Properties

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ABSTRACT: A novel dendronized aromatic polyamide with a polyamide backbone and chloromethylene-end-functionalized polyamide dendrons is reported for the first time. An attempt at a one-pot synthesis of end-functionalized dendronized polymers with a macromonomer strategy without protection and deprotection procedures is also reported for the first time. The results from Fourier transform infrared and NMR spectral analysis indicated that perfect coverage of the chloromethyl groups in the periphery of the resulting polymers was obtained. Data from gel permeation chromatography analysis showed a typical weight-average molecular weight (M_w) of 76,678 and a polydispersity of 2.44 for the first-generation polymers and an M_w of 41,554 and a polydispersity of 2.74 for the second-generation polymers. The solubility in solvents for the resulting polymers was improved remarkably because of the introduction of the dendritic fragments and the existence of the periphery functional groups. Both the glass-transition temperature and onset decomposition temperature decreased versus those of the linear aromatic polyamides, but the 50% weight loss temperature was still up to 723°C. The X-ray diffractograms indicated only an amorphous peak in the wide-angle region of 24–25°. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3087–3096, 2007

Key words: macromonomers; polyamides; synthesis

INTRODUCTION

Dendronized polymer,[1] the term coined by Schlüter et al.,[2] is a merger of two concepts: dendrimers and polymers. In other words, a dendronized polymer is a special kind of graft copolymer[3,4] or, in the case of complete coverage, a comb polymer[3,4] with dendritic side chains pending at every repeating unit along the polymer backbone. Dendronized polymers originally appeared in a patent filed by Tomalia and Kirchhoff[5] in 1987 and now have become a promising new field attracting considerable attention from researchers in organic chemistry, polymer synthesis, and materials science, as can be seen in recently published reviews.[1,6–10]

The synthetic strategies of dendronized polymers can be divided conceptually into three different categories: a graft-to strategy (also termed a convergent route), a graft-from strategy (also termed a divergent route), and a macromonomer strategy. All these strategies have their advantages and disadvantages, and there is no universally optimal strategy. Nevertheless, on the basis of the number of publications, the macromonomer route is the most commonly used strategy by far because of the resulting polymers with a quantitative degree of dendron attachment.[9]

Although dendronized polymers have been developed remarkably, there are still some problems remaining, such as how to improve the molecular weights of dendronized polymers and narrow the distributions of the molecular weights and how to have functional groups in the periphery (here they are called functionalized dendronized polymers).[10] In particular, the latter hamper their further modifications and applications. Reports on the synthesis of functionalized dendronized polymers are increasing. For example, functionalized first-generation and second-generation dendronized styrenes, acrylates, and methacrylates carrying amino groups decorated with *Teoc*, *Boc*, or *Cbz* in their periphery were polymerized by Schlüter and coworkers.[11–14] Functionalized dendronized polyacrylates decorated with glucose units in the periphery were presented by the same group.[15] Schlüter et al.[11] also synthesized functionalized polystyrenes with hydroxyl in the periphery. Series of functionalized dendronized poly(methacrylate)s and their derivatives with ester groups in the periphery were reported by Chessa et al.,[16] Xi et al.,[17,18] and Draheim and Ritter.[19] However, the functional groups in the aforementioned functionalized dendronized polymers were all obtained by means of protection and deprotection procedures; that

is, before polymerization, a protection procedure was adopted to avoid unfavorable reactions and gelation, and a deprotection procedure was necessary after polymerization. This strategy brought additional steps of synthesis; moreover, the efficiency of the protection/deprotection reaction influenced the perfect attachment of functional groups in the periphery.

Linear polyamides are commonly available polymers, and dendrimers with amide bonds are also popular topics in the synthesis of dendritic macromolecules, including polyamidoamines,[20–23] polyamides,[24–26] polyaramides,[27–43] poly(ester amide)s,[26] and poly(ether amide)s.[26,37–41] However, reports on dendronized polymers with amide bonds are relatively scarce. Li and coworkers[44,45] synthesized dendronized polyamides with polyether dendrons. A Schlüter-type dendron is a kind of dendron with an amide bond, and a series of dendronized polystyrenes, polyacrylates, and polymethacrylates with Schlüter-type dendrons were presented by Schlüter's group.[11–15,46–50] Nevertheless, dendronized polymers with both a polyamide backbone and polyamide dendrons have seldom been reported, so they are synthetically attractive and challenging.

Thionyl chloride ($SOCl_2$) is a well-known activating agent for the preparation of amides as well as acid chlorides from carboxylic acids.[51] It is an inexpensive, commercially available reagent and has been used in the synthesis of linear polyamides[52] and polyamide dendrimers[39–41] successfully.

Here a novel dendronized aromatic polyamide with a polyamide backbone and chloromethylene-end-functionalized polyamide dendrons is reported. Meanwhile, we easily synthesized the dendrons and macromonomers and developed a one-pot method for the preparation of functionalized dendronized polymers by a macromonomer strategy without protection and deprotection procedures, using $SOCl_2$ as a versatile and common condensing reagent. Therefore, a facile approach for obtaining functionalized dendronized polymers was explored.

EXPERIMENTAL

Measurements

Infrared (IR) spectra were recorded with a WQF-410 Fourier transform infrared spectrometer (Beijing, China). ^{1}H- and ^{13}C-NMR was recorded with an Inova 400 spectrometer (Palo Alto, CA). Mass spectra were measured with an LCQ-Advantage sensitive MS[n] ion trap system (San Jose, CA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were twice carried out on a Netzsch STA 449C (Netzsch, Germany) under a flowing nitrogen atmosphere at a heating rate of 10°C/min. The inherent viscosity was measured in N,N-dimethyl-

formamide (DMF; 0.5 g/dL) at 25°C with a suspended-level Ubbelohde viscometer. Gel permeation chromatography (GPC) analysis was performed on an Alltech (Altech Associate, Inc., Deerfield, IL), model 626 high-performance liquid chromatography (HLPC) pump equipped with a UVIS-201 detector with polystyrene standards. PL HFIP gel columns were used. The flow rate was 1.0 mL/min, and the column temperature was 30°C. DMF containing 0.01 mol/L lithium bromide (LiBr) was used as an eluent. X-ray diffraction analysis was performed on a Bruker (Madison, WI) D8 Advance diffractometer with Cu Kα_1 radiation.

Materials

3,5-Diaminobenzoic acid (**2**; 98%) and 5-aminoisophthalic acid (**5**; 95%) were purchased from ABCR GmbH (Karlruke, Germany). Chloroacetyl chloride (**1**), N-methyl-2-pyrrolidone (NMP), $SOCl_2$, 4,4′-oxy-dianiline (4,4′-ODA or **8**), N,N′-carbonyl diimidazole (CDI), lime chloride ($CaCl_2$), DMF, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), ethanol, sulfuric acid (96%), LiBr, lithium chloride (LiCl), triethylamine (TEA), acetone, ethyl ether, chlohydric acid (HCl; 36%), and triphenyl phosphite (TPP) were all analytical-grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) Pyridine (Py) was also analytical-grade and was purchased from Shanghai ShiYi Chemicals Reagent Co., Ltd. (Shanghai, China). All the agents were used as received without further purification.

GI dendron (3)

In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **2** (3.04 g, 20.0 mmol) and NMP (25 mL). The solution was stirred at room temperature until **2** was dissolved in NMP absolutely. It was cooled with a −20 to −15°C saturated brine/ice bath for 0.5 h, and then **1** (6.78 g, 60.0 mmol) was added under nitrogen. The reaction mixture was stirred for another 0.5 h at that temperature. Then, the saturated brine/ice bath was replaced by an ice/water bath, and the reaction was carried out for 9 h at 0°C and for 1 h at room temperature. The reaction mixture was poured into HCl/water (1/20 v/v), and the precipitate was collected and dried. The crude product was redissolved in NMP, and the resulting solution was reprecipitated with ethanol/water (1/10 v/v). The precipitate was collected by filtration, washed with water, and dried in a vacuum at 90°C to afford a white powder. The yield was 96%.

IR (KBr): 1689 (carboxyl C=O), 1653, 1560 (amide C=O), 1610, 1450 cm^{-1} (aromatic). ^{1}H-NMR (DMSO-d_6): 4.23 (s, 4H, CH_2), 7.92 (d, 2H, ArH), 8.16 (q, 1H, ArH), 10.52 (s, 2H, CONH). ^{13}C-NMR (DMSO-d_6): 43.76, 114.23, 115.77, 131.99, 139.27, 165.34, 166.97.

Mass spectrometry (MS; atmospheric pressure ionization-electronic-spray (API-ES)): 303 (100) [M − 2], 304 (14) [M − 1], 305 (74) [M].

GI dendron (4)

3 and **2** were dried in a vacuum at 120°C for 4 h before being used. In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **3** (3.05 g, 10.0 mmol) and NMP (15 mL). After **3** was dissolved in NMP absolutely at room temperature, the solution was cooled with an ice/water bath for 0.5 h. Then, 1.20 equiv of $SOCl_2$ (1.42 g, 12.0 mmol) with respect to **3** were added under nitrogen. The reaction mixture was stirred for 0.5 h at 0°C and for 0.5 h at room temperature. Then, it was placed in a 90°C oil bath under reduced pressure for 0.5 h to remove excessive $SOCl_2$. Cooled to room temperature in air and in an ice/water bath for 0.5 h under nitrogen, a solution of 0.48 equiv of **2** (0.73 g, 4.8 mmol) with respect to **3** in NMP (10 mL) was added to the reaction mixture. The reaction was performed at 0°C for 10 min and at room temperature for 20 h. The reaction mixture was poured into HCl/water (1/20 v/v). The precipitate was collected by filtration, washed with water, and dried in a vacuum at 90°C to yield a gray powder. The yield was 98%.

IR (KBr): 1680 (br, carboxyl C=O), 1680, 1550 (amide C=O), 1606, 1454 cm^{-1} (aromatic). ^{1}H-NMR (DMSO-d_6): 4.24 (m, 8H, CH$_2$), 7.82 (d, 4H, ArH), 8.10 (d, 2H, ArH), 8.17 (t, 2H, ArH), 8.50 (d, 1H, ArH), 10.56 (s, 4H, CONH), 10.57 (s, 2H, CONH). ^{13}C-NMR (DMSO-d_6): 43.63, 113.56, 114.56, 116.57, 116.95, 131.54, 136.49, 138.95, 139.56, 165.26, 165.88, 167.13. MS (+ centroid atmosphere pressure chemical ionization (+c APCI)): 724.5 (48) [M − 2]$^+$, 726.5 (77) [M]$^+$, 728.5 (35) [M + 2]$^+$, 802.1 (86) [M + DMSO − 2], 804.0 (100) [M + DMSO], 806.0 (57) [M + DMSO + 2].

G1 macromonomer (6)

3 and **5** were dried in a vacuum at 120°C for 4 h before being used. In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **3** (3.05 g, 10.0 mmol) and NMP (15 mL). After **3** was dissolved in NMP absolutely at room temperature, the solution was cooled with an ice/water bath for 0.5 h. Then, 1.20 equiv of $SOCl_2$ (1.42 g, 12.0 mmol) with respect to **3** were added under nitrogen. The reaction mixture was stirred for 0.5 h at 0°C and for 0.5 h at room temperature. Then, it was placed in a 90°C oil bath under reduced pressure for 0.5 h to remove excessive $SOCl_2$. Cooled to room temperature in air and in an ice/water bath for 0.5 h under nitrogen, a solution of 0.960 equiv of **5** (1.83 g, 9.60 mmol) with respect to **3** and TEA (10.3 mmol, 1.04 g) in NMP (20 mL) was added to the reaction

mixture. The reaction was performed at 0°C for 1 h and at room temperature for 20 h. The reaction mixture was poured into HCl/water (1/20 v/v). The precipitate was collected by filtration, washed with water, and dried in a vacuum at 90°C, and a gray powder was obtained. The yield was 99%.

IR (KBr): 1691 (br, carboxyl C=O), 1691, 1560 (amide C=O), 1606, 1452 cm^{-1} (aromatic). ^{1}H-NMR (DMSO-d_6): 4.30 (s, 4H, CH$_2$), 7.88 (d, 2H, ArH), 8.20 (s, 2H, ArH), 8.23 (s, 2H, ArH), 8.64 (d, 1H, ArH), 10.59 (s, 2H, CONH), 10.75 (s, 1H, CONH), 13.28 (br, 2h, COOH). ^{13}C-NMR (DMSO-d_6): 43.55, 113.37, 114.28, 124.71, 125.07, 131.70, 136.03, 138.98, 139.77, 165.02, 165.82, 166.50. MS (+c APCI): 359.4 (100) [M − C$_2$H$_2$(CH$_2$)$_6$]$^+$, 361.3 (58) [M − C$_2$H$_2$(CH$_2$)$_6$ + 2]$^+$, 545.4 (38) [M + DMSO]$^+$, 547.4 (24) [M + DMSO + 2]$^+$.

G2 macromonomer (7)

4 and **5** were dried in a vacuum at 120°C for 4 h before being used. In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **4** (2.18 g, 3.00 mmol) and NMP (10 mL). After **4** was dissolved in NMP absolutely at room temperature, the solution was cooled with an ice/water bath for 0.5 h. Then, 1.40 equiv of $SOCl_2$ (0.50 g, 4.2 mmol) with respect to **4** were added under nitrogen. The reaction mixture was stirred for 10 min at 0°C and for 1 h at room temperature. Then, it was placed in a 90°C oil bath under reduced pressure for 0.5 h to remove excessive $SOCl_2$. Cooled to room temperature under nitrogen, a solution of 0.96 equiv of **5** (0.55 g, 2.9 mmol) with respect to **4** and TEA (3.1 mmol, 0.31 g) in NMP (10 mL) was added to the reaction mixture. The reaction was performed at room temperature for 20 h. The reaction mixture was poured into HCl/water (1/20 v/v). The precipitate was collected by filtration, washed with water, and dried in a vacuum at 90°C, and a gray powder was obtained. The yield was 94%.

IR (KBr): 1680 (br, carboxyl C=O), 1680, 1549 (amide C=O), 1604, 1452 cm^{-1} (aromatic). ^{1}H-NMR (DMSO-d_6): 4.30 (s, 8H, CH$_2$), 7.88 (d, 4H, ArH), 8.05 (d, 2H, ArH), 8.19 (s, 2H, ArH), 8.23 (s, 1H, ArH), 8.48 (s, 2H, ArH), 8.67 (d, 2H, ArH), 10.59 (t, 4H, CONH), 10.66 (s, 2H, CONH), 10.75 (s, 1H, CONH), 13.23 (br, 2H, COOH). ^{13}C-NMR (DMSO-d_6): 43.56, 113.18, 114.28, 115.53, 115.77, 124.63, 125.01, 131.72, 135.59, 136.41, 138.95, 139.42, 139.89, 165.02, 165.80, 166.09, 166.52. MS (+c APCI): 678.1 (100) [M − C$_{14}$H$_{28+2}$NCO]$^+$, 679.2 (64) [M − C$_{14}$H$_{28+2}$NCO + 1]$^+$, 680.2 (16) [M − C$_{14}$H$_{28+2}$NCO + 2]$^+$, 890 (5) [M]$^+$.

General polycondensation procedure

In a flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser were placed **6**

(0.94 g, 2.0 mmol) and SOCl$_2$ (10 mL). The solution was stirred under reflux at 110°C for 24 h and then distilled under reduced pressure for 1 h at that temperature to remove excessive SOCl$_2$. NMP (30 mL) were added to a flask under nitrogen, and the resulting mixture was stirred at that temperature until it turned into a homogeneous solution. The solution was cooled to room temperature and then cooled in an ice/water bath for 0.5 h. Then, 0.7 equiv of **8** (0.28 g, 1.4 mmol) with respect to **6** were added under nitrogen. The reaction was carried out at 0°C for 2 h and at room temperature for 24 h. The reaction mixture was poured into HCl/water (1/2 v/v), and the precipitate was collected by filtration. The crude product was dipped into HCl/water (1/1 v/v) again for 2 h to remove unreacted **8** absolutely. The precipitate was filtered and washed with water (200 mL) four times, with acetone (100 mL) three times, and with ethyl ether (100 mL) one time. The pale brown product was obtained after it was dried at 60°C in a vacuum.

PG1s (9)

The yield was 52%.

IR (KBr): 1707 (carboxyl C=O), 1676, 1543 (amide C=O), 1603, 1498, 1448 (aromatic), 1227 cm^{-1} (oxyphenylene). ^{1}H-NMR (DMSO-d_6): 4.28 (d, 4H, CH$_2$), 7.04 (d, 4H, ArH), 7.28 (d, 4H, ArH), 7.87 (m, 2H, ArH), 8.18 (s, 2H, ArH), 8.28 (s, 2H, ArH), 8.57 (q, 2H, ArH), 10.53 (s, 2H, CONH), 10.61 (s, 2H, CONH), 10.76 (s, 1H, CONH). ^{13}C-NMR (DMSO-d_6): 43.53, 113.32, 114.26, 118.69, 122.04, 131.48, 134.58, 135.96, 136.12, 138.98, 139.42, 139.58, 164.92, 165.00, 165.85, 166.73.

PG2s (10)

The yield was 47%.

IR (KBr): 1672, 1541 (amide C=O), 1603, 1496, 1446 (aromatic), 1221 cm^{-1} (oxyphenylene). ^{1}H-NMR (DMSO-d_6): 4.28 (d, 8H, CH$_2$), 7.08 (t, 4H, ArH), 7.31 (d, 4H, ArH), 7.88 (m, 4H, ArH), 8.06 (d, 2H, ArH), 8.18 (d, 2H, ArH), 8.28 (S,1H, ArH), 8.46 (d, 2H, ArH), 8.67 (t, 2H, ArH), 10.54 (s, 2H, CONH), 10.61 (t, 4H, CONH), 10.66 (s, 2H, CONH), 10.76 (d, 1H, CONH). ^{13}C-NMR (DMSO-d_6): 43.64, 113.61, 114.57, 115.77, 119.11, 119.88, 122.58, 124.91, 125.09, 131.84, 135.80, 136.50, 138.99, 139.45, 165.29, 165.98, 166.62.

RESULTS AND DISCUSSION

Synthesis of the dendrons

Facile syntheses of polyamide dendrons from unprotected AB$_2$ building blocks with SOCl$_2$ as a condensing agent have been reported in the literature.[39–41]

The convergent synthesis is carried out by a two-step method involving (1) the activation of carboxylic groups with SOCl$_2$ and (2) condensation with an unprotected AB$_2$ building block. Here, the suitable AB$_2$ building block should contain one carboxylic group and two amino groups. In the literature, the authors selected 3,5-bis(4-aminophenoxy)benzoic acid as an unprotected AB$_2$ building block, which was synthesized by them from 3,5-dihydroxybenzoic acid and 4-fluoronitrobenzene in the presence of sodium carbonate.[53] In this study, we selected **2**, which was commercially available, as an unprotected AB$_2$ building block. Although the steric hindrance was higher in **2** than in 3,5-bis(4-aminophoxy)benzoic acid, the desired structures were still obtained through corresponding changes in the activation and reaction conditions.

Another improvement in this study in comparison with the literature is the adjustment of the molar ratio of SOCl$_2$ to the carboxylic group. As described in the literature, the molar ratio of SOCl$_2$ to the carboxylic group is very important for the quantitative activation and prevention of unfavorable reactions such as the reaction of SOCl$_2$ with amines. With purified SOCl$_2$ (e.g., SOCl$_2$ was distilled under nitrogen over TPP and then stored at 0°C under nitrogen), the reaction of 1.04 equiv of SOCl$_2$ with respect to carboxylic acid provided the corresponding amide in a quantitative yield, so 1.04 equiv of SOCl$_2$ with respect to the carboxylic acid was employed in the literature. In this study, to avoid the inconvenience of purification and to use commercially available SOCl$_2$ directly, a higher molar ratio of SOCl$_2$ to the carboxylic group (e.g., 1.20 equiv) was employed. However, to prevent unfavorable reactions, excessive SOCl$_2$ was distilled under reduced pressure before the addition of the unprotected AB$_2$ building block. Similarly, the quantitative formation of the corresponding amide was observed.

The syntheses of **3** and **4** are shown in Scheme 1. **2** was reacted with **1** to give **3** in a 96% yield after
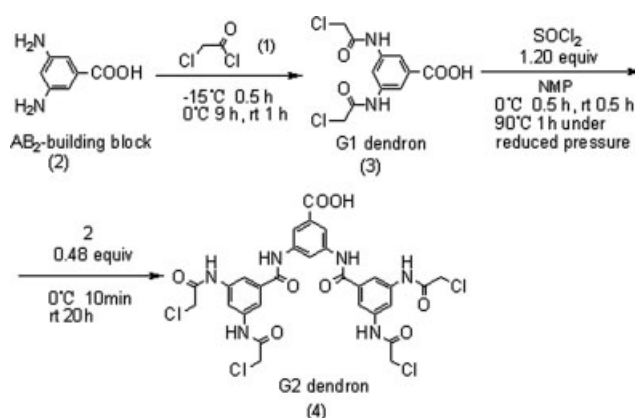
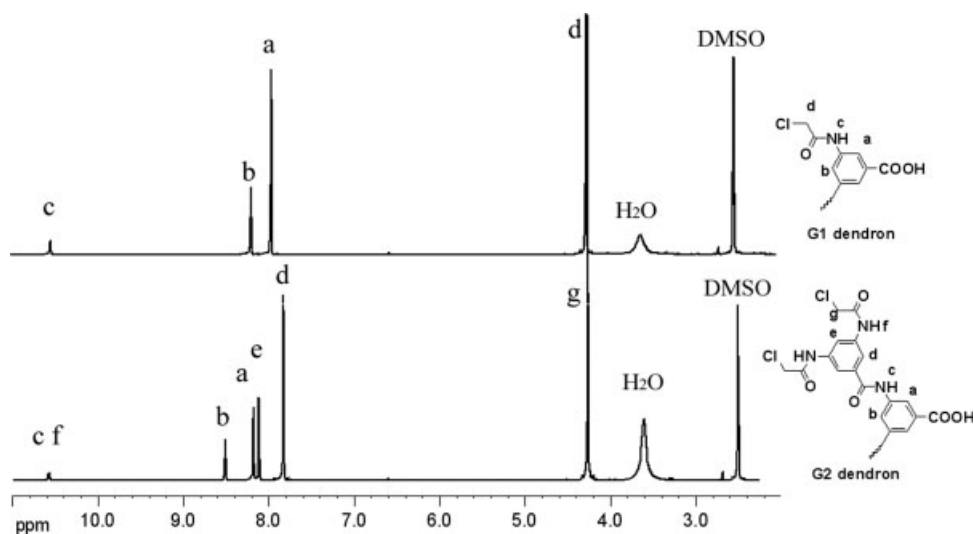**Scheme 1** Synthesis of the dendrons.

Figure 1 ^{1}H-NMR spectra of the dendrons.

precipitation in water. **4** was synthesized by a two-step procedure, as described in the preceding paragraph, in a 98% yield after workup. Because of the high steric hindrance in AB$_2$, the reaction time was prolonged correspondingly, and the activation conditions of the carboxylic groups and the conditions for condensation were independently set, depending on the generation of the dendron.

The structures of these dendrons were characterized with IR, ^{1}H- and ^{13}C-NMR, and mass spectra. In the IR spectrum of **3**, the strong characteristic absorption at 1689 cm^{-1} was ascribed to carboxylic groups, and the absorption at 1653 and 1560 cm^{-1} was attributed to amide carbonyl groups. ^{1}H-NMR spectra of all dendrons showed signals corresponding to methylene protons, amide protons, and aromatic protons at 4.23–4.24, 10.52–10.57, and 7.82–8.50 ppm, respectively, as shown in Figure 1. The MS spectra of **3** and **4** indicated their molecular weights to be 305 and 725.5 Da, which were very close to the calculated molecular weights of 305 and 726 Da, respectively. All these satisfactory findings clearly indicated the formation of the desired structure.
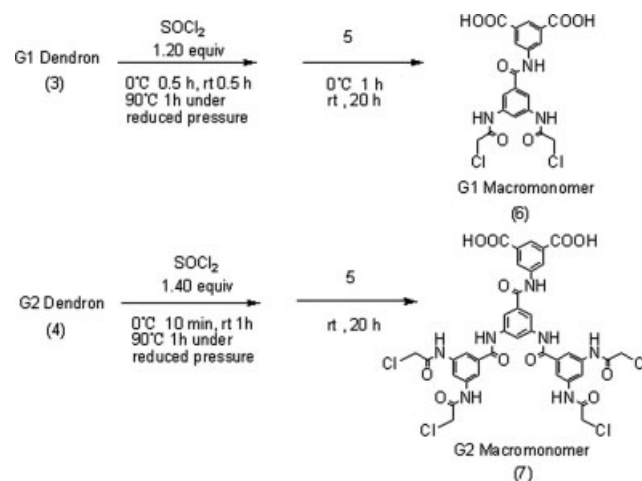
Synthesis of the macromonomers

The synthesis of the macromonomers was carried out according to the same two-step procedure used in the synthesis of dendrons. **5** was used as an A$_2$B building block and contained one amino group and two carboxylic groups. As shown in Scheme 2, the amino group of **5** was reacted with the activated carboxylic groups of dendrons with SOCl$_2$ as a condensing reagent. Therefore, the introduction of two carboxylic groups made the dendrons become macromonomers that were suitable for polycondensation.

The structures of these macromonomers were also characterized with IR, NMR, and MS measurements. In the IR spectrum of **6**, the strong and broad characteristic absorption at 1691 cm^{-1} was ascribed to carbonyl groups of carboxylic groups and amide, and the absorption at 1560 cm^{-1} was attributed to the amide group. ^{1}H-NMR spectra of all macromonomers showed signals corresponding to methylene protons, amide protons, aromatic protons, and carboxylic protons at 4.30, 7.85–8.67, 10.59–10.75, and 13.23–13.28 ppm, respectively, as shown in Figure 2.

Synthesis of the functionalized dendronized polyamides

The polymerization of dendronized polyamides was conducted with the macromonomers and 4,4'-ODA in the presence of SOCl$_2$ as an activating agent, as shown in Scheme 3. TPP/Py, SOCl$_2$, and CDI were
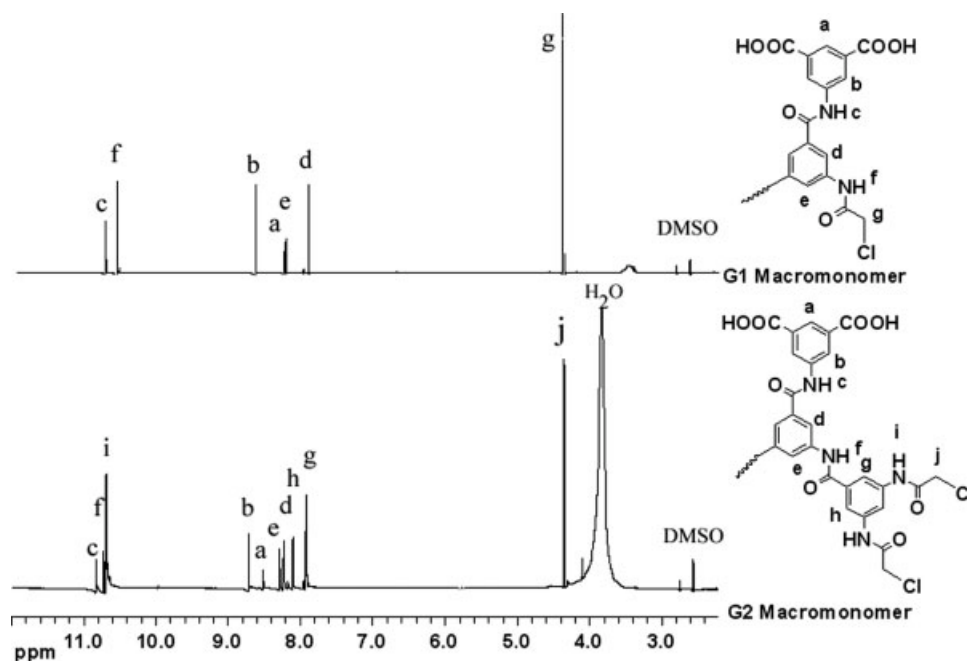

Scheme 2 Synthesis of the macromonomers.

**Figure 2** ^{1}H-NMR spectra of the macromonomers.

all efficient condensing agents for the formation of the amide. The resulting polymers prepared in the presence of different condensing agents are shown in Table I.

Although TPP/Py and CDI are more easily handled, they are not suitable for the synthesis of functionalized dendronized polyamides because the chloromethyl groups in the periphery of the macromonomers are active and easily react with amino groups of 4,4′-ODA at high temperatures when TPP/Py and CDI are used as activating agents. This unfavorable reaction will result in gelation, as shown in Table I. Hence, in the syntheses of functionalized dendronized polymers, protection and deprotection procedures have usually been adopted to avoid unfavorable reactions and gelation.[11–19]

The aforementioned problems could be resolved through the use of SOCl$_2$ as a condensing agent because the polycondensations were always conducted at room temperature, although the activation of carboxylic groups was performed at a high temperature. At a low temperature, unfavorable reactions and gelation did not happen. More importantly, SOCl$_2$ had no influence on the chloromethyl groups in the periphery of the resulting polymers; this was confirmed by IR and NMR measurements subsequently. Therefore, the protection and deprotection procedures did not need to be used here. Because the carboxylic groups in the macromonomers could not be converted into acid chloride completely in 1 day, the stoichiometric ratio of 4,4′-ODA influenced the molecular weight of the resulting products strongly, and the efficiency of conversion varied with the gen-

eration and structure of the macromonomer, as shown in Table I. As demonstrated by experiments, the efficiency of conversion was about 60% for **6** and 70% for **7**. The addition of CaCl$_2$ also influenced the molecular weight of the products obviously. The molecular weight of the products without CaCl$_2$ was higher than that with CaCl$_2$.

The structures of the functionalized dendronized polyamides were confirmed by IR and NMR measurements. In the IR spectra of all the resulting polymers, a new absorption peak attributed to symmetric vibrations of aromatic ether groups was observed at 1227 (PG1s) or 1221 cm^{-1} (PG2s), and it indicated
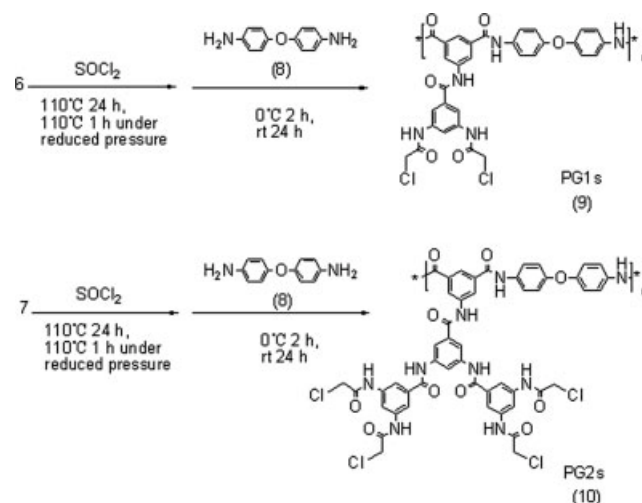
Scheme 3 Synthesis of the functionalized dendronized polyamides.

TABLE I
Some Synthetic Details and Results of the Polymerization

Sample	Condensing agent	4,4′-ODA (equiv)	CaCl$_2$ (wt %)	Inherent viscosity	GPC	
					M_w	M_w/M_n
PG1s-4	TPP/Py	1.0	0	Gel		
PG2s-2	CDI	1.0	0	Gel		
PG1s-6	SOCl$_2$	0.6	6	0.05	24,679	3.165
PG1s-7	SOCl$_2$	0.7	6	0.10	55,356	2.646
PG1s-8	SOCl$_2$	0.6	0	0.17	76,678	2.441
PG2s-3	SOCl$_2$	0.6	6	0.09	23,737	2.239
PG2s-4	SOCl$_2$	0.7	6	0.31	41,554	2.740

the existence of a 4,4′-ODA unit. A peak attributed to the carboxylic group at 1707 cm^{-1} in PG1s disappeared in PG2s, and this indicated PG1s with carboxylic end groups and PG2s with amino end groups. The peaks at 1676 and 1543 cm^{-1} in PG1s, or the ones at 1672 and 1541 cm^{-1} in PG2s, attributed to amide carbonyl groups, were in accordance with those in the corresponding macromonomers. Figure 3 shows the ^{1}H-NMR spectra of the functionalized dendronized polyamides. All the methylene, amide, and aromatic protons in the spectra of the macromonomers could be found in those of the corresponding resulting polymers. The agreement of the signal at 4.28 ppm assigned to the methylene proton in the polymers with that in the macromonomers indicated the perfect coverage of the chloromethyl groups in the periphery of the polymers and no influence on the chloromethyl groups during the polycondensation. Besides, two new peaks assigned to aromatic protons were observed at 7.08 and 7.32 ppm, and they indicated the incorporation of the 4,4′-ODA unit. However, in the ^{13}C-NMR spectra of PG2s, the signals of aromatic protons in the backbone could not be found because of the shielding effect of the dendrons. It was clear that the desired

functionalized dendronized polyamides were obtained.

Some properties of the functionalized dendronized polyamides

The molecular weights and inherent viscosities of the resulting polymers were measured by conventional means (GPC) with reference to standard polystyrene for calibration and with a suspended level Ubbelohde viscometer, and they are summarized in Table I. It is well known that GPC typically underestimates the molecular weights of dendronized polymers[54,55] because of the quite different hydrodynamic volumes of the dendronized polymers from those of the linear polystyrenes that are used as calibration materials for GPC columns. However, the data in Table I show that the moderate molecular weights of the resulting polymers were still achieved with moderate polydispersity. The weight-average molecular weights (M_w's) for PG1s and PG2s were up to 76 and 41 kg/mol with polydispersities of 2.44 and 2.74, respectively.

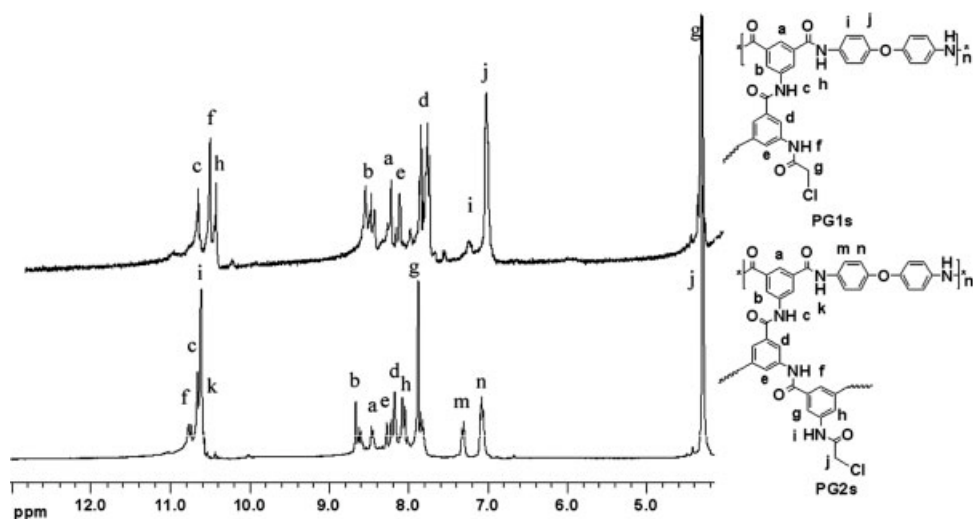Obviously different from those of conventional polyamides, the inherent viscosities of the resulting

Figure 3　^{1}H-NMR spectra of the functionalized dendronized polyamides.

TABLE II
Solubility of the Functionalized Dendronized Polyamides

Solvent	Functionalized dendronized polyamide		Dendronized polyamide[a]		Linear aromatic polyamide[b]
	G1	G2	G1	G2	
DMF	+	+	+−	+	−
DMF/LiCl[c]	+	+	+	+	−
DMAC	+	+	+−	+	−
DMSO	+	+	+−	+	−
NMP	+	+	+	+	−
NMP/LiCl[c]	+	+	+	+	+
Sulfuric acid	+	+	+	+	+

+ = soluble; − = insoluble; +− = partially soluble.
[a] Synthesized in a related work, the structure of the backbone and side dendritic fragments was identical to that of the functionalized dendronized polyamides, except that the chloromethyl groups in the periphery were substituted by phenyl groups.
[b] Synthesized in ref. 45.
[c] The concentration of LiCl was 5% (w/w).

polymers were all very low, as reported in the literature.[44,45] This phenomenon may be caused by the existence of side dendrons. Systematic research on the relationship between the viscosities of dendronized polymers and their molecular weights has not been reported, although it has been noted that the viscosities of dendrimers are very low and the relationship between their viscosities and molecular weights differs from that of linear polymers.[56,57]

Table II presents the solubility behavior of the resulting functionalized dendronized polyamides. In comparison with dendronized polyamides without functional groups in the periphery that were synthesized in our laboratory[58] and conventional linear aromatic polyamides,[45] the solubility of the functionalized dendronized polyamides was improved remarkably. PG1s and PG2s were both easily dissolved in aprotic polar solvents such as DMF with or without LiCl, DMAc, DMSO, NMP with or without LiCl, and sulfuric acid. However, the dendronized polyamides without functional groups in the periphery were soluble in NMP and DMF with lithium salt and partially soluble in DMF, DMAc, and DMSO. The linear aromatic polyamides were soluble only in sulfuric acid and partially soluble in NMP with lithium salt. It has been reported that the interaction of polymers with their environment depends largely on the polymer architecture and molecular interactions such as hydrogen bonding.[59,60] Therefore, it can be deduced that the solubility of the dendronized polyamides improved because of the pendant dendritic fragments and the decreased formation of the hydrogen bonds among the polymer chains. On the other hand, the polar functional groups, namely, chloromethyl groups, in the periphery of the functionalized dendronized polyamides increased the interactions between the polymer molecules and polar solvents, so the solubility of the functionalized dendronized polyamides was further improved in comparison with the dendronized polyamides.

The thermal properties of the resulting polymers were investigated with DSC and TGA. The glass-transition temperatures (T_g's) of the resulting polymers were in a narrow range of 156–157°C. It seems that there were few differences between the T_g's of PG1s and PG2s, which had different generation dendritic fragments. It has been reported that the glass transition of dendrimers primarily depends on the molecular structure, including the generation number of the branching step and the nature of the end groups.[61] Unfortunately, the relationship between the glass transition and structures of dendronized polymers is not clear so far because of the structural and architectural complexity of dendronized polymers. However, a decrease in the intermolecular interactions will undoubtedly be in favor of the motion of the polymer chains, and this will improve the solubility and at the same time lower the T_g's. Hence, the T_g's of the functionalized dendronized polyamides were much lower than the literature values of linear aromatic polyamides.[45]

The thermograms of the resulting polymers are depicted in Figure 4, and the relevant data are shown in Table III. The onset decomposition temperatures (T_{onset}'s) for PG1s and PG2s were 163 and 165°C, respectively, which were lower than those of the dendronized polyamides, which were 285–292°C.[58] This decrease was due to the existence of the chloromethyl groups in the periphery of the resulting polymers. It was reported that under heating conditions chloromethyl groups reacted with amino groups and carboxylic groups,[62] which were at the end of the resulting polymer chains, and con-
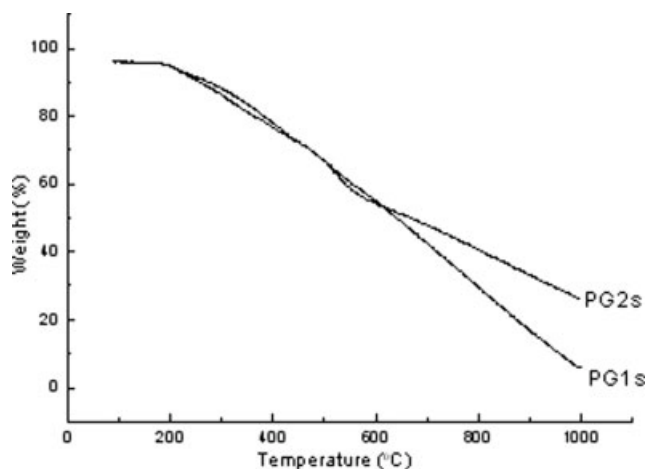
Figure 4 TGA curves of the functionalized dendronized polyamides.

Figure 5 X-ray diffractograms of the functionalized dendronized polyamides.

sequently resulted in the formation of networks in the polymers. For the same reason, the 10% weight loss temperature ($T_{10\%}$) for PG1s was 340°C, and it was 320°C for PG2s. However, the 50% weight loss temperature ($T_{50\%}$) still remained high, although T_{onset} and $T_{10\%}$ were lowered. Moreover, the thermal stability at even higher temperatures of the resulting polymers was especially remarkable because of the formation of the network described previously. Therefore, the thermal stability of PG2s at high temperatures was superior to that of PG1s because the content of chloromethyl groups in PG2s was higher than that in PG1s.

X-ray diffractograms recorded from both PG1s and PG2s at room temperature are shown in Figure 5. The diffractograms indicated only an amorphous peak in a wide-angle region, and the position, intensity, and width were little different for PG1s and PG2s. The 2θ of the peak was 24.3°, corresponding to a real space distance of 3.66 Å for PG1s, whereas for PG2s, it was 25.4°, corresponding to a real space distance of 3.50 Å. It has been reported that the peak can be attributed to spatial correlations between some repetitive elements such as the dendron's phenyl rings.[50] However, a sharp peak at a small angle, which would indicate the formation of columnar mesophases[63] or reflect the thickness of dendronized polymers,[50] could not be found in this study. This meant that the resulting polymers with the first- and
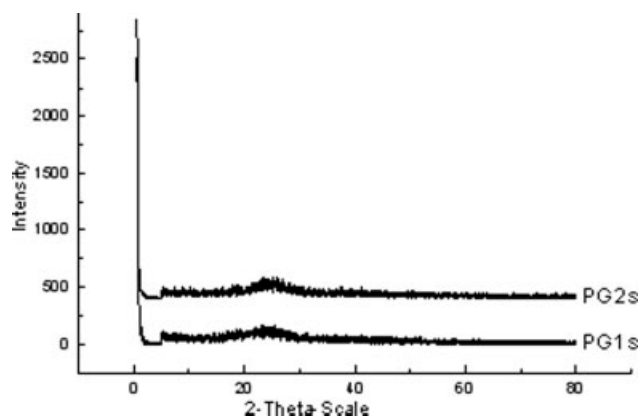
second-generation dendritic fragments were still not cylindrical objects that highly excluded each other in space and whose thickness, consequently, could be detected by X-ray diffraction. At the same time, the supramolecular column and/or cubic phases could not form because of a lack of intermolecular hydrogen bonding in these functionalized dendronized polymers. Therefore, the resulting polymers exhibited quite an amorphous character.

CONCLUSIONS

Functionalized dendronized aromatic polyamides with chloromethyl groups in the periphery were prepared successfully by the macromonomer route with $SOCl_2$ as an activating agent without protection/deprotection procedures. The rapid synthesis of the dendrons and macromonomers and the elimination of protection/deprotection procedures made the synthesis of the functionalized dendronized polymers more facile and provided more perfect coverage of functional groups in the periphery of the dendronized polymers. Consequently, it could afford a broader application field for the functionalized polymers to be prospected. The structures of the resulting dendrons, macromonomers, and polymers were confirmed with IR and NMR spectra.

GPC measurements showed the resulting polymers with moderate molecular weights and polydispersities. However, the inherent viscosities were all rather low, as measured by a suspended-level Ubbelohde viscometer. The solubility in organic solvents of the resulting polymers was improved remarkably because of the introduction of the dendritic fragments and the existence of the periphery functional groups. T_g and T_{onset} decreased in comparison with those of linear polyamides because of the decreased intermolecular interaction of the resulting polymers, but the thermal stability at high temperatures of the resulting polymers was especially remarkable

TABLE III
Thermal Properties of the Functionalized Dendronized Polyamides

Sample	T_g (°C)	T_{onset} (°C)	$T_{10\%}$ (°C)[a]	$T_{50\%}$ (°C)[a]
PG1s	157	163	340	677
PG2s	156	165	320	723

[a] The temperatures of 10 and 50% weight loss after the deduction of volatiles before 100°C.

because of the formation of networks resulting from the reaction of chloromethyl groups with amino or carboxylic end groups of the polymer chains. The X-ray diffractograms indicated only an amorphous peak in a wide-angle region of $2\theta = 24$–$25°$.

This work constitutes a step toward surface-functionalized, cylindrical nanoobjects. We are currently investigating the influence of reaction conditions on the molecular weight of the resulting polymers and the use of the resulting polymers as macroinitiators in atom transfer radical polymerization to prepare dendronized brushes. On the other hand, the chloromethyl groups in the periphery can be converted into other functional groups, such as amino and hydroxyl groups, to explore the wider use of the resulting polymers.

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