Macromolecules **2000,** *33,* 4639−4646

Hyperbranched Polyimides for Gas Separation Applications. 1. Synthesis and Characterization

Jianhua Fang, Hidetoshi Kita, and Ken-ichi Okamoto*

Department of Advanced Materials Science & Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan

Received December 21, 1999; Revised Manuscript Received April 4, 2000

ABSTRACT: A series of wholly aromatic hyperbranched polyimides were successfully prepared by condensation polymerization of a triamine monomer, tris(4-aminophenyl)amine (TAPA), and a series of commercially available dianhydride monomers such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), and pyromellitic anhydride (PMDA). The synthesis involves the formation of hyperbranched polyamic acid precursors in the first step and the thermal or chemical imidization in the subsequent step, which is similar to the conventional two-step method for the synthesis of linear polyimides. Different monomer addition orders resulted in different hyperbranched polymers even if the same kinds of monomers but different molar ratios were used. When a dianhydride solution was added to the TAPA solution (manner 1), an amine-terminated hyperbranched polyimide was obtained, whereas the addition of TAPA solution to a dianhydride solution (manner 2) yielded an anhydride-terminated hyperbranched polyimide. The appropriate molar ratios of TAPA to a dianhydride are 1:1 for manner 1 and 1:2 for manner 2. From ^{1}H NMR spectra the branching degrees of the amine-terminated hyperbranched polyimides were estimated to be 0.64, 0.72, and 0.68 for 6FDA−TAPA, DSDA−TAPA, and PMDA−TAPA, respectively. All the anhydride-terminated polyimides were found wholly branched. Gel permeation chromatography (GPC) measurement revealed that both the amine-terminated and anhydride-terminated 6FDA−TAPA polyimides had moderate number-averaged molecular weights, but the latter had very broad molecular weight distribution.

Introduction

Dendritic polymers have received increasing attention in recent years because they are expected to have unique properties when compared to their linear analogues. The highly branched structure and a large number of terminal functional groups are two important structural features of dendritic polymers, which clearly distinguish them from linear (nonbranching) polymers. Dendrimers are perfectly branched and monodispered macromolecules. The synthesis of a dendrimer involves multistep procedures (i.e., protection, coupling, and deprotection cycles), leading to high cost and difficulty in large-scale preparation. Hyperbranched polymers do not have the well-defined (perfect) architectures as dendrimers, and they are generally comprised of three parts: linear (L), dendritic (D), and terminal (T) units. Nevertheless, hyperbranched polymers are thought to have similar physical properties to dendrimers and can be used to replace dendrimers for most cases.[1] Since hyperbranched polymer can be simply prepared by direct “one-step” polymerization of multifunctional monomers, they are of more significance than dendrimers from the viewpoint of industrial applications.

Many hyperbranched polymers have been synthesized such as polyphenylene,[2] poly(ether ketone),[3] poly(4-chloromethylstyrene),[4] *m*-polyaniline,[5] polycarbonate,[6] polyesters,[7] aromatic polyamides,[8] and so on. However, very few papers deal with the synthesis of hyperbranched aromatic polyimides. It is well-known that aromatic polyimides represent an important class of high-performance polymeric materials because of their many outstanding key properties such as high mechanical strength, high modulus, unusual thermoxidative stability, excellent electrical properties, and superior chemical resistance. Because of these merits, polyimides have found wide applications in high-temperature adhesive, photoresist, nonlinear optical material, Langmuir−Blodgett (L−B) film, and membrane separation. The development of hyperbranched polyimides may extend our understandings on the “structure−property” relationship.

Polyimides have also been identified as the high-performance membrane materials for gas separations.[9−14] The high gas permeability of polyimides is generally attributed to the large fractional free volume which is closely related to their highly rigid structure, while the high selectivity is due to the high diffusion selectivity and/or the high solubility selectivity. On the other hand, it is reported that there are many open and accessible cavities (typically several angstroms in size) in a rigid hyperbranched polymer, which are formed due to the periphery of neighboring branches.[1,2] Thus, we can imagine that these cavities may function as the pathways for the transport of gas molecules. On the basis of these considerations, we tried to develop a series of wholly aromatic hyperbranched polyimides for gas separations.

Hyperbranched polymers are typically prepared by self-condensation reaction of AB$_2$-type monomers. Here, A and B represent two kinds of functional groups which can react with each other but cannot undergo self-reaction. Linear polyimides are generally prepared by polymerization of dianhydride and diamine monomers. However, one cannot expect to synthesize a hyperbranched polyimide simply from a monomer containing one anhydride and two amine groups (or one amine and two anhydride groups) because such a kind of AB$_2$-type

---

* To whom correspondence should be addressed.

10.1021/ma9921293 CCC: $19.00

monomer seems unavailable due to the too high reactivities of anhydride and amine groups. To solve this problem, one approach is to preincorporate imide ring to a trifunctional monomer. Harrison and Feast reported the synthesis of a type of hyperbranched polyimides from a series of AB_2 monomers containing a cyclopentadienone ring (A) and two maleimide groups (B_2) via Diels−Alder reaction.[15] Kricheldorf et al. synthesized a poly(ester imide) from a trifunctional imide monomer.[16] Maier et al. synthesized a heterocyclic polyimide from a monomer containing a maleimide group (A) and an azine group (B_2) through a crisscross cycloaddition polymerization.[17] However, strictly speaking, these polymers are not wholly aromatic hyperbranched polyimides. On the other hand, hyperbranched polymers can also be prepared from ($A_2 + B_3$)-type monomers.[8c,18] In this paper, we report our attempts on the synthesis of a series of wholly aromatic hyperbranched polyimides by polymerization of commercially available dianhydrides (A_2) and a triamine monomer, tris(4-aminophenyl)amine (B_3). Film formation and gas permeation properties of these hyperbranched polyimides will be reported in a subsequent paper.

Experimental Section

Materials. Tris(4-nitrophenyl)amine was purchased from Aldrich and was used as received. Phthalic anhydride (PTA), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), and pyromellitic anhydride (PMDA) were purified by sublimation in vacuo before use. *N*,*N*-Dimethylacetamide (DMAc) was distilled under reduced pressure and dehydrated with 4 A molecular sieves. 1,4-Dioxane was used without further purification.

Measurements. Infrared (IR) spectra were recorded on a Horiba FT-200 spectrometer, in 50 scans at a resolution of 4 wavenumbers, as KBr pellets. ^1H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. Inherent viscosity was measured in DMAc at 35 °C with an Ubbelohde viscometer. Differential scanning calorimetry (DSC) was performed with a Seiko DSC-5200 at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) was performed with a HLC-8020 apparatus using a Shodex KD-80M column. The eluant was NMP with a flow rate of 1.0 mL/min. Polymer solutions in NMP were filtered through a 0.5 μm PTFE filter before injected into the column. Molecular weights were calculated against poly(ethylene oxide) standards. Thermogravimetric analysis (TGA) of the polymers was obtained in nitrogen with a TA 7000 thermogravimetric analyzer at a heating rate of 10 °C/min.

Synthesis of Tris(4-aminophenyl)amine (TAPA). In a 1000 mL four-neck flask a suspension of 15.2 g (0.4 mmol) of tris(4-nitrophenyl)amine and 1.0 g of Pd/C (10 wt %) in 720 mL of dioxane/ethanol (2/1) was heated to reflux under nitrogen atmosphere. Then 80 mL of hydrazine monohydrate was added dropwise over 5 h. After the addition was completed, the reaction mixture was further refluxed for 20 h. After cooling to room temperature the mixture was filtered, and the filtrate was poured into 4 L of water. The precipitate was collected by filtration and dried in vacuo (10.2 g, 89%). The crude product was recrystallized from ethanol to give gray, shiny crystals; mp 246 °C (241−244 °C, lit.[19]). ^1H NMR (DMSO-d_6), δ (ppm): 6.58 (6H, ArH), 6.43 (6H, ArH), 4.72 (6H, NH_2). IR (KBr, cm^{-1}): 3406, 3336, 1618, 1502, 1331, 1261, 1117, 829.

Synthesis of Model Compound 1. In a 100 mL thoroughly dried four-neck flask 0.290 g (1.0 mmol) of TAPA was dissolved in 3 mL of DMAc with magnetic stirring under N_2 flow. To this solution was added dropwise 0.148 g (1.0 mmol) of phthalic anhydride (PTA) in 2 mL of DMAc through a syringe over 0.5 h. The reaction mixture was further stirred at room temperature for 2 h. Then 10 mL of *m*-xylene was added, and the mixture was heated to reflux for 5 h with a Dean-Stark apparatus. After cooling to room temperature, the solution was poured into water, and the precipitate was washed with water and methanol successively and dried in vacuo. A 0.24 g sample of crude product was obtained. It was purified by column chromatography with silica gel using the mixture of ethanol/cyclohexane (1/2, by volume) as the eluant. ^1H NMR (DMSO-d_6), δ (ppm): 7.95−7.86 (4H, ArH of phthalic anhydride residues), 7.08 (2H at position a, $J = 8.9$ Hz), 6.89 (4H at position c, $J = 8.6$ Hz), 6.63 (2H at position b, $J = 8.9$ Hz), 6.58 (4H at position d, $J = 8.6$ Hz), 5.04 (4H, NH_2).

Synthesis of Model Compound 2. The above procedure for the synthesis of model compound **1** was followed except that 0.296 g (2.0 mmol) of PTA was used; the final reaction solution was poured into methanol, and the precipitate was washed with methanol. A 0.32 g sample of crude product was obtained. It was also purified by column chromatography, and the mixture of ethanol/cyclohexane (1/3) was used as the eluant. ^1H NMR (DMSO-d_6), δ (ppm): 7.98−7.88 (4H, ArH of phthalic anhydride residues), 7.31 (d, 4H at position a, $J = 8.6$ Hz), 7.09 (d, 4H at position b, $J = 8.9$ Hz), 6.95 (d, 2H at position c, $J = 8.5$ Hz), 6.65 (d, 2H at position d, $J = 8.5$ Hz), 5.20 (2H, NH_2).

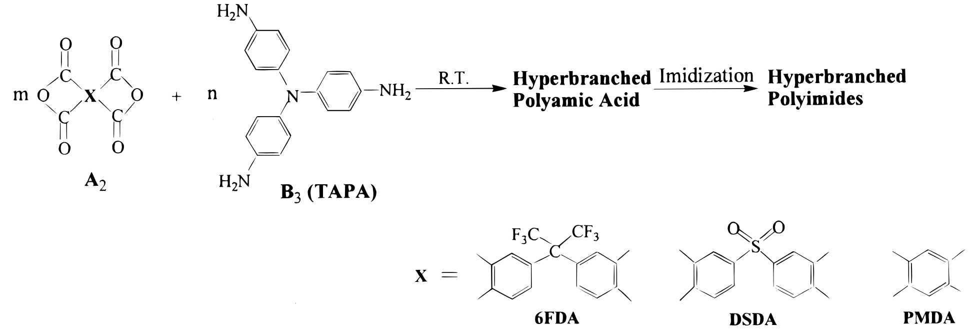
Synthesis of Model Compound 3. To a 100 mL thoroughly dried four-neck flask were charged 0.290 g (1.0 mmol) of TAPA and 5 mL of DMAc under N_2 flow. The contents were magnetically stirred at room temperature. To this solution, 0.467 g (3.15 mmol) of phthalic anhydride (PTA) was added in one portion. The reaction mixture was stirred overnight. Next day 10 mL of *m*-xylene was added, and the mixture was heated to reflux for 5 h with a Dean-Stark apparatus. After cooling to room temperature, the mixture was filtered, and the yellow solid product was washed with methanol and dried in vacuo.

Synthesis of Amine-Terminated Hyperbranched Polyimides (Manner 1). A 1.5 mmol aliquot of TAPA was dissolved in 10 mL of DMAc in a 100 mL thoroughly dried four-neck flask under N_2 flow. The contents were stirred with a magnetic stirring bar at room temperature, and 1.5 mmol of dianhydride (6FDA, DSDA, and PMDA) in 5 mL of DMAc was added dropwise through a syringe over 1.5 h. After the addition was finished, the reaction mixture was further stirred for 3 h. Then 10 mL of *m*-xylene was added, and the mixture was heated to 160 °C for 5 h with a Dean-Stark apparatus. After cooling to room temperature, the mixture was poured into methanol (for 6FDA−TAPA) or directly filtered (for DSDA−TAPA and PMDA−TAPA). The precipitate was washed with methanol and dried in vacuo.

Synthesis of Anhydride-Terminated Hyperbranched Polyimides (Manner 2). In a 100 mL thoroughly dried four-neck flask 1.0 mmol of dianhydride (6FDA, DSDA, PMDA) was dissolved in 10 mL of DMAc under N_2 flow. The mixture was stirred with a magnetic stirring bar at room temperature. A 0.5 mmol aliquot of TAPA in 10 mL of DMAc solution was added dropwise through a syringe over a period of 2 h. After the complete addition of TAPA solution, the reaction mixture was further stirred for 3 h. Then a mixture of 1.0 g of triethylamine and 3.0 g of acetic anhydride was added, and the reaction mixture was stirred at room temperature and 60 °C for 3 and 5 h, respectively. After cooling to room temperature, the mixture was poured into water (for 6FDA−TAPA) or directly filtered (for DSDA−TAPA and PMDA−TAPA), and the precipitate was dried in vacuo.

Chemical Modification. The 6FDA-based polyamic acid precursors prepared by the same procedures and scales as described above were used for chemical modification. That is, to the polyamic acid solution prepared by manner 1 was added the mixture of 1.5 g of triethylamine and 4.5 g of acetic anhydride, and the solution mixture was stirred at room temperature and 60 °C for 3 and 5 h, respectively. After cooling to room temperature, the mixture was poured into methanol,

Scheme 1



m / n = 1 / 1 (when a dianhydride was added to TAPA solution)
2 / 1 (when TAPA was added to a dianhydride solution)

and the precipitate was dried in vacuo. In the case of the polyamic acid solution prepared by manner 2, 0.056 g (0.6 mmol) of aniline was added, and the reaction mixture was stirred at room temperature for 5 h. Then the mixture of 1.0 g of triethylamine and 3.0 g of acetic anhydride was added, and the solution mixture was stirred at room temperature and 60 °C for 3 and 5 h, respectively. After cooling to room temperature, the mixture was poured into methanol, and the precipitate was dried in vacuo.

Results and Discussion

Polymerization. Hyperbranched polymers are generally prepared from AB_2-type monomers. However, for synthesizing hyperbranched polyimides, we cannot simply start from a monomer containing one anhydride and two amine groups (or one amine and two anhydride groups) because, as mentioned in the Introduction, anhydride and amine groups are too reactive to exist in the same molecule independently. The copolymerization of A_2 and B_3 monomers is an alternative but relatively less developed method. By the use of this method, Frechet et al. have succeeded in preparing hyperbranched aliphatic polyethers using a diepoxy compound as the A_2 monomer and a trihydroxy compound as the B_3 monomer.[18a] Jikei et al. have succeeded in preparing a hyperbranched aromatic polyamide from *p*-phenylenediamine (A_2) and trimesic acid (B_3).[8c] No cross-linking occurred when the monomer concentrations were controlled. In this paper we use commercially available dianhydrides (6FDA, DSDA, and PMDA) as A_2 and a triamine, TAPA, as B_3 to synthesize a series of hyperbranched polyimides. The synthesis involves two steps as shown in Scheme 1. The dianhydrides and TAPA were condensation polymerized in DMAc to form hyperbranched polyamic acid precursors, and subsequently the precursors were thermally or chemically converted to the final hyperbranched polyimides.

The polymerization was affected by many factors such as monomer addition, monomer molar ratio, and concentrations. Two kinds of monomer addition orders, named manner 1 and manner 2, were employed for the condensation polymerization of dianhydrides and TAPA. Manner 1 refers to the addition of a dianhydride solution to TAPA solution in DMAc, while manner 2 is the reverse order. In each case, the monomer should be added so slowly that the concentration of dianhydride (manner 1) or TAPA (manner 2) approached zero to avoid any high local concentration. When monomer solids were directly added or even if the addition of monomer solution was not slow enough, gelation occurred immediately. Figure 1 shows a diagram of the polymer chain propagation processes. In the case of manner 1, initially once the dianhydride was added, it would react with TAPA immediately, and one dianhydride molecule could react with two TAPA molecules. With the addition of dianhydride monomer, more TAPA molecules and subsequently low molecular weight oligomer molecules would be reacted. It can be deduced that n number of dianhydride molecules can react with $(n + 1)$ number of TAPA molecules. When molecular weight grew large enough, the numbers of the reacted dianhydride and TAPA approached being equal. Therefore, the appropriate molar ratio between the dianhydride and TAPA is 1:1, and correspondingly, the molar ratio between anhydride and amine groups of the monomers is 2/3. As a result, no free anhydride groups exist in the polymers, and these polymers are amine-terminated. Any use of excess dianhydride will cause insoluble gel. Figure 2 shows the chemical structure (schematic) of the obtained amine-terminated hyperbranched polyimides using 6FDA−TAPA as an example. On the other hand, for manner 2, initially once a TAPA molecule was added, three dianhydride molecules would be reacted immediately. With the addition of TAPA, more dianhydride molecules and then the low molecular weight oligomer molecules (anhydride-terminated) would be reacted. It can also be deduced that $(3^n - 1)/2$ number of TAPA is required for the condensation reaction with 3^n number of dianhydride molecules, and therefore the appropriate molar ratio between the dianhydride and TAPA is 2:1 (the molar ratio between anhydride and amine groups in the monomers: 4/3). The obtained polymers are thus anhydride-terminated, and their chemical structure (schematic) is shown in Figure 3 using 6FDA−TAPA as an example. Just as in the case of manner 1, any use of excess TAPA will lead to gelation immediately. This clearly indicates that, although the same kinds of monomers were used, different hyperbranched polymers could be obtained by controlling monomer addition order. However, the polymerization of AB_2-type monomers can only form B-terminated hyperbranched polymers.

Monomer concentration is another important factor. It was found that the total solid content should be kept below 0.2 mol/L for manner 1 and 0.075 mol/L for manner 2, respectively. Higher concentration will lead to insoluble gel.

To protect the terminal functional groups, different imidization methods were employed for these two types of polyamic acid precursors. The amine-terminated polyamic acids were thermally imidized in solution in the presence of xylene (azeotrope for the removal of water), while the anhydride-terminated ones were

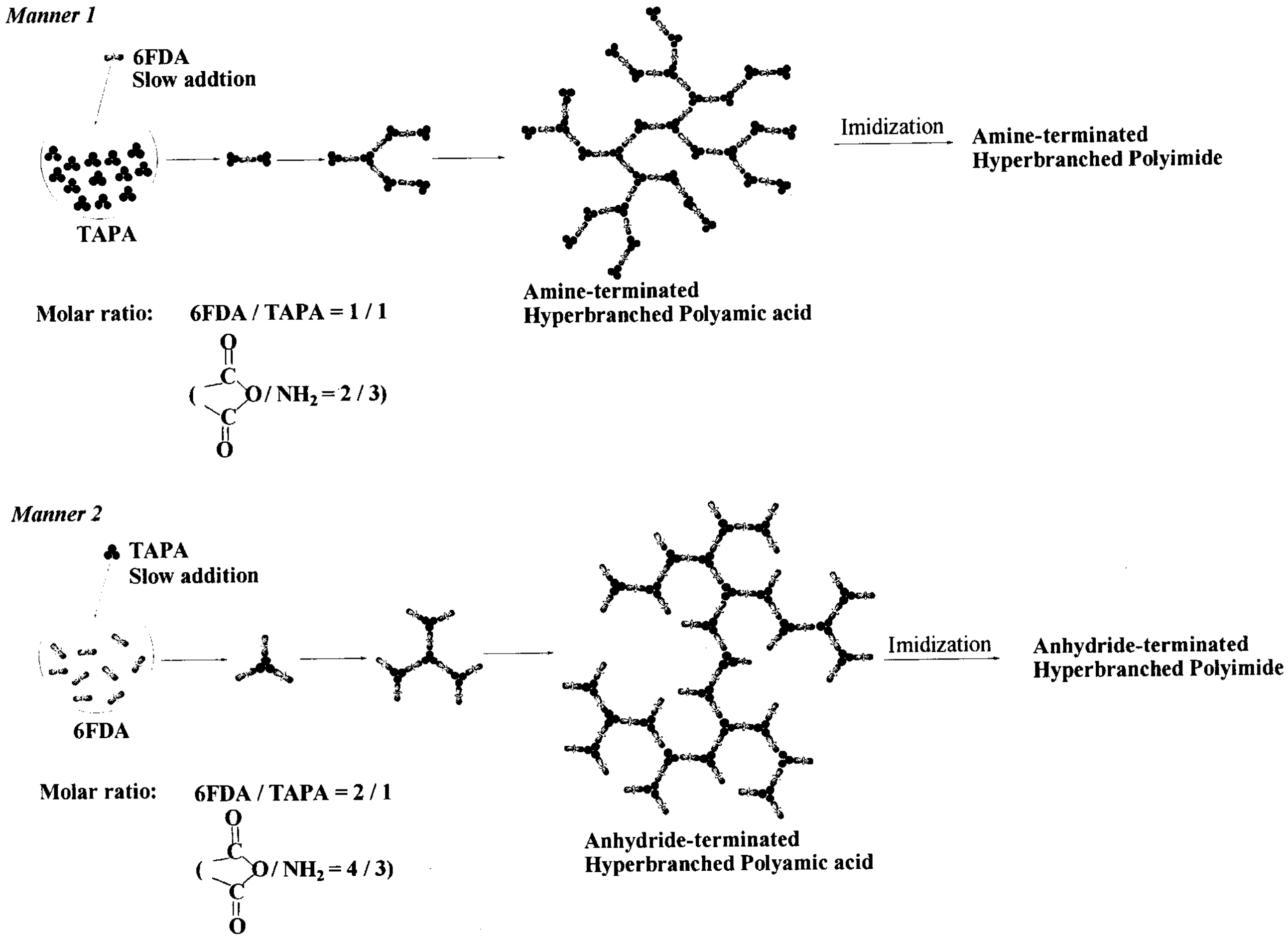


Figure 1. Polymerization of dianhydrides and TAPA by different monomer addition manner.

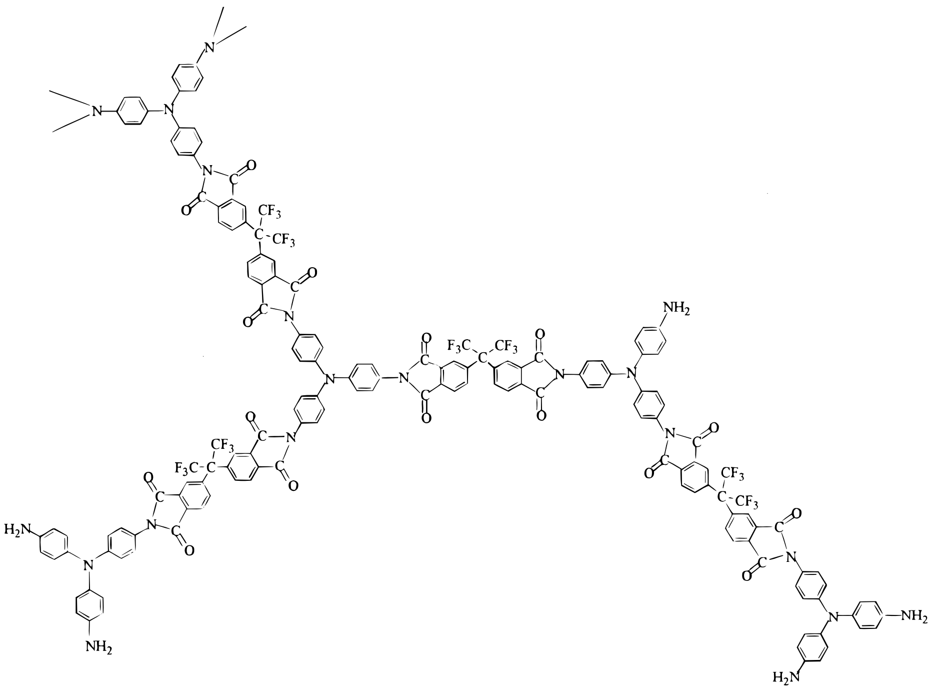


Figure 2. Chemical structure of the amine-terminated 6FDA–TAPA hyperbranched polyimide.

chemically converted to polyimides using the mixture of excess acetic anhydride and triethylamine. IR spectra confirmed that complete imidization was achieved for all the polyimides. Figure 4 shows the IR spectra of both amine-terminated and anhydride-terminated 6FDA–TAPA polyimides. The bands around 1784 (1786) cm^{-1} (C=O asymmetrical stretching), 1720 (1722) cm^{-1} (C=O symmetrical stretching), 1377 cm^{-1} (C–N stretching), and 721 cm^{-1} (C=O bending) are the characteristic absorption bands of polyimide. However, no character-

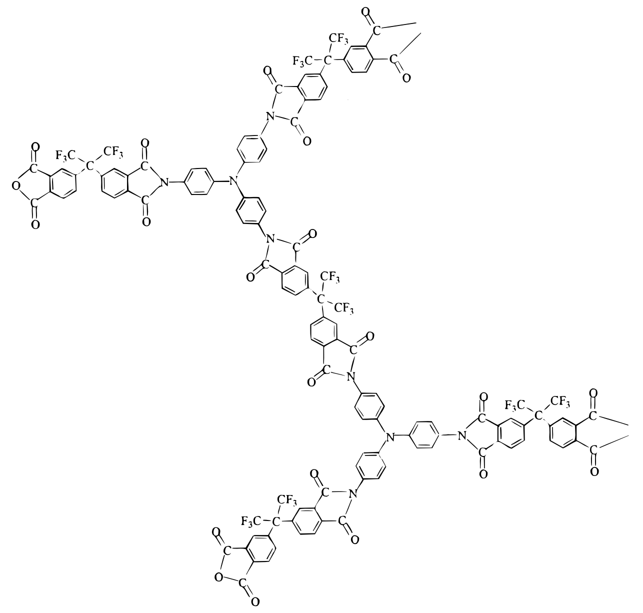


Figure 3. Chemical structure of the anhydride-terminated 6FDA−TAPA hyperbranched polyimide.

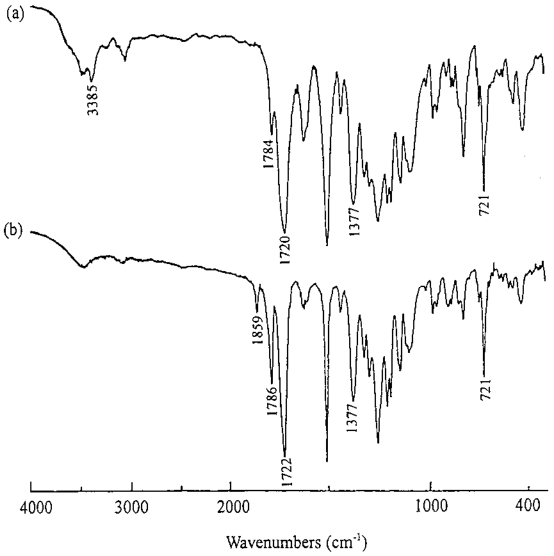


Figure 4. IR spectra of 6FDA−TAPA hyperbranched polyimides: (a) amine-terminated; (b) anhydride-terminated.

istic band of polyamic acid (around 1680 cm^{-1}) was found. In addition, the bands around 3385 and 1859 cm^{-1} are attributed to the stretching of N−H of terminal amine groups in the amine-terminated 6FDA−TAPA and the stretching of C=O of the terminal anhydride groups in the anhydride-terminated 6FDA−TAPA, respectively.

Characterization. The structural perfection of hyperbranched polymers is generally characterized by the degree of branching (DB), which is defined by Frechet as follows:[20]

$$DB = (D + T)/(D + T + L) \qquad (1)$$

where D, T, and L refer to the numbers of dendritic, terminal, and linear units in the polymer, respectively. Experimentally, DB is usually determined from ^1H NMR or ^{13}C NMR spectroscopy by comparing the integration of the peaks for the respective units in the hyperbranched polymers.[20] Figure 5 shows the ^1H NMR spectra of the amine-terminated and anhydride-terminated 6FDA−TAPA polyimides in DMSO-d_6. For the amine-terminated polyimide, the peaks in the range 8.14−7.74 ppm are assigned to the hydrogens of 6FDA residues, while the peaks in the range 7.42−6.58 ppm correspond to the hydrogens in the phenyl rings of TAPA residues which contain the information on degree of branching. The broad peak at 5.48 ppm is attributed to the hydrogens of the free amine groups in terminal and linear units. To make clear the detailed assignment of the peaks in the range 7.42−6.58 ppm, three kinds of model compounds were synthesized from PTA and TAPA as shown in Scheme 2. The TAPA residues in model compounds **1**, **2**, and **3** are similar to the counterparts in terminal, linear, and dendritic units of the hyperbranched polyimide, respectively. For comparison purpose, their ^1H NMR spectra except **3** are also shown in Figure 5. The ^1H NMR spectrum of compound **3** was not obtained because of its insolubility in common organic solvents. Nevertheless, the assignment of the peaks in the range 7.42−6.58 ppm of the amine-terminated 6FDA−TAPA polyimide can still be achieved by comparison to the ^1H NMR spectra of model compounds **1** and **2** as well as that for the anhydride-terminated 6FDA−TAPA polyimide. Compound **1** has four distinct peaks at 7.08 (**H**a), 6.89 (**H**c), 6.63 (**H**b), and 6.58 ppm (**H**d). Compound **2** also has four distinct peaks but with different chemical shifts at 7.31 (**H**a), 7.09 (**H**b), 6.95 (**H**c), and 6.65 ppm (**H**d). It is obvious that for the amine-terminated 6FDA−TAPA polyimide the peaks around 7.08, 6.89, and 6.58 ppm should be attributed to both terminal and linear units (peaks in this region are overlapped). The peak around 7.27 ppm should be independent of the terminal units but be related to the linear ones, while the peak around 7.42 ppm is related to neither terminal units nor linear ones. Note that these two peaks (7.42 and 7.27 ppm) also appeared in the ^1H NMR spectrum of the anhydride-terminated 6FDA−TAPA polyimide. For the anhydride-terminated 6FDA−TAPA polyimide, no peak corresponding to amine hydrogens was observed, indicating that no free amine groups existed in the polymer. Furthermore, since only two distinct peaks corresponding to TAPA residues were observed (7.42 and 7.25 ppm); i.e., there were only two kinds of hydrogen in the phenyl rings of TAPA residues. Peaks in the range 8.17−7.70 ppm are due to the hydrogens of 6FDA residues, of which the chemical shifts are similar to those of the amine-terminated 6FDA−TAPA polyimide. Therefore, for the amine-terminated 6FDA−TAPA polyimide, the peak at 7.42 ppm should be ascribed to the dendritic part only, and the peak at 7.27 ppm is attributed to both dendritic and linear parts (overlapped). According to eq 1, the DB is thus estimated to be 0.64. For the anhydride-terminated 6FDA−TAPA polyimide, since all the amine groups of TAPA monomer have been reacted (i.e., TAPA residues are completely "dendritic") as mentioned above, the polyimide should have the "completely branched" structure (DB = 1). However, it should be noted that although the anhydride-terminated 6FDA−TAPA polyimide is "fully branched" with regard to TAPA units, the polymer is still less perfect in structure than common dendrimers due to the random polymerization process. Maier et al. have also observed such a phenomenon.[17] This indicates DB alone is sometimes not so sufficiently effective for the char-

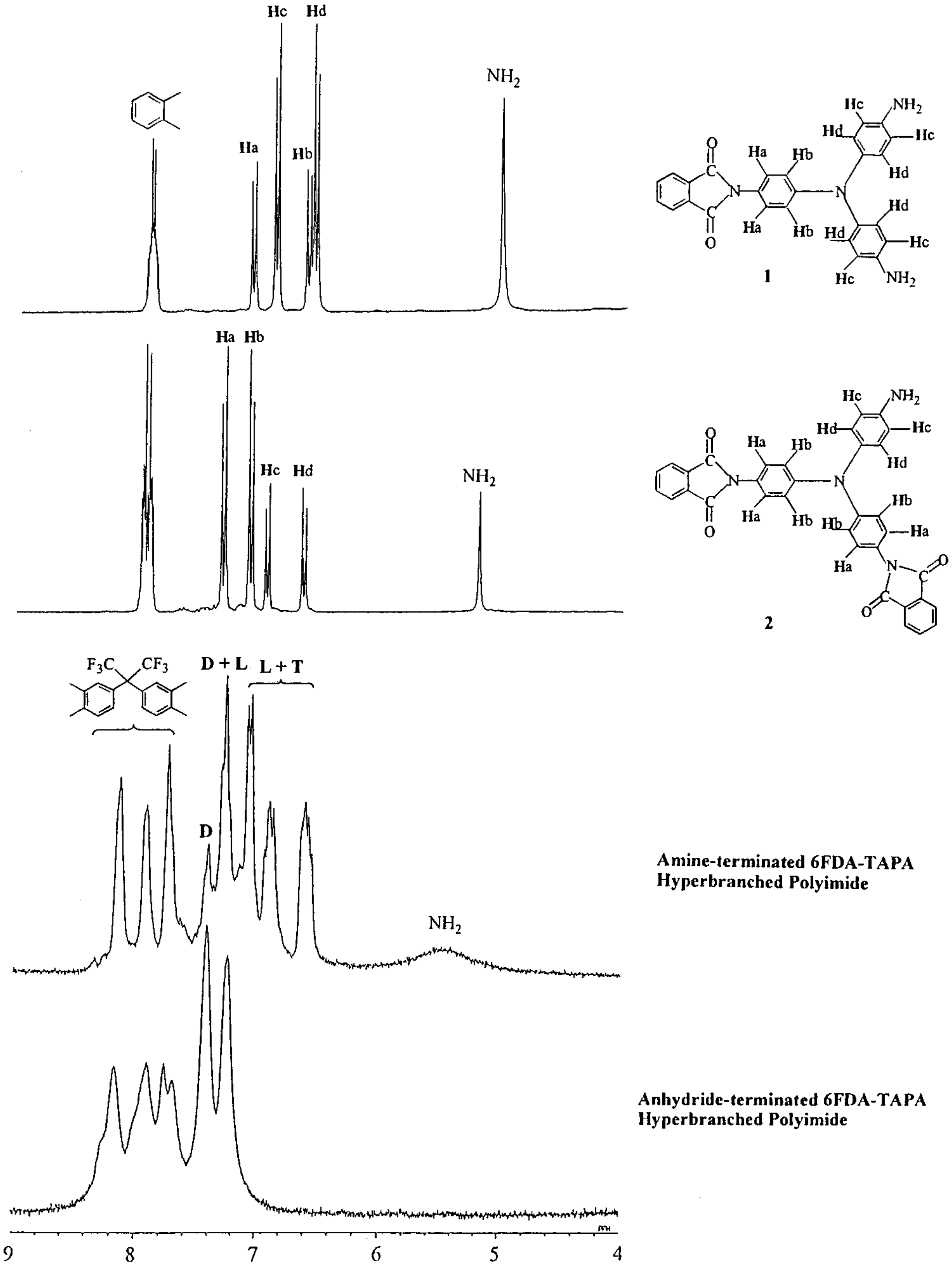


Figure 5. ^{1}H NMR spectra of model compounds and 6FDA–TAPA hyperbranched polyimides.

acterization of structural perfection of hyperbranched polymers.

For the amine-terminated DSDA–TAPA and PMDA–TAPA hyperbranched polyimides, their ^{1}H NMR spectra were not obtained due to the insolubility in common organic solvents. However, their polyamic acid precursors are soluble, and also there is no change in the degree of branching before and after imidization; the ^{1}H NMR spectra of these two precursors were measured. Using the same analyzing approach discussed above for the amine-terminated 6FDA–TAPA hyperbranched polyimide, the DB values were estimated to be 0.72 and 0.68 for DSDA–TAPA and PMDA–TAPA, respectively. The anhydride-terminated DSDA–TAPA and PMDA–TAPA hyperbranched polyimides also have the "fully branched" structures (DB = 1) just as in the case of the anhydride-terminated 6FDA–TAPA polyimide.

The solubility properties, inherent viscosity, and glass transition temperatures (T_g) of the prepared hyperbranched polyimides were investigated. 6FDA-based polyimides were found readily soluble in DMAc, 1-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO) and partially soluble in acetone, tetrahydrofran (THF), and 1,4-dioxane, but insoluble in benzene. DSDA- and PMDA-based polyimides were insoluble in all the tested solvents. This is similar to the case of their linear analogous polymers (6FDA-based linear polyimides are known for their excellent solubility in comparison to other polyimides). As shown in Table 1, the amine-terminated 6FDA–TAPA polyimide showed a moderate inherent viscosity (0.76 dL/g), whereas the inherent viscosity of the anhydride-terminated one was unusually high (1.92 dL/g), which greatly deviates from the fact that hyperbranched polymers generally have fairly low inherent viscosity (in comparison with their linear analogues). This is likely due to its high weight-averaged molecular weight (M_w = 150 000) as shown in Table 2. Although this polymer had only moderate number-averaged molecular weight (M_n = 8400), the molecular weight distribution was unusually broad (for

Scheme 2

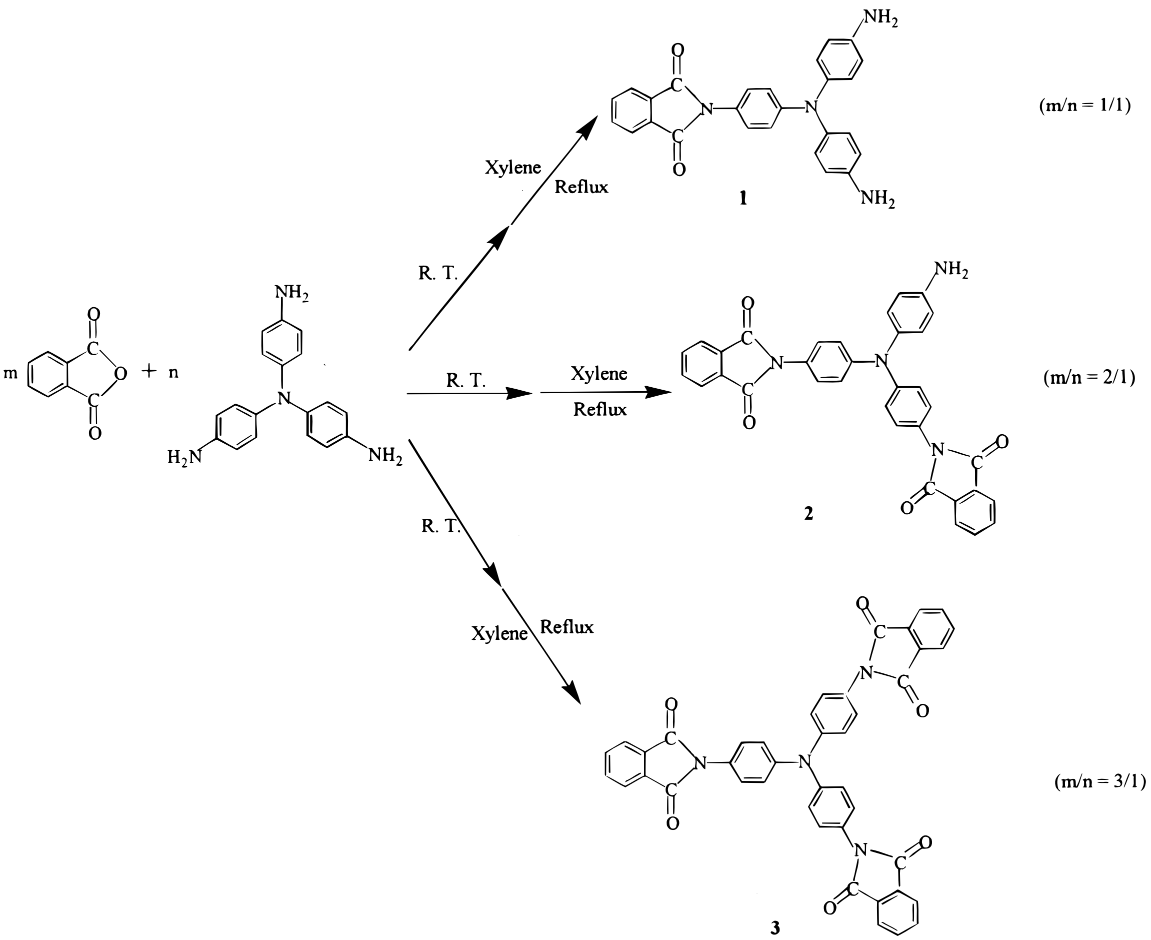


Table 1. Solubility, Inherent Viscosity, and Glass Transition Temperatures of the Prepared Hyperbranched Polyimides

polyimide		viscosity (dL/g)	T_g[a] (°C)	solubility in DMAc
6FDA–TAPA	amine-terminated	0.76	339	soluble
	anhydride-terminated	1.92	320	soluble
DSDA–TAPA	amine-terminated		312	insoluble
	anhydride-terminated		295	insoluble
PMDA–TAPA	amine-terminated		NM	insoluble
	anhydride-terminated		NM	insoluble

[a] NM = not measured.

Table 2. Molecular Weights of 6FDA-TAPA Hyperbranched Polyimides

polyimide	M_n	M_w	M_w/M_n
amine-terminated	6 400	37 000	5.8
anhydride-terminated	8 400	150 000	18
acetic anhydride-modified	12 000	77 000	6.4
aniline-modified	10 000	160 000	16

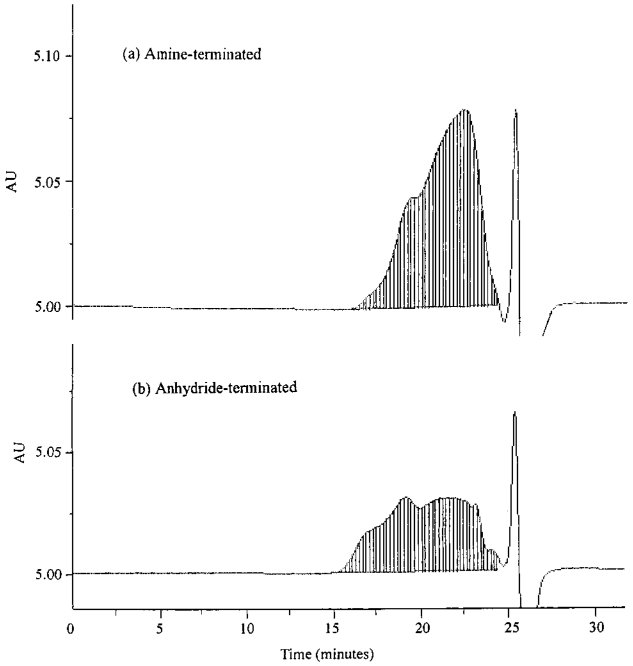


Figure 6. GPC traces of 6FDA–TAPA hyperbranched polyimides: (a) amine-terminated; (b) anhydride-terminated.

GPC traces see Figure 6), indicating that the polymer contains very high molecular weight series. The real molecular weight of the polymer may be even larger than the value estimated from poly(ethylene oxide) standards because dendritic macromolecules generally have smaller size than linear polymers with the same molecular weight and can hardly be expanded in solution. The unusual broad molecular weight distribution should be ascribed to the specific characteristics of the polymerization process of $A_2 + B_3$ monomers and the monomer addition manner. As discussed in the polymerization section, with the addition of TAPA to the reaction solution, initially three 6FDA molecules and/or then three anhydride end-capped low molecular weight oligomers were required to react with one TAPA molecule to form a larger polymer molecule. Since the growth of "polymer" molecules was completely random, a very broad molecular weight distribution was ob-

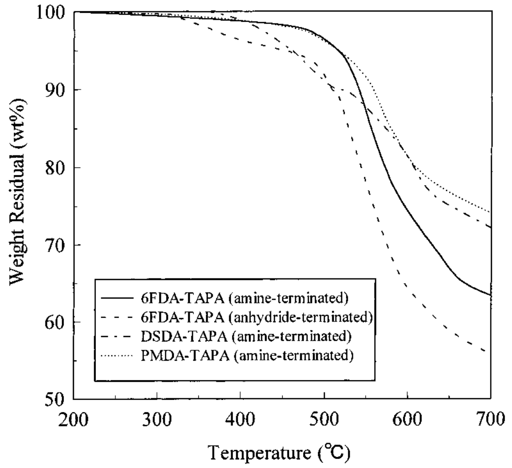


Figure 7. Thermogravimetric curves of hyperbranched polyimides in nitrogen.

tained. This turned more serious at the post stage of polymerization because the diffusion of the newly added TAPA molecules turned difficult due to the increased viscosity of the polymer solution. In the case of the amine-terminated 6FDA−TAPA polyimide, since the polymerization was achieved by the addition of 6FDA molecules to TAPA solution and with the addition of one 6FDA molecule only two TAPA or "polymer" molecules were consumed, the molecular weight distribution was more narrow than that of the anhydride-terminated one. To examine whether the terminal functional groups (amine or anhydride) had any effects on the measurement of molecular weight distribution, these two kinds of polyimides were chemically modified. That is, the amine-terminated 6FDA−TAPA polyimide was allowed to react with acetic anhydride to convert the terminal amino groups to acetamido groups and the anhydride-terminated 6FDA−TAPA polyimide to react with aniline to convert the terminal anhydride groups to imido groups. As shown in Table 2, it is clear that both of the chemically modified polyimides showed similar molecular weight distribution to their original ones, indicating that the results of molecular weight distribution determined by GPC are reliable.

From Table 1 we can also find that the anhydride-terminated polyimides display lower T_g than the corresponding amine-terminated ones. This is probably because the amine-terminated polymers have stronger macromolecular interaction resulting from the hydrogen bond between the terminal amine groups. The different branching structure is another possible reason.

The thermogravimeteric analysis (TGA) on the obtained hyperbranched polyimides was carried out as shown in Figure 7. It is obvious that the amine-terminated 6FDA−TAPA and PMDA−TAPA polyimides show fairly good thermal stability. The anhydride-terminated 6FDA−TAPA polyimide, however, is less thermally stable than the corresponding amine-terminated one. This is likely related to the differences in terminal functional groups and the content of 6FDA residue. Nevertheless, it still had the temperature of 5 wt % loss over 450 °C in N_2.

Conclusions

(1) A series of hyperbranched polyimides were successfully prepared from dianhydrides (A_2) and TAPA (B_3) by controlling the concentration and molar ratio of monomers.

(2) Different monomer addition order resulted in different hyperbranched polyimides. When a dianhydride solution was added to the TAPA solution (manner 1), an amine-terminated hyperbranched polyimide was obtained, whereas the addition of TAPA solution to a dianhydride solution (manner 2) yielded an anhydride-terminated hyperbranched polyimide.

(3) The appropriate molar ratios between TAPA and a dianhydride are 1:1 for manner 1 and 1:2 for manner 2. Any use of excess dianhydride (manner 1) or TAPA (for manner 2) will cause insoluble gel.

(4) The anhydride-terminated 6FDA−TAPA polyimide had very broad molecular weight distribution.

Acknowledgment. This work was supported partly by a Grant-in-aid for Developmental Scientific Research (No. 10450296) from the ministry of Education, Science, and Culture of Japan and also by Petroleum Energy Center and Japan High Polymer Center as the R & D project for membrane for petroleum component separation.

References and Notes

(1) Young, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.

(2) Young, H. K.; Owen, W. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.

(3) (a) Morikawa, A. *Macromolecules* **1998**, *31*, 5999. (b) Shu, C.-F.; Leu, C. M. *Macromolecules* **1999**, *32*, 100. (c) Shu, C.-F.; Leu, C.-M.; Hung, F.-Y *Polymer* **1999**, *40*, 6591.

(4) Weimer, M. W.; Frechet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955.

(5) Spetseris, N.; Ward, R. E.; Meyer, T. Y. *Macromolecules* **1998**, *31*, 3158.

(6) Bolton, D. H.; Wooley, K. L. *Macromolecules* **1997**, *30*, 1890.

(7) Trollsas, M.; Hedrick, J.; Mecerreyes, D.; Jerome, R.; Dubois, P. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 3187.

(8) (a) Young, H. K. *J. Am. Chem. Soc.* **1992**, *114*, 4947. (b) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215. (b) Jikei, M.; Chon, S.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* **1999**, *32*, 2061.

(9) Stern, S. A.; Mi, Y.; Yamamoto, H.; St. Clair, A. K. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1989**, *27*, 1897.

(10) Coleman, M. R.; Koros, W. J. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1994**, *32*, 1915.

(11) Kim, T. H.; Koros, W. J.; Husk, G. R.; O'Brien, K. C. *J. Membr. Sci.* **1988**, *37*, 45.

(12) Okamoto, K.; Noborio, K.; Hao, J.; Tanaka, K.; Kita, H. *J. Membr. Sci.* **1997**, *134*, 171.

(13) Tanaka, K.; Osada, Y.; Kita, H.; Okamoto, K. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1995**, *33*, 1907.

(14) Okamoto, K.; Tanaka, K.; Kita, H.; Ishida, M.; Kakimoto, M.; Imai, Y. *Polym. J.* **1992**, 24.

(15) Harrison, R. M.; Feast, W. J. *ACS Polym. Mater. Sci. Eng.* **1997**, *77*, 162.

(16) Kricheldorf, H. R.; Bolender, O.; Wollheim, T. *High Perform. Polym.* **1998**, *10*, 217.

(17) Maier, G.; Zech, C.; Voit, B.; Komber, H. *Macromol. Chem. Phys.* **1998**, *199*, 2655.

(18) (a) Emrick, T.; Chang, H.; Frechet, J. M. J. *Macromolecules* **1999**, *32*, 6380. (b) Russo, S.; Boulares, A.; Da Rin, A. *Macromol. Symp.* **1999**, *143*, 309.

(19) Miller, R. D.; Burland, D. M.; Jurich, M.; Lee, V. Y.; Moylan, C. R.; Thackara, J. I.; Twieg, R. J.; Verbiest, T.; Volksen, W. *Macromolecules* **1995**, *28*, 4970.

(20) Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

MA9921293