Synthesis of Hyperbranched Aromatic Polyamide by Direct Polycondensation Method

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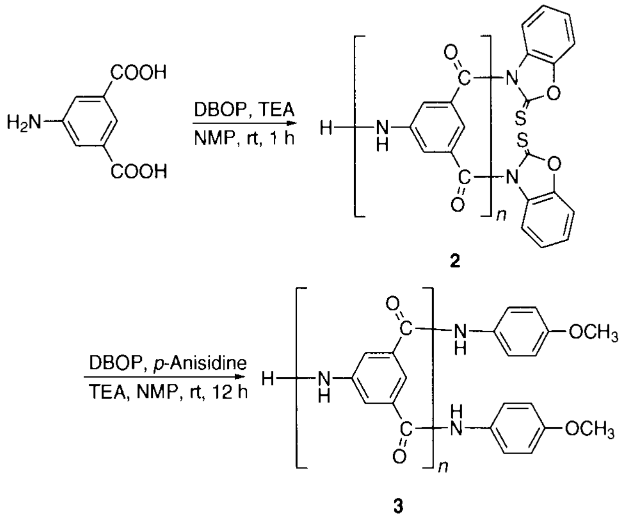
A hyperbranched aromatic polyamide was prepared from 5-aminoisophthalic acid by the direct polycondensation method using diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) as a condensing agent. The resulting polymer was further reacted with *p*-anisidine to give methoxy-end-capped polymer (**3**). IR spectrum of **3** indicates the end-capping was achieved completely. MALDI-TOF MS spectrum of **3** indicates presence of no side-reaction. Number average molecular weight of **3** could be determined by its ^{1}H NMR spectrum and was 1 800.

Dendrimers have been attracted much interests because of their unique architecture and their novel properties. Hyperbranched polymers are a relatively new class of highly branched materials which are easily accessible, and can be prepared in large quantities in contrast to the synthesis of the dendrimers. They are generally prepared when maltifunctional AB_n monomers are allowed to react in an less controlled one step polymerization. A wide variety of hyperbranched polymers have been reported in the literature including polyesters,[1, 2] polyethers,[3] polyphenylene-ethynylene,[4] polycarbonates[5] and polyamides.[6] For the synthesis of them, synthesis of the reactive AB_n monomer, for example, acid chloride possessing some amino groups, is required. Such reactive monomers are difficult to be prepared and/or purified, and this provides serious limitation for preparation of wide range of the hyperbranched polymers. Melt polycondensation of hydroxydicarboxylic monomer at high temperature was also examined to prepare the hyperbranched polyester, but side reactions involving ether-linkage[2] and cyclic structure[1] were found.

Direct polycondensation method is very useful for the preparation of condensation polymers.[7-9] That requires no active acyl monomers and proceeds under mild condition. Thus we are interested in applying direct polycondensations for the synthesis of hyperbranched polyamides. This method should reduce the reaction steps in monomer synthesis, and accomplish wide variety of the hyperbranched polymers to be prepared. In this paper, we report the synthesis of a hyperbranched aromatic polyamide, which has already been prepared from 5-aminoisophthaloyl dichloride by Kim,[6] by direct polycondensation method from 5-aminoisophthalic acid (**1**) with diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP)[9] as a condensing agent.

Polymerization was carried out by mixing **1**, equimolar triethylamine and two molar equivalents of DBOP in NMP at room temperature for 1 h. The mixture was poured into methanol and the precipitate was filtered. The resulting polymer (**2**) should have active amide terminal groups as shown in Scheme 1. **2** was soluble in aprotic polar solvents such as DMSO, DMF, DMAc and NMP, and insoluble in toluene, THF, acetone and pyridine. Weight average molecular weight (Mw) of **2** was determined by GPC (DMF) with polystyrene calibration, and was 30 000 (Mw/Mn = 1.51) which is comparable to that reported by Kim.[6]



Scheme 1.

The molecular weight of polyamides determined by GPC generally shows no exact value because the value is relative to polystyrene. One of the methods to determine the exact molecular weight of polyamides is quantitative analyses of terminal groups. We attempted to cap the terminal carboxylic groups of **2** by *p*-anisidine in order to analyze the terminal groups by ^{1}H NMR spectroscopy. The end-capped hyperbranched polyamides was prepared by addition of *p*-anisidine and DBOP (each 10 molar equivalents

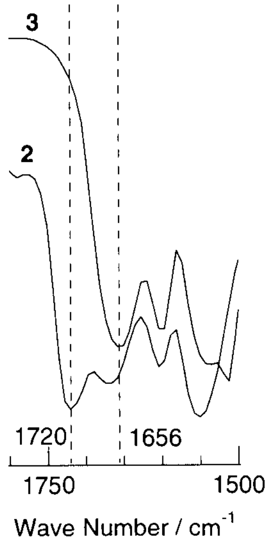
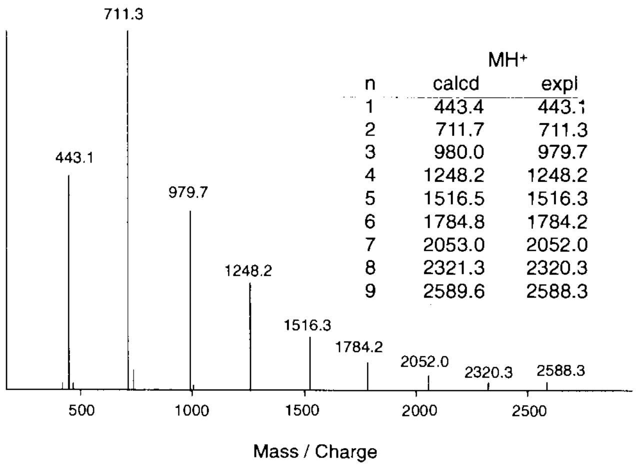


Figure 1. IR spectrum of **2** and **3** (KBr).

to **1**) after the reaction described above. The resulting polymer (**3**) was soluble not only in the aprotic polar solvents but also in THF and pyridine. The Mw (GPC with DMF) of **3** was 32 000 (Mw/Mn = 1.21) and comparable to that of **2**.

Figure 1 shows carbonyl region of IR spectrum of **2** and **3**. In the spectrum of **2**, a peak at 1720 cm^{-1}, which is assigned to C=O stretching of the carbonyl group in the active amide, was observed besides the amide absorbance at 1 650 cm^{-1}. On the contrary, the spectrum of **3** showed no peaks at 1 720 cm^{-1}. Thus the end-capping was achieved completely and the all terminal groups in **3** are methoxy groups. MALDI-TOF MS spectrum of **3** (Figure 2) was also suggested the complete end-capping. The spectrum shows peaks only at small molecular weight region below 2 000 because high molecular weight polar compounds such as polyamides are hard to ionize due to their strong intermolecular interaction. The appeared peaks were, however, observed clearly at regular intervals of 268. That intervals are agreed with the molecular weight of the repeating units (268.3). Thus the reaction causes no side reaction and all terminal groups were end-capped. The number average molecular weight (Mn) of **3** could be estimated by comparing the number of the aromatic protons and that of the methoxy protons in its ^{1}H NMR spectrum and was 1 800 which corresponds to the 6-mer. The larger molecular weight resulted from the GPC measurement might be caused by rigid structure of **2** and **3**. Kim reported the molecular weight of the polyamide prepared from 5-aminoisophthaloyl dichloride to be 30 600 estimated by GPC.[6] Our GPC results (Mw = 32 000) corresponds to that of them. Thus the smaller molecular weight indicated by the ^{1}H NMR does not support any limitation of this direct polycondensation method.



	MH+	
n	calcd	expl
1	443.4	443.1
2	711.7	711.3
3	980.0	979.7
4	1248.2	1248.2
5	1516.5	1516.3
6	1784.8	1784.2
7	2053.0	2052.0
8	2321.3	2320.3
9	2589.6	2588.3

Figure 2. MALDI-TOF MS spectrum of **3**. Dihydroxybenzoic acid (DHBA) was used as a matrix.

In conclusion, the direct polycondensation method was successfully applied to synthesis of the hyperbranched polyamides without any side reactions under the mild condition. Absence of side reaction was confirmed by MALDI-TOF MS spectrum and exact molecular weight could be determined by ^{1}H NMR spectrum. Using more flexible monomer such as aliphatic compounds would be improve the molecular weight of the product.

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