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 homopolymers were synthesized by self-acid-assisted polycondensation (SAAP) through mono-halogen substituted thiophene derivative monomers. Detailed characterization of the obtained polymers was 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 spontaneously polymerized successfully through a 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 path for exploring other conjugated polythiophenes through such a facile method.

Introduction

Conjugated polymers have wide application in light-emitting diodes,1,2 field-effect transistors,3,4 photovoltaic cells,5,6 and other opto-electronic devices. Due to their universal usage in modern materials science, a lot of scientific efforts have been devoted to designing universal synthesis methods, which cover polycondensation through C–C10,11 or C–H coupling10,11 and other means.12 For instance, Pd-promoted Suzuki coupling8 and Stille coupling9 were introduced for conjugated polymer synthesis in 1989 and have become the primary choice for most researchers. Meanwhile, as far as new methods to form conductive polythiophene are concerned, an environmentally friendly and facile method for solid state polymerization (SSP) was invented in 2003 and had great success in 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 moderately to highly conductive polymers because of the generation of an 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 and fluorescence spectra properties and of course conductivity and so on. It appears that conjugated polymers play a brilliant role in the organic electronics field which ranges from OLED, OPV to OFET, and at the same time, conductive polymers like PEDOT-PSS, which is a typical sample, mainly serve as electrode materials or as buffer layers in organic electronics devices. Triggered by the SSP progress, we think about how to use such a simple heat treatment method to synthesize neutral conjugated polymers directly. However, such a facile method was lacking before 2011.

Recently, Officer15 and our group16 independently fortunately found that PEDOT can be formed just by the simple heating of mono-bromo substituted 3,4-ethylenedioxythiophene (Br-EDOT). Meanwhile, T. M. Swager group17a successfully synthesized corresponding polymers based on mono chloro-substituted EDOT derivatives in the presence of a Lewis acid. The latest progress concerning the Brønsted acid effect was reported.17b We have already verified that such a heat promoted polymerization is acid dependent16 and named such a type of reaction as self-acid-assisted polycondensation (SAAP). This interesting result encouraged us to further design more complicated monomers and to try to probe the success rate based on SAAP by changing the thiophene derivative structures, halogen effects as well as halogen positions in the designed monomers. In addition, a soluble polymer was designed by introducing long alkoxy chains into monomer because of no report concerning polymer molecular weight and the lack of a detailed characterization so far.
Furthermore, it is generally believed that, compared with symmetrical molecules, unsymmetrical molecules are really hard nuts to crack but play a big role in molecular design to synthesize multi-functional polymers with unique optical, electronic and physical properties. Therefore, it is necessary to explore unsymmetrical monomers 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 polythiophenes.

Experimental

Most chemicals were purchased from Wuhan Shenshi Chemicals Co., Ltd and were used without further purification unless otherwise noted. 3,4-Ethynledioxiythiophene (EDOT) was purchased from Suzhou Yacoo Co., Ltd. Diethyl ether anhydrous solvent was distilled from commercial diethyl ether with CaH2. 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 and 5-bromo-7-thiophen-2-yl-2,3-dihydro-thiophen-3,3'-dioxide were synthesized according to previous reports.

Monomer 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 literature21 except for the change of 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 CH2Cl2 (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 CH2Cl2 and washed with H2O and brine, and dried over MgSO4. After filtration, the solvent was removed to yield a yellow solid (310 mg, 85%).1H NMR: δ (CDCl3, ppm): 6.26 (s, 1H), 4.32–4.33 (m, 8H, 4.23 (m, 8H), 1.79 (m, 2H), 1.50 (m, 6H), 1.32 (m, 18H), 0.89 (t, 3H). 13C NMR: δ (CDCl3, ppm): 6.91 (d, 2H), 4.29 (d, 4H).

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 Et2O, and filtered through Celite. The organic phase was washed with water and brine and dried over MgSO4. After filtration, the 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%).1H NMR: δ (CDCl3, ppm): 6.91–6.93 (d, 2H), 6.22 (1H), 4.29–4.21 (d, 4H), 13C NMR: δ (CDCl3): 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 desired compound was synthesized by the modification of a previous method.25 Anhydrous THF (30 mL) was slowly added dropwise to a solution of lithium disopropylamide (prepared by the addition of butyllithium to disopropylamine, 10 mmol), with the temperature maintained at 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, with the temperature maintained at around −50 °C. Then the reaction mixture was warmed to −20 °C and stirred at this temperature for 15 min. The reaction mixture was cooled to −78 °C and 2-isopropanoyl-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, and dried with MgSO4. The solvent was removed via rotary evaporation, and the residue was distilled. The product yield was 1.86 g (60%).1H NMR (CDCl3): 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 (S-S-OC8, 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 was dissolved in 15 ml of toluene. A K2CO3 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(C6H5)3]4 were added to the mixture. The reaction mixture was cooled at −78 °C, stirred for 1 h and warmed to room temperature and stirred for 12 h. The mixture was poured into water, extracted with ether, and dried with MgSO4. The solvent was removed via rotary evaporation, and the residue was distilled. The product yield was 1.86 g (60%).1H NMR (CDCl3): 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).

Polymer Chemistry
δ (CDCl₃) 152.8, 135.6, 127.0, 123.8, 121.6, 117.7, 115.7, 72.1, 32.0, 30.0, 26.1, 22.9, 14.6. Anal. Calcld for C₁₄H₁₇BrOS₂: C, 48.69%; H, 4.96%; S, 12.1%. 1H NMR (CDCl₃): 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). 13C NMR (CDCl₃): 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. Calcld for C₁₄H₁₆BrOS₂: 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 the SSP procedure previously reported. Briefly, each monomer (0.05–0.2 g) was incubated from room temperature to 60–100 °C for 1–72 h and dried in a vacuum at room temperature to give a black powder of the 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. Diffuse reflectance IR spectra were measured on a Perkin-Elmer FTIR spectrometer. Absorption IR spectra for the characterization of the compounds were obtained by chloroform solution. The UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrophotometer. The UV–vis absorption spectra of the polymers and the corresponding monomers were recorded in 0.1 M Bu₄NClO₄ in acetonitrile, a 1 cm² area of the polymers and as the working electrode for electrochemical measurements in 0.1 M Bu₄NClO₄ in acetonitrile, a 1 cm² area of the working, counter, and reference electrodes, respectively (CH Instruments 604D electrochemical system). The X-ray diffraction (XRD) pattern was obtained by a Bruker D8 Advanced X-ray diffractometer using Cu-Kα (1.54 Å) radiation at room temperature. The thermal properties of the polymers were measured on a Netsch STA449C thermal analyzer at a heating rate of 10 °C min⁻¹ under nitrogen at a flow rate of 20 cm³ 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 the 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 monomers and their behavior through SAAP**

All monomers were synthesized as shown in Scheme 1. Monomers 1 and 2 were obtained by bromination and iodination of bis-EDOT respectively. Monomers 3 and 4 were synthesized using Stille coupling reactions. With the selective lithium reagent LDA, boronane was introduced at 5-position of 3-hexylthiophene. Then, after Suzuki coupling and then NBS bromination, 6 and 7 were obtained respectively.

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

**XRD patterns of the monomers and respective polymers**

Fig. 1 shows XRD patterns of the selected monomers and their respective polymers. We can see that all monomers show sharp peaks in the range of 10–60°, which are a characteristic feature of crystal compounds and an indication of relatively long-range order. However, most sharp peaks disappear except for leaving a wide broad peak around 22–26° once they change into the 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 30.4° for the bromo-substituted derivative while peaks at 11.6, 15.5, 16.0, 20.3, 21.1, 23.4, 24.2, 25.0, and 29.9° for the iodo-substituted one. Their featured XRD patterns reveal that their crystal structures might be quite different after halogen change. After the SAAP process, only two peaks are left for PEDOT-Br at 26.1, 13.0°, which can be assigned to the crystal phase of (020) and (200) respectively. Therefore, its polymer structure is almost the same as that in our previous
It is noted that in the case of E-E-I, its corresponding polymer has an almost amorphous phase because of its broad weak peak at 26.1°, indicating that the bromo-substituted monomer is inclined to form higher orderness of molecule packing once it forms PEDOT.

In the case of Br-E-S, it shows quite different XRD patterns with peaks appearing at 11.3, 16.0, 18.6, 21.7, 23.6, 24.8, 26, 27, 28.1, 29.7, and 37.7. In addition, after SAAP, only a very weak peak around 26° was observed, revealing that 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 a similar absorption curves shape while the others are typical non-doped polymers because of the lower absorption value in the near-IR region. Due to the moderate absorption in the near-IR region around 800–1000 nm, which is the featured absorption for a p-type polymer, it is believed that these PEDOT polymers were oxidized mostly. We reported previously that the PEDOT obtained through SAPP using Br-EDOT is partly oxidized. Therefore, the polymer can be easily oxidized using the bis-EDOT dimer as the starting monomer.
However, in the case of P(E-S), it shows a weak absorbance at 700 nm, indicating that it is more difficult to oxidize than PEDOT. That is to say, after introducing thiophen units, it can stabilize the polymer as it prevents oxidation to some extent. Furthermore, after further introducing alkyloxy chains, as in the case of P(S-S-OHexy), it shows the lowest value in the near-IR region if we normalize these curves. These experimental results reveal that the more push electron groups of oxygen it has, the easier it will be oxidized.

Due to the fact that we first obtain the soluble homopolymer of P(S-S-OHexy) through SAAP, its fluorescence spectra were examined in CHCl₃ solution, as shown in Fig. 2b. When excited within their \( \pi-\pi^* \) bands, it exhibits a strong luminescence maximum at around 560 nm, with \( E_0-0 \) transition energies of 2.37 eV. Though molecular weight has an influence on the peak value for absorption spectra³⁰ and there are peaks overlapped in solid P(S-S-OHexy) films, blue shift²⁰ was observed in its film absorbance, indicating the formation of H-aggregates.

FTIR spectroscopy and thermal stability
Polymers' FTIR spectra are shown in Fig. 3. The characteristic absorption peaks of the first two PEDOT systems are almost the same indicating that PEDOT has exactly the same structure in the bulky phase whether the starting monomer is bromo or iodo substituted. Meanwhile, P(E-S) exhibits similar IR curves to those of PEDOT polymers. In detail, 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. In addition, all of them have featured peaks at 696 cm\(^{-1}\) related to in-plane deformation of the C–S–C of the thiophene ring.\(^{32}\)

However, P(S-S-C\(_6\)OHexy) containing long alkyloxy chains has quite different fingerprints. In this case, except for the general featured peaks possessed by polythiophene, it shows a 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 the alkyloxy chain in the polymer matrix, peaks of 696 cm\(^{-1}\) (deformation of C–S–C), 897 cm\(^{-1}\) (C–S stretching),\(^{16}\) 1267 cm\(^{-1}\) (C–O stretch)\(^{37}\) and 1417 cm\(^{-1}\) (O–C–O wag) demonstrate a strong intensity, indicating that the alkyloxy chain would increase the thiophene ring vibration and free rotation of the C–O bond.

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

Photo picture and conversion yield
In most cases, after SAAP is performed over 60 °C or even higher for several hours, the light yellow or yellow solid of monomers changed to sky-blue or black powder, as shown in Fig. 5. These experimental results were similar to those in our previous report concerning the SAAP for Br-EDOT\(^{16}\) and other SSP-based polythiophene systems.\(^{13}\) We found that most monomers gave high yield up to 95% at 60 °C within several hours except for S-S-Ohexy-Br, and high temperature shortens the reaction time generally. However, in the case of S-S-Ohexy-Br, it requires higher temperature and takes a longer time to complete polymerization.

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

Electrochemical behavior of the 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 the FTO electrode. As shown in Fig. 6, except for P(S-S-OHexy), most polymers show broad reduction peaks at approx. 0.1 V. Meanwhile, except for PEDOT-Br, others do not show distinct oxidation peaks. In addition, the onset oxidation potentials for PEDOT-Br, PEDOT-I, P(E-S) and P(S-S-OHexy) are –0.5, –0.45, –0.2 and 0.7 V, respectively, which indicates that the more push electrons of oxygen atoms they have, the easier they will 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 the 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 an iodo atom in the starting monomer. At present, we cannot understand this kind of result clearly but this might be due to their different crystalline phases. Because of the smaller C–I bond energy (C–Br of 276 kJ mol$^{-1}$ and C–I of 240 kJ mol$^{-1}$), it may result in quick polymerization rate and in obtaining more amorphous phase. Such a primitive explanation is well supported by the fact that PEDOT-I has poor polymer chain packing (see the XRD analysis section in Fig. 1), which results in a poor charge storage capability. In addition, further electrochemical impedance spectra (in the ESI†) reveal that PEDOT-Br has a better charge transfer ability compared with that of PEDOT-I.

**Molecular 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 molecular weight, and its typical $^1$H-NMR is presented in the ESL†

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Yield (%)</th>
<th>Retention time</th>
<th>$M_n$ a (g mol$^{-1}$)</th>
<th>DP b</th>
<th>PDI c</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 °C</td>
<td>80 °C (2 days)</td>
<td>&gt;90</td>
<td>17.9</td>
<td>91 548</td>
<td>346</td>
</tr>
<tr>
<td>90 °C (6 h)</td>
<td>&gt;90</td>
<td>25.6</td>
<td>996</td>
<td>4</td>
<td>1.98</td>
</tr>
<tr>
<td>100 °C (6 h)</td>
<td>&gt;90</td>
<td>26.0</td>
<td>2869</td>
<td>11</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 1 summarizes the reaction conditions investigated, the product yield, $M_n$, and the PDI of the P(S-S-OHexy). As can be seen, as the temperature increases, $M_n$ increases drastically along with the PDI in the range of 1.1–2, which is good news for us in our aim to rationally control the molecular distribution for different uses. In addition, extending time up to two days results in an $M_n$ of 91 548 with a PDI of 2.96. Therefore, several thousands to nearly hundred thousands molecular weight would be obtained by well controlling the temperature and reaction time under SAAP.

**Conclusions**

In this study, PEDOTs and different homopolythiophenes were prepared by SAAP from mono-halogen substituted thiophene...
derivative monomers, and the monomers’ structural effects, especially the bromo-substituted positions, were investigated in detail. We intended to probe the relationship between the monomers’ structure and their success rate under SAAP. Our study reveals that halogen atoms, halogen positions and molecular structures have a great effect on the monomers’ SAAP behavior. We can draw a conclusion that as far as monomer design is concerned, the bromo or iodo atom has almost no behavior. We can draw a conclusion that as far as monomer

Acknowledgements

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References