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# Chain-Growth Polymerization of 2-Chlorothiophenes Promoted by Lewis Acids

Baltasar Bonillo and Timothy M. Swager\*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139, United States

Supporting Information Placeholder

**ABSTRACT:** Lewis acids promote the polymerization of several 2-chloroalkylenedioxythiophenes providing high molecular weight conjugated polymers. The proposed mechanism is a cationic chain-growth polymerization, as confirmed by end-capping reactions and a linear correlation of molecular weight with percent conversion. The “living” character of this process was used to prepare new block copolymers.

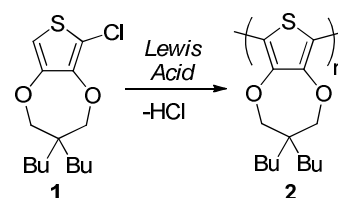
There is an ongoing need for the development of methodologies for the synthesis of conjugated polymers<sup>1</sup> in support of their applications in flexible opto-electronic devices.<sup>2</sup> Among this class of materials, polythiophenes stand out as one of the most important classes of materials and display desirable charge transport, optical absorptions, and stability. The major routes to these materials include oxidative and cross-coupling polymerizations. The latter has undergone intense investigation since variants were shown to exhibit living chain growth character thereby allowing the preparation of polyalkylthiophenes with high molecular weight and narrow polydispersity.<sup>3</sup> Nevertheless, there remains a need to generate additional syntheses of established architectures as well as new materials based on the requirement of high molecular weight polymers with mechanical resistance and better processing.<sup>3a,4</sup>

We and others<sup>5</sup> have noticed the violent autopolymerization of 3-alkoxy-2-bromothiophenes. Officer and co-workers<sup>5b</sup> reported the polymerization of several bromothiophenes, in neat form or catalyzed by HBr, and proposed a cationic mechanism with the elimination of HBr to obtain a conjugated polymer. Although this uncontrolled nature of that reaction did not provide useful polythiophenes, we targeted this reactivity as offering the potential for a controlled chain-growth polymerization.

To avoid the instability of alkoxybromothiophenes we decided to develop alkoxychlorothiophene monomers. The lower acidity of the eliminated HCl is also desirable to prevent polymer degradation and/or competing side reactions.<sup>5b</sup> Chloro-dibutylpropylenedioxythiophene (Cl-ProDOT), **1**, was used as a model monomer for the initial development of the polymerization conditions. The stability of **1** allowed its purification and we screened its reactivity under classical cationic polymerization conditions.<sup>6</sup> For example, treatment of a solution of **1** in dichloromethane with 25% of boron trifluoride provided poly-di-butyl(ProDOT) **2** in a 29% yield (entry 1, Table 1). This reaction gave the polymer in a doped/protonated state and after neutralization with hydrazine a purple solid was obtained with a molecular weight of 4000 g/mol and a PDI of 1.41. This polymer was characterized by NMR, GPC

and MALDI-TOF (see Supporting Information) and our NMR data is in agreement with the literature.<sup>7</sup>

## Scheme 1



With the goal of optimizing the reaction conditions to improve the yield, increase the molecular weight, and lower the polydispersity, a systematic study was carried out and summarized in Table 1. The polymerization qualitatively exhibits a fast initiation after the addition of a small amount of the Lewis acid, however, to obtain a high polymer yield additional Lewis acid (0.15-0.3 eq.) is required. This feature is likely a consequence of the fact that the polymerization formally generates HCl, which builds up and reacts with free Lewis acid to create a very strong Brønsted acid. Under these conditions the growing polymer is protonated reducing the degree of ionization of the chain end and HCl complexation of the Lewis acid lowers its effectiveness as a catalyst.<sup>8</sup> As detailed in Table 1, we investigated (1-bromoethyl)benzene (RBr) as an initiator, however in general **1** is able to self-initiate polymerization when reacted with a suitable Lewis acid. After screening a number of Lewis acid catalysts, we have determined that SnCl<sub>4</sub> displayed the best performance giving better yields and higher molecular weights with lower catalyst loadings. We also found that the resulting polymers produced with SnCl<sub>4</sub> were more readily neutralized than those produced with AlCl<sub>3</sub>, TiCl<sub>4</sub>, FeCl<sub>3</sub> or Sc(OTf)<sub>3</sub>. Slight changes were observed for SnCl<sub>4</sub> polymerizations with different solvents and reaction temperatures (Table 1, entries 14-22). In some cases a dark precipitate formed and superior results were obtained in homogenous reaction mixtures using *ortho*-dichlorobenzene (*o*-DCB) as solvent at 120°C (Table 1, entry 20). It is worth pointing out that a strong Brønsted acid, like TfOH, also promoted the polymerization of **1** (entry 23).

Based on our own intuition and the literature,<sup>5b,9</sup> we propose a transformation of **1** → **2** that begins with the reaction of SnCl<sub>4</sub> and **1** to give a zwitterion **3** (Scheme 2). Reaction with other monomer gives dimer **4** and elimination of SnCl<sub>5</sub><sup>-</sup> produces **5**. Monomer addition reactions produce a composition shown as **6**, which may have a complex structure with units as show, units that are cationic and protonated, and neutral thiophene units. HCl elimination during workup provides **2**.

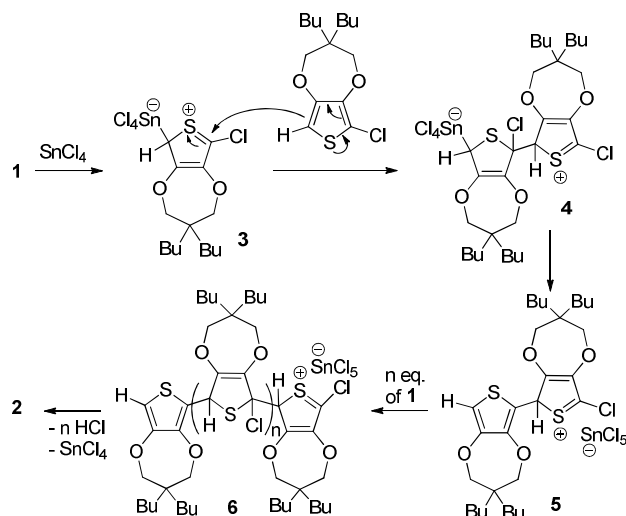
**Table 1.** Polymerization of **1** promoted by Lewis acids.<sup>a</sup>

entry	Lewis acid (%) <sup>b</sup>	Reaction Conditions	Yield (%)	Mn (g/mol), PDI <sup>c</sup>
1	BF <sub>3</sub> ·Et <sub>2</sub> O (25)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 3d	29	4000, 1.41
2	BF <sub>3</sub> ·Et <sub>2</sub> O (20)	Toluene, r.t., 2d	47	6000, 1.58
3	AlCl <sub>3</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 3d	72	8700, 1.64
4	AlCl <sub>3</sub> (50)	THF, reflux, 3d	-	-
5	AlCl <sub>3</sub> (20)	RBr, <sup>d</sup> CH <sub>2</sub> Cl <sub>2</sub> , r.t., 2d	86	9000, 2.15
6	FeCl <sub>3</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 2d	90	7000, 1.60
7	TiCl <sub>4</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 2d	75	4000, 1.49
8	Sc(OTf) <sub>3</sub> (50)	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub> , 100°C, 2d	29	6500, 2.25
9	AuCl <sub>3</sub> (25)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 3d	17	4000, 1.43
10	AgOTf (100)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 3d	50	9000, 1.65
11	Cp <sub>2</sub> ZrMe <sub>2</sub> , Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> (15)	RBr, CH <sub>2</sub> Cl <sub>2</sub> , r.t., 4d	trace	4000, 2.07
12	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> (25)	RBr, CH <sub>2</sub> Cl <sub>2</sub> , r.t., 4d	23	10000, 1.66
13	SbCl <sub>5</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 2d	85	3600, 1.30
14	SnCl <sub>4</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 3d	85	9500, 1.55
15	SnCl <sub>4</sub> (15)	Toluene, 100°C, 2d	90	11000, 1.54
16	SnCl <sub>4</sub> (20)	RBr, CH <sub>2</sub> Cl <sub>2</sub> , r.t., 2d	82	10000, 1.74
17	SnCl <sub>4</sub> (15)	Toluene, 80°C, 2d	85	11000, 1.64
18	SnCl <sub>4</sub> , EtAlCl <sub>2</sub> (15)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 1d	67	11000, 1.68
19	SnCl <sub>4</sub> , NaBARF <sub>4</sub> <sup>e</sup> (20)	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 2d	91	7800, 1.75
20	SnCl <sub>4</sub> (15)	<i>o</i> -DCB, 120°C, 2d	95	11000, 1.43
21	SnCl <sub>4</sub> (100)	Cs <sub>2</sub> CO <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , r.t., 7d	60	6800, 1.60
22	SnCl <sub>4</sub> (30)	Cs <sub>2</sub> CO <sub>3</sub> , Toluene, reflux, 3d	40	6500, 1.54
23	TfOH (25)	<i>o</i> -DCB, 120°C, 2d	84	15000, 2.60

<sup>a</sup>All reactions were run at 0.15 M in monomer. <sup>b</sup>% of Lewis acid added to obtain a total conversion from the monomer. <sup>c</sup>Number-average molecular weights (Mn) and polydispersity indices (PDI) were determined by gel permeation chromatography relative to PS standards. <sup>d</sup>RBr = (1-bromoethyl)benzene (5%). <sup>e</sup>ArF = 3,5-bis-(trifluoromethyl)phenyl.

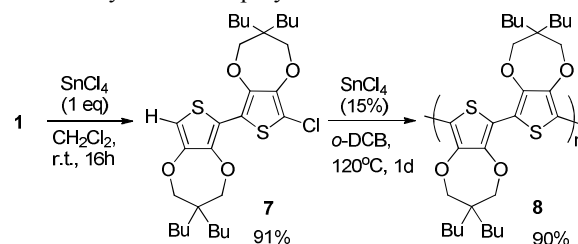
of each monomer and we expect that the situation may be more complex with the polymer being protonated by highly acidic SnCl<sub>4</sub>H species generated *in situ*.

### Scheme 2. Mechanistic proposal for polymerization of **1**.



Interestingly when a solution of **1** in dichloromethane at room temperature was treated with one equivalent of SnCl<sub>4</sub>, the dimer **7** is isolated in a high yield, thereby suggesting the viability of intermediate **5** in the polymerization. The corresponding polymer **8** (Mn 20,000 g/mol, PDI 2.25) was prepared by treatment of **7** with catalytic amount of SnCl<sub>4</sub> (Scheme 3) and **8** is spectroscopically identical to **2**.

### Scheme 3. Synthesis and polymerization of dimer **7**.



The relatively low (<2) polydispersities<sup>10</sup> found for most of the entries in Table 1 support our proposed chain-growth mechanism.<sup>11</sup> To prove this feature we investigated the molecular weight as a function of conversion for **1** in *o*-DCB and SnCl<sub>4</sub> (25%) catalyst. Figure 1 shows these data as well as the variation of the polydispersity with monomer conversion. The linear relationship between the molecular weight and conversion and the relative constant polydispersity confirms a chain-growth process.

To exploit the cationic chain-growth nature of this polymerization<sup>12</sup> process we have demonstrated end-capping with nucleophiles. Specifically, quenching a polymerization of **1** with excess sodium phenoxide salts (Scheme 3) results in end-capping with this group as confirmed by NMR spectroscopy. Quenching with salt **10a** yielded an isolated polymer product with <sup>19</sup>F-NMR signals at -63 ppm indicating the incorporation of the 3-trifluorophenoxy moiety. When the salt **10b** was used the corresponding polymeric product showed a peak around 0.35 ppm in the <sup>1</sup>H-NMR spectra, and, assuming the incorporation of one 4-trimethylsilylphenoxy group per polymer chain, a molecular weight of 5500 g/mol was calculated based on the NMR integrals, which is in relative agreement with the GPC molecular weight estimation of 6500 g/mol.

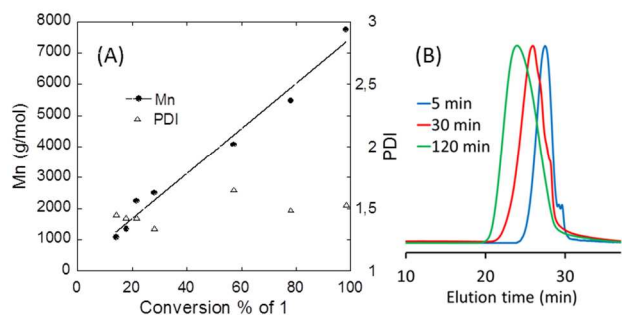
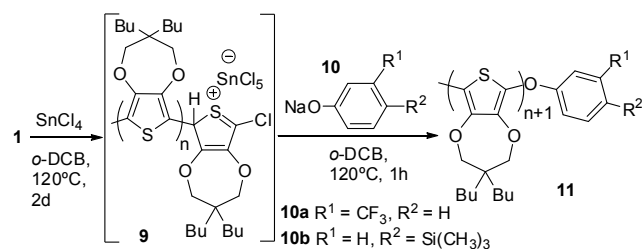
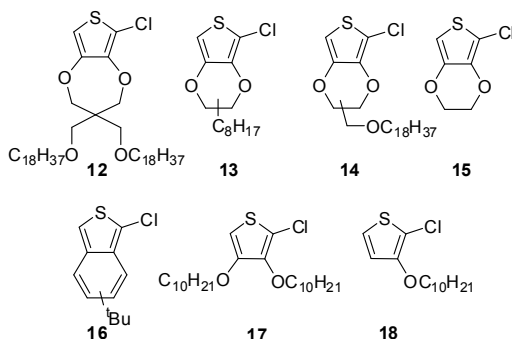


Figure 1. (A)  $M_n$  (●) and  $PDI$  (△) values of polymer **2** as a function of monomer conversion in the polymerization of **1** with 25% of  $\text{SnCl}_4$  in *o*-DCB at  $120^\circ\text{C}$ . (B) GPC curves at 5, 30 and 120 min.

**Scheme 4.** End-capping experiments with sodium phenoxide salts.



Our method can be extended to the other 2-chlorothiophene monomers shown in Chart 1 and the polymerization results for monomers **9-15** are summarized in Table 2. The polymerization of **12** promoted by  $\text{SnCl}_4$  gave a previously reported polymer<sup>13</sup> with  $M_n$  of 20,000 g/mol and a  $PDI$  of 1.37. **13** provided a poorly soluble polymer in 89% yield and the soluble portion displayed a  $M_n$  of 2800 g/mol.<sup>14</sup> A longer C18 alkyl chain in **14** provided only a modest improvement in the  $M_n$  (5000 g/mol,  $PDI$  of 1.22) as a result of limited solubility.<sup>15</sup>



**Chart 1.** 2-Chlorothiophene monomers.

**Table 2.** Polymerization of monomers **12-18** with  $\text{SnCl}_4$  in *o*-dichlorobenzene at  $120^\circ\text{C}$ .

Monomer	Yield (%)	$M_n$ (g/mol)	$PDI$
<b>12</b>	90	20,000	1.37
<b>13</b> <sup>a</sup>	89	2800 <sup>b</sup>	1.23
<b>14</b> <sup>a</sup>	93	5000	1.22
<b>15</b>	91	- <sup>c</sup>	-
<b>16</b> <sup>a</sup>	70	5000	1.40
<b>17</b>	56	3000	1.54
<b>18</b>	55	2000	1.30

<sup>a</sup> Mixture of regioisomers. <sup>b</sup> Fraction soluble in THF. <sup>c</sup> Not soluble.

Polyethylenedioxythiophene (PEDOT) is widely used in the fabrication of polymer electronic devices as a result of its high conductivity and stability.<sup>16</sup> Consequently we have evaluated our method in the synthesis of PEDOT by the treatment of **15** with  $\text{SnCl}_4$ . These conditions gave the corresponding polymer in a conductive doped state (pressed pellet  $\sigma = 50 \text{ S/cm}$ ) as a dark blue solid in a 91% yield. The complete insolubility of this material precludes molecular weight determination.

Chlorobenzo[*c*]thiophene **16** is unstable at room temperature in its neat form or a concentrated solution. The polymerization of **16** was carried out in dichloromethane at  $-78^\circ\text{C}$  using  $\text{SnCl}_4$  to give a polymer consistent with literature characterization<sup>17</sup> in 70% yield ( $M_n = 5000 \text{ g/mol}$ ). The higher reactivity of **16** to polymerization is understood to be the result of the aromatization of the benzene ring during the chain growth process.

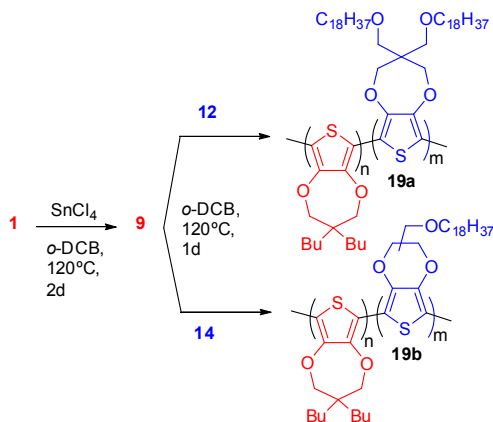
Straight chain alkoxy thiophene monomers **17** and **18** were also investigated to determine the polymerization's scope. Monomer **17** provided a polymer<sup>18</sup> with a  $M_n$  of 3000 g/mol, however, the <sup>1</sup>H-NMR suggests side reactions of the carbocation intermediates produced some branched structures or irregular 2,3 or 2,4 substitution patterns. In the case of **18** a cleaner polymer was obtained, albeit with a low  $M_n$  (2000 g/mol). Nevertheless, the <sup>1</sup>H-NMR (see SI) revealed a completely regioregular head-to-tail structure.<sup>19</sup>

Considering the chain-growth and "living" character of this polymerization we have applied it to the synthesis of block copolymers. Conjugated block copolymers are of interest to generate materials that self-assemble into defined nanostructures.<sup>20</sup> We first investigated if thiophene-thiophene block polymers could be synthesized. A solution of **1** was treated with  $\text{SnCl}_4$  and heated in *o*-dichlorobenzene at  $120^\circ\text{C}$ . When the disappearance of the monomer was confirmed by thin layer chromatography an aliquot was taken to analyze the first block and a solution of **12** or **14** in the same solvent was added to reaction crude and the reaction was kept at  $120^\circ\text{C}$  for another day (see SI). The block copolymers **19a** and **19b** from monomers **1** and **12** or monomers **1** and **14** were respectively synthesized (Table 3) and purified by Soxhlet extraction. This procedure may remove some homopolymer and in general our experiments were hindered by the low solubility of the first block homopolymer **1**.

**Table 3.** Block copolymers **19**.

Polymer	First Block Polymer $M_n$ (g/mol), $PDI$	Yield (%)	$M_n$ (g/mol)	$PDI$
<b>19a</b>	5000, 1.45	55	14000	1.60
<b>19b</b>	5000, 1.39	60	10000	1.71

**Scheme 5.** Synthesis of block copolymers **19a/b**.



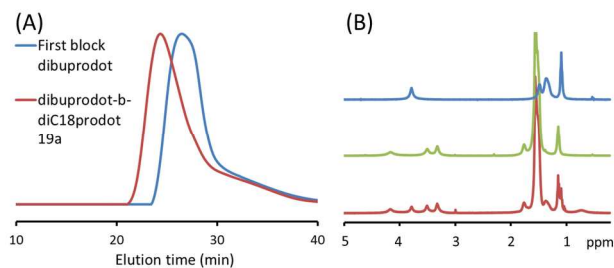
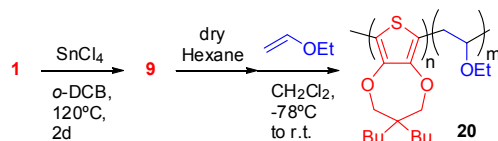


Figure 2. (A) GPC curves of **9** quenched from a block polymer synthesis (blue trace) before addition of **12** and of the final block copolymer **19a** (red trace). (B) <sup>1</sup>H-NMR spectra of homopolymers **9** (blue trace), poly-**12** (green trace), and block copolymer **19a** (red trace).

An optimized procedure required diluted monomer concentrations (80 mM) in the polymerization and consequently the first block  $M_n$  is smaller than those reported in Table 1. For both **19a** and **19b**, we succeeded in creating materials  $n/m \approx 1$  by NMR analysis. Obtaining higher  $n/m$  ratios for **19b** is complicated by low solubility of the block copolymer, which created an inhomogeneous reaction.

We have further extended this method to the synthesis of rod-coil copolymers,<sup>21</sup> taking advantage of the cationic mechanism of the polymerization. These investigations further probe the “living” character and require that our “living chain” is competent to initiate a classic cationic polymerization (Scheme 6). A consideration in our system is the need for excess Lewis acid and the protonation of the polymer backbone. Hence, after the **1** is consumed the first block was precipitated and washed with dry hexane to remove excess acid. The resulting solid was then dissolved in dichloromethane, cooled at  $-78^\circ\text{C}$  and ethylvinylether (EVE) was added to produce a block copolymer, **20**, with a  $M_n$  of 12000 g/mol, PDI of 1.78, and  $n/m \approx 1$ .

**Scheme 6.** Synthesis of a copolymer of **1** and ethylvinylether.



In summary, we report a “living” chain-growth synthesis to create polythiophenes from the reaction of 2-chlorothiophene monomers and Lewis acids. The molecular weights and polydispersities are comparable to previous methods reported in the literature. The living character enabled the synthesis of all conjugated thiophene-thiophene block copolymers and polythiophene-poly(ethylvinylether) rod-coil block copolymers. Although this transformation has limited scope at present, it demonstrates the ability to polymerize an aromatic monomer through a classical cationic methodology, by making use of HCl elimination reactions to regain aromatic stability during the polymerization. We expect that the concept of an ionic addition-elimination based scheme can be extended to create other polyaromatic semiconducting polymers.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and compound characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

tswager@mit.edu

### Notes

The authors declare no competing financial interests.

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- (10) GPC chromatographs of **1** showed a severe “tailing” probably due to a strong interaction between the polymer and the columns. This likely produces an overestimation of the polydispersities.
- (11) No fractionation of the polymer was observed during the isolation.
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