SYNTHESIS OF CHITOSAN-GRAFT-POLYANILINE WITH THE CONDUCTIVE POTENTIAL

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Abstract. Chitosan (CS) is one of the most plenteous polymers in nature and gets ubiquitous in many fields such as pharmaceutical and medical industries, wastewater treatment, agriculture, etc. due to its remarkable biodegradability and friendliness to human beings and ecology. Recently, nature-originated conductive materials have been gaining more attention than other materials because they can be utilized in reality, while others are difficult to decompose after use. Understandably, polyaniline (PANI), which is one of the prominent conductive polymers with a distinguished conjugated structure, simple synthesis, cost-effectiveness, environmental stability, and conductivity, was grafted with CS (CS-graft-PANI) to produce a copolymer possessing a combination of properties between CS and PANI. Although there have been several researches related to this copolymer, the grafting efficiency and electrical conductivity were relatively low. Therefore, this paper aims at obtaining a higher efficiency and electrical conductivity of CS-graft-PANI copolymer by systematically adjusting the synthesis parameters including the volume of acid solution to dissolve aniline, initiator concentration, acetic acid concentration to dissolve CS, the initiator methods and dopants. As a result, the best copolymer product reached a graft efficiency of 69.4\% and grafting percentage of 78.5\% with an electrical conductivity of 7.96\times10^{-3} Scm\textsuperscript{-1}. The chemical composition and morphology were determined by Fourier-transform Infrared Spectroscopy and Scanning Electron Microscope while the thermal characteristic was also carefully detected via Thermogravimetric Analysis.

Keywords: ammonium persulfate, chitosan graft polyaniline, conductive material, \textit{p}-toluene sulfonic acid.

Classification numbers: 2.9.3, 2.10.1, 2.10.2.

1. INTRODUCTION

Chitosan (CS) is one of the potential materials in the contemporary era due to its second-most richness in nature after cellulose, and possession of exceptional functions of biopolymers.
Besides, CS itself owns a lot of superb properties such as non-toxic, non-allergenic to human beings, biodegradable (due to containing breakable glycosidic bond [1]), naturally biocompatible, bioabsorbable, and good film-forming ability [2 - 4]. Derived from chitin in the shells of crustaceans (crabs, shrimps, etc.), mollusks, or insects, CS can be utilized to reduce the solid garbage in the environment and is used in some fields such as pharmaceutical and medical industries, wastewater treatment and agriculture, etc. [2 - 5]. Other exceptional properties that make CS stand out from the other polysaccharides are antimicrobial and bacteriostatic activities. CS was demonstrated to be effective against a wide range of both gram-negative and gram-positive bacteria [2, 4]. However, there are several drawbacks that CS needs to be improved to broaden its practical applications such as highly selective solubility, brittleness, and average mechanical properties. For example, CS was grafted with n-butyl acrylate to enhance its flexibility and mechanical properties with strong antibacterial characteristics [2, 6]. Gu et al. [7] synthesized CS graft poly(ε-caprolactone) to produce micelles for drug delivery in the pharmaceutical field. In textile industries, CS and methoxypolyethylene glycol were combined to form copolymers as a multi-functional finishing agent for coating cotton fabrics with the aim of enhancing strength and antibacterial activity [8].

Recently, the tremendous conductive ability of CS graft polyaniline (CS-graft-PANI) has been gaining much attention. Although the structure of PANI is similar to that of polypyrroles, polythiophenes, and polyphenylene vinylenes, etc. with the conjugated double bond or π electron delocalization in the molecule, PANI are more preferable due to the cost-effectiveness, simple synthesis, good optical and reasonably electrical properties with excellent environmental stability [9]. Moreover, PANI is an organic-based oxidative polymer [10] containing benzenoid units and oxidized quinoid units on the backbone [11]. To generate a semiconductor, a state of half-oxidized emeraldine must be achieved, which encloses an alternating sequence of two benzenoid units and one quinoid unit [12]. The conductivity of this polymer is intrinsically related to the chemical structure, morphology, dopants, and extrinsically correlated to the atmosphere and temperature [13]. However, the solubility and mechanical weakness are two of the noticeable disadvantages of PANI that have appealed to many researchers to improve. Therefore, a combination of CS and PANI is a perfect mutual complement to their characteristics [14]. In this way, Marcasuzaa et al. [15] successfully synthesized CS-graft-PANI-based hydrogels and found out that their conductivity was roughly 10^-5 - 10^-2 S cm^-1 depending on molecular weight and grafting percentage. Ramaprasad et al. [16] also published the grafting of PANI onto radiation crosslinked CS, which exhibited a change in volume conductivity from 10^-11 to 10^-8 S cm^-1, and surface conductivity from 10^-10 to 10^-2 S cm^-1. Most importantly, this group of authors found that the electrical property can be enhanced when the product was doped with 1 M HCl solution. At the same time, Tiwari and Singh [17] analyzed their best CS-graft-PANI copolymer sample and showed that with the sample possessing the highest grafting percentage, the conductivity reached at 4.03 × 10^-2 S cm^-1. Moreover, pH was found to strongly affect the electrical conductivity (the higher the pH, the lower the conductivity).

In this paper, a CS-graft-PANI copolymer was synthesized with the oxidative method using (NH4)2S2O8 as an initiator and HCl as a dopant. Moreover, p-toluene sulfonic acid (PTSA), which acts as a dopant, greatly contributes to an increase in the conductivity of polymers [15-17]. Thus, herein, PTSA was used in the reaction as a new dopant to examine the conductivity of CS-graft-PANI copolymer in comparison with the use of a traditional dopant such as HCl.

2. MATERIALS AND METHODS

2.1. Materials
Chitosan (CS) (deacetylation degree of 71 %, Chitosan VN, Vietnam), ammonium persulfate (APS) (Xilong, China), HCl (98 %, Xilong, China), N-methyl pyrrolidinone (NMP), p-toluene sulfonic acid (PTSA) (Merk, Germany), acetic acid (AA) (China) were directly used without purification. Aniline (98%, Xilong, China) was distilled before use.

2.2. Methods

2.2.1. Polymerization of polyaniline

First, 0.01 mol of aniline was dissolved in 1 M HCl solution with different volumes (8 - 48 mL) and stirred for 30 min to homogenize the solution at ambient temperature. Meanwhile, a solution of APS in HCl was prepared by dissolving an amount of APS (in molarity varying from 0.005 to 0.0125) into 8 mL of 1 M HCl solution. The reactor system was cooled down to 5 °C, then APS solution was added dropwise to the system. This process lasted 5 h at 5 °C. The precipitated product was filtered and washed with distilled water. Then, acetone was used to eliminate oligomers and excess monomers from PANI. The PANI product was dried in the vacuum desiccator at 50 °C for 6 h. PANI was submerged in 3 % NH₄OH solution for 24 h to carry out undoping process, and then carefully washed to remove alkali before being dried in a vacuum oven. The PANI products were evaluated by the efficiency (H %), Fourier-transform Infrared Spectroscopy, UV-Vis and electrical conductivity.

2.2.2. Chitosan graft PANI (CS-graft-PANI)

![Reaction scheme of CS-graft-PANI.](image)

The synthesizing mechanism is clearly shown in Figure 1. First, 0.005 mol of aniline was added to different volumes (8 and 16 mL) of 1 M HCl solution at ambient temperature and stirred homogeneously. Meanwhile, 30 g of 1 wt.% CS solution at different concentrations of acetic acid (0.5 - 2 %) was added to the reactor system to create a uniform mixture before reducing the temperature to 5 °C. After that, APS solution (at an APS/Aniline molar ratio of 1.0 - 1.3 in 4 mL of 1 M HCl solution) was introduced drop by drop into the reaction to carry out the
graft polymerization for 5 h. When the reaction was finished, a 5 % NaOH solution was added into the mixture to neutralize the excess HCl. At the following stage, the products including polymer, oligomer PANI and CS-graft-PANI copolymer were precipitated in methanol. This mixture was then washed with distilled water, NMP and acetone orderly to eliminate the excessive reactants, PANI homopolymer, and oligomer from CS-graft-PANI [18]. CS-graft-PANI copolymer was dried in a vacuum desiccator at 50 °C for 6 h before characterizations.

2.2.3. Characterization method

The yield of undoping reaction was determined with the equation: \( H(\%) = \frac{m_{\text{undoped PANI}}}{m_{\text{monomer}}} \times 100 \); in which \( m_{\text{undoped PANI}} \) is the mass of PANI after being undoped with NH$_3$OH, \( m_{\text{monomer}} \) is the mass of used monomer. The yield of graft reaction was calculated with the graft efficiency (E %) and graft percentage (G %). \( E(\%) = \frac{W_g}{W_m + W_0} \times 100 \); \( G(\%) = \frac{W_g - W_0}{W_0} \times 100 \); in which \( W_g \) is the weight of CS-graft-PANI, \( W_m \) is the weight of monomer, \( W_0 \) is the weight of initial CS. The samples prepared for Fourier-transform Infrared Spectroscopy (FTIR) measurement were powdery and measured by a Tensor 27 (Bruker, Germany). The samples used in Ultraviolet-visible spectroscopy (UV-Vis) were in the form of aqueous solution and were measured with a Spectrophotometer V-630. Electrical conductivity (EC) was determined by an Olympus Tokyo - 302466 using the 4-point DC-resistance technique, where samples were compressed into pellets with a diameter of 1 cm under a pressure of 1000 kg.cm$^{-2}$. The surface morphology of the products was inspected by JOEL Scanning Electron Microscope (SEM) with powder samples. Thermogravimetric Analysis was conducted by Labsys Evo (TG-DSC 1600 °C) from 0 to 700 °C at a rate of 10°C min$^{-1}$ in N$_2$ atmosphere.

3. RESULTS AND DISCUSSION

3.1. The factors affecting the synthesis process of PANI

3.1.1. The effect of volume of 1 M HCl solution to dissolve aniline

*Table 1.* The effect of a) 1 M HCl solution volume; and b) APS concentration on the efficiency H %. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>( V_{\text{HCl}} ) (mL)</th>
<th>Aniline (mol)</th>
<th>APS (mol)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>48</td>
<td>0.01</td>
<td>0.005</td>
<td>31</td>
</tr>
<tr>
<td>P2</td>
<td>32</td>
<td>0.01</td>
<td>0.005</td>
<td>43</td>
</tr>
<tr>
<td>P3</td>
<td>16</td>
<td>0.01</td>
<td>0.005</td>
<td>48</td>
</tr>
<tr>
<td>P4</td>
<td>8</td>
<td>0.01</td>
<td>0.005</td>
<td>46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>APS (mol)</th>
<th>Aniline (mol)</th>
<th>( V_{\text{HCl}} ) (mL)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3</td>
<td>0.005</td>
<td>0.01</td>
<td>16</td>
<td>48</td>
</tr>
<tr>
<td>P5</td>
<td>0.0075</td>
<td>0.01</td>
<td>16</td>
<td>61</td>
</tr>
<tr>
<td>P6</td>
<td>0.01</td>
<td>0.01</td>
<td>16</td>
<td>79</td>
</tr>
<tr>
<td>P7</td>
<td>0.0125</td>
<td>0.01</td>
<td>16</td>
<td>70</td>
</tr>
</tbody>
</table>

In this experiment, HCl acted as not only a doping reagent but also a reaction medium. As can be seen in Table 1a, when the volume of 1 M HCl solution was increased from 8 to 16 mL, H % changed insignificantly from 46 to 48 %. However, continuing to increase the volume to 32 mL and 48 mL caused a dramatic decrease in H % to 43 and 31 %, respectively. This can be explained that due to the considerable rise of the total HCl volume (to 48 mL) at a rather small APS/Aniline molar ratio of 0.5, the contact probability between reactive centers and monomers was decreased, leading to a reduction in chain propagation, and accordingly reduction of H % (to 31 %). In brief, with 0.01 mol of aniline, 16 mL of 1 M HCl solution was suitable to carry out
the reaction to form PANI and achieve the highest H % (48 %). However, similar to almost all previous papers, H % is lower than 50 % due to the low molar concentration of APS [19].

3.1.2. The effect of APS concentration

In Table 1b, with the same amount of aniline (0.01 mol) dissolved in 16 mL of 1 M HCl solution, when the initiator APS increased from 0.005 to 0.01 mol, the quantity of reactive centers steadily increased to propagate polymer chains, thereby gradually increasing H % from 48 to 79 %. However, APS concentrations in excess of 0.01 mol may easily lead to chain termination and chain transfer, reducing the H % and molecular weight of PANI.

3.1.3. Evaluation of the PANI doped with HCl - P6 sample

![Figure 1](image-url)

Figure 1. Chemical structure of P6 sample evaluated by: a) FTIR spectrum of PANI doped with Cl with the illustrated Benzenoid (B) and Quinoid (Q) structures in b); c) UV-Vis spectrum.

P6 sample with the highest H % was evaluated by FTIR spectrum (Figure 2a), UV-Vis curve (Figure 2c) and EC. FTIR spectra sufficiently show the peaks of PANI structure such as 3441 cm⁻¹ (N-H stretching), 2922 - 2850 cm⁻¹ (CH stretching), 1594 and 1464 cm⁻¹ (stretching vibration of the quinoid ring and benzenoid zing (Figure 2b)), 1291 - 1238 cm⁻¹ (C-N stretching of aromatic amine ring), 1117 cm⁻¹ (N=Q=N of quinoid ring), 791 cm⁻¹ (stretching vibration of benzene rings with the para substitution).

Figure 2c shows that there are 2 electron-transition steps at 344 and 633 nm. The peak at 344 nm is related to the π-π* transition of the benzenoid ring, and the latter transition corresponds to the localized polaron bands and transition process from polaron to π* [20]. The intensity of the PANI peaks in the UV-Vis spectra is very high, correlating with the best samples in the previous paper [21]. The EC of P6 sample reached 0.45 Scm⁻¹, which is relatively high but lower than that of the sample in the referred paper (0.742 Scm⁻¹) [17]. This indicates the low molecular weight of synthesized PANI.

3.2. The factors affecting the synthesis process of CS-graft-PANI

3.2.1. The effect of acetic acid concentration on G % and E %
In the graft copolymerization, the effect of acetic acid on G % and E % was evaluated by changing its concentration from 2 % to 1 %, and 0.5 % (corresponding to C1, C2 and C3 samples in Table 2, respectively) while other parameters were kept constant. As can be seen, an AA concentration of 2 % caused an ineffective polymerization process with G of 17.7 % and E of 46.1 % while a decrease in AA concentration to 1 % and 0.5 % greatly improved G % and E %. Both G % and E % reached the highest values of 41.5 % and 55.3 %, respectively, when CS was dissolved in the lowest AA concentration of 0.5 %. This can be explained that with high concentrations of AA, the number of H⁺ increased excessively, leading to a higher density of positive electrons at -NH₂ groups in CS molecules [22] (see Figure 1). As a result, difficulty in transferring H⁺ for dehydration may occur, preventing the formation of reactive centers, thereby reducing the chain propagation of PANI and subsequently lowering G % and E%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V_HCl (mL)</th>
<th>Aniline (mol)</th>
<th>APS/Aniline (mol/mol)</th>
<th>AA concentration (%)</th>
<th>G (%)</th>
<th>E (%)</th>
<th>Initiation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>8</td>
<td>0.005</td>
<td>1.0</td>
<td>2.0</td>
<td>17.7</td>
<td>46.1</td>
<td>1</td>
</tr>
<tr>
<td>C2</td>
<td>8</td>
<td>0.005</td>
<td>1.0</td>
<td>1.0</td>
<td>33.3</td>
<td>52.3</td>
<td>1</td>
</tr>
<tr>
<td>C3</td>
<td>8</td>
<td>0.005</td>
<td>1.0</td>
<td>0.5</td>
<td>41.5</td>
<td>55.3</td>
<td>1</td>
</tr>
<tr>
<td>C4</td>
<td>8</td>
<td>0.005</td>
<td>1.1</td>
<td>0.5</td>
<td>65.4</td>
<td>64.7</td>
<td>1</td>
</tr>
<tr>
<td>C5</td>
<td>8</td>
<td>0.005</td>
<td>1.2</td>
<td>0.5</td>
<td>73.3</td>
<td>67.8</td>
<td>1</td>
</tr>
<tr>
<td>C6</td>
<td>8</td>
<td>0.005</td>
<td>1.3</td>
<td>0.5</td>
<td>79.6</td>
<td>70.5</td>
<td>1</td>
</tr>
<tr>
<td>C7</td>
<td>8</td>
<td>0.005</td>
<td>1.2</td>
<td>0.5</td>
<td>78.5</td>
<td>69.4</td>
<td>2</td>
</tr>
</tbody>
</table>

3.2.2. The effect of APS/Aniline molar ratio on G % and E %

In the reaction to synthesize PANI, the highest H % was achieved at an APS/Aniline molar ratio of 1.0 (Section 3.1.2). However, the copolymerization process was carried out with the participation of both aniline and CS. Consequently, increasing the amount of initiator can greatly affect the copolymerization process and copolymer product. As can be seen from Table 2, when the APS/Aniline molar ratio increased from 1.0 to 1.3 (corresponding to samples C3 to C6), the molar concentration of the APS initiator increased, enabling the quantity of reactive centers to go up and simultaneously enabling the unreacted monomer to go down. This is the reason why the values of both G % and E % increased. However, if this ratio was too high (e.g. 1.3 mol/mol), although G and E were higher than that of using 1.2 mol/mol, the sample showed the excessive oxidation phenomenon, depriving the conductive structure of copolymer [23]. This result was verified by comparing the chemical structure in FTIR spectra (Figure 3). There were several typical peaks of PANI and CS appearing in the spectra of both C5 and C6 samples: O-H stretching of CS and NH stretching in PANI at around 3444 cm⁻¹, CH stretching at 2924 - 2854 cm⁻¹, C=O stretching in CS at 1649 cm⁻¹. The stretching vibration of conductive structure in PANI was at 1113 cm⁻¹ (N=Q=N) that also appeared in samples C5 and C6. However, the intensity of this N=Q=N peak in the spectrum of the sample with the ratio of 1.2 is higher than that of the sample with the ratio of 1.3 (when compared to the intensity of C=O groups in CS at 1649 cm⁻¹). In addition, an outstanding peak appearing at 2361 cm⁻¹ in the spectra of sample C5 is attributed to the presence of diazonium salt [24], which facilitates the conductivity of polymers [25]. This peak is also shown in the spectra of pure PANI (Figure 2a) while the similar peak in the spectra of sample C6 is relatively small. Moreover, the stretching vibration of benzene ring with the para-substituted position was at 800 cm⁻¹ in sample C5 while this peak did
not appear in sample C6. All of these peaks theoretically demonstrated that thanks to the conjugated double bond in N=Q=N structure and p-substituted benzene ring, the conductive ability of sample C5 was superior to that of sample C6. As a result of the actual experiments, the EC of samples C5 and C6 was detected with the result of $7.56 \times 10^{-3}$ S cm$^{-1}$ and $7.23 \times 10^{-3}$ S cm$^{-1}$, respectively, which obviously confirm the above hypothesis.

3.2.3 The effect of initiation methods on $G\%$ and $E\%$

The same ratio of APS/Aniline (1.2 mol/mol) and the same amount of 1 wt.% CS solution at an AA concentration of 0.5 % were used to synthesize copolymer by 2 different initiation methods. The first method was used from the beginning, which was given in Section 2.2.2: the initiator was added dropwise into the mixture of CS and aniline. Therefore, the initiator could attack and create the reactive centers in both CS and aniline, resulting in a $G$ of 73.3 % and an $E$ of 67.8 %. However, to optimize the $G\%$ and $E\%$, the second method was discovered, which was slightly modified from the first method: a half amount of the initiator was added dropwise into the CS solution to activate the reactive centers in CS first, then aniline was inserted into the reactor flask before adding drop by drop the remaining amount of the initiator into the mixture to carry out the graft copolymerization. The results in Table 2 (samples C5 and C7) show that when all the conditions were fixed but the method was slightly changed, both $G\%$ and $E\%$ of the latter method was higher than that of the first method ($G = 78.5$ % and $E = 69.4$ %, respectively). Furthermore, the FTIR spectra of sample C7 in Figure 4a showed the stretching C-N vibration at 1299 cm$^{-1}$, and stretching vibration of conductive structure (N=Q=N) of PANI at 1105 cm$^{-1}$, which was considerably increased (nearly double that intensity of C=O stretching vibration in CS at 1639 cm$^{-1}$) compared with sample C5 in Figure 3c. This demonstrates that sample C7 possessed more conjugated structure (N=Q=N) than sample C5, thereby making the EC of sample C7 ($7.96 \times 10^{-3}$ S cm$^{-1}$) higher than that of sample C5 ($7.56 \times 10^{-3}$ S cm$^{-1}$). The conductivity of the copolymer mainly depends on $G\%$ since the higher the $G\%$, the more PANI can be grafted onto the CS chains while PANI plays a role in determining the conductivity of the copolymer.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{FTIR spectrum of a) sample C6, b) sample CS, c) sample C5.}
\end{figure}
3.3. The effect of dopant reagents on conductivity of CS-graft-PANI copolymer

In this paper, two kinds of dopant were used to investigate their effect on the conductivity of the final doped copolymer: (i) PTSA was used to dope onto the PANI chain of CS-graft-PANI copolymer by immersing 1 g of CS-graft-PANI copolymer in 20 mL of 1 M PTSA for 24
h, (ii) HCl was used instead of PTSA with the same process. The conductive results in Figure 4b showed that the conductivity of copolymer doped with HCl was lower than that of PANI (roughly 56 times). On the other hand, sample C7 doped with HCl was slightly higher than PTSA.

\[\text{Figure 6. TGA graph of a) C7}_{\text{PTSA}}; \text{ b) C7}_{\text{HCl}}.\]

Comparing Figure 6a with Figure 6b, there were similarly 3 stages of weight reduction [26]: (i) The first stage (50 - 160 °C): PTSA-doped copolymer reached a point of losing weight of 6.67 % at 85.53 °C while the weight of HCl-doped copolymer was reduced by 8.52 % at 83.87 °C. This was due to the evaporation of solvent or moisture, and the separation of small molecules doped in the PANI segments [26]. The weight of copolymer doped with PTSA decreased less than that of copolymer doped with HCl due to the degradation of unsteady Cl doped on PANI chains, leading to the quicker decrease in copolymer weight. (ii) The second stage (160 - 260 °C): This stage can be explained by the degradation of CS chains [26], which leads to the similarity of the two samples. (iii) The final stage (260 - 400 °C): The PTSA-doped copolymer witnessed a decline in the weight by 14.37 % at 325 °C while the HCl-doped copolymer experienced a reduction in the weight by 13.59 % at 333 °C. This stage is the deterioration of the PANI chains [26]. At the same time, the molecular weight of PTSA dopant is much higher than that of Cl (190.22 and 35.5, respectively). These PTSA molecules were completely segmented and destroyed, leading to a greater reduction in the weight of the PTSA-doped copolymer.

4. CONCLUSIONS

The most efficient conditions for the synthesis of emeraldine-structured PANI with the highest H of 79 % and EC of 0.45 Scm\(^{-1}\) were the temperature of 5 °C for 5 h, the use of 16 mL of 1 M HCl solution and APS/Aniline molar ratio of 1.0. In the CS-graft-PANI copolymerization process, 0.05 mol of aniline dissolved in 8 mL of 1 M HCl solution reacted with 30 g of 1 wt.% CS solution in 0.5 % acetic acid solution, resulting in the highest G (41.5 %) and E (55.3 %). Meanwhile, the concentration of acetic acid exceeding 0.5% would reduce G and E % due to the effect on CS chains. Besides, the APS/Aniline ratio also influenced the copolymerization efficiency and emeraldine structure of PANI on CS chains, leading to the highest value of EC \((7.56\times10^{-3} \text{ Scm}^{-1})\), corresponding to a G value of 73.3 % and an E value of 67.8 % at an APS/Aniline molar ratio of 1.2. Apart from the first method, which concurrently activated both aniline and CS, the modified method using a half amount of APS to initiate CS first and then putting aniline into the mixture before adding the remaining amount of APS
enabled G and E to increase to 78.5 % and 69.4 %, respectively. Meanwhile, the EC of the copolymer using this innovative method also increased to $7.96 \times 10^3$ S cm$^{-1}$. Furthermore, different dopants inevitably led to changes in EC and thermal properties of the final products.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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