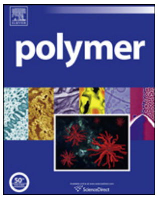
Polymer 50 (2009) 5065–5070

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Synthesis and application of conducting graft copolymer with viable processability

Youyi Xia [a,b], Qing Su [a], Yun Lu [a,*]

[a] Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China
[b] Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, PR China

ARTICLE INFO

Article history:
Received 9 July 2009
Received in revised form
16 August 2009
Accepted 24 August 2009
Available online 4 September 2009

Keywords:
Graft copolymer
Polypyrrole side chain
Processability

ABSTRACT

A soluble and processable conducting copolymer, poly(acrylonitrile-co-vinyl acetate)-graft-polypyrrole, noted as P(AN-co-VA)-g-PPY, has been synthesized successfully by graft polymerization of pyrrole in a colloid of P(AN-co-VA) within DMF/HCl solution. FTIR, ^{1}HNMR, EPR, DSC, GPC and elemental analysis results confirm that the polypyrrole side chains have grown onto P(AN-co-VA) chain backbones and the maximum PPY content reached 15.46 wt% under the experimental conditions. The conducting P(AN-co-VA)-g-PPY copolymer can be dissolved in organic solvents and easily processed to the film with strong stretching strength as high as 30 MPa and high conductivity as high as 10^{-1} S/cm. By control of the amounts of P(AN-co-VA) and pyrrole, the property adjustment between electronic conductivity and stretching strength of P(AN-co-VA)-g-PPY film can be achieved, which is of signality for different practice applications. As an example, the noble metal microstructures including tortuous Ag wire and hierarchically hedgehog-like Au sphere have been obtained via a reduction of silver nitrate or hydrogen tetrachloroaurate using the as-prepared conducting film without any additives, which may open up a thinking room for us to search new microstructures and new materials.

1. Introduction

Conjugated polymers which are conducting, semiconducting, light emitting or absorbing are essential ingredients in a host of advanced applications [1]. Such materials are usually accompanied by conformational rigidity, which tends to inhibit solubility that in turn impedes both molecular characterization and materials processing. The conducting polymers belonging to polyenes or polyaromatics such as polyacetylene, polyaniline, polypyrrole, polythiophene, poly(p-phenylene), poly(phenylene vinylene) classes have been studied extensively, but poor solubility in most of the common solvents and low thermoplasticity render the processing of conducting polymers research to prepare soluble forms of conducting polymers [2–4]. For conducting polymers with aromatic and heteroaromatic units, introducing some substituted groups either alkyloxy group or long-chain alkyl group into the monomer to make available soluble, well-defined products have already been reported [5–7]. However, the side chain substitution may cause thermal instability of the doped polymers [8], meanwhile, the free-standing conducting polymer films with flexibility could hardly obtained due to the rigidity of the main chains. By using electrochemical polymerization with potentiostatic or galvanostatic conditions, free-standing as well as self-supporting conducting polymer films of desired thickness have also been generated [9,10]. Unfortunately, such conducting polymer film is usually restricted in size due to the limit of electrode dimension. Another effort which has been made is the studies on composites containing conducting polymers and an inert polymer matrix [11–13], which offered a desirable processability for the composite but a relative low electrical conductivity. Recently, significant experimental attempt has been focused on chemical copolymerization between the heteroaromatic monomers and conventional polymers, mainly relating to the synthesis and characterization of the copolymers. Little has dealt with about the practicable processability, let-alone the mechanical strength character of the materials resulted from those copolymers [14–20]. Therefore, synthesizing new and processable conducting polymers as well as discovering the broad range of physical phenomena and chemical flexibility is still a challenge for us to further open up opportunities for new technological application.

In this work, we reported a facile grafting approach by choosing a commercial random copolymer, poly(acrylonitrile-co-vinyl acetate), as the main chain and a conducting polypyrrole with heteroaromatic units as the side chain. A processable conducting

---

[*] Corresponding author. Tel.: +86 25 83686423; fax: +86 25 83317761.
E-mail address: yunlu@nju.edu.cn (Y. Lu).

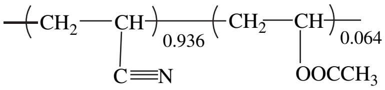
0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.08.039

polymer with high solubility in organic solvents has been synthesized and the homogeneous, reproducible thin film with conductivities as high as 10^{-1} S/cm and stretching strength as high as 30 MPa has been obtained. In addition, because of technological interests and applications for the aforesaid film, an example of potential use is discussed. For instance, Ag wires and Au spheres with hierarchical structure are further fabricated via a direct reduction of silver nitrate or hydrogen tetrachloroaurate using the as-prepared conductive film without any additives, which would be very useful in photography, catalysis, biological labeling, optoelectronics and so on.

2. Experimental part

2.1. Materials

Pyrrole (PY) monomer was purchased from Aldrich, and distilled under reduced pressure. $FeCl_3$ and *N,N′*-dimethylformamide (DMF) was analysis grade and used as received without further purification. P(AN-co-VA) containing 90 wt% AN units was supplied by Anqing Petrochemical Group of China, and the chemical structure of which is given as



$$-\!\left(CH_2-\underset{\underset{\displaystyle C\equiv N}{|}}{CH}\right)_{0.936}\!-\!\left(CH_2-\underset{\underset{\displaystyle OOCCH_3}{|}}{CH}\right)_{0.064}\!-$$

Also, it has a mensurated number average molecular weight (M_n) of 7.70×10^4 g/mol and polydispersity (M_w/M_n) of 1.47.

2.2. Synthesis and film-formation of P(AN-co-VA)-g-PPY copolymer

P(AN-co-VA) (0.20 g) was dissolved in DMF (20 mL) containing 280 μL of PY, to which hydrochloric acid solution (36.5 wt%) was added to ensure that the reaction system is maintained under acidic environment (pH = 3–5). Under N_2 atmosphere, the formed P(AN-co-VA) colloid was stirred for 6 h at room temperature. Then, according to the same method for polymerization of PY described in our previous work [21], 60 mL of aqueous solution containing 0.648 g of $FeCl_3$ oxidant was added in 30 min. After continuously stirring for 24 h, the P(AN-co-VA)-g-PPY copolymer is synthesized and can be collected via being filtered and dried in vacuum at 40 °C. The preparation of copolymer film was achieved by casting the solution containing the dissolved P(AN-co-VA)-g-PPY of 0.20 g in 20 mL DMF into the glass dish under environmental temperature. The pure P(AN-co-VA) film was also prepared according to the same experimental procedure for comparison. The typical film thickness was about 0.2 mm.

2.3. The grafted PPY content calculation of the P(AN-co-VA)-g-PPY copolymer

According to the results of element analysis and ^{1}H NMR, the grafted PPY content (W_{PPY}) in the P(AN-co-VA)-g-PPY copolymer was respectively estimated by the following two equations:

$$\frac{\dfrac{W_{PPY}\times 48}{M_{PY}-2}+\dfrac{90\%\times(1-W_{PPY})\times 36}{M_{AN}}+\dfrac{10\%\times(1-W_{PPY})\times 48}{M_{VA}}}{\dfrac{W_{PPY}\times 14}{M_{PY}-2}+\dfrac{90\%\times(1-W_{PPY})\times 14}{M_{AN}}}=\frac{W_c}{W_N} \qquad (1)$$

$$\frac{\dfrac{W_{PPY}\times 3}{M_{PY}-2}}{\dfrac{90\%\times(1-W_{PPY})\times 3}{M_{AN}}+\dfrac{10\%\times(1-W_{PPY})\times 3}{M_{VA}}}=\frac{I_1}{I_2} \qquad (2)$$

where M_{PY}, M_{AN} and M_{VA} are the molecular weights of PY, AN and VA, respectively. W_C and W_N are the weights of carbon and nitrogen in the P(AN-co-VA)-g-PPY copolymer. I_1 is the total integration of peaks at 7.0–7.1 and 6.5–6.8 ppm in the ^{1}H NMR spectrum of P(AN-co-VA)-g-PPY copolymer, while I_2 is the total integration of peaks at 1.8–2.4 and 3.0–3.3 ppm.

2.4. Preparation of noble metal microstructures

Without any additives added, two pieces of 1 cm^2 of P(AN-co-VA)-g-PPY film(10^{-1} S cm^{-1}) were immersed into 10^{-2} mol L^{-1} of $AgNO_3$ and $HAuCl_4$ aqueous solutions, respectively, for 48 h at room temperature. The noble metal microstructures were formed on the P(AN-co-VA)-g-PPY film and collected after being scraped from the surfaces of films with a knife, filtered, washed, and dried under environmental temperature.

2.5. Instruments and measurements

Molecular weight and its distributions, for the P(AN-co-VA)-g-PPY samples, were determined by gel permeation chromatography (Waters 1515) using a series of two linear Styragel columns HT3, HT4, and an oven temperature of 60.8 °C. Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30.8 °C) were used. The eluent was DMF + 1 g/L LiBr at a flow rate of 1.0 mL/min. A series of six polystyrene standards with molecular weights ranging from 800 to 400,000 g/mol were used for calibration. Scanning electron microscopy (SEM) and optical microscope experiments were performed with a JSM-5610 and XPT-7 microscope, respectively. Attenuated Total Reflectance Fourier-transform infrared (ATR-FTIR) spectra of film samples were obtained on a BrukerVECTOR22 spectrometer equipped with a narrow band mercury cadmium telluride detector. P(AN-co-VA) and P(AN-co-VA)-g-PPY samples were dissolved in DMSO-d_6 for ^{1}H NMR mensuration on a Bruker DR × 500 instrument. The elemental composition of P(AN-co-VA)-g-PPY was measured on the CHN-O-Rapid elemental analysis instrument. EPR signals were recorded on a Bruker EMX-10/12 Spectrometer (X-band) at room temperature. DSC measurements were carried out using Perkin–Elmer Pyris 1 with a scanning rate of 20 K/min in argon. The electrical conductivity of the P(AN-co-VA)-g-PPY films at room temperature was determined by using four-point probe technique. The mechanical properties were measured at room temperature using an Instron 4301 (Instron, USA) universal testing machine. Briefly, the film samples prepared according to the ASTM standard D 882-01(45 × 5 × 0.2 mm, length × width × thickness) were tested at a rate of 10 mm min^{-1}. Young's modulus was calculated from the linear part of the initial slope. For each sample, the test was performed 5 times. The result was averaged and a standard deviation was reported.

3. Results and discussion

3.1. Synthesis and characterization of the conducting P(AN-co-VA)-g-PPY copolymer

It is foremost important to design the reasonable structure and achieve the synthesis under appropriate polymerization conditions for a processable conducting polymer. As the selected main chains, P(AN-co-VA) copolymer offered the conformational flexibility and the reactive functional group (–CN), which could ensure the graft polymerization of heteroaromatic monomers onto the main chain and the solubility, viable processability and mechanical performance of final products. For pyrrole molecule, a five-member heteroaromatic monomer, 2 or 3 position of the pyrrole ring may occur a reaction similar to Gatterman reaction [22,23] with the nitrile group at acidic condition, which could provide a “site” for growing of conjugated side chains. In the graft polymerization of pyrrole to P(AN-co-VA) main chains, how to keep the acidic environment and resolving of P(AN-co-VA) matrix at the same time is crucial. In our case, a colloid of P(AN-co-VA) in DMF/HCl solution is the real reaction location. The details of the reactive process could be described as shown in Fig. 1, in which, as we noticed, it is the nitrile groups as the grafted sites that induct the pyrrole monomer and its cation radical to propagate gradually, getting the PPY conjugated side chains on the P(AN-co-VA) backbone.

The first evidence for the graft polymerization could be acquired from the structure characterization of P(AN-co-VA)-g-PPY film. The FTIR spectrum of P(AN-co-VA) (Fig. 2a, underside) shows the characteristic band at 2240 cm^{-1} for –CN stretching and 1740 cm^{-1} for –CO stretching. Besides above-mentioned bands of P(AN-co-VA), some characteristic absorption peaks (1540, 1294, 1155 and 1018 cm^{-1}) related to polypyrrole, corresponding to the pyrrole ring fundamental vibration and the =C–H in-plane vibration [24], respectively, can be observed in the spectrum of P(AN-co-VA)-g-PPY sample(Fig. 2a, upside). These results indicate spectroscopically that PPY is successfully grafted onto P(AN-co-VA) chains. Fig. 2b (underside) shows ^{1}H NMR spectrum of pure P(AN-co-VA), in which the characteristic peaks of P(AN-co-VA) is mainly located at 1.8–2.4 and 3.0–3.3 ppm. Compared with that of P(AN-co-VA) film, the ^{1}H NMR spectrum (Fig. 2b, upside) of P(AN-co-VA)-g-PPY dissolved in DMSO-d_6 solution displays two groups of new peaks at 7.0–7.1 and 6.5–6.8 ppm, respectively, which are assigned to hydrogens in PPY rings [17]. It is well known that pure PPY is insoluble in DMSO, while P(AN-co-VA)-g-PPY polymer can be dissolved in several organic solvents such as DMF and DMSO. The solution behavior of P(AN-co-

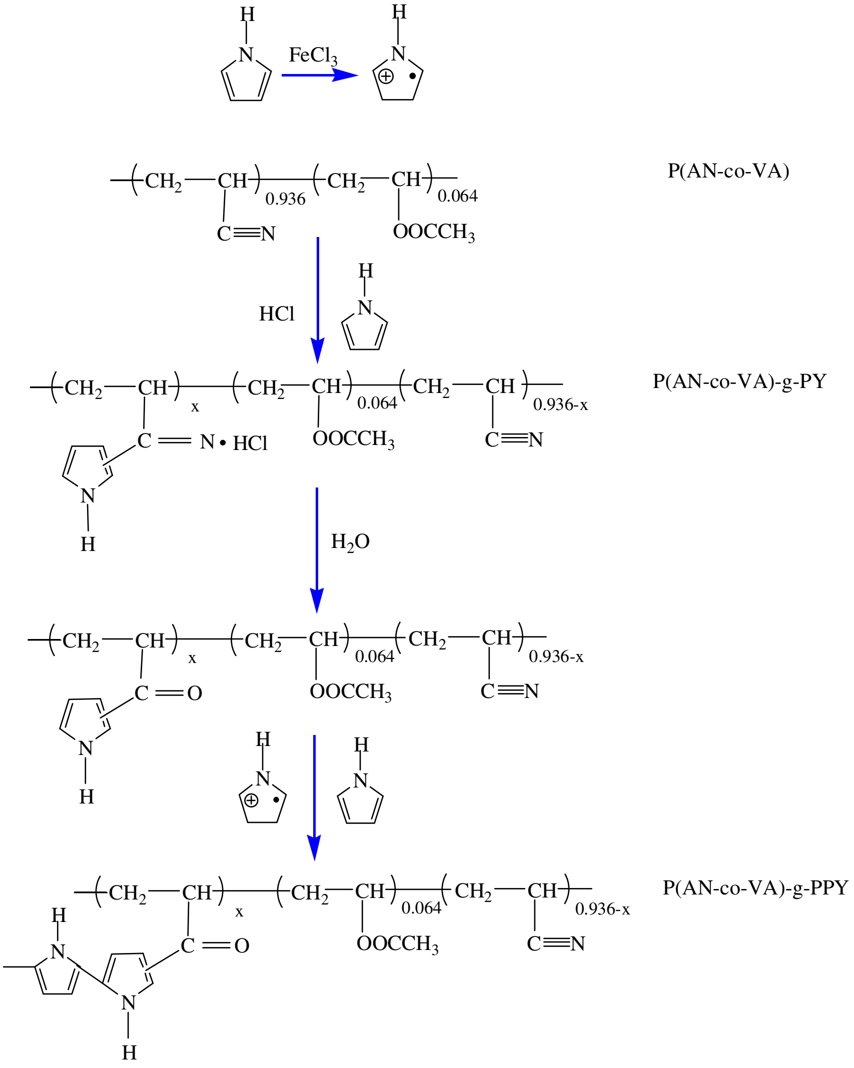


Fig. 1. Illustration of synthetic approach of P(AN-co-VA)-g-PPY polymer.

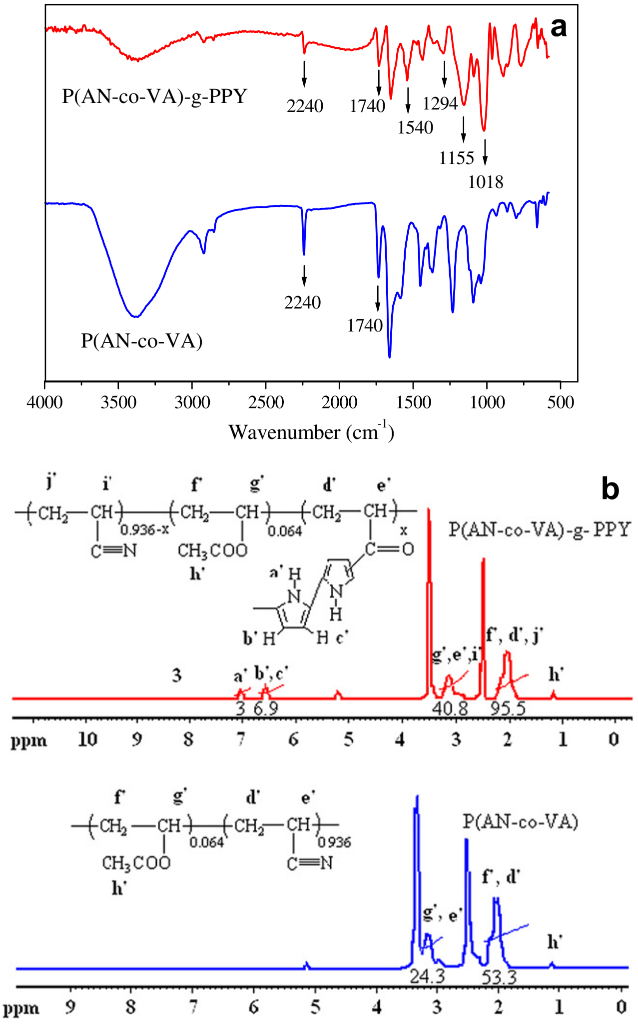


Fig. 2. FTIR (a), ^{1}HNMR (b) spectra of the P(AN-co-VA) and P(AN-co-VA)-g-PPY.

VA)-g-PPY as same as that of P(AN-co-VA) confirms further the successful grafting of PPY onto P(AN-co-VA).

The second evidence for the graft polymerization could be illustrated by EPR spectra of the samples before and after the graft reaction (Fig. 3). According to expectation, pure P(AN-co-VA) shows no EPR signal (Fig. 3a). By contraries, pure PPY powder exhibits a strongly sharp signal with a line width of 16.10 G (Fig. 3c), displaying a high concentration of cation radicals. Exhilaratingly, for the P(AN-co-VA)-g-PPY, we also observe an EPR signal ever if it is weak, indicating the existence of PPY cation radicals on P(AN-co-VA) chains (Fig. 3b). The EPR signal line width of 5.87 G for P(AN-co-VA)-g-PPY shows a large difference (10.23 G) compared with that of PPY powder, suggesting that the located chemical environment of the PPY cation radicals in the two different samples is rather dissimilar, and the interaction among the cation radicals in P(AN-co-VA)-g-PPY is weaker than that in PPY powder due to the presence of P(AN-co-VA) backbone. The value of spectrum splitting gene (g-value) of P(AN-co-VA)-g-PPY copolymer is 2.0041, very closing to the g-value of a free electron (2.0023), attesting to the strong activity of the cation radicals in P(AN-co-VA)-g-PPY copolymer.

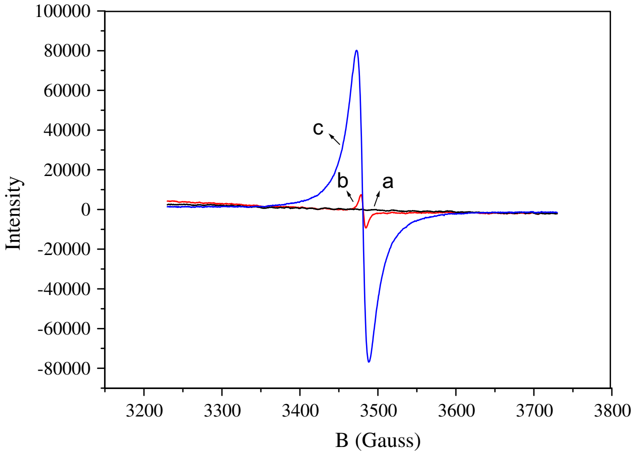


Fig. 3. EPR spectra of P(AN-co-VA) (a), P(AN-co-VA)-g-PPY (b) and PPY (c).

The third evidence for the graft polymerization could be supplied by measuring molecular weights of the P(AN-co-VA)-g-PPY copolymers. The molecular weights of the P(AN-co-VA) and P(AN-co-VA)-g-PPY polymers are listed in Table 1, respectively. As can be seen, the P(AN-co-VA)-g-PPY copolymers with different conductivities all have the increased molecular weights compared with pure P(AN-co-VA). Moreover, the more the amount of pyrrole added to polymerization systems, the higher the molecular weight as well as the conductivity of the copolymer, confirming well again the successful grafting of PPY onto P(AN-co-VA).

It is noticeable that although the measured molecular weight of P(AN-co-VA)-g-PPY increased comparing with that of P(AN-co-VA) owing to the graft of PPY, the PPY content in the copolymer should not be simply calculated from the molecular weights of P(AN-co-VA) and P(AN-co-VA)-g-PPY. This is because the molecular weight measured by GPC is a relative value, which is related to the effective size occupied by those polymer chains in solution or their hydrodynamic volumes [25]. The conjugated PPY macromolecule chain is rigid, which may result in the P(AN-co-VA)-g-PPY molecules with lower PPY content showing larger hydrodynamic volume. In such case, the molecular weight of P(AN-co-VA)-g-PPY measured by GPC may be not in accord with its absolute molecular weight. In this work, we estimated the grafted PPY content according to the results of element analysis and NMR. For the same samples, the data calculated from the two methods were relatively closed, as shown in Table 1. Considering that both the long relaxation time and the complex polymer conformational distribution in solution may make the peaks in the NMR spectrum broader or more complicated [26], we think that the graft ratio calculated from the result of

Table 1
Molecular weights of P(AN-co-VA)-g-PPY copolymers with different conductivities.

Samples	PY/P(AN-co-VA) (wt%)	Conductivity (S/cm)	M_n (g/mol)	M_w (g/mol)	PDI	PPY content (wt%)
a	–	–	7.70×10^4	1.13×10^5	1.40	–
b	67	10^{-5}	1.09×10^5	1.51×10^5	1.39	7.41[a]/6.86[b]
c	100	10^{-3}	1.39×10^5	1.84×10^5	1.32	10.52[a]/9.98[b]
d	134	10^{-1}	2.34×10^5	3.13×10^5	1.34	15.46[a]/15.02[b]

[a] Element analysis method.
[b] NMR method.

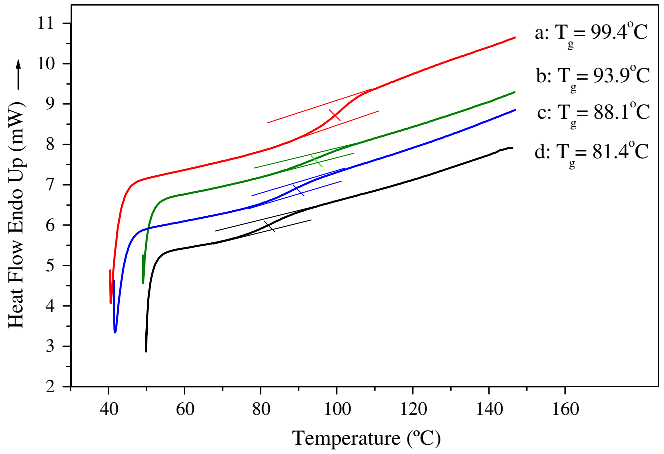


Fig. 4. DSC patterns of P(AN-co-VA) (a) and P(AN-co-VA)-g-PPY copolymers (b, c, d).

element analysis should be more appropriate than that from the integration of peaks in NMR spectrum.

Usually, polymer exhibits different physical properties before and after graft. In this work, the glass transition temperatures (T_g) of P(AN-co-VA) and P(AN-co-VA)-g-PPY copolymers are measured. As shown in Fig. 4, the P(AN-co-VA)-g-PPY copolymers (b, c, d) with different PPY contents all have the decreased T_g compared with pure P(AN-co-VA) (a) and the T_g decreases gradually with the increase of PPY content, which can be ascribed to the presence of side PPY chains. On the one hand, the considerable steric hinderance and stiffness of the side PPY chains will depress the P(AN-co-VA)-g-PPY main chain segments mobility and raise the T_g. On the other hand, the introduction of side PPY chains is to increase the number of chain end groups [27], therefore, an extra amount free volume is produced, which will tend to decrease the T_g. In our case, it is proposed that the latter is more prominent so that there is an effective lowering of T_g after graft copolymerization.

3.2. The morphology, properties and functionalization of the conducting P(AN-co-VA)-g-PPY copolymer film

According to the strategy used in this work to synthesize processable conducting P(AN-co-VA)-g-PPY polymer, a homogeneous and black polymer film is finally obtained by evaporation of DMF in the polymer solution on glass substrate. Fig. 5 shows the appearances of P(AN-co-VA) film before and after the graft reaction observed with the optical microscope and SEM. Compared with the slightly yellow pure and insulating P(AN-co-VA) film, the P(AN-co-VA)-g-PPY film displays a color of black with metallic shine and a surface as smooth as that of P(AN-co-VA) film. The film can be made easily in different size according to the demand and cut handily into various shapes depending on end use.

Table 2
Mechanical properties of P(AN-co-VA) and P(AN-co-VA)-g-PPY copolymer film with different conductivities.

Sample	Conductivity (S/cm)	Mechanical parameters		
		Strain at break (%)	Stress at break (MPa)	Young's modulus (MPa)
a	–	22.3 ± 0.2	31.5 ± 0.2	1257 ± 25
b	10^{-5}	18.5 ± 0.1	31.1 ± 0.2	1434 ± 20
c	10^{-3}	17.7 ± 0.1	31.0 ± 0.2	1504 ± 20
d	10^{-1}	16.1 ± 0.1	30.8 ± 0.2	1878 ± 20

The stretching properties and conductivities of pure P(AN-co-VA) and P(AN-co-VA)-g-PPY film are shown in Table 2. Compared to no information of stretching properties given in some analogous conductive polymer film [28–30], satisfactorily, it can be found that P(AN-co-VA)-g-PPY film keeps the good stretching strength similar to pure P(AN-co-VA) film, assuring its possibly practical applications. With the conductivity increasing, Young's modulus of these P(AN-co-VA)-g-PPY films also increases, while the strain at break decreases gradually. The results indicate that these P(AN-co-VA)-g-PPY films have bigger rigidity, due to the rigid PPY segments on P(AN-co-VA) chains which make conformation of total chains being changed more difficultly under stress. In terms of conductivity, pure P(AN-co-VA) film is non-conductive, while P(AN-co-VA)-g-PPY film has the maximum conductivity of 10^{-1} S cm^{-1}, which is higher than some analogous conductive conjugated polymers composites [28,31]. In addition, this value is constant after aging 180 days at room temperature, suggesting the good environmental stability in the presence of oxygen. Certainly, this value is slightly lower than the corresponding neat PPY particles, which can be ascribed to the presence of insulated P(AN-co-VA) chains in the film. From the experimental data in Table 2, it can also be found that the performance adjustment between conductivity and stretching properties can be achieved for idiographic demand. For instance, in order to make the P(AN-co-VA)-g-PPY solution spun to antistatic fiber, the moderate conductivity may be selected, thus the spun fiber can afford good flexibility and elongation.

Based on the as-prepared conductive P(AN-co-VA)-g-PPY film, its functionalization has been tried to expand its practicality. For instance, without any additives, the well-defined microstructures of noble metals such as Ag wire and Au sphere have been obtained

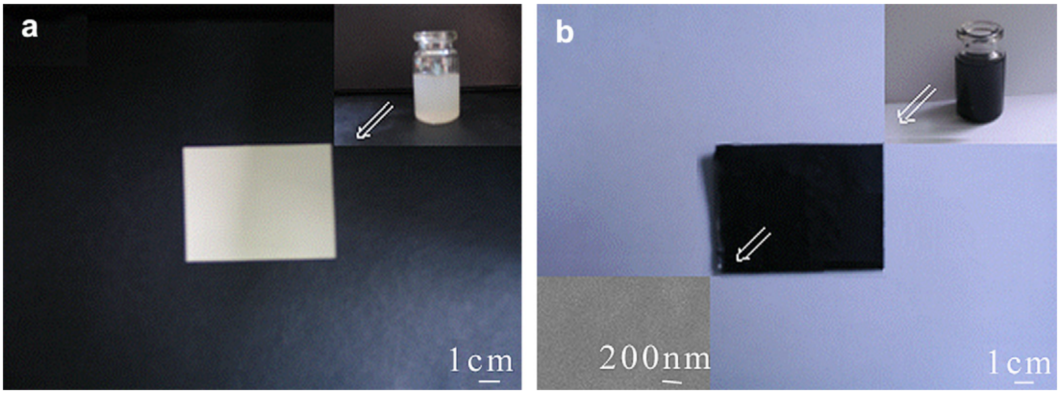


Fig. 5. The appearances of the insulating P(AN-co-VA) film (a) and P(AN-co-VA)-g-PPY film (b) with a conductivity of 10^{-1} S cm^{-1} [the left inset is the SEM image of P(AN-co-VA)-g-PPY film].

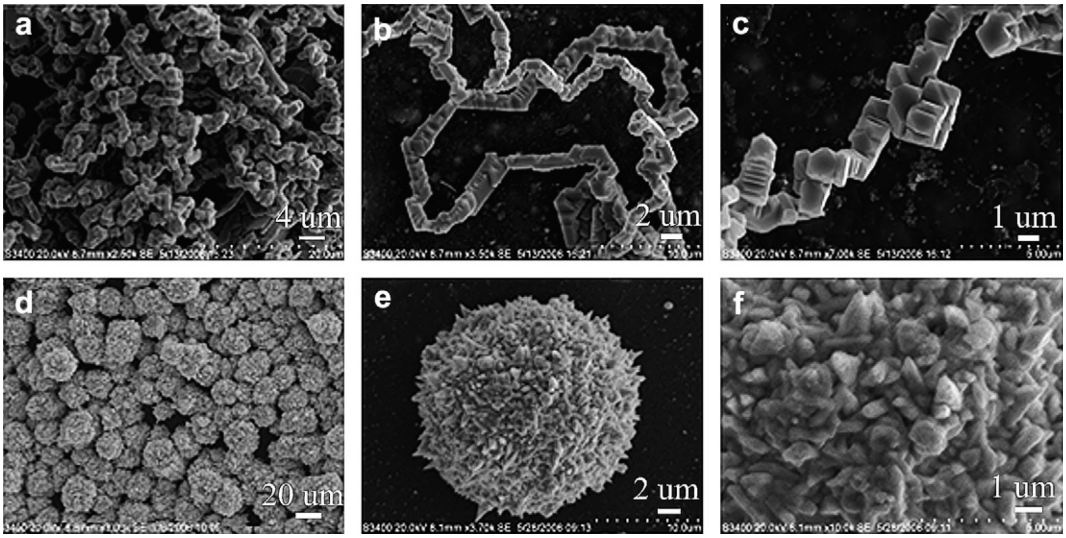


Fig. 6. SEM images of the synthesized silver microwires (a, b, c) and Au microspheres with hierarchical structure (d, e, f) using the as-prepared conductive film (10^{-1} S cm^{-1}).

via the reduction of silver nitrate or hydrogen tetrachloroaurate using the as-prepared conductive film. It can been seen from Fig. 6 that tortuous Ag microwires and hierarchically hedgehog-like gold microspheres can be formed respectively after the conductive polymer film (10^{-1} S/cm) was immersed directly into $AgNO_3$ and $HAuCl_4$ aqueous solutions for 48 h at room temperature without any added reducing agent or structure-directing agent, which can be ascribed to the reduction of the doped polypyrrole side-chains in the grafting copolymer according to postsynthesis reductive mechanism of conductive polymers [32]. Obviously, it is interesting that why Ag (I) is reduced to tortuous microwires, while Au (III) is reduced to hierarchically hedgehog-like microspheres with particles and pricks as building blocks under experimental conditions. It is suggested that the side PPY chains of the conducting copolymer film play dual reducing and structure-directing roles during the formation of Au microspheres with hierarchical structure. Detailed formation process and the potential use of the as-prepared noble metal microstructures are being investigated and will be reported in the next work.

4. Conclusions

In summary, we developed a simple approach for synthesis of a novel P(AN-co-VA)-g-PPY conducting copolymer with soluble and processable property, which can be scaled up easily for producing industrial amounts of the polymer. Via graft polymerization of pyrrole in a colloid of P(AN-co-VA) within DMF/HCl solution, the polypyrrole side chains can grow onto the P(AN-co-VA) backbone by the reaction of pyrrole rings and functional –CN groups, which has been confirmed by FTIR, ^{1}HNMR, EPR, GPC and elemental analysis. The cast P(AN-co-VA)-g-PPY film exhibits an attractive integrated performance including high conductivity of 10^{-1} S/cm, strong stretching strength of 30 MPa, and easy handling in air or cutting into different shapes. By control of the amounts of P(AN-co-VA) and pyrrole, the performance adjustment between conductivity and stretching strength can be achieved, which is extremely significant for various practical applications such as EMI shielding, electrochromic displays, microelectronic devices and surface anti-electrostatic. In particular, the conductive film can be used to further prepare the noble metal microstructures with well-defined and controlled morphologies, which would be very useful in photography, catalysis, biological labeling, optoelectronics and so on.

Acknowledgements

We are grateful for the support from the National Natural Science Foundation of China (Nos. 20574034, 50773030) and Testing Foundation of Nanjing University.

References

[1] Skotheim TA, Reynolds JR. Handbook of conducting polymers. 3rd ed. BocaRaton, FL: CRC Press; 2007.
[2] Rumbau V, Pomposo JA, Eleta A, Rodriguez J, Grande H, Mecerreyes D, et al. Biomacromolecules 2007;8:315–7.
[3] Nguyen MT, Kasai P, Miller JL, Diad AF. Macromolecules 1994;27:3625–31.
[4] Ito S, Murata K, Teshima S, Aizawa R, Asako Y, Takahashi K, et al. Synth Met 1998;96:161–3.
[5] Jen KY, Oboodi R, Elsenbaumer RL. Polym Mater Sci Eng 1985;53:79–81.
[6] Sugimoto R, Takeda S, Gu HB, Yoshino K. Chem Express 1986;1:635–9.
[7] Sato M, Tanaka S, Kaeriyama K. Chem Commun 1986;6:873–8.
[8] Koizumi H, Dougauchi H, Ichikawa T. J Phys Chem B 2005;109:15288–90.
[9] Shi GQ, Jin S, Xue G, Li C. Science 1995;267:994–6.
[10] Yang XM, Dai TY, Zhu ZX, Lu Y. Polymer 2007;48:4021–7.
[11] Levine K, Iroh JO. J Mater Chem 2001;11:2248–52.
[12] Fan ZF, Wang Z, Duan MR, Wang JX, Wang SC. J Membr Sci 2008;310:402–8.
[13] Park HS, Kim YJ, Hong WH, Lee HK. J Membr Sci 2006;272:28–36.
[14] Park YH, Shin HC, Lee YK, Son YK. Macromolecules 1999;32:4615–8.
[15] Li NY, Shan D, Xue HG. Eur Polym J 2007;43:2532–9.
[16] Tarkuc S, Sahin E, Toppare L, Colak D, Cianga I, Yagci Y. Polymer 2006;47: 2001–9.
[17] Bae WJ, Kim KH, Jo WH. Macromolecules 2005;38:1044–7.
[18] Hosseini SH, Dabiri M, Ashrafi M. Polym Int 2006;55:1081–9.
[19] Lienkamp K, Wegner G. Macromol Rapid Commun 2007;28:1112–4.
[20] Kızılcan N, Öz NK, Ustamehmetoğlu B, Akar A. Eur Polym J 2006;42:2361–8.
[21] Yang XM, Zhu ZX, Dai TY, Lu Y. Macromol Rapid Commun 2005;26:1736–40.
[22] Zhao YL, He SQ, Xu CD. Pandect of heterocyclic chemistry. China: High Education Press; 1992. p. 163.
[23] Michael JSD, Gerald Jr JG. J Am Chem Soc 1966;88:1349–52.
[24] Yang XM, Dai TY, Lu Y. Polymer 2006;47:441–7.
[25] Hiemenz PC, Lodge TP. Polymer chemistry. Boca Raton: CRC Press; 2007.
[26] Walczak RM, Leonard JK, Reynolds JR. Macromolecules 2008;41:691–700.
[27] Brydson JA. Plastics materials. London: Newnes-Butterworths; 1975.
[28] Park YH, Park CR. Synth Met 2001;118:187–92.
[29] Bhat NV, Sundaresan E. J Appl Polym Sci 1991;42:1615–22.
[30] Park YH, Han MH. J Appl Polym Sci 1992;45:1973–82.
[31] Ng SC, Chan HSO, Xia JF, Yu WL. J Mater Chem 1998;8:2347–52.
[32] Zhang X, Manohar SK. J Am Chem Soc 2005;127:14156–7.