

STUDIES ON THE POLYPYRROLE/POLYELECTROLYTE MOLECULAR COMPOSITES

BAO Jingseng (宝净生), XU Chaochou (徐朝涛) and CAI Wei (蔡 玮)

(Institute of Chemistry, Academia Sinica, Beijing 100080)

ABSTRACT

The polyelectrolyte of propane sulfonate (PS) grafted PPTA copolymers ———PPTA-PS, PPTA[O]-PS, PPTA[C]-PS were prepared and used as electrolyte in the process of electrochemical polymerization of pyrrole to form the molecular composite polypyrrole (PPY)/Polyelectrolyte.

The preparation and liquid crystalline property of three kinds of polyelectrolyte, the electrical conductivity, mechanical properties, SEM and thermoproperties of PPY/polyelectrolyte are presented in detail.

INTRODUCTION

It is well known that polypyrrole (PPY) film synthesized by electrochemical polymerization shows high electrical conductivity with good stability in air,^[1] but is hard and brittle with very poor flexibility.^[2] Some methods were used to improve its mechanical properties.^[3] We have recently obtained the conducting composite films from polypyrrole and polyurethane, these films maintained super-high flexibility of polyurethane matrix, and high stability and conductivity.^[4,5]

In this paper, the improvement of mechanical properties of PPY by electrochemical preparation of conductive composite films from pyrrole (PY) and polyelectrolytes of PPTA system are studied in detail. Poly (p-phenylene-terephthalamide) (PPTA), copolymer of PPTA which contains 4,4'-diaminodiphenyl ether (PPTA [O]) and 4,4'-diaminodiphenyl methane (PPTA [C]) were obtained by low temperature polycondensation. Soluble polyelectrolytes of PPTA system were synthesized by graft copolymerization of PPTA and PPTA copolymers with 1,3-propane sulfone. The poly (p-phenyleneterephthalamide propane sulfonate) (PPTA-PS) and PPTA [O]-PS, PPTA [C]-PS were used as electrolytes in the electrochemical polymerization of PY. The molecular composites of PPT/PPTA-PS, PPY/PPTA[O]-PS and PPTA[C]-PS with better conductivity and tensile strength were obtained.

EXPERIMENTAL

1. Materials

Pyrrole was purified by distillation over NaOH under N₂, b. p. 130—131°C /760 mm Hg.; Dimethyl sulfoxide (DMSO) was purified by vacuum distillation over calcium hydride under N₂, b. p. 58—59°C /6mmHg and finally dried over 4Å molecular sieve.; Sodium hydride (NaH) is suspended in paraffin (contains

This work was supported by the National Natural Science Foundation of China.

Received February 22, 1992

80%) and 1, 3- propane sultone (m.p. 31 — 33 °C) was used without further purification.

PPTA, PPTA[O] and PPTA[C] were synthesized in our laboratory with inherent viscosity of 2.90, 3.66 and 2.44 respectively.

2. Characterization of composites conductivity

The electrical conductivity was measured by four-point probe method. The liquid crystalline picture was taken by polarized microscope. The mechanical properties were measured on Instron-1122 instrument. IR spectra were taken by Perkin-Elmer 180 spectrophotometer. The thermal properties were measured under N₂ atmosphere on the Du Pont Type 1090 Analyzer coupled to the TGA model with the heating rate of 20 °C / min., X-ray diffraction spectra were obtained by using the diffractometer with CuK α -radiation.

3. Synthesis of polyelectrolytes

For the preparation of PPTA-PS, a 500-ml three-necked flask equipped with condenser, drying tube, nitrogen inlet tube dropping funnel and stirrer was used. The apparatus was swept by dry nitrogen, 0.025M (0.75g) of sodium hydride and 150 ml of DMSO were placed in the flask at 30 °C. The temperature was raised to 70 °C after 20 minutes and the mixture was maintained at 70 — 75 °C under nitrogen with stirring. About 40 minutes was required for the sodium hydride to be consumed completely. 0.025M amide unit (3.0g) of PPTA was added at 30 °C for 4hrs. Then, 0.025M (3.05g) of 1,3- propane sultone was added and the mixture was stirred at 40 °C for 24 hrs. The PPTA-PS was precipitated in THF, filtered, and washed several times with THF. The isolated product was dried in a vacuum oven. PPTA[O]-PS. and PPTA[C]-PS were prepared in the similar way.

4. Preparation of conductive composite films

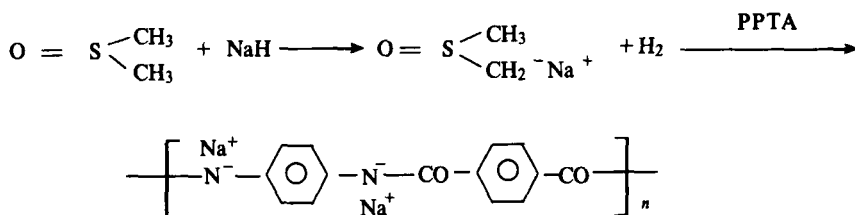
Electrochemical polymerization was carried out in acetonitrile (ACN)/ethylene glycol (EG) (50/50) solution which contain 0.2M of freshly distilled pyrrole and one of the polyelectrolytes such as PPTA-PS, PPTA[O]-PS and PPTA[C]-PS was used as the supporting electrolyte. The one compartment glass cell is equipped with a Nickel counter electrode. The current densities 3 — 5 mA/cm² and reaction time 10 — 30 minutes.

The PPY/PPTA-PS, PPY/PPTA[O]-PS and PPY/PPTA[C]-PS conductive composite films were rinsed with distilled water and then dried at 50 °C, and the flexible conductive composite films were obtained.

RESULTS AND DISCUSSION

1. Preparation of the polyelectrolytes

Firstly, the metalation reaction of PPTA was carried out in DMSO with the sodium methylsulfinylcarbanion(I) solution which was formed from the reaction of powdered sodium hydride with excess of dry DMSO. The scheme of the metalation reaction can be represented by



Low molecular weight PPTA ($\eta_{\text{inh}} = 2.90$) was used. The color of the reactants mixture changed from the suspension of PPTA in DMSO to the transparent deep red solution of metalated PPTA in DMSO after 4 hrs. The time required for the metalation reaction depends on several factors such as the reactant concentrations, the porosities of PPTA samples, and particle sizes. A metalation time of 4 hrs was enough to dissolve PPTA in the solution containing sodium methylsulfinylcarbanion.

Secondly, N-substituted PPTA (poly-p-phenyleneterephthalamide propane sulfonate) was obtained from the reaction of metalated PPTA and 1, 3-propane sultone in DMSO at 40 °C according to the following scheme:

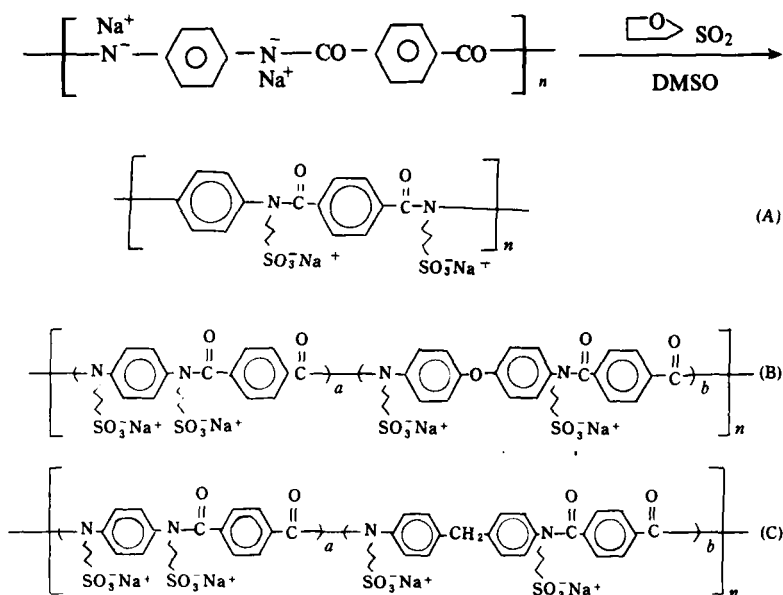


Fig. 1 Structure of Polyelectrolytes (a=80%, b=20%)
(A) PPTA-PS ; (B) PPTA[O]-PS; (C) PPTA[C]-PS

The preparation of PPTA[O]-PS and PPTA[C]-PS are the same as PPTA-PS and their structures are shown in Fig. 1 which showed that the content of PPTA[O] and PPTA[C] in the copolymers is 20% respectively, and the conc. H_2SO_4 solution of PPTA[O] and PPTA[C] has lyotropic liquid crystalline behaviour. They showed nematic textures when the solution concentration above their critical concentration (C^*).

The IR spectra of the polyelectrolytes are shown in Fig. 2. which showed that the absorption peaks at 1630 cm^{-1} , 1550 cm^{-1} and 1320 cm^{-1} were attributed

to amide I, II and III bands, respectively. The strong absorptions at 1200 and 1045 cm^{-1} were due to S=O stretching of side groups in aralkylated polymers. But the absorption of 3170 cm^{-1} (N-H stretching) disappeared, which represented the N-H of main chain in the PPTA, PPTA[O] and PPTA[C] polymers were substituted by propanesulfonic acid according to Fig.1 reaction. Three kinds of polyelectrolytes were prepared.

2. Preparation of the polypyrrole/polyelectrolyte composites

As it was reported^[5], mixture of organic solvents was better for use to prepare the polypyrrole (PPY). Polypyrrole/polyelectrolyte composites were prepared by the electrochemical polymerization of pyrrole in acetonitrile (ACN)/ ethylene glycol (EG) containing 0.2M of freshly distilled pyrrole and polyelectrolytes (PPTA-PS, PPTA[O]-PS, PPTA[C]-PS) as supporting electrolyte with Ni electrode at current density 3—5 mA/cm^2 . The experimental results were shown in Table 1.

Table 1 Conductivity and mechanical properties of PPY/polyelectrolyte composites

Composite film	Conductivity (S/cm)	Tensile strength (MPa)	Elongation at break (%)
PPY/PPTA-PS	2.08	79.95	7.3
PPY/PPTA[O]-PS	1.57	79.63	6.0
PPY/PPTA[C]-PS	2.64	79.33	6.7

The composite were homogeneous films which can be peeled off from the electrode surface. These flexible self-supporting composite films are much easier to peel off than pure PPY films.

3. Conductivity and mechanical properties of PPY/polyelectrolyte composite films

The conductivity and mechanical properties of PPY/polyelectrolyte composite films depend on the electropolymerization conditions, such as concentration of PY, different kinds and amount of electrolytes, different kind of solvents, current density and time of electropolymerization etc. Effect of main factors during the electropolymerization for preparing the PPY/PU (polyurethane) composites were studied in detail^[5]. Based on our previous work, three kinds of PPTA system polyelectrolyte were synthesized which were used for supporting electrolytes in the electropolymerization reaction. Three kinds of PPY/PPTA system polyelectrolyte composite were prepared. The stress-strain curves for conductive composites were shown in Figure 3. The experimental results showed that the three kind composite films with best mechanical properties, the tensile strength and elongation of PPY/PPTA system polyelectrolytes composite films were around 80 Mpa and

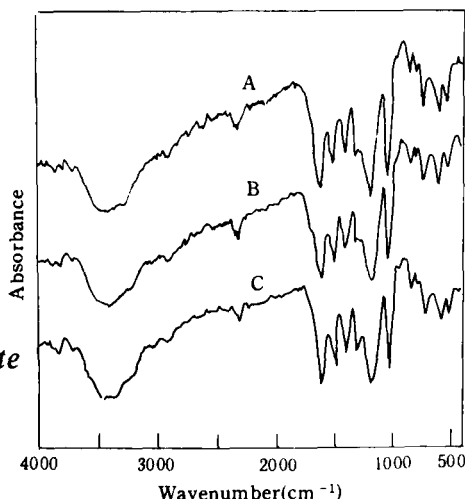


Fig. 2 IR spectra of the polyelectrolytes

(A --- PPTA-PS, B --- PPTA[O]-PS
C --- PPTA[C]-PS)

ranged from 6—8% respectively. The mechanical properties of composites were much better than that of pure polypyrrole.

Table 1 shows the conductivity and mechanical properties of PPY/PPTA system polyelectrolyte of molecular composites. Experimental results show that the three kind composites all have excellent mechanical properties and electrical conductivity when the special PPTA system polyelectrolytes are used as the supporting electrolyte for preparing PPY/polyelectrolyte molecular composites.

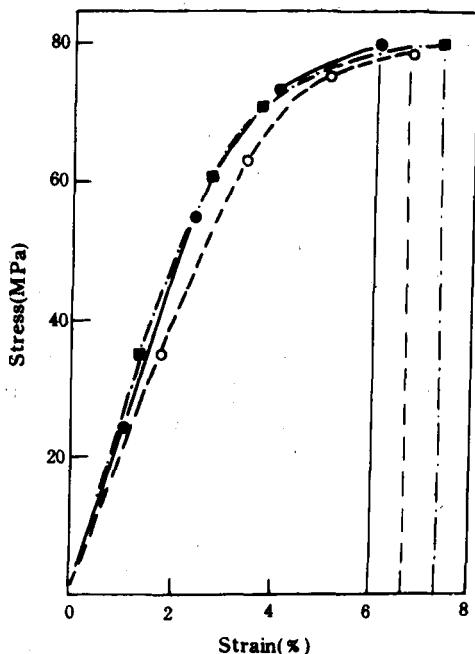


Fig. 3 Stress-strain curves of molecular composites

(■) PPY/PPTA-PS; (●) PPY/PPTA(O)-PS; (○) PPY/PPTA(C)-PS

4. Thermostability of PPY/polyelectrolyte composite films

The results of thermogravimetric analyses (TGA) are shown in Table 2.

Table 2 Thermostability of PPY/polyelectrolyte composite films

Temp. (°C)	PPY and composites	PPY and PPY/polyelectrolyte films			
		PPY	PPY/PPTA-PS	PPY/PPTA(O)-PS	PPY/PPTA(C)-PS
10	Wt. loss (%)	310	400	360	380
20		400	520	480	500

The TGA measured at heating rate of 20 °C /min. and the temperature for weight loss of 10% of PPY/PPTA-PS, PPTA/PPTA(O)-PS and PPTA/PPTA(C)-PS are 400 °C, 360 °C and 380 °C respectively.

5. SEM of PPY/polyelectrolyte composite films

The SEM of PPY/polyelectrolyte composite films are shown in Figure 4. The SEM pictures of A are faces to solution and B are faces to electrode. SEM

pictures of A showed typical morphology of polypyrrole.

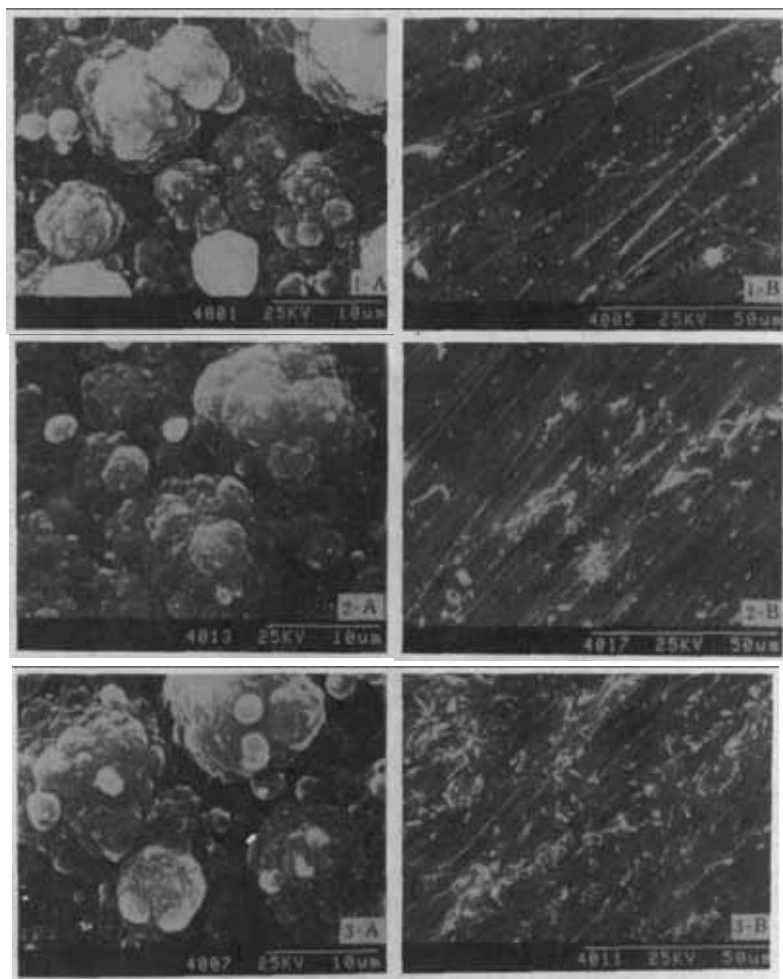


Fig. 4 SEM of PPY/polyelectrolyte composites 1) PPY/PPTA-PS; 2) PPY/PPTA(C)-PS; 3) PPY/PPTA(O)-PS A: Face to solution; B: Face to electrode

CONCLUSION

1. Three kinds of polyelectrolyte PPTA-PS, PPTA-(O)-PS and PPTA(C)-PS were obtained by the metalation of PPTA, PPTA-(O), PPTA-(C) with NaH, then grafted with 1,3- propane sultone.
2. Three kinds of molecular composite PPY/PPTA-PS, PPY/PPTA(O)-PS, PPY/PPTA(C)-PS with the PPTA-PS, PPTA(O)-PS, PPTA(C)-PS electrolyte on Ni slice working electrode.
3. The mechanical properties are better than those using low molecular weight electrolyte. The tensile strength of the PPY/poly-electrolyte are 79.33 — 79.95

Mpa, and elongation at break are 6.0 — 7.3%.

4. The electrical conductivity of the composite films are 1.5 — 2.64 S/cm.

Keywords :

Polypyrrole; Poly (p — phenylene terephthalamide); Polyelectrolyte; Conductive composite

REFERENCES

- [1] Bi, X.T.; Yuo, Y.; Dan, Y.; Young, Q. and Quin, R., *Polymer Communications*, **1985**; (6), 445.
- [2] (a) Diaz, A.F.; Kanazawa, K.K. and Gardini, G.P., *J. Chem. Soc., Chem. Commun.*, **1979**, 635.
(b) Diaz, A.F. and Hall, B.S., *IBM J. Res. Develop.*, **1983**, 27, 342.
(c) Tourillon, G. and Garnier, F., *J. Electroanal. Chem.*, **1982**, 135, 173.
- [3] Paoli, M. D.; Waltman, R.J.; Diaz, A.F. and Bargon, J., *J. Polym. Sci. Polym. Chem. Ed.*, **1985**, 23, 1687.
- [4] Bi, X.T. and Pei, Q.B., *Synth. Met.*, **1987**, 133, 301.
- [5] Bao, J.S.; Daroux, M. L.; Litt, M.; Yeager, E. B., *Chinese J. Polym. Sci.*, **1990**, 8 (2) 149.