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Effect of Monomers' Structure on Self Acid Assisted-Polycondensation for the Synthesis of Poly(3,4-ethylenedioxythiophene) and Homopolythiophene

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Poly(3,4-ethylenedioxythiophene) (PEDOT) and thiophene based homopolymer were synthesized by self acid-assisted polycondensation (SAAP) through mono-halogen substituted thiophene derivative monomers. Detailed characterizations of the obtained polymers were carried out by X-ray diffraction (XRD), Cyclic Voltammetry (CV), Infrared spectrum (IR), UV-Vis absorbance spectroscopy, Fluorescence spectroscopy (FR) and Thermogravimetric analysis (TGA). Most synthesized monomers can be spontaneous polymerized successfully through simple annealing process at moderate temperature, indicating that they are suitable for SAAP. Moreover, our results reveal that substituted halogen (bromo or iodo) positions play an important role in SAAP, which may pave a wide way for exploring the other conjugated polythiophene through such facile method

Keywords: Self acid assisted polycondensation (SAAP), Poly(3,4-ethylenedioxythiophene), Mono-halogen substituted thiophene derivative, Homopolythiophene

Introduction

Conjugated polymers have wide application in light-emitting diodes[1-2], field-effect transistors[3-4], photovoltaic cells[5-7], and other opto-electronic devices. Due to their universal usage in modern material science, a lot of scientific efforts have been devoted to explore universal synthesis methods, which cover polycondensation through C-C[8-9] or C-H coupling[10-11] and other means.[12] For instance, Pd-promoted Suzuki coupling[8] and Stile coupling[9] were introduced for the conjugated polymer synthesis in 1989 and also have been become the primary choices for most researchers. Meanwhile, as far as new methods to form conductive polythiophene are concerned, an environmentally friendly and facile method of solid state polymerization (SSP) was invented in 2003 and had great success on the synthesis of Poly(3,4-ethylenedioxythiophene) (PEDOT) and its analogue.[13] Unfortunately, it makes slow progress mainly due to the shortage of suitable monomers[14]. In addition, SSP requires symmetrical di-halogen substituted monomers and usually produces moderate to high conductive polymers because of the generation of oxidant of bromine or iodine during its polycondensation procedure.

It is generally accepted that due to their electronic state difference, conjugated polymers share most properties with their conductive polymers but differ in other characteristics such as UV-visible, fluoresce spectra properties and of course conductivity and so on. It seems that conjugated polymers play a brilliant role in organic electronics field which ranges from OLED, OPV to OFET and at the same time conductive polymer like PEDOT-PSS, which is a typical sample, mainly serves as electrode materials or as buffer layers in organic electronics devices. Triggered by SSP progress, we think about how to use such simple heat treatment method to synthesize neutral conjugated polymer directly. However, such facile method was lacking before 2011.

Recently, Officer[15] and our group[16] independently fortunately found PEDOT can be formed just by simple heating of mono-bromo substituted 3,4-ethylenedioxythiophene (Br-EDOT). Meanwhile, Swager T. M. group[17a] successfully synthesized corresponding polymers based on mono choloro-substituted EDOT derivatives in the existence of Lewis acid. And the latest progress concerning of Brønsted acids effect was reported.[17b] We already verified such heat promoted polymerization is acid

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†Electronic supplementary information (ESI) available: ^{1}H, ^{13}C NMR and ^{1}H of P(S-S-OHexy).

depending[16] and named such type reaction as self acid-assisted polycondensation (SAAP). This interesting result encourages us to further design more complicated monomers and try to probe the success rate based on SAAP through changing thiophene derivatives structures, halogen effects as well as halogen positions in the designed monomers. In addition, soluble polymer was designed by introducing long alkyloxy chain in monomer because of no report concerning polymer molecule weight and lacking of detailed characterization till now.

Furthermore, it is generally believed that compared with symmetrical molecules, unsymmetrical molecules are really hard nuts to crack but play a big role in molecule design to make multi-functional polymers with unique optical, electronic and physical properties. Therefore, it is necessary to explore unsymmetrical monomer suitable for facile SAAP, which offers amazing advantages of solvent free, trace metal free and so on. Here, we present our latest result and prove that SAAP is a versatile approach to synthesize different conjugated polythiophene.

Experimental

Most chemicals were purchased from Wuhan Shenshi Chemicals Co., Ltd. and were used without further purification unless otherwise noted. 3,4-Ethylenedioxythiophene (EDOT) was purchased from Suzhou Yacoo Co., Ltd. Diethyl ether anhydrous solvent was distilled from commercial diethyl ether with CaH_2. 2,3,2',3'-Tetrahydro-[5,5']bi[thieno[3,4-b][1,4]dioxinyl] (bis-EDOT)[18], 5,7-dibromo-2,3-dihydro-thieno[3,4-b][1,4]dioxine,[13] tributyl-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-stannane[19], 3-hexyloxy-thiophene,[20] 5-bromo-7-thiophen-2-yl-2,3-dihydro-thieno[3,4-b][1,4]dioxine (**3**)[21] were synthesized according to previous reports.

Monomers synthesis and acid assisted-polycondensation

7-Bromo-2,3,2',3'-tetrahydro-[5,5']bi[thieno[3,4-b][1,4]dioxinyl] (E-E-Br, 1)

The target compound was synthesized according to the literature[22] except change N-bromosuccinimide (NBS) to 1 eq. A 10-mL Schlenk flask equipped with a stirring bar was charged with bis-EDOT (280 mg, 1.0 mmol) in dry CH_2Cl_2 (30 mL). N-bromosuccinimide (NBS) (170 mg, 1.0 mmol) was added, and the reaction was allowed to stir at 0 °C for 2 h. The slightly blue mixture was dissolved in 500 ml of CH_2Cl_2 and washed by H_2O, and brine, and dried over $MgSO_4$. The solvent was evaporated to give a yellowish solid 310 mg (85%). ^{1}HNMR: δ ($CDCl_3$, ppm): 6.27 (s, 1H), 4.32-4.23 (m, 8H). ^{13}C NMR: δ (DMSO) 141.6, 140.5, 137.9, 136.7, 98.9, 84.9, 65.8, 65.6, 65.5, 65.0. Anal. Calcd for $C_{12}H_9BrO_4S_2$: C, 39.9%; H, 2.51%; S, 17.75. Found: C, 39.82%; H, 2.77%; S, 17.93%.

7-Iodo-2,3,2',3'-tetrahydro-[5,5']bi[thieno[3,4-b][1,4]dioxinyl] (E-E-I, 2)

The target compound was synthesized according to the literature method.[23] Briefly, A hexane solution of n-BuLi (0.42 ml, 2.4 M 1.0 mmol) was added dropwise to a solution of bis-EDOT (280 mg, 1 mmol) in THF (20 ml) at –78°C. The mixture was stirred for 1 hour at this temperature. Then iodine (0.27 g, 1.0 mmol) in THF (7 ml) was slowly added while the red color disappeared simultaneously. The mixture was allowed to reach room temperature. After 1 hour of stirring at room temperature, water was added and the mixture was extract with diethyl ether. The combined organic layers were washed with aqueous Na_2SO_3, saturated $NaHCO_3$ solution, water and brine. The organic phase was dried over $MgSO_4$. After filtration and removing the solvent in vacuo, the product was purified by recrystallization from ether as light yellow powder (0.3 g, 75%). Purification was achieved by filtration over a short column of silica gel (SiO_2, CH_2Cl_2/diethyl ether, 1/1). ^{1}HNMR: δ ($CDCl_3$, ppm): 6.26 (s, 1H), 4.34-4.23 (m, 8H). which is consisted with reported result.[24]

5-(5-Bromo-thiophen-2-yl)-2,3-dihydro-thieno[3,4-b][1,4]dioxine (E-S-Br, 4)

A 100 mL round-bottom flask was charged with 2,5-dibromothiophene (0.48 g, 2 mmol), tetrakis(triphenylphosphine)palladium (0) (230 mg, 0.2 mmol), tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (0.86 g, 2 mmol), and anhydrous DMF (20 ml) and heated to 80 °C with stirring for 72 h. The reaction mixture was then cooled down to room temperature, diluted with Et_2O, and filtered through Celite. The organic phase was washed with brine and water and dried over $MgSO_4$. After filtration, solvent was removed to yield the crude product which was then chromatographed on silica using petroleum ether as the eluent. The desired product was a crystalline yellow solid (0.42 g, yield 70%). ^{1}HNMR: δ ($CDCl_3$, ppm): 6.91-6.93 (d, 2H), 6.22 (1H), 4.29-4.21 (d, 4H). ^{13}C NMR: δ ($CDCl_3$) 142.0, 137.8, 136.6, 129.9, 122.7, 111.6, 110.8, 97.5, 65.3, 64.8.

2-(4-Hexyloxy-thiophen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (5)

The desire compound was synthesized by modification of previous method.[25] Anhydrous THF (30 ml) was slowly added dropwise to a solution of lithium diisopropylamide (prepared by addition of butyllithium to diisopropylamine, 10 mmol), the temperature being maintained around -15 ˚C. The reaction mixture was cooled to -60˚C, and a solution of 3-hexyloxy-thiophene (1.84 g, 10 mmol) in anhydrous THF (10 ml) was slowly added dropwise, the temperature being maintained around -50 ˚C. Then the reaction mixture was warmed up to -20 ˚C and stirred at this temperature for 15 min. The reaction mixture was cooled to -78 ˚C and 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (2.2 ml, 10 mmol) was added to the solution, and the resulting mixture was stirred at –78 °C for 1 h and warmed to room temperature and stirred for 12 h. The mixture was poured into water, extracted with ether, dried with $MgSO_4$. The solvent was removed via rotary evaporation, and the residue was distilled. The product yield was 1.86 g (60%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.25 (s, 1H), 6.57 (s, 1H), 6.26 (s, 1H) 3.82 (t, 2H), 1.79 (m, 2H), 1.44-1.40(m, 6H) 1.32 (m, 18H), 0.89 (t, 3H).

4-Hexyloxy-[2,2']bithiophenyl (6, S-S-OC$_6$)

2-Bromo-thiophene (0.16 g, 1 mmol) and 0.31 g (1 mmol) of 2-(4-hexyloxy-thiophen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (**5**) were dissolved in 15 ml of toluene. A K_2CO_3 solution (30 ml, 2 M) and 0.03 g of trimethylbenzylammonium chloride were added to the mixture. The reaction mixture was degassed by several freeze/thaw cycles before 4 mg of $Pd[P(C_6H_5)_3]_4$ were added under nitrogen. The mixture was refluxed for 48 h and the organic phase was separated and evaporated. The product was purified by column chromatography (eluent: hexane/chloroform, 7:3) and freeze dried. Yield: 0.19 g (70%) of a yellow oil.

^{1}H NMR ($CDCl_3$): δ (ppm) 7.20-7.18 (d, 1H), 7.15-7.14 (d, 1H), 7.00-6.98 (d, 1H), 6.85 (d, 1H), 6.11 (s, 1H), 3.93 (t, 2H), 1.79 (m, 2H), 1.50-1.44 (m, 6H), 0.93 (t, 3H). ^{13}C NMR: δ ($CDCl_3$) 152.8, 135.6, 127.0, 123.8, 122.7, 121.6, 117.7, 115.7, 72.1, 32.0, 30.0, 26.1, 22.9, 14.6. Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.11%; H, 6.81%; S, 24.07. Found: C, 63.15%; H, 6.55%; S, 23.76%.

5-Bromo-4-hexyloxy-[2,2']bithiophenyl (S-S-OC$_6$-Br, 7)

The compound was synthesized by a similar bromination procedure and got yellow oil **1**. Yield: 0.6 g (70%); ^{1}H NMR ($CDCl_3$): δ (ppm) 7.22-7.21 (d, 1H), 7.09 (d, 1H), 7.00-6.98 (d, 1H), 6.80 (s, 1H), 4.06-4.02 (t, 2H), 1.76 (m, 2H), 1.46-1.33 (m, 6H), 0.91 (t, 3H). ^{13}C NMR: δ ($CDCl_3$) 154.7, 137.2, 135.6, 128.1,125.0, 123.8, 114.0, 90.5, 72.6, 31.8, 29.7, 25.7, 22.8, 14.3. Anal. Calcd for $C_{14}H_{17}BrOS_2$: C, 48.69%; H, 4.96%; S, 18.57. Found: C, 48.82%; H, 5.18%; S, 18.77%.

Self acid assisted-polycondensation:

The **SAAP** procedure was similar to SSP procedure as previous reported.[13,16] Briefly, each monomer (0.05-0.2 g) was incubated at room temperature to 60-100ºC for 1-72 h and dried in vacuum at room temperature to give black powder of corresponding polymers.

Other Characterizations

IR spectra for the characterization of the compounds were recorded on a Perkin-Elmer FTIR spectrometer. Absorption spectra were measured on a Unicam UV 300 spectrophotometer at wavelengths from 300 to 1000 nm. Different polymers deposited on fluorine doped tin oxide (FTO) substrate were prepared by heating drop-casted monomers and the obtained FTO/polymers substrate were used UV-Vis measurement and as working electrode for electrochemical measurements. For a three-electrode electrochemical measurements in 0.1 M Bu_4NClO_4 in acetonitrile, a 1 cm^2 area of FTO/polymer substrate, platinum foil, and Ag/AgCl served as the working, counter, and reference electrodes, respectively (CH Instruments 604D electrochemical system). X-ray diffraction (XRD) pattern was obtained by Bruker D8 advanced X-ray diffractometer by using Cu-Ka (1.54 Å) radiation at room temperature. The thermal properties of the polymers were measured on a Netzsch STA449C thermal analyzer at a heating rate of 10 ^oC min^{-1} in nitrogen at a flow rate of 20 cm^3 min^{-1}. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) equipped with a Waters 2690 separation module and a Waters 2410 refractive index detector (Waters Co., Milford, MA). N,N-Dimethylformamide (DMF) was used as eluent at a flow rate of 0.5 ml min^{-1} with the temperature maintained at 30 °C, and the results were calibrated against polystyrene standards.

Results and Discussion

Synthesis of monomer and their behavior under SAAP

All monomers were synthesized as shown in Scheme 1. Monomer **1** and **2** were obtained by bromination and iodination of bis-EDOT respectively. Monomer **3** and **4** were synthesized through Stille coupling reactions. With the selective lithium reagent of LDA, borolane was introduced at 5-position of 3-Hexyloxy-thiophene. Then followed by Suzuki coupling, later on NBS bromination, **6** and **7** were obtained respectively.

All SAAP experiments were carried out in a plastic vial under 60-100 ºC for 24 h. Compared with the typical 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine (DBEDOT)'s SSP procedure[13] as mentioned above, instead of the generation of elementary halogen, hydrobromic acid is produced in our SAPP. Therefore, the obtained polymer PEDOT should be in neutral state because of nonexistence of strong oxidant in the experiment. In addition, such polymerization is self-accelerated process because of generation of hydrobromic acid or hydroiodic acid and the proton is involved in their chain propagation.[16] Our SAAP test shows that all can form corresponding polymers smoothly except for monomer **4**, indicating that SAAP can successfully form homopolymers through these designed unsymmetrical monomers and the bromo-substitution position is a key factor for their success. In details, halogen substituted in the 7-position of EDOT dimer (bis-EDOT) is effective, indicating SAAP can be employed successfully in dimer. According to the SAAP results for monomers of **3** and **4**, it is clear that bromo-substituted position in EDOT unit directly results in a successful SAAP and this also indicates that bromo atom should be close to oxygen atom on the molecule level. Such interesting phenomenon is well explained by acid-assisted polymerization mechanism as proposed previously.[16,26] Finally, the success of monomer **7** has verified that alkyloxy chain is an effective way for the synthesis of soluble polymer through SAAP. In our study, we did not check chloro-substituted thiophene derivative under SAAP because C-Cl bond energy (328 kJ/mol) is too strong to be broken by heat-treatment, resulting in the failure of initiation of polymerization.[13,17]

XRD patterns of the monomers and respective polymers

Figure 1 shows XRD patterns of the selected monomers and their respective polymers. We can see that all monomers show sharp peaks in the rage of 10-60º, which are featured characteristic for crystal compounds and for an indication of relatively long-range order. However, most sharp peaks disappear except for leaving a wide broad peak around 22-26º once they change into corresponding polymers through SAAP, indicating the existence of amorphous phase in their polymer matrix.

For the first two PEDOT systems, it is obvious that after halogen substitution of bis-EDOT, these monomers show different XRD patterns with peaks at 11.9, 12.3, 18.2, 21.8, 23.9, 24.8, 27.2, and 30.4º for bromo-substituted derivative while peaks at 11.6, 15.5, 16.0, 20.3, 21.1, 23.4, 24.2, 25.0, and 29.9º for iodo-substituted one. Their featured XRD patterns reveal that their crystal structures might be quite different after halogen change. After SAAP process, only two peaks left for PEDOT-Br at 26.1, 13.0º, which can be assigned to crystal phase of (020) and (200) respectively.[27] Therefore, its polymer structure is almost the same as our previous reported of SAAP of Br-EDOT.[16] It is noted that in the case of E-E-I, its corresponding polymer has almost amorphous phase because of its broad weak peak at 26.1º, indicating bromo substituted monomer is inclined to form higher order-ness of molecule packing once it forms PEDOT.

While in the case of Br-E-S, it shows quite different XRD pattern with peaks appeared at 11.3, 16.0, 18.6, 21.7, 23.6, 24.8, 26, 27, 28.1, 29.7, 37.7. In addition, after SAAP, only a very weak peak around 26º was observed, revealing P(E-S) has more amorphous phase than those of PEDOT systems. We did not check P(S-S-OHexy) and its monomer because of the latter's oily phase at room temperature.

Absorption of all polymers and fluorescence of P(S-S-OHexy)

It is obvious that the first two (PEDOT-Br and PEDOT-I) have similar absorption curves shape while the others show typical non-doped polymer because of the lower absorption value at near-IR region. Due to the moderate absorption at near-IR region around 800-1000 nm, which is the featured absorption for p-type polymer, [28,29] it is believed that these PEDOT polymers were oxidized mostly. We reported[16] previously that PEDOT obtained through SAPP by Br-EDOT shows partly oxidized. Therefore, the polymer can be easily to oxidized when using bis-EDOT dimer as starting monomer. However, in the case of P(E-S), it shows weak abs at 700 nm, indicating it is more difficult to be oxidized than PEDOT. That is to say, after introducing thiophen unit, it can stabilize polymer due to its preventing oxidation to some extent. Furthermore, after further introducing alkyloxy chain, as in the case of P(S-S-OHexy), it shows the lowest value near-IR region if we normalized these curves. These experimental results reveal that the more push electron group of oxygen it has, the easier it will be oxidized.

Due to the fact that we first obtain soluble homopolymer of P(S-S-OHexy) through SAAP, therefore, its fluorescence spectra was examined in $CHCl_3$ solution, shown in Fig 2b. When excited within their π–π* bands, it exhibits a strong luminescence maximum at around 560 nm, with $E_{0\text{-}0}$ transition energies of 2.37 eV. Though molecule weight have influence with peak value for absoptiong spectra[30] and there are peaks overlapped in solid P(S-S-OHexy) film, blue shift[30] was observed in its film absorption, indicating the formation of H-aggregates.

FTIR spectroscopy and thermal stability

Polymers' FTIR spectra were shown in Figure 3. The characteristic absorption peak of the first two PEDOT systems are almost same indicating that PEDOT have exactly same structure in bulky phase whether the starting monomer is bromo or iodo substituted. Meanwhile, P(E-S) exhibits similar IR curve compared with those PEDOT polymers. In details, these three samples peaks at 1510, 1473, 1321 and 1192 cm^{-1} were assigned to the stretching of C=C and C-C in the thiophene ring.[31,32] In addition, all of them have featured peaks at 696 cm^{-1} related to in-plane deformation of C-S-C of thiophene ring.[32]

However, P(S-S-C_6OHexy) containing long alkyloxy chains has quite different fingerprints. In this case, except for the general featured peaks owned by polythophene, it shows strong intensity at 2954 and 2854 cm^{-1} which have been assigned respectively to the asymmetric C-H stretching vibrations of -CH_3 and the symmetric C-H stretching vibration in -CH_2- moieties[33]. Meanwhile, 804 cm^{-1} is characteristic of the 2,3,5-trisubstituted thiophene ring.[34,35] Moreover, after introducing alkyloxy chain in polymer matrix, peaks of 696 cm^{-1} (deformation of C-S-C), 897 cm^{-1} (C-S stretching),[36] 1267 cm^{-1} (C-O stretch)[37] and 1417 cm^{-1} (O-C-O wag) demonstrate strong intensity, indicating alkyloxy chain would increase thiophen ring vibration and free rotation of C-O bond.

The thermal stability of the polymers was investigated with thermogravimetric analysis (TGA) (Fig. 4). It is obviously that the 10% weight-loss temperatures for most polymers were up to 250 °C, which were high enough for their future applications as active materials in most opto-electronic devices.

Photo picture and conversion yield

In most cases, after SAAP is over 60°C or even higher for several hours, light yellow or yellow solid of monomers changed to sky-blue or black power, as shown in Fig. 5. These experimental results were similar to our previous report concerning of SAPP for Br-EDOT[16] and the other SSP-based polythiophene systems.[13] And we found that most monomers gave high yield up to 95% under 60 °C within several hours except for S-S-Ohexy-Br and high temperature shortens reaction time generally. However, in the case of S-S-Ohexy-Br, it requires higher temperature and takes longer time to complete polymerization.

Taking oily or liquid state of monomer into consideration, it seems that solid state of monomers may have quick reaction rate under SAAP. And this interesting phenomena reminds us that these suitable monomers crystal structures may be favorable for construction of corresponding polymers. At present, we attribute these experimental facts to the flexible alkyloxy chain, which may retard molecule aggregation and molecule rearrangement during SAAP process. We assume that such monomer needs to be reconstructed at the initial stage of heating, then C-Br bond breaks and SAAP occurs smoothly. Anyway, our experiments verify again that SAAP is a versatile and effective means for the conjugated homopolythiophenes synthesis.

Electrochemical behavior of corresponding polymers

The cyclic voltammetry experiments were performed with a scan range from -0.8 to 0.7 V (vs Ag/AgCl) on these thin polymer films deposited on FTO electrode. As shown in Fig. 6, except for P(S-S-OHexy), most polymers show broad reduction peak appears approx. at 0.1 V. Meanwhile, except for PEDOT-Br, others do not show distinct oxidation peaks. In addition, the oxidation onset for PEDOT-Br, PEDOT-I, P(E-S) and P(S-S-OHexy) are -0.5, -0.45, -0.2 and 0.7V respectively, which indicate that the more push electron of oxygen atoms have, the easier to be oxidized. Such interesting results are entirely consistent with their UV-Visible spectra as discussed above. Because PEDOT polymers are well-investigated systems, we determined other two polymers' energy level through CV measurements. The onset oxidation and reduction potentials of P(E-S) and P(S-S-OHexy) were -0.60/-2.16 V and 0.32/-1.11 V vs. Fc/Fc^+, respectively, corresponding to HOMO/LUMO (-4.83/-3.27 eV) and (-5.75/-4.32 eV), respectively.

As shown in Fig 6a and b, their CV curves are quite different although the bromo was replaced by iodo atom in the starting monomer. At present, we cannot understand this kind results clearly but this might be due to their different crystalline phase. Because of the smaller C-I bond energy (C-Br of 276 kJ/mol and C-I of 240 kJ/mol), it may result in quick polymerization rate and getting more amorphous phase. And such primitive explanation is well supported by the fact that PEDOT-I has poor polymer chain packing (see XRD analysis section) which results in poor charge storage capability. In addition, further electrochemical impedance spectra (in supporting information) reveals that PEDOT-Br has better charge transfer ability compared with that of PEDOT-I.

Molecule weight of P(S-S-OHexy) vs temperature dependence
Because of the insolubility of the other three polymers, the soluble P(S-S-OHexy) was chosen as a typical model compound to further characterize especially concerning of molecular weight and its typical ^{1}H-NMR was presented in supporting information. Table 1 summarizes reaction conditions investigated, product yield, Mn, and PDI of the P(S-S-OHexy). As can be seen that along with the temperature increase, M_n increase drastically along with the DP in the range of 1.1-2, which is a good news for us to rational control molecule distribution for different usage. In addition, extending time up to two days results M_n of 91,548 with PDI 2.96. Therefore, several thousand to near hundred thousand of molecule weight would be obtained through well controlling temperature and reaction time under SAAP.

Conclusions

In this study, PEDOTs and different homopolythiophen were prepared by SAAP from mono-halogen substituted thiophen derivative monomers and the monomers' structure effects, especially the bromo-substituted positions were investigated in details. We intended to probe the relationship between monomers' structure and their success rate under SAAP. Our study reveals that halogen atoms, halogen positions and molecule structures have great effect on the monomers' SAAP behavior. We can draw a conclusion that as far as monomer design is concerned, bromo or iodo atom has almost no difference in SAAP. However, halogen atoms should close to alkyloxy or ethylenedioxy, which definitely guarantees its SAAP success. Our investigation not only helps to broaden SAAP database, but also supplies fundamental information to understand such promising polymerization approach. In addition, through simple temperature and time controlling, we can obtain low to high molecule weight scale polymers.

Furthermore, our success of preparation of unsymmetrical homopolythiophene may offer an alternative way to synthesize other conjugated polythiophenes, which may have plenty usage in lots of optical-electronic devices. Further expanding studies for other thiophene derivatives and their corresponding polymers application in organic-electronic field are under way in our lab.

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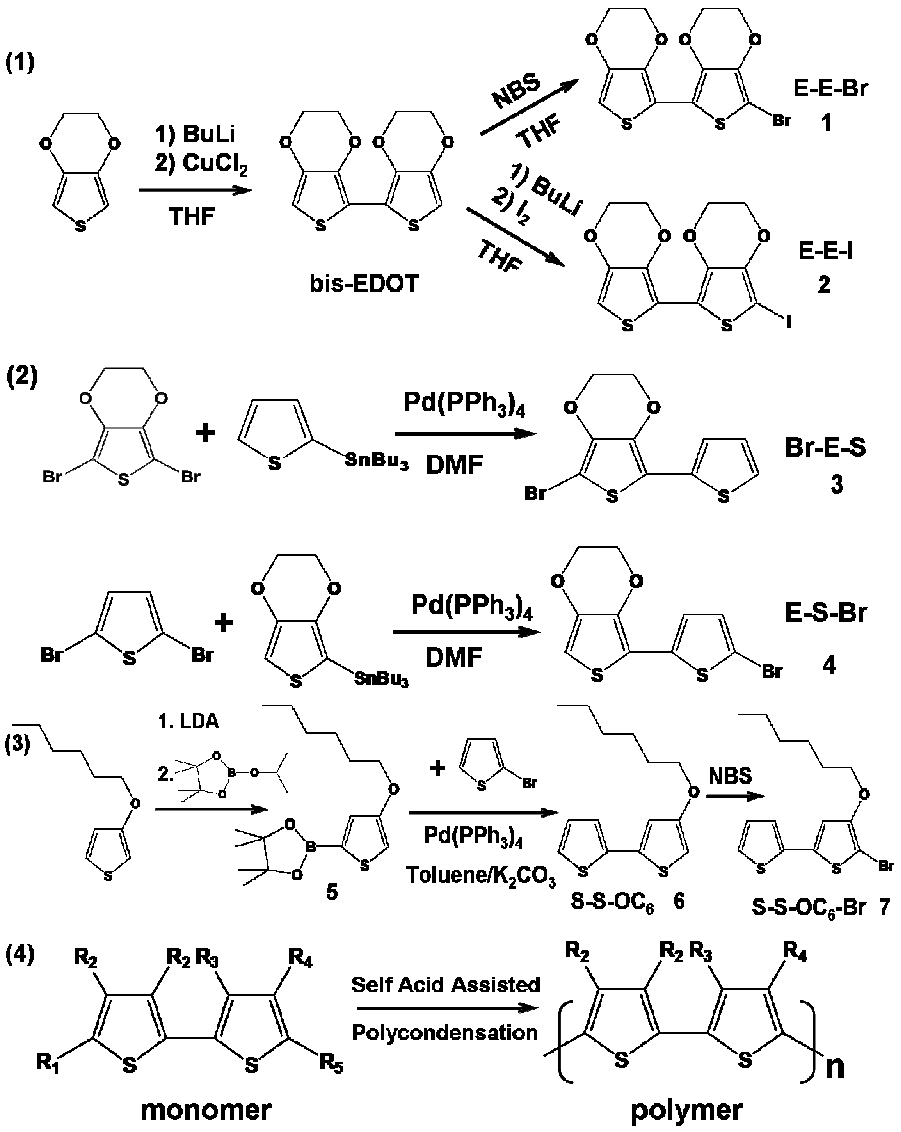

E-E-Br (1): R_1 = H; R_2, R_3, R_4 = -OCH$_2$-; R_5 = Br	PEDOT-Br
E-E-I (2): R_1 = H; R_2, R_3, R_4 = -OCH$_2$-; R_5 = I	PEDOT-I
Br-E-S (3): R_1 = Br; R_2 = -OCH$_2$-; R_3, R_4, R_5 = H	P(E-S)
E-S-Br (4): R_1, R_3, R_4 = H; R_2 = -OCH$_2$-; R_5 = Br	No reaction
S-S-OC$_6$-Br (7): R_1, R_2, R_3 = H; R_4 = -OC$_6$H$_{13}$; R_5 = Br	P(S-S-OHexy)

Scheme 1. Synthesis of the monomers and corresponding polymers.

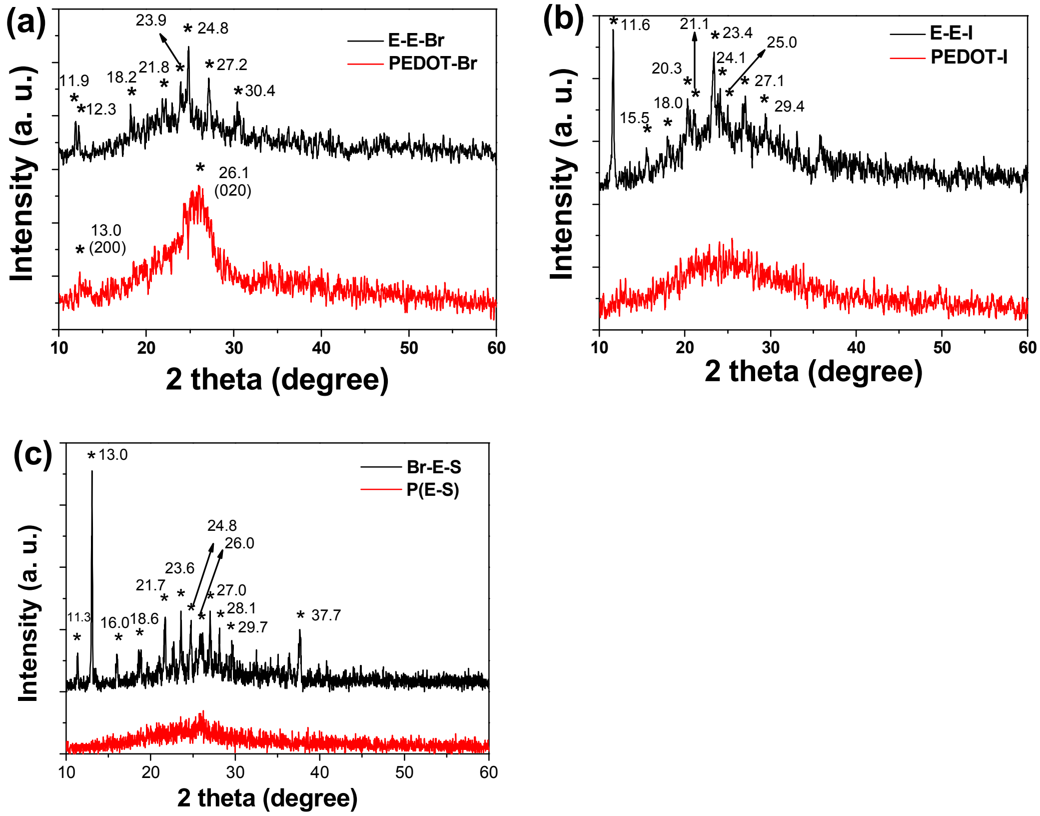

Figure 1. XRD spectra of (a) E-E-Br and PEDOT-Br, (b) E-E-I and PEDOT-I and (c) Br-E-S and P(E-S).

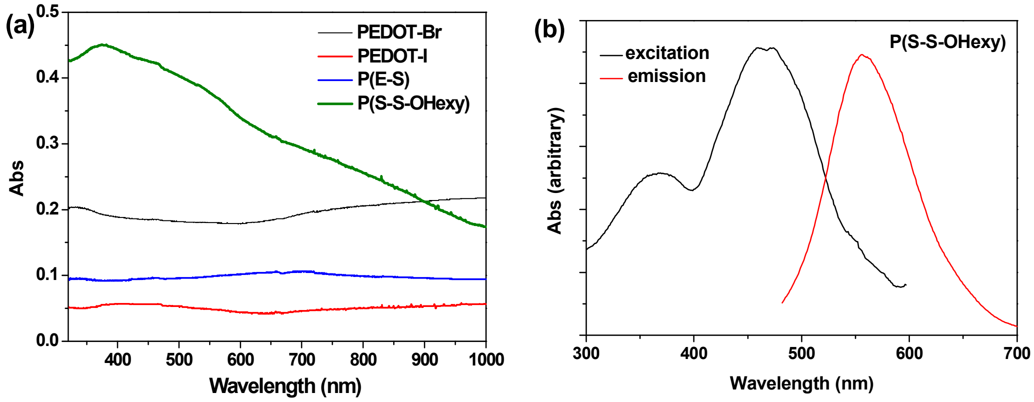

Figure 2. (a) Absorbance spectra of corresponding polymers films and (b) absorption (dark line) and emission (red line) spectra of P(S-S-OHexy) in $CHCl_3$. The emission spectra was obtained using the same solvent by excitation at 450 nm.

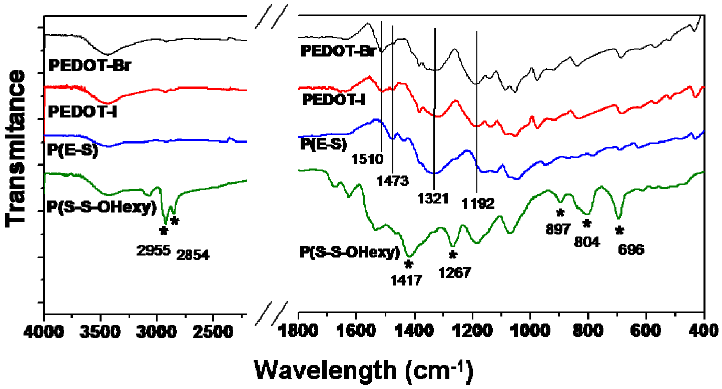

Figure 3 FTIR spectra for the all these polymers.

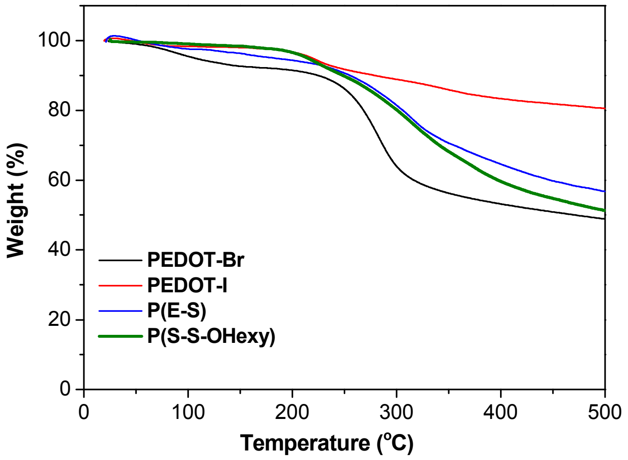

Figure 4 TGA curves of the polymers with a heating rate of 10 °C min^{-1} under nitrogen.

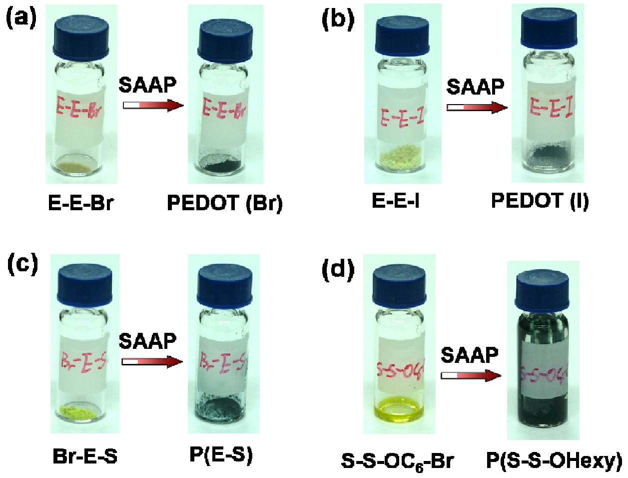

Figure 5 picture of the monomers after heat treatment under SAAP.

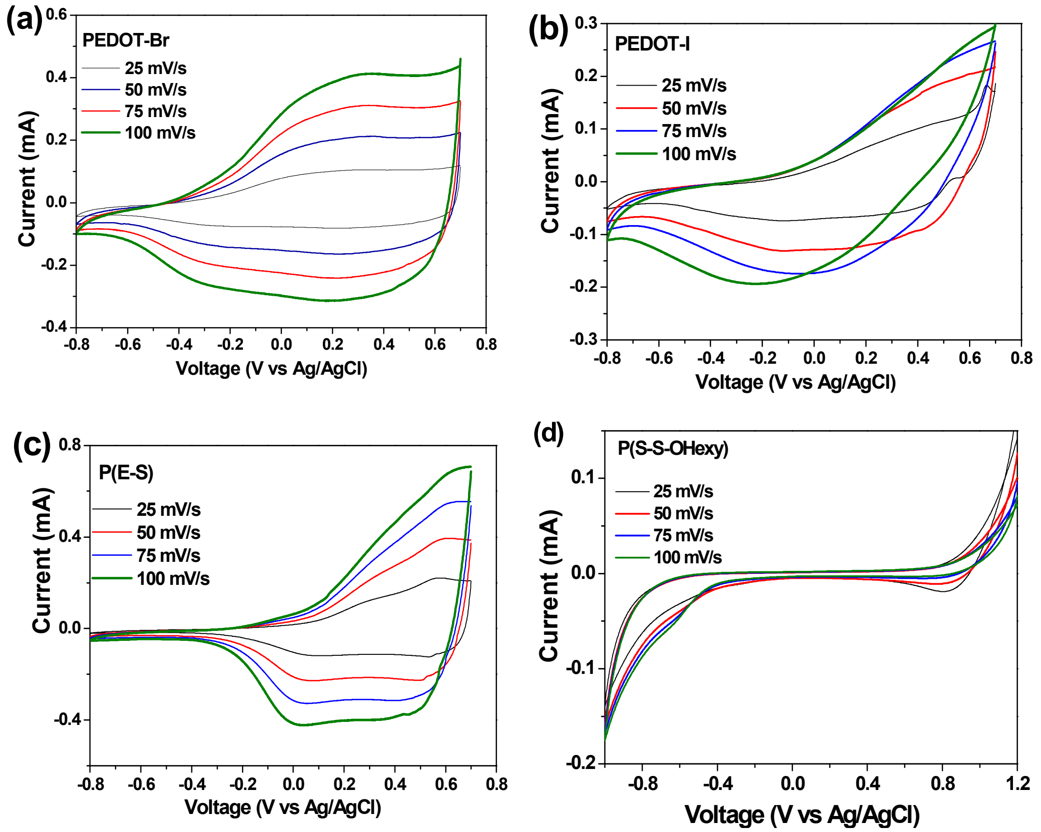

Fig. 6. The CVs of all polymers films in acetonitrile solution containing 0.1 M Bu_4NClO_4 taken at various scan rates.

Table 1. Effect of SAAP temperature on the Molecular Weight and PDI.

Temperature	Yield (%)	Retention time	M_n(g mol^{-1})^a	DP^b	PDI^a
60°C	-	-	-	-	-
80°C (2 days)	> 90	17.9	91,548	346	2.96
90°C (6 h)	> 90	25.6	996	4	1.98
100°C (6 h)	> 90	26.0	2869	11	1.18

a Molecular weights and PDI were determined by GPC with respect to polystyrene standards. b Degree of polymerization (DP) was calculated based on the Mn values determined by GPC.