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Uncatalyzed synthesis of polypyrrole with viologen side groups and its chemical properties

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Abstract A substituted polypyrrole (PPr) with viologen side groups (**polymer-1**) was obtained from the reaction of *N*-aminopyrrole with 1-hexyl-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium dihalide (**salt-1**). A model compound (**model-1**) was synthesized by the reaction of *N*-aminopyrrole with *N*-(2,4-dinitrophenyl)-4-(4-pyridyl)pyridinium chloride (**salt-2**). UV–vis spectra revealed that **polymer-1** had an expanded π-conjugation system along the polymer chain: the polymer showed an onset position of absorption at a wavelength approximately 200 nm longer than the corresponding wavelength of **model-1**. **Polymer-1** received an electrochemical oxidation of the pyrrole ring and reduction of the viologen group within the polymer.

Introduction

Polypyrrole (PPr) is one of the most important conductive polymers because of its usability in capacitors, batteries, and sensors [1–5]. PPrs are synthesized by electrochemical polymerization and using various catalyst systems with transition metal complexes and Lewis acids [6–18]. Non-substituted PPrs have very low solubility in organic solvents, although substituted PPrs show improved solubilities. Recently, water-soluble PPrs with a sulfonic acid group were synthesized [9, 19–25]. They showed high electric conductivity because of self-doping via protonation of the polymer backbone by the sulfonic acid group. However, the conductivity of these sulfonated PPrs is highly pH-dependent; acidic conditions are required for a substantial increase in conductivity. Moreover, this doping condition presents a harsh and corrosive environment for industrial applications. In addition, the development of metal-free synthesis for PPrs is attractive because it offers many potential advantages with regard to cost, safety, and environmental concerns. PPrs synthesized using catalyst systems with transition metal complexes and Lewis acids often contain metal contaminations or metal counter anions, which is undesirable for utilization of the polymers as materials for electric devices. In contrast, uncatalyzed synthesis method can provide metal-free pure PPrs that are suitable for electric devices.

To find a milder environment for doping, we explored the use of viologen (1,1′-disubstituted 4,4′-bipyridinium dications), a well-known redox agent, to convert PPrs from an insulating to a conducting state. Recently, we reported the synthesis of polyanilines and polyphenylenes with viologen side groups and described their electrochromism and self-doping properties [26]. The self-doping nature of polymers that contain a viologen side group can be explained by electron transfer from the polymer backbone to the viologen groups. In the case of these polymers, the viologen side groups were introduced by a reaction between the amino groups in the polymers and a Zincke salt, 1-hexyl-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium dihalide (**salt-1**). In addition, we reported the uncatalyzed synthesis of an ionic polyphenylacetylene through 1-alkyl-1′-(4-ethynylphenyl)-4,4′-bipyridinium dihalide which was generated by the reaction of 4-ethynylbenzene with **salt-1**; this intermediate compound caused self-polymerization, initiated by the halogen ion(s) in the viologen groups [27]. In this study, this process was extended to the polymerization of *N*-aminopyrrole through the reaction with **salt-1**; an intermediate compound, 1-hexyl-1′-(*N*-pyrrolyl)-4,4′-bipyridinium dihalide causes self-polymerization via coupling

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between the radicals on the pyrrole ring that are generated by electron transfer from the pyrrole ring to the viologen group. PPrs with viologen side groups will show solubility in organic solvents and self-doping nature because of the presence of the viologen groups. An investigation of the chemical properties of PPrs containing the viologen moiety would provide a greater understanding of the chemical properties of PPrs and aid in the development of new functional materials. Studies have previously been conducted on PPrs containing the viologen moiety with a non-conjugated alkyl spacing group between the polymer backbone and the viologen moiety. PPrs containing the viologen moiety without a spacing group could easily cause electron transfer from the polymer backbone to the viologen moiety, leading to improved electrical properties. To the best of our knowledge, however, there have been no studies on PPrs containing the viologen moiety bonded to the polymer backbone without a spacing group.

In this article, we report the synthesis of PPr containing viologen side groups without a spacing group between the polymer backbone and the viologen moiety using an uncatalyzed system with a Zincke salt. We also describe the synthesis of a model compound (**model-1**) along with the optical, electrochemical, and thermal properties of these newly synthesized polymer and **model-1**.

Experimental

Materials and measurements

Solvents were dried, distilled, and stored under nitrogen. **Salt-1** and *N*-(2,4-dinitrophenyl)-4-(4-pyridyl)pyridinium chloride (**salt-2**) were prepared according to the literature [26, 28]. Other reagents were purchased and used without further purification. Reactions were carried out using standard Schlenk techniques under nitrogen.

The IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer and a JEOL AL-400 spectrometer, respectively. Elemental analysis was carried out on a Yanagimoto MT-5 CHN corder. UV–vis spectra were obtained on a JASCO V-560 spectrometer. GPC analyses were carried out using a Waters 150C with polystyrene gel columns with a DMF solution of LiBr (6 mM) as an eluent and a RI detector. The ground-state geometry of the repeating unit of polypyrrole (PPr) with viologen side groups (**polymer-1)** was optimized with a Gaussian 09 computer program at the density functional theory (DFT) level using B3LYP/6-31G* functional [29]. Cyclic voltammetry was performed in a dichloromethane solution containing 0.10 M $[Et_4N]BF_4$ with a Hokuto Denko HSV-110. Electric conductivity measurements were carried out on an Advantest R8340A ultra high resistance meter using a two-probe method. TGA curve was obtained by a Rigaku Thermo plus TG8120.

Synthesis of **polymer-1**

Salt-1 (1.58 g, 3.0 mmol) was dissolved in EtOH (30 mL) at 60 °C. *N*-aminopyrrole (0.27 g, 3.3 mmol) was added to the EtOH solution. After the reaction solution was refluxed for 12 h, the solvent was removed under vacuum. The resulting solid was washed with acetone and water and dried in vacuo to obtain **polymer-1** as a black powder (0.76 g, 60%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): 4.64 (2H), 1.25 (6H), 0.87 (3H). Calcd for $(C_{20}H_{23}N_3BrCl\cdot1.5H_2O)_n$: C, 59.45; H, 6.03; N, 5.78. Found: C, 59.67; H, 5.89; N, 5.70.

Synthesis of **model-1**

Salt-2 (0.54 g, 1.5 mmol) was dissolved in EtOH (30 mL) at 80 °C. *N*-aminopyrrole (0.24 g, 3.0 mmol) was added to the EtOH solution. After the reaction, the solution was refluxed for 12 h, and the solvent was removed under vacuum. The resulting solid was washed with acetone, acetonitrile, and chloroform in this order and dried in vacuo to yield black solid. The black solid was extracted with water, and the solvent was removed in vacuo to yield a black solid, which was reprecipitated from acetone. **Model-1** was collected by filtration, dried in vacuo, and obtained as a black solid (0.15 g, 40%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): 9.68 (d, $J = 6.8$ Hz, 2H), 8.96 (d, $J = 5.6$ Hz, 2H), 8.85 (d, $J = 6.4$ Hz, 2H), 8.23 (s, 2H), 7.67 (s, 2H), 6.45 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): 153.6, 150.0, 149.9, 145.8, 125.9, 122.8, 121.2, 109.7.

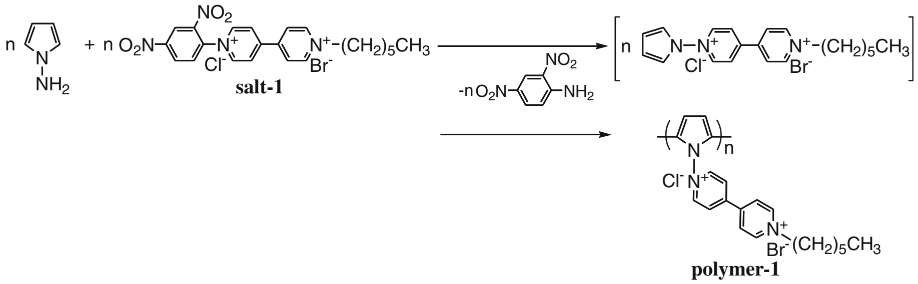
Results and discussion

Synthesis

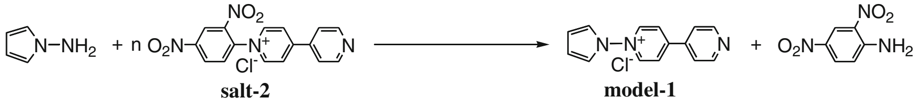
The reaction of *N*-aminopyrrole with **salt-1** resulted in the elimination of 2,4-dinitroaniline and the polymerization of the pyrrole group, yielding a **polymer-1**, in 60% yield (Scheme 1). The low yield of the isolated polymer was apparently due to the formation of a low molecular weight product, which was eventually removed during the purification process.

In order to evaluate the structure and chemical properties of **polymer-1**, the **model-1** was synthesized. The reaction of *N*-aminopyrrole with **salt-2** yielded the **model-1** (Scheme 2).

Scheme 1 Synthesis of polypyrrole with viologen side groups (**polymer-1**)



Scheme 2 Synthesis of a model compound (**model-1**)



Model-1 was soluble in polar organic solvents such as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO); however, **polymer-1** was partly soluble in the solvents. GPC measurement suggested that the M_n and M_w values of the DMF-soluble part of **polymer-1** were 4,590 and 5,000, respectively. The intrinsic viscosity of the DMSO-soluble part of **polymer-1** at a concentration of 0.10 gd L^{-1} was 0.39 dL g^{-1}.

NMR and IR spectra

Figure 1 shows the ^{1}H NMR spectra of **polymer-1** and **model-1** in DMSO-d_6. Peak assignments are shown in the figure. Peaks corresponding to the hexyl protons were observed in the range of δ 0.87–4.64 in the ^{1}H NMR spectrum of **polymer-1**. However, peaks corresponding to the pyrrole and pyridinium rings in **polymer-1** were not observed, probably because of the presence of radical species in the polymer backbone, which were generated by electron transfer from the polymer backbone to the viologen group. It has been reported that radical species in π-conjugated polymers often decrease the intensities of ^{1}H NMR signals corresponding to the protons in the polymer [30]. The peaks corresponding to the protons at the 3- and 4-positions of the pyrrole ring in **model-1** shifted to lower magnetic field positions as compared to those in *N*-aminopyrrole. This was because of the presence of the electron-withdrawing pyridinium ring in the **model-1**.

Figure 2 shows the IR spectra of *N*-aminopyrrole, **salt-1**, and **polymer-1**. The disappearance of the absorption peaks due to the ν(N–H) of the amino group and ν(N–O) of **salt-1** along with the appearance of the new absorption peak due to the ν(C=N) of the viologen group at 1635 cm^{-1} in the IR spectrum of **polymer-1** support the Zincke reaction between *N*-aminopyrrole and **salt-1**. The absorption of the ν(C=N) in the polymer backbone overlaps with that of the ν(C=N) in the viologen group.

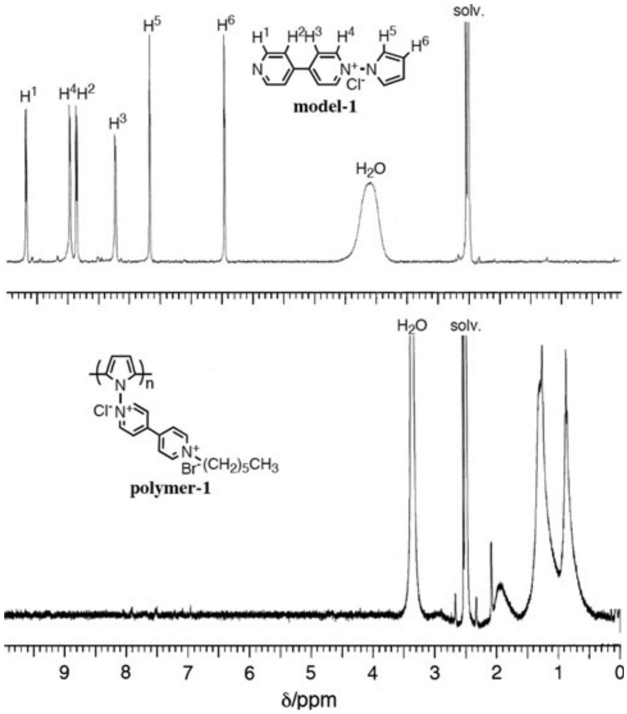


Fig. 1 ^{1}H NMR spectra of **polymer-1** and **model-1** in DMSO-d_6

UV–vis spectra

Figure 3 shows the UV–vis spectra of **polymer-1** in DMSO and **model-1** in MeOH. **Model-1** shows an absorption peak at 265 nm. **Polymer-1** shows a very broad absorption in the range of 250–600 nm. The onset position shifted by approximately 200 nm, and the new wavelength is greater than the corresponding wavelength of **model-1**. These results reveal that **polymer-1** has an expanded π-conjugation system along the polymer chain. It has been reported that polyphenylenes bearing viologen side groups show absorption peaks in the range of 500–700 nm corresponding to the viologen radical cation, which is generated by electron transfer from the polymer backbone to the

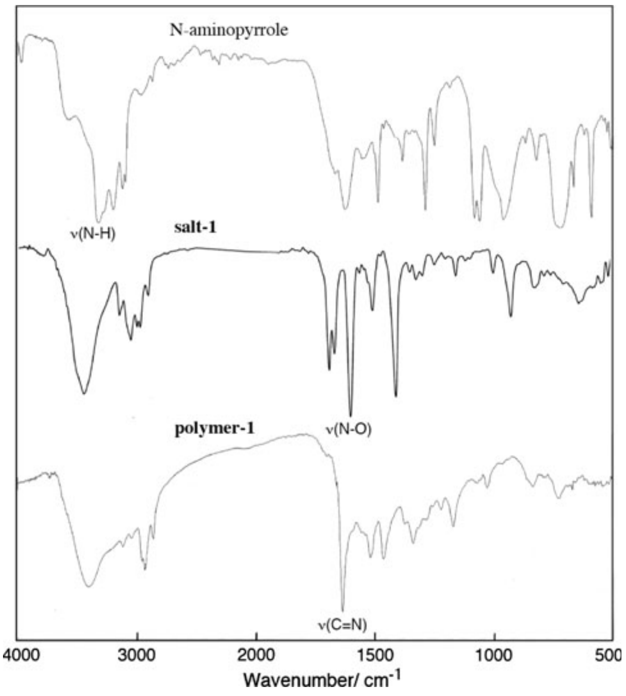


Fig. 2 IR spectra of *N*-aminopyrrole, **salt-1**, and **polymer-1**

viologen group [26]. However, such absorption corresponding to the viologen radical cation was not observed in the UV–vis spectrum of **polymer-1** under nitrogen. This result suggests the presence of few radical species in the polymer backbone, which, in turn, corresponds to a restriction of electron transfer from the polymer main chain to the viologen group because of twisting between the pyrrole ring and viologen group. In order to obtain information on twisting between the pyrrole ring and viologen group, computational calculations at the DFT level of **model-2** were carried out. **Model-2** with a methyl group at the *N* atom of the pyridinium ring is suitable for rapid calculations. The computational calculations reveal that the pyrrole ring of **model-2** is located perpendicular to the plane of the viologen group, as shown in Fig. 4. However, the small number of radical species still affects the magnetic properties of the polymer, resulting in the disappearance of the ^{1}H NMR signal of the protons corresponding to the polymer backbone, as mentioned above.

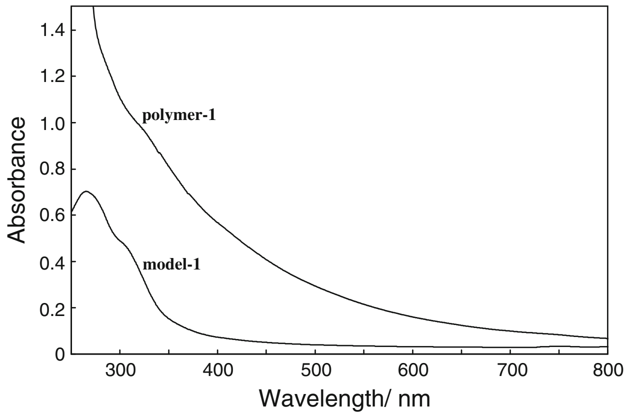


Fig. 3 UV–vis spectra of **polymer-1** in DMSO and **model-1** in MeOH

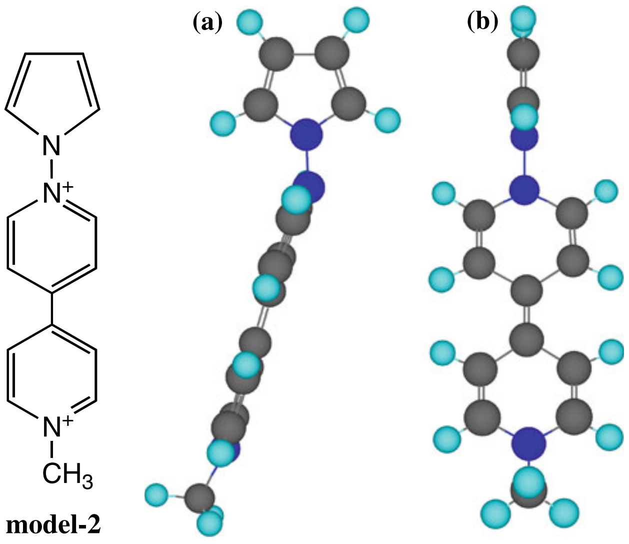


Fig. 4 A computer calculated structure of **model-2**

Electrochemical and electric properties

The results of cyclic voltammetry measurements suggest that a cast film of **polymer-1** on a Pt plate undergoes a two-step electrochemical reduction in the viologen moiety in a dichloromethane solution of 0.10 M $[NEt_4]BF_4$. As depicted in Fig. 5, the cyclic voltammogram of **polymer-1** shows the first peak cathode potential *E*pc(1) and the second peak cathode potential *E*pc(2) at −1.35 and −2.36 V vs. Ag^+/Ag, respectively; these are coupled with anode potentials *E*pa(1) and *E*pa(2) at −1.12 and −2.17 V vs. Ag^+/Ag, respectively. An anodic peak corresponding to the electrochemical oxidation of pyrrole ring is observed at 0.77 V vs. Ag^+/Ag. However, the corresponding reduction (*p*-dedoping) peak does not appear in the cyclic voltammogram; this is likely because of the formation of a stable adduct between the electrochemically oxidized polymer and BF_4^-. Electrochemically oxidized π-conjugated polymers have been reported to form stable adducts with BF_4^- during cyclic voltammetry measurements [31]. The peaks due to the electrochemical reduction disappeared in the second scan, indicating that **polymer-1** is unstable toward an electrochemical reaction.

The electric conductivity (σ) of **polymer-1** was 2.4×10^{-5} Scm^{-1}. This value is lower than that of sulfonic acid-doped polypyrrole ($\sigma = 8 \times 10^0$ Scm^{-1} [32]). However, semiconductive **polymer-1** may be applicable as a material

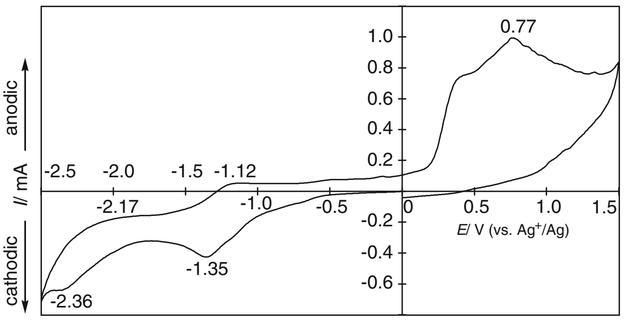


Fig. 5 Cyclic voltammogram of a cast film of **polymer-1** on a Pt plate in a dichloromethane solution of $[Et_4N]BF_4$ (0.10 M). The scan rate was 50 mV s^{-1}

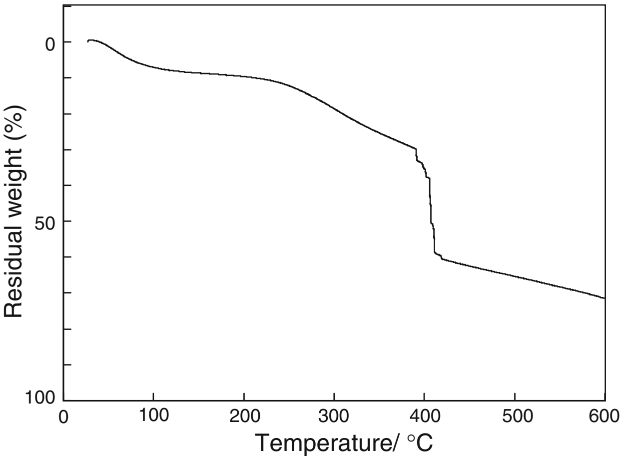


Fig. 6 TG curve of **polymer-1** under nitrogen atmosphere with a heating rate of 10 °C min^{-1}

for electric devices such as diodes and field effect transistors that need semiconductive materials rather than high conductive materials. The lower conductivity of **polymer-1** might be due to the ring twisting along the polymer backbone, which in turn was induced by the steric hindrance of the bulky viologen moiety.

Thermal properties

Figure 6 shows the TGA curve of **polymer-1** under a nitrogen atmosphere. The weight loss of **polymer-1** in the range of 80–200 °C corresponds to the thermal loss of hydrated water in the polymer. The content of hydrated water in **polymer-1** was confirmed by its IR spectrum and by elemental analysis. **Polymer-1** exhibits a two-stage thermal decomposition in the ranges of 200–380 and 380–400 °C. These weight losses may originate from the thermal decomposition of the viologen moiety and the polymer backbone, respectively.

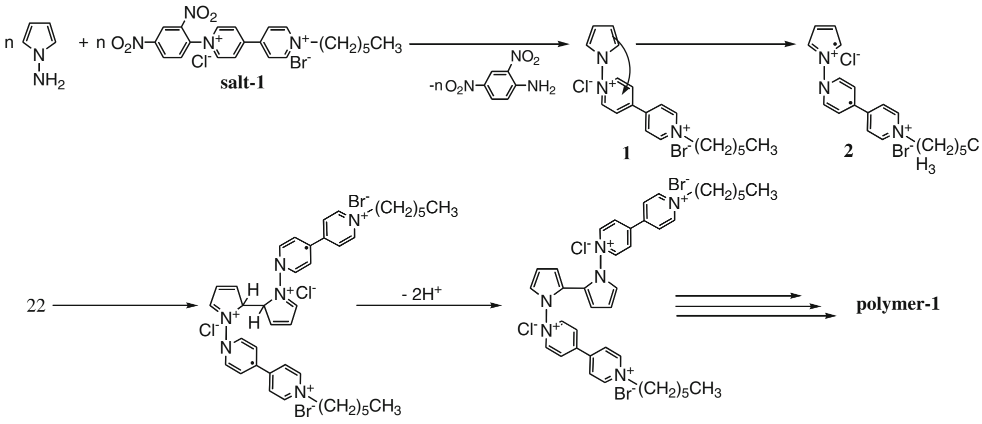
Reaction pathway

Scheme 3 shows a possible reaction mechanism for the polymerization of *N*-aminopyrrole with **salt-1**. This scheme shows the first reaction of *N*-aminopyrrole with **salt-1**, which yields an intermediate species (**1**). The polymerization of the pyrrole ring starts via coupling between the radical cationic species (**2**) that are generated as a result of electron transfer from the pyrrole ring to the viologen group in **1**. Polymerization of the pyrrole ring did not occur in the reactions of *N*-aminopyrrole with **salt-2**. These results show that electron transfer from the pyrrole ring to the viologen group is important for initiation of polymerization. A radical coupling mechanism for the polymerization of pyrrole has been proposed in the literature [33].

Conclusions

PPr containing viologen side groups (**polymer-1**) was obtained by the reaction of *N*-aminopyrrole with **salt-1**. The UV–vis spectra suggested that the polymer had an expanded π-conjugation system along the polymer chain. **Polymer-1** was electrochemically active in film. From the results obtained in this study, it can be concluded that the

Scheme 3 A possible reaction mechanism



4,4′-bipyridinium salts used herein may be used for the uncatalyzed synthesis of well-defined ionic PPrs.

References

1. Maksymiuk K (2006) Electroanal 18:1537
2. Geetha S, Rao CRK, Vijayan M, Trivedi DC (2006) Anal Chim Acta 568:119
3. Kim BC, Ko JM, Wallace GG (2008) J Power Sources 177:665
4. Yamamoto H, Kanemoto K, Oshima M, Isa I (1999) Electrochem 67:855
5. Kudoh Y, Kojima T, Fukuyama M, Tsuchiya S, Yoshimura S (1996) J Power Sources 60:157
6. Zang J, Li CM, Bao SJ, Cui X, Bao Q, Sun CQ (2008) Macromolecules 41:7053
7. Saravanan C, Shekhar RC, Palaniappan S (2006) Macromol Chem Phys 207:342
8. Wu AM, Kolla H, Manohar SK (2005) Macromolecules 38:7873
9. Sahin Y, Aydin A, Udum YA, Pekmez K, Yildiz A (2004) J Appl Polym Sci 93:526
10. Pringle JM, Efthimiadis J, Howlett PC, Efthimiadis J, MacFarlane DR, Chaplin AB, Hall SB, Officer DL, Wallace GG, Forsyth M (2004) Polymer 45:1447
11. Ge DT, Wang JX, Wang Z, Wang SC (2002) Synth Met 132:93
12. Bazzaoui M, Bazzaoui EA, Martins L, Martins JI (2002) Synth Met 128:103
13. Duchet J, Legras R, Demoustier-Champagne S (1998) Synth Met 98:113
14. Ishizu K, Tanaka H, Saito R, Maruyama T, Yamamoto T (1996) Polymer 37:863
15. An H, Haga Y, Yuguchi T, Yosomiya R (1994) Angew Macromol Chem 218:137
16. Nakata M, Shiraishi Y, Taga M, Kise H (1992) Macromol Chem Phys 193:765
17. Rapi S, Bocchi V, Gardini GP (1998) Synth Met 24:217
18. Machida S, Miyata S, Techagumpuch A (1989) Synth Met 31:311
19. Hür E, Bereket G, Sahin Y (2006) Mater Chem Phys 100:19
20. Havinga EE, Hoeve W, Meijer EW, Wynberg H (1989) Chem Mater 1:650
21. Bae WJ, Kim KH, Jo WH, Park YH (2005) Macromolecules 38:1044
22. Nabid MR, Entezami AA (2004) J Appl Polym Sci 94:254
23. Jang KS, Lee H, Moon B (2004) Synth Met 143:289
24. Stankovic S, Stankovic R, Ristic M, Pavlovic O, Vojnovic M (1997) React Funct Polym 35:145
25. Geckeler KE, Arsalani N, Rivas BL (1997) Macromol Rapid Commun 18:503
26. Yamaguchi I, Mizoguchi N, Sato M (2009) Macromolecules 42:4416
27. Yamaguchi I, Higashi J, Sato M (2009) J Mater Sci 44:6408. doi:10.1007/s10853-009-3884-y
28. Yamaguchi I, Higashi H, Shigesue S, Shingai S (2007) Tetrahedron Lett 48:7778
29. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03, Revision A.1. Gaussian, Inc, Pittsburgh
30. Yamamoto T (1996) Chem Lett 25:703
31. Ranger M, Leclerc M (1998) Can J Chem 76:1571
32. West K, Bay L, Nielsen MM, Velmurugu Y, Skaarup S (2004) J Phys Chem B 108:15001
33. Lacroix JC, Maurel F, Lacaze PC (2001) J Am Chem Soc 123:1989