

Polymer Communication

Water soluble polyaniline and its blend films prepared by aqueous solution casting

Y.H. Geng^a, Z.C. Sun^b, J. Li^a, X.B. Jing^{b,*}, X.H. Wang^a, F.S. Wang^a

^a*Polymer Chemistry Laboratory, CAS and SINOPEC, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China*

^b*Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China*

Received 12 October 1998; received in revised form 14 January 1999; accepted 30 January 1999

Abstract

Polyaniline (PAN) was doped with phosphonic acid containing hydrophilic tails. The solubility of the doped PAN in water was controlled by changing the length of hydrophilic chain in the dopant. When poly(ethylene glycol) monomethyl ether (PEGME) with molecular weight $M_w = 550$ was used as the hydrophilic chain of the dopant, the doped PAN was entirely soluble in water. The film cast from aqueous solution showed good electrochemical redox reversibility. Aqueous solution blending of PAN with poly(ethylene glycol) (PEG, $M_w = 20\,000$) and poly(*N*-vinyl pyrrolidone) (PVP, $M_w = 360\,000$) was achieved. Percolation threshold of the composite film was lower than 3 wt.%. Electrical conductivity of the composite film was in the range of 10^{-1} – 10^{-5} S cm⁻¹, depending on molecular weight of the acid and the content of PAN in the composite. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; Hydrophilic dopant; Phosphonic acid

1. Introduction

Polyaniline (PAN) is a well-known conducting polymer. It shows unique features such as electric conductivity, chemical or electrochemical redox reversibility and thus it exhibits a great potential to be used in many fields, such as electrode materials [1], static electricity dissipation [2], metal anti-corrosion and marine-fouling prevention [3,4]. Because PAN is insoluble or infusible, great efforts have been made to realize its solution processing or melt processing by improving its solubility in organic solvent and its miscibility with other melt-processable polymers. Two methods were adopted. One was to introduce flexible substituents onto the benzene rings or nitrogen atoms [5–12] of PAN. The other was doping PAN with functional organic acid such as camphorsulfonic acid (CSA) and dodecyl benzene sulfonic acid (DBSA) [13–17]. In the latter case, based on the improved processability of PAN caused by the solubility of the dopants in organic solvents or miscibility with conventional polymers, conducting composites of PAN

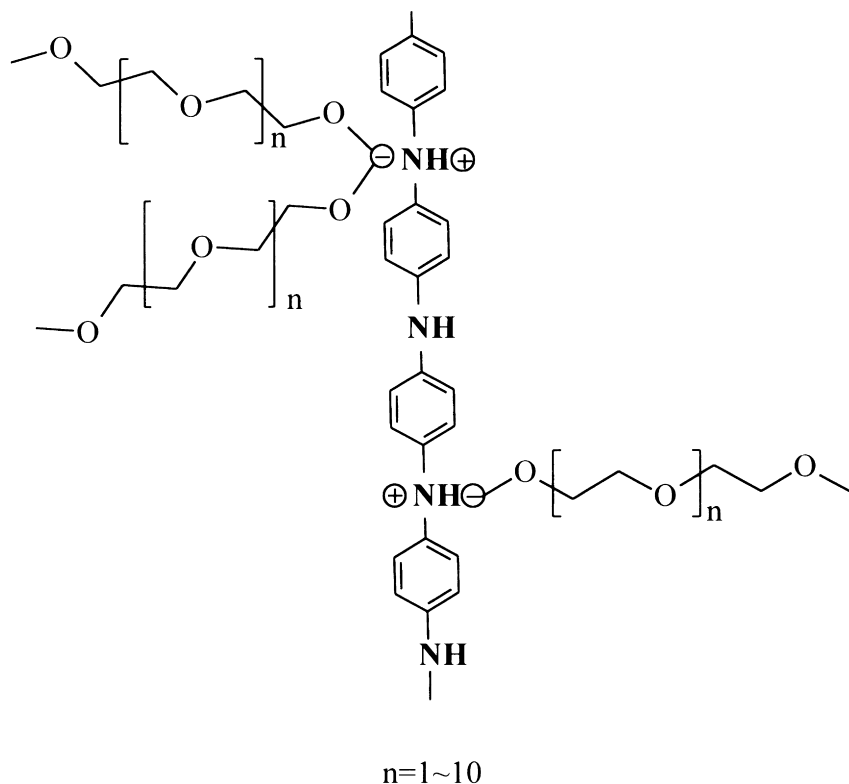
with other insulating polymers were made with quite low conduction percolation threshold [18,19].

Recently, owing to the consideration of environmental protection, preparation of water-soluble PAN is required, especially when PAN is used as a component of aqueous coatings. Two methods were reported to prepare water soluble or dispersible PAN. One was grafting a sulfonic or phosphoric acid group onto the benzene ring or nitrogen atom [6–12]. The other was synthesizing PAN in the presence of a water-soluble polymeric stabilizer [20–24]. Obviously, these methods were time-consuming and expensive. Few reports were found in the literature to employ water-soluble dopants.

In this article, we introduced hydrophilic chains into phosphoric acid to synthesize water-soluble dopants and to prepare the doped PAN with the molecular structure shown in Scheme 1. Because of the hydrophilic nature of the poly(ethylene glycol) monomethyl ether (PEGME), the doped PAN was soluble in water or dispersible in the solution of water-soluble polymers. Further, conducting blends or composites of PAN with water-soluble polymers such as poly(ethylene glycol) (PEG) and poly(vinyl pyrrolidone) (PVP) were prepared. Their morphological structure and properties in the form of casting films were examined as a function of the host-polymer, the content of PAN in

* Corresponding author. Tel.: + 86-431-5682801; fax: + 86-431-5685656.

E-mail address: xbjing@ns.ciac.jl.cn (X.B. Jing)



Scheme 1. Structure of PA-doped PAN.

the composites and the length of hydrophilic tails in the dopant.

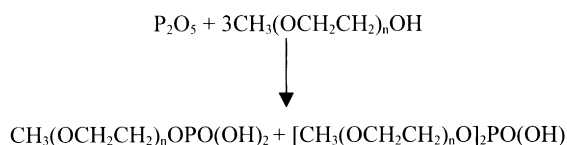
2. Experiments

2.1. Materials

PEG ($M_w = 20\,000$), PVP ($M_w = 360\,000$) and PEGMEs were purchased from Aldrich. Diethylene glycol monomethyl ether (DEGME), P_2O_5 and benzene were of analytical grade. PAN was prepared in our own laboratory [25]. The chemicals to synthesize PAN were of analytic grade and used as received without further purification.

2.2. Synthesis of the acidic phosphonate and preparation of PAN film

Three PEGMEs, DEGME, PEGME-350 and PEGME-550, in which 350 and 550 stand for the molecular weight of PEGME, were used as starting materials. Corresponding phosphonic acids (PA) prepared were designated as PA-DEG, PA-350 and PA-550.



Scheme 2. Scheme of synthesis of organic acidic phosphonate.

To prepare the PA, 0.3 mol PEGME in 50 ml benzene was added into a dispersion of 0.1 mol P_2O_5 (14.16 g) in 50 ml benzene. The mixture was heated to $70^\circ C$ and stirred for 3 h. After removing residual P_2O_5 and solvent, a colorless transparent liquid was obtained. It was a mixture of mono- and bi-hydroxyl acids with a molar ratio of 1:1 as shown in Scheme 2. So the average molecular weight of the dopants was estimated to be 253, 596 and 896 g mol^{-1} for PA-DEG, PA-350 and PA-550, respectively.

The solutions were prepared by adding PAN–PA mixture (molar ratio is 1:0.5), PEG or PVP into distilled water and by stirring at room temperature for 72 h. Their concentrations are 10.0, 5.0 and 5.0 g per 100 ml, respectively. The (PEG or PVP)/PAN/PA composite solution was prepared by adding PAN/PA solution slowly into PEG or PVP solution under stirring. The films were prepared by casting the solutions onto glass substrates and drying at room temperature. The samples were vacuum dried at $40^\circ C$ for 24 h prior to measurements.

2.3. Instruments

UV–Vis spectra were recorded on UV-3000 spectrometer. Differential scanning calorimetry (DSC) experiments were carried out on Perkin–Elmer-DSC 7 thermal analysis system under nitrogen atmosphere at heating and cooling rate of $5^\circ C\text{ min}^{-1}$. Wide angle X-ray diffraction (WAXD) patterns were recorded on Rigaku X-ray diffractometer at room temperature at a scan rate of 2° min^{-1} . Cyclic

Table 1
Solubility of PAn doped with the phosphonic acids in various solvents ('i': insoluble, 'p': partially soluble and 's': completely soluble)

Dopant	Acetone	Ethanol	Chloroform	Water	NMP
PA-DEG	i	i	i	i	s
PA-350	i	i	p	p	s
PA-550	p	p	s	s	s

voltammogram curves were recorded on the Model 283 Potentiostat/Galvanostat from EG&G Princeton Applied Research at a scan rate of 20 mV min⁻¹. Electrical conductivity was measured by a standard four-probe method.

3. Results and discussion

Solubilities of PAn doped with PA-DEG, PA-350 and PA-550 are shown in Table 1. PAn doped with PA-DEG is only soluble in NMP, a polar solvent. With increasing length of hydrophilic chain in the dopant, solubility of the doped PAn increases. PAn/PA-350 is not soluble in water but is dispersible in aqueous solution of PEG ($M_w = 20\ 000$) when the PEG concentration is up to 10 wt.%. Electrical conductivity of the film cast from this dispersion is about 1.7×10^{-2} S cm⁻¹. When PA-550 is used, doped PAn is completely soluble in water, NMP and chloroform, partially soluble in ethanol and acetone. Free-standing films can be cast from water, chloroform and NMP solutions. These indicate that we can prepare water-soluble PAn/PA by increasing the length of hydrophilic chain in the dopant. UV-Vis spectra of the films are shown in Fig. 1. In the spectra of the films cast from chloroform, acetone, ethanol and water solutions, there are three peaks at 325, 430 and 750–800 nm, characteristic of doped PAn. In the spectrum of the film cast from NMP solution, there is a shoulder at around 620 nm in addition to absorption bands at 325, 430 and above 900 nm, indicating incomplete doping of PAn. This is caused by the

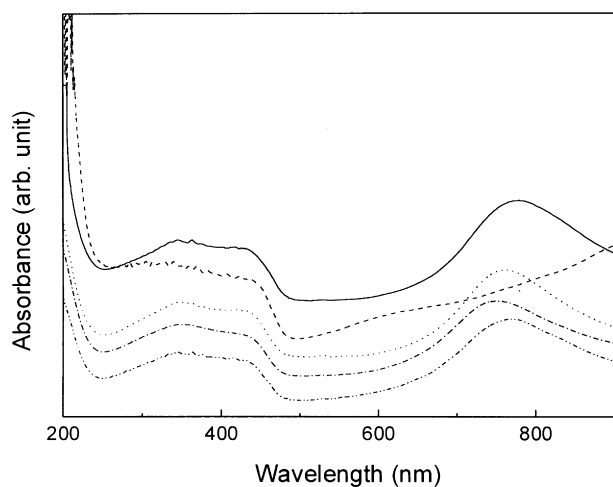


Fig. 1. UV-Vis spectra of PAn/PA-550 films cast from chloroform (.....), ethanol (-----), acetone (.....), NMP(-----) and water (—) solutions.

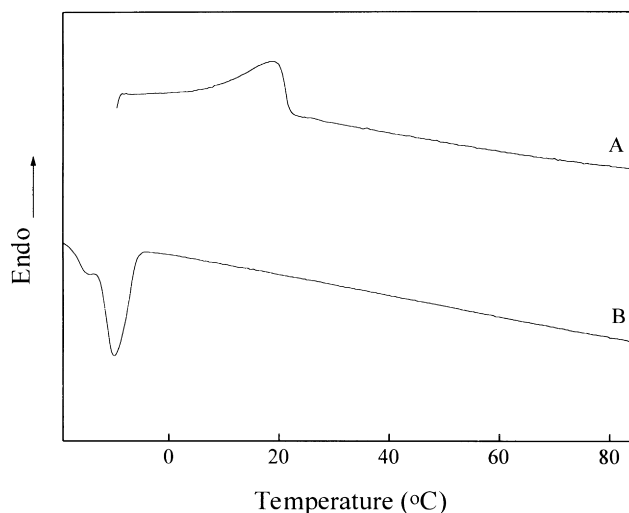


Fig. 2. DSC thermograms of PAn/PA-550 at a scan rate of 5°C min⁻¹ under N₂: A—heating curve; B—cooling curve.

weak basicity of NMP and weak acidity of the dopant, and often observed in NMP solution of doped PAn [26]. There is a reversible phase transformation in DSC spectra of PAn/PA-550 at 19.1 and -9.8°C for heating and cooling curve, respectively, due to melting and crystallization of hydrophilic PEGME segments in the dopant (Fig. 2). Similar phase transformation was also observed by Zheng et al. [27,28] for PAn grafted by alkyl segments on nitrogen atoms.

Cyclic voltammograms (CV) of PAn/PA-550 film were recorded using PA-DEG as electrolyte ($0.4\ \text{mol l}^{-1}$, Fig. 3). There are two couples of redox peaks, similar to PAn doped with inorganic protonic acid [29,30]. The small difference between the oxidation and the reduction potential of the second redox process indicates a good electrochemical reversibility of PAn/PA-550. The CV curves at the 10th and 5th cycle almost superimpose indicating a good electrochemical stability of PAn/PA-550. PAn/PA-350 also shows a similar electrochemical behavior.

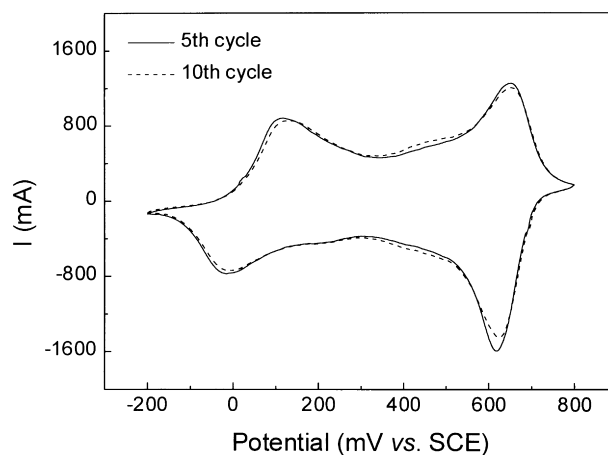


Fig. 3. Cyclic voltammogram of PAn/PA-550 film, Pt plate was used as working and counter-electrode, scan rate: 10 mV S⁻¹.

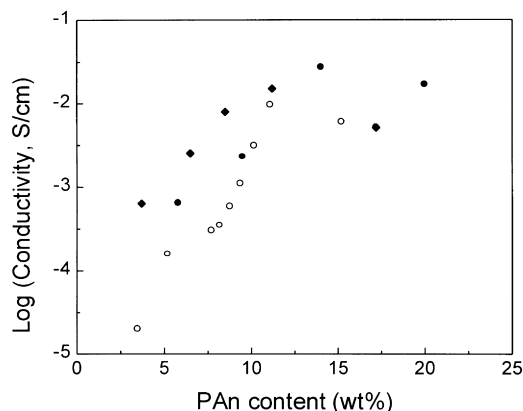


Fig. 4. Dependence of electrical conductivity of PEG/PAn/PA-350 (○), PEG/PAn/PA-550 (●) and PVP/PAn/PA-500 (◆) composite films on PAN content.

Based on the improved solubility of PAn/PA-350 and PAn/PA-550 in water, we can prepare composite films of PAn and other water soluble polymers, such as PEG and PVP, by solution blending and casting. The dependence of electrical conductivity of the composite film on PAN content is shown in Fig. 4. When PAN content is lower than 10 wt.%, the conductivity of the films increased with increasing PAN content, whereas at a PAN content of above 10 wt.% the conductivity was almost independent of it. Electrical conductivity of PEG/PAn/PA-550 film containing 3.5 wt.% PAn and PVP/PAn/PA-550 film containing 3.7 wt.% PAn is about 1.2×10^{-5} and $6.5 \times 10^{-4} \text{ S cm}^{-1}$, respectively, indicating a good dispersion of PAn in the composite and a conducting network can be formed at a low PAN content. Thus percolation threshold of PEG/PAn/PA-550 and PVP/PAn/PA-550 composite should be lower than 3 wt.%. When PEG is used, the composite film changes to semi-transparent with increasing PEG content because of crystallization of PEG, observed by

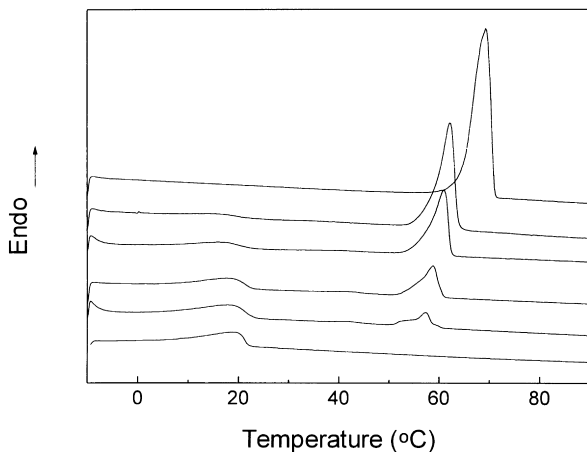


Fig. 5. DSC thermograms of PEG/PAn/PA-550 composite, from top to bottom, PEG content (wt.%): 100, 60, 40, 20, 10, 0.

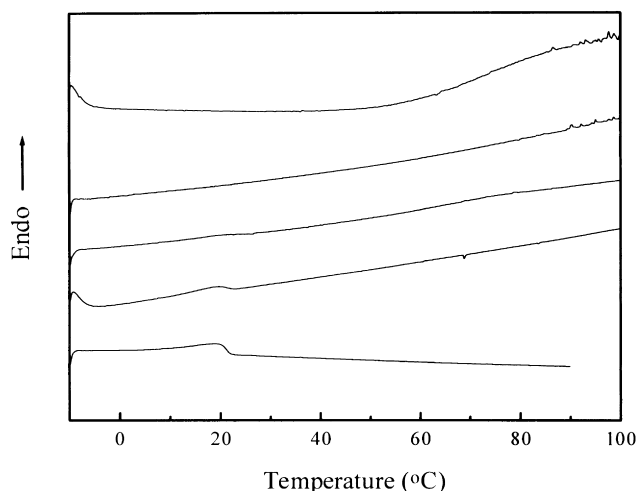


Fig. 6. DSC thermograms of PVP/PAn/PA-550 composite, from top to bottom, PVP content (wt.%): 100, 70, 50, 33, 0.

polarized optical microscopy. PVP/PAn/PA films are green and transparent at any content of PVP.

In DSC thermograms of PEG/PAn/PA-550 composite (Fig. 5), there are two endothermic peaks at 15–20 and 55–70°C, corresponding to melting of PAn/PA-550 and PEG, respectively. The melting point of PEG in the composite decreases sharply compared with pure PEG, whereas the normalized enthalpy of PEG melting in the composite changes little and only decreases 13% in the composite containing 10 wt.% PEG. From X-ray measurements, crystal structure of PEG in the composite is similar to that of pure PEG. However, normalized enthalpy of PAn/PA-550 in the composite decreases rapidly with increasing PEG content. Thus PEGME segments in PA-550 significantly interact with PEG chains. At the temperature close to the PEG melting point, PEGME segments can act as solvent or plasticizer and lower the melting point of PEG. In DSC thermograms of PVP/PAn/PA-550 composite (Fig. 6), the endothermic peak of PAn/PA-550 decreases more rapidly with increasing PVP content than in the case of PEG/PAn/PA-550 composite. The peak disappears for PVP/PAn/PA-550 containing 50 wt.% PVP. This indicates that PEGME segments in the dopant distribute themselves uniformly in the composite with PVP because of the non-crystalline nature of PVP.

4. Conclusions

Water-soluble PAn can be prepared by doping PAn with organic PA containing PEG segments. The solution cast films of PA doped PAn exhibit good conducting and electrochemical properties. The composite films of PAn with PEG or PVP prepared by solution blending show low conductivity percolation threshold (<3.0 wt.%).

Acknowledgements

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

References

- [1] Gustafsson G, Cao Y, Heeger AJ, et al. *Nature* 1992;357:478.
- [2] Trivedi DC, Dhawan SK. In: Prasad PN, Nigrm JK, editors. *Frontier of polymer research*, New York: Plenum Press, 1992. pp. 419.
- [3] Deberry DW. *J Electrochem Soc, Electrochem Sci Tech* 1985;132:1022.
- [4] Wang X-H, Li J, Zhang J-Y, Sun Z-C, Yu L, Jing X-B, Wang F-S, Sun Z-X, Ye Z-J. *Synth Met* 1999.
- [5] Clark RL, Yang SC. *Synth Met* 1989;29:E337.
- [6] Wang XH, Li J, Wang X, Jing XB, Wang FS. *Synth Met* 1995;69:147.
- [7] Yue J, Epstein AJ. *J Am Chem Soc* 1990;112:2800.
- [8] Wei XL, Wang YZ, Long SM, Bobeczko C, Epstein AJ. *J Am Chem Soc* 1996;118:2545.
- [9] Chen SA, Hwang GW. *Macromolecules* 1996;29:5950.
- [10] Chen SA, Hwang GW. *J Am Chem Soc* 1995;117:10 055.
- [11] Chan HSO, Ho PKH, Ng SC, Tan BTG, Tan KL. *J Am Chem Soc* 1995;117:8517.
- [12] DeArmitt C, Armes SP, Winter J, Uribe FA, Gottesfeld S, Mombourquette C. *Polymer* 1993;34:158.
- [13] Cao Y, Heeger AJ. *Synth Met* 1992;48:91.
- [14] Heeger AJ. *Synth Met* 1993;55–57:3471.
- [15] Tzou K, Gregory RV. *Synth Met* 1993;53:365.
- [16] Yang CY, Cao Y, Smith P, Heeger AJ. *Synth Met* 1993;53:293.
- [17] Virtanen E, Laakso J, Ruohonen H, Väkiparta K, Järvinen H, Jussila M, Passiniemi P, Osterholm J-E. *Synth Met* 1997;84:113.
- [18] Tallman DE, Wallace GG. *Synth Met* 1997;90:13.
- [19] Han MG, Im SS. *J Appl Polym Sci* 1998;67:1863.
- [20] Aldissi M, Armes AP. *Prog Org Coatings* 1991;19:21.
- [21] Vincent B, Waterson J. *J Chem Soc, Chem Commun* 1990;9:683.
- [22] Liu J-M, Yang SC. *J Chem Soc, Chem Commun* 1991;21:1592.
- [23] Sun LF, Liu J-M. *Polym Prep* 1992;33(2):379.
- [24] Liu CF, Maruyama T, Yamamoto T. *Polym J* 1993;25:363.
- [25] Geng YH, Sun ZC, Li J, Jing XB, Wang FS. *Synth Met* 1998;96:1.
- [26] Geng YH, Li J, Jing XB, Wang FS. *Synth Met* 1997;77:97.
- [27] Zheng WY, Levon K, Laakso J, Osterholm J-E. *Macromolecules* 1994;27:7754.
- [28] Zheng WY, Levon K, Taka T, Laakso J, Osterholm J-E. *J Polym Sci Part B—Polym Phys* 1995;33:1289.
- [29] Wang BC, Tang JS, Wang FS. *Synth Met* 1986;13:329.
- [30] Huang W-S, Humphrey BD, MacDiarmid AJ. *J Chem Soc, Faraday Trans 1* 1986;82:2385.