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Synthesis of Well-Defined Poly(*p*-benzamide) from Chain-Growth Polycondensation and Its Application to Block Copolymers

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Summary: Poly(*p*-benzamide) with a defined molecular weight and a low polydispersity and block copolymers containing this well-defined aramide was synthesized. Phenyl 4-(4-octyloxybenzylamino)benzoate (**1b**) polymerized at room temperature in the presence of base and phenyl 4-nitrobenzoate (**2a**) as an initiator in a chain-growth polycondensation manner to give well-defined aromatic polyamides having the 4-octyloxybenzyl groups as a protecting group on nitrogen in an amide. It was confirmed by a model reaction that deprotection of this protecting group proceeded completely with trifluoroacetic acid (TFA) without breaking the amide linkage. The utility of this approach to poly(*p*-benzamide) with a low polydispersity was demonstrated by the synthesis of block copolymers of poly(*p*-benzamide) and poly(*N*-octyl-*p*-benzamide) or poly(ethylene glycol). The SEM images of the supramolecular assemblies of the former block copolymer showed µm-sized bundles and aggregates of flake structures.

Keywords: block copolymer, chain-growth polycondensation, living polymerization, polyamide, self-assembly

Introduction

The self-assembly of well-defined polymers containing condensation polymers or oligomers in part has recently received a great deal of attention due to their surprising properties or functionality.[1] The condensation polymer units in those polymers are prepared by conventional polycondensation and possess broad molecular weight distribution[2] except for several

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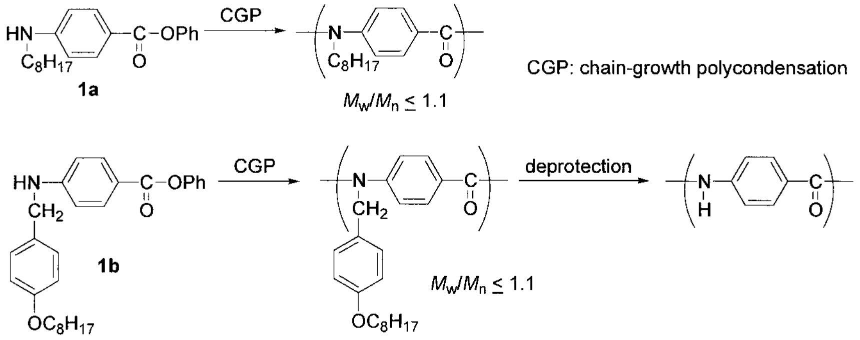
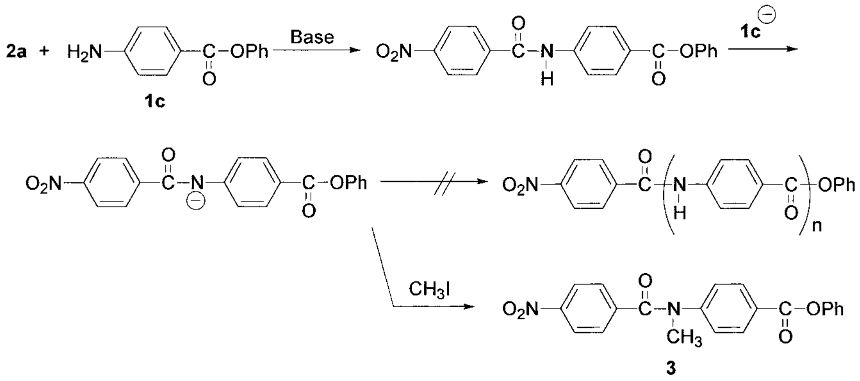
examples.[3] General synthetic method for condensation polymers with low polydispersities would promote the development of new materials based on self-organization. We have recently succeeded in synthesizing *N*-alkyl aromatic polyamides having defined molecular weights and low polydispersities by chain-growth polycondensation of phenyl 4-(octylamino)benzoate (**1a**), where the monomer reacts with the polymer end group selectively, not with other monomers.[4] From the point of view of self-assemble materials and fabrication materials, well-defined *N*-unsubstituted aromatic polyamide, poly(*p*-benzamide), is very attractive. In this paper, we report the synthesis of poly(*p*-benzamide) having defined molecular weights and low polydispersities by chain-growth polycondensation of monomer **1b** bearing the *N*-protecting group, followed by deprotection, and also synthesis of block copolymers[5] of poly(*p*-benzamide) and *N*-alkyl aromatic polyamides or poly(ethylene glycol) (PEG).



Polycondensation of 1c

We first attempted the polycondensation of phenyl 4-aminobenzoate (**1c**), which leads directly to poly(*p*-benzamide), in the presence of phenyl 4-nitorbenzoate (**2a**) as an initiator under the same conditions as the chain-growth polycondensation of **1a**.[4] However, not polyamide but the *N*-methylated 1:1 adduct **3** of **1c** and **2a** was obtained after quenching with iodomethane. The observed reaction is accounted for by involvement of the abstraction of the amide proton with the aminyl anion of **1c**. The anion generated on the amide bond between **2a** and **1c** is such a strong electron-donating group that the phenyl ester at the *para*-position of the anion is deactivated for polymerization, resulting in **3** after methylation of the amide anion. This result indicates that monomers having the primary amino group are not applicable to the chain-growth polycondensation for aromatic polyamides.

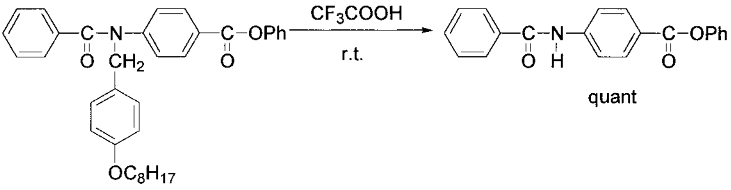


Polycondensation of 1b

The polymerization of monomers bearing the secondary amino group substituted by a protecting group was studied. 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. 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 **2a** and base (*N*-triethylsilyl-*N*-octylaniline, CsF, and 18-crown-6)[4] in THF at room temperature. The polymerization proceeded homogeneously and was completed in 4 h to yield a polyamide with M_n of 3700[6] and M_w/M_n of 1.07. The calculated M_n value based on feed ratio of $[\mathbf{1b}]_0/[\mathbf{2a}]_0$ was 3600, and therefore the polyamide was synthesized in a controlled fashion. A living polymerization nature was also ascertained by a linear correlation between the M_n values and monomer conversion, retaining low polydispersities. Unfortunately, however, the polyamides were precipitated during polymerization when the feed ratios of $[\mathbf{1b}]_0/[\mathbf{2a}]_0$ were more than 10.

Deprotection

Deprotection of the 4-octyloxybenzyl groups on nitrogen in the polymer obtained was carried out in trifluoroacetic acid (TFA)[7] to precipitate polymer during reaction. This polymer was only soluble in H_2SO_4, and it was not confirmed whether deprotection took place quantitatively without scission of the amide linkages in polymer. For this reason, model compound **4** was treated with TFA at ambient temperature for 72 h, resulting in complete deprotection without breaking the amide and ester linkages.



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Block Copolymers of *N*-H and *N*-Octyl Aromatic Polyamide

According to the above results, a soluble block copolymer of poly**1a** and poly(*p*-benzamide) was synthesized. Thus, **1a** was polymerized in the presence of **2a** and base in THF at room temperature to give a prepolymer.[4] A fresh feed of **1b** and *N*-triethylsilyl-*N*-octylaniline[4] was added to the prepolymer in the reaction mixture. 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, indicating a successful production of the block copolymer of **1a** and **1b** with a controlled molecular weight (Table 1).

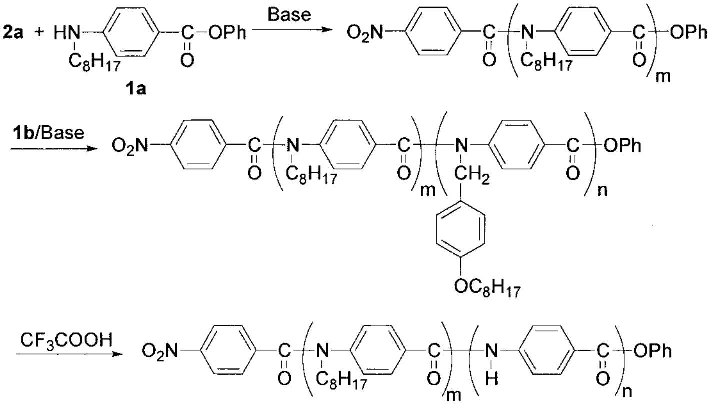


Table 1. Synthesis of block coplymers of poly**1a** and poly**1b**.

1st segment[a]			diblock copolymer		
M_n(calcd)	M_n[b]	M_w/M_n[c]	M_n(calcd)	M_n[b]	M_w/M_n[c]
1370	1170	1.13	3030	2000	1.11
1420	2410	1.13	4770	4630	1.10
2460	2900	1.10	7270	8130	1.08
2470	2490	1.10	5900	6420	1.10
2530	2410	1.14	4270	4150	1.12
4230	4730	1.08	7160	8890	1.06
4800	4600	1.09	6530	6070	1.08
4830	6100	1.08	11500	11900	1.08

Polymerization was initiated with **2a** in THF at 25 °C in all cases.

[a] Poly**1a**.

[b] Estimated by ^{1}H NMR.

[c] Estimated by GPC based on polystyrene standards (eluent: THF).

The block copolymer obtained was then stirred in 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, DMF. In the ^{1}H NMR spectrum of the product, the signal of the benzylmethylene protons of poly**1b** units at 4.90 ppm completely disappeared. The GPC chromatogram of the product (Figure 1B) in the low molecular weight region slightly shifted toward the lower moleculer weight region, while keeping the low polydispersity. Consequently, deprotection of the 4-octyloxybenzyl groups proceeded quantitatively without scission of the amide linkage in polymer, and a soluble diblock copolymer of aromatic *N*-H polyamide and *N*-octyl polyamide was successfully synthesized.

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 μm-sized bundles were formed as well as aggregates of flake structures;

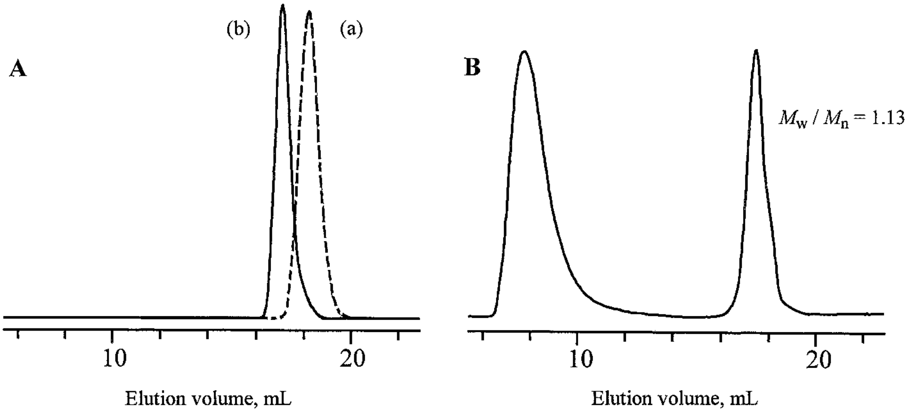


Fig. 1. GPC profile of polymer (eluent: THF). (A) Synthesis of the block copolymer of **1a** and **1b** by monomer addition method: (a) poly**1a** as a prepolymer ($[\mathbf{1a}]_0/[\mathbf{2a}]_0 = 9.6$), M_n = 2490, $M_w/M_n = 1.10$; (b) poly**1a**-*b*-poly**1b** as a postpolymer ($[\text{added } \mathbf{1b}]_0/[\mathbf{2a}]_0 = 10.2$), 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.

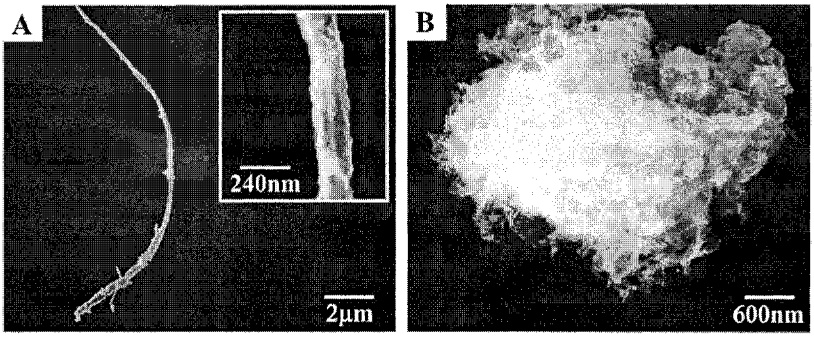
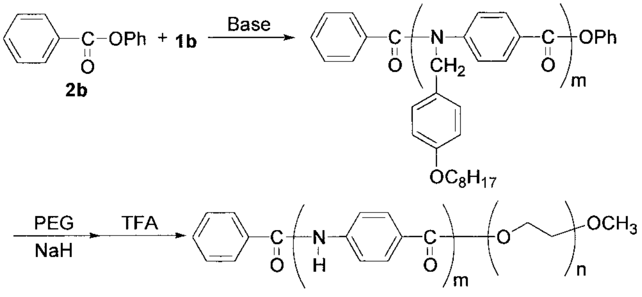


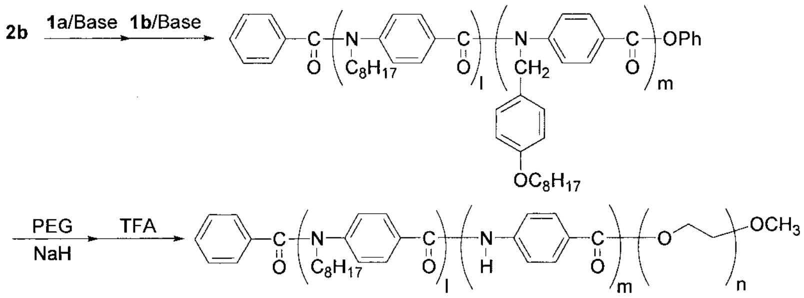
Fig. 2. SEM images (A, B) of the supramolecular assemblies of the block copolymer of poly(*N*-octyl-*p*-benzamide) and poly(*p*-benzamide) from the copolymer solution in THF dried at 25 °C on a silicon wafer and sputter coated with carbon. (A) is magnified in the inset in (A).

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 μm 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.

Block Copolymers of *N*-H Aromatic Polyamide and PEG

The polymer end group of poly**1b** is the phenyl ester, which would be applicable to the reaction with anionic living polymer end groups to yield other kind of block copolymers containing poly(*p*-benzamide) after deprotection. We tried the synthesis of block copolymers of poly(*p*-benzamide) and PEG. Phenyl benzoate (**2b**) was used instead of **2a** for the chain-growth polycondensation of **1b**, because the amide linkage of **2a** unit and **1b** was cleaved during the deprotection of 4-octyloxybenzyl group with TFA. The reaction of poly**1b** with monomethylated PEG in the presence of NaH yielded a block copolymer of poly**1b** and PEG, which was then treated with TFA to give a block copolymer of poly(*p*-benzamide) and PEG. Unfortunately, this block copolymer was poor solubility in common organic solvents, and it was difficult to characterize the polymer. For the production of a soluble block copolymer containing poly(*p*-benzamide) and PEG, the block copolymer of poly**1a** and poly**1b**, mentioned in the above section, was used. Thus, the block copolymer of poly**1a** and poly**1b** reacted with monomethylated PEG (M_n = 2000, M_w/M_n = 1.05) in the presence of NaH to give the triblock copolymer of poly**1a**, poly**1b**, and PEG (M_n = 3200, M_w/M_n = 1.15). Treatment of this block copolymer with TFA yielded the soluble triblock copolymer of *N*-octyl and *N*-H aromatic polyamide and PEG (M_n = 3380, M_w/M_n = 1.20). The GPC elution curves showed a peak in the higher molecular weight region both in the THF and DMF solution, implying that this block copolymer also self-assembles. Further studies about this supramolecular structure are currently under way.





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 soluble diblock copolymers of poly(*p*-benzamide) and poly(*N*-octyl-*p*-benzamide) and of poly(*p*-benzamide) and PEG, and a triblock copolymer of poly(*p*-benzamide), poly(*N*-octyl-*p*-benzamide) and PEG. The first block copolymer was arranged in a supramolecular self-assembly in THF to give intriguing μm-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.

Acknowledgment

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