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Communications to the Editor

Synthesis of Hyperbranched Aromatic Polyamide from Aromatic Diamines and Trimesic Acid

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Recently, dendritic macromolecules have drawn the attention of various research groups because of their unique physical and chemical characteristics.[1−5] Dendrimers are prepared through divergent or convergent approaches which are composed of stepwise synthesis. Hyperbranched polymers are analogues of dendrimers, which have less controlled structures. It is reported that the thermal properties and solubility of hyperbranched polymers are similar to those of dendrimers when these polymers have the same repeating units.[6]

Aromatic polyamides (aramids) are accepted as one of the important high-performance polymers.[7] Gelled networks composed of aramid segments have also been investigated as rigid fractal polymers.[8−12] Direct connection of aromatic rings by amide bonds gives exceptional heat and flame resistance and high tensile strength and modulus. Unfortunately, all aramids are generally characterized by poor processability. It is worthwhile to introduce hyperbranched structures in order to improve the poor processability caused by the rigid repeating unit in the linear aramids. Kim has reported the synthesis of hyperbranched aromatic polyamides from AB_2 and A_2B monomers.[13]

In general, hyperbranched polymers are synthesized by self-polycondensation of AB_n type monomers which have one "A" functional group and n "B" functional ones. However, most of the AB_n molecules are not commercially available and the preparation of such a designed monomer takes a longer time in comparison with the following polymerization. On the other hand, many difunctional monomers (A_2) are commercially available as monomers for linear condensation polymers. Furthermore, some trifunctional monomers (B_3) used for branching or cross-linking agents are also available. Polymerization of A_2 and B_3 monomers generally leads not only to branching but also to cross-linking and cyclization reactions. In most cases, when three-dimensional structure is developed, the polymer becomes a gel or highly cross-linked material which is insoluble in any organic solvents.[14−16] Critical conversion of the A functional group for gelation can be calculated to be 0.87 when equimolar amounts of A_2 and B_3 monomers are reacted.[17] Flory has also pointed out that the polymerization of AB_x monomers proceeds without gelation to form hyperbranched polymers. If the first condensation of A_2 and B_3 molecules is faster than the following propagation, a AB_2 type molecule would be formed as an intermediate molecule and accumulated in solution. Therefore, hyperbranched polymers might be prepared through intermediate AB_2 molecules formed from A_2 and B_3 monomers. In this paper, a direct polymerization of diamines and triacid was investigated as a new route to synthesize hyperbranched polyamides from A_2 and B_3 monomers, as shown in Scheme 1. In the scheme, A, B, and ab represent an amino, a carboxyl, and an amido group, respectively. When one amido (ab) was formed from the A_2 and B_3, unreacted functional groups are denoted by A′ for the amino group and B′ for the carboxylic group.

Scheme 1

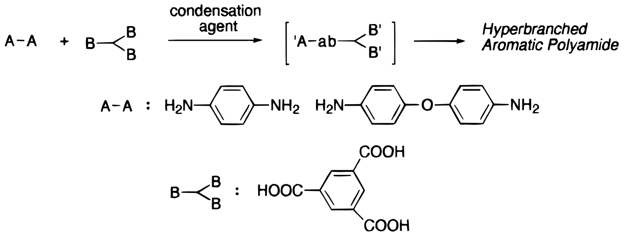

Table 1. Direct Polycondensation of Diamines and Trimesic Acid in the Presence of Condensation Agents[a]

code	diamine	NMP (mL)	$P(OPh)_3$ (mmol)	pyridine (mL)	LiCl (g)	yield (%)	η_{inh}[b] (dL/g)
PD-01	PD	80	30	7.5	0	92	0.96
PD-02		80	30	7.5	0	87	0.70
PD-03		50	30	7.5	0	gel	
PD-04		80	20	5.0	0	74	0.31
PD-05		80	25	5.0	0	72	0.29
PD-06		80	20	5.0	1	93	0.72
ODA-01	ODA	80	30	7.5	0	88	0.49
ODA-02		80	30	7.5	0	93	0.75
ODA-03		80	20	5.0	1	gel	
ODA-04		100	20	5.0	1	gel	

[a] The polymerization was carried out with an equimolar amount of an diamine (10 mmol) and trimesic acid (10 mmol) in the presence of triphenyl phosphite and pyridine at 80 °C for 3 h. [b] Measured at a concentration of 0.5 g/dL in DMF containing LiBr (0.01 mol/L) at 30 °C.

Equimolar amounts of the diamines *p*-phenylene diamine (PD) and 4,4′-oxyphenylene diamine (ODA) and trimesic acid (TMA) were allowed to polymerize in the presence of triphenyl phosphite and pyridine as condensation agents. A typical experiment is as follows (PD-02 in Table 1). A three-necked flask was charged with 1.08 g (10 mmol) of PD, 2.10 g (10 mmol) of TMA, 7.5 mL of pyridine, and 80 mL of *N*-methylpyrrolidinone (NMP). Triphenyl phosphite (7.82 mL, 30 mmol) was added to the solution after the monomers were dissolved

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completely. The mixture was heated at 80 °C for 3 h and then poured into 500 mL of methanol containing 10 mL of 12 N aqueous HCl. The precipitated product was collected by filtration and purified by reprecipitation from NMP solution into methanol. The product was washed with hot methanol and dried in vacuo at 100 °C for 12 h. The reaction conditions and results of the polymerization are summarized in Table 1.[18]

It is reported that the direct polymerization of aromatic diamines (A_2) and aromatic tricarboxylic acids (B_3) resulted in gelation within 10−20 min when the feed ratio of amino and carboxyl groups was equal to 1.[8,9] In this work, the ratio was set to 2:3 in all experiments and the $A_2 + B_3$ polymerization could be controlled to form soluble polymers by consideration of reaction conditions. For the polymerization of PD and TMA, no gelation occurred for the polymerization at 80 °C for 3 h with the total monomer concentration of 0.21 mol/L (3.3 wt %). A powdery polymer was obtained with a reasonable reproducibility (PD-01 and PD-02). Since the resulting polymer was soluble in aprotic polar solvents, such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide, NMP, and dimethyl sulfoxide, it was completely different from gel and highly cross-linked materials. In the IR spectrum of the resulting polymer, a broad absorption band from 3400 to 3200 cm^{-1} and a strong carbonyl absorption at 1659 and 1713 cm^{-1} were observed. These data suggested the formation of the amide and the existence of a carboxyl group in the polymer. The proton of the carboxyl group was also observed as a broad peak at 13.47 ppm in the ^1H NMR spectrum. The integration ratio for the peaks attributed to aromatic protons of the PD unit and of the TMA unit was 3.0:4.5, which indicated that the PD unit was incorporated slightly more than the TMA unit. The degree of branching (DB) is one of the most important parameters for characterization of hyperbranched polymers. Although the DB of the resulting polymer could not be determined because of its complex structure, the percentage of trisubstituted TMA units against all TMA units can be calculated by the integration of the ^1H NMR peaks. Multiple peaks attributed to TMA protons were observed from 8.60 to 8.95 ppm. The peak at 8.77 ppm, assigned to a trisubstituted TMA unit by using a model compound,[19] gave the percentage 32. The trisubstituted TMA unit corresponds to the dendritic unit of the hyperbranched polymer if the $A'B'_2$ intermediate molecule in Scheme 1 was used as a starting material for the self-condensation. It is interesting to note that the percentage 32 was close to 25, which was the expected value statistically when the DB of the corresponding hyperbranched polymer was 0.5.[20−22] The inherent viscosity of the resulting polymer was as high as that reported for the sol fraction of rigid polyamide networks.[9,11]

When the amount of NMP was decreased to 50 mL (the total monomer concentration was 0.31 mol/L or 4.9 wt %), gel formation was observed in 2 h at the same reaction conditions (PD-03). Three equivalents of triphenyl phosphite to TMA was required to achieve a high inherent viscosity when the polymerization was carried out without lithium chloride (LiCl). Addition of LiCl accelerated the polymerization, as reported in the literature.[23] The polymer having a high viscosity was obtained from the polymerization with 2 equiv of triphenyl phosphite in the presence of LiCl (PD-06).

Table 2. End-Capping Reaction of the Resulting Polymers by *p*-Anisidine[a]

sample	W_{init}[b] (g)	W_{end}[b] (g)	ΔW[b] (g)	M_{COOH}[c]	f[d]	M_w[e]	η_{inh}[f] (dL/g)
PD-02	1.86	2.36	0.50	387	0.73	285 000	0.70
ODA-01	2.86	3.15	0.29	1027	0.36	86 700	0.53

[a] The end-capping reaction was carried out with 4.31 g (35 mmol) of *p*-anisidine and the resulting polymer in the presence of triphenyl phosphite (35 mmol) and pyridine (10 mL) in NMP (140 mL) at 100 °C for 3 h. [b] W_{init} and W_{end} represent the weight of the sample at the beginning and the end of the reaction, respectively. $\Delta W = W_{end} - W_{init}$. [c] Molecular weight per one carboxylic acid group calculated from W_{init} and ΔW. [d] $f = M_{AB_2\ unit}/M_{COOH}$. [e] Determined by GPC measurements with a laser light-scattering detector in DMF containing LiBr (0.01 mol/L). [f] Measured at a concentration of 0.5 g/dL in DMF containing LiBr (0.01 mol/L) at 30 °C.

4,4′-Oxyphenylene diamine (ODA) was another candidate for a A_2 monomer. A powdery polymer was formed by the direct polymerization with TMA in the presence of 3 equiv of triphenyl phosphite with a reasonable reproducibility (ODA-01 and ODA-02). IR and ^1H NMR spectroscopic data[18] indicated the formation of an amide bond and the existence of a carboxylic acid, similar to the case for the PD−TMA system. The integration ratio of aromatic peaks attributed to TMA and the ODA in ^1H NMR was 3.0:10.0, which also indicated that ODA unit was incorporated more than TMA unit. The peak at 8.76 ppm assigned to trisubstituted TMA protons occupied 60% of the multiple peaks of all TMA protons (8.65−8.87 ppm). The percentage implies that the trisubstituted TMA unit was formed more than that in the PD−TMA polymer. Gelation occurred when the polymerization was carried out with LiCl even if the amount of NMP was increased to 100 mL (ODA-03 and ODA-04).

To evaluate the amount of carboxylic acid groups in the resulting polymers, *p*-anisidine was reacted with PD-02 and ODA-01 (end-capping reaction), as shown in Table 2. The end-capping reaction was carried out with 4.31 g (35 mmol) of *p*-anisidine and the resulting polymer in the presence of triphenyl phosphite (35 mmol) and pyridine (10 mL) in NMP (140 mL) at 100 °C for 3 h.[24] The absorption at 1713 cm^{-1} attributed to carboxylic acid disappeared, and a new peak at 1179 cm^{-1} attributed to the ether bond in the methoxy group appeared after the end-capping reaction. The molecular weight per one carboxylic acid group M_{COOH} can be calculated by the amount of reacted *p*-anisidine (ΔW). A new parameter (f) calculated by the division of the molecular weight of the $A'B'_2$ unit by M_{COOH} represents the deviation of resulting polymers from the corresponding hyperbranched polymers. The M_{COOH} and f values indicated that the resulting polymers contained many carboxylic acid groups whose amount was less than that of the corresponding hyperbranched polymer ($f = 1.0$). GPC measurements for PD−TMA and ODA−TMA polymers failed because of the strong adsorption of samples on columns. The end-capping reaction enabled us to evaluate the molecular weight by GPC measurements.[25] Each molecular weight was high enough, and the M_w for PD-02 was larger than that for ODA-01. The molecular weight increased when the measurement was carried out at a higher concentration of the sample. This phenomenon suggested that aggregation of the polymers would occur in DMF even if LiBr were added to avoid the aggregation. Further studies about the estimation of an accurate molecular

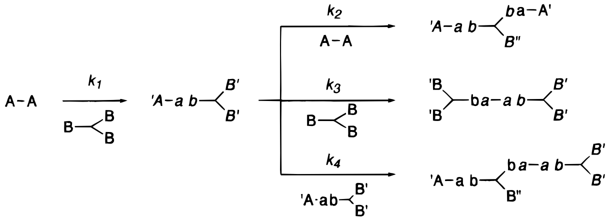

Figure 1. Reaction path for the initial stage of the polymerization of A_2 and B_3 momoners.

weight are in progress. The molecular weight distrubutions (M_w/M_n) for PD-02 and ODA-01 were 5.26 and 4.93, respectively, which implies a broad molecular weight distribution. Each inherent viscosity in DMF was not changed noticeably by the end-capping reaction in both cases.

The end-capping reaction of PD-02 by *p*-toluic acid was preliminarily investigated in order to evaluate the amino groups. After the end-capping reaction by condensation agents, no change was observed in IR spectroscopy and a very small peak at 2.37 ppm attributed to the methyl protons of *p*-toluic acid was observed in ^1H NMR. The results suggest that PD-02 has a very small amount of amino groups.

The glass transition temperature was not clearly observed for all resulting polymers by means of DSC, as reported in the case of the rigid aromatic fractals.[12] Thermal decomposition was observed from 276 °C for the PD−TMA polymer and 268 °C for the ODA−TMA polymer.[26] The onset temperature increased about 20 °C for both polymers by the end-capping reaction with *p*-anisidine. The temperatures for 10% weight loss for the PD−TMA and the ODA−TMA polymers were 473 and 507 °C, respectively. During TGA measurements, the sample weight decreased a few percent around 100 °C for all samples and the weight increase was observed when the preheated sample (230 °C) was cooled to 30 °C. The weight change is attributed to desorption and adsorption of water. The hygroscopicity may be caused by amide bonds because the same phenomenon was observed for the polymer prepared from PD and isophthalic acid.

Possible reaction paths at the initial stage of the polymerization are illustrated in Figure 1 with corresponding rate constants (k_1, k_2, k_3, and k_4). After an $A'B'_2$ type intermediate is formed by the first condensation of A_2 and B_3 molecules, there are three reaction paths for the $A'B'_2$ molecule: condensation with A_2 (k_2), B_3 (k_3), and the $A'B'_2$ molecule (k_4). If k_1 is much larger than k_2, k_3, and k_4, the $A'B'_2$ type molecules would be accumulated in the reaction mixture, which is suitable for the formation of hyperbranched polymers. In this work, the amine functional group in the $A'B'_2$ type molecules (A′) is deactivated by the formation of an amide bond in comparison with the original amino group (A) because the electron-donating tendency of the amino group is decreased by the formation of an amide bond in the para position of the ring system. Therefore, k_3 and k_4 should be smaller than k_1. However, B′, which represents the carboxylic acid group in the $A'B'_2$ type molecule, might have the same reactivity as that of B in the B_3 molecule. That is, k_2 should be almost the same as k_1.

Table 3. Proton Affinity of Monomers and Corresponding $A'B'_2$ Molecules

	PA (kcal/mol)		
monomer	A_2[a]	$A'B'_2$[a]	ΔPA[b]
PD	233.17	228.28	4.89
ODA	231.71	229.30	2.41

[a] Proton affinity of A_2 monomer and $A'B'_2$ molecules, respectively. [b] $\Delta PA = PA_{A2} - PA_{A'B'2}$.

We have tried to estimate the deactivation effect of the amino group in the $A'B'_2$ molecules by an ab initio molecular orbital calculation.[27] Proton affinity (PA) is defined by the difference in total energy before and after protonation. It has been reported that the PA of aromatic diamines is proportional to the pK_a.[28] In addition, the reactivity of aromatic amines for nucleophilic reaction can be estimated quantitatively by pK_a values.[29,30] Therefore, the reactivity would be estimated by the discussion of PA without isolation of products. PA values for diamines and corresponding $A'B'_2$ molecules are listed in Table 3. PA decreased after the formation of the amide bond for both cases of PD and ODA, which implies that the amino groups in the $A'B'_2$ molecules are deactivated by the formation of amide bonds. That is, k_3 and k_4 in Fugue 1 are smaller than k_1. The ether bond in ODA acted as a spacer and made the ΔPA smaller than that of PD. We assume that ΔPA affects the *f* values in Table 2. Kinetic data from experiments will give a quantitative discussion.

In summary, the direct polycondensation of aromatic diamines (A_2) and trimesic acid (B_3) has been investigated as a new and convenient route to synthesize hyperbranched aromatic polyamides. The polymerization can be controlled to avoid gelation, and powdery polymers were isolated by investigation of reaction conditions. The resulting polymers were soluble in organic solvents and contained large amount of carboxylic acid groups, which is similar to the case for conventional hyperbranched polymers prepared from AB_2 type monomers. The reactivity change of monomers and intermediate molecules during the polymerization affected the structure of the resulting polymers.

Acknowledgment. The molecular orbital calculations were carried out at the Computer Center of the Tokyo Institute of Technology and the Computer Center of the Institute for Molecular Science, and we thank them for their generous permission to use the Cray C90 and the DEC alpha server 8400, and the IBM SP2, respectively.

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(17) The branching coefficient and conversion of functional groups can be related by the following equation: $\alpha = rp_b^2 = p_a^2/r$. The critical branching coefficient (α_c) was 0.5 and the r (B/A) was 1.5 in this work. Therefore, when p_a reaches 0.87, α becomes 0.5 and gelation occurs statistically.

(18) PD-TMA: IR (KBr, cm^{-1}) 3313, 3077, 1713, 1659, 1613, 1557, 1514, 1449, 1404, 1314, 1248, 1113, 1017, 920, 834, 731, 699, 675, 525. ^{1}H NMR (DMSO, δ_{ppm}) 13.47 (br, COOH), 10.62, 10.52, 9.91 (amido proton), 8.78, 8.75, 8.72, 8.70, 8.62 (m, aromatic protons from TMA), 7.94, 7.82, 7.80, 7.71, 7.69, 7.58 (m, aromatic protons from PD). ^{13}C NMR (DMSO, δ_{ppm}) 165.75, 165.51, 163.97, 163.71, 163.42, 152.86, 135.55, 135.34, 135.17, 134.07, 134.01, 133.95, 131.78, 131.63, 131.42, 131.24, 130.37, 128.95, 122.10, 122.20, 121.91, 120.61, 119.21, 118.33, 118.27, 118.17, 118.14, 117.92. ODA-TMA: IR (KBr, cm^{-1}) 3338, 3135, 3072, 1711, 1659, 1609, 1538, 1501, 1451, 1410, 1316, 1237, 1169, 1109, 1015, 920, 880, 831, 735, 517. ^{1}H NMR (DMSO, δ_{ppm}) 12.65 (br, COOH), 10.62, 9.90 (amido proton), 8.78, 8.73, 8.71, 8.68, 8.61 (m, aromatic protons from TMA), 7.83, 7.80, 7.58, 7.55, 7.23, 7.21, 7.17, 7.07, 7.05, 6.98, 6.95 (m, aromatic protons from ODA). ^{13}C NMR (DMSO, δ_{ppm}) 165.81, 165.56, 164.02, 163.77, 135.45, 135.30, 134.66, 131.81, 131.66, 131.48, 131.31, 130.41, 130.31, 120.66, 120.62, 119.25.

(19) The model compound *N*,*N′*,*N″*-triphenyl-1,3,5-benzenetriamide was prepared from 1,3,5-benzenetricarbonyl trichloride and aniline.

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(22) The hyperbranched polymer with its DB of 0.5 must have linear units of 50%, dendritic units of 25%, and terminal units of 25% when the degree of polymerization is high enough.

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(24) End-capped polymer from PD-02: IR (KBr, cm^{-1}) 3301, 3075, 1661, 1610, 1547, 1514, 1443, 1406, 1314, 1246, 1179, 1111, 1032, 919, 831, 771, 700, 525, 450. ^{1}H NMR (DMSO, δ_{ppm}) 10.61, 10.46, 10.44, 9.91 (amido proton), 8.73, 8.70, 8.68 (m, aromatic protons from TMA), 7.94, 7.85, 7.59 (m, aromatic protons from PD), 7.74, 7.70, 6.97, 6.95 (dd, aromatic protons from *p*-anisidine), 3.76 (s, methyl H). End-capped polymer from ODA-01: IR (KBr, cm^{-1}) 3304, 3135, 3072, 1663, 1607, 1536, 1499, 1410, 1316, 1238, 1171, 1109, 1032, 1015, 878, 831, 727, 519, 448. ^{1}H NMR (DMSO, δ_{ppm}) 10.61, 10.45, 9.91 (amido proton), 8.69, 8.67 (m, aromatic protons from TMA), 7.85, 7.82, 7.08, 7.05 (dd, aromatic protons from ODA), 7.73, 7.70, 6.96, 6.93 (dd, aromatic protons from *p*-anisidine), 3.75 (s, methyl H).

(25) GPC measurements are carried out in DMF containing LiBr (0.01 mol/L) at a concentration of 0.5−0.7 g/L. Absolute molecular weight was calculated with a laser-light scattering detector connected to the GPC system directly. The specific refractive increment was determined to be 0.242 mL/g.

(26) Thermal gravimetric analysis was carried out at a heating rate of 20 °C/min in N_2. The onset temperature was determined from the plateau line around 200 °C because of its hygroscopicity.

(27) The caluclation was carried out with the Gaussian 94 program with HF/6-31G**. Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

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