Transition-Metal-Free Controlled Polymerization of 2-Perfluoroaryl-5-trimethylsilylthiophenes

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S *Supporting Information*

ABSTRACT: A catalytic amount of fluoride anion promoted the polymerization of 2-pentafluorophenyl-5-trimethylsilylthiophene, providing a high-molecular-weight conjugated polymer in a chain-growth-like manner. The resulting polymer with a controlled molecular weight and a low molecular weight distribution was obtained in a high yield. The mechanism involves a pentacoordinated fluorosilicate as a key intermediate. The active polymerization end also initiated the second polymerization to afford well-defined block copolymers.

Over the past decades, the design and synthesis of π-conjugated polymers have been active areas of research because of their applications as optoelectronic materials, such as organic field-effect transistors (FETs) and organic electroluminescent (EL) devices. Transition-metal catalyzed C−C coupling polycondensations are one of the most important synthetic methods for these polymers.[1] For example, Kumada−Tamao−Corriu coupling and Suzuki−Miyaura coupling are employed for the synthesis of conjugated polymers. However, the molecular weight (MW) and polydispersity of the polymers synthesized in such a way are not well controlled. As an alternative for these conventional step-growth polycondensations, chain-growth polymerization has been demonstrated recently.[2,3] The polymerization affords conjugated polymers with a controlled MW and low polydispersity index (PDI), but requires transition-metal catalysts.[4]

Herein, we report an alternative controlled polymerization of 2-perfluoroaryl-5-trimethylsilylthiophenes catalyzed by the fluoride anion. The polymerization requires no transition-metal catalyst and also proceeds in a chain-growth-like manner to afford the polymers with a controlled MW and low PDI.

We designed 2-pentafluorophenyl-5-trimethylsilylthiophene **1** as a monomer and examined the polymerization with a catalytic amount of the fluoride anion (Scheme 1). This is because the fluoride anion catalyzed carbon−silicon bond activation resulting in a nucleophilic pentacoordinate silicate[5,6] and the S_NAr reaction of perfluoroaryl groups[7,8] have been well studied.[9] The polycondensation of hexafluorobenzene and bis(trimethylsilyl)thiophenes was recently reported, but not controlled.[10]

The addition of a catalytic amount of the fluoride anion to **1** smoothly promoted the polymerization. Table 1 summarizes the polymerization results. For example, the reaction of **1** with 5 mol % tetrabutylammonium fluoride (TBAF) as a fluoride anion source in tetrahydrofuran (THF) at room temperature for 2 h led to poly(tetrafluorophenylene-thienylene) **2** with a MW of 6700 and a PDI of 1.55 in 93% yield (entry 2).[11,12] When the polymerization of **1** was examined with varying mol % of TBAF to the monomer, the MW of the polymer was increased with increasing monomer to TBAF ratio, while the PDIs were relatively low (entries 1−3). The addition of **1** to a solution of TBAF also gave the polymer (entry 4). Tetramethylammonium fluoride, however, was not a good initiator, because it remained undissolved in THF. Metal fluorides, such as potassium fluoride and cesium fluoride, in the presence of 18-crown-6 were not effective, but potassium fluoride/cryptand[2.2.2] was effective (entries 6−8) for the polymerization of **1**. Among the fluorosilicates examined (entries 9,10), tetrabutylammonium difluorotriphenylsilicate (TBAT)[13] initiated the polymerization to give **2** with a relatively low PDI.

The structure of the polymer is highly regulated, as demonstrated by ^{1}H, ^{13}C, and ^{19}F NMR analyses (Figure S1 in the Supporting Information). The ^{1}H NMR spectrum of **2** showed three major signals around 0.8, 1.4, and 4.0 ppm from the side chain on the thienylene units, along with a small signal at 6.7 ppm arising from the thienyl group at the polymer end. In the ^{19}F NMR spectrum of the polymer, a strong signal and three weak types of signals, which are assigned to the 1,4-tetrafluorophenylene units in the main chain and the pentafluorophenyl group at the polymer end, respectively, were observed. Thus, the NMR spectra are consistent with a highly regulated structure for the polymer main chain, indicating that the polymerization process itself must be highly regioselective. In addition, because the polymer ends are designated as the pentafluorophenyl and the thienyl groups, the integral ratio of the peaks from the side chain on the main chain and the end group in the NMR spectra assessed the number-

Scheme 1. Polymerization of 1
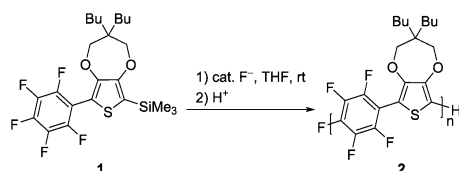
Table 1. Polymerization of 1 Catalyzed by Fluoride Anion[a]

entry	F⁻ (mol %)	reaction conditions	yield (%)	M_n[b,c]	PDI[b,c]
1	Bu₄NF (TBAF) (10)	THF, rt, 2 h	81	4900	1.30
2	Bu₄NF (TBAF) (5)	THF, rt, 2 h	93	6700 (7900)	1.55 (1.34)
3	Bu₄NF (TBAF) (0.5)	THF, rt, 2 h	89	13 800 (15 300)	1.71 (1.35)
4	Bu₄NF (TBAF) (5)	THF, rt, 20 h[d]	54	6300	2.01
5	Me₄NF (5)	THF, rt, 2 h	0	–	–
6	KF (5)/18-C-6 (10)	THF, 80 °C, 5 days	0	–	–
7	CsF (5)/18-C-6 (10)	toluene, 80 °C, 5 days	0	–	–
8	KF (5)/cryptand[2.2.2] (10)	THF, rt, 20 h	83	6900	1.57
9	[(Me₂N)₃S]⁺[Me₃SiF₂]⁻ (5)	THF, rt, 2 h	95	20 500	3.19
10	Bu₄N⁺[Ph₃SiF₂]⁻ (5)	THF, rt, 2 h	93	7740	1.94

[a]All reactions were run with [**1**] = 0.3 mmol in 5 mL of solvent. [b]The number-average MW (M_n) and PDI were determined by SEC using polystyrene standards. [c]The figures in parentheses are the weight-average MW (M_w) and PDI determined by SEC-MALS. [d]A THF solution of **1** was added to a TBAF solution.

averaged MW (M_n) of ca. 5200, in reasonable agreement with the MW estimated by size-exclusion chromatography (SEC) (Table 1, entry 2). In addition, matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectra also show that the polymer has the pentafluorophenyl and the thienyl groups at the ends (Figure S2 in the Supporting Information).

In view of the controlled MW and the relatively low PDIs (<2) found for most of the entries in Table 1, the polymerization proceeds in a chain-growth-like manner under these conditions. To prove this feature, we investigated the MW of the polymers formed as a function of monomer conversion with 5 mol % TBAF. Figure 1 shows the M_n and
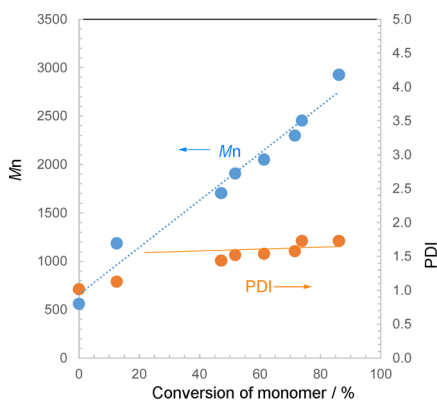

Figure 1. M_n and PDI of polymer **2** formed as a function of monomer conversion in the polymerization of **1** with **5** mol % TBAF.

PDI as a function of monomer conversion (see also Table S1 and Figure S3 in the Supporting Information). The polymerization of **1** was almost completed within a few minutes. The linear relationship between the M_n and conversion, and the nearly constant and relatively low PDI, support the chain-growth process.

As a control experiment, the reaction of hexafluorobenzene and bis(trimethylsilyl)thiophene with 5 or 10 mol % TBAF in THF at room temperature was examined, but no polymer was found (see Supporting Information).[14]

We further evaluated metal alkoxide/cryptand[2.2.2] as an initiator for the polymerization (Scheme 2). The addition of 5 mol % potassium *tert*-butoxide in the presence of 10 mol % cryptand[2.2.2] initiated the polymerization of **1** efficiently to give polymer **3a** with an M_n of 10 700 and a PDI of 1.75 in 82%

**Scheme 2. Reactions of 1 with Potassium Alkoxides**
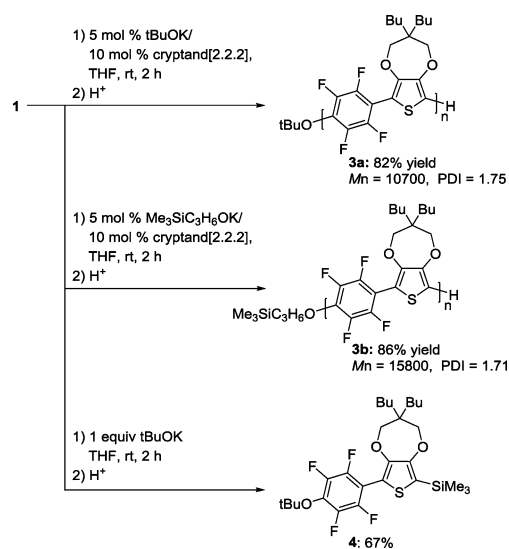
yield. Potassium 3-trimethylsilylpropoxide also gave **3b**. ^{1}H NMR spectra of **3b** showed peaks at around 0 and 6.7 ppm arising from the trimethylsilyl and thienyl groups at the polymer ends, respectively, where the observed integral ratio was in good agreement with the calculated value (calcd for Me₃Si-/thienyl-H 9.0, found 8.0) within the experimental errors (Figure S4 in the Supporting Information). To elucidate the initial step of the polymerization for this case, the reaction of **1** with a 1 equiv amount of potassium *tert*-butoxide, followed by the addition of ethanol, was examined. This reaction exclusively gave 2-(4′-*tert*-butoxytetrafluorophenyl)-5-trimethylsilylthiophene **4**, indicating that *tert*-butoxide attacks on the pentafluorophenyl group of **1**.

Scheme 3 shows a possible polymerization mechanism. In the initial step of the reaction, a fluoride anion attacks the trimethylsilyl group of **1** to form a pentacoordinate silicate. The silicate is quite reactive and could regioselectively attack the 4-position of the pentafluorophenyl group of **1** to reproduce a fluoride anion. Then, the fluoride anion catalyzes the polymerization to give polymer **2**. In the polymerization, the reactivity of the trimethylsilyl group and/or the silicate at the polymer end is changed by replacing the 4-position of the pentafluorophenyl group of **1**. Watson et al. discussed the change in the reactivity by substitution in the reaction of bis(trimethylsilyl)thiophene and hexafluorobenzene.[10] Further,

Scheme 3. Possible Polymerization Mechanism of 1
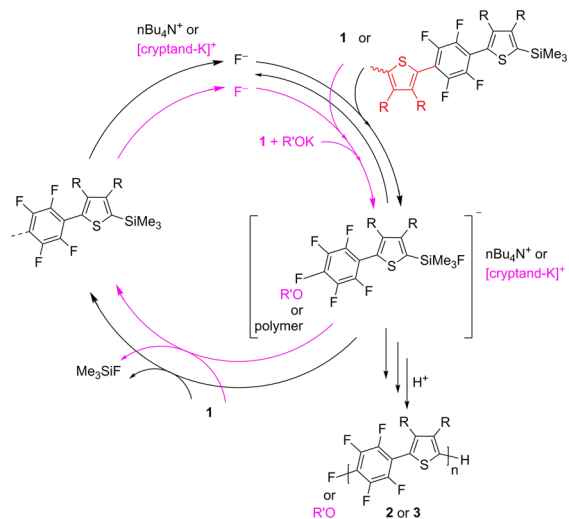
the fluoride anion would transfer intramolecularly to the trimethylsilyl group at the polymer end in the polymerization of **1**, where there may be an anion−π interaction[15] that produces an associated pair to allow the polymerization to proceed via chain growth. This is because of the lack of polymerization of bis(trimethylsilyl)thiophene and hexafluorobenzene under our conditions as the control experiment. A further detailed description of the polymerization mechanism requires further studies. On the other hand, when using metal alkoxides as an initiator, the initial step of the polymerization occurs by the attack of the alkoxide on the pentafluorophenyl group of **1** to give a fluoride anion, resulting in the formation of a pentacoordinate silicate, and then the polymerization proceeds in the same way as mentioned above.

Next, to exploit the chain-growth nature of this polymerization process, we demonstrated end-capping (Scheme 4). The

Scheme 4. End-Capping with 5
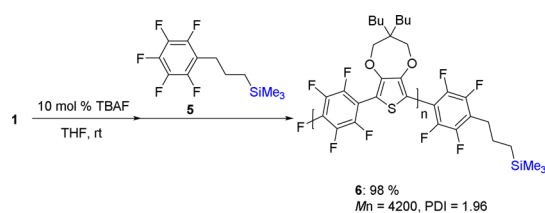
addition of an excess amount 3-(pentafluorophenyl)propyl-trimethylsilane **5** to the reaction mixture of **1** terminated the polymerization to give end-capped polymer **6**, as confirmed by NMR spectroscopy (Figure S5 in the Supporting Information). We also applied the "living" character of this growing end to the synthesis of well-defined block copolymers (Scheme 5). After polymerization of **1** with a catalytic amount of TBAF, a part of the mixture was studied to analyze the MW of the first block, and then a solution of **1** or **7** was added to the reaction mixture to afford block copolymer **2′** or **8**, respectively.[16] As shown in Figure 2, the SEC curves of the polymer obtained at the end of the reaction shifted toward a higher molecular weight than those of the first polymerization. The first/second block ratio (n/m) of **8** was found to be 0.60 by ^{1}H NMR analysis (Figure S6 in the Supporting Information).

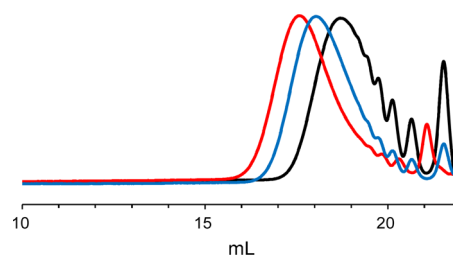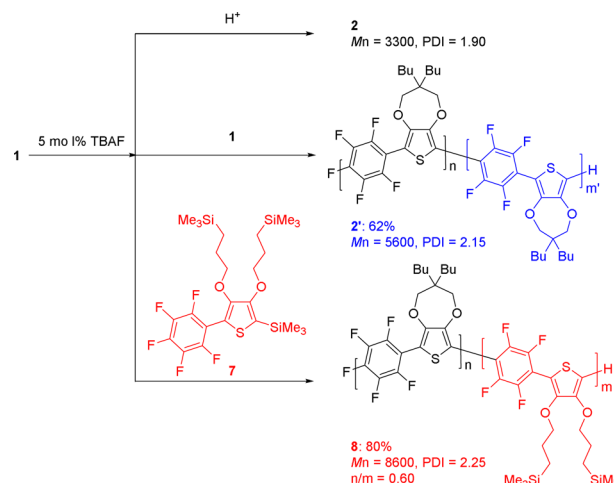**Scheme 5. Synthesis of Block Copolymers**

Figure 2. SEC curves (RI) obtained by the first polymerization of **1** (polymer **2**, black) and sequential addition of **1** (polymer **2′**, blue) and **7** (polymer **8**, red) after the first polymerization of **1**.

Further, we extended our method to the polymerization of nonafluorobiphenyl and heptafluoronaphthyl-substituted thiophenes (Scheme 6). The reaction of (nonafluorobiphenyl)-

Scheme 6. Polymerization of Perfluoroaryl-Substituted Trimethylsilylthiophene 9a,b
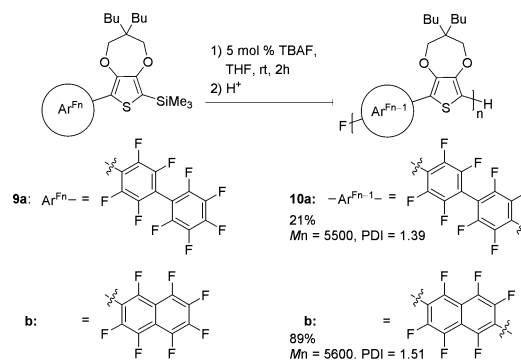
trimethylsilylthiophene **9a** with 5 mol % TBAF gave polymer **10a** with an M_n of 5500 and a PDI of 1.39 in a moderate yield. (Heptafluoronaphthyl)trimethylsilylthiophene **9b** was also polymerized by the addition of 5 mol % TBAF to give polymer **10b** with an M_n of 5600 and a PDI of 1.51 in a good yield. The structures of these polymers were highly ordered, as evidenced by NMR analyses (Figure S7 in the Supporting Information), indicating that the polymerizations of perfluoroarylthiophene **9** also proceed with high regioselectivity on the perfluoroaryl groups.

In summary, we have demonstrated the transition-metal-free controlled polymerization of 2-perfluoroaryl-5-trimethyl-silylthiophenes promoted by the fluoride anion. The polymerization proceeds in a chain-growth-like manner to afford polymers with a controlled MW and low PDI. In addition, because the polymerization end is active, the block copolymers are prepared by addition of a second monomer to the polymerization mixture. The polymerization in this report would be an alternative synthetic method for well-controlled π-conjugated polymers. The present initiation- and termination-defined controlled polycondensation will open a new avenue of macromolecular 3-D modeling architecture with the stiffness as well as conductivity of the π-conjugated main chain as the growth-controlled building block. Further study along this line is currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization of new compounds and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(14) Our polymerization conditions were quite different from the reported conditions by Watson and Wang:[10] ([bis(trimethylsilyl)thio-phene] = 0.2 M in toluene, 10 mol % CsF, 20 mol % 18-crown-6, 80 °C, 5 days).

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(16) The polymerization of 2-(pentafluorophenyl)-3,4-bis(3-trimethylsilylpropoxy)-5-trimethylsilylthiophene 7 with 5 mol % TBAF gave a polymer with an M_n of 7700 and a PDI of 1.40 in 78% yield.