Synthesis and Characterization of Aromatic Block Copolyamides by Condensative Chain Polymerization

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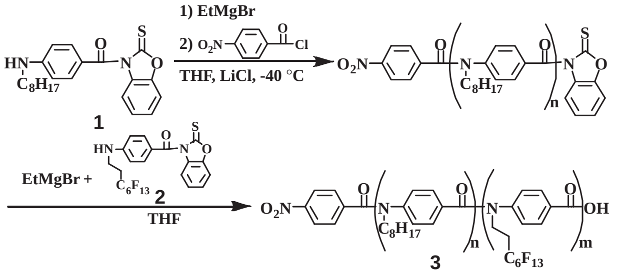
Aromatic block copolyamides with well-controlled molecular weights (MWs) and narrow polydispersities (PDIs) were successfully prepared by the condensative chain polymerization of 3-[4-(*N*-octylamino)benzoyl]benzoxazoline-2-thione (**1**) and 3-[4-(*N*-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorooctylamino)-benzoyl]benzoxazoline-2-thione (**2**). The formation of the block copolymers was confirmed by GPC, DSC, and NMR analyses. The thin film formed on mica was analyzed using atomic force microscopy (AFM), and the results indicated the existence of phase segregation.

Recently, condensative chain polymerization has been developed for the synthesis of condensation polymers with controlled molecular weights (MWs) and narrow polydispercity indexes (PDIs),[1] and well-controlled polymers such as polyamides,[2] poly(ether ketone)s,[3] poly(ether sulfone)s,[4] polyethers,[5] polythiophenes,[6] and polyphenylenes[7] have been successfully prepared. The MWs and PDIs of these polymers can be controlled simply by changing the molar ratios of the initiator and the monomer.

Condensative chain polymerization can introduce functional units in a polymer main chain, which is generally not accessible for addition polymerization. Therefore, the synthesis and phase segregation of condensation block copolymers would be interesting for the preparation of novel functional materials if the PDI can be well controlled. However, there have been few reports pertaining to this topic; well-controlled diblock aramide with a molecular weight of 6200 was prepared from phenyl 4-(4-octyloxybenzylamino)benzoate and phenyl 4-(octylamino)-benzoate, and the resulting block copolyamides produced supra-molecular assemblies.[8] There has been no observation of any clear phase segregation with ordered structures.

As a part of the program on the synthesis of well-defined condensation polymers, we reported the synthesis of poly(*N*-alkyl-*p*-benzamide)[2] and poly(*N*-fluoroalkyl-*p*-benzamide).[9] Based on these findings, we investigated the synthesis, characterization, and phase segregation of novel aromatic block copolyamides from **1** and **2** via condensative chain polymerization.

Block copolyamides **3** were synthesized by the sequential monomer addition of **2** after the quantitative conversion of **1** (Scheme 1 and the preparation detail in Supporting Information). The polymerization was initiated by employing nitrobenzoyl chloride in the presence of LiCl (see Supporting Information). Table 1 summarizes the results of the block copolymerization of **1** with **2**. All the polymers of **3** were obtained in excellent yields and with narrow PDIs. Changing the feed ratio of the two monomers can vary the unit ratio of the block copolymers.



Scheme 1. Synthesis of block copolyamides **3**.

Table 1. Synthesis of block copolyamides **3**[a]

Run	Feed (n/m)	Yield[b] /%	M_n(NMR)[c]	PDI[d]	Composition of the polymer (n/m)[c]
1	60/40	92	13000	1.20	60/40
2	50/50	86	14800	1.14	55/45
3	30/70	92	23400	1.16	34/66
4	70/30	85	20600	1.19	72/28

[a]Conditions; $[M_{1st}]_0 = 0.334$ M, $[LiCl]_0/[M]_0 = 10$, $[EtMgBr]_0/[M]_0 = 1.0$, in THF at −40 °C for 3 h. [b]MeOH insoluble part. [c]Determined by ^{1}H NMR. [d]Determined by GPC ($CHCl_3$, PSt standard).

Figure 1a shows the GPC profiles of the prepolymer obtained by the condensative chain polymerization of **1** and the post polymer after the second stage polymerization of **2**. The peak of the profile is shifted to the high-MW region, and the post polymer maintains a narrow PDI of 1.20, indicating the formation of the block copolymer. The number average molecular weights (M_ns) of the first block were estimated by GPC and ^{1}H NMR spectroscopy to be 4600 and 7800, respectively, which indicates that the the size of the polyamide is reduced in chloroform at the above-mentioned conditions. The expected M_n value is calculated from the feed ratios of the monomer and initiator to be 7300, which agrees well with the value estimated from ^{1}H NMR spectroscopy. The M_n value of the post polymer determined by ^{1}H NMR spectroscopy is 13000, which is close to the calculated value of 13300. The polymerization solution was poured into methanol to isolate the polymer. The structure of the block copolymer was characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy. All the signals assignable to both units were also observed in the ^{13}C NMR spectrum (Figure 1b). The ^{13}C NMR spectrum that is expanded from 169 to 170 ppm is depicted in Figure 1c. Two signals due to amide carbonyls adjacent to hydrocarbon and fluorocarbon units are observed at 169.3 and

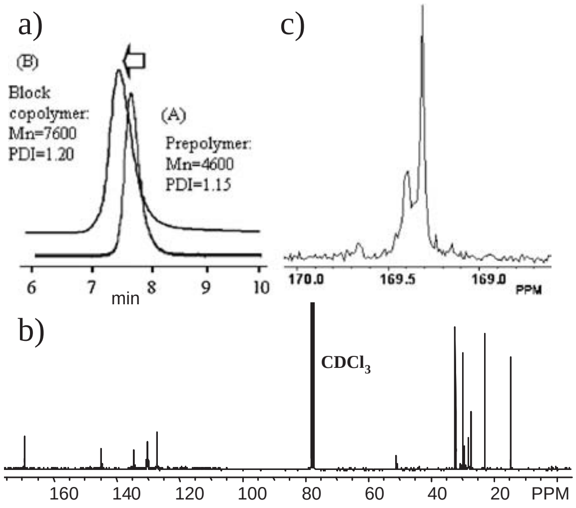


Figure 1. a) GPC ($CHCl_3$, PSt Standard) traces (UV detector) of prepolymer (A) and block copolymer (B). b) ^{13}C NMR ($CDCl_3$) spectrum of the block copolymer. c) The expanded ^{13}C NMR spectrum of carbonyl signals from 169 to 170 ppm.

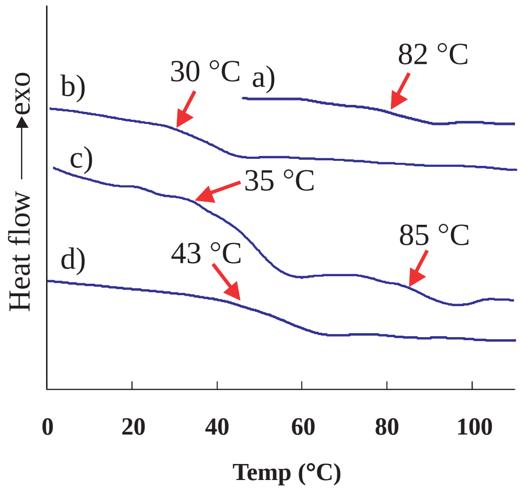


Figure 2. DSC profiles of the homopolymers obtained with monomers **2** (a) and **1** (b), the block copolymer (c), and the random copolymer (d).

169.4 ppm, indicating that the post polymer obtained under the conditions described above is most probably the corresponding block copolymer.

The DSC profiles of the homo-, random, and block copolymers are shown in Figure 2. The T_g values of the homopolymers obtained using the monomers **1** and **2** are observed to be 30 °C (Figure 2b) and 82 °C (Figure 2a), respectively. While only one transition is observed at 43 °C for the random copolymer (Figure 2d), the block copolymer shows two glass-transition temperatures corresponding to each unit, indicating the formation of the block copolymer (Figure 2c).

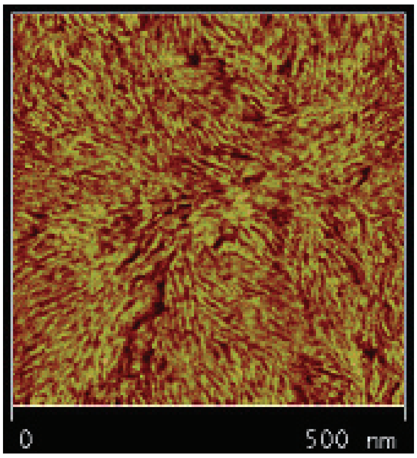


Figure 3. Tapping-mode phase contrast image of the annealed block copolymer film.

To observe the phase segregation, the block copolymer was dissolved in trifluorotoluene and cast on mica. The film was annealed at 150 °C for 3 days under nitrogen to promote the phase segregation. The surface profile of the specimen (Figure 3) was investigated using AFM. Figure 3 shows an AFM tapping-mode phase contrast image, where a clear contrast elastic modulus between the two segments can be observed.

In summary, we have demonstrated the synthesis of aromatic block copolyamides with a narrow PDI by the condensative chain polymerization of **1** with **2**. The ^1H and ^{13}C NMR spectroscopy, GPC, and DSC profiles indicated the formation of the corresponding block copolymers. The AMF profile also showed micro phase segregation in the block copolymers. The detailed morphology of the block copolymers is now under investigation.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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