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Direct Polycondensation of Carboxylic Acids and Amines Catalyzed by 3,4,5-Trifluorophenylboronic Acid

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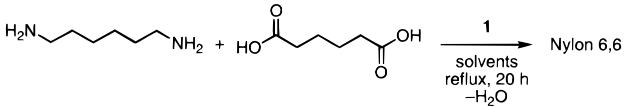
Introduction. Polyamides are used in the production of synthetic fibers and engineering resins. Aromatic polyamides are particularly well-known as high-performance polymers due to their excellent thermal, mechanical, and chemical properties.[1] There are three conventional methods for the synthesis of polyamides. One is thermal polymerization, which is a well-known industrial process for aliphatic polyamides with high molecular weight. However, it is difficult to obtain aromatic polyamides with a high molecular weight by molten polycondensation.[1b,2,3] This has been explained primarily by the low reactivity of aromatic amines compared with that of aliphatic amines because of the resonance effect of phenyl groups. The second method is polymerization of acids and amines in the presence of a stoichiometric amount of condensing agents. The third method involves low-temperature solution polymerization, where activated acyl derivatives such as acid chlorides are reacted with amines to form polyamides. This approach is still useful for preparing aromatic polyamides even though the use of acid halides is environmentally undesirable. Direct polycondensation that produces only a stoichiometric amount of water as a byproduct is the most ideal route, both environmentally and industrially. As far as we know, there are no known reusable catalysts for this route to produce polyamides under thermal conditions.

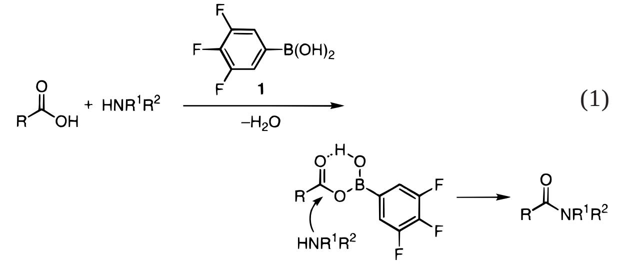
We recently found that 3,4,5-trifluorophenylboronic acid (**1**) is a highly effective catalyst for the amide condensation of amines and carboxylic acids (eq 1).[4] Arylboronic acids bearing electron-withdrawing substituents at the aryl group behave as water-, acid-, and base-tolerant thermally stable Lewis acids and can be easily handled in air. An active (acyloxy)boron complex **2** is generated in situ by the condensation of **1** with carboxylic acids.[4] In this paper, we describe a successful direct thermal amide polycondensation catalyzed by **1** to form not only aliphatic polyamides but also aromatic polyamides and polyimides.

Table 1. Direct Polycondensation of Hexamethylenediamine and Adipic Acid[a]



entry	cat. **1** (mol %)	solvent	yield (%)	M_n[c]	M_w[c]
1	10	*o*-xylene−*m*-cresol[b]	85	4690	22400
2	10	*o*-xylene	89	2680	8330
3	10	toluene−*m*-cresol[b]	83		
4	0	toluene−*m*-cresol[b]	0		

[a] The reaction was carried out in a flask fitted with a pressure-equalized addition funnel (containing a cotton plug and ca. 4 g of 4 Å molecular sieves (pellets) and functioning as a Soxhlet extractor) surmounted by a reflux condenser under Ar. [b] A 20 v/v % of *m*-cresol was added. [c] Two linear Shodex HFIP 806M GPC columns were employed. The polymer was run at 0.06 wt % in HFIP containing 0.005 M CF_3CO_2Na with a nylon 6,6 standard.



(1)

Results and Discussion. Initially, the direct polycondensation of hexamethylenediamine and adipic acid to form nylon 6,6 was examined under various conditions. The results are summarized in Table 1. The polycondensation of a 1:1 salt of hexamethylenediamine and adipic acid in the presence of 10 mol % of **1** was carried out at reflux in *o*-xylene with removal of water (4 Å molecular sieves in a Soxhlet thimble) for 20 h to obtain nylon 6,6 in 89% yield (entry 2). The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the nylon obtained were estimated to be 2680 and 8330, respectively, from GPC for elution by hexafluoro-2-propanol (HFIP). It seems that the insolubility of nylon 6,6 in *o*-xylene makes high polymer formation difficult. Since nylon 6,6 dissolves in *m*-cresol, polycondensation was carried out in a 1:3 (v/v) mixed solvent of *m*-cresol and *o*-xylene at reflux in the presence of 10 mol % of **1** (entry 1). The ratio of *m*-cresol in the solvents was determined to be 20 v/v %, since excess *m*-cresol inhibits the catalytic activity of **1**. The M_n and M_w values were increased to 4690 and 22 400, respectively. Heating the reaction mixture to over 150 °C was not effective for obtaining a higher molecular weight of nylon 6,6, presumably due to side reactions. Interestingly, nylon 6,6 was not obtained at all in a control experiment without catalyst **1** under thermal conditions (entry 3 versus entry 4). This simple procedure may be one of the most effective methods of synthesizing oligomeric nylon 6,6, although the polymer molecular weights were never high enough.

Next, we explored whether direct polycondensation catalyzed by **1** could be used to prepare aramids that were more thermally stable than nylons. The polycondensation of isophthalic acid (**3**) and 1,4-phenylenediamine (**4**) was examined under the monocarboxamide condensation conditions described previously; the reaction mixture was heated at reflux in mesitylene (bp 162−164 °C) with azeotropic removal of water (4 Å molecular sieves in a Soxhlet thimble) in the presence of catalytic amounts of **1**.[4] However, the reaction did not proceed at all, and the starting materials were recovered. Among the various solvents and reaction

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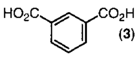
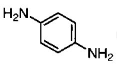
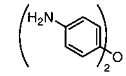
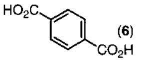
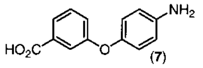
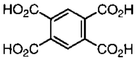
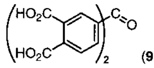
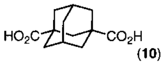
Table 2. Direct Polycondensation of Amines and Carboxylic Acids[a]

entry	carboxylic acid	amine	conditions[b]	yield (%)	η_{inh}[f] (dL/g)	M_n /10^4	M_w /10^4
1	 (**3**)	 (**4**)	**A**	>99	0.90	–	–
2			**A**[c]	>99	–	1.15[g]	2.83[g]
3			**B**[c]	84	–	–	–
4			**C**[c]	34	–	–	–
5	**3**	 (**5**)	**A**	>99 [58][e]	0.60	–	–
6			**A**[c]	95	–	2.74[g]	17.30[g]
7	 (**6**)	**4**	**A**[c]	92	0.45	–	–
8			**D**[d]	98	1.19	–	–
9	**6**	**5**	**A**[c]	95	0.30	–	–
10			**D**	98	0.90	–	–
11	 (**7**)		**A**[c]	65	–	–	–
12			**D**[c]	78 [38][e]	–	–	–
13	 (**8**)	**5**	**A**[c]	97	–	–	–
14	 (**9**)	**4**	**E**	93	–	–	–
15	**9**	**5**	**E**	96	–	–	–
16	 (**10**)	**4**	**A**[c]	65	–	–	–
17			**D**[c]	>99	0.30	–	–
18	**10**	**5**	**A**[c]	85	–	–	–
19			**D**[c]	91	0.60	–	–
20	**6**	$H_2N(CH_2)_9NH_2$ (**11**)	**E**	94	–	1.03[h]	22.92[h]

[a] Unless otherwise noted, a 10:1 (w/w) mixed solvent of *m*-terphenyl and NBP was used. [b] A: **1** (1 mol %), 300 °C (2 days). B: **1** (10 mol %), 300 °C (2 h). C: no catalyst (2 h). D: **1** (10 mol %), 300 °C (2 days). E: **1** (10 mol %), 200 °C (1 day) → 250 °C (1 day) → 300 °C (1 day). [c] A 3:1 (w/w) mixed solvent of *m*-terphenyl and NBP was used. [d] 5:1 (w/w) mixed solvent of *m*-terphenyl and NBP was used. [e] Referential data by noncatalyzed thermal polycondensation of Kakimoto and his colleagues.[3] [f] Inherent viscosity measured in concentrated sulfuric acid at a concentration of 0.0667 g/dL at 25 °C. [g] Two linear TSK-gel-GMH$_{XL}$ GPC columns were employed. The polymer was run at 0.2 wt % in NMP containing 0.05 M LiCl and 0.05 M H_3PO_4 with a polystyrene standard. [h] Three linear G1000HHR-GMHHR-Hx2 GPC columns were employed. The polymer was run at 2.5 mg/mL in HFIP containing 0.01 M CF_3CO_2Na with a poly(methyl methacrylate) standard.

temperatures screened, we found that the desired high molecular weight aramid could be obtained quantitatively as a white solid by heating the reaction mixtures in the presence of only 1 mol % of **1** in a 10:1 (w/w) mixed solvent of *m*-terphenyl and *N*-butyl-2-pyrrolidinone (NBP) at 300 °C (bath temperature) under a slow argon flow to remove water for 2 days (condition A; entry 1 in Table 2). When the reaction was carried out without an argon flow, the reaction mixture gradually changed to black. Although the polycondensation proceeded slowly at 300 °C in the absence of **1**, the reaction was obviously promoted by catalyst **1** (entry 3 versus entry 4 in Table 2). NBP was added to partially dissolve the resulting aramid, and the optimal ratio to maintain the catalytic activity of **1** was found to be 9–25 wt % in solvent. The addition of more than 25 wt % of NBP lowered the chemical yield of the aramid, since the high polarity of NBP inhibits the catalytic activity of **1**. Catalyst **1** could be recovered in good yield (ca. 80%) from filtrates after the reaction by flash column chromatography on silica gel.

To explore the generality and scope of the boronic acid **1**-catalyzed direct polycondensation to aramids and semiaromatic nylons, various structurally diverse carboxylic acids and amines were examined under the optimal reaction conditions (Table 2).[5] The structure of polymer was confirmed by IR and ^{1}H NMR measurements. In the table there are included several important commercial products such as poly[*N*,*N*′-(1,4-phenylene)-terephthalamide], poly[*N*,*N*′-(1,4-phenylene)-3,3′,4,4′-benzophenonetetracarboxylic imide], and nylon 9,T.

In most cases, the reaction proceeded cleanly in the presence of 1–10 mol % of **1** at 300 °C, and the desirable aramids were obtained as a white or light brown solid in quantitative yields. For example, GPC indicated that M_n and M_w values were 27 400 and 173 000 based on standard polystyrene for poly(*p*,*p*′-oxydiphenylene isophthalamide) which was obtained in the polycondensation of **3** and **5** (entry 6), and the inherent viscosity was 0.60 dL/g (entry 5). In contrast, Kakimoto and his colleagues have reported that the noncatalyzed thermal polycondensation of **3** and **5** at 260 °C gives the corresponding polyamide as a black solid in 68% crude yield and 0.20 dL/g inherent viscosity.[3] Similarly, AB monomer, 3-(4-aminophenoxy)benzoic acid, which is less soluble than AA+BB-type monomers, was condensed in the presence of **1**. The polyamide was then produced in a moderate yield (up to 78%, entry 12),[6] but this result was much better than the chemical yield (38%) in the noncatalyzed thermal polycondensation.[3,6]

Furthermore, the imide polycondensation between an aniline unit and a phthalic acid unit proceeded quantitatively without the isolation of amide–carboxylic acid under the same conditions with amide polycondensation (entry 13). The polycondensation of 3,3′,4,4′-benzophenonetetracarboxylic acid (**9**) and **4** or **5** was performed under the milder condition E (200 °C → 250 °C → 300 °C) because the reaction mixture was gradually changed to black if the reaction initiated at 300 °C (entries 14 and 15). The IR spectra of polyimides produced (entries 13–15) were identified with those of authentic samples.

The polycondensation to semiaromatic nylons successfully proceeded in the presence of **1** (entries 16–20). Ten mole percent of **1** was needed to give the corresponding polyamides in high yield for the polycondensation of 1,3-diadamantanedicarboxylic acid (**10**) and **4** or **5** (entries 17 and 19). The milder condition E was optimal in the synthesis of nylon 9,T[7] as well as in the synthesis of ploy[*N*,*N*′-(1,4-phenylene)-3,3′,4,4′-benzophenonetetracarboxylic imide] (entry 20). Although not enough high molecular weight nylon 6,6 could be obtained by the present polycondensation, nylon 9,T was obtained in 94% yield, and its M_n and M_w values were 10 300 and 229 200, respectively.

Conclusion. 3,4,5-Trifluorophenylboronic acid (**1**) was shown to be a highly effective catalyst for the direct polycondensation to aramids, semiaromatic nylons, and polyimides. However, it is difficult to obtain high molecular weight nylons which are good for practical levels by themselves using the present procedure. We believe that our catalytic direct polycondensation will find use as an environmentally and industrially ideal condensation method in the near future.

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References and Notes

(1) (a) Sandler, S. R.; Karo, W. *Polymer Synthesis*, 2nd ed.; Academic Press: San Diego, 1992; Vol. I, Chapter 4. (b)

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(2) Mark, H. F.; Atlas, S. M.; Ogata, N. *J. Polym. Sci.* **1962**, *61*, S49.

(3) For the successful thermal self-polycondensation of 3,5-bis-(4-aminophenoxy)benzoic acid as an AB_2-type monomer, see: Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* **1998**, *31*, 5964. According to this paper, an AB_2-type monomer gives rise to a much higher reactivity and M_n than the corresponding AB-type and AA+BB-type monomers in noncatalyzed thermal polymerization.

(4) Ishihara, K.; Ohara, S.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4196.

(5) A representative polymerization procedure (method A) is as follows. A flame-dried, 25 mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a reflux condenser was charged with carboxylic acids (1 mmol), amines (1 mmol), catalyst **1** (0.01 mmol), NBP (0.4 g), and *m*-terphenyl (3.6 g). The mixture was heated under a slow argon flow (ca. 20 mL/min) under the conditions indicated in Table 2 and brought to reflux with the removal of water. After the reaction was completed, the resulting mixture was cooled to ambient temperature and diluted with acetone (ca. 30 mL), and the solvents were removed by filtration. The crude solid obtained was washed by heating at reflux in methanol (15 mL) for 1 h, and the solvents were removed by filtration. Washing in methanol was repeated three times. Finally, the desired polyamides were obtained as white or light brown powder by drying under vacuum at 100 °C for 1 h. The filtrate obtained by treatment with acetone was concentrated and purified by flash chromatography on silica gel using hexanes−ethyl acetate (1:1 to 0:1) to recover catalyst **1** as a white solid (ca. 80%).

(6) The M_n value of the sample obtained in the noncatalyzed thermal polycondensation of **7** has been determined as 2800 by ^{1}H NMR analysis according to Kakimoto et al.[3] In our case, the M_n value could not be determined by the same method because amine and carboxylic acid groups which are the end groups of the resulting product were not clearly observed in IR and ^{1}H NMR spectra. Therefore, the M_n value of our sample would be expected to be much higher.

(7) 9,T = nonamethyleneterephthalamide.

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