Rapid Synthesis of Hyperbranched Aromatic Polyetherimides

D. Scott Thompson,[†,‡] **Larry J. Markoski,**[‡] **and Jeffrey S. Moore***[,†,‡]

School of Chemical Sciences and the Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, Illinois 61801

Received December 28, 1998

ABSTRACT: High molecular weight hyperbranched polyetherimides have been synthesized in a single-pot reaction in as little as 2.5 min from an easily synthesized and scalable AB_2 monomer using a rapid catalytic arylation method. NMR integration experiments and model compound studies revealed a degree of branching (DB) of 67% for hyperbranched polyetherimide **4** relative to the expected statistical value of 50%. Molecular weights were determined by gel permeation chromatography in two different solvent systems and varied widely. The polymers are highly soluble in common organic solvents and are among the most thermally stable hyperbranched polymers yet prepared.

Introduction

In recent years, interest in the single-step synthesis of hyperbranched polymers has rapidly increased.[1] Our involvement in this field has risen not only from the point of synthetic novelty but also from the potential uses highly branched polymers might have in the processing and property enhancement of linear commodity polymers. Although hyperbranched polymers do not have perfectly defined structures, they retain many of the important features of dendritic macromolecules (i.e., multiple end groups, high solubility, and reduced viscosities relative to their linear counterparts). Thus, they may be considered practical alternatives to dendrimers for use in applications where the perfectly regular structure of highly branched macromolecules is less important. While there have been many reports on the synthesis and characterization of hyperbranched polymers,[1,2−10] little work has been done to efficiently synthesize large quantities of thermally stable polymers for testing potential applications. If hyperbranched materials are to be used as additives in commodity polymers and thermosets, the backbone must have thermal and hydrolytic stabilities that are equal to or better than those of the major component, while delivering enhanced processability and physical properties.

One commercially important class of high-performance polymers that has yet to be studied in the hyperbranched form is the aromatic polyetherimide. We feel that hyperbranched materials of this class would be ideal for use as specialty additives in linear high-performance polymers. Linear polyetherimides are known for their excellent thermooxidative stability, chemical resistance, and mechanical properties. These characteristics make them useful for specialty applications such as wire enamels, sterilizable medical equipment, aircraft engine parts, and others.[11]

While many methods have been developed for the synthesis of polyetherimides,[12] one of two methods is typically employed. The first involves the condensation of diamines and dianhydrides to form poly(amic)acid precursors that are subsequently imidized by chemical or thermal treatment.[13] The second involves aromatic nucleophilic substitution reactions between phenolate salts and nitrophthalimides.[14] To prepare hyperbranched polyetherimides, it is important to use a method that involves stable "AB_2" monomers that are easily synthesized and purified. Neither of the aforementioned methods meets these criteria. Purification of amino anhydride monomers is complicated because of oligomerization upon heating and drying; thus, few amino anhydrides are known.[15] The use of aromatic nucleophilic substitution reactions between phenolate salts and aromatic nitrophthalimides also has disadvantages. Oxidatively sensitive phenolate salts require strict adherence to anhydrous conditions in order to achieve high conversion. The formation of product is accompanied by a nitrite salt that must be removed after polymerization, and the nitrite ion can participate in unwanted side reactions.[16] Another limitation is that reactions using benzenediol salts give poor yields due to electron transfer between the nitrophthalimide and the benzenediol dianion.[17]

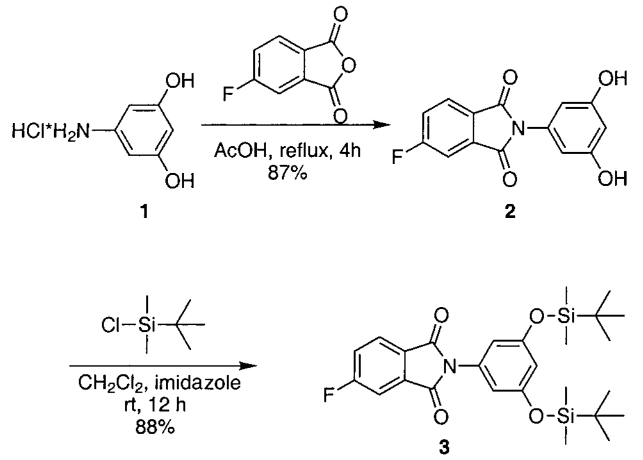
Krickeldorf has published a series of reports on the synthesis of polyetherketones and polyethersulfones using an arylation method involving trimethylsilyl (TMS) protected diphenols, activated difluorides, and catalytic amounts of CsF.[18] Using a method similar to that reported by Kricheldorf, Bryant and St. Clair described the synthesis of linear polyetherimides derived from TMS-protected 3- and 4-hydroxyphenyl-4-fluorophthalimide AB monomers.[19] Inherent viscosities as high as 1 dL/g were reported. In our hands, we found the TMS protecting groups to be quite labile, preventing the monomers from being purified to greater than 96%. This lability is likely enhanced at elevated temperatures. The free phenols are not reactive under the polymerization conditions and act as chain terminators. Changing the TMS groups to *tert*-butyldimethylsilyl (TBDMS) ethers circumvented the monomer stability problem and allowed for the rapid, efficient synthesis of high molecular weight polymers. We recently reported that this arylation method can be used to synthesize small molecule aromatic etherimides rapidly and in high yield.[20] This paper details the successful extension of this chemistry to the synthesis of the hyperbranched polyetherimide **4** and its characterization in terms of molecular weight, degree of branching, and thermal stability.

[†] School of Chemical Sciences.

[‡] Beckman Institute for Advanced Science and Technology.

10.1021/ma982008n CCC: $18.00

Scheme 1. Monomer Synthesis



Results and Discussion

Synthesis. The synthesis of monomer **3** was accomplished in two steps from the hydrochloride salt of 3,5-dihydroxyaniline[21] (**1**; Scheme 1). Reaction of **1** with 4-fluorophthalic anhydride in refluxing acetic acid afforded 3,5-dihydroxyphenyl-4-fluorophthalimide (**2**) in good yield.[22] The TBDMS protecting groups were installed by stirring TBDMS chloride in methylene chloride with imidazole.[23] The reaction was high-yielding, and purification was straightforward involving separation of the imidazole salts by filtration and recrystallization of monomer **3** from heptane.

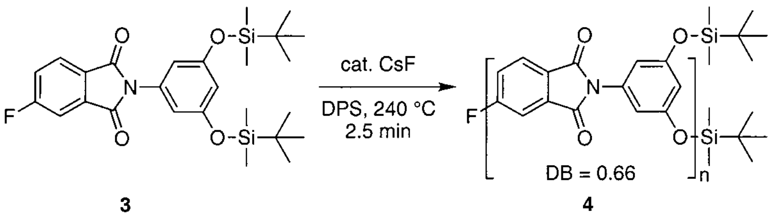
The polycondensation of **3** was performed by preheating a silicon oil bath to 240 °C (Scheme 2). A polymerization vessel containing monomer, diphenylsulfone, and catalyst was quickly immersed in the bath. The solid reagents melted immediately, forming a slightly yellow molten solution. Within seconds of melting, the reaction mixture began bubbling vigorously and TBDMS fluoride evolution was observed. The mixture was stirred until bubbling ceased (approximately 2.5 min after all solids had melted), and the reaction mixture was then removed from heat and cooled. Before solidification, the reaction mixture was taken up in hot toluene followed by acetone, which was then removed in vacuo yielding a white powder. This powder was slurried in hot ethanol, and the insoluble polymer was separated from the DPS by filtration and isolated as a white amorphous powder.

Degree of Branching. An important characteristic of any hyperbranched polymer is its degree of branching (DB).[24] The DB for polymer **4** has been determined by a combination of model compound studies and proton NMR integration experiments. Scheme 3 shows the model reaction performed to determine the theoretical DB, assuming reactivity is independent of molecular size. Samples of 1 equiv of B_2 monomer **5** and 1 equiv of fluorophthalimide **6** were reacted under the same conditions used for polymerization of **3**. A quantitative recovery of material yielded a 1:1:1 mixture of unreacted **5**, monoarylated product **7**, and diarylated product **8**.[25] The DB is then estimated from eq 1.

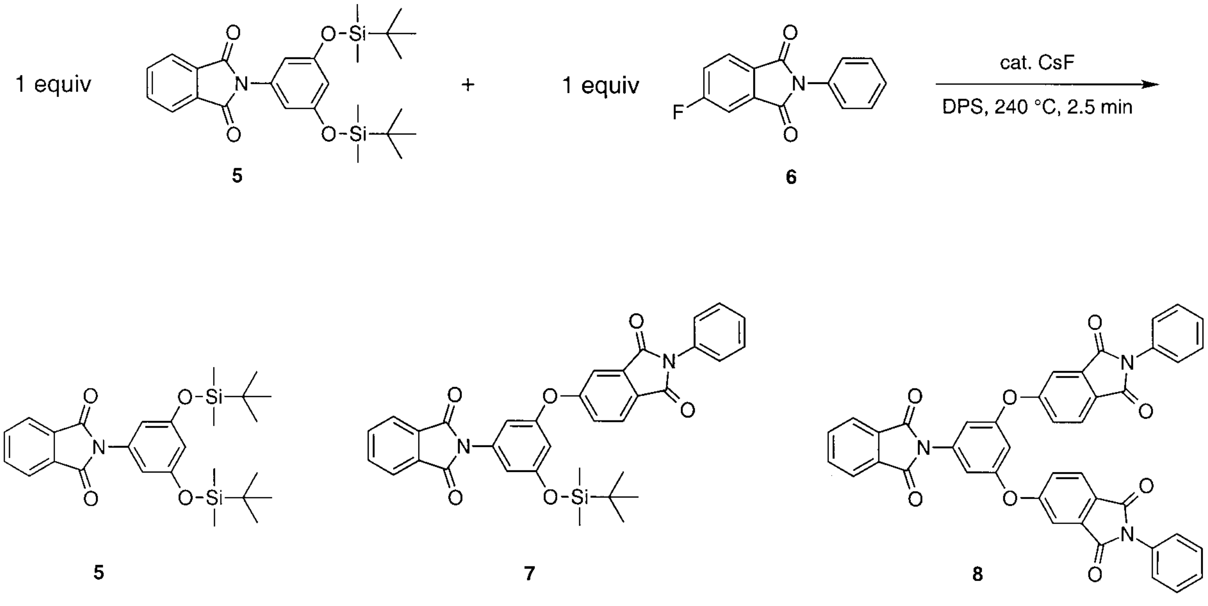
$$\mathrm{DB} = \frac{[\mathbf{8}] + [\mathbf{5}]}{[\mathbf{8}] + [\mathbf{7}] + [\mathbf{5}]} \tag{1}$$

On the basis of this definition, the degree of branching of the hyperbranched polymer is predicted to be 67%.

Scheme 2. Synthesis of Hyperbranched Polyetherimide (HBPEI)



Scheme 3. Model Reaction Used to Estimate the Degree of Branching (DB)



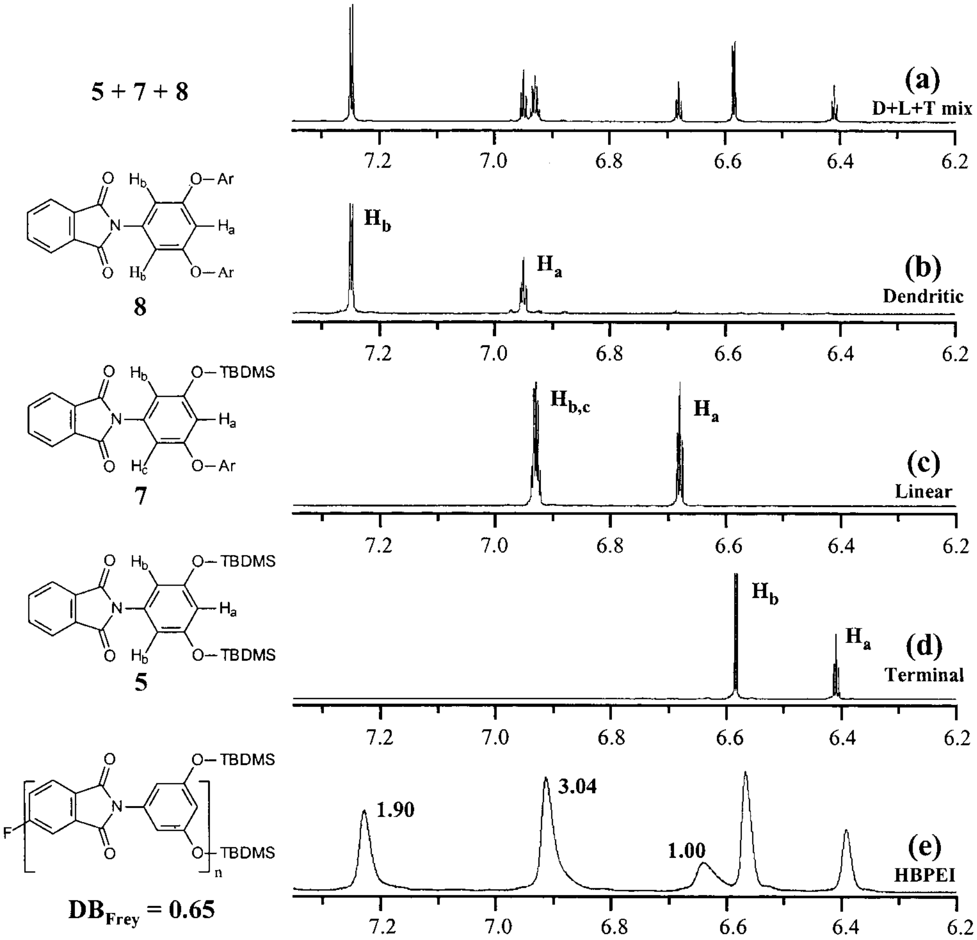


Figure 1. NMR Spectra of the aromatic region used to determine degree of branching: (a) NMR of known mixture of model compounds **5**, **7**, and **8**; (b) NMR of dendritic model compound **8**; (c) NMR of linear model compound **7**; (d) NMR of terminal model compound **5**; (e) NMR of hyperbranched polyetherimide **4**.

Figure 1 shows proton NMR data from the aromatic region of the hyperbranched polyetherimide **4**, the three model compounds **5**, **7**, and **8**, and a known mixture of the three model compounds. As seen in Figure 1b–d, distinct proton resonances are observed for the dendritic, linear, and terminal units. Dendritic model compound **8** shows a doublet at 7.25 ppm (H_b) and a triplet at 6.96 ppm (H_a). Linear model compound **7** shows two overlapping triplets at 6.93 ppm (H_b) and a triplet at 6.68 ppm (H_a). Terminal model compound **5** shows a doublet at 6.58 ppm (H_b) and a triplet at 6.41 ppm (H_a). To verify the accuracy of NMR integrations for the determination of DB, we prepared a known mixture of the three model compounds and determined their molar ratios from NMR integrations to within 0.01% (Figure 1a).[26] The NMR of hyperbranched polymer **4** is shown in Figure 1e. The broad peak at 7.23 ppm corresponds to the dendritic proton H_b. The peak at 6.92 ppm includes the overlapping signals from linear protons H_b and H_c and dendritic proton H_a. The linear proton H_a resonates at 6.64 ppm. The peak at 6.58 ppm corresponds to the terminal proton H_b, and the linear proton H_a appears at 6.40 ppm. Frey has recently given a more accurate expression for the calculation of the DB from NMR integration experiments.[24c] The DB from the NMR integration according to Frey's definition is calculated as

$$DB_{\mathrm{Frey}} = \frac{2[D]}{2[D] + [L]} \qquad (2)$$

Table 1. GPC Data for Hyperbranched PEI 4

GPC conditions	M_n (kDa)	M_w (kDa)	PDI
THF[a]	19.2	47.5	2.5
NMP/LiBr[b]	9.3	100.4	10.7

[a] Relative to linear PS standards. [b] On the basis of Universal calibration.

On the basis of this formula, the degree of branching can be calculated from integrated intensities of the peaks shown in Figure 1e. The DB_{Frey} calculated using the integration of the dendritic protons H_b (1.90) and linear proton H_a (1.00) gives a value of 66%.[27] This value is in excellent agreement with the DB determined from the model compound study.

Molecular Weight and Characterization. The molecular weight of the hyperbranched polyetherimide was determined by gel permeation chromatography (GPC) using two different GPC solvent systems with two different methods of detection. The results of the GPC analysis are shown in Table 1. The data obtained from each GPC system showed excellent reproducibility in duplicate runs. The data, however, illustrate the difficulty in determining the molecular weights of hyperbranched polymers. The GPC methods used depend on comparison to narrow molecular weight linear polystyrene standards. In addition, the elution profile of the HBPEI appears to be highly sensitive to the mobile phase used, and molecular weights determined from each system differ widely. This behavior may be due to aggregation and/or adsorption to the column.

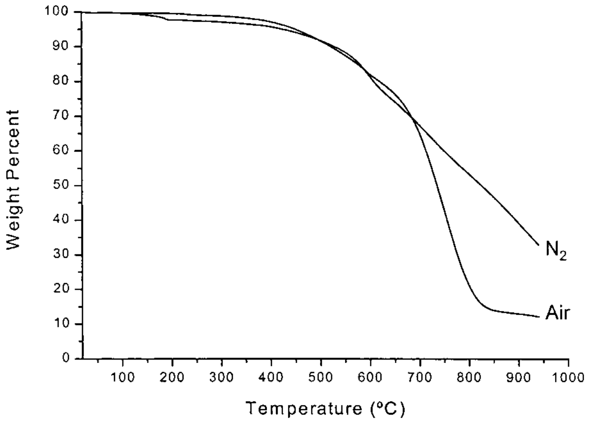


Figure 2. Thermal gravimetric analysis of hyperbranched polyetherimide **4** with a heating rate of 10 °C/min. A 10% weight loss occurs at 530 °C.

Table 2. Change in M_n vs Extent of Reaction

extent of reaction	M_n (kDa)
97	12.4
98	18.5
99	36.9
99.9	367.6

Table 3. Thermal Stabilities Reported for Hyperbranched Polymers

polymer type	ref	10% weight loss (°C)
polyphenylene	1b	>550
polyamide	3g	480−530
polyetherketone	6a	470
polyetherketone	*a*	500

[a] Hawker, C. J.; Chu, F. *Macromolecules* **1996**, *29*, 4370−4380.

NMR was also used to characterize the extent of reaction and the number-average molecular weight by end group analysis. In the limit of complete reaction, the number of end groups or B groups (TBDMS) equals the number of repeat units plus 1. Thus, in the case of complete reaction, the ratio of TBDMS groups to repeat units would equal 1. The integration of proton resonances for this theoretical case would lead to a 1:1 ratio based on the integration of the methyl group protons of the TBDMS group to the aryl protons of the polymer. The extent of reaction can be determined by measuring the ratio for the hyperbranched polymer and dividing by the theoretical ratio calculated for 100% completion. The experimental ratio is 0.94, indicating that the reaction has gone to 94% completion. Given the number of moles of starting monomer and the extent of reaction, the number-average molecular weight (M_n) is 6.3 kDa. This analysis, however, is very sensitive to small changes in integrated intensities and thus cannot provide reliable molecular weight information for extents of reaction exceeding 90% (Table 2).[28] While the calculated number-average molecular weight by this approach is in doubt, it is evident from the ratio of integrations that the TBDMS end groups are largely intact.

The hyperbranched polyetherimide is highly soluble in all common organic solvents with the exception of hexane, ethanol, methanol, and water. Initial experiments have shown that removal of the silyl protecting groups with TBAF yields a polymer soluble in slighty alkaline water.

The thermal stability of the polymer was determined by thermogravimetric analysis (TGA) in air and nitrogen. The thermal curves are shown in Figure 2. The polymers exhibit exceptional thermal stability in air with 10% weight loss occurring at 530 °C (Table 3).[29] Similar thermal stability is observed under inert atmosphere. Differential scanning calorimetry (DSC) showed no perceptible glass transition temperature (T_g) before decomposition. Optical microscopy, however, showed a visual softening temperature near 300 °C. These observations suggest that the polymer molecules have few intermolecular entanglements. We are currently investigating the effect of end group modifications on the properties of these new hyperbranched molecules.

Conclusions

The first synthesis of an aromatic hyperbranched polytherimide was performed with an easily prepared and purified 4-fluorophthalimide derived monomer, **3**. Our synthetic method is extremely rapid, and the resulting polymer has a high degree of branching (66%), indicating an enhanced rate of reaction of the linear units over terminal units in the course of the polymerization. The polymers are highly soluble in common organic solvents and are among the most thermally stable hyperbranched polymers yet prepared. Further investigations regarding the nature of the enhancement in the degree of branching and the use of this material in blends with linear polyetherimides are in progress.

Acknowledgment. This material is based on work supported by the U.S. Army Research Office MURI under Grant DAAG55-97-0126. D. Scott Thompson thanks Rohm and Haas for their support of an ACS Division of Organic Chemistry fellowship.

References and Notes

(1) For comprehensive reviews of the literature prior to 1998 see the following. (a) Malmström, E.; Hult, A. *J.M.S.−Rev. Macomol. Chem. Phys.* **1997**, *C37* (3), 555−579. (b) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685−1698.

(2) Hyperbranched polyester reports published after reviews in ref 1. (a) Kricheldorf, H. R.; Bolender, O. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*(6), 903−918. (b) Tao, X. T.; Zhang, Y. D.; Wada, T.; Sasabe, H.; Suzuki, H.; Watanabe, T.; Miyata, S. *Adv. Mater.* **1998**, *10*, 226−230. (c) Kricheldorf, H. R.; Stukenbrock, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 31−38. (d) Fomine, S.; Rivera, E.; Fomina, L.; Ortiz, A.; Ogawa, T. *Polymer* **1998**, *39*, 3551−3558. (e) Kricheldorf, H. R.; Stukenbrock, T.; Friedrich, C. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *36*, 1397−1405. (f) Kricheldorf, H. R. *Pure Appl. Chem.* **1998**, *70*, 1235−1238. (g) Trollsas, M.; Atthoff, B.; Chesson, H.; Hedrick, J. L. *Macromolecules* **1998**, *31*, 3439−3445. (h) Trollsas, M.; Hedrick, J. L. *Macromolecules* **1998**, *31*, 4390−4395. (i) Feast, W. J.; Hamilton, L. M.; Hobson, L. J.; Rannard, S. P. *J. Mater. Chem.* **1998**, *8*, 1121−1125. (j) Trollsas, M.; Hawker, C. J.; Remenar, J. F.; Hedrick, J. L.; Johanson, M.; Ihre, H.; Hult, A. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2793−1798. (k) Kricheldorf, H. R.; Bolender, O. *High Perform. Polym.* **1998**, *10*, 217−229. (l) Hahn, S. W.; Yun, Y. K.; Jin, J. I.; Han, O. H. *Macromolecules* **1998**, *31*, 6417−6425. (m) Kricheldorf, H. R.; Stukenbrock, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2347−2357.

(3) Hyperbranched polyamides, polyamidoamines, and polyamines. (a) Haba, O.; Tajima, H.; Ueda, M.; Nagahata, R. *Chem. Lett.* **1998**, *4*, 333−334. (b) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1998**, *31*, 5964−5966. (c) Russo, S.; Boulares, A.; Mariani, A. *Macromol. Symp.* **1998**, *128*, 13−20. (d) Suzuki, M.; Yoshida, S.; Shiraga, K.; Saegusa, T. *Macromolecules* **1998**, *31*, 1716−1719. (e) Spetseris, N.; Ward, R. E.; Meyer, T. Y. *Macromolecules* **1998**, *31*, 3158−3161. (f) Hobson, L. J.; Feast, W. J. *Polymer* **1998**, *40*, 1279−1297. (g) Yang, G.; Mitsutoshi, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215−2220.

(4) Hyperbranched polyureas. Kumar, A.; Meijer, E. W. *Chem. Commun.* **1998**, *16*, 1629−1630.

(5) Hyperbranched polyphenylenes. Morgenroth, F.; Mullen, K. *Tetrahedron* **1997**, *53*, 15349−15366.

(6) Hyperbranched polyethers and polyetherketones. (a) Martinez, C. A.; Hay, A. S. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35* (1), 57−90. (b) Mueller, A.; Kowaleski, T.; Wooley, K. L. *Macromolecules* **1998**, *31*, 776−786. (c) Jin, R. H.; Motokucho, S.; Andou, Y.; Nishikubo, T. *Macromol. Rapid Commun.* **1998**, *19*, 41−46. (d) Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 10180−10186. (e) Morikawa, A. *Macromolecules* **1998**, *31*, 5999−6009.

(7) Hyperbranched polysilanes and polysiloxanes reports after reviews in ref 1. (a) Londergan, T. M.; Weber, W. P. *Polym. Bull.* **1998**, *40*, 15−20. (b) Miravet, J. F.; Fréchet, J. M. J. *Macromolecules* **1998**, *31*, 3461−3468. (c) Interrante, L. V.; Rushkin, I.; Shen, O. *Appl. Organomet. Chem.* **1998**, *12*, 695−705. (d) Kadokawa, J.; Sato, M.; Karasu, M.; Tagaya, H.; Chiba, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2373−2376.

(8) Hyperbranched polystyrenes and polyacrylates. (a) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955−970. (b) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901−915. (b) Malmstrom, E. E.; Hawker, C. J. *Macromol. Chem. Phys.* **1998**, *199*, 923−935. (c) Fomina, L.; Guadarrama, P.; Fomine, S.; Salcedo, R.; Ogawa, T. *Polymer* **1998**, *39*, 3551−3558.

(9) Others hyperbranched polymers. (a) Puskas, J. E.; Grasmuller, M. *Macromol. Symp.* **1998**, *132*, 117−126. (b) Kim, J. S.; Pawlow, J. H.; Wojcinski, L. M.; Murtuza, S.; Kacker, S.; Sen, A. *J. Am. Chem. Soc.* **1998**, *120*, 1931−1933. (c) Londergan, T. M.; You, Y. J.; Thompson, M. E.; Weber, W. P. *Macromolecules* **1998**, *31*, 2784−2788. (d) Kadokawa, J.; Sato, M.; Karasu, M.; Tagaya, H.; Chiba, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2373−2376.

(10) Theoretical papers. (a) Lach, C.; Frey, H. *Macromolecules* **1997**, *31*, 2381−2383. (b) Radke, W.; Litvinenko, G.; Muller, A. H. E. *Macromolecules* **1998**, *31*, 239−248. (c) Hanselmann, R.; Holter, D.; Frey, H. *Macromolecules* **1998**, *31*, 3790−3801.

(11) (a) Odian G. G. *Principles of Polymerization*; Wiley and Sons: New York, 1991; p 160. (b) Takekoshi, T. Applications of Polyimides as Photosensitive Materials. In *Polyimides: fundamentals and applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; pp 743−758. (c) Takekoshi, T. Polyimides in High Performance Electronics Packaging and Optoelectronic Applications. In *Polyimides: fundamentals and applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; pp 743−758.

(12) Takekoshi, T. Synthesis of Polyimides. In *Polyimides: fundamentals and applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; pp 743−758.

(13) Harris, F. W. Synthesis of Aromatic Polyimides from Dianhydrides and Diamines. In *Polyimides*; Blackie, Chapmann and Hall: New York, 1990; pp 1−37.

(14) Takekoshi, T. Other Synthetic Routes to Polyimides. In *Polyimides*; Blackie, Chapmann and Hall: New York, 1990; pp 38−57.

(15) Wang, Z. Y.; Qi, Y.; Bender, T. P.; Gao, J. P. *Macromolecules* **1997**, *30*, 764−769.

(16) Williams, F. J.; Donahue, P. E. *J. Org. Chem.* **1977**, *42*, 3414−3419.

(17) White, D. M.; Takekoshi, T.; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Louks, G. R.; Manello, J. S.; Matthews, O.; Schluenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1635−1658.

(18) (a) Kricheldorf, H. R.; Bier, G. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2283−2289. (b) Kricheldorf, H. R.; Bier, G. J. *Polymer* **1984**, *25*, 1151−1156. (c) Kricheldorf, H. R.; Meier, J.; Schwart, G. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 529−534. (d) Kricheldorf, H. R.; Schwart, G.; Erxleben, J. J. *Makromol. Chem.* **1988**, *189*, 2255−2267. (e) Kricheldorf, H. R.; Delius, U. *Makromol. Chem.* **1989**, *190*, 1277−1288. (f)) Kricheldorf, H. R. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 365−388.

(19) (a) Bryant, R. G.; St. Clair, T. L. *Abstracts of the 4th International Conference on Polyimides*, Ellenville, NY, October/November, 1991; p II-69. (b) Takekoshi, T. U.S. Patent number 1993000096393.

(20) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Tetrahedron Lett.*, in press.

(21) Thorn, M. A.; Denny, G. H.; Babson, R. D. *J. Org. Chem.* **1975**, *40*, 1556−1558.

(22) 3,5-Dihydroxyphenyl-4-fluorophthalimide (**2**). To a 100 mL round-bottom flask was added 19.8 g (121 mmol) of the hydrochloride salt of 3,5-dihydroxy aniline **1**, 50 mL of glacial acetic acid, and 22.2 g (134 mmol) of 4-fluorophthalic anhydride. The mixture was stirred at reflux for 4 h. The reaction was removed from heat, and the product **2** was precipitated in 1 L of water and isolated by filtration as an off-white solid. The product was dried under vacuum at 100 °C overnight (14.71 g, 87%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 9.634 (bs, 2H), 7.981 (dd, J = 8.40, 4.55, 1H), 7.792 (dd, J = 7.41, 2.28, 1H), 7.670 (ddd, J = 9.39, 8.37, 2.28), 6.285 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz): δ 167.0, 166.2, 165.8, 165.8, 165.0, 158.5, 134.7, 134.6, 133.1, 127.8, 127.8, 126.3, 126.2, 121.7, 121.4, 111.3, 111.1, 105.8, 102.6. MS (EI) (calcd for C$_{14}$H$_8$FNO$_4$, 273.0437; found 273.0439): *m/e* 273 (100), 229 (9), 94 (6), 71 (6), 57 (8).

(23) 3,5-Di-*tert*-butyldimethylsilyloxyphenyl-4-fluorophthalimide (**3**). To a 500 mL round-bottom flask was added 24.1 g (88.2 mmol) of 3,5-dihdroxyphenyl-4-fluorophthalimide (**2**) 27.95 g (185 mmol) of *tert*-butyldimethylsilyl chloride, 12.6 g (185 mmol) of imidazole, and 250 mL of CH$_2$Cl$_2$. The reaction was stirred at ambient temperature for 12 h. The imidazole salts were removed by filtration, and the CH$_2$Cl$_2$ was removed in vacuo. The white solid was recrystallized from heptane (38.7 g, 88%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 7.953 (ddd, J = 8.25, 4.55, 0.31, 1H), 7.607 (ddd, J = 7.31, 2.30, 0.33, 1H), 7.475 (ddd, J = 8.96, 8.26, 2.35), 6.577 (d, J = 2.20, 2H), 6.415 (t, J = 2.19, 1H), 1.001 (s, 18H), 0.247 (s, 12H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz): δ 168.2, 166.5, 166.2, 166.2, 157.3, 135.1, 135.1, 133.3, 128.2, 128.2, 126.7, 126.6, 122.2, 122.0, 112.5, 112.3, 111.9, 111.6, 26.0, −4.2. MS (EI): *m/e* 502 (18), 501 (44), 445 (42), 444 (100), 388 (11), 222 (15), 148 (13), 73 (34). Anal. Calcd for C$_{26}$H$_{36}$FNO$_4$Si$_2$: C, 62.24; H, 7.23; N, 2.79. Found: C, 61.93; H, 7.11; N, 2.85.

(24) (a) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583−4588. (b) Hawker, C. J.; Chu, F. *Macromolecules* **1996**, *29*, 4370−4380. (c) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30−35.

(25) All model compounds characterized by ^{1}H NMR, ^{13}C NMR, MS, and EA.

(26) Comparison of calculated degrees of branching from molar ratios of a known mixture and from NMR integrations of mixture (Figure 1a). The degree of branching equation defined by Hawker and Fréchet was used to determine DB:

$$\mathrm{DB} = \frac{[\mathrm{D}] + [\mathrm{L}]}{[\mathrm{D}] + [\mathrm{L}] + [T]}$$

$$\mathrm{DB}_{\text{known}} = \frac{[1.12 \times 10^{-5}] + [7.03 \times 10^{-6}]}{[1.12 \times 10^{-5}] + [7.96 \times 10^{-6}] + [7.03 \times 10^{-6}]} = 0.696$$

The DB value calculated from NMR integrations is within 0.01% of that calculated using the known molar amounts.

(27) The degree of branching was calculated several ways using combinations of the integration values shown in Figure 1e. All values calculated fall between 65.4% and 67.5%.

(28) A positive error of 2% in the integration of the methyl group protons would result in a change of extent of reaction to 96% and a change in molecular weight to 9.3 kDa. As the extent of reaction approaches 98% and higher, the error in molecular weights becomes exponentially larger (see Table 2).

(29) (a) The corressponding linear AB polymer derived from polymerization of 3-*tert*-butyldimethylsilyloxyphenyl-4-fluorophthalimide has a 10% weight loss of 582 °C. (b) The highest thermal stabilties reported in the hyperbranched polymer literature are listed in Table 3.

MA982008N