Preparation and Properties of Hyperbranched Aromatic Polyimides via Polyamic Acid Methyl Ester Precursors

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ABSTRACT: An AB_2 type monomer, an isomeric mixture of 3,5-bis(4-aminophenoxy)diphenyl ether-3′,4′-dicarboxylic acid monomethyl ester (**6**), was synthesized starting from 3,5-dimethoxyphenol. A hyperbranched polyamic acid methyl ester precursor was prepared from self-polycondensation of the AB_2 type monomer in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) as a condensing agent. End-capping reactions of free amine end groups of the precursor with acetyl, *n*-heptanoyl chloride, and 4-methylphthalic anhydride were carried out. By chemical imidization of these precursors in the presence of acetic anhydride and pyridine, hyperbranched aromatic polyimides which were soluble in NMP, DMF, and DMSO were successfully prepared. By gel permeation chromatography measurement with a laser light scattering detector, weight-average molecular weights (M_w) of hyperbranched aromatic polyimides were found to be 37 000−188 000. From IR and ^{1}H NMR analyses, it was found that both end-capping and subsequent chemical imidization reactions proceeded quantitatively. The degree of branching (DB) of hyperbranched aromatic polyimides were around 0.50. By thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements of the hyperbranched aromatic polyimides, 5 wt % thermal loss temperatures (T_5) were observed to be above 395 °C, and T_g values were 189, 138, and 186 °C for the end groups of acetoamide, *n*-heptanoamide, and 4-methylphthalimide, respectively. The densities of the transparent films of the hyperbranched polyimides having acetoamide end groups were found to be less than 1.35, which were lower than those of their linear analogues. The film, prepared from the hyperbranched polyimide with 4-methylphthalimide end groups, had a lower dielectric constant and birefringence and a shorter cutoff wavelength than the film of poly(4,4′-oxydiphenylene pyromellitimide).

Introduction

Aromatic polyimides are well-known as important high performance polymers. Numerous researches on the syntheses and applications of aromatic polyimides have been reported over the past few decades owing to their outstanding properties with high thermal stability. Most commercialized aromatic polyimides are produced through a two-step method. The method is composed of the preparation of polyamic acids as soluble precursors and the subsequent cyclization to form insoluble polyimides. Polyamic acids in solution are usually unstable in storage for long period because hydrolytic cleavage reaction readily takes place. To improve the stability, polyamic acid ester derivatives[1] have been studied. Polyamic acid esters can afford solutions with higher concentration compared with parent polyamic acids because of lower solution viscosity. Therefore, thicker polyimide films can be obtained by using the polyamic acid ester precursors with one process of film cast.

Recently, dendritic macromolecules have attracted considerable attention due to new physical and chemical properties caused by their unique structures. These dendritic macromolecules which possess many functional end groups and branching points are mainly classified into dendrimers and hyperbranched polymers.[2−6] Although dendrimers are monodispersive with well-defined and perfectly branched structures, their preparations require stepwise reactions involving protection and deprotection with further purification. On the other hand, hyperbranched polymers are polydispersed macromolecules with irregular and randomly branched structures, which can be produced on a large scale by the one-step polymerization of AB_x monomers. As compared to their linear analogues, hyperbranched polymers possess good solubility in organic solvents and lower viscosity. In addition, introduction of various functional groups into hyperbranched structures can be easily achieved by chemical modification of end groups. Hyperbranched polymers have been produced mainly by condensation reactions, which had been applied to the syntheses of hyperbranched polyphenylenes,[7] polyesters,[8] polyamides,[9] polyethers,[10] poly(ether−ketone)s,[11] and poly(siloxysilane)s.[12] In the case of hyperbranched polymers with heterocyclic structures, the syntheses of hyperbranched poly(phenylquinoxaline)s,[13] poly(ester−imide)s,[14] poly(ether−imide)s,[15] and polycarbazoles[16] were already reported to date. These heterocyclic hyperbranched polymers, prepared by a one-step method from AB_2 type monomers containing heterocyclic structures, had high thermal stability and good solubility. In a recent communication, we reported the two-step preparation of hyperbranched polyimides, in which the imide heterocyclic ring was formed from a hyperbranched polyamic acid methyl ester precursor.[17] The precursor was prepared by direct self-polycondensation of an AB_2 type monomer in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP)[18] as a condensing agent. Even if the hyperbranched polyimides exhibit limited solubility in organic solvents, the processability might be improved by utilizing the precursors without chemical modification of end groups. In addition, for future blend materials which comprise of linear and hyperbranched polyimides, the two-step preparation via precursors would result in better compatibility than the one-step one.

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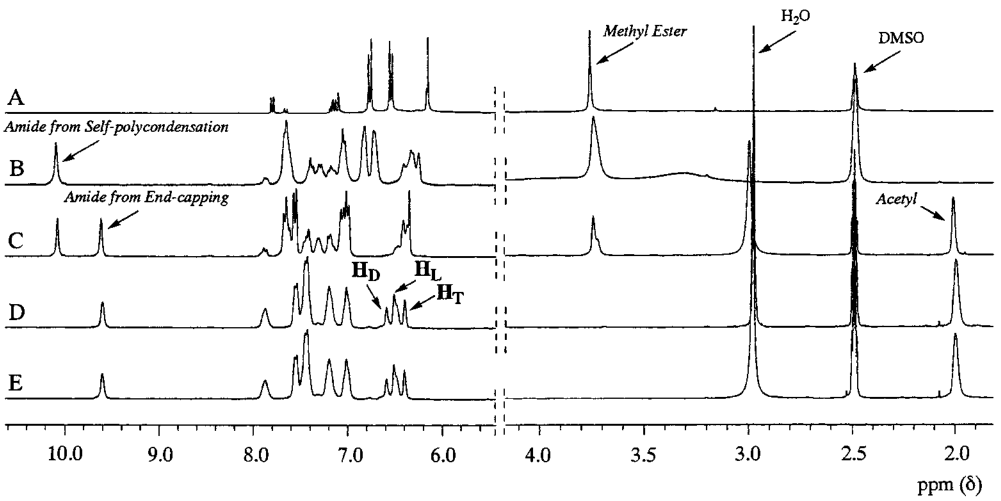
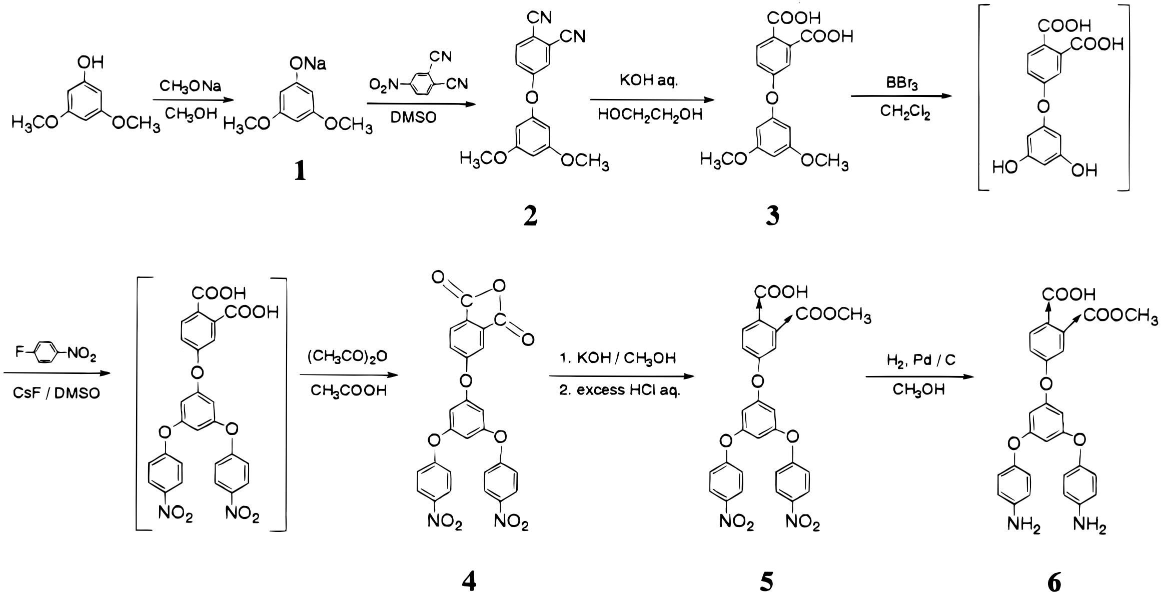


Figure 1. ^{1}H NMR spectra of (A) AB_2 type monomer **6** in DMSO-d_6 at room temperature and (B) polymers **7**, (C) **9**, (D) **8**, and (E) **11** at 100 °C.

Scheme 1



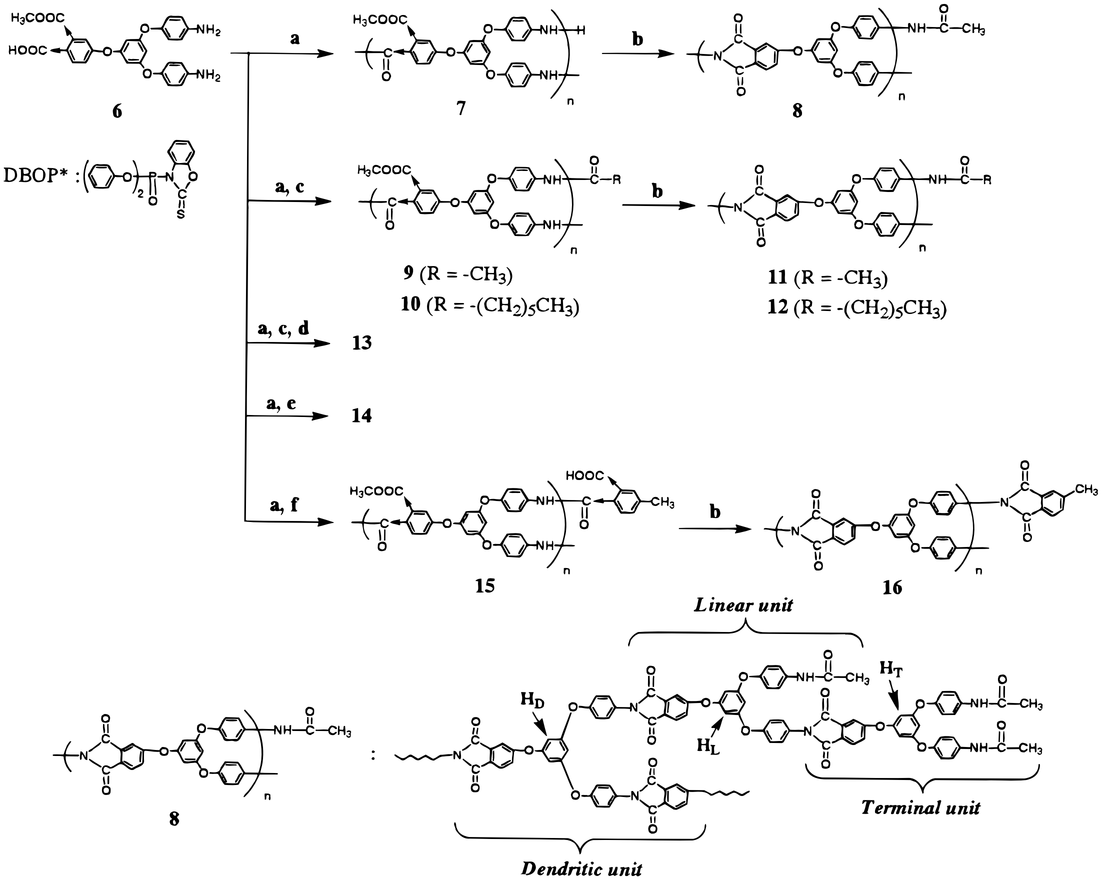
In this paper, we report details on the preparation and properties of hyperbranched aromatic polyimides having various end groups via hyperbranched polyamic acid methyl ester precursors.

Results and Discussion

Monomer Synthesis. An isomeric mixture of 3,5-bis(4-aminophenoxy)diphenyl ether−3′,4′-dicarboxylic acid monomethyl ester (**6**) was prepared starting from 3,5-dimethoxyphenol, as shown in Scheme 1. 4-(3,5-Dimethoxyphenoxy)phthalonitrile (**2**) was prepared by the nucleophilic substitution reaction of 4-nitrophthalonitrile with sodium 3,5-dimethoxyphenoxide (**1**), which was obtained by the reaction of 3,5-dimethoxyphenol with sodium methoxide. Basic hydrolysis reaction successfully converted the phthalonitrile derivative **2** to phthalic acid compound **3**. Cleavage of the methyl ether bond in **3** with boron tribromide gave a resorcinol derivative which contained a small amount of impurities. This was followed by the introduction of the nitrophenoxy group by nucleophilic substitution reaction with 4-nitrofluorobenzene in the presence of cesium fluoride. Subsequent dehydration reaction of nitro phthalic acid in the mixture of acetic anhydride and acetic acid afforded nitro anhydride **4**, which was precipitated as a pure crystalline compound. The AB_2 type monomer **6** was obtained by the ring-opening reaction of **4** with methanol and subsequent reduction of the nitro group in **5**. The structure of **6** was characterized by ^{1}H NMR (spectrum A in Figure 1) and the IR spectrum and confirmed by elemental analysis. From the ^{1}H NMR spectrum, the ratio of the two isomers for *p*-,*m*-methyl ester substitution was 1:3.8.

Polymer Syntheses. As reported previously,[17] the self-polycondensation of **6** was carried out in the presence of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP) as a condensing agent (step **a** in Scheme 2). The use of a small volume (1.5 mL) of *N*-methyl-2-pyrrolidinone (NMP) turned the polymerization mixture to gel in 10 min. Using a higher volume (3 mL), the polymerization reaction proceeded homogeneously and resulted in a white powdery product **7** in 86% yield (Table 1). However, the isolated **7** was insoluble or formed a gel in various organic solvents.[17]

Scheme 2[a]



[a] Key: **a**, DBOP*, $(CH_3CH_2)_3N$, NMP, room temperature, 3 h; **b**, $(CH_3CO)_2O$, pyridine, DMSO or DMF, 100 °C, 24 h; **c**, RCOCl, room temperature, 3 h; **d**, 100 °C, 24 h; **e**, $(CH_3CO)_2O$, pyridine, 100 °C, 24 h; **f**, $(4\text{-}CH_3)C_6H_3(CO)_2O$, room temperature, 3 h.

Table 1. Preparation of Hyperbranched Aromatic Polyamic Acid Methyl Ester Precursors and Polyimides

polymer	NMP (mL) in **a**[a]	appearance in **a**[b]	yield (%)[c]	M_w (M_w/M_n)[d]	η_{inh} (dL/g)[e]	DB[f]
7	1.5	gel				
	3	H	86	gel	gel	
8	3	H	84	188 000 (3.0)	0.29	0.48
9	2.25	H	82	112 000 (2.5)	0.27	
	3	H	80	70 000 (2.1)	0.23	
11	2.25	H	78	50 000 (1.6)	0.21	0.47
	3	H	80	37 000 (1.6)	0.18	0.49
13	2.25	H	81	38 000 (1.5)	0.17	0.50
14	2.25	H	84	38 000 (1.6)	0.17	0.51

[a] Self-polycondensation reactions of AB_2 monomer **6** (0.60 g, 1.24 mmol) were carried out in the presence of 0.57 g (1.48 mmol, 1.2 equiv) of DBOP and 0.17 mL (1.24 mmol, 1 equiv) of triethylamine in 1.5−3 mL of NMP at room temperature for 3 h in nitrogen. [b] Appearance of the polymerization mixture. H: homogeneous solution throughout the reaction. [c] After reprecipitation in methanol containing 0.1 wt % lithium chloride. [d] Determined by GPC measurements with a laser light scattering detector in DMF containing lithium bromide (0.01 mol/L) as an eluent. The specific refractive increments (d*n*/d*c*) were 0.152 mL/g for **9**, 0.168 mL/g for **8**, **11**, **13**, and **14**. [e] Measured at a concentration of 0.5 g/dL in NMP at 30 °C. [f] Determined by ^1H NMR analysis.

Without isolation of **7**, acetyl chloride was added to the polymerization mixture as an end-capping agent for the free amine end groups of **7**, and then the mixture was maintained at room temperature for 3 h (step **c** in Scheme 2). Pouring the resulting solution into methanol containing lithium chloride (0.1 wt % $LiCl/CH_3OH$) and reprecipitating from *N*,*N*-dimethylformamide (DMF) solution into 0.1 wt % $LiCl/CH_3OH$ gave a light yellow powdery product, **9**, in 80% yield. The resulting polymer **9** turned soluble in NMP, DMF and DMSO. From GPC measurement with a laser light scattering detector, a weight-average molecular weight (M_w) of **9** was 70 000 with a polydispersity index (M_w/M_n) of 2.1. The inherent viscosity (η_{inh}) was 0.23 dL/g (Table 1). In the ^1H NMR spectrum of **9** (spectrum C in Figure 1), as compared with that of **7** (spectrum B), two new peaks arisen from the end- capping were observed at 9.60 and 2.00 ppm, which were assigned to amide and acetyl protons, respectively. The integration ratio of peaks for the amide proton (10.10 ppm) generated from the self-polycondensation, amide (9.60 ppm) from the end-capping, and methyl ester (3.75 ppm) and acetyl protons (2.00 ppm) was found to be 1:1:3:3. The resulting ratio was quite consistent with the ratio calculated from quantitative end-capping. In the IR spectrum of **9**, the peak intensity at 1669 cm^{-1} assigned to the amide group increased significantly in comparison with that of **7**. These results indicated that the end-capping reaction of **7** with acetyl chloride proceeded quantitatively.

Imidization reactions of **7** and **9** were carried out by thermal and chemical methods. Both heat treatments of **7** and **9** at 300 °C for 1 h under vacuum gave insoluble products.[17] The chemical imidization of **9** was carried out in the presence of acetic anhydride and pyridine in DMF at 100 °C for 24 h, as shown in Scheme 2 (step **b**). The resulting product **11** was recovered as a light yellow powder with 80% yield, which was soluble in NMP, DMF, and DMSO. Polymer **11** had M_w of 37 000, M_w/M_n of 1.6, and η_{inh} of 0.18 dL/g (Table 1). In the ^1H NMR spectrum of **11** (spectrum E in Figure 1), as compared

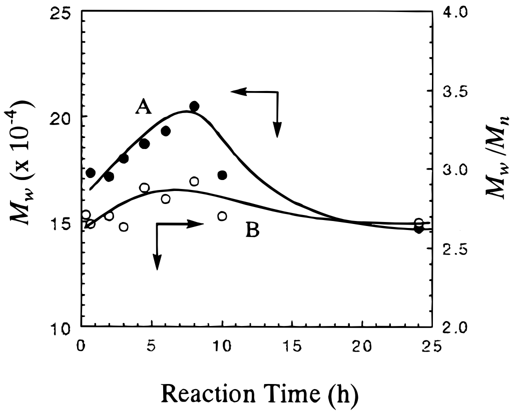


Figure 2. Reaction time dependence on (A) M_w and (B) M_w/M_n of polymer **9**.

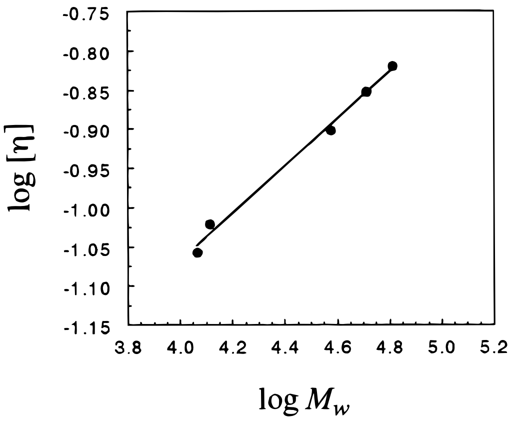


Figure 3. Relationship between log [η] and log M_w of polymer **11** in DMF containing lithium bromide (0.01 mol/L).

with that of **9** (spectrum C), the amide (10.10 ppm) from the self-polycondensation and the methyl ester (3.75 ppm) peaks disappeared. Two peaks at 2.00 and 9.60 ppm arisen from end-capping remained. In the IR spectrum, two absorptions characteristic of the imide group were clearly observed at 1720 and 1780 cm^{-1} with the characteristic amide absorption at 1669 cm^{-1}. The resulting polymer **11** had the same ^{1}H NMR and IR spectra as those of **8** (spectrum D), prepared from **7**. From these results, it was found that the treatment with acetic anhydride and pyridine of the end-capped precursor **9** quantitatively produced the hyperbranched aromatic polyimide **11**.

Polymer **11** had lower M_w and η_{inh} values (37 000 and 0.18 in Table 1) than those (188 000 and 0.29) of **8**, although both polymers were prepared through the same polymerization conditions. Preparing from the self-polycondensation of **6** in 2.25 mL of NMP, the resulting polyimide **11** had slightly higher M_w and η_{inh} values (50 000 and 0.21) than those of the case of 3 mL. Polymers **13** and **14**, whose repeating units were expected to be the same as those of **8** and **11**, were prepared by two other synthetic routes. The first route for the preparation of **13** was composed of the polymerization (step **a**), the end-capping with acetyl chloride (step **c**), and the subsequent heat treatment of the reaction mixture at 100 °C for 24 h (step **d**). The other, for the preparation of **14** (step **a** and **e**), included the addition of acetic anhydride and pyridine to the polymerization mixture after self-polycondensation of **6** and the immediate heat treatment at 100 °C for 24 h. By ^{1}H NMR and IR analyses, it was confirmed that resulting polyimides **13** and **14** showed the same ^{1}H NMR and IR spectra as those of **8** and **11.** The polymers **13** and **14** had almost the same M_w and η_{inh} values (38 000 and 0.17), and these values were also lower than those of **8**. From these results, it was found that **11**, **13**, and **14**, which were prepared without isolation of **7**, had lower M_w and η_{inh} values than those of **8**, which was obtained from isolated **7**. According to the gelation of **7** after isolation, we assume that **8** formed aggregation in the GPC eluent and NMP, and the molecular weight of **8** was overestimated.

Reaction time dependence on M_w and M_w/M_n of polymer **9** were investigated. As shown in Figure 2, M_w of **9** was 173 000 at 40 min and increased to around 210 000 at 8 h, and a subsequent decrease of M_w was observed (curve A). The M_w/M_n ranged from 2.6 to 2.9 (curve B). In the case of polyimide **11** prepared from **9**, M_w was measured to be in the range 52 000−68 000 with a change of M_w/M_n from 1.3 to 1.5. In each GPC curve for **9** obtained by a refractive index detector, a shoulder peak was observed on the higher molecular weight side of the main peak. On the other hand, there was no shoulder peak in that for **11**. From these results, it seemed that polymer **9** aggregated in the GPC eluent.

The degree of branching (DB) of hyperbranched polymer was defined as the ratio of the sum of dendritic and terminal units vs total units (linear, dendritic, and terminal units).[19] As shown in the previous communication,[17] DB of the resulting hyperbranched aromatic polyimide **8** (spectrum D in Figure 1) was determined to be 0.48 by ^{1}H NMR analysis using the model compound. By the same manner, DB values of **11**, **13**, and **14** were found to be in the range 0.47−0.51 (Table 1) and were independent of the M_w and η_{inh} values.

Relationship between M_w and intrinsic viscosity [η] for polymer **11** is shown in Figure 3. A shape factor, α, which was defined by the Mark−Houwink equation ($[\eta] = KM^{\alpha}$) was calculated to be 0.30 from the slope drawn by the least-squares method. The fact that the α value was found to be noticeably lower than 0.5 indicated that polymer **11** had highly branched structures.

The end-capping reactions of polyamic acid esters with other substituents and the subsequent chemical imidizations were examined in the similar method as described above. Polymer **10** was prepared by the end-capping reaction of **7** with *n*-heptanoyl chloride (step **c** in Scheme 2). In the ^{1}H NMR spectrum of **10**, five new peaks were observed. These peaks were assigned to an amide (9.53 ppm) and *n*-hexyl protons (2.28−2.30, 1.60, 1.29, 0.86 ppm). The integration analysis indicated that this end-capping reaction proceeded quantitatively. After the chemical imidization of **10** to form **12**, the amide (10.10 ppm) generated from the self-polycondensation and the methyl ester protons (3.75−3.88 ppm) disappeared, and the peaks for the amide (9.51 ppm) and *n*-hexyl protons (2.27, 1.59, 1.28, 0.85 ppm) from the end-capping were slightly shifted to higher fields. Using 4-methylphthalic anhydride as the end-capping agent, polymers **15** and **16** were successfully prepared and characterized in the same manner as for polymers **10** and **12**.

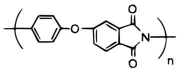
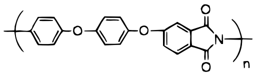
Polymer Properties. Thermal properties and solubility of the resulting polymers are summarized in Table 2. In the thermogravimetric (TG) curve of polymer **7**, weight loss (6.7 wt %) caused by the elimination of methanol was observed at the range of 180−230 °C,

Table 2. Thermal Properties and Solubility of Resulting Polymers

polymer	$T_5{}^a/T_g{}^b$(°C)	solubility^c NMP	DMF	DMSO	THF
7		gel	gel	gel	−
8	395/193	++	++	++	−
9		++	++	++	−
10		++	++	++	++
11	425/189	++	++	++	−
12	405/138	++	++	++	++
15		++	++	++	−
16	455/186	++	++	+	++

[a] T_5 (5 wt % loss temperature) was determined by TG at a heating rate of 10 °C/min in nitrogen. [b] Determined by DSC at a heating rate of 10 °C/min in nitrogen on second heating. [c] Key: (++) soluble at room temperature; (+) soluble on heating; (−) insoluble.

Table 3. Densities of Cast Films from Resulting Polymers

Polymer	Density (g/cm^3)^a
8	1.344
9	1.329
11	1.332
	1.405^b
	1.376^c

[a] Measured by the sink−float method in the mixture of tetrachloromethane and toluene at 30 °C. [b] Prepared from the precursor with inherent viscosity of 0.22 dL/g. [c] With 0.31 dL/g.

which was close to the calculated weight loss of 6.8 wt %. Also from TG analyses of polymers **9**, **10**, and **15**, thermal imidizations were found to be completed below 250 °C. From DSC analyses, glass transition temperatures (T_g) of the resulting hyperbranched aromatic polyimides were all at around 190 °C except for **12**. Polymer **12** with *n*-hexyl group had a much lower T_g value (138 °C) than others. In most cases, resulting polymers exhibited good solubility in NMP, DMF, and DMSO. The precursor **10** and polyimides **12** and **16** were soluble even in THF. Polyimides **8** and **11** were soluble at a concentration of 400 mg/mL in NMP at 100 °C.

Transparent yellow films were prepared by casting from NMP or DMF solutions of hyperbranched polymers onto glass plates, followed by heating. All resulting films were brittle, which would be caused by the low solution viscosity of the hyperbranched polyimides. Films prepared from precursor **9** and polyimides **8** and **11** with acetoamide end groups had close density values, as shown in Table 3. As compared with films of linear analogues, it was found that hyperbranched polymer films had noticeably lower density values than those of their linear analogues. This result seems to suggest that hyperbranched polymers inherently have structures with much loose packing than linear ones.

Table 4. Dielectric and Optical Properties of Polyimide Films

polyimide	ϵ^a	$n_{av}{}^b$	Δn^c
16	2.94	1.661	0.006
ODA−PMDA	3.33	1.691	0.053

[a] Measured with ITO−Al−polyimide−Al device at 23 °C under 100 kHz (polyimide film thickness of 2.2 μm for **16** and 1.5 μm for ODA−PMDA). [b] Average value of in-plane and out-of-plane refractive indices at 23 °C determined by prism coupling method using He−Ne laser (**16**, 4.9 μm; ODA−PMDA, 5.1 μm). [c] Difference between in-plane and out-of-plane refractive indices.

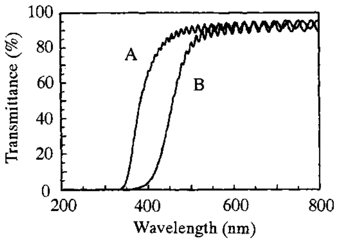


Figure 4. UV−vis spectra of films for (A) polymer **16** (thickness of 4.9 μm) and (B) poly(4,4′-oxydiphenylene pyromellitimide) (5.1 μm).

In Table 4, dielectric and optical properties of the film of **16** are summarized and compared with those of the film of poly(4,4′-oxydiphenylene pyromellitimide) (ODA−PMDA), where both films were prepared by casting from γ-butyrolactone solutions. The film of **16** had a dielectric constant (ϵ) of 2.94, which was lower than that of the ODA−PMDA film. Although there were not so much differences in the refractive index (n_{av}) between **16** and the ODA−PMDA polyimide, birefringence (Δn) of **16** was observed to be noticeably lower in comparison with that of the ODA−PMDA polyimide. This result suggests that polymer **16** has more isotropic structures than the ODA−PMDA polyimide. It is well-known that, for the film of ODA−PMDA polyimide, the polymer chains aggregate and form highly oriented structures during thermal treatment.[20] We assume that less aggregation and orientation of polymer chains take place in the film of **16**. Figure 4 shows UV−vis spectra of both polyimide films. It was found that polymer **16** had a shorter cutoff wavelength than the ODA−PMDA polyimide. The looser packing between imide rings might result in a lesser charge-transfer effect.

Conclusion

Hyperbranched aromatic polyimides having various end groups were successfully prepared via polyamic acid methyl ester precursors. The resulting hyperbranched polyimides had high molecular weight with DB values of ca. 0.5, and exhibited good solubility in NMP, DMF, DMSO, and THF. The 5 wt % thermal loss temperatures (T_5) were observed at above 395 °C, and T_g values were detected at 189, 138, and 186 °C for the end groups of acetoamide, *n*-heptanoamide and 4-methylphthalimide, respectively. Films prepared from hyperbranched polymers with acetoamide end groups had lower densities than their linear analogues. The hyperbranched polyimide film with 4-methylphthalimide end groups possessed lower dielectric constant, birefringence, and shorter cutoff wavelength than the film of poly(4,4′-oxydiphenylene pyromellitimide). These results imply looser packing structures of hyperbranched polymers.

Experimental Section

Chemicals. *N*-Methyl-2-pyrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine were distilled from calcium hydride under reduced pressure. Dichloromethane, acetic anhydride, and acetyl chloride were used after distillation in the presence of calcium chloride, magnesium, and phosphorus pentachloride, respectively. Other solvents and reagents were used as received.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 (300 MHz) spectrometer. IR spectra were recorded on a Shimadzu FT/IR-8100 spectrophotometer. Differential scanning calorimetry (DSC), thermogravimetry (TG), and differential thermal analysis were performed with a Seiko DSC 6200 and TG/DTA 6200, respectively. Gel permeation chromatography (GPC) was performed with a JASCO HPLC 880 PU fitted with polystyrene–divinylbenzene columns (two Shodex KD 806 M and 802) and a Shodex RI-71 refractive index detector in DMF containing 0.01 mol/L of lithium bromide as an eluent. The molecular weights were determined by laser light scattering measurements using a mini DAWN apparatus (Wyatt Technology Co.) and a Shimadzu RID-6A refractive index detector. Specific refractive increments (d*n*/d*c*) of polymers were measured in DMF at 690 nm by using Optilab 903 apparatus (Wyatt Technology Co.). Density of the cast films was measured using a density gradient column.

Monomer Preparation. Synthesis of Sodium 3,5-Dimethoxyphenoxide (1). To a 300-mL round-bottomed flask fitted with a dropping funnel and a nitrogen inlet tube was added 3.479 g (64.4 mmol) of sodium methoxide under nitrogen in ice–water bath. To the flask was added 40 mL of dry methanol dropwise to keep the reaction temperature at 0–3 °C. After sodium methoxide was dissolved completely in methanol, a methanol (40 mL) solution of 9.928 g (64.4 mmol) of 3,5-dimethoxyphenol was added dropwise. After addition, the reaction mixture was maintained for 20 min at that temperature and for 1 h at room temperature, and then evaporated to remove methanol. The light yellow powdery product was obtained after drying overnight at 80 °C under vacuum, giving 11.287 g: yield 99%; ^{1}H NMR (DMSO-d_6) δ 5.19–5.22 (t, 1H, Ar–H), 5.42–5.43 (d, 2H, Ar–H), 3.52 (s, 6H, methoxy) ppm.

Synthesis of 4-(3,5-Dimethoxyphenoxy)phthalonitrile (2). To a 1000-mL round-bottomed flask fitted with a nitrogen inlet tube were added 7.531 g (42.8 mmol) of **1**, 7.401 g (42.8 mmol) of 4-nitrophthalonitrile, and 160 mL of DMSO under nitrogen. The reaction mixture was stirred for 1 h at room temperature and then was poured into a 5 N hydrochloric acid aqueous (HCI(aq)) solution to precipitate. The product was collected by filtration and washed with a 1.2 N HC1(aq) solution, giving 10.870 g after drying overnight at 80 °C under vacuum: 91% yield; ^{1}H NMR (DMSO-d_6) δ 8.05–8.08 (d, 1H, Ar–H), 7.75–7.76 (d, 1H, Ar–H), 7.37–7.41 (dd, 1H, Ar–H), 6.42–6.44 (t, 1H, Ar–H), 6.33–6.34 (d, 2H, Ar–H), 3.73 (s, 6H, methoxy) ppm; IR (KBr) 2230 cm^{-1} (cyano group). Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.57; H, 4.32; N, 9.99. Found: C, 68.40; H, 4.53; N, 10.01.

Synthesis of 4-(3,5-Dimethoxyphenoxy)phthalic Acid (3). To a 500-mL round- bottomed flask fitted with a condenser were added 10.00 g (35.7 mmol) of **2**, 15 g (267.3 mmol) of potassium hydroxide, 100 mL of ethylene glycol, and 50 mL of water. The reaction mixture was stirred for 3 h under reflux. After cooling to room temperature, the reaction mixture was poured into 400 mL of water in an ice–water bath and acidified with 40 mL of 12 N HCI(aq) solution to precipitate. The product was collected by filtration and washed with 1.2 N HCI(aq) solution, giving 10.527 g after drying overnight at room temperature under vacuum: 93% yield; ^{1}H NMR (DMSO-d_6) δ 7.73–7.76 (d, 1H, Ar–H), 7.09–7.14 (m, Ar–H, 2H), 6.37–6.39 (t, Ar–H, 1H), 6.26–6.28 (d, Ar–H, 2H), 3.72 (s, 6H, methoxy) ppm; IR (KBr) 1690 cm^{-1} (carboxyl group). Anal. Calcd for $C_{16}H_{14}O_7$: C, 60.38;H, 4.43. Found: C, 60.09; H, 4.50.

Synthesis of 3,5-Bis(4-nitrophenoxy)diphenyl Ether-3′,4′-dicarboxylic Anhydride (4) Starting from 3. To a 1000-mL round-bottomed flask fitted with a dropping funnel and a nitrogen inlet tube were added 16.960 g (58.4 mmol) of **3** and 330 mL of dry dichloromethane under nitrogen. To the flask in ice–water bath was added 75 g (299 mmol) of boron tribromide dropwise to keep the reaction temperature at 0–3 °C, and then the reaction mixture was maintained for 1 h at that temperature and for 20 h at room temperature. The resulting reaction mixture was poured into 1500 mL of cold water. The aqueous solution of upper layer was extracted with 2000 mL of diethyl ether and the extract was washed with 1800 mL of 0.6 N HCl(aq) solution. Next, 800 mL of diethyl ether was added to the organic solution of lower layer, and the resulting solution was washed with 2000 mL of 0.6 N HCl(aq) solution. The combined diethyl ether extract was treated with anhydrous magnesium sulfate and then evaporated to remove diethyl ether. A 12.780 g yield of the light yellow gummy product was obtained after drying overnight at room temperature under vacuum and provided for the next step without further purification.

To a 500-mL three-necked flask fitted with a condenser, nitrogen inlet, and outlet tubes, 40.690 g (267.9 mmol) of cesium fluoride was added through nitrogen. After the flask was dried with a heating gun, 12.780 g of the resulting product in the previous step, 10.10 mL (95.9 mmol) of 4-fluoronitrobenzene, and 190 mL of DMSO were added to the flask. The reaction mixture was maintained at 115 °C for 24 h and then poured into 2000 mL of cold water to precipitate the product. The precipitate was collected by filtration and washed with 1000 mL of water. A 25.02 g yield of the light yellow powdery product was obtained after drying overnight at room temperature under vacuum. This product was provided for the next step without further purification.

To the 500-mL of round-bottomed flask fitted with a condenser and a nitrogen inlet tube were added 25.02 g of the resulting product in the previous step, 20 mL of dry acetic anhydride and 260 mL of glacial acetic acid under nitrogen. The reaction mixture was stirred for 2 h under reflux. During the reaction, the orange powdery precipitate was observed in the reaction mixture. After the reaction, the product was collected by filtration and washed with acetic anhydride and glacial acetic acid, giving 16.132 g after drying overnight at 130 °C under vacuum: 58.9% yield starting from **3**; IR (KBr) 1850, 1780 cm^{-1} (anhydride group). Anal. Calcd for $C_{26}H_{14}N_2O_{10}$: C, 60.71; H, 2.74; N, 5.45. Found: C, 60.66; H, 2.82; N, 5.39.

Synthesis of an Isomeric Mixture of 3,5-Bis(4-nitrophenoxy)diphenyl Ether–3′,4′-Dicarboxylic Acid Monomethyl Ester (5). To the 200-mL round-bottomed flask fitted with a nitrogen inlet tube were added 10.042 g (19.5 mL) of **4** and methanol (100 mL) solution of 1.7 g (30.3 mmol) of potassium hydroxide under nitrogen. The reaction mixture became a homogeneous solution in 3 h at room temperature, and was maintained for 1 h. The reaction mixture was filtered, and the resulting filtrate was poured into 1500 mL of 0.6 N HCl(aq) solution to precipitate. The product was collected by filtration, washed with 0.6 N HCl(aq) solution, and dried overnight at room temperature under vacuum, giving 9.770 g after reprecipitation once into a 0.6 N HCl(aq) solution from potassium hydroxide/methanol solution: 92% yield; ^{1}H NMR (DMSO-d_6) δ 8.22–8.27 (m, 4H, Ar–H), 7.83–7.86 (dd, 0.79H, Ar–H), 7.71–7.74 (d, 0.21H, Ar–H), 7.26–7.37 (m, 6H, Ar–H), 6.85–6.90 (m, 3H, Ar–H), 3.77–3.78 (s + s, 3H, methyl ester) ppm; IR (KBr) 1730 cm^{-1} (carboxyl, ester group). Anal. Calcd for $C_{27}H_{18}N_2O_{11}$: C, 59.35; H, 3.32; N, 5.13. Found: C, 58.80; H, 3.32; N, 5.02. From the ^{1}H NMR analysis, the ratio of two isomers was 1:3.8 for *a p*-:*m*-methyl ester substitution.

Synthesis of an Isomeric Mixture of 3,5-Bis(4-aminophenoxy)diphenyl Ether–3′,4′-Dicarboxylic Acid Monomethyl Ester (AB$_2$ Monomer, 6) To a 90-mL autoclave were added 7.468 g (5.5 mmol) of **5**, 0.741 g of 10% palladium–charcoal, and 70 mL of dry methanol. The mixture was stirred under 8 atm of hydrogen at room temperature for 48 h, filtered with Celite, and then evaporated to remove methanol. The light brown powdery product was obtained after drying at 45 °C under vacuum for 70 h, giving 6.460 g: 97% yield; ^{1}H NMR (DMSO-d_6) δ 7.79–7.82 (d, 0.79H, Ar–H), 7.67–7.69 (d, 0.21H, Ar–H), 7.26–7.37 (m, 6H, Ar–H), 7.11–7.20 (m, 2H, Ar–H), 6.75–6.80 (m, 4H, Ar–H), 6.54–6.58 (m, 4H, Ar–H), 6.13–6.19 (m, 3H, Ar–H), 3.77 (br, 3H, methyl ester) ppm. Anal. Calcd for $C_{27}H_{22}N_2O_7$: C, 66.66; H, 4.56; N, 5.76. Found: C, 66.12; H, 4.56; N, 5.61. From the ^{1}H NMR analysis, the ratio of two isomers was 1:3.8 for *p*-:*m*-methyl ester substitution.

Polymer Preparation. Direct Self-polycondensation of 6 (Preparation of Polymer 7). To a 50-mL three-necked flask fitted with nitrogen inlet and outlet tubes were added 0.603 g (1.24 mmol) of **6**, 0.568 g (1.48 mmol) of (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonic acid diphenyl ester (DBOP), 0.17 mL (1.24 mmol) of triethylamine, and 3 mL of NMP through nitrogen. The reaction mixture was maintained for 3 h at room temperature and diluted with 6 mL of NMP. The resulting solution was poured into 350 mL of methanol containing 0.1 wt % lithium chloride (0.1 wt % LiCl/CH_3OH), and the precipitated polymer was collected by filtration. The product was dried overnight at room temperature under vacuum, giving 0.504 g: 86% yield; ^{1}H NMR (DMSO-d_6, 100 °C) δ 10.10 (s, 1H, amide-H), 6.65−7.86 (m, 11H, Ar−H), 6.23−6.41 (m, 3H, Ar−H), 3.75 (br, 3H, methyl ester) ppm; IR (KBr) 1663 (amide), 1725 cm^{-1} (ester group).

End-Capping Reaction A typical experiment (preparation of polymer **9**) is shown as follows. After the polymerization mixture was stirred for 3 h, the NMP (6 mL) solution of 2.80 mL (39.4 mmol, 32 equiv) of acetyl chloride was added dropwise to the mixture in ice−water bath. After addition, the reaction mixture was maintained for 0.5 h at that temperature and for 3 h at room temperature, and diluted with 20 mL of NMP. The resulting solution was poured into 2000 mL of 0.1 wt % LiCl/CH_3OH to precipitate. The resulting precipitated polymer was collected by filtration, and dissolved in DMF. After reprecipitation, the product (polymer **9**) was filtered, and dried overnight at room temperature under vacuum, giving 0.506 g: 80% yield; weight-average molecular weight, M_w = 70 000, polydispersity index M_w/M_n = 2.1; inherent viscosity, η_{inh} = 0.23 dL/g; ^{1}H NMR (DMSO-d_6, 100 °C) δ 10.10 (s, 1H, amide-H), 9.60 (s, 1H, amide-H), 7.00−7.67 (m, 11H, Ar−H), 6.35−6.41 (m, 3H, Ar−H), 3.75 (br, 3H, methyl ester), 2.00 (s, 3H, acetyl) ppm; IR (KBr) 1671 (amide), 1727 cm^{-1} (ester group).

Polymer **10** was prepared by end-capping reaction of **7** with enanthyl chloride (2.50 mL, 16.2 mmol, 13 equiv) by the similar procedure for the preparation of **9**: 97% yield; ^{1}H NMR (DMSO-d_6, 100 °C) δ 10.08 (s, 1H, amide-H), 9.53 (s, 1H, amide-H), 6.99−7.89 (m, 12H, Ar−H), 6.35−6.37 (m, 3H, Ar−H), 3.75−3.80 (br, 3H, methyl ester), 2.28−2.30 (m, 2H, methylene), 1.60 (s, 2H, methylene), 1.29 (s, 6H, propylene), 0.86 (s, 3H, methyl) ppm; IR (KBr) 1663 (amide), 1728 (ester), 3070−2870 cm^{-1} (hexyl group).

Polymer **15** was prepared by the end-capping reaction of **7** with 4-methylphthalic anhydride (1.310 g, 8.08 mmol, 13 equiv) by the similar procedure used for the preparation of **9**: 83% yield; ^{1}H NMR (DMSO-d_6, 100 °C) δ 10.10 (s, 1H, amide-H), 9.98 (s, 1H, amide-H), 7.05−7.90 (m, 14H, Ar−H), 6.40−6.42 (br, 3H, Ar−H), 3.75 (br, 3H, methyl ester), 2.38 (s, 3H, methyl) ppm; IR (KBr) 1659 (amide + amic acid), 1725 cm^{-1} (ester group).

Chemical Imidization. A typical experiment (preparation of polymer **8**) is shown as follows. To a 50-mL three-necked flask through nitrogen were added 0.453 g of **7**, 1.10 mL (11.7 mmol) of acetic anhydride, 0.70 mL (8.7 mmol) of pyridine, and 7 mL of DMSO. The reaction mixture was stirred for 24 h at 100 °C and diluted with 20 mL of DMSO. The resulting solution was poured into 1800 mL of 0.1 wt % LiCl/CH_3OH to precipitate. The resulting precipitated polymer was collected by filtration, and dissolved in DMF. After reprecipitation, the product (polymer **8**) was filtered, washed with hot 0.1 wt % LiCl/CH_3OH, and dried overnight at 120 °C under vacuum, giving 0.398 g: 86% yield; M_w = 188 000, M_w/M_n = 3.0; η_{inh} = 0.29 dL/g; 5 wt % loss temperature: T_5 = 395 °C, glass transition temperature: T_g = 193 °C; ^{1}H NMR (DMSO− d_6, 100 °C) δ 9.60 (s, 1H, amide-H), 7.00−7.88 (m, 11H, Ar−H), 6.40−6.60 (m, 3H, Ar−H), 2.00 (s, 3H, acetyl) ppm; IR (KBr) 1670 (amide), 1720, 1780 cm^{-1} (imide group); Anal. Calcd for $C_{28}H_{18}N_2O_6$: C, 70.28; H, 3.79; N, 5.85. Found: C, 67.74; H, 3.53; N, 5.55.

Polymer **11** was prepared by chemical imidization of **9** by the similar procedure for the preparation of **8**: 80% yield; M_w = 37 000, M_w/M_n = 1.6; η_{inh} = 0.18 dL/g; T_5 = 425 °C, T_g = 189 °C; ^{1}H NMR (DMSO-d_6, 100 °C) δ 9.60 (s, 1H, amide-H), 7.00−7.88 (m, 11H, Ar−H), 6.40−6.60 (m, 3H, Ar−H), 2.00 (s, 3H, acetyl) ppm; IR (KBr) 1670 (amide), 1720, 1780 cm^{-1} (imide group).

Polymer **12** was prepared by chemical imidization of **10** by the similar procedure used for the preparation of **8**: 79% yield; T_5 = 405 °C, T_g = 138 °C; ^{1}H NMR (DMSO-d_6, 100 °C) δ 9.51 (s, 1H, amide-H), 7.02−7.89 (m, 11H, Ar−H), 6.40−6.60 (m, 3H, Ar−H), 2.27 (s, 2H, methylene), 1.59 (s, 2H, methylene), 1.28 (s, 6H, propylene), 0.85 (s, 3H, methyl) ppm; IR (KBr) 1671 (amide), 1721, 1779 (imide), 3070−2860 cm^{-1} (hexyl group).

Polymer **13** was prepared by heating treatment at 100 °C for 24 h after end-capping reaction with acetyl chloride without isolation of **9**: 81% yield; M_w = 38 000, M_w/M_n = 1.5; η_{inh} = 0.17 dL/g; ^{1}H NMR (DMSO-d_6, 100 °C) δ 9.60 (s, 1H, amide-H), 7.02−7.88 (m, 11H, Ar−H), 6.40−6.60 (m, 3H, Ar−H), 2.00 (s, 3H, acetyl) ppm; IR (KBr) 1670 (amide), 1720, 1780 cm^{-1} (imide group).

Polymer **14** was prepared by chemical imidization in a procedure similar to that for the preparation of **8** without isolation of **7**: 84% yield; M_w = 38 000, M_w/M_n = 1.6; η_{inh} = 0.17 dL/g; ^{1}H NMR (DMSO-d_6, 100 °C) δ 9.60 (s, 1H, amide-H), 7.02−7.89 (m, 11H, Ar−H), 6.41−6.60 (m, 3H, Ar−H), 2.00 (s, 3H, acetyl) ppm; IR (KBr) 1670 (amide), 1720, 1780 cm^{-1}(imide group).

Polymer **16** was prepared by chemical imidization of **15** by a procedure similar to that for the preparation of **8**: 89% yield; T_5 = 455 °C, T_g = 186 °C; ^{1}H NMR (DMF-d_7, 100 °C) δ 7.05−7.98 (m, 14H, Ar−H), 6.57−6.66 (s + s, 3H, Ar−H), 2.51 (s, 3H, methyl) ppm; IR (KBr) 1721, 1779 cm^{-1}(imide group).

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References and Notes

(1) Nishizaki, S.; Moriwaki, T. *Kogyo Kagaku Zasshi* **1970**, *73*, 1873.

(2) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *G. Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(3) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176.

(4) Voit, B. I. *Acta Polym.* **1995**, *46*, 87.

(5) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci.—Pure Appl. Chem.* **1996**, *A33*, 1399.

(6) Malmoström, E.; Hult, A. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555.

(7) Kim, Y. H.; Webster, O. W. *Ibid.* **1990**, *112*, 4592. Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561. Kim, Y. H.; Beckerbauer, R. *Macromolecules* **1994**, *27*, 1968.

(8) Johansson, M.; Malmstörm, E.; Hult, E. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 619. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. Turner, S. R.; Voit, B. I.; Mourey, T. M. *Macromolecules* **1993**, *26*, 4617. Kricheldorf, H. R.; Stöber, O. *Macromol. Rapid. Commun.* **1994**, *15*, 87. Malmstörm, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, *28*, 1698.

(9) Uhrich, K. E.; Boegeman, S.; Fréchet, J. M. J.; Turner, S. R. *Polym. Bull.* **1991**, *25*, 551. Kim, Y. H. *Adv. Mater.* **1992**, *4*, 764. Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1998**, *31*, 5964. Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1999**, *32*, 2215. Jikei, M.; Chon, S.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanabe, J. *Macromolecules* **1999**, *32*, 2061.

(10) Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583. Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J. *Polym. Mater. Sci. Eng.* **1991**, *64*, 237.

(11) Chu, F.; Hawker, C. J. *Polym. Bull.* **1993**, *30*, 265. Miller, T. M.; Neeman, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356. Miller, T. M.; Neeman, T. X.; Kwock, E. W.; Stein, S. M. *Macromol. Symp.* **1994**, *77*, 35. Shu, C.-F.; Leu, C.-M. *Macromolecules* **1999**, *32*, 100.

(12) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(13) Srinivasan, S. A.; Tweieg, R.; Hedrick, J. L.; Hawker, C. J. *Macromolecules* **1996**, *29*, 8543. Hedrick, J. L.; Hawker, C. J.; Miller, R. D.; Tweieg, R.; Srinivasan, S. A.; Trollsas, M. *Macromolecules* **1997**, *30*, 7607.

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

(15) Thompson, D. S.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1999**, *32*, 4764.

(16) Tao, X.; Zhang, Y.; Wada, T.; Sasabe, H.; Watanabe, T.; Miyama, S. *Adv. Mater.* **1998**, *10*, 226. Zhang, Y.; Wang, L.; Wada, T.; Sasabe, H. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1359.

(17) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 1111.

(18) Ueda, M.; Kameyama, A.; Hashimoto, K. *Macromolecules* **1988**, *21*, 19. Ueda, M.; Mori, H. *Macromol. Chem.* **1993**, *194*, *511*.

(19) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(20) Hasegawa, M.; Kochi, M.; Mita, I.; Yokota, R. *Eur. Polym. J.* **1989**, *25*, 349.

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