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## ARTICLE

# Chain-growth cationic polymerization of 2-halogenated thiophenes promoted by Bronsted acids

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Bronsted acids are found to be effective and generally applicable catalysts for inducing the cationic chain-growth polymerization of a wide variety of 2-halogenated-3-substituted-thiophenes, having hydrogen, alkyl, alkylthio, alkoxy, and dialkoxy substituent groups. The effectiveness of the cationic polymerization depends on the acid strength and the electron density of the 2-halothiophene monomer. For the most electron-rich monomer, like EDOT, the polymerization can be initiated essentially with any acid that is stronger than acetic acid. While for the electron poor 2-bromothiophene, it only workable with the strongest acid, e.g., trifluoromethanesulfonic acid. Using this new polymerization method, highly solution-processable and conductive poly(alkylthiophene)s with a conductivity of greater than 180 S/cm, can be conveniently prepared. Control experiments indicated that Lewis acid like  $\text{BF}_3$  and  $\text{SnCl}_4$  (0.5 equiv) can also induce the polymerization of 3-alkylthio-2-bromothiophenes similarly, but their polymerization failed totally in the presence of trace amount of acid scavenger (e.g., <0.1 equiv  $\text{NEt}_3$ ). On the other hand, the similar polymerization with Bronsted acid did not show any noticeable reverse effect under the same condition. The polymerization with Bronsted acid may involve the coupling between the monomer (as the nucleophile) and its protonated form (as the electrophile), followed by the elimination of HBr (or HCl) to convert the unstable nonconjugated dimeric intermediate **11** (Scheme 2) into the more stable conjugated chain growing species **12**, which then initiate the polymerization by repeating the propagation steps of coupling with additional monomer and then undergoing HX-elimination to regenerate the chain-growing centres.

## Introduction

Conjugated polymers (CPs) are highly interested due to their great application potentials for organic electronic devices such as polymer light emitting diodes (PLEDs), field-effect transistors (FETs), solar cells, and high storage capacitors.<sup>1-4</sup> Among the conjugated polymers, polythiophenes (PTs) are particularly interested due to their high conductivity, easy processability, and environmental and thermal stability.<sup>5</sup> Conventionally, PTs were synthesized either from thiophenes via oxidative polymerization, using metal-containing oxidants such as  $\text{FeCl}_3$ , or from 2,5-dibromothiophenes via metal-catalyzed polycondensation polymerization using combined reagents of Mg metal and Ni(0) catalyst.<sup>6</sup> Recently, such metal-catalyzed polycondensation method has been modified by McCullough's and Reike's groups, for making highly regioregular poly(3-substituted thiophenes) from 2,5-dibromo-3-substituted-thiophenes and/or 2-bromo-3-substituted-thiophenes using various metal-containing reagents in combination with a sterically crowded Ni catalyst,  $\text{Ni}(\text{dppf})\text{Cl}_2$ .<sup>7</sup> Most recently, Lemaire and others have demonstrated that a novel direct arylation method<sup>8</sup> can also be used for making polythiophenes from 2-bromo-3-alkylthiophenes under elevated temperatures using Pd complexes as the sole catalyst.<sup>9</sup>

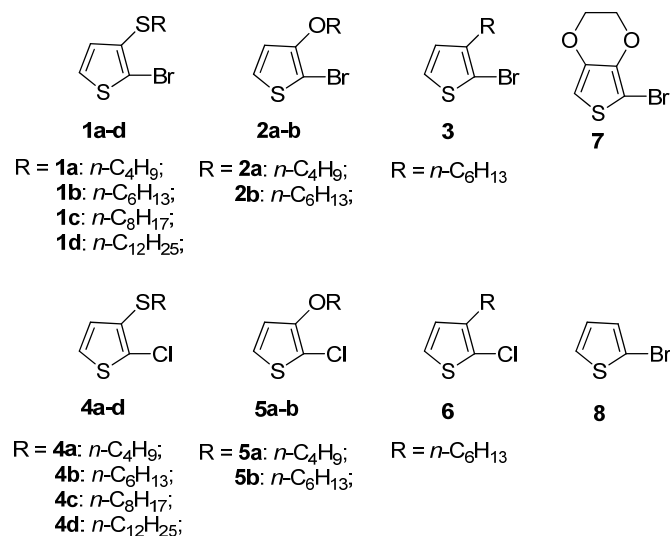
However, all the polythiophenes prepared from the above mentioned methods have encountered a common problem of being contaminated with transition metal impurities that might cast a

detrimental effect on shortening the shelf-life of their corresponding application devices. Since the removal of these strongly coordinative transition metal ions away from these highly electron-rich and conjugated polymer matrices are difficult and tedious,<sup>10</sup> it would be great advantageous to develop a new and generally applicable polymerization method for making polythiophenes without the need of using transition metal catalyst.

In this regards, Wudl<sup>11</sup> and Skabara<sup>12</sup> have discovered a solid-state polymerization chemistry based on a well-ordered crystal of 2,5-dibromo-3,4-ethylenedioxythiophene and 2,5-dibromo-3,4-ethylenedithio-thiophene, respectively. Reynold had demonstrated a liquid-state self-polymerization method based on the neat liquid of 2,5-diiodo-3,4-ethylenedioxyppyrrrole.<sup>10b</sup> Officer and coworkers have also investigated into the spontaneous self-polymerization phenomena for some 3-alkoxy-2-bromo-thiophenes.<sup>13</sup> Most recently, Swager has reported a chain-growth polymerization of 2-chloro-3,4-alkylenedioxythiophene as promoted by some Lewis acids,<sup>14</sup> via a cationic chain-growing centre having a nonconjugated polymer backbone structure.

All the above novel polymerization chemistry and phenomena are mainly associated with the highly reactive alkoxy- and dialkoxy-thiophene systems. Recently, we have also independently discovered another metal-free cationic chain-growth polymerization chemistry of 2-halothiophenes as promoted by Bronsted acids,<sup>15</sup> which is found

to be not only applicable to the highly reactive alkoxythiophenes and dialkoxythiophenes, and 3,4-ethylenedioxythiophenes (EDOTs), but also works well for the less reactive alkylthiophene and thiophene, and even for the unsubstituted 2-bromothiophene (Scheme 1). The mechanistic aspects for this Bronsted acid induced cationic chain-growth polymerization and their differences from the Lewis acid catalyst system will be discussed in details.



**Scheme 1.** Various 2-halogenated thiophenes workable for Bronsted-acid-catalyzed polymerization.

## Results and discussion

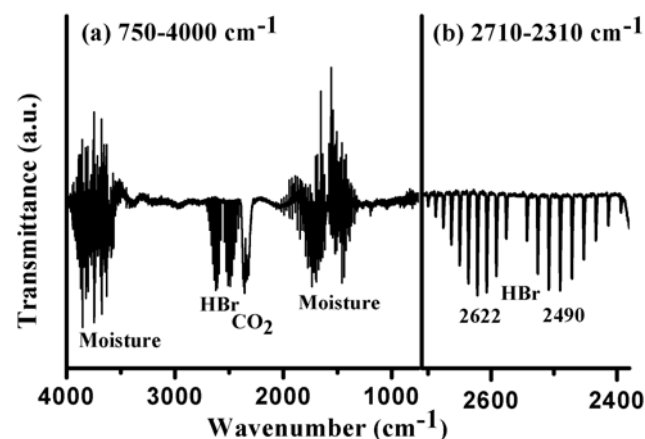
### Preparation and characterization of poly(3-butylthiophene) from 2-bromo-3-butylthiophene (BBTT)

In our previous attempt to synthesize 2-bromo-3-butylthio-5-iodothiophene as the monomer for making regioregular poly(3-butylthiophene) via McCullough's and Reike's methods, we have accidentally discovered the addition of some strong protonic acid had triggered the polymerization of 2-bromo-3-butylthiophene (**1a**). During the study, we had first tried to carry out the iodination of **1a** with NIS (*N*-iodosuccinimide) reagent in acetic acid solvent medium and got a rather poor yield of ~40%. Then, the same reaction was attempted in a stronger acid medium like trifluoroacetic acid (TFA), aiming for getting higher yields, we however found that as soon as 2-bromo-3-butylthiophene was charged to the TFA solvent medium, it reacted violently and explosively to form a dark brown sticky mass, even before the addition of NIS. After thorough investigations, we believed that a conjugated polythiophene material was somehow obtained and the polymerization might have been going through a cationic polymerization mechanism as promoted by the TFA. Hence, we then conducted a more extended investigation to find out the applicable scope for this new polymerization chemistry.

Typical experiments were done by adding 0.5 equiv of TFA into a solution of **1a** in a given solvent medium (e.g., toluene) under nitrogen atmosphere at a given temperature, the pale yellow reaction solution turned to dark brown immediately with the violent evolution of some gaseous byproduct instantly. The reaction solution became more viscous with time and could even turn into a whole solid mass under certain conditions. The concurrently evolved gas during the

polymerization period was monitored by FTIR, showing a typical spectrum (Fig. 1) for a gas molecule of HBr.<sup>16</sup> The resultant products, denoted as PBTT-Br, were confirmed by UV-vis spectra and GPC analyses as conjugated polythiophenes.

The results summarized in Table 1 indicated that the polymerization went effectively well as long as greater than ca. 0.1 equiv (e.g. 0.1–4 equiv) of TFA was used. When less than 0.05 equiv of TFA was used, the polymerization did initiate at the beginning, but somehow stopped at ~10% monomer conversion. This may be caused by the fact that the resultant polythiophenes would compete for the Bronsted acid for their own doping reaction. But, when greater than 2 equiv of TFA was used, the reaction went too fast to be conveniently controlled. So, 0.1 to 0.5 equiv of TFA was chosen for most of the studies. Regarding to the Bronsted acids, we found that acetic acid is too weak to initiate the polymerization, while methanesulfonic acid (MSA) is somehow difficult to give reproducible results probably due to its much higher polarity (which cause the phase separation phenomenon at the very beginning of the addition); and TFA is the suitable choice (Table 1 entries 1–4). A wide variety of solvent medium, such as toluene (Tol), THF, DCM, tetrachloroethane (TCE), chlorobenzene (CB), and *o*-dichlorobenzene (*o*-DCB) (entries 5–10), can be employed and give similar results. Although, longer reaction hours (e.g. 24 h) can provide higher molecular weight polymer (Table 1, entries 11–12), the PDI was also somehow increased significantly. After a thorough study, we found that high molecular weight polymers can be best obtained by performing the polymerization at higher reaction temperature (e.g., 100 °C) for a longer period (e.g. 24–48 h) with a lower equivalent amount (0.05 equiv) of a stronger but less polar Bronsted acid (e.g., trifluoromethanesulfonic acid, TFMSA) in TCE (Table 1, entries 13–16).



**Fig. 1** The FTIR spectrum for the evolved gas collected during the polymerization of BBTT: (a) full range and (b) expanded region for the HBr byproduct. CO<sub>2</sub> and H<sub>2</sub>O in the atmosphere along the pathway of the IR beam were also detected.

We found that Lewis acid BF<sub>3</sub> (0.5 equiv) also worked as an effective catalyst for the polymerization of 2-bromo-3-butylthiophene (which was also accompanied with HBr evolution), but at a significantly slower rate than TFA (0.5 equiv). Interestingly, the addition of only a small amount (0.1 equiv.) of NEt<sub>3</sub> (acted as a potential acid scavenger) inhibited the polymerization completely. On the other hand, addition of 0.1 equiv of acetic acid helps to boost up its polymerization reactivity significantly. Similar reaction behaviours have also been observed when a much stronger Lewis acid, e.g., SnCl<sub>4</sub> was used. While, the

addition of 0.1 equiv  $\text{NEt}_3$  to the polymerization solution of 2-bromo-3-butylthiophene with Bronsted acid catalyst (either 0.5 equiv TFA or 0.5 equiv MSA) did not show any noticeable reverse effects to their polymerization activity. Probably, the initiation step for the Lewis acid induced polymerization of 2-brominated-thiophenes have also involved an initial trace amount of Bronsted acid (the acid sources may be provided by an acid impurity or an acidic byproduct resulted from the interaction of moisture and the Lewis acid), which might help to create the initial chain propagating species. By adding 0.1 equiv of  $\text{NEt}_3$ , the acid impurity seems to be completely scavenged and the polymerization activity was totally inhibited, even though excess amount of free  $\text{BF}_3$  or  $\text{SnCl}_4$  (at least greater than 0.4 equiv.) was still available within the same reaction solution.

**Table 1 Polymerization of 2-bromo-3-butylthiophene**

En	Acid (equiv)	Reaction conditions <sup>a</sup>	$\lambda_{\text{max}}^b$ (nm)	Yd <sup>c</sup>	$M_w$ , PDI <sup>d</sup>
1	AA (0.50)	Neat, rt, 72 h	-	0%	No reaction
2	TFA (0.50)	Neat, rt 2 h	451		$1.3 \times 10^3$ , 1.98
3	MSA (0.50)	Neat, rt 2 h	447		$1.0 \times 10^3$ , 1.51
4	TFA (0.10)	Tol, rt, 3h	450		$1.3 \times 10^3$ , 1.38
5	TFA (0.50)	Tol, rt, 3 h	455		$1.5 \times 10^3$ , 1.51
6	TFA (0.50)	THF, rt, 3h	448		$1.3 \times 10^3$ , 1.12
7	TFA (0.50)	DCM, rt, 3h	464		$1.5 \times 10^3$ , 1.15
8	TFA (0.50)	TCE, rt, 3 h	460		$1.5 \times 10^3$ , 1.20
9	TFA (0.50)	CB, rt, 3 h	460		$1.5 \times 10^3$ , 1.16
10	TFA (0.50)	<i>o</i> -DCB, rt, 3 h	456		$1.5 \times 10^3$ , 1.19
11	TFA (0.10)	Tol, rt, 24 h	462		$3.9 \times 10^3$ , 4.77
12	TFA (0.50)	Tol, rt, 24 h	461		$3.8 \times 10^3$ , 4.60
13	TFA (0.50)	Tol, 50°C, 3 h	470		$2.5 \times 10^3$ , 1.43
14	TFMSA (0.05)	TCE, 100°C, 3 h	456	75%	$2.5 \times 10^3$ , 1.31
15	TFMSA (0.05)	TCE, 100°C, 8 h	475	80%	$4.2 \times 10^3$ , 1.57
16	TFMSA (0.05)	TCE, 100°C, 24 h	482	85%	$6.1 \times 10^3$ , 1.91

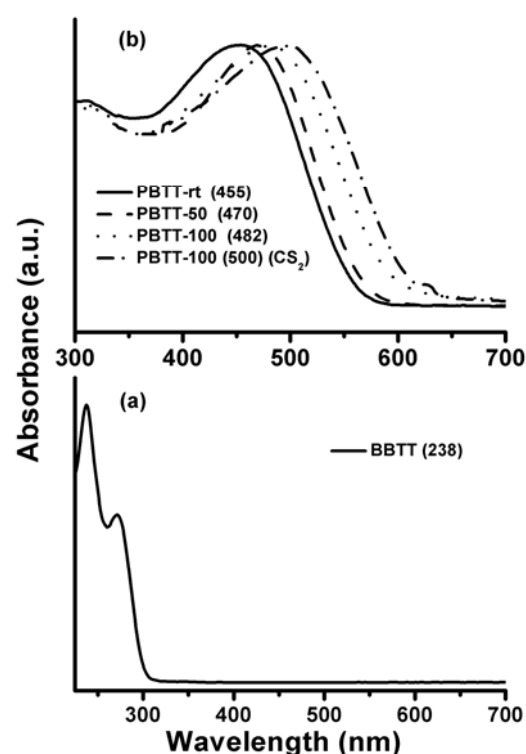
<sup>a</sup> Polymerizations were carried out with 3 volumes of solvents. Solvent: Tol: toluene; TCE: 1,1,2,2-tetrachloroethane; CB: chlorobenzene; *o*-DCB: 1,2-dichlorobenzene;

<sup>b</sup> Measured with their dilute THF solutions.

<sup>c</sup> Yd: yield. For entries 2-13, tacky polymer mixtures were obtained with essentially quantitative yields; for entries 14-16, solid polymer powders were obtained.

<sup>d</sup>  $M_w$  weight average molecular weight;  $M_n$  number average molecular weight; PDI: polydispersity ( $= M_w/M_n$ );  $M_w$  and  $M_n$  were determined by GPC using THF as eluant and calibrated against polystyrene standards.

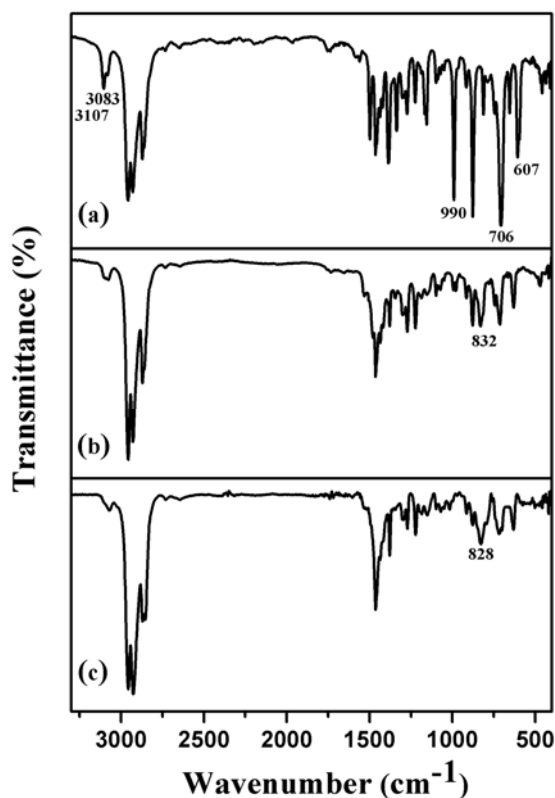
The UV-vis and GPC studies for the resultant PBTT-Br indicated that accompanied with increased  $M_w$  of the resultant polymers from  $1.5 \times 10^3$  (entry 5), through  $2.5 \times 10^3$  (entry 13),  $6.1 \times 10^3$  (entry 16), the UV absorption  $\lambda_{\text{max}}$  (Fig. 2) of the polymers also concurrently red-shifted from  $\sim 455$  nm to 482 nm (in  $\text{CHCl}_3$ ) or  $\sim 500$  nm (in  $\text{CS}_2$ ) (Fig. 2). The poly(butylthiophene), PBTT-Cl, prepared from 2-chloro-3-butylthiophene at 100 °C reported in the later section showed further red-shifted  $\lambda_{\text{max}}$  to  $\sim 500$  nm (in  $\text{CHCl}_3$ ) and 519 nm (in  $\text{CS}_2$ ). Regarding to the high molecular weight poly(3-butylthiophene)s obtained at 100 °C, the absorption  $\lambda_{\text{max}}$  is quite close to the  $\lambda_{\text{max}}$  found for highly regioregular poly(alkylthiophene)s ( $\sim 500$  nm),<sup>17a-b</sup> but much higher than the random poly(butylthiophene)s prepared by oxidative polymerization with  $\text{FeCl}_3$  ( $\sim 436$  nm)<sup>17c</sup> and by metal-catalyzed condensation with Ni catalyst ( $\sim 396$  nm).<sup>17d</sup> The UV-vis results suggest that our high molecular weight polymers should have a reasonable extent of regioregularity, as expected based on the electronic and steric influences from the asymmetrically distributed substituent groups.



**Fig. 2** The UV-vis spectrum for: (a) the starting monomer **BBTT**; and (b) the polymer product **PBTT-Br**.

The IR spectral data in Fig. 3 for the monomer **BBTT** (Fig. 3a) and the polymer **PBTT-Br** (Fig. 3b and 3c) clearly demonstrated that the resultant polymer is linked through the C-2 and C-5 positions. Accompanied with the polymerization, the original C-Br stretching peak (at  $990 \text{ cm}^{-1}$ ) and the  $\alpha$ -proton vibrational peaks (at  $3107 \text{ cm}^{-1}$  for the stretching and  $706 \text{ cm}^{-1}$  for the bending) in **BBTT** (Fig. 3a) decreased significantly. In addition, the vinylic =C-H bending peak at  $880 \text{ cm}^{-1}$  in **BBTT** (for the  $\beta$ -proton of the monomer; Fig 3a) also reduced greatly, while a new and broader vinylic =C-H bending peak appeared at  $\sim 830 \text{ cm}^{-1}$  in **PBTT-Br** (Fig. 3b and 3c), which is attributable to the  $\beta$ -proton of 2,3,5-trisubstituted thiophene repeat unit.

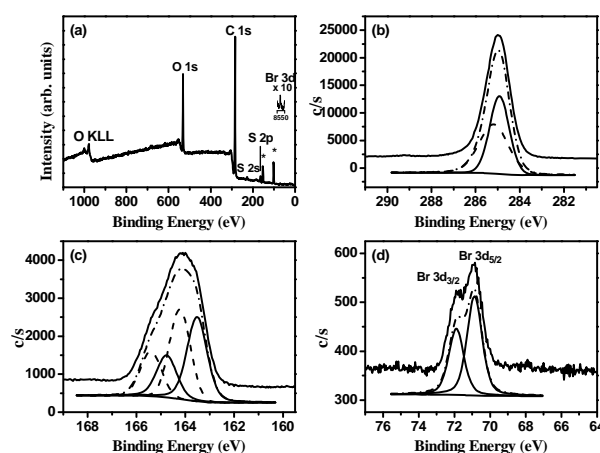
The loss of the Br group and the formation of polythiophene backbone structure can be clearly confirmed by the XPS study. The XPS spectrum (Fig. 4) for a 3 h PBTT-Br specimen cast on silicon wafer showed a typical spectral features for poly(3-butylthiophene)s.<sup>18</sup> The S 2p peak can be resolved via curve deconvolution into two sets of S 2p<sub>2/3</sub> and S 2p<sub>1/2</sub> lines, with a set of S 2p<sub>2/3</sub> (163.5 eV) and S 2p<sub>1/2</sub> (164.75 eV) lines accounting for the S of the alkylthio group and another set of S 2p<sub>2/3</sub> (164.2 eV) and S 2p<sub>1/2</sub> (165.4 eV) lines for the S of the thiophene ring. (XPS data has been calibrated by setting the peak maximum of the C 2p line at 285 eV). Accordingly, the C 2p line can also be resolved into two peaks (in 1:1 ratio) at 284.9 (C-C) and 285.2 (C-S) eV for the C atoms bound with C and S, respectively. Furthermore, a much reduced Br peak (with a Br/S atomic ratio of ~0.035) was also observed at ~70.9 eV that can be resolved into a single set of Br 3d<sub>5/2</sub> and Br 3d<sub>3/2</sub> lines at 70.85 eV and 71.9 eV, respectively, accounting for a covalently bonded C-Br group instead of a bromide anion (at ~68.8eV). Regarding to the high M<sub>w</sub> PBTT-Br sample obtained at 100 °C for 24 h, the amount of the residual Br group was found to be further reduced as expected, but the residual amount was too little to be measured with reliable precision.



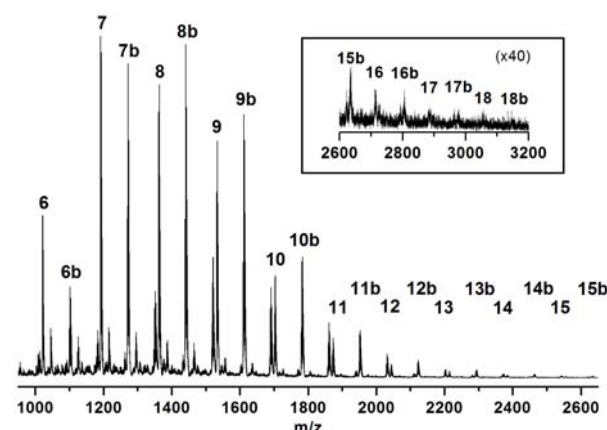
**Fig. 3** IR spectra for: (a) the monomer BBTT, and (b)-(c) for the polymer PBTT-Br prepared: (b) with 0.5 equiv TFA at rt for 3h; and (c) with 0.05 equiv of TFMSA at 100 °C for 24 h.

The presence of the C-Br group on the individual polymer chains can be further confirmed with the MS spectrum of MALDI-TOF (matrix-assisted laser desorption and ionization time-of-flight mass spectrometry). The MS spectrum of MALDI-TOF for the 3 h PBTT-Br sample (Fig. 5) showed a homologous series of polymers **6b-18b** with an equal mass difference of 170 (the mass of one repeat unit) between the next homolog. Further close comparison between the

measured and the calculated mass data (Table S1, ESI<sup>†</sup>) clearly confirmed that polymers **6b-18b** contains 6-18 repeat units plus a single bromo group per chain. The formation of a series of polymer **6b-18b** strongly suggested that the Bronsted-acid-induced cationic polymerization might have been mainly gone through a head-to-tail coupling fashion and possibly via a cationic intermediate that contains a single bromo group per growing polymer chain. Interestingly, the Mass spectrum also observed a homologous series of polymers **6-18** that contains 6-18 repeat units but without the bromo group. Similar data behaviour was also observed for the high M<sub>w</sub> PBTT-Br prepared at 100 °C (as illustrated in Fig. S42; supplementary data). Thus, polymer **6-18** may be most likely derived from **6b-18b** via the photo-induced halogen-cleavage during the Laser irradiation and desorption treatment process (Nd:YAG laser; 337 nm), which is the well known photochemical behavior for aryl halides.<sup>19</sup> Similar Laser-induced dehalogenation phenomena can also be recognized from the MALDI spectra previously reported for the polymers yielded from the solid-state-polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene<sup>11</sup> and 2,5-dibromo-3,4-ethylenedithio- thiophene,<sup>12</sup> respectively.



**Fig. 4** XPS spectra for the 3 h PBTT-Br sample cast on silicon wafer: (a) survey spectrum (0-1100 eV) and the chemical state spectra for (b) C 1s, (c) S 2p, and (d) Br 3d. The chemical state spectra have been resolved into peaks (shown by solid traces and/or broken traces) of various chemical states by de-convolution. The dash-dot traces are the traces of the sum of the deconvoluted peaks. The lines labelled with \* are Si 2p and Si 2s lines for the Si wafer.



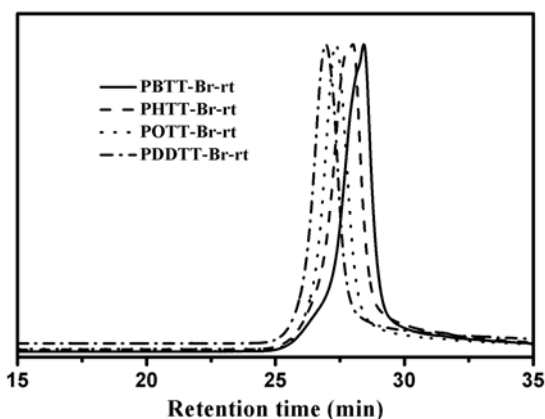
**Fig. 5** MALDI-TOF mass spectrum for PBTT-Br (rt, 3h sample).

Inset is the 40× magnified spectrum for the polymers with 15 to 18 repeat units.

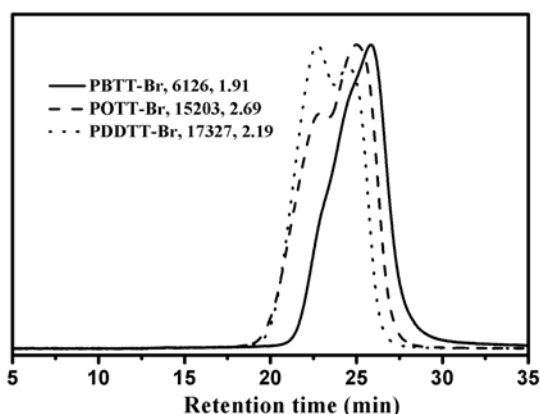
Interestingly, the non-brominated analogue, i.e., butylthiophene (BTT), however did not show any polymerization activity even after being treated with a stronger acid (MSA 0.5 equiv) for 2 days. It produced only a low yield of nonconjugated dimer (~30%) with most of the starting monomer (>60%) being recovered, showing similar reaction behaviors as previously reported for the reaction between EDOT (ethylenedioxythiophene) and a strong protonic acid (e.g.,  $\text{CF}_3\text{CO}_2\text{H}$ ,  $\text{H}_2\text{SO}_4$ ),<sup>20</sup> which yielded non-conjugated dimers and trimers in 60%, together with the unreacted monomer in 40%.

### Polymerization of other monobrominated-thiophenes

Similar to 2-bromo-3-butylthiophene, other 2-bromo-3-alkylthiophenes also underwent rapid polymerization with 0.5 equiv amount of TFA at rt to give low molecular weight polymers with  $M_w$  ranging from  $2 \times 10^3$ – $3 \times 10^3$  (Table 1 entry 5 and Table 2 entries 1-3; Fig. 6).



**Fig. 6** The GPC traces for the poly(3-alkylthiophene)s, PATTs, prepared with 0.5 equiv TFA at rt for 3h from the corresponding 2-bromo monomers.



**Fig. 7** The GPC traces for the poly(3-alkylthiophene)s, PATTs, prepared with 0.05 equiv of TFMSA at 100 °C for 24 h from the corresponding 2-bromo monomers.

When similar polymerizations were performed at 100 °C for 24 h using only one-tenth or one-fifth amount (i.e., 0.05 or 0.1 equiv) of TFMSA as the catalyst, the molecular weights of resultant poly(3-alkylthiophene)s increased by about 3-8 times to the range of  $6.1 \times 10^3$  and  $1.7 \times 10^4$  (Table 1, entry 16; Table 2, entries 4-5; Fig. 7), possibly due to the combination effects of fewer initiation number and higher propagation rate.

**Table 2** Polymerization of other 2-bromo-thiophenes

En	Monomer; Polymer	Reaction conditions <sup>a</sup>	$\lambda_{\text{max}}$ <sup>b</sup> (nm)	Yd <sup>c</sup>	$M_w$ , PDI <sup>d</sup>
1	<b>1b</b> , BHBT; PHTT-Br	Tol, rt, 3 h TFA (0.05)	460		$2.0 \times 10^3$ , 1.25
2	<b>1c</b> , BOTT; POTT-Br	Tol, rt, 3 h TFA (0.50)	464		$2.4 \times 10^3$ , 1.21
3	<b>1d</b> , BDDTT; PDDTT- Br	Tol, rt, 3 h TFA (1.00)	466		$3.1 \times 10^3$ , 1.16
4 <sup>e</sup>	<b>1c</b> , BOTT; POTT-Br	TCE, 100 °C, 24 h TFMSA (0.05)	492	85%	$1.5 \times 10^4$ , 2.69
5 <sup>e</sup>	<b>1d</b> , BDDTT; PDDTT- Br	TCE, 100 °C, 24 h TFMSA (0.10)	492	85%	$1.7 \times 10^4$ , 2.19
6	<b>2a</b> , BBOT; PBOT-Br	Tol, rt, 3 h; TFA (0.50)	510	55%	$2.0 \times 10^3$ , 1.69
7	<b>2a</b> , BBOT; PBOT-Br	Tol, rt, 24 h TFA (0.50)	521	60%	$2.4 \times 10^3$ , 1.74
8	<b>2b</b> , BHOT; PHOT-Br	Tol, rt, 3 h TFA (0.50)	494	55%	$2.1 \times 10^3$ , 1.47
9	<b>7</b> , BEDOT; PDOT-Br	$\text{CHCl}_3$ , rt, 1 h TFA (0.50)	498 <sup>f</sup>	95%	Insol.
10	<b>3</b> , BHT; PHT-Br	TCE, 100 °C, 3 h TFMSA (0.05)	400	53%	$2.7 \times 10^4$ , 16.7 <sup>g</sup>
11	<b>3</b> , BHT; PHT-Br	TCE, 100 °C, 24 h TFMSA (0.05)	400	71%	$4.4 \times 10^4$ , 34 <sup>g</sup>
12	<b>8</b> , BT; PT-Br	$\text{CHCl}_3$ , rt, 3 h TFMSA (0.1)	450 <sup>f</sup>	70%	partially soluble
13	<b>8</b> , BT; PT-Br	TCE, 100 °C, 3 h TFMSA (0.1)		90%	insol.

<sup>a</sup> Polymerizations were carried out with 3 volumes of solvents.

<sup>b</sup> Measured for their dilute chloroform solutions.

<sup>c</sup> For entries 1-3 low molecular weight polymer mixtures were obtained with essentially quantitative yields; for entries 4-12 solid powders were obtained.

<sup>d</sup> Refer to the footnote d of Table 1.

<sup>e</sup> The GPC traces for POTT-Br and PDDTT-Br have been further resolved into two peaks. The  $M_w$ /PDI data for the high and low molecular weight components are 27637/1.96 and 4868/1.27 for POTT-Br; and are 27095/1.68 and 5899/1.22 for PDDTT-Br, respectively.

<sup>f</sup> UV-vis spectra were measured based on the soluble oligomers.






<sup>g</sup> Polymer samples of the PBHT-Br contained substantial amount of gel.

Interestingly, for the polymers with longer alkylthio groups, such as octylthio and dodecylthio, the high temperature polymer samples were found to show a clear bimodal GPC peak (Fig. 7). The  $M_w$ /PDI data for the high molecular weight component was found to be 27637/1.96 (POTT-Br) and 27095/1.68 (PDDT-Br) respectively; while the  $M_w$ /PDI data for the low molecular weight component was found to be 4868/1.27 (POTT-Br) and 5899/1.22 (PDDT-Br) (entries 4-5 and footnote e; Table 2). The PDI values of the high molecular weight components (1.68-1.96) are in general greater than the corresponding low molecular weight components (1.22-1.27), implied that the high molecular weight components might have been derived from the low molecular weight components through the secondary couplings between the polymer chains.

This polymerization method is also applicable to the highly reactive thiophene system, such as the 2-bromo-3-alkoxythiophene and 2-bromo-3,4-dialkoxythiophene systems (Table 2 entries 6-9). For these highly reactive monomer systems, extra care in handling is required to prevent the spontaneous self-polymerization. The storage of the monomer in an inert organic solvent medium such as hexane would be helpful. To perform the polymerization, prior to the addition of the Bronsted acid to induce the polymerization, the hexane solvent was replaced by toluene by mixing toluene to the hexane solution (~1 M) of a given monomer followed by rotovaping to remove the unwanted hexane.

For 2-bromo-3-butoxythiophene (BBOT) and 2-bromo-3-hexoxythiophene (BHOT) highly soluble solid polymer powders with a higher molecular weight ( $2.0\text{-}2.4 \times 10^3$ ) than its butylthio-substituted analogue can be obtained even at rt with 0.5 equiv TFA for 3 h (Table 2, entries 6-8). While under the same reaction conditions, 2-bromo-3,4-ethylenedioxythiophene (BEDOT) polymerized extremely fast to give insoluble polymer powder (Table 2, entry 9). This polymerization method is also extendable to other less reactive monomer systems such as 2-bromo-3-hexylthiophene (BHT) (Table 2 entries 10-11); but higher reaction temperature, longer reaction time, and stronger Bronsted acid are needed. Interestingly, even the simplest thiophene, like 2-bromothiophene (BT) can also be effectively polymerized at rt or at 100 °C to give partially soluble reddish brown or insoluble dark blue solid powder, respectively (Table 2, entries 12-13), as long as a sufficiently strong acid, such as TFMSA (0.1 equiv), is used.

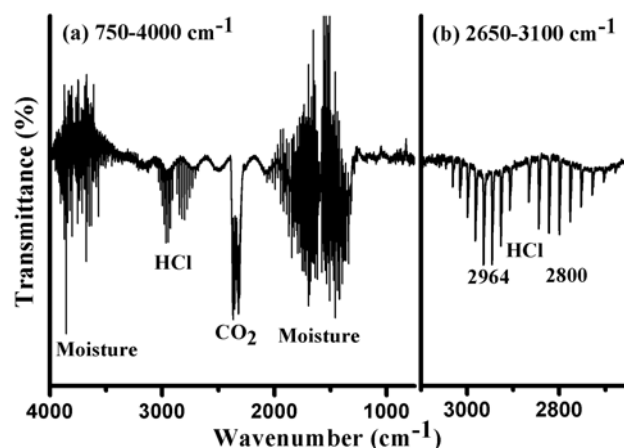
**Table 3** The effective Bronsted acids for the polymerization of various 2-bromo-thiophenes<sup>a,b</sup>

					
CH <sub>3</sub> CO <sub>2</sub> H	X	X	X	X	X
CH <sub>2</sub> ClCO <sub>2</sub> H	X	X	X	X	Δ
CHCl <sub>2</sub> CO <sub>2</sub> H	X	X	Δ	Δ	O
CCl <sub>3</sub> CO <sub>2</sub> H	X	X	Δ	Δ	O
CF <sub>3</sub> CO <sub>2</sub> H	X	Δ	O	O	O
CH <sub>3</sub> SO <sub>3</sub> H	X	O	O	O	O
CF <sub>3</sub> SO <sub>3</sub> H	O	O	O	O	O

<sup>a</sup> The polymerizations were tested at rt with 1 M monomer solution in CHCl<sub>3</sub> using 0.1 equiv of acid.

<sup>b</sup> Polymerization rate – O: Fast; Δ: Slow; X: No reaction.

The effective Bronsted acids for inducing the cationic chain polymerization of a variety of 2-bromo-3-substituted-thiophenes were surveyed and summarized in Table 3. The results clearly showed that the most electron rich thiophene EDOT-Br, can be effectively polymerized by almost any acid that is stronger than acetic acid. While the least electron-rich thiophene, i.e., the unsubstituted 2-bromothiophene, only works with the strongest acid, CF<sub>3</sub>SO<sub>3</sub>H. Apparently, the polymerization started with an acid-base interaction between the acid catalyst and the 2-bromo-thiophene monomer.



**Fig. 8** The FTIR spectrum for the evolved gas collected during the polymerization of 2-chloro-3-butylthiophene, CBTT: (a) full range and (b) expanded region for the HCl product. The CO<sub>2</sub> and H<sub>2</sub>O in the atmosphere along the pathway of the IR beam were also detected.

**Table 4** Polymerization of various 2-chloro-thiophenes<sup>a</sup>

En	Monomer; Polymer	$\lambda_{\max}^b$ (nm)	Yd <sup>c</sup>	$M_w$ , PDI <sup>d</sup>
1	<b>4a</b> , CBTT; PBTT-Cl	500	75-80%	$4.7 \times 10^3$ , 1.58
2	<b>4c</b> , COTT; POTT-Cl	508	78%	$6.3 \times 10^3$ , 1.56
3	<b>4d</b> , CDDTT; PDDTT-Cl	502	80%	$7.0 \times 10^3$ , 1.3
4	<b>5a</b> , CBOT; PBOT-Cl	555	85%	$2.3 \times 10^3$ , 1.31
5	<b>5b</b> , CHOT; PHOT-Cl	523	83%	$2.8 \times 10^3$ , 1.35
6 <sup>e</sup>	<b>6</b> , CHT; PHT-Cl	421	72%	$2.6 \times 10^4$ , 3.88
7	<b>6</b> , CHT; PHT-Cl	415	70%	$9.7 \times 10^3$ , 2.13

<sup>a</sup> Polymerizations were carried out in TCE (3 volumes) for 24 h at 100 °C (entries 1-6) or at 50 °C (entry 7) with 0.05 equiv (entries 1-2 and 4-7) or 0.1 equiv (entry 3) of TFMSA.

<sup>b</sup> Measured for their dilute chloroform solutions.

<sup>c</sup> Yd: yield. Solid polymer powders were obtained in all cases.

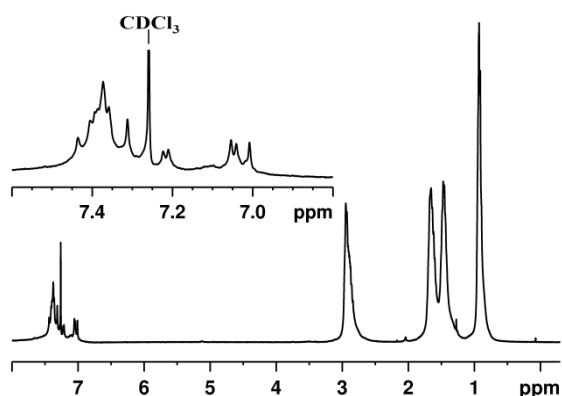
<sup>d</sup> see the footnote d of Table 1

<sup>e</sup> The GPC analysis for PHT-Cl (entry 6) showed a clear bimodal peak that can be further resolved by deconvolution into two peaks. The  $M_w$ /PDI data for the high and low molecular weight components are 30208/1.82 and 4891/2.06, respectively.

### Polymerization of 2-chloro-3-alkylthiophene

Regarding to the case of 2-chloro-3-butylthiophene, neither acetic acid nor trifluoroacetic acid is capable of initiating its polymerization at rt. But, when a stronger acid like MSA or TFMSA was added, the polymerization can also be initiated immediately even at rt and simultaneously released HCl gas (fume) as monitored by the FTIR spectroscopy (Fig. 8), similar to its bromo-analogue. The evolution of HCl gas also underwent continuously throughout the polymerization course. While for the Lewis acid ( $\text{SnCl}_4$ ) induced polymerization of 2-chloro-3,4-alkylene-dioxythiophene reported by Swager et al., such HCl elimination phenomena was not noticed during their polymer growing process, and the polymerization is believed to go through a cationic chain-growing centre having a nonconjugated polymer backbone structure.<sup>14</sup> The results suggest that there may still exist some fundamental mechanistic differences between the Bronsted acid and the Lewis acid catalysts. Additional works are still needed to further clarify their different behaviours.

Since the polymerization of 2-chloro-3-butylthiophene went much slower at rt than its bromo-analogue, the corresponding polymerizations are studied mostly at higher reaction temperature (e.g., 50 °C or 100 °C) for longer time (e.g., 24 h). The poly(3-butylthiophene), PBTT-Cl, prepared from 2-chloro-3-butylthiophene, shows similar structural features as the polymer prepared from its bromo-analogue, PBTT-Br, as confirmed by the IR and MALDI spectra. The polymer obtained at 100 °C for 24 h showed a UV-vis absorption  $\lambda_{\text{max}}$  at ~500 nm (in  $\text{CHCl}_3$ ) and 519 nm (in  $\text{CS}_2$ ) (as illustrated in Fig. S44; supplementary data). Like the bromo-analogue, the MALDI mass spectrum of PBTT-Cl (as illustrated in Fig. S43; supplementary data) also showed a homologous series of polymers **6c-14c** (bearing with a single Cl atom per chain) and a homologous series of polymers **6-14** (having no Cl atom), both display an equal mass difference of 170 (the mass of one repeat unit) between the next homologs. The peak intensities for the Cl-containing polymer chains are however far lower than those peaks for Cl-free polymer chain. This may be caused by the higher susceptibility of an aryl chloride to photo-induced halogen-cleavage toward the 337 nm laser beam.<sup>19</sup> The GPC studies indicated that the  $M_w$  of PBTT-Cl prepared at 100 °C increased gradually with the polymerization time from  $3.5 \times 10^3$  (PDI 1.32; 3 h sample), through  $4.0 \times 10^3$  (PDI 1.43; 8 h), to  $4.7 \times 10^3$  (PDI 1.58; 24 h).



**Fig. 9** The  $^1\text{H}$  NMR spectrum of PBTT-Cl in  $\text{CDCl}_3$ .

Furthermore, the  $^1\text{H}$  NMR spectrum (Fig. 9) indicated that the high molecular weight PBTT-Cl has a reasonably high regioregularity (>90%), showing a major peak appeared at 7.38 for the head-to-tail (H-T) coupled chain,<sup>21-23</sup> and some minor peaks at 7.22 and between 7.0-7.1, possibly for the aromatic protons of the end groups and/or the  $\beta$ -proton of the oligomers.

The obtained PBTT-Cl are highly solution processable and are soluble in common organic solvents, such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , TCE, THF, NMP, DMF,  $\text{CS}_2$ , xylene, toluene, chlorobenzene, and *o*-dichlorobenzene. The conductivity of this highly regio-regular PBTT-Cl was measured with a 4-in-line probe and found to be ~180 S/cm, based on a 5  $\mu\text{m}$  thick film spin cast on a glass substrate and doped in a close chamber saturated with  $\text{I}_2$  vapor.

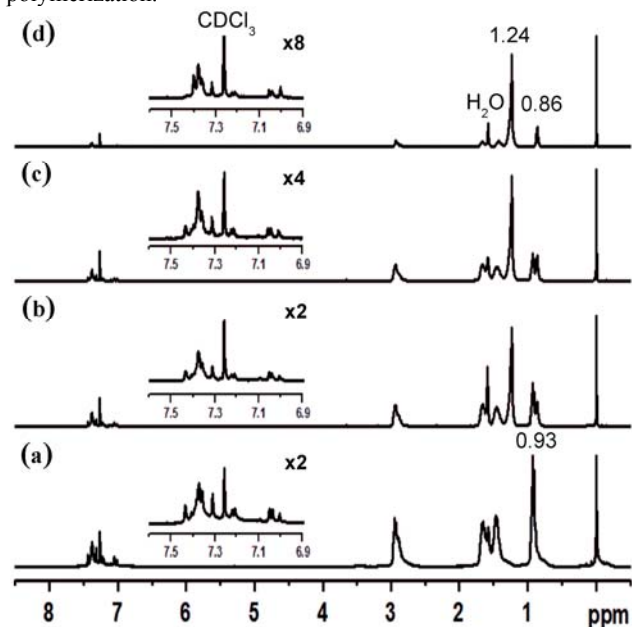
### Copolymerization of 2-chloro-3-butylthiophene and 2-chloro-3-dodecylthiophene

The “long-living” nature of the chain growing centres was confirmed by the success in making the block copolymers of 2-chloro-3-butylthiophene and 2-chloro-3-dodecylthiophene via sequential polymerization. The experiment was done by performing the polymerization of 2-chloro-3-butylthiophene (1 equiv) with 0.05 equiv TFMSA at 100 °C for 3 h to form the initial PBTT-Cl polymer chains,<sup>24</sup> then about half amount of the reaction solution was removed and worked up to yield a polymer sample having only the first polymeric block, i.e., the poly(3-butylthiophene) block. To the remaining polymerization solution, an equal volume and concentration of a pure second monomer solution in TCE (containing only 0.5 equiv of 2-chloro-3-dodecylthiophene but without the acid catalyst) was added. As the second monomer solution was charged, an instant and obvious evolution of HCl gas was observed. The polymerization was then continued for additional 5 and 21 h, and the second and the third samples were then taken (which are denoted as the 8 h and 24 h samples), accordingly. The  $^1\text{H}$  NMR spectra (Fig. 10a-c) of these three polymer samples together with a control homopolymer sample of 2-chloro-3-dodecylthiophene (obtained at 100 °C with 0.05 equiv TFMSA for 24 h; Fig. 10d) are summarized in Fig. 10. The  $^1\text{H}$  NMR results clearly showed that the primary chain growing centres generated in the first 3 h have successfully initiated the polymerization (i.e., copolymerization) of the second monomer and sustained its polymerization activity continuously throughout the 24 h polymerization period, as indicated by the continuous increase of the  $^1\text{H}$  NMR peaks at  $\delta$ 1.24 and 0.85 that are solely associated with the dodecylthio group of the second monomer component. Interestingly, the 24 h sample indeed showed both the terminal  $-\text{CH}_3$  groups for the butylthio (at  $\delta$ 0.86) and the dodecylthio (at  $\delta$ 0.93) in 1:1 ratio, same as the overall monomer feed ratio. In addition, the UV-vis study clearly indicated that all the three samples showed only a single component absorption peak with  $\lambda_{\text{max}}$  at ~500 nm as for the high molecular weight poly(3-alkylthiophene)s. Furthermore, the UV-Vis monitoring for the reaction solution after the addition of the second monomer did not show any spectral evidences for the formation of low molecular weight poly(3-dodecylthiophene)s during the copolymerization periods (i.e. in between 3-24 h). The results and observations suggest that the polymerization of the second monomer was mostly initiated and proceeded on the existing polymer chains of the initial poly(3-butylthiophene) block.

The GPC results for the three samples in Fig. 11a are consistent with our expectation that the average molecular weight of the polymer chains increased continuously and significantly from  $3.8 \times 10^3$  (PDI = 1.38; 3 h sample of the initial polymer block) through  $5.0 \times 10^3$



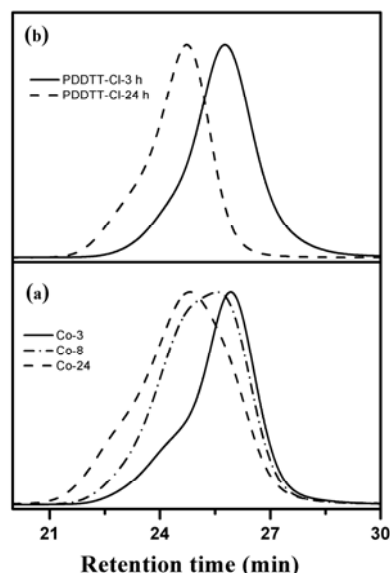
(PDI = 1.44; 8 h sample of copolymer) and to  $7.0 \times 10^3$  (PDI = 1.63; 24 h sample of copolymer); and their molecular weights are comparable with the homopolymer control samples of PBTT-Cl (obtained in 3 h,  $M_w$   $3.5 \times 10^3$ ; PDI 1.32) and PDDTT-Cl (obtained in 24 h,  $M_w$   $7.0 \times 10^3$ , PDI 1.3). Interestingly, no any new polymer chains with a lower molecular weight than the initial polymer block was detected in either the 8 h or the 24 h copolymer samples suggested that the copolymerization might be essentially starting from the initial polymer blocks that were somehow still active for polymerization.



**Fig. 10**  $^1\text{H}$  NMR for the polymer samples obtained from the copolymerization experiment: (a) the initial polymer block sampled at 3 h after the initiation of the polymerization of **4a**; (b)-(c) the resultant copolymers sampled at 5 h and 21 h (denoted as the 8 h and 24 h samples), respectively, after the addition of the second monomer **4d**; (d) the control homopolymer sample of 3-dodecylthiothiophene obtained in 24 h under the same reaction conditions.

### Plausible mechanism

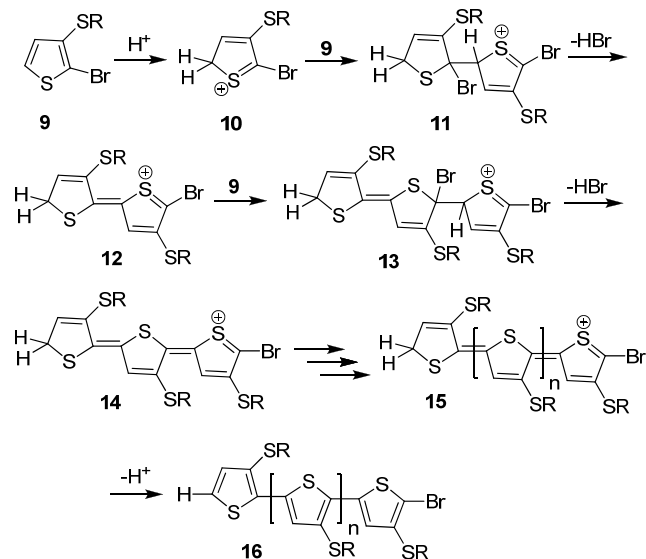
Although further studies are still needed to understand the actual polymerization mechanism, we would like to propose a plausible polymerization mechanism as shown in Scheme 2. The protonation of monomer **9** at the C-5 site (the most electron rich site) will boost up the electrophilicity at the bromine-substituted C-2 site and enhance its reactivity toward another monomer nucleophile to form the coupled dimeric intermediate **11**, which will then undergo a fast elimination of HBr (probably through a concerted reaction similar to a typical E2 elimination) to form a highly stable cationic intermediate **12**, which will then initiate the chain-growth cationic polymerization, by repeating the propagation steps of (1) coupling first with another thiophene monomer, and then (2) undergoing HBr-elimination to regenerate the chain growing species. The high stability of intermediate **12** is understandable, because its resonance form **12'** (Scheme 3) represents one of the most stable cationic system due to the multiple resonance stabilization mechanisms provided by the lone pair electrons of the neighboring S and Br atoms and the highly conjugated backbone  $\pi$  bonding system. The easiness in undergoing HBr-elimination is probably facilitated by the



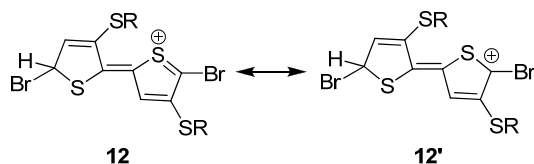
**Fig. 11** (a) The GPC traces for the 3 h (Co-3; solid line), 8 h (Co-8; dash line) and 24 h (Co-24; dash-dot line) samples taken from the copolymerization experiment; (b) the control homopolymer samples of PBTT-Cl (3 h; solid line) and PDDTT-Cl (24 h; dash line).

molecular geometry arrangement resulted from the ring coupling step, which places the H and the Br atoms on the opposite side of the newly formed C-C bond. To minimize the steric repulsion, the two neighboring bulky thiophene rings would tend to adapt an anti coplanar conformation, so that they could separate from each other as far as possible. This steric arrangement tendency would then facilitate the C-H and C-Br groups to adapt an anti-periplanar conformation, favoring a concerted elimination of HBr. To exam this assumption, DFT calculation was performed in gas phase at the B3LYP/6-31G\*\* level with Gaussian 03 for finding out the most stable structure of the coupled dimeric intermediate **11** (Fig. 12). The calculated stable structure indeed displays a rather large dihedral angle of H-C-C-Br as expected; it is  $179.4^\circ$  for the 2-bromothiophene system,  $173.1^\circ$  for the 2-bromo-3-methylthiophene system, and  $172.9^\circ$  for the 2-bromo-3-butylthiophene system. The calculated stable structure has been examined in term of vibrational frequency calculations with all positive values.

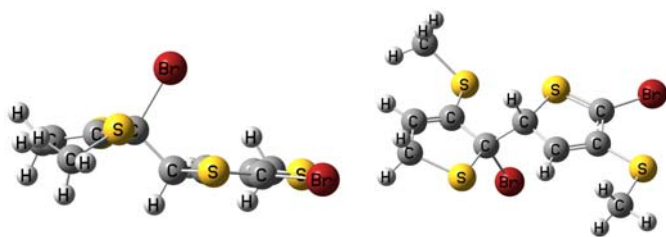
The readiness in undergoing HBr-elimination is clearly supported by the immediate pressure build-up right after the addition of the Bronsted acid catalyst. Furthermore, the evolution of HBr gas (fume) was found to undergo concurrently and continuously throughout the polymerization process, suggested that the HBr elimination must have occurred in every chain coupling event, which would help to maintain the polymer chain growing species in its relatively stable highly conjugated structure throughout the chain-growing process (Scheme 2). The close observations (with TLC, UV-vis, and  $^1\text{H}$  NMR) for the polymerization of 2-bromo-3-butylthiophene (at rt with 0.05 equiv of TFMSA) indicated that high molecular weight polymers ( $M_w > 1.6 \times 10^3$ ) had formed since the very beginning of the polymerization (within 5 min) even when most of the monomer (>65%) was still untouched. The results imply that the polymerization undergoes essentially via a chain-growth polymerization mechanism.



**Scheme 2** The plausible mechanism for a chain-growth cationic polymerization induced by the Bronsted acid.



**Scheme 3** The resonance form of intermediate 12.



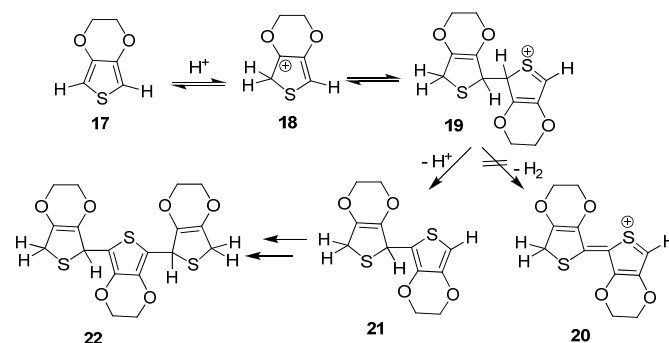
**Fig. 12** The calculated stable structure for the coupled dimeric intermediate 11 (displayed herewith a methylthiophene analogue for a better viewing clarity) based on the DFT calculation in gas phase at the B3LYP/6-31G\*\* level with Gaussian 03. The dihedral angle of H-C-C-Br is 173.1°.

Regarding to the 2-chlorothiophene analogues, the stronger electron-withdrawal chlorine (than bromine) would reduce the basicity of the monomer and disfavour the initial protonation of the monomer; the much stronger C-Cl bond (vs. C-Br) should have also hindered the HCl-elimination (vs. HBr-elimination) and slow down the chain propagation.

Most interestingly, although the initial polymerization of 2-bromothiophene is far more difficult than 2-bromo-3-alkylthiophenes and 2-bromo-3-alkylthiophenes (and requires the use of the most strong acid like TFMSA) due to its much poorer basicity, the polymerization propagation rate of 2-bromothiophene is however faster than 3-alkylthiophenes and 3-alkylthiophenes, judging from the apparent rates of HBr gas evolution and the color

change of the reaction solution. The easier HBr-elimination of the 2-bromothiophene system may be attributed to its more favorable dihedral angle of H-C-C-Br (179.4°) in its coupled intermediates.

Actually, the ability in undergoing fast HBr-elimination is the key for the Bronsted acids to work as an effective polymerization catalyst for 2-halogenated thiophenes. This may be accountable for why a highly basic and strong nucleophile like EDOT fails to undergo acid-catalyzed polymerization.<sup>20</sup> As illustrated in Scheme 4, owing to the difficulty in eliminating H<sub>2</sub> in the absence of oxidative catalyst (like FeCl<sub>3</sub>), the unstable dimeric intermediate 19 fail to convert into the more conjugated and relatively stable dimeric intermediate 20. Instead, it loses one acidic proton to resume the aromaticity for one of ring to gain back its stability partly, forming the non-conjugated dimer 21, which can undergo another cycle of coupling reaction to form the non-conjugated trimer 22.



**Scheme 4** The plausible formation mechanism for the non-conjugated dimer and trimer from EDOT by reacting with strong acid, like TFA or H<sub>2</sub>SO<sub>4</sub>.

## Experimental Section

### Characterization methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Varian Unity 400 MHz spectrometer. IR spectra were measured using Perkin-Elmer 2000 Fourier Transform infrared (FTIR) spectrometer, based on pressed KBr pellets and cast thin film on silicon wafer. UV-vis spectra for the polymer solutions (in THF) were recorded with Hitachi U-3501 spectrophotometer. The molecular weight analysis for the polymers was performed on a gel permeation chromatography (GPC) system equipped with three Waters styragel columns (installed in a 40 °C oven) and a UV detector (set at the λ<sub>max</sub> of the analyzed polymers) using THF as the mobile phase (at 1 mL/min). The molecular weight was calibrated against polystyrene standards. The MALDI-TOF MS (matrix-assisted laser desorption and ionization time-of-flight mass spectrometry) spectra for the polymer mixtures were acquired using a Bruker Daltonics, Autoflex III smartbeam LRF200-CID time-of-flight mass spectrometer with a Nd:YAG laser (355 nm) in positive ion and linear mode. Sample solution (0.1wt% in THF) were spotted (0.5 μL) onto a matrix-assisted laser desorption/ionization plate, followed by the addition of 0.5 μL solution of α-cyano-4-hydroxycinnamic acid (CHCA) (prepared in 1:1 co-solvent of H<sub>2</sub>O/CH<sub>3</sub>CN plus 0.1 wt% of trifluoroacetic acid) as the matrix. Spectra have been first calibrated with Peptide Standard and then with CHCA as an additional internal standard.

### Chemicals

3-Alkylthiophenes, 3-alkoxythiophenes, and 3-hexylthiophene are prepared from 3-bromothiophene according to the literature reported procedure.<sup>17a,25</sup> 2-Bromothiophene, 3-bromothiophene, 3,4-ethylenedioxythiophene were purchased from Aldrich. Alkyl disulfides, *n*-butanol, *n*-hexanol, *n*-butyllithium, *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), hydrazine hydrate, trifluoroacetic acid (MSA), trifluoromethanesulfonic acid (TFMSA), methanesulfonic acid (MSA), boron trifluoride diethyl etherate (BF<sub>3</sub>.Et<sub>2</sub>O), ammonium chloride, sodium hydroxide, chloroform, hexanes, 1,1,2,2-tetrachloroethane (TCE), 1,2-dichlorobenzene, chlorobenzene, chloroform, carbon disulfide, and dichloromethane were purchased from Aldrich, Acros and Alfa-Aesar and they were used as received without further purifications. THF and toluene were dried according to standard procedures before the use.

#### Typical experiment for the bromination of 3-alkylthiophenes Synthesis of 2-bromo-3-butylthiophene (BBTT)

3-Butylthiophene (BTT) (2.00 g, 11.61 mmol, 1.00 equiv) was taken in a 50 mL single neck round bottom flask along with chloroform (26.0 mL). The homogeneous solution was added with solid *N*-bromosuccinimide (2.17 g, 12.19 mmol, 1.05 equiv) portionwise for a period of one hour at rt (18 °C). During the addition of NBS, the colorless solution turned to pale yellow heterogeneous mixture (white solid was precipitated). The reaction mixture was stirred at rt for 3 hours and monitored by TLC. After 3 hours, the reaction mixture was diluted with chloroform (52 mL) and washed successively with 5 wt% NaOH (50 mL) and two times with water (50 mL each time). The separated organic solution was dried over anhydrous magnesium sulfate and concentrated to get a pale yellow liquid, which was distilled at 90-95 °C under vacuum (0.39 torr). The desired product BBTT was obtained as a colorless liquid (2.47 g, 84.6%).  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.25 (d, 1 H, *J* 6.00), 6.92 (d, 1 H, *J* 5.60), 2.85 (t, 2 H, *J* 7.40), 1.60-1.53 (m, 2 H), 1.48-1.39 (m, 2 H), 0.91 (t, 3 H, *J* 7.40).  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>; CDCl<sub>3</sub>): 133.04, 130.04, 125.82, 113.55, 34.74, 31.56, 21.66, 13.57.  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3107 (m), 3083 (m), 2859 (s), 2930 (s), 2872 (s), 2859 (s), 1500 (s), 1464 (s), 1437 (m), 1422 (m), 1384 (s), 1337 (s), 1271 (m), 1223 (m), 1154 (s), 1099 (w), 1072 (w), 1052 (w), 990 (s), 916 (w), 880 (s), 811 (m), 747 (w), 706 (s), 658 (m), 607 (s), 459 (m).

#### Synthesis of 2-chloro-3-butylthiophene (CBTT)

3-Butylthiophene (BTT) (5.00 g, 29.02 mmol, 1.00 equiv) was taken in a 50 mL single neck round bottom flask along with acetonitrile (50.0 mL) and added with acetic acid (0.52 g, 0.50 mL, 8.71 mmol, 0.30 equiv). The homogeneous solution was added with solid *N*-chlorosuccinimide (NCS) (4.07 g, 30.47 mmol, 1.05 equiv) portionwise for a period of 30 min at rt (23 °C). During the addition of NCS, the colorless solution turned to pale blue heterogeneous mixture (white solid was precipitated). The reaction mixture was stirred at rt for 30 min and monitored by TLC. After 30 min, the reaction mixture was diluted with chloroform (100 mL) and washed successively with 5 wt% NaOH (75 mL) and two times with water (75 mL each time). The separated organic solution was dried over anhydrous magnesium sulfate and concentrated to get a pale brown liquid. The pale brown liquid was purified by column chromatography using hexane as eluent in silica gel to get the desired product CBTT as a colorless liquid (5.74 g, 82%).  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.09 (d, 1 H, *J* 5.60), 6.91 (d, 1 H, *J* 5.60), 2.83 (t, 2 H, *J* 7.40), 1.59-1.52 (m, 2 H), 1.45-1.40 (m, 2 H), 0.90 (t, 3 H, *J* 7.20).  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>; CDCl<sub>3</sub>): 129.87 (CH), 129.81 (C),

129.20 (C), 122.60 (CH), 34.60 (CH<sub>2</sub>), 31.62 (CH<sub>2</sub>), 21.63 (CH<sub>2</sub>), 13.56 (CH<sub>3</sub>).

The syntheses and the corresponding spectroscopic data for other 2-bromo-3-substituted-thiophenes and 2-chloro-3-substituted-thiophenes containing various alkyl, alkoxy, and alkylthio, and dialkyl substituents are summarized in the Supplementary Section.

#### Typical experiment for the polymerization of 2-bromo-3-alkylthiophenes

##### Preparation of poly(3-butylthiophene) (PBTT) at rt

A solution of BBTT (0.50 g; 1.99 mmol) in 1.50 mL of toluene was added with trifluoroacetic acid (0.077 mL; 99% pure; *d* 1.48; 0.114 g; 0.995 mmol; 0.50 equiv) in a single neck round bottom flask under nitrogen atmosphere at room temperature (rt; 25 °C). After the addition, the colorless liquid became red-brown liquid, which then, within 5 minutes, turned into a dark blue color solution with the evolution of lot of smoke. The thick mass was stirred for 3 h at rt. Then, the thick blue color mass was diluted in dichloromethane (20 mL), washed successively with 5 wt% aqueous sodium hydroxide solution (20 mL) and two times with water (20 mL each time). The resulting red-brown color solution was concentrated in a rotavapor to get a thick gummy red brown color mass in quantitative yield. The obtained product was confirmed to be poly(3-butylthiophene) by NMR and IR spectroscopic studies.  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.43 (br m), 7.37 (br m), 7.32 (br m), 7.22 (br m), 7.05 (br m), 7.00 (s), 2.90 (br m, 2 H), 1.63 (br m, 2 H), 1.45 (br m, 2 H), 0.91 (br m, 3 H).  $\nu_{\text{max}}$ /cm<sup>-1</sup>: 3099 (m), 3077 (m), 2956 (s), 2928 (s), 2870 (s), 2859 (s), 1532 (m), 1465 (s), 1436 (m), 1419 (m), 1378 (m), 1346 (m), 1272 (m), 1224 (m), 1156 (w), 1188 (w), 1099 (m), 1072 (w), 980 (m), 914 (w), 878 (m), 832 (m), 815 (m), 745 (w), 713 (m), 628 (m), 475 (m).  $\lambda_{\text{max}}$ (THF)/nm 454.

##### Typical experiment for the polymerization of 2-bromo-3-alkylthiophenes

##### Preparation of poly(3-butylthiophene) (PBTT-Br) from BBTT at 100 °C

A solution of BBTT (0.50 g; 1.99 mmol) in 1.50 mL of 1,1,2,2-tetrachloroethane (TCE) was heated to 100 °C and added with trifluoromethanesulfonic acid (0.012 mL; 99% pure; *d* 1.696; 0.021 g; 0.138 mmol; 0.05 equiv) in a single neck round bottom flask under nitrogen atmosphere at room temperature. After the addition, the colorless liquid turned into a dark blue color solution with the evolution of lot of smoke. The thick mass was stirred at 100 °C for 24 h. Then, the thick blue color mass was cooled to rt and diluted with dichloromethane (3 mL). The diluted mass was added with 3 drops of hydrazine hydrate, stirred at rt for 2 h and added slowly into 200 mL of methanol containing 1 mL of hydrazine hydrate. The resulting red-brown color precipitate was stirred at rt for 6 h and filtered, washed with methanol and dried under vacuum. The product was obtained as a brown color solid in 85% yield (0.29 g) and it was confirmed to be poly(3-butylthiophene) by NMR and IR spectroscopic studies.  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.36 (br m), 7.31 (br m), 7.21 (br m), 7.04 (br m), 2.91 (br m, 2 H), 1.62 (br m, 2 H), 1.45 (br m, 2 H), 0.91 (br m, 3 H).  $\lambda_{\text{max}}$ (chloroform)/nm 482;  $\lambda_{\text{max}}$ (carbon disulfide)/nm 500.

##### Typical experiment for the polymerization of 2-chloro-3-alkylthiophenes

### Preparation of poly(3-butylthiophene) (PBTT-Cl) from CBTT at 100 °C

A solution of CBTT (0.50 g; 2.42 mmol) in 1.50 mL of 1,1,2,2-tetrachloroethane (TCE) was heated to 100 °C and added with trifluoromethanesulfonic acid (0.011 mL; 99% pure;  $d$  1.696; 0.018 g; 0.121 mmol; 0.05 equiv) in a single neck round bottom flask under nitrogen atmosphere. After the addition, the colorless liquid turned into a dark blue color solution with the evolution of lot of smoke. The thick mass was stirred at 100 °C for 24 h. Then, the thick blue color mass was cooled to rt and diluted with dichloromethane (3 mL). The diluted mass was added with 3 drops of hydrazine hydrate, stirred at rt for 2 h and added slowly into 200 mL of methanol containing 1 mL of hydrazine hydrate. The resulting red-brown color precipitate was stirred at rt for 6 h and filtered, washed with methanol and dried under vacuum. The product was obtained as a brown color solid in 78% yield (0.32 g) and it was confirmed to be poly(3-butylthiophene) by NMR study.  $\delta_{\text{H}}$ (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ): 7.44 (br s), 7.41-7.36 (br m), 7.23-7.21 (br m), 7.06-7.01 (br m), 2.95-2.86 (br m, 2 H), 1.66-1.60 (br m, 2 H), 1.47-1.46 (br m, 2 H), 0.93-0.91 (br m, 3 H).  $\lambda_{\text{max}}$ (chloroform)/nm 500.

### Conclusions

Bronstead acids are found to be effective and generally applicable catalysts for inducing the cationic chain-growth polymerization of a wide variety of 2-halogenated-3-substituted-thiophenes, having alkyl, alkylthio, alkoxy, and dialkoxy substituent groups. The studies indicated that the polymerization initiated, in general, more readily when a stronger acid or a more electron-rich thiophene monomer is employed. Accompanied with the polymerization, evolution of HBr or HCl gas undergoes continuously and simultaneously with the growth of the polymer chains. The results indicated that 2-bromo-3-substituted-thiophenes undergo the cationic polymerization more readily than their 2-chloro analogues, with faster initiation and propagation rates, probably due to their stronger basicity and the easier elimination of HBr vs HCl. While, as expected, the less reactive 2-chloro-3-substituted-thiophenes have actually yielded more regioregular polymers, such as PBTT-Cl. Using this method, highly solution-processable and conductive polythiophenes, e.g., poly(3-butylthiophene) (PBTT-Cl, with a conductivity of  $>180$  S/cm) can be conveniently prepared. Most interestingly, even the simple unsubstituted 2-bromothiophene can be readily converted into high molecular weight polymer using a strong acid like TFMSA.

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### Notes and references

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Electronic Supplementary Information (ESI) available: For experimental procedures and additional results on NMR, UV, GPC and MALDI-TOF Mass, See DOI: 10.1039/b000000x/

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**Chain-growth cationic polymerization of 2-halogenated thiophenes promoted by Bronsted acids**

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Bronsted acids are found to be effective and generally applicable catalysts for inducing the cationic chain-growth polymerization of a wide variety of 2-halogenated-3-substituted-thiophenes.

