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Communication

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

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Supporting Information

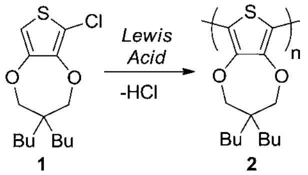
ABSTRACT: Lewis acids promote the polymerization of several 2-chloroalkylenedioxythiophenes, providing high-molecular-weight conjugated polymers. The proposed mechanism is a cationic chain-growth polymerization, as confirmed by end-capping reactions and a linear correlation of molecular weight with percent 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[1] in support of their applications in flexible optoelectronic devices.[2] Among this class of materials, polythiophenes stand out as one of the most important types 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 (MW) and low polydispersity index (PDI).[3] Nevertheless, there remains a need to generate additional syntheses of established architectures as well as new materials based on the requirement of high-MW polymers with mechanical resistance and better processing.[3a,4]

We and others[5] have noticed the violent autopolymerization of 3-alkoxy-2-bromothiophenes. Officer and co-workers[5b] 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 the 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.[5b] Chlorodibutylpropylenedioxythiophene (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.[6] For example, treatment of a solution of **1** in CH_2Cl_2 with 25% BF_3 provided poly(di-Bu-ProDOT) (**2**) in 29% yield (Scheme 1 and Table 1, entry 1). This reaction gave the polymer in a doped/protonated state, and after neutralization with N_2H_4, a purple solid with a MW of 4000 g/mol and a PDI of 1.41 was obtained. This polymer was characterized by NMR spectroscopy, gel-permeation chromatography (GPC), and MALDI-TOF mass spectrometry [see the Supporting Information (SI)], and our NMR data were in agreement with the literature.[7]

Scheme 1



With the goal of optimizing the reaction conditions to improve the yield, increase the MW, and lower the PDI, a systematic study was carried out (Table 1). The polymerization qualitatively exhibited a fast initiation after the addition of a small amount of the Lewis acid, but to obtain a high polymer yield, additional Lewis acid (0.15−0.3 equiv) was 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.[8] As detailed in Table 1, we investigated (1-bromoethyl)benzene (RBr) as an initiator, but in general, **1** was able to self-initiate polymerization when reacted with a suitable Lewis acid. After screening a number of Lewis acid catalysts, we determined that $SnCl_4$ displayed the best performance, giving better yields and higher MW with lower catalyst loading. We also found that the polymers produced with $SnCl_4$ were more readily neutralized than those produced with $AlCl_3$, $TiCl_4$, $FeCl_3$, or $Sc(OTf)_3$. Slight changes were observed for $SnCl_4$ polymerizations with different solvents and reaction temperatures (entries 14−22). A dark precipitate formed in some cases, and superior results were obtained in homogeneous reaction mixtures using *o*-dichlorobenzene (*o*-DCB) as the solvent at 120 °C (entry 20). It is worth pointing out that a strong Brønsted acid (TfOH) also promoted the polymerization of **1** (entry 23).

On the basis of our own intuition and the literature,[5b,9] we propose that the **1** → **2** transformation begins with the reaction of $SnCl_4$ and **1** to give zwitterion **3** (Scheme 2). Reaction with another monomer gives dimer **4**, and elimination of $SnCl_5^-$ produces **5**. Monomer addition reactions produce a composition

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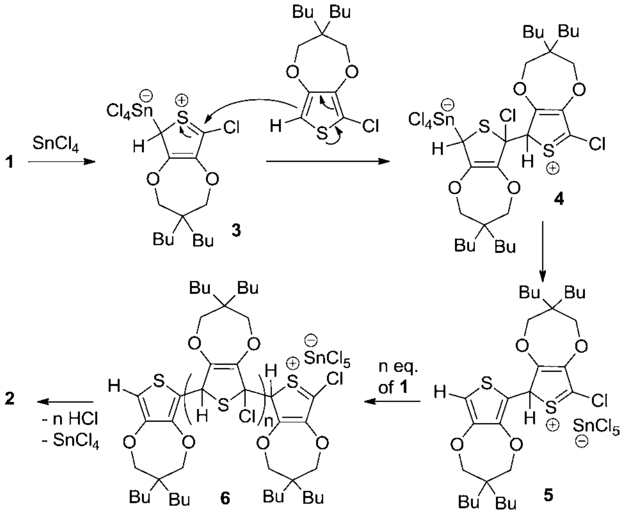
Table 1. Polymerization of 1 Promoted by Lewis Acids[a]

entry	Lewis acid (%)[b]	reaction conditions	yield (%)	M_n (g/mol), PDI[c]
1	$BF_3 \cdot Et_2O$ (25)	CH_2Cl_2, rt, 3 days	29	4000, 1.41
2	$BF_3 \cdot Et_2O$ (20)	toluene, rt, 2 days	47	6000, 1.58
3	$AlCl_3$ (20)	CH_2Cl_2, rt, 3 days	72	8700, 1.64
4	$AlCl_3$ (50)	THF, reflux, 3 days	–	–
5	$AlCl_3$ (20)	RBr,[d] CH_2Cl_2, rt, 2 days	86	9000, 2.15
6	$FeCl_3$ (20)	CH_2Cl_2, rt, 2 days	90	7000, 1.60
7	$TiCl_4$ (20)	CH_2Cl_2, rt, 2 days	75	4000, 1.49
8	$Sc(OTf)_3$ (50)	$C_2H_2Cl_4$, 100 °C, 2 days	29	6500, 2.25
9	$AuCl_3$ (25)	CH_2Cl_2, rt, 3 days	17	4000, 1.43
10	AgOTf (100)	CH_2Cl_2, rt, 3 days	50	9000, 1.65
11	Cp_2ZrMe_2, $Ph_3CB(C_6F_5)_4$ (15)	RBr, CH_2Cl_2, rt, 4 days	trace	4000, 2.07
12	$Ph_3CB(C_6F_5)_4$ (25)	RBr, CH_2Cl_2, rt, 4 days	23	10000, 1.66
13	$SbCl_5$ (20)	CH_2Cl_2, rt, 2 days	85	3600, 1.30
14	$SnCl_4$ (20)	CH_2Cl_2, rt, 3 days	85	9500, 1.55
15	$SnCl_4$ (15)	toluene, 100 °C, 2 days	90	11000, 1.54
16	$SnCl_4$ (20)	RBr, CH_2Cl_2, rt, 2 days	82	10000, 1.74
17	$SnCl_4$ (15)	toluene, 80 °C, 2 days	85	11000, 1.64
18	$SnCl_4$, $EtAlCl_2$ (15)	CH_2Cl_2, rt, 1 day	67	11000, 1.68
19	$SnCl_4$, $NaBAr^F_4$[e] (20)	CH_2Cl_2, rt, 2 days	91	7800, 1.75
20	$SnCl_4$ (15)	o-DCB, 120 °C, 2 days	95	11000, 1.43
21	$SnCl_4$ (100)	Cs_2CO_3, CH_2Cl_2, rt, 7 days	60	6800, 1.60
22	$SnCl_4$ (30)	Cs_2CO_3, toluene, reflux, 3 days	40	6500, 1.54
23	TfOH (25)	o-DCB, 120 °C, 2 days	84	15000, 2.60

[a] All reactions were run with 0.15 M monomer. [b] Percent Lewis acid added to obtain total conversion from the monomer. [c] The number-average MW (M_n) and PDI were determined by GPC relative to polystyrene standards. [d] RBr = (1-bromoethyl)benzene (5%). [e] Ar^F = 3,5-bis(trifluoromethyl)phenyl.

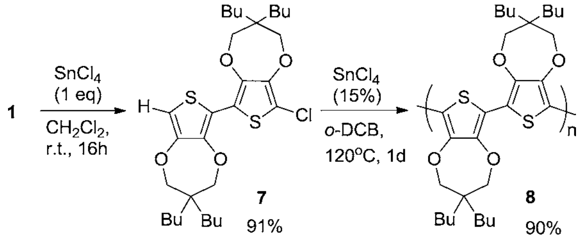
Scheme 2. Mechanistic Proposal for the Polymerization of 1



shown as **6**, which may have a complex structure with units as shown, units that are cationic and protonated, and neutral thiophene units. HCl elimination during workup provides **2**.

Interestingly when a solution of **1** in CH_2Cl_2 at room temperature was treated with 1 equiv of $SnCl_4$, dimer **7** was isolated in high yield, thereby suggesting the viability of intermediate **5** in the polymerization. The corresponding polymer **8** (M_n = 20 000 g/mol, PDI = 2.25) was prepared by treatment of **7** with a catalytic amount of $SnCl_4$ (Scheme 3), and **8** was spectroscopically identical to **2**.

Scheme 3. Synthesis and Polymerization of Dimer 7



The relatively low PDIs (<2)[10] found for most of the entries in Table 1 support our proposed chain-growth mechanism.[11] To prove this feature, we investigated the MW as a function of conversion for **1** in o-DCB with 25% $SnCl_4$ catalyst. Figure 1 shows these data as well as the variation of the PDI with monomer conversion. The linear relationship between the MW and conversion and the relatively constant PDI confirm the chain-growth process.

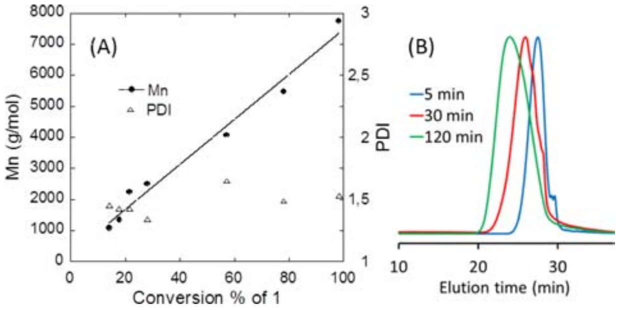
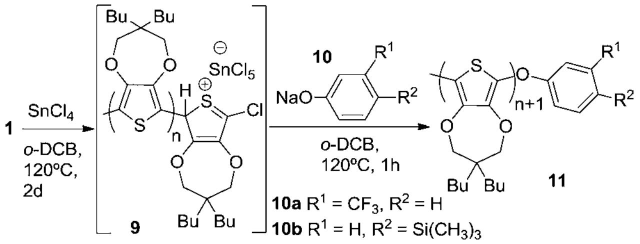


Figure 1. (A) M_n (●) and PDI (△) of polymer **2** as functions of monomer conversion in the polymerization of **1** with 25% $SnCl_4$ in o-DCB at 120 °C. (B) GPC curves at 5, 30, and 120 min.

To exploit the cationic chain-growth nature of this polymerization process,[12] we demonstrated end-capping with nucleophiles. Specifically, quenching a polymerization of **1** with excess sodium phenoxide salts (Scheme 4) resulted in phenoxide end-capping, as confirmed by NMR spectroscopy. Quenching with salt **10a** yielded an isolated polymer product with an ^{19}F NMR signal at −63 ppm indicating the incorporation of the 3-

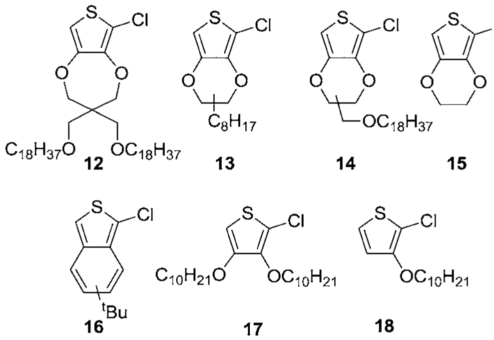
Scheme 4. End-Capping Experiments with Sodium Phenoxide Salts



trifluoromethylphenoxy moiety. When salt **10b** was used, the corresponding polymeric product showed a peak around 0.35 ppm in the ^{1}H NMR spectrum; with the assumption that one 4-trimethylsilylphenoxy group was incorporated per polymer chain, the MW was calculated from the NMR integrals to be 5500 g/mol, in relative agreement with the GPC MW estimate of 6500 g/mol.

Next, we extended our method to 2-chlorothiophene monomers **12−18** (Table 2). The polymerization of **12** promoted by $SnCl_4$ gave a previously reported polymer[13] with M_n = 20 000 g/mol and PDI = 1.37. **13** provided a poorly soluble polymer in 89% yield, and the soluble portion had M_n = 2800 g/mol.[14] The longer C18 alkyl chain in **14** provided only a modest improvement in M_n (5000 g/mol, PDI = 1.22) as a result of the limited solubility.[15]

Table 2. Polymerization of Monomers 12−18 with $SnCl_4$ in *o*-DCB at 120 °C



monomer	yield (%)	M_n (g/mol)	PDI
12	90	20000	1.37
13[a]	89	2800[b]	1.23
14[a]	93	5000	1.22
15	91	–[c]	–
16[a]	70	5000	1.40
17	56	3000	1.54
18	55	2000	1.30

[a]Mixture of regioisomers. [b]Fraction soluble in THF. [c]Not soluble.

Poly(ethylenedioxythiophene) (PEDOT) is widely used in the fabrication of polymer electronic devices as a result of its high conductivity and stability.[16] Consequently, we evaluated our method in the synthesis of PEDOT by treating **15** with $SnCl_4$. These conditions gave the corresponding polymer in a conductive doped state (pressed pellet, σ = 50 S/cm) as a dark-blue solid in 91% yield. The complete insolubility of this material precluded MW determination.

Chlorobenzo[*c*]thiophene **16** is unstable at room temperature in its neat form or in a concentrated solution. Polymerization of **16** in CH_2Cl_2 at −78 °C using $SnCl_4$ gave a polymer consistent with literature characterization[17] in 70% yield (M_n = 5000 g/mol). The higher reactivity of **16** toward polymerization is understood to be the result of the aromatization of the benzene ring during the chain-growth process.

Straight-chain alkoxythiophene monomers **17** and **18** were also investigated to determine the scope of the polymerization. Monomer **17** provided a polymer[18] with M_n = 3000 g/mol, although ^{1}H NMR analysis suggested that 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, ^{1}H NMR analysis (see the SI) revealed a completely regioregular head-to-tail structure.[19]

Considering the chain-growth and "living" character of this polymerization, we applied it to the synthesis of block copolymers. Conjugated block copolymers are of interest in generating materials that self-assemble into defined nanostructures.[20] We first investigated whether thiophene−thiophene block polymers could be synthesized. A solution of **1** was treated with $SnCl_4$ and heated in *o*-DCB at 120 °C. When the disappearance of the monomer was confirmed by thin-layer chromatography, an aliquot was taken to analyze the first block, and then a solution of **12** or **14** in the same solvent was added to the crude reaction mixture. The reaction was continued at 120 °C for another day (see the SI) and afforded block copolymer **19a** or **19b**, respectively (Scheme 5 and Table 3). **19a** and **19b** were purified by Soxhlet extraction, which may remove some homopolymer. In general, our experiments were hindered by the low solubility of the first block, homopolymer **1**.

Scheme 5. Synthesis of Block Copolymers 19a and 19b

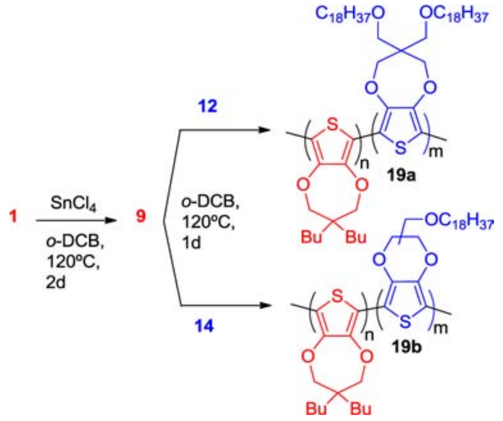


Table 3. Data for Block Copolymers 19

polymer	M_n (g/mol), PDI of first block	yield (%)	M_n (g/mol)	PDI
19a	5000, 1.45	55	14000	1.60
19b	5000, 1.39	60	10000	1.71

An optimized procedure required diluted monomer concentrations (80 mM) in the polymerization, and consequently, the M_n of the first block was smaller than those reported in Table 1. For both **19a** and **19b**, we succeeded in creating materials with $n/m \approx 1$ as determined by NMR analysis (Figure 2B). Obtaining higher n/m ratios for **19b** was complicated by the low solubility of the block copolymer, which created an inhomogeneous reaction.

We further extended this method to the synthesis of rod−coil copolymers,[21] taking advantage of the cationic mechanism of the polymerization. These investigations further probed the "living" character and required that our "living chain" be competent to initiate a classic cationic polymerization (Scheme 6). A consideration in our system was the need for excess Lewis acid and protonation of the polymer backbone. Hence, after **1** was consumed, the first block was precipitated and washed with dry hexane to remove excess acid. The resulting solid was then dissolved in CH_2Cl_2 and cooled to −78 °C, and subsequent addition of ethyl vinyl ether (EVE) produced block copolymer **20** with M_n = 12 000 g/mol, PDI = 1.78, and $n/m \approx 1$.

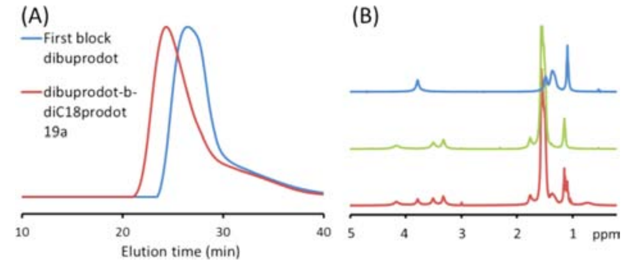
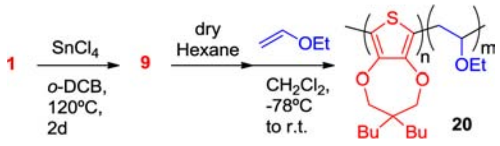


Figure 2. (A) GPC curves of **9** quenched from a block polymer synthesis before the addition of **12** (blue trace) and of the final block copolymer **19a** (red trace). (B) ^{1}H NMR spectra of homopolymers **9** (blue trace) and poly(**12**) (green trace) and the block copolymer **19a** (red trace).

Scheme 6. Synthesis of a Copolymer of 1 and EVE



In summary, we have reported a "living" chain-growth synthesis to create polythiophenes from the reaction of 2-chlorothiophene monomers and Lewis acids. The MWs and PDIs are comparable to those for previous methods reported in the literature. The living character enabled the synthesis of all-conjugated thiophene−thiophene block copolymers and polythiophene−poly(ethyl vinyl ether) 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 semiconductive 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.

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Notes

The authors declare no competing financial interest.

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(10) GPC chromatograms of **1** showed severe "tailing", probably due to a strong interaction between the polymer and the column. This likely produced an overestimation of the PDIs.

(11) No fractionation of the polymer was observed during the isolation.

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