ELSEVIER

Polymer 41 (2000) 6931–6934

polymer

Polymer Communication

Enhanced electrical conductivity of polypyrrole prepared by chemical oxidative polymerization: effect of the preparation technique and polymer additive

H.C. Kang, K.E. Geckeler*

Laboratory of Applied Macromolecular Chemistry, Department of Materials Science and Engineering, Kwangju Institute of Science and Technology, 1 Oryong-dong, Puk-gu, Kwangju 500-712, South Korea

Received 15 November 1999; received in revised form 6 January 2000; accepted 8 February 2000

Abstract

The electrical conductivity of chemically prepared polypyrrole in aqueous solution was found to be strongly dependent on the preparation technique and polymer additive. Owing to the hygroscopic nature of polypyrrole, it is essential to remove residual water. Accordingly, the conductivity can be enhanced by about two orders of magnitude when using a preparation technique that includes a washing treatment with organic solvents and drying under vacuum at elevated temperatures to attain maximum removal of water. Thus, the electrical conductivity of polypyrrole is affected not only by reported factors such as the ratio of oxidant to pyrrole, reaction temperature, and reaction time, but also by the preparation technique. Additionally, a significant enhancement of the conductivity up to 90 S cm^{-1} by using of poly(ethylene glycol) as an additive during the polymerization could be achieved. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Additive; Polypyrrole; Electrical conductivity

1. Introduction

Although polypyrrole (PPY) has been prepared by electrochemical polymerization, the alternative approach of chemical oxidative polymerization has been also pursued, because it allows mass production within a short time. Chemical preparation of PPYs by using various conditions (change of solvent, oxidant, dopant, ratio of oxidant to pyrrole, reaction temperature, reaction time, etc.) has been reported in the literature [1,2]. Especially in the aqueous system, PPY showed a high conductivity when the ratio of ferric chloride to pyrrole was reduced, however, the yield was then also decreased. In addition, the reaction temperature has to be low (0–5°C) to obtain good conductivities, if the ferric salt is used.

Recent studies also showed that the addition of polymers can influence the conductivity by sterical stabilization of the polypyrrole chains [1]. To this end, water-soluble polymers of molecular masses over 20,000 g mol^{-1} such as methyl cellulose, poly(vinyl alcohol-*co*-acetate), poly(ethylene oxide), poly(vinylpyrrolidone), poly(2-vinylpyridine), poly(vinylmethylether), and others, were studied. When using these additives, conductivities of a broad range (1×10^{-9}–12 S cm^{-1}) have been obtained [1]. Specifically, for poly(ethylene oxide) with a molar mass of 130,000 g mol^{-1} a conductivity of 2×10^{-3} S cm^{-1} was found [3]. Further, low-molecular surfactants such as sodium dodecylbenzene sulfonate, sodium alkylnaphthalene sulfonate, and sodium alkylsulfonate were investigated [4–6].

The influence of air and oxygen-free atmosphere has been also studied recently for the application of polypyrrole as a solid electrolyte for capacitors [7]. In this investigation, covalently bonded oxygen was detected by FT-IR spectroscopy. Interestingly, no difference in the thermostability of oxidized and native PPY was found. In line with these studies, the thermal stability of the electrical conductivity was also found to be enhanced by using an antioxidative dopant [8]. Thus, the conductive stability was increased by aromatic sulfonates such as 2-hydroxy-5-sulfobenzoic acid up to 150°C in air. The pronounced effect is explained and confirmed by IR spectroscopy with deuterized PPY by a thermal stabilization mechanism involving the suppression of proton dissociation from the 1-position and maintaining the conjugated structure by supplying protons from the dopant.

Very recently, other approaches, e.g. the use of binary

---

* Corresponding author. Tel.: + 82-62-970-2316; fax: + 82-62-970-2338.

E-mail address: keg@kjist.ac.kr (K.E. Geckeler).

PII: S0032-3861(00)00116-6

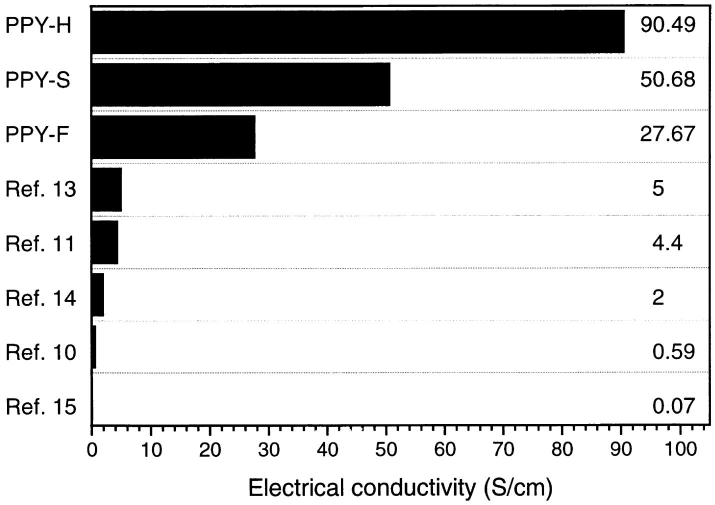

Fig. 1. Comparison of electrical conductivities of polypyrroles reported in literature which were prepared by chemical oxidative polymerization using ferric chloride without additive and with additive (PPY-H).

solvent systems consisting of boron trifluoride/ethyl ether for the synthesis of high-quality polypyrrole, have been described [9]. However, so far the effect of low-molecular telechelics such as bifunctional poly(oxyethylene) derivatives has not been studied.

In this study, we focus on the effect of the preparation technique and of a polymer additive on the electrical conductivity of PPY when ferric chloride is used as an oxidant in the aqueous phase.

2. Experimental

2.1. Materials

Pyrrole (Acros, 99%) was distilled under reduced pressure prior to use. Poly(ethylene glycol) (PEG 1000) was a gift from Clariant, Switzerland. Anhydrous ferric chloride (Sigma), 37% hydrochloric acid (Junsei), methanol (Junsei), and acetone (Oriental Chemical Inc.) were used as received.

2.2. Preparation of PPY using organic solvent treatment (PPY-S)

$FeCl_3$ (1.42 g, 8.75 mmol) was dissolved in 50 ml of 1 M HCl under nitrogen at 0°C. After 30 min, distilled pyrrole (1.22 ml, 17.56 mmol) was added in one step. The color of the mixture changed quickly first to green and then to black. After another 30 min, the mixture was filtered and the residue was washed thoroughly with methanol and then with acetone several times. The final product was dried in vacuo at 40°C for at least 12 h. Yield: 0.163 g (14%).

2.3. Preparation of PPY using freeze-drying (PPY-F)

The same procedure was used as for PPY-S, however, the product was washed with distilled water instead of organic solvents and then dried by freeze-drying. Yield: 0.119 g (10.1%).

2.4. Preparation of PPY using a polymer additive (PPY-H)

The same procedure was used as for PPY-S, however, the polymerization was carried out in the presence of poly(ethylene glycol) (PEG 1000) and then dried under vacuum (see Fig. 2).

2.5. Polymer characterization

The synthesis of PPY was monitored by IR spectrometry (Perkin–Elmer, IR 2000 series). IR spectra of the PPYs obtained were identical to those reported: stretching vibration ($3420\ cm^{-1}$, broad band) and bending vibration ($1445\ cm^{-1}$) of N–H bond, stretching vibration ($3126\ cm^{-1}$, broad band) of C–H bond, stretching vibration ($1539\ cm^{-1}$) and bending vibration ($1445\ cm^{-1}$) of C=C bond, stretching vibration ($1190\ cm^{-1}$) of C–N bond, stretching vibration ($1290\ cm^{-1}$) of C–C bond, and bands ($1398\ cm^{-1}$ and $1167\ cm^{-1}$) of the pyrrole ring.

The amount of residual water and the mass loss were determined by TGA (Thermal Analyst, TA2100 series).

2.6. Electrical conductivity measurements

After pressing a pellet of PPY, the conductivities of PPYs prepared by the different techniques were measured using the four-probe method (Bio-Rad Microscience, Hall measurement system HL5500) at room temperature (RT). PPY-F: 27.67 ± 0.40 ($n = 3$); PPY-S: 50.68 ± 0.14 ($n = 3$).

3. Results and discussion

Oxidative chemical polymerization in the presence of HCl and ferric chloride was used for the preparation of

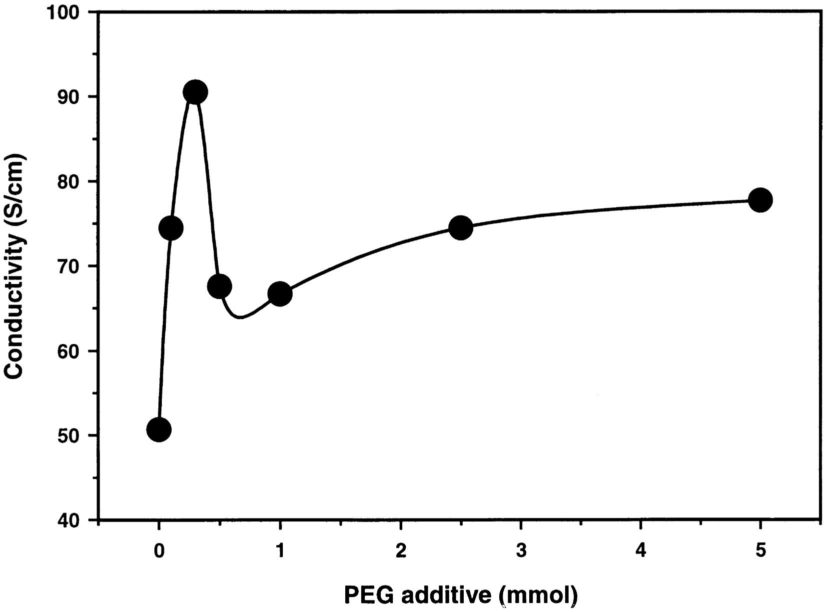

Fig. 2. Conductivity of polypyrrole prepared by chemical oxidation as a function of poly(ethylene glycol) additive.

the polypyrrole samples as reported previously [10]. Different procedures after finishing the reaction were employed. In the first technique, the polymer was washed thoroughly with methanol, then with acetone several times, and finally dried in vacuo at elevated temperature (PPY-S). For comparison, samples using the same procedure, however, replacing the organic solvents by water and final freeze-drying (PPY-F) were prepared.

The electrical conductivities of PPY-S and PPY-F showed salient differences due to the different preparation methods described above (Table 1). In the drying method, conductivities increased in the following order: vacuum drying at above RT after solvent treatment > freeze-drying > vacuum drying at RT without washing treatment. This confirms that the degree of water removal in the polymer is an important factor for the electrical conductivity value obtained for PPY in aqueous media. The exposure of PPY-F to water is longer because the removal speed of water is slower when using the freeze-drying method, and also the polymer is in contact with an aqueous environment while drying. When insoluble PPY was treated by easily volatile solvents such as methanol and acetone, most of the water was removed due to its miscibility with these solvents. Then the solvents including residual water were evaporated by drying in vacuo at elevated temperature. When the vacuum drying method was applied, temperature and washing treatment did affect the conductivity of PPY, as shown by the data in Table 1.

The residual solvent content of PPY-S and PPY-F was found to be 6.07% at 150°C and 4.84% at 129°C, respectively. Although a comparison between the residual solvent contents for two polymers is difficult, the temperatures of decomposition were found to be saliently different (180°C for PPY-S and 150°C for PPY-F). The effect on the solvent removal rate may also explain the data of the real decomposition of polymer at 250°C, as the mass loss after evaporating the residual solvent was determined to be 5.03% for PPY-S and 5.73% for PPY-F, respectively. However,

Table 1
Comparison of experimental conditions and properties of polypyrroles prepared by different techniques (1 M HCl (50 ml), $FeCl_3$ (1.42 g, 8.75 mmol), pyrrole (1.22 ml, 17.56 mmol), reaction time: 30 min)

	PPY[a]	PPY-F	PPY-S	PPY-H[b]
Washing treatment	None	Water	Methanol, acetone	Methanol, acetone
Drying method	in vacuo	Freeze drying	in vacuo	in vacuo
Drying temp. (°C)	~25	−20/~25	~40	~40
Thermal stability (mass loss at 250°C in %)	–	10.57	11.10	10.09–11.31
Solvent content (%)	–	4.84[c]	6.09[d]	5.82–6.58[d]
Conductivity ($S\ cm^{-1}$)	0.59	27.67	50.68	66.67–90.49

[a] Data from Ref. [10].
[b] In the presence of PEG additive.
[c] Mass loss at 129°C. For most samples, except for PPY-F, the mass loss between 120°C and 170°C is negligible due to solvent evaporation.
[d] Mass loss at 150°C.

although the material was dried additionally at high temperatures in vacuo, it was difficult to remove completely residual water from PPY. This can be traced back to its hygroscopic nature when it was exposed to atmospheric laboratory conditions previously. Reportedly, oxygen defects induced in the presence of water during the oxidative polymerization of pyrrole lead to a reduction of the conductivity of PPY [11]. Consequently, the electrical conductivity can be enhanced by optimizing the preparation method aiming at a minimization of water content and/or of the contact time with water of the polymer.

In the literature, the electrical conductivities of PPYs prepared by chemical oxidation using ferric chloride without adding other compounds showed mostly low values ($<10\ \mathrm{S\ cm^{-1}}$) [10–15] as shown in Fig. 1. On the other hand, one value was reported to be about $110\ \mathrm{S\ cm^{-1}}$ [12]. This value, however, was measured under different conditions (under vacuum). Unfortunately, we could not reproduce this high conductivity for PPY when using the conditions of the experimental method reported. However, a lower conductivity value ($18.66\ \mathrm{S\ cm^{-1}}$) was found. In addition, the yield using that procedure was also lower (1.4%) compared to 14% when using our technique. In that Ref. [12], no yield is mentioned. Under the reported conditions, the conductivity of PPY prepared using the solvent technique has been 86 times and the yield about 3 times higher than previously reported values [10] using a similar procedure.

In addition, the effect of a polymer additive on the electrical conductivity of polypyrrole using the oxidative polymerization process was studied. Thus, the conductivity of polypyrrole prepared in the presence of poly(ethylene glycol) (PEG) additive (PPY-H) was found to be higher than those of polypyrrole synthesized without additive. Interestingly, there was a strong dependence of the conductivity of polypyrrole on the amount of additive (Fig. 2).

After an initial steep increase up to about $90\ \mathrm{S\ cm^{-1}}$ for 0.3 mmol of added PEG, the conductivity consolidated to $77.67\ \mathrm{S\ cm^{-1}}$ when 5 mmol PEG were added. This behavior can be explained by a competition between kinetic and stabilizing effects during the polymerization process. For relatively low amounts of additive (up to 0.3 mmol) the stabilizing effect is more pronounced, thus indicating reduced cross-linking and less structural defects. However, at higher amounts, the kinectic effects were favored. Because PEG shows relatively basic properties in the presence of HCl in aqueous solution, the polymerization rate can be increased due to the enhanced removal of protons by PEG during the reaction.

The decomposition temperatures of the different polymer products showed a similar behavior, however, the final decomposition point of PPY with the highest conductivity was found to be quite different compared to PPY without PEG (642°C without PEG (PPY-S), 612°C with PEG (PPY-H)). The reason for the decrease of thermal stability seems to be an entropy decrease due to the lower cross-linking degree in the structure of polypyrrole when using the polymer additive.

When using chemical polymerization for the preparation of PPY, the conductivity can be quite different. By using the treatment with organic solvents and drying in vacuo, conductivities for PPY of about two orders of magnitude higher and also higher yields could be attained. Additionally, the conductivity could be enhanced up to about $90\ \mathrm{S\ cm^{-1}}$ by using poly(ethylene glycol) as a polymer additive during the oxidative polymerization. Consequently, conductivity is affected not only by the amount of oxidant, ratio of oxidant to pyrrole, reaction temperature, and reaction time, but also by the preparation technique and polymer additive.

Acknowledgements

This work was financially supported by KISTEP, Korea (Grant no. I-04-017).

References

[1] Mandal BM, Banerjee P, Bhattacharyya SN. Polypyrrole (processable dispersions). In: Salamone JC, editor. Polymeric materials encyclopedia, Boca Raton: CRC Press, 1996. p. 6670–8.

[2] Rodriguez J, Grande HJ, Otero TF. Polypyrroles: from basic research to technological applications. In: Nalwa HS, editor. Handbook of organic conductive molecules and polymers, vol. 2. Chichester: Wiley, 1997. p. 415–68.

[3] Armes SP, Aldissi M, Idzorek GC, Keaton PW, Rowton LJ, Stradling GL, Collopy MT, McColl DB. J Colloid Interf Sci 1991;141:119.

[4] Kudoh Y. Synth Met 1996;79:17.

[5] Kudoh Y, Akami K, Matsuya Y. Synth Met 1998;95:191.

[6] DeArmitt C, Armes SP. Langmuir 1993;9:652.

[7] Satoh M, Ishikawa H, Yageta H, Amano K, Hasegawa E. Synth Met 1997;84:167.

[8] Takeoka S, Hara T, Fukushima K, Yamamoto K, Tsuchida E. Bull Chem Soc Jpn 1998;71:1471.

[9] Wan XB, Liu XR, Xue G, Jiang LX, Hao JJ. Polymer 1999;40:4907.

[10] Geckeler KE, Arsalani N, Rivas BL. Macromol Rapid Commun 1997;18:503–8.

[11] Thieblemont JC, Gabelle JL, Planche MF. Synth Met 1994;66:243.

[12] Machida S, Miyata S, Techagumpuch A. Synth Met 1989;31:311–8.

[13] Simmons MR, Chaloner PA, Armes SP, Kang ET, Tan KL, Loh FC. Polymer 1996;37:2743.

[14] Sak-Bosnar M, Budimir MV, Kovac S, Kukulj D, Duic L. J Polym Sci Part A: Polym Chem 1992;30:1609.

[15] Mathys GI, Truong VT. Synth Met 1997;89:103.