

## Chain-Growth Polycondensation for Well-Defined Aramide. Synthesis of Unprecedented Block Copolymer Containing Aramide with Low Polydispersity

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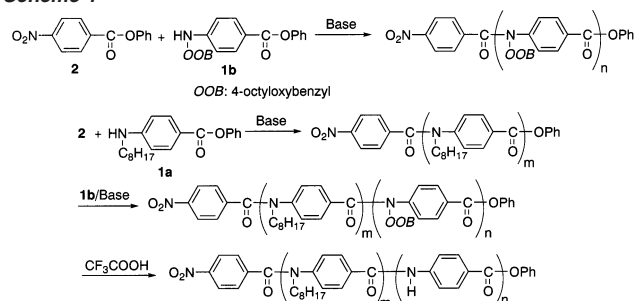
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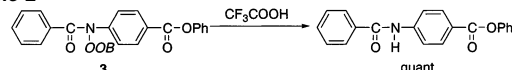
Aramids such as Kevlar and poly(*p*-benzamide) are known to be one of the most tough organic fabrication materials and have been used as a content of bulletproof jackets, and so on. The toughness of aramides stems from intermolecular hydrogen bonding of amide bonds and  $\pi$ - $\pi$  stacking of aromatic rings.<sup>1</sup> We have recently achieved control over molecular weight and polydispersity of poly(*N*-octyl-*p*-benzamide)s<sup>2</sup> by chain-growth polycondensation<sup>3</sup> of phenyl 4-(octylamino)benzoate (**1a**), in which monomer **1a** reacts with the polymer end group selectively, not with other monomers. However, the physical properties of this well-defined polyamide may not be as good as those of aramides because the *N*-alkylated polyamide, which is soluble in most of organic solvents, does not form intermolecular hydrogen bonding. An extension of our work of the chain-growth polycondensation for polyamides will be the synthesis of aramides with defined molecular weights and low polydispersities. The well-defined aramides awake our interest in not only the physical properties compared to those with broad molecular weight distributions but also supramolecular self-assembly of soluble block copolymers<sup>4</sup> containing aramides with low polydispersities. Those aramide block copolymers<sup>5</sup> are expected to be arranged to form intriguing nanostructures by virtue of multiple hydrogen bondings between the same length polymers. Herein we report an approach to a well-defined poly(*p*-benzamide) through the chain-growth polycondensation of **1b** having the *N*-protecting group followed by deprotection and the synthesis of a block copolymer of poly(*N*-octyl-*p*-benzamide) and poly(*p*-benzamide) with a low polydispersity (Scheme 1). Furthermore, we have found that this polyamide diblock copolymer self-assembles to form supramolecular micro-order bundles.

The *N*-protecting group of monomer was first studied.<sup>6</sup> On the basis of peptide chemistry, the amino group of monomer was protected as the *tert*-butyl carbamate (Boc), but this monomer did not polymerize.<sup>7</sup> Monomer protected with the methoxyethoxymethyl (MEM) group was too unstable to be isolated. Monomer with the methoxybenzyl group was not freely soluble in the solvent for polymerization. Eventually, phenyl 4-(4-octyloxybenzylamino)benzoate (**1b**) was prepared and polymerized in the presence of 10 mol % of phenyl 4-nitrobenzoate (**2**) and base (*N*-triethylsilyl-*N*-octylaniline, CsF, and 18-crown-6)<sup>2</sup> in THF at room temperature (Scheme 1). The polymerization proceeded homogeneously and was completed in 4 h to yield a polyamide with  $M_n$  of 3700<sup>8</sup> and  $M_w/M_n$  of 1.07. The calculated  $M_n$  value based on feed ratio of  $[\mathbf{1b}]_0/[\mathbf{2}]_0$  was 3600, and therefore the polyamide was synthesized in a controlled fashion.<sup>9</sup> Unfortunately, however, the polyamides were

### Scheme 1



### Scheme 2



precipitated during polymerization when the feed ratios of  $[\mathbf{1b}]_0/[\mathbf{2}]_0$  were more than 10.<sup>10,11</sup>

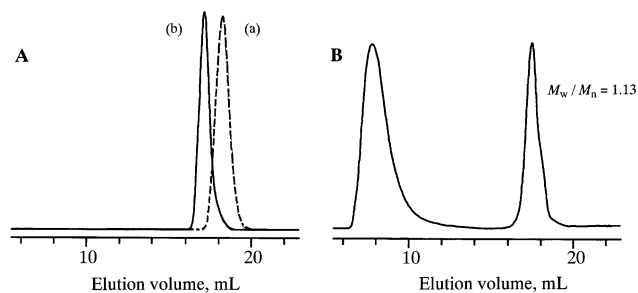
The 4-octyloxybenzyl (OOB) groups on amide nitrogens in the polymer obtained were attempted to be removed by trifluoroacetic acid (TFA),<sup>12</sup> but polymer was precipitated during reaction. This polymer was only soluble in  $H_2SO_4$ , and it could not be confirmed whether deprotection took place quantitatively without scission of the amide linkages of polymer. Accordingly, model compound **3** was treated with TFA at ambient temperature for 72 h, resulting in complete deprotection without breaking the amide and ester linkages (Scheme 2).

We next synthesized a soluble block copolymer containing poly(*p*-benzamide) not only because deprotection of poly**1b** unit can be identified directly by analysis of the block copolymer but also because very strong intermolecular forces of well-defined poly(*p*-benzamide) must have the block copolymer self-assemble in an unprecedented manner. Thus, **1a** was polymerized in the presence of **2** ( $[\mathbf{1a}]_0/[\mathbf{2}]_0 = 9.6$ ) and base in THF at room temperature to give a prepolymer<sup>2</sup> ( $M_n = 2490$  ( $M_n(\text{calcd}) = 2470$ ),  $M_w/M_n = 1.10$ ). A fresh feed of **1b** and *N*-triethylsilyl-*N*-octylaniline<sup>2</sup> was added to the prepolymer in the reaction mixture (Scheme 1). The added **1b** feed was smoothly polymerized. The GPC chromatogram of the product (Figure 1A (b)) clearly shifted toward the higher molecular weight region, while retaining the narrow distribution ( $M_n = 6420$  ( $M_n(\text{calcd}) = 5900$ ),  $M_w/M_n = 1.10$ ), indicating a successful production of the block copolymer of **1a** and **1b** with a controlled molecular weight.<sup>13</sup> The block copolymer obtained was then treated with TFA at ambient temperature for 72 h, followed by purification with a preparative HPLC to yield a yellowish solid, which was soluble in THF,  $CHCl_3$ ,  $CH_2Cl_2$ , and DMF. In the <sup>1</sup>H NMR spectrum of the product, the signal of the benzylmethylene protons of the amide protecting groups in the poly**1b** unit at 4.90

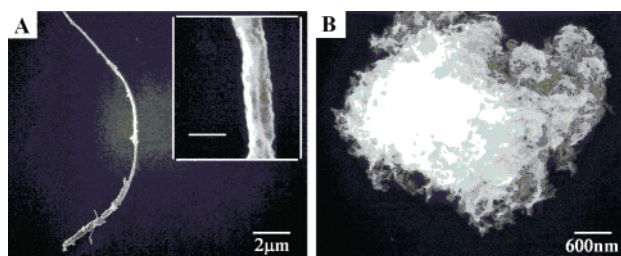
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**Figure 1.** GPC profile of polymer (eluent: THF). (A) Synthesis of the block copolymer of **1a** and **1b** by monomer addition method: (a) poly**1a** as a prepolymer ( $[1a]_0/[2]_0 = 9.6$ ,  $M_n = 2490$ ,  $M_w/M_n = 1.10$ ); (b) poly**1a**-*b*-poly**1b** as a postpolymer ( $[added\ 1b]_0/[2]_0 = 10.2$ ,  $M_n = 6420$ ,  $M_w/M_n = 1.10$ ). (B) The block copolymer of poly(*N*-octyl-*p*-benzamide) and poly(*p*-benzamide) obtained by the deprotection of the 4-octyloxybenzyl groups on poly**1a**-*b*-poly**1b** with TFA.



**Figure 2.** SEM images (A, B) of the supramolecular assemblies of the block copolymer of poly(*N*-octyl-*p*-benzamide) and poly(*p*-benzamide) from the copolymer solution in THF dried at 25 °C on a silicon wafer and sputter coated with carbon. (A) is magnified in the inset in (A).

ppm completely disappeared. The GPC chromatogram of the product (Figure 1B) in the low molecular weight region slightly shifted toward the lower molecular weight region, while keeping the low polydispersity. Consequently, deprotection of the 4-octyloxybenzyl groups proceeded quantitatively without scission of the amide linkage of polymer, and a soluble diblock copolymer of aromatic *N*-H polyamide and *N*-octyl polyamide was successfully synthesized (Scheme 1).

It should be noted that the GPC chromatogram (eluent: THF) of the above block copolymer showed a large peak in the high molecular weight region as well as the peak corresponding to the block copolymer (Figure 1B). The observed high molecular weight region peak implies that this block copolymer was arranged in a supramolecular self-assembly in THF. Scanning electron microscopy (SEM) was used to visualize the supramolecular assemblies of the block copolymer after drying the THF solution on a silicon wafer. Surprisingly, the SEM images revealed that  $\mu\text{m}$ -sized bundles were formed as well as aggregates of flake structures;<sup>14</sup> the reason for the formation of two kinds of structures is unclear at present time (Figure 2). The length of the bundles was in the range of 4–15  $\mu\text{m}$  and their diameter was in the range of 150–250 nm. The DMF solution of the block copolymer, however, did not show the high molecular weight peak in the GPC chromatogram, and the bundle structures were not observed in the SEM, either. The SEM image of homopolymer of **1a** having the *N*-octyl groups also did not show the bundle structures even by use of the THF solution. Therefore, the hydrogen bondings of the poly(*p*-benzamide) unit of the block copolymer are probably responsible for supramolecular bundle structures. Further studies by X-ray diffraction methods will be essential to achieving a detailed understanding of the supramolecular structures of the block copolymer.

In conclusion, our chain-growth polycondensation method for well-defined aromatic polyamides has been developed to the synthesis of poly(*p*-benzamide) with a low polydispersity by the

polycondensation of **1b** followed by deprotection with TFA. By this method we synthesized a soluble diblock copolymer of poly(*p*-benzamide) and poly(*N*-octyl-*p*-benzamide) with a narrow molecular weight distribution, which was arranged in a supramolecular self-assembly in THF to give intriguing  $\mu\text{m}$ -sized bundles probably by virtue of the multiple intermolecular hydrogen bondings of the poly(*p*-benzamide) unit. The self-assembly of block copolymers and star polymers containing the well-defined poly(*p*-benzamide) units will be a versatile protocol for nanoarchitectures of aromatic polyamides. Experiments along these lines are in progress.

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**Supporting Information Available:** Synthesis and polymerization of monomer **1b** and the synthesis of diblock copolymer of **1a** and **1b**, followed by deprotection (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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- Phenyl 4-aminobenzoate, which would lead directly to poly(*p*-benzamide), did not polymerize under our polymerization conditions.
- The observed low reactivity of the Boc-protected monomer may be caused by steric hindrance of the monomer, because it did not react even with 4-nitrobenzoyl chloride.
- The  $M_n$  value of polyamide was estimated by the  $^1\text{H}$  NMR spectra based on the ratios of signal intensities of the repeating units to those of the initiator unit.
- A living polymerization nature was also ascertained by a linear correlation between the  $M_n$  values and monomer conversion, retaining low polydispersities.
- Longer poly**1b** units (DP = 20) could be introduced to the block copolymer of **1a** and **1b** in the postpolymerization from poly**1a** without precipitation (see ref 13).
- The polymer solubility was not changed even though the dodecyloxy group was introduced to monomer instead of the octyloxy group in **1b**.
- For examples of the deprotection of the 4-methoxybenzyl group with TFA, see: (a) Brooke, G. M.; Mohammed, S.; Whiting, M. C. *Chem. Commun.* **1997**, 1511–1512. (b) Miki, Y.; Hachiken, H.; Kashima, Y.; Sugimura, W.; Yanase, N. *Heterocycles* **1998**, *48*, 1–4. (c) Bouzide, A.; Sauve, G. *Tetrahedron Lett.* **1999**, *40*, 2883–2886.
- Other block copolymers (**1a**)<sub>*n*</sub>-(**1b**)<sub>*m*</sub> were also synthesized in a controlled fashion.  $n = 5$ ,  $m = 10$ :  $M_n = 4630$  ( $M_n(\text{calcd}) = 4770$ ),  $M_w/M_n = 1.10$ .  $n = 10$ ,  $m = 5$ :  $M_n = 4150$  ( $M_n(\text{calcd}) = 4270$ ),  $M_w/M_n = 1.12$ .  $n = 10$ ,  $m = 14$ :  $M_n = 8130$  ( $M_n(\text{calcd}) = 7270$ ),  $M_w/M_n = 1.08$ .  $n = 17$ ,  $m = 9$ :  $M_n = 8890$  ( $M_n(\text{calcd}) = 7160$ ),  $M_w/M_n = 1.06$ .  $n = 20$ ,  $m = 5$ :  $M_n = 6070$  ( $M_n(\text{calcd}) = 6530$ ),  $M_w/M_n = 1.08$ .  $n = 20$ ,  $m = 20$ :  $M_n = 11900$  ( $M_n(\text{calcd}) = 11500$ ),  $M_w/M_n = 1.08$ .
- Similar bundles were also observed in the SEM image of the block copolymer without the terminal nitro group, which was obtained by successive chain-growth polycondensation of **1a** and **1b** initiated with phenyl benzoate instead of **2**, followed by deprotection.

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