

SYNTHESIS OF STAR-SHAPED AROMATIC POLYAMIDES CONSISTING OF CYCLOSILOXANE CORE

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Star-shaped aromatic polyamides were prepared, in order to obtain soluble aromatic polyamides which exhibited the similar physical properties to those of the ordinary linear polyamides. Two kinds of core molecules consisting of tetracyclosiloxane with tetracarboxyl or octacarboxyl groups were prepared, and tetra- or octa-armed star-shaped aromatic polyamides were synthesized by polycondensation of 4-aminobenzoic acid initiated at the carboxyl groups of these core molecules. Then, the terminal carboxyl groups of the star-shaped polymers were end-capped by the reaction with *p*-toluidine. In addition, the star-burst aromatic polyamides were prepared by the similar procedure using 4-aminobenzoic acid and 5-aminoisophthalic acid as monomers. It was found that these branched aromatic polyamides were soluble in DMSO and other aprotic polar solvents, and maintained the unique characteristics of linear aromatic polyamides such as thermal stability and crystallinity.

Key words: cyclosiloxane, star-shaped polymer, aromatic polyamides, solubility, thermal stability.

1. INTRODUCTION

Recently, the multi-armed macromolecules, such as hyper-branched polymers¹⁾, dendrimers²⁾, and star-shaped polymers³⁾, have been focused in much attention due to their unique architectures and properties. Generally speaking, the multi-armed macromolecules exhibit the low viscosity, the amorphous solid property and the facility to introduce functional end groups. In addition, one of the unique characteristics is the higher solubility rather than the linear polymers with the same backbone component. Therefore, the syntheses of multi-armed macromolecules consisted of aromatic polyesters, polyamides and poly(phenylene sulfide)s, etc., have been reported to obtain the soluble polymers, the linear ones of which are insoluble⁴⁾⁻⁷⁾. Yang et al. reported that the hyper-branched aromatic polyamides were prepared from AB₂ type monomers and were soluble in some organic solvents⁶⁾. In this case, the soluble polymers were successfully obtained, however, the peculiar properties of aromatic polyamides, such as crystallinity and thermal stability, were lost, owing to that the segment length of the monomer units became very short.

In our previous paper⁸⁾, we have reported that the octa-armed star-shaped aromatic polyamides were prepared by polycondensation of 4-aminobenzoic acid initiated at the amino or carboxyl groups of the core molecules containing cyclosiloxane component, and were soluble in DMSO and other aprotic polar solvents, which maintained the peculiar properties of linear

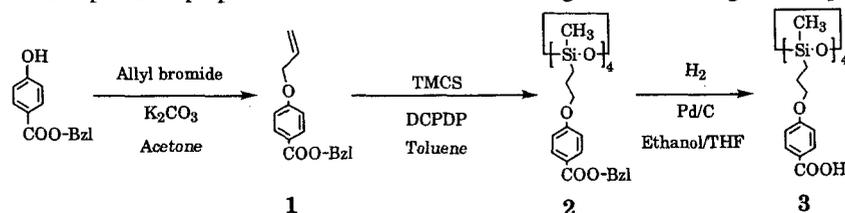
aromatic polyamides. In this paper, the star-shaped aromatic polyamides with different number of branches and star-burst structures were prepared by the similar procedure, in order to investigate the effect of branched structure on the solubility, the crystallinity and the thermal stability of these polyamides.

2. RESULTS AND DISCUSSION

2.1 Preparation of star-shaped polyamides

As shown in Scheme 1, the core molecule (3) consisting of tetracyclosiloxane component with tetracarboxyl groups was prepared by hydrosilylation of benzyl 4-allyloxybenzoate (1) and tetramethylcyclotetrasiloxanes with Pt catalyst to afford 2, followed by hydrogenation reduction with H₂/Pd. The product, 3, was a white solid and stable in air.

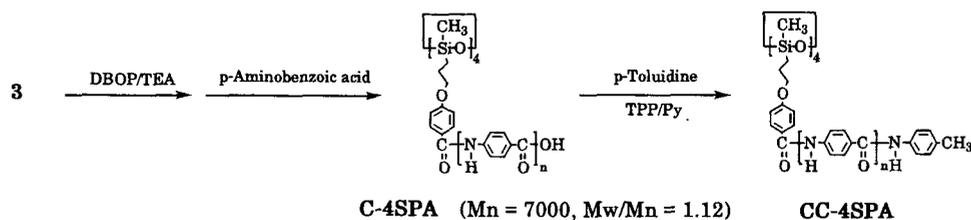
Scheme 2 represents the synthetic procedure of tetra-armed star-shaped polyamide (C-4SPA). C-4SPA was prepared from the core molecule, 3, with 4-aminobenzoic acid as a monomer and diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)-phosphonate (DBOP) as a condensation agent. DBOP has been known to activate a carboxyl group to proceed a polycondensation reaction⁷⁾. Therefore, after DBOP was reacted with 3, the equivalent amount of monomer was added in this reaction, then, the additions of DBOP and monomers were repeated three times. However, the average degree of polymerization of each branch was 2.0 of the monomer unit, which was determined by calculating the ratio of integration of proton peaks at



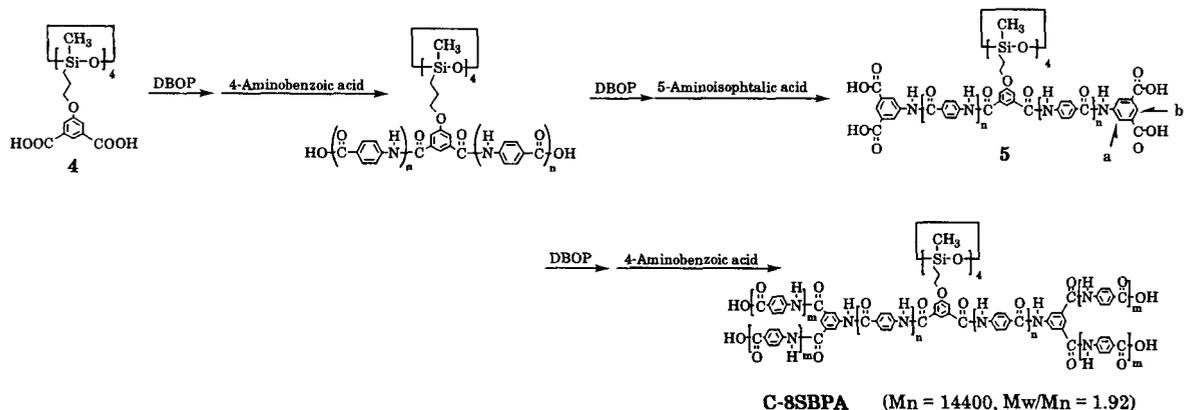
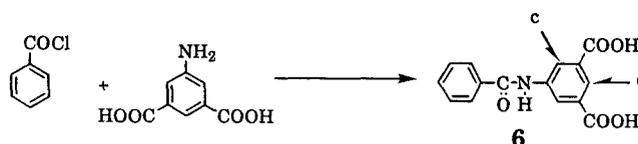
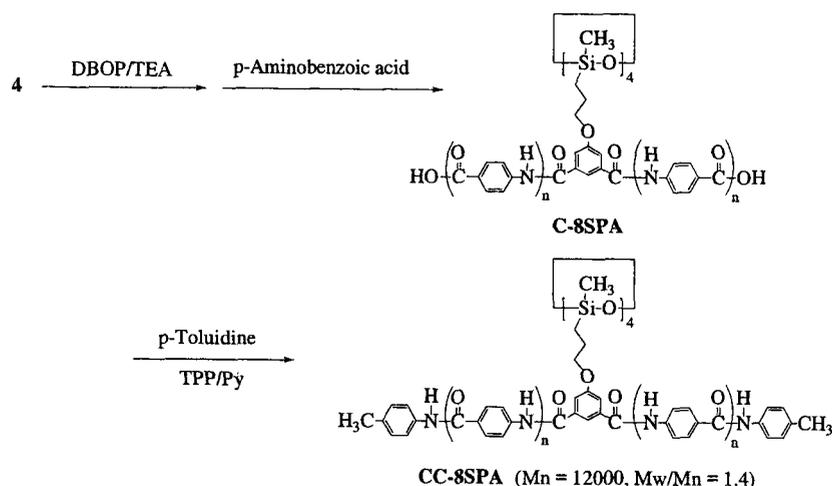
Scheme 1 Synthesis of a core molecule containing tetracarboxyl groups (3)

Si-methyl and phenylene units in its $^1\text{H-NMR}$ spectrum. According to the gel permeation chromatography (GPC), the number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of **C-4SPA** were 7,000 and 1.12, respectively. Furthermore, **CC-SPA** was prepared by end-capping the carboxyl groups of **C-4SPA** by the reaction with *p*-toluidine. A star-burst polymer (**C-8SBPA**) was prepared from the core molecule, **4**, with octacarboxyl groups by polycondensation of 4-aminobenzoic acid and 5-aminoisophthalic acid as monomers, as shown in

Scheme 3. In the $^1\text{H-NMR}$ spectrum of the intermediate, **5**, a proton signal was observed at 8.69 ppm, which was not observed in the star-shaped polyamides. It was thought that this proton signal was attributed to *a* or *b* proton of benzene ring shown in Scheme 3. Then, the model compound, **7**, was prepared to identify the proton signal at 8.69 ppm. As it was observed that the proton signals of *c* and *d* of **6** in Scheme 4 were 8.62 and 8.20 ppm, respectively, the proton signal at 8.69 ppm was identified as the proton of *a* position in the benzene ring of **5**. Further, the average



Scheme 2 Syntheses of tetra-armed star-shaped polyamides

Scheme 3 Synthesis of **C-8SBPA** from **4**Scheme 4 Synthesis of a model compound (**6**)

Scheme 5 Syntheses of octa-armed star-shaped polyamides.

Table 1 Solubility of star-shaped polyamides^{a)}

	THF	DMF	NMP	DMSO	DMA ^c
C-8SPA	×	○	△	○	○
CC-8SPA	×	×	△	○	○
C-4SPA	×	○	△	○	○
CC-4SPA	×	×	×	△	△
C-8SBPA	×	○	△	○	○
PA	×	×	×	×	×

a) Solubility was determined in concentration of 10 mg/ml. ○: soluble, △: soluble after heating at about 100°C, ×: insoluble.

Table 2 Thermal stability of star-shaped polyamides.

	C-8SPA	CC-8SPA	C-4SPA	CC-4SPA	C-8SBPA	PA
T _m (°C) ^{a)}	—	—	—	—	—	—
T _{d0} (°C) ^{b)}	390.5	381.1	364.0	386.8	375.4	391.8
T _{d10} (°C) ^{c)}	462.1	463.0	449.8	443.9	461.1	481.8

a) The melting temperature (T_m) was not observed by DSC measurement up to 350°C.

b) Temperature at which the weight loss started in N₂, determined by TGA.

c) Temperature of 10 % weight loss in N₂, determined by TGA.

substitution ratio of the terminal branched structure of **5**, which was derived from the reaction with 5-aminoisophthalic acid, was calculated to be about 30 % from the integration ratio between the protons of Si-methyl and those of *a*. Then, the polycondensation of 4-aminobenzoic acid was initiated at carboxyl groups of **5** to afford **C-8SBPA**. According to the GPC measurement, M_n and M_w/M_n of the obtained **C-8SBPA** were 14400 and 1.92, respectively.

2.2 Characterizations of star-shaped polyamides

The physical properties of these branched polyamides, **C-4SPA**, **CC-4SPA** and **C-8SBPA**, were compared with those of octa-armed star-shaped polymers (**C-8SPA** and **CC-8SPA** in Scheme 5), the preparation of which was described in the previous paper⁸⁾, and the linear polyamide, poly(4-aminobenzoic acid) (**PA**).

As shown in Table 1, all of star-shaped and star-burst polymers were soluble in some aprotic polar solvents, although the solubility of **C-4SPA** and **CC-4SPA** was relatively lower than the others. On the other hand, the solubility of **C-8SBPA** was not changed as compared with that of **C-8SPA**. The thermal properties of these samples were also investigated by using differential scanning calorimetry (DSC) and thermal gravimetry (TGA), the results of which were summarized in Table 2. For all of the samples, neither glass transition nor melting temperature was observed by DSC up to 350°C. By TGA, the temperatures of degradation start and 10 wt.% weight loss of these polymers were observed at about 380°C and 460°C, respectively, which were similar values of **PA**. Therefore, it was confirmed that these branched polymers maintained the high thermal stability of the linear aromatic polyamide, **PA**.

The wide angle X-ray scattering (WAXS) of these polyamides was measured at room temperature. It was found that the WAXS pattern of the branched polyamides exhibited the broad hallow in the wide angle region, whereas that of **PA** showed the sharp peaks as

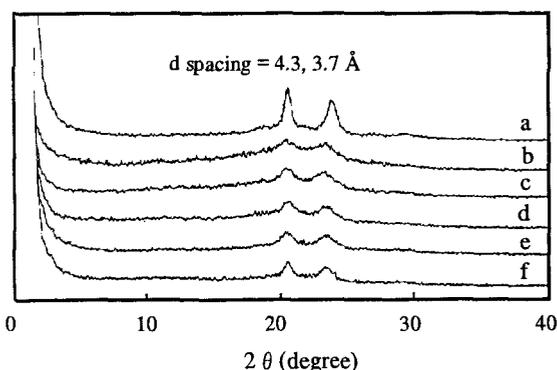


Figure 1 X-ray diffraction patterns of polyamides after annealing at 260°C for 30 min. a : **PA**, b : **C-8SBPA**, c : **C-8SPA**, d : **CC-8SPA**, e : **C-4SPA**, f : **CC-4SPA**

shown in Figure 1 (curve a). While, the sharp peaks in the wide angle region appeared for the branched polyamides after annealing these polyamides at 260°C for 30 min as seen in Figure 1 (curves b-f).

From these results, it was concluded that these star-shaped aromatic polyamides were soluble in DMSO and other aprotic polar solvents, and maintained the unique characteristics of linear aromatic polyamides, such as thermal stability and crystallinity. Therefore, it is expected that thin films can be easily produced from the organic solutions of these star-shaped polyamides, which would be applicable for some electric materials and others by harnessing the characteristics of aromatic polyamides. However, in the polymerization of 4-aminobenzoic acid or 5-aminoisophthalic acid initiated at the core molecule, the reaction did not proceed quantitatively owing the low reactivity of the monomers. Then, the investigation of polymerization with other monomers, for example, 4-amino-4'-carboxydiphenyl ether and 4-amino-3',5'-dicarboxydiphenyl ether, is now in progress.

3. EXPERIMENTAL

3.1 Synthesis of benzyl 4-allyloxybenzoate (1)

Benzyl 4-hydroxybenzoate (10.0 g, 43.8 mmol) and allyl bromide (6.36 g, 52.6 mmol) were dissolved in 100 ml of acetone (100 ml). Then, potassium carbonate (6.20 g, 43.81 mmol) was added to the solution, and it was refluxed with stirring for 4 h. Diethyl ether (100 ml) was added and the insoluble salts were filtrated off. After the filtrate was concentrated, the residue was purified by silica gel column chromatography (eluent; hexane/chloroform = 1/1 vol.) to afford 12.4 g of **1** as a transparent liquid. Yield: 98 %.

3.2 Synthesis of 1,3,5,7-tetrakis(3-(4-(benzyloxy-carbonylphenoxy)propyl)tetramethylcyclotetrasiloxane (2)

Under an argon atmosphere, **1** (2.40 g, 8.95 mmol), 1,3,5,7-tetramethyltetracyclosiloxane and dicyclopentadienylplatinum (II) chloride (DPPC) were dissolved in toluene. Then, the mixture was stirred at 80 °C for 4 h. After the filtration of the mixture was carried out through a small amount of silica gel, the filtrate was concentrated and purified by silica gel column chromatography (eluent; hexane/ chloroform= 1/1 vol.) to afford 1.30 g of **2** as a transparent liquid. Yield: 52 %.

3.3 Synthesis of 1,3,5,7-tetrakis(3-(4-carboxylphenoxy)propyl)tetramethylcyclotetrasiloxane (3)

In an autoclave, **2** (1.27 g, 0.98 mmol) was dissolved in 10 ml of the mixture of THF/ethanol (3/2 vol.) and 150 mg of Pd-C powder was added. After degassing in the autoclave, the atmosphere was substituted with 40 atm of hydrogen. Then, the mixture was stirred for 20 hour at r.t. After Pd-C powder was filtrated off through celite, the filtrate was concentrated and the residue was purified by recrystallization from hexane/THF to afford 0.96 g of **3** as a white solid. Yield: 79 %.

3.4 Synthesis of 3,5-dicarboxylbenzanilide (6)

Under an argon atmosphere, 5-amino- isophthalic acid (0.30 g, 1.66 mmol) was dissolved in NMP. Then, benzoyl chloride (0.28 g, 1.99 mmol) was added dropwise, and the mixture was stirred for 1 h at r.t. The reaction mixture was then poured into an excess amount of water to precipitate the product. The precipitate was filtered and washed with methanol to afford 0.34 g of **6** as a white solid. Yield: 72 %.

3.5 Syntheses of C-4SPA and CC-4SPA

3 (0.10 g, 0.11 mmol) and DBOP (0.18 g, 0.46 mmol) were dissolved in 0.4 ml of NMP, and 0.07 ml of triethylamine was added to the solution. Then, the mixture was stirred at 40°C for 2 h. The solution of 4-aminobenzoic acid (monomer, 58.0 mg, 0.42 mmol) in 0.4 ml of NMP was added to the mixture, and it was stirred at 40°C for 22 h. After the additions of DBOP and the monomer were repeated five times in this reaction condition, the mixture was poured into an excess amount of methanol to precipitate the product. The precipitate was filtered to afford 0.25 g of **C-4SPA** as a white solid. Yield: 62 %.

Under an argon atmosphere, **C-4SPA** (40 mg) and p-toluidine (30 mg, 0.49 mmol) were dissolved in 0.3 ml of NMP. Triphenyl phosphite (TPP, 0.13 ml) and

pyridine (0.04 ml) were added to the solution. The mixture was stirred at 100°C for 24 h. The reaction mixture was then poured into an excess amount of methanol to precipitate the product. The precipitate was filtered to afford 45 mg of **CC-4SPA** as a white solid.

3.6 Synthesis of C-8SBPA

Under an argon atmosphere, **4** (0.10 g, 0.09 mmol) and DBOP (0.30 g, 0.73 mmol) were dissolved in 0.6 ml of NMP, and 0.6 ml of triethylamine was added to the solution. The mixture was stirred at 40°C for 2 h. The solution of 4-aminobenzoic acid (97 mg, 0.71 mmol) in 0.6 ml of NMP was added to the mixture, and this mixture was stirred at 40°C for 22 h. Then, the additions of DBOP, triethylamine and the monomer were repeated four times in this reaction condition. After DBOP and triethylamine were added again to the mixture, the solution of 5-aminoisophthalic acid (129 mg, 0.71 mmol) was added and was stirred at 40°C for 22 h. The mixture was poured into an excess amount of methanol to precipitate the product (**5**), which was dried *in vacuo* at 60°C.

The obtained **5** (0.10 g, 0.033 mmol) and DBOP (0.14 g, 0.36 mmol) were dissolved in 1.2 ml of NMP under an argon atmosphere, and 0.05 ml of triethylamine was added to the solution. The mixture was stirred at 40°C for 2 h. Then, the solution of 4-aminobenzoic acid (45 mg, 0.33 mmol) in 0.6 ml of NMP was added, and the mixture was stirred at 40°C for 22 h. After the additions of DBOP and the monomer were repeated five times in this reaction condition, the mixture was poured into an excess amount of methanol to precipitate the product. The precipitate (**5**) was filtered to afford 250 mg of **C-8SBPA** as a white solid. Yield: 28 %.

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