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The synthesis of novel aromatic polyamides with precisely pendant dendritic blocks

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Summary

A novel category of polyamides with precisely pendant Percec-type dendritic fragments has been successfully synthesized. Their structures were confirmed by FT-IR and ^{1}H-NMR spectra. The solubilities of these polyamides were greatly improved, especially the one with second generation dendritic blocks can be dissolved in normal organic solvents such as ethyl acetate, acetone, ether, hexane, etc.

Introduction

Dendrimers have received considerable scientific and technological attention firstly due to their unique architecture and those fascinating branching strategies (1-4). Further interest in their functional construction and application potential has been then increasing (5-10). It has been observed that dendrimers display unusual properties different from their linear analogs including solubility, viscosity, thermal and other properties (11-14). As a consequence of the search for materials with improved properties many investigators have studied the so-called hybrid linear-dendritic copolymers. Fréchet et al. have reported several families of hybrid block copolymers based on polyether dendrimers linked to polyethylene oxide, polyethylene glycol, polyester and polystyrene and have studied the properties of these nanoscopic supermolecules (15-17). Percec et al. have prepared linear polystyrene and polymethacrylate jacked with dendritic coats and have demonstrated that the polymeric shape can be controlled from spheroidal to cylindrical polymers as a function of backbone multiplicity Nc (18-20). Tomalia et al. have synthesized dendrimer hybrids derived from a linear poly(ethyleneimine) core and dendri poly(amidoamine) and illustrated their transformation from random coil to extended cylindrical conformation as a function of generation level enhancement (21). The polymers with a rigid-rod chain decorated with dendritic fragments were showed by Schlüter et al., which have been believed to be all cylindrically shaped structures (22-24).

The present work involves the synthesis of polymerizable diamines bearing two generations of Percec-type dendritic fragments and their polycondensation with diacid chlorides, leading to the formation of novel aromatic polyamides with precisely pendant dendritic blocks. These are expected to be cylindrical polymers of Schlüter type. It is well known that aromatic polyamides are a class of high performance polymers due to their excellent mechanical strength and thermal stability. However, rigidity of the backbone

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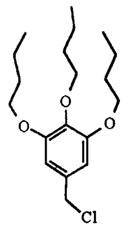
and strong hydrogen bonding results in insolubility in most organic solvents and difficult to process. These novel aromatic polyamides bearing pendant dendritic blocks are expected to maintain good thermal stability by restricting segmental mobility and improve solubility due to decreased packing and crystalinity as those aramides with other bulky pendent groups (25).

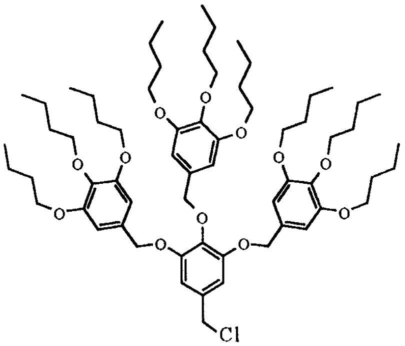
Experimental

^{1}H NMR spectra were recorded on Varian 200 NMR spectrometer (200Hz). Mass spectra were measured with Kratos AEI-MS-50 and BIFLEX III instruments. IR spectra were performed on PERKIN-ELMER 683 spectrometer. Elemental analyses were taken by a ST02 GC instrument. Melting points were determined on a X5 Meltemp apparatus and were uncorrected. THF was dried and distilled over sodium. CH_2Cl_2 was dried with calcium hydride and distilled upon use. N, N-dimethyl acetamide was purified by vacuum distillation over phosphorus pentoxide. Terephthaloyl chloride was recrystallized from dry hexane right before use. The other reagents were all analytical grade and used without further purification.



1

G1-CH_2Cl



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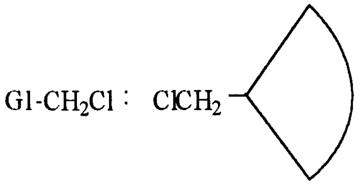
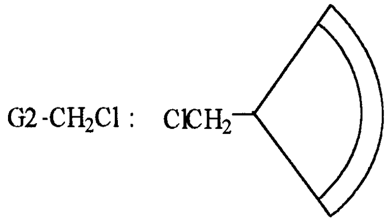
G2-CH_2Cl





Two Percec-type dendritic fragments **1**(first generation) and **2**(second generation) were provided according to the synthesis by Percec et al. (26). The precursor of diamines with dendritic fragments, compound **3**, was made according to the method of Yamashiro (27). The preparation of polymerazable diamines bearing dendritic blocks and their polycondensation were illustrated in Scheme 1 and Scheme 2 respectively.

G1-CH_2Cl (3,4,5-tributyloxy benzyl chloride) (1)

To a stirring solution of 3,4,5-tributyloxy benzyl alcohol (2.60g, 8.0 mmol, prepared by the reduction of methyl 3,4,5-tributyloxy benzoate) and CH_2Cl_2 (50ml) containing DMF (5ml) $SOCl_2$ (0.82ml, 11.2mmol) was added dropwise. After 15 min, the solvent was removed on a rotary evaporator. The product was dissolved in Et_2O, washed twice with saturated $NaHCO_3$ solution, then twice with water. The organic layer was dried over $MgSO_4$. After the solvent was removed, 2.5g of crude product of G1-CH_2Cl was obtained as pale yellow oil. Yield 91%. It was used in the next step without further purification. ^{1}H-NMR($CDCl_3$): δ = 0.98 (m, 9H), 1.48 (m, 6H), 1.76(m, 6H), 4.0(m, 6H), 4.52(s, 2H), 6.60(s, 2H). MS (m/z, %): 342(M^+, 38%), 286(M^+-C_4H_8, 45%), 230(M^+-2xC_4H_8, 35%), 174(M^+-3xC_4H_8, 100%), 139(M^+-3xC_4H_8-Cl, 55%)

G2-CH2Cl (2)

G1-CH_2Cl (9.8g, 29mmol), Methyl 3,4,5-trihydroxy benzoate (1.9g, 10mmol) and anhydrous K_2CO_3 (30g, 0.22mol) were mixed in DMF (150ml). The mixture was stirred and heated at 65°C for 3 hours and then the solvent was evaporated under vacuum. The residue was dissolved with Et_2O, washed with dilute HCl and water, dried over $MgSO_4$. After the solvent was removed, the crude product was purified by recrystallization from acetone at 0°C to yield 7.4g of G2-$COOCH_3$ as a white waxy solid. Yield: 65%. m.p.: 61-63 °C. ^{1}H-NMR ($CDCl_3$): δ= 0.92(m, 27H), 1.48(m, 18H), 1.70(m, 18H), 3.78-3.90 (m, 18H), 5.06(s, 6H), 6.64(d, 6H), 7.40(s, 2H). Then G2-$COOCH_3$ (5.2g, 4.7mmol) was reduced with $LiAlH_4$ (0.28g, 7.27mmol) in dry THF to provide G2-CH2OH and followed by the chlorination of G2-CH_2OH (2.47g, 2.3mmol) with $SOCl_2$ (0.23ml, 3.22 mmol). The reaction procedure is similar to that of G1-CH_2Cl. Yield of G2-CH2Cl (a white waxy solid): 92%. m.p. 52-53°C. ^{1}H-NMR($CDCl_3$): δ= 0.98(m, 27H), 1.50(m, 18H), 1.75(m, 18H), 3.90(m, 18H), 4.50(d, 2H), 5.00(d, 6H), 6.62(t, 8H). Elemental analysis: Calcd: C, 70.27; H, 8.94. Found: C, 70.33, H, 8.86.

4,4'-dinitro-2, 2'-dihydroxy-diphenyl(3)

6-Iodo-3-nitroanisol was first obtained from o-anisidine in the usual way (27). Under CO_2 atmosphere, the 6-Iodo-3-nitroanisol (23.12g, 82.9mmol) was heated with copper bronze(11g, 172mmol) and nitrobenzene(10ml) at 210-220°C for about 6 hours. Then the reaction mixture was submitted to a steam distillation and the residue was pulverized after dried and extracted with ether and benzene in succession. The extract was rescrystallized from benzene to give 4.7g of 4,4'-dinitro-2, 2'-dimethoxy-diphenyl as pale yellow solid. Yield 37%. m.p. 255-256°C(reported m.p. 257-258°C) 1H-NMR($CDCl_3$): δ=3.89(s, 6H), 7.4-7.8(m, 6H). MS (m/z, %): 304(M^+, 100%), 243(M^+-NO_2-CH_3, 16.7%), 228(M^+-NO_2-2xCH_3, 10.9%), 197(M^+-2xNO_2-CH_3, 11.1%). Then 4,4'-dinitro-2, 2'-dimethoxy-diphenyl(0.85g, 2.8mmol), hydrobromic acid (40%, 9.1ml), acetic acid (5.6ml) and acetic anhydride (5.6ml) were added into a 50ml three-necked flask and heated to reflux for 48 hours. The reaction mixture was then diluted with water after concentration, the solid was separated out and extracted with 15% sodium hydroxide aqueous solution. The extract was neutralized and the precipitates were extracted with benzene after dried. The residue was purified by recrystallization from ethanol to give 0.62g of compound **3** as yellow solid. Yield 80%. m.p. 251-253 °C (reported m.p. 253-254 °C) ^{1}H-NMR(DMSO): δ=7.48(d)-7.75(d) (6H). NIS (m/z, %): 276(M+, 100%), 184(M+-2xNO_2, 15.3%).

Dinitro compounds with dendritic blocks 4a (G1-biph-NO2) and 4b (G2-biph-NO_2)

Typical procedure: G1-CH_2Cl or G2-CH_2Cl (1 mmol), compound 3 (0.5 mmol), K_2CO_3(10 mmol), catalytic amount of KI and acetone(30ml) were added into a 100ml round-bottom flask. The mixture was heated to reflux with stirring for 24-48 hours. Then acetone was removed by vacuum distillation. The residue was added water and extracted with ether. The combined extracts were treated with $MgSO_4$ and the filtrate was dried by a rotary evaporator. The crude product was purified by recrystallization, 4a from petroleum ether and 4b from ethanol. Both 4a and 4b are pale yellow powder.

Compound **4a**: Yield 82%. m. p. 116-118 °C, H-NMR($CDCl_3$): δ= 0.95(t, 18H), 1.45(m, 12H), 1.68(m, 12), 3.78(t,8H), 3.88(t,4H), 4.98(s,4H), 6.34(s,4H), 7.45(d)~7.92(m)(4H). ^{13}C-NMR($CDCl_3$): δ=13.74, 13.83, 19.10, 19.18, 31.29, 32.23, 68.55, 70.74, 72.93, 104.52, 107.37, 115.77, 130.45, 131.47, 133.12, 148.66, 153.17, 156.31. Elemental analysis: Calcd. C, 67.55; H, 7.71; N, 3.15; Found: C, 67.48, H, 7.66; N, 3.19.

Compound **4b**: Yield 78%. m. p. 99-101 °C. ^{1}H-NMR(CD_3COCD_3): 0.92(m, 54H), 1.45 (m, 36H), 1.67(m, 36H), 3.80(m, 36H), 4.8~5.28(t, 16H), 6.64(t, 16H), 7.7(d)~8.1(m)(6H). ^{13}C-NMR(CD_3COCD_3): δ=14.15, 19.83, 68.91, 71.58, 73.02, 75.33, 105.99, 106.15, 108.15, 116.65, 132.77, 134.08, 138.159, 149.54, 153.85, 157.23. Elemental analysis: Calcd. C, 70.35; H, 8.38; N, 1.17; Found: C, 69.89; H, 8.23; N, 1.16.

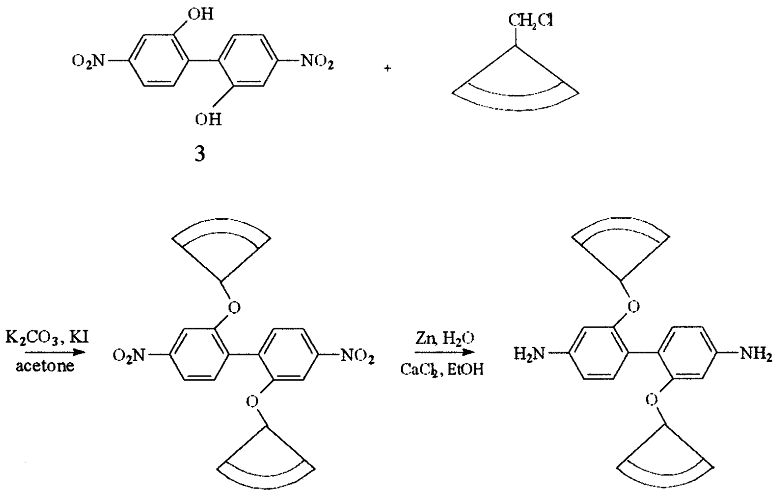
Diamine compounds with dendritic blocks 5a (G1-biph-NH_2) and 5b (G2-biph-NH_2)

Typical procedure: In a 50 ml three-necked flask, compound **4a** or **4b** (1.0mmol), Zn powder (53mmol), $CaCl_2$ (1.26mmol) and 30ml 78% ethanol were added. The mixture was refluxed for about 2 hours. The solids were filtered and rinsed with ether. The combined filtrates were dried with $MgSO_4$ and evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether: ethyl acetate=4:1). Both compound 5a and 5b are viscous yellow liquid.

Compound **5a**: Yield 45%. ^{1}H-NMR(CD_3Cl): 0.95(m, 18H), 1.5(m, 12H), 1.72(m, 12H), 3.85(m, 12H), 4.8(s, 4H), 6.3(s, 2H), 6.35(d, 2H), 6.4(s, 4H), 7.05(d, 2H). MS (MALDI-TOF): 851.7. Elemental analysis: Calcd. C, 72.43; H, 8.75; N, 3.38; Found: C, 72.21; H, 8.53; N, 3.16.

Compound **5b**: Yield 20%. ^{1}H-NMR(CD_3Cl): 0.85(m, 54H), 1.4(m, 36H), 1.65(m, 36H), 3.8(m, 36H), 4.8(m, 16H), 6.24(s, broad, 2H), 6.42(s, 2H), 6.52(d, 16H), 7.0(s, broad, 2H). MS (MALDI-TOF): 2331.4. Elemental analysis: Calcd. C, 72.13; H, 8.82; N, 1.20; Found: C, 71.87; H, 8.65; N, 1.08.

Scheme1:



3

4a(G1-biph-NO_2)
4b(G2-biph-NO_2)

5a(G1-biph-NH_2)
5b(G2-biph-NH_2)

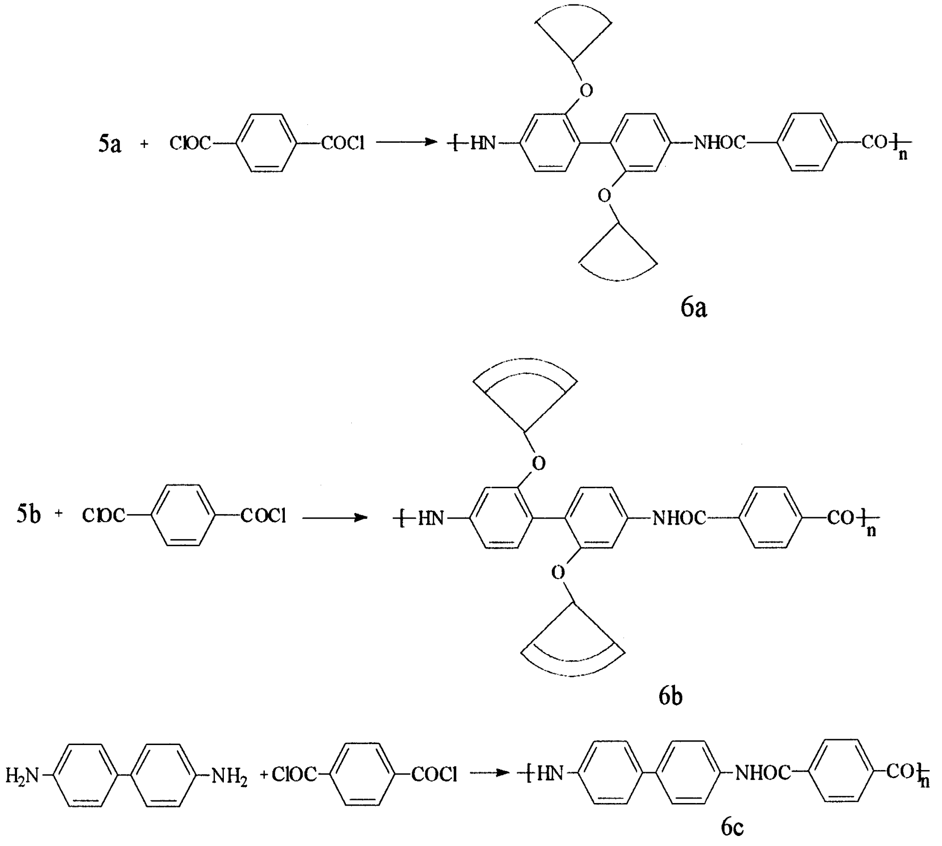
Polycondensation:

Typical procedure: To a three-necked flask fitted with a nitrogen inlet and $CaCl_2$ drying tube was placed **5a** or **5b** (0.2mmol) and N, N-dimethylacetamide (1.7ml). The solution was cooled with ice bath for 15min, then powdered terephthaloyl chloride (0.2mmol) was added with rapid stirring. The ice bath was removed after 30min and the reaction was continued for another 10-24 hours at room temperature. The polymer was isolated by precipitation, 6a in ether and 6b in methanol. Both 6a and 6b are yellowish solids after dried under vacuum.

Dendritic polyamide **6a**: Yield 80%. ^{1}H-NMR(DMF-d7): 0.92(m, 18H), 1.5(m, 12H), 1.7(m, 12H), 3.85(m, 12H), 5.1(s, 4H), 6.65(s, 4H), 7.39~8.4(10H), 10.6(s, 1H). IR (KBr, cm^{-1}): 3320, 2860, 2920, 2960, 1650, 1580, 1520, 1500, 1430, 1320, 1230, 1100, 1010.

Dendritic polyamide **6b**: Yield 90%. ^{1}H-NMR(CDCl$_3$): 0.9(m, 54H), 1.4(m, 36H), 1.7(m, 36H), 3.82(m, 36H), 4.9(m, 16H), 6.58(d, 16H), 7.6, 7.8, 8.2, 8.54(10H). IR (KBr, cm^{-1}): 3400, 2950, 2920, 2860, 1650, 1590, 1500, 1430, 1330, 1230, 1100, 1010.

Scheme 2:



Results and Discussion

Hybrid dendritic-linear copolymers have been referred to as architectural copolymers derived from a combination of linear and dendritic macromolecular architectures (21). Rodlike, cylindrical dendrimers were formed generally by two approaches, either through the dendronization of polymeric backbones with functional groups to which dendritic fragments can be attached or by the polymerization of reactive dendrons. We chose the second route in order to synthesize novel polyamides bearing precisely pendant dendritic fragments considering the difficulties to have the polymer backbones completely reacted by the first route. Dinitro biphenyl compounds **4a** and **4b** were chosen as the monomers carrying dendritic blocks since it has been reported that a monomer bearing two dendritic fragments per benzene ring reduced the coupling rate and favor side reactions (22). The coupling reaction of compound 3 and G1-CH$_2$Cl or G2-CH$_2$Cl is different from the well-known C-alkylation of phenol. It was found that potassium carbonate/ potassium iodide/acetone was the only reaction media resulted in good yield and potassium carbonate/acetone, potassium carbonate/DMF or potassium carbonate/potassium iodide/DMF were all failed. The possible explanation might be come from the catalytical function of iodide anion. Benzyl chloride is not such an active group that it can not be easily replaced directly by the phenoxy anion, but it can be substituted by iodide anion in the presence of potassium iodide to yield benzyl iodide as an intermediate, which was then readily replaced by phenoxy anion. The major side product is the one with only one phenol group replaced and the other left unreacted as potassium salt, which can be easily removed by washing with water. The product can be easily dissolved in most solvents such as hexane, petroleum ether, ether, ethyl acetate, acetone, benzene, etc.

The reduction of dinitro biphenyl compound **4a** and **4b** leads to the polymerizable diamine compounds **5a** and **5b**. The reduction was firstly tried by Fe powder under acidic condition but side reactions made the purification process too tedious and difficult, which may be attributed to the possible cleavage of the benzyloxy groups of **4a** and **4b** by acids. We then decided to select basic or neutral conditions but the reductions by zinc powder in the presence of NaOH or by polysodiumsulfide all failed. Finally the reaction succeeded via zinc powder with $CaCl_2$ in the mixture of ethanol and water. During the reduction, there accompanied still a side reaction that caused it difficult to separate the main product from the mixture so the yield was relatively low. Both compound **5a** and **5b** are viscous yellow liquid. They are soluble in most solvents such as acetone, alcohol, ether, ethyl acetate, hexane and scarcely in methanol.

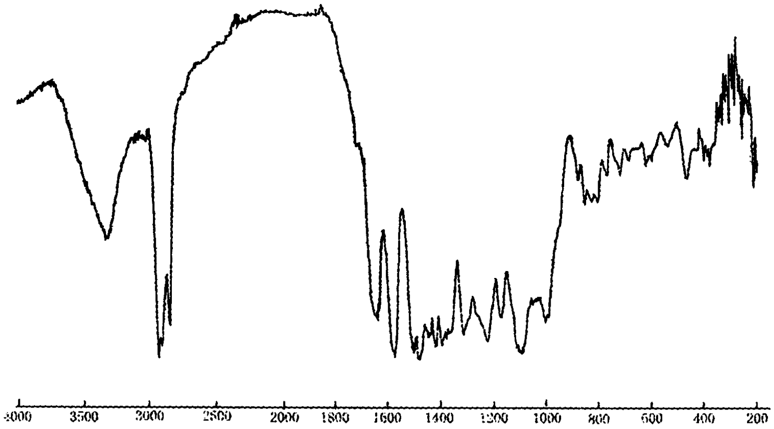
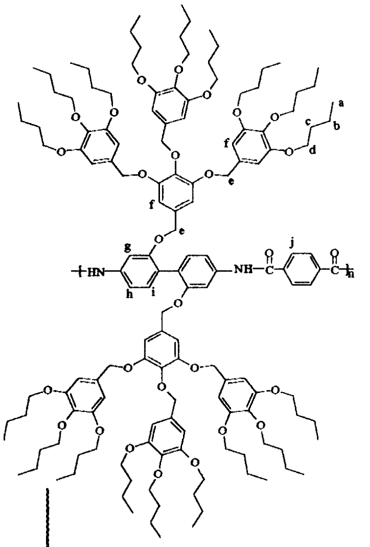


Fig.1 IR spectra of polyamide **6b**



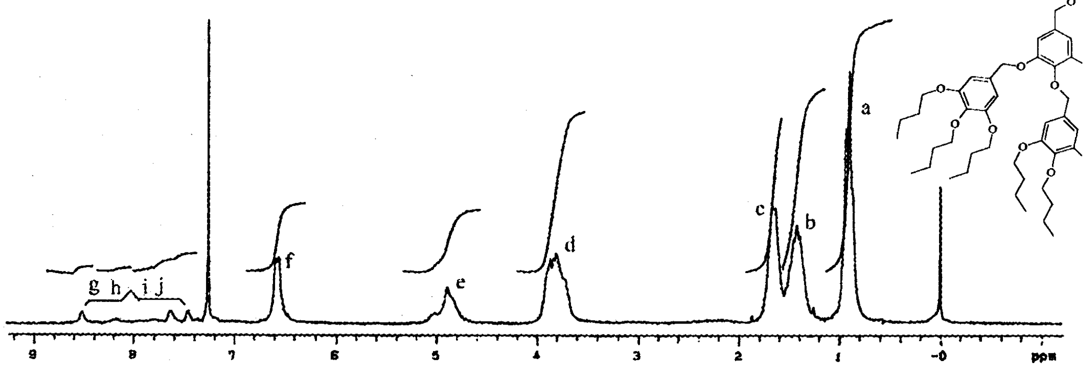


Fig.2 ^{1}H-NMR($CDCl_3$) spectra of polyamide **6b**

The polycondensations were conducted by the low-temperature solution method (scheme 2) using stoichiometric amounts of dendritic biphenyldiamine **5a** or **5b** with terephthaloyl chloride. These exothermic polymerizations were carried out at 0°C, then were allowed to slowly warm to room temperature and the stirring was continued for 10-24 hours. Polycondensation of biphenyldiamine with terephthaloyl chloride (Polyamide **6c**) was also carried out for comparison. Polyamides **6a** and **6b** remained dissolved in the solvents all along the reaction while polyamide **6c** precipitated from the solvent very quickly. The polyamide **6a** was recovered from the reaction mixture by precipitating in ether, the polyamide **6b** in methanol and the yields are high.

The structures of all polymers are basically characterized by IR and ^{1}H-NMR spectra. The assignments for the pendant dendritic fragments of the polyamides are consistent with the monomers. IR spectra of all aramides (polyamide **6b** in Fig. 1 as an example) showed characteristic absorption at 3300-3400 cm^{-1} (NH stretching), 1650-1660 cm^{-1} (amide I band, C=O stretching), around 1580 cm^{-1} (amide II band, interaction of NH bending) and 1320-1330 cm^{-1} (aromatic CN stretching), which confirmed the amide structure. Also ^{1}H-NMR spectra (polyamide **6b** in Fig.2 as an example) were all in good agreement with corresponding aramide structures.

Table.1 Solubilities of dendritic polyamides

	polymer	6a	6b	6c
	η(dl/g)[a]	0.88	0.16	
Solubility	DMF	+	+	+-
	DMA	+	+	+-
	ether	-	+	-
	chloroform	-	+	-
	acetone	-	+	-
	hexane	-	+	-
	ethyl acetate	-	+	-
	THF	-	+	-
	Petroleum ether	-	+	-

Note: + soluble; - insoluble ; +- partially soluble

[a] Inherent viscosity was measured in an Ostwald viscometer in DMA at 30℃

The inherent viscosities of the polyamides **6a** and **6b** ranged from 0.15-0.90 dl/g (Table 1) but **6c** was not measured due to its bad solubility in DMA. It has been noted that the relationship between the viscosities of dendrimers and their molecular weights differs from that of linear polymers (10, 11). Even GPC data could not indicate the real molecular weights of hybrid dendritic-linear copolymers since it is not reasonable to assume that PS is a good reference for these copolymers (24). So it is difficult to predict the molecular weights based on our results reported here. The Solubilities of these novel dendritic polyamides are much improved compared with normal aramides. Polyamide **6a** (with the first generation dendritic blocks) is soluble in DMF and DMA while polyamide **6b** (with the second-generation dendritic blocks) can be dissolved in most organic solvents even in hexane and petroleum ether. It is assumed that cylindrical architectures are formed by these precisely pendant dendritic fragments wrapped on the rigid backbone of the polyamides and decreased the formation of the hydrogen bonds among the polymer chains, which contributes to the improved solubility of these novel polyamides. Further studies on the thermal properties of these novel polyamides are in progress.

Acknowledgments

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