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Journal Name

PAPER

A simple method to fabricate poly(aniline-co-pyrrole) with highly improved electrical conductivity via pre-polymerization

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A highly conductive aniline and pyrrole copolymer (P(An-Py)) was fabricated by properly controlling pre-polymerization time. The electrical conductivity of P(An-Py) by proper pre-polymerization achieved the same order of magnitude (10^{-1} S/cm) with their homopolymers, or even slightly higher, which was unrelated to the molar ratio of two monomers. Only by 15 mins pre-polymerization, the electrical conductivity of P(1An-3Py) and P(1An-1Py) improved more than 3 orders of magnitude and 4 times, respectively. Electron microscopic analysis showed there was no obvious change in the morphology of the copolymers with pre-polymerization. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) revealed that the copolymers backbone contained many small aniline chains after pre-polymerization. The number of quasi-hydrogen bonding between N of pyrrole and adjacent free H⁺ of protonated aniline was greatly reduced. As a result, the number of free H⁺ of protonated aniline chain in copolymer was significantly increased, thus the carrier concentration and electrical conductivity increased sharply. Our results suggested that properly controlling the pre-polymerization time before copolymerization was a simple but effective way to highly improve the conductivity of copolymers that aniline and other monomer copolymerized.

Introduction

Conductive polymers, owing to their good electrical, electrochemical and optical properties, were extensively used in light-emitting diodes^{1, 2}, anti-corrosion materials³, batteries⁴⁻⁶, hydrogen storage materials⁷, electromagnetic shielding materials⁸, capacitors⁹ and sensors¹⁰. Conductive polymers mainly include polystyrene acetylene, polystyrene, polyaniline (PANI), polypyrrole (PPy), poly phenylene acetylene and polythiophene, etc. PANI and PPy had been widely investigated¹¹⁻¹⁴ because of its low cost, environmental stability and high electrical conductivity. However, due to their big π -conjugated structure, they were mostly insoluble, which limited their large-scale commercial applications.

In order to adjust their conjugated structure, improve the processibility and combine the unique properties of both homopolymers, a lot of studies had been performed to fabricate poly(aniline-co-pyrrole) by electrochemical¹⁵⁻¹⁷ or chemical oxidation¹⁸⁻²⁰ approaches and their related properties were investigated²¹⁻²³. Some works controlled the copolymers structure by inverse microemulsion²⁴ or template methods²⁵⁻²⁷. However, when the content of pyrrole was higher than aniline, the conductivity of copolymers were greatly reduced and lose their original electrical properties. So how to remain the conductivity of

copolymers is urgent to be solved. Only a few researches were reported about this. Antony et al²⁸ synthesized poly(aniline-co-pyrrole) using a special kind of anionic amphiphilic dopant as a template. The electrical conductivity of copolymer was unchanged with molar ratio of aniline and pyrrole. But this method exists many deficiencies, such as high cost due to the difficulties in obtaining the dopant and the complicated fabrication process, which hinder the large-scale production and practical application.

The present investigation is committed to fabricate poly(aniline-co-pyrrole) copolymer with high electrical conductivity by simple process and low cost raw materials. The main idea is to pre-polymerize monomers and control pre-polymerization time properly before copolymerization. We found that the electrical conductivity of P(An-Py) by proper pre-polymerization achieved the same order of magnitude (10^{-1} S/cm) with their homopolymers, and moreover it was not affected by the component of monomers. Such a simple and effective experimental method is very suitable for industrial production and reduces raw material and synthetic costs.

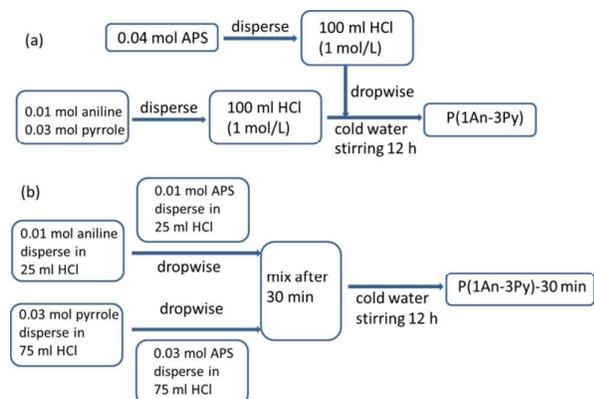
Experimental Section

Materials

Aniline and pyrrole monomers used in this study were supplied by Sinopharm Chemical Reagent Co. Ammonium persulfate (APS), hydrochloric acid (HCl) and ethanol were also provided by Sinopharm Chemical Reagent Co. All the chemicals were analytical pure and used directly without further treatment.

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Scheme 1 Synthesis process of (a) P(1An-3Py), (b) P(1An-3Py)-30 min.

Preparation of copolymer without pre-polymerization

The copolymer was synthesized by in-situ chemical oxidative polymerization. 0.91 ml (0.01 mol) aniline and 2.08 ml (0.03 mol) pyrrole were dispersed into 100 ml (1 mol/L) HCl solution with 20 min stirring. Then the mixture poured into three neck flask with continually stirring in cold water bath (6–8 °C). 9.128 g (0.04 mol) ammonium persulfate (APS) dissolved in 100 ml (1 mol/L) HCl solution, then dropped (1 d/s) in flask for reaction 12 h. The resulting mixture was filtered and the residue was washed thoroughly in turn with deionized water and ethanol for three times. The obtained powders were dried at 60 °C at least 24 h. This copolymer denoted as P(1An-3Py) and the numbers represented the ratio of aniline and pyrrole. The schematic representation of the synthesis process of P(1An-3Py) was illustrated in Scheme 1(a). P(1An-1Py), P(3An-1Py), polypyrrole and polyaniline were fabricated with the same process.

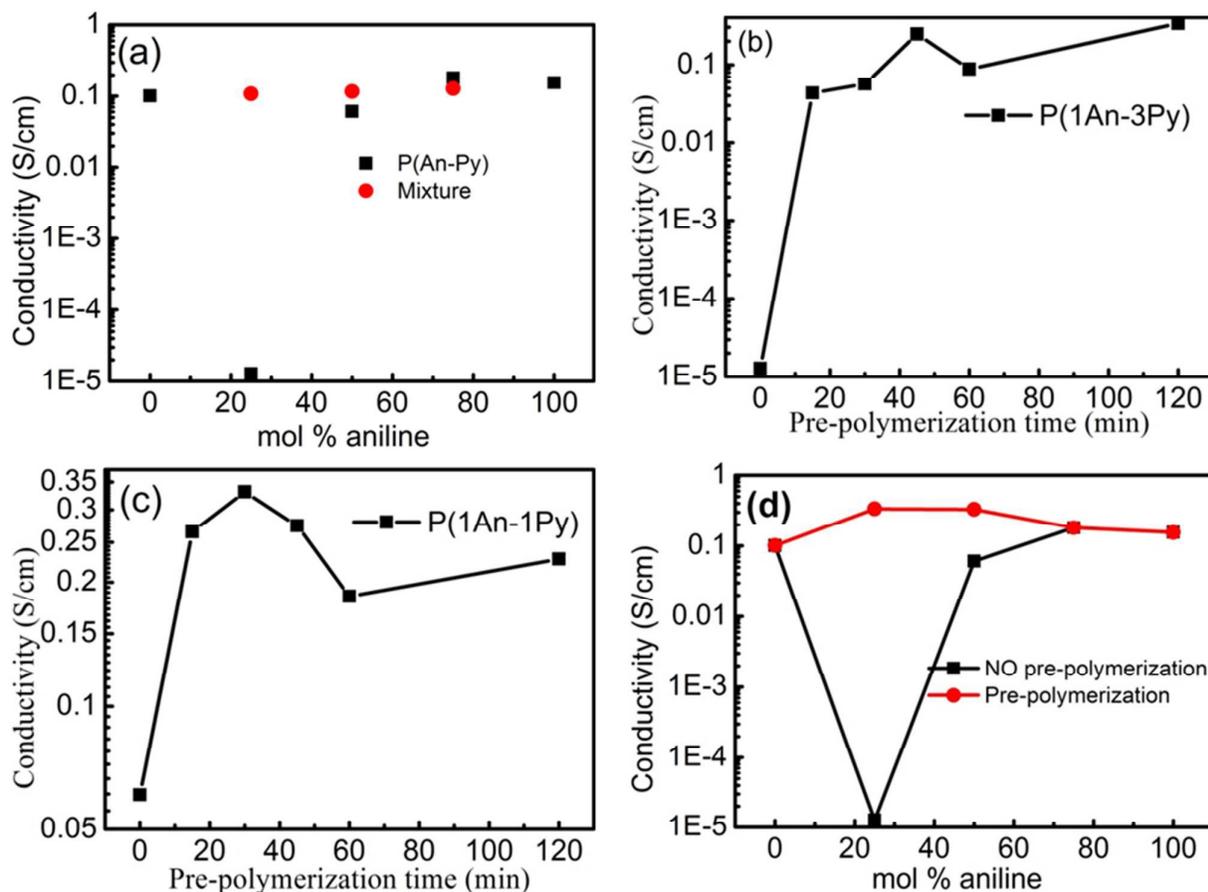


Fig. 1. (a) Conductivity of P(An-Py) in dependence on the monomer mixture P composition (squares). The conductivity of PANI and PPy homopolymer mixtures of corresponding composition is shown for comparison (circles). The dependence of the conductivity on the pre-polymerization time of the prepared (b) P(1An-3Py), (c) P(1An-1Py) copolymers. (d) Conductivity of P(An-Py) with proper pre-polymerization (circles) and no pre-polymerization (squares).

Preparation of copolymer with pre-polymerization

The copolymer was also synthesized by in-situ chemical oxidative polymerization. 0.91 ml (0.01 mol) aniline and 2.08 ml (0.03 mol) pyrrole were dispersed into 25 ml and 75 ml (1 mol/L) HCl solution with 20 min stirring, respectively. Poured the two mixture into three neck flask separately and continued to stir in cold water bath (6~8 °C). 2.282 g (0.01 mol) and 6.846 g (0.03 mol) APS dissolved in 25 ml and 75 ml (1 mol/L) HCl solution, respectively, and dropped into the flask for reaction 30 min, then mixed the solutions of the two flasks for reaction another 12 h. The resulting mixture was filtered and the residue was washed thoroughly with deionized water and ethanol for three times, respectively. The obtained powders were dried at 60 °C at least 24 h. This copolymer denoted as P(1An-3Py)-30min. The schematic representation of the synthesis process of P(1An-3Py)-30min was illustrated in Scheme 1(b). Other copolymers with different pre-polymerization time were fabricated with the same process except the pre-polymerization time.

Characterization

These copolymer powders were pressed into wafers with a thickness of about 1 mm and a diameter of 13 mm at a constant pressure of 25 MPa with pressure holding time of 30 s. The electrical conductivity of the samples was measured by a dc kelvin bridge and a standard four-probe technique at room temperature. When the conductivity of the samples was below 10^{-3} S/cm, a multimeter was used. Prior to measurements, circular copper electrodes were deposited on both sides of the pellets. The carrier concentration and carrier mobility were measured by a Hall Effect measurement instrument (HM2000) at room temperature. The field emission scanning electron microscopy (FESEM) imaging was performed with a JSM6700F (JEOL) field emission scanning electron microscope. Infrared spectra of the copolymers were recorded using Perkin-Elmer 5700 FT-IR spectrometer in the range of 4000-400 cm^{-1} with the copolymer samples dispersed in KBr pellets. The XPS measurements of samples were made on a RBD upgraded Perkin-Elmer PHI-5000C ESCA system.

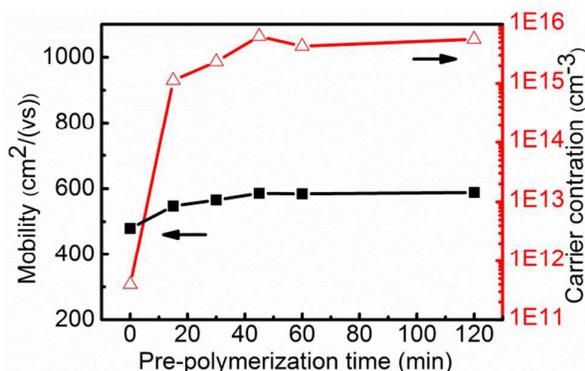


Fig. 2. The dependence of the carrier concentration and mobility on the pre-polymerization time of the prepared P(1An-3Py).

Results and discussion

Conductive properties

The conductivity of P(An-Py) depended on monomer composition, which was shown in Fig. 1(a). The conductivity of homopolymers blends was also given for comparison. The conductivity of all the proportion of PANI and PPy blends and their homopolymer was in the same order of magnitude, which had been a high value. When aniline content was lower than 50%, the conductivity of copolymer was 4 orders of magnitude lower than that of the corresponding blend. As the content of aniline increased to over 50%, the copolymer's conductivity was slightly higher than corresponding blend. The conductivity of P(1An-1Py) achieved a half of corresponding mixture. Fig. 1(b) and 1(c) were the conductivity of P(1An-3Py) and P(1An-1Py) with different pre-polymerization time, respectively. The conductivity of P(1An-3Py) greatly improved 3 orders of magnitude only by pre-polymerizing 15 mins. Increasing the pre-polymerization time, the conductivity continued to raise an order of magnitude. For P(1An-1Py), the conductivity could remarkably enhance 4 times only by 15 minutes' pre-polymerization. Continue to pre-polymerize, the conductivity of P(1An-1Py)-30min reached the maximum and was 5 times higher than P(1An-1Py). Fig. 1(d) was the conductivity of P(An-Py) with proper pre-polymerization and no pre-polymerization. As long as pre-polymerizing proper time, the conductivity of P(An-Py) could reached or even slightly higher than their homopolymers.

Carrier concentration and mobility

Fig. 2 shown the dependence of the carrier concentration and mobility on the pre-polymerization time of the prepared P(1An-3Py). The carrier concentration of P(1An-3Py) greatly improved 3 orders of magnitude only by 15 minutes' pre-polymerization. Finally it improved 4 orders of magnitude with continually pre-polymerized. Meanwhile, when the pre-polymerization time increased, the carrier mobility of P(1An-3Py) just slightly improved. The conductivity of material is determined by carrier concentration and mobility. Combined Fig. 2 with Fig. 1(b), it was obvious that the change of conductivity was similar to carrier concentration. Namely, the increase of the conductivity of this copolymer could be attributed to the change of carrier concentration.

SEM

Fig. 3 was the SEM image of the prepared P(1An-3Py) copolymers with different pre-polymerization time. The particles of P(1An-3Py) were irregular spherical with the diameter about 500 nm and aggregated together. After pre-polymerization, the morphology and diameter of copolymers were unchanged. P(1An-1Py) also had the same phenomenon (Supporting Information Fig. 1). Usually, the morphology of PANI and PPy were rod-like and spherical, respectively. Pre-polymerization just changed monomers arrange in the small areas and did not form long aniline chain. So the morphology and diameter of copolymers were unchanged with pre-polymerization. It revealed that the change of conductivity by pre-polymerization was irrelated to the morphology.

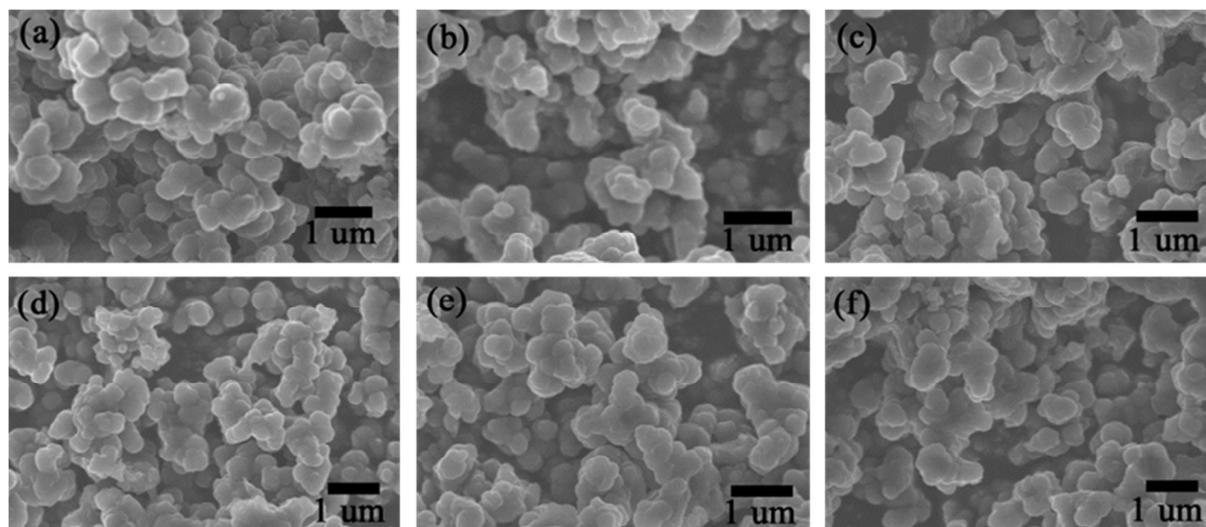


Fig.3. SEM image of the prepared P(1An-3Py) copolymers with different pre-polymerization time: (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 120 min.

FT-IR spectra

FTIR spectra of P(1An-3Py) copolymers with different pre-polymerization time and the mixture of PANI and PPy (1:3 on the molar basis of constitutional units) were shown in Fig. 4. All the spectra of samples showed a same broad absorption band at the wavenumbers higher than 2000 cm^{-1} (so the Fig. 4 only shown the beginning of this band). The spectrum of P(1An-3Py) copolymer showed 1541 cm^{-1} , which was combined with quinone stretching vibration in the phenyl ring and C-C stretching vibration in the pyrrole ring. The band at 1473 cm^{-1} was combined with benzene in the phenyl ring and C-N stretching vibration in the pyrrole ring.^{19, 20} The peak at 1316 cm^{-1} was assigned to C-H or C-N in-plane deformation modes. The peak at 1203 cm^{-1} was assigned to C-N stretching vibration of aniline and pyrrole directly connected.²⁷ The band at 1110 cm^{-1} could be attributed to C-H in-plane bending on the 1,2,4-substituted benzene of PANI.²⁵ We could deduce that the pyrrole units in the copolymer were likely to be attached to the 1, 2, or 4 position on the benzene ring. The band of C-H and N-H in-plane deformation vibration was assigned to 1048 cm^{-1} and the band of C-C out-of-plane ring deformation vibration correspond to 965 cm^{-1} .

The spectrum of mixture of PANI and PPy (1:3) showed a series of characteristic peaks of PANI and PPy homopolymers, which was the same with copolymer of P(1An-3Py), such as 1541 cm^{-1} , 1473 cm^{-1} , 1048 cm^{-1} and 965 cm^{-1} . Differently, the mixture appeared characteristic peaks of 1295 cm^{-1} , 1187 cm^{-1} and 1097 cm^{-1} , corresponding to C-N stretching modes of the leucoemeraldine, combined C-N stretching vibration with C-H, N-H bending vibration, and C-H, N-H in-plane bending vibration, respectively.

When the pre-polymerization time increased, the peak at 1316 cm^{-1} moved to 1295 cm^{-1} . The peak at 1203 cm^{-1} gradually disappeared and the peak at 1187 cm^{-1} enhanced. The band at

1110 cm^{-1} gradually shifted to 1097 cm^{-1} . These changes illustrated that the proportion of aniline and pyrrole directly connected in the P(1An-3Py) copolymer gradually decreased with the pre-polymerization time increased. Correspondingly, aniline chain segments gradually formed.

XPS

Fig. 5 was XPS N1s core-level spectra of the P(1An-3Py) and P(1An-3Py)-30 min. Each curve was resolved into two peaks which are -NH- and N^+ . The binding energy of -NH- of P(1An-3Py) was 399.6 eV. The peak over 400 eV was assigned to N^+ , and the area content of the peak was 8.6 %.

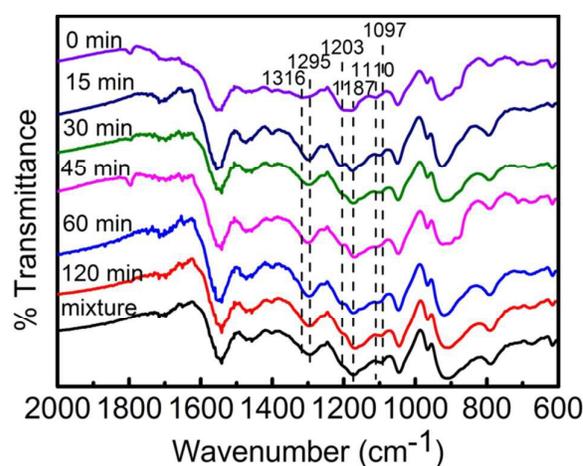


Fig.4. FTIR spectra of P(1An-3Py) copolymer with different pre-polymerization time and the mixture of PANI and PPy (1:3 on the molar basis of constitutional units).

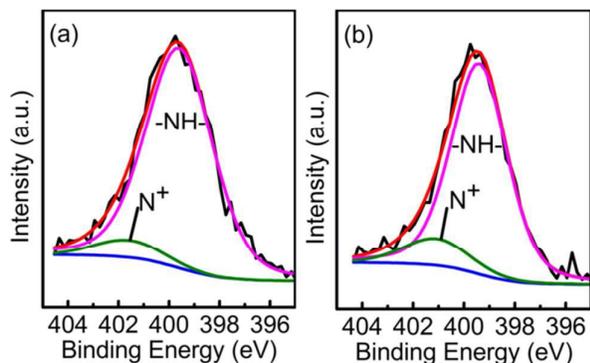


Fig.5. XPS N1s core-level spectra of (a), P(1An-3Py) and (b), P(1An-3Py)-30 min.

For P(1An-3Py)-30 min, the peaks of -NH- and N^+ were located at 399.4 eV and about 400 eV, respectively. The content of N^+ was

raised by 4 %, up to 12.6 %. When aniline connected to pyrrole, the binding energy of -NH- was higher than aniline connected to each other.^{13,18} After pre-polymerization, the binding energy of -NH- was decreased 0.2 eV. It revealed that the proportion of aniline connected to pyrrole decreased, which the aniline small chain in copolymer increased. The XPS was in good correlation with the FTIR and the conductivity.

Conductive mechanism

According to the research of the predecessors,²⁹⁻³¹ the structure unit of PANI was tetramer of benzene: quinone = 3:1. The high electrical conductivity of PANI was achieved by doping and the most common dopant was proton acid. Proton acid was preferred to the N of quinone ring. When these N were protonated, the proton charge delocalized near aromatic ring and just like each N with a 0.5 positive charge. While the original benzene and quinone structure disappeared after proton acid doping. The proton of doping delocalized between two near N and all proton of delocalization connected, thus formed conjugated system with high electrical conductivity (Fig. 6).

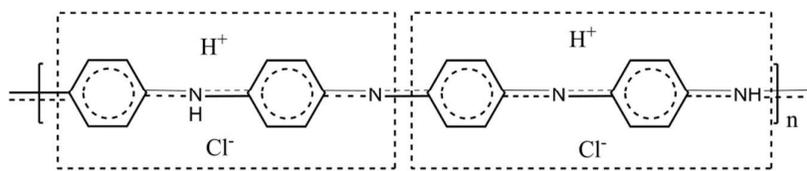


Fig.6. Mechanism of PANI doped by HCl.

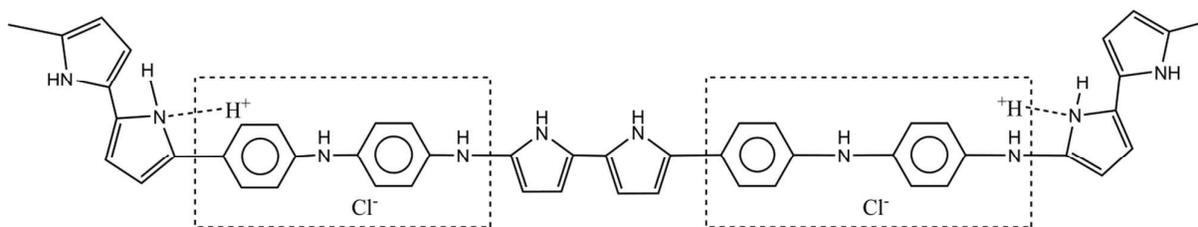


Fig.7. Mechanism of P(1An-3Py) doped by HCl.

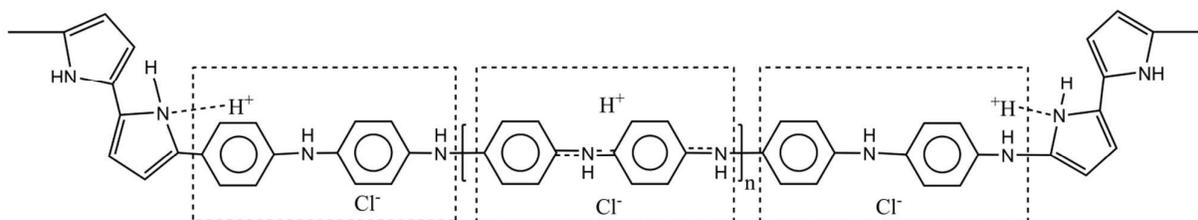


Fig.8. Mechanism of P(An-Py) doped by HCl with pre-polymerization.

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The conductivity of P(An-Py) increased with mol % of aniline and had a mutation when mol % of aniline was 50 %. Lim et al¹⁸ studied monomer reactivity ratio for aniline and pyrrole, $r_{An}=0.13$ and $r_{Py}=2.16$, respectively. It revealed that aniline tended to combine with pyrrole. When the content of aniline was low, i.e. P(1An-3Py), aniline almost connected with pyrrole directly or formed thumbnail aniline chain. On the one hand, aniline disrupted big conjugated system of pyrrole chain, thus made pyrrole chain non-conductivity. On the other hand, when aniline connected with pyrrole directly, the H⁺ of protonation aniline formed quasi-hydrogen bonding with N of adjacent pyrrole. It resulted from the strong electronegativity of N. Hence, the H⁺ had been fixed, and the conductive mechanism of aniline could not form and the conductivity of the copolymer was very low (Fig. 7).

Only by 15 min pre-polymerization, the electrical conductivity of P(1An-3Py) and P(1An-1Py) improved more than 3 orders of magnitude and 4 times, respectively. P(1An-3Py) formed many short aniline chains after pre-polymerization. As aniline could not connect with pyrrole directly, the H⁺ of protonation aniline could shift on the aniline chain freely and the mechanism of aniline could form (Fig. 8). N⁺ formed due to the strong interaction between the delocalized H⁺ of aniline chain and the lone pair electrons on the N. It was consistent with XPS. The high electrical conductivity of P(3An-Py) and P(1An-1Py) with no pre-polymerization could be attributed to the relatively high content of aniline. This meant copolymer formed many short aniline chains in the later stage reaction. The mechanism was similar to P(An-Py) with pre-polymerization. When the content of conductive aniline chain achieved a certain amount, the electrical conductivity of the copolymer could reach the same order of magnitude to the homopolymers.

Conclusions

In this paper, a highly conductive poly(aniline-co-pyrrole) was fabricated by proper pre-polymerization. The conductivity of P(1An-3Py) was only 1.28×10^{-5} S/cm, but it could be significantly improved 3 orders of magnitude after pre-polymerization for only 15 mins, and it could be further increased by an order of magnitude with longer pre-polymerization time. As for P(1An-1Py), the conductivity could be promoted more than 4 times, up to 0.265 S/cm and it could reach 0.331 S/cm with continued pre-polymerization. The conductivity of P(3An-1Py) was higher than that of the corresponding proportion blend. In a word, the electrical conductivity of P(An-Py) by proper pre-polymerization could achieve the same order of magnitude (10^{-1} S/cm) as their homopolymers, or even slightly higher than them, which had nothing to do with the molar ratio of two monomers.

The morphology and the size of copolymers were unchanged after pre-polymerization, however, the number of quasi-hydrogen bonding between N of pyrrole and adjacent free H⁺ of protonated aniline was greatly declined. Consequently, the number of free H⁺ of protonated aniline chain in copolymer significantly increased, leading to the increase of the carrier concentration and the electrical conductivity. This

method of properly pre-polymerization before copolymerization was a simple but effective method to markedly promote the conductivity of copolymer, which could be applied to other copolymers of aniline with other monomers and suitable for large-scale industrial production.

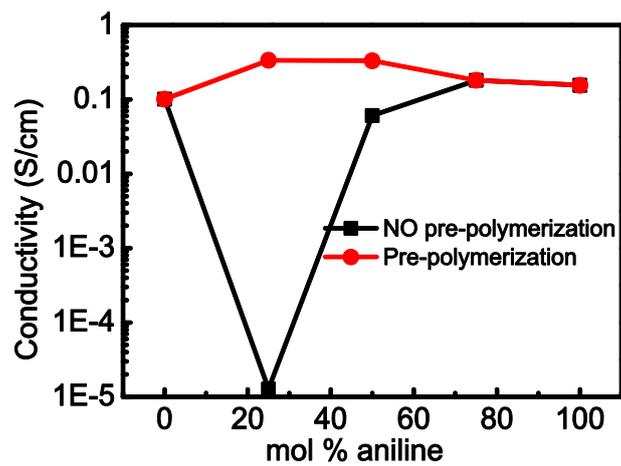
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