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Nanoparticles of Polypyrrole and Their Effect on Mediating Li Ion Transport from Liquid Electrolyte to Cathode

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ABSCTRACT

Nano-scale particles of polypyrrole (PPy) have been synthesized by polymerizing the respect monomer in the presence of its substituted homologue with oxyethylene (POE) oligomers as the substitute groups. The polymerization was carried out by introducing an aqueous solution of oxidant into the tetrahydrofurane (THF) solution of the monomers. The particles obtained possess brush-like architectures in the dispersing medium, and their sizes in dry state fall into the range of 10 to 40 nm according to TEM analysis. When dispersed by a low content (< 0.1 wt %) in an aprotic organic solvent, the nanoparticles synthesized have been found to affect the conduction of lithium ion. The effect is interpreted as a significant reduction in the electrical resistance at the electrode/electrolyte interface according to gain-phase impedance measurement. This has been attributed to the mediating role of the graft POE chains on the colloidal particles.

INTRODUCTION

The conventional procedures of the preparation of conducting polymer colloids rely on emulsion polymerization by using water-soluble polymers, such as poly(vinyl alcohol-*co*-vinyl acetate), PEO, and cellulosic derivatives etc., as steric stabilizers [1]. In this way, the stabilizer is physically adsorbed onto the surface of the PPy particles. The average particle diameter of the colloidal particles varies over the range 66~300 nm. Recently, Simmons et al. have reported a "reactive stabilizer" route leading to colloidal PPy [2]. By this method, water-soluble monomers such as N-vinylpyrrolidone was copolymerised with various vinylic (bi)thiophene comonomers to obtain water-soluble statistical copolymers. After the *in situ* polymerization of the pyrrole monomer, resulting PPy particles were typically 100~150 nm in diameter. The present paper proposes an alternative approach that results in even smaller PPy nanoparticles. By this method, large organic molecules containing polyoxyethylene (PEO) moiety are bound to pyrrole or aniline molecule via a spacer, tolylene diisocyanate (TDI). Besides the synthesis of the PPy nanoparticles, their application for improving ionic conductivity of liquid electrolyte of lithium is also explored in this study.

EXPERIMENTAL DETAILS

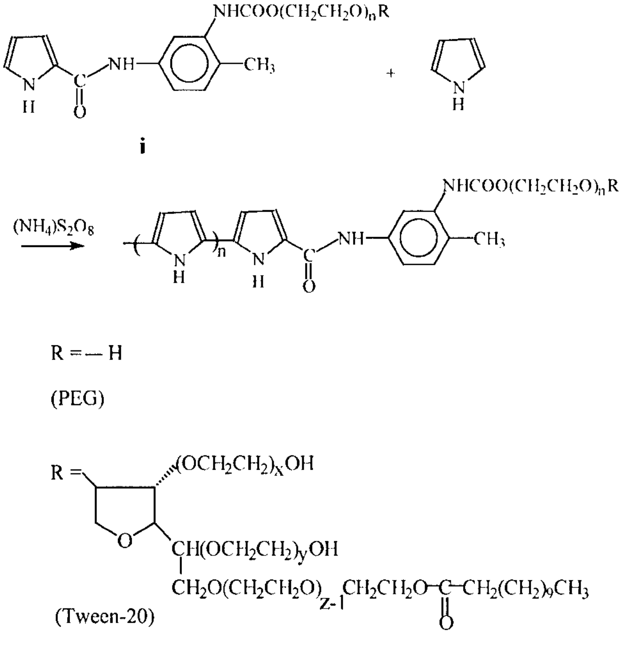
Preparation of the grafted polypyrrole nanoparticles

THF 40ml, pyrrole (0.70ml, 10.1 mmol), TDI (1.45ml, 10.1mmol) were added into a 100ml conical flask. The mixture was stirred for 36h at room temperature. Then oxyethyl-containing oligomer (11 mmol) and dibutyl tin dilauriate (DBTDL, ca. 0.3 ml) were added into the solution. After that, the reaction was allowed to extend for 24 more hours at room temperature. An aqueous solution consisting of $(NH_4)_2S_2O_8$ (2.77g, 12.1 mmol) and deionized water (DIW) 40ml was introduced into the organic solution, and the two-liquid-phase mixture was stirred for 8 h at room temperature for carrying out the oxidation polymerization of the pyrrole and its derivatives as shown in Scheme 1.

The resulting PPy colloids were subjected to a high-speed centrifugation (11,000 rpm for 2h on Jouan M14.11) to sediment the PPy colloids. The clear supernatant was decanted off, and the sediment was dispersed into THF/DIW (1:1 vol) mixture by mechanical agitation; the dispersion was then subjected to the centrifugation. The cycle of centrifugation and dispersion was repeated twice for purifying the colloids.

Preparation of the colloidal dispersions in aprotic organic solvents

In a typical procedure, the colloids of PPy derivatives obtained after purification was dried at 60°C overnight, the solid was then dispersed into DMSO by mechanical agitation and followed by ultrasonication. Consequently, a very stable colloidal dispersion of PPy derivatives in DMSO (~0.2 wt%) was prepared.



Scheme 1. Grafting the oxyethyl oligomer chain to PPy nanoparticles

TEM measurement

The colloids of the PPy derivatives were diluted with DIW to 200 ppm. Dip a carbon-coated copper grid in the dispersion once and let it dry at room temperature. The TEM measurements were conducted on a Philips CM300 FEG.

Dispersing the colloidal particles into LiBr-DMSO solution

In the DMSO colloidal dispersion, the maximum concentration is about 0.2wt%. A slightly over load of solid poly(Py-*co*-Py-TDI-PEG600) would cause difficulty in dispersing the colloid uniformly in DMSO. In most cases, the 0.1wt% dispersion was used as the medium for dissolving LiBr to make a liquid electrolyte.

Evaluation of the electrical properties of the colloidal dispersion

AC impedance measurements were conducted on a Solarton SI 1260 Impedance/Gain-Phase Analyzer. The amplitude of the sinusoidal excitation signal was 10 mV. DC conductivities were measured with a Hioki 3540mΩ HiTester. For both AC and DC measurements liquid samples are placed in a rectangular shape cell with two parallel brass sheets as electrodes.

DISCUSSION

It is known that pyrrole units in polypyrrole (PPy) are linked through their α-carbons [3]. As such, when the reaction mixture is subjected to oxidizing polymerization, the bare pyrrole molecules would polymerize first to form PPy nuclei and the growth of the nuclei would be terminated upon the participation of the α-substituted pyrrole molecules **i**. Accordingly, the poly(ethylene glycol) chains are attached chemically to the surface of PPy particles, leading to brush-like PPy colloidal particles as illustrated in *Scheme 1*. Table 1 summarizes three types of PPy nanoparticles synthesized, which differ in the structure of the surface-grafted oxyethylene oligomer.

Table 1. Identification of the various nanoparticles synthesized

Oligomer branch	Polypyrrole
PEG600	poly(Py-*co*-Py-TDI-PEG600)
PEG1000	poly(Py-*co*-Py-TDI-PEG1000)
Tween 20	poly(Py-*co*-Py-TDI-Tween20)

Studies based on TEM observation

TEM images of poly(Py-*co*-Py-TDI-PEG600) (Fig. 1a) and poly(Py-*co*-Py-TDI-PEG1000) (Fig. 1b) show quite different mean particle sizes between the two, the former having an average diameter around 30nm whereas the latter an average diameter smaller than 10nm. As the TEM sample of poly(Py-*co*-Py-TDI-PEG600) was prepared after separation and re-dispersion processes, it is likely that the elementary particles underwent agglomeration in the separation step. The resulting agglomeration could not be broken down any more. On the contrary, the TEM sample of poly(Py-*co*-Py-TDI-PEG1000) was prepared without being separated from the polymerization system as it could not form sediment by centrifugation.

The DC measurement of the colloidal dispersion in DMSO containing soluble LiBr

As dimethyl sulfoxide (DMSO) is an aprotic polar organic solvent, it is therefore a suitable liquid medium for studying Li ion conduction. DMSO itself has a conductivity (S/cm) of minus nine power of order (Table 2). When 0.42 wt % of LiBr is dissolved in it, the conductivity of the solution is boosted by one thousand times owing to a large degree of dissociation of LiBr via the co-ordination of DMSO molecules to Li^+ ions. Similarly, when poly(Py-*co*-Py-TDI-PEG600) colloid (~0.1 wt%) is dispersed in pure DMSO, the conductivity of the dispersion also inflates by one thousand times because the number of colloidal particles per unit of volume is considerably large.

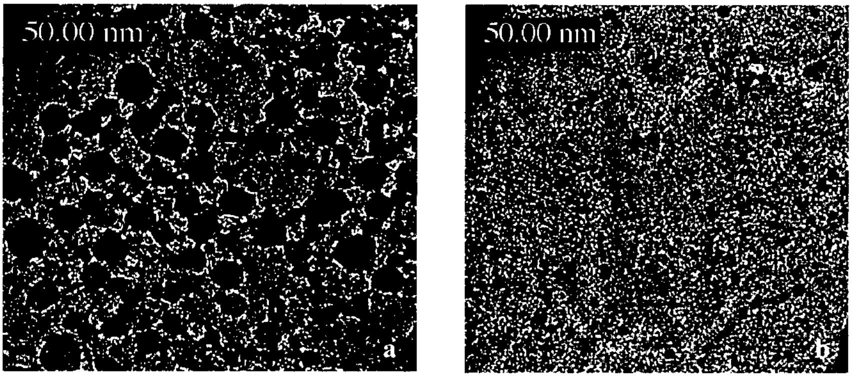


Fig. 1 TEM of (a) poly(Py-*co*-Py-TDI-PEG600) and (b) poly(Py-*co*-Py-TDI-PEG1000)

Table 2. *Effect of the PPy colloids on the conductivity of the electrolyte**

Solid content of the DMSO dispersion (wt%)		LiBr		
		0	0.42wt%	0.88wt%
Poly(Py-*co*-Py-TDI-PEG600)	0	2.0E-09	3.4E-06	1.1E-05
	0.096%	2.7E-06	2.5E-05	2.2E-05
Poly(Py-*co*-Py-TDI-Tween20)	0	2.0E-09	3.4E-06	1.1E-05
	0.094%	2.6E-06	8.2E-05	7.3E-05

* The unit of the data in the table is S/cm.

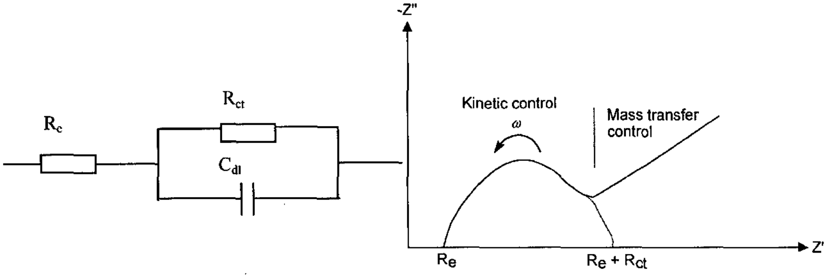
A simple estimation can give the picture of how it is. Assume that the particles have spherical shape with the average diameter of 70 nm. If the mass density of poly(Py-*co*-Py-TDI-PEG600) is taken as 1, 0.1 wt % of poly(Py-*co*-Py-TDI-PEG600) particles dispersing in DMSO means that there are about 6×10^{12} particles in 1 ml of dispersion. Frequent collisions among the particles allow electrons to be transferred throughout the DMSO medium.

Apparently, only conducting polymer colloids can offer this function. It is interesting to note that as poly(Py-*co*-Py-TDI-PEG600) (~0.1 wt%) is dispersed into the solution of LiBr in DMSO, the conductivity of the resulting liquid system is seven times greater than that of the LiBr solution (0.42 wt %). However, when the LiBr concentration is doubled, the enhancing effect of the colloid becomes less obvious (Table 2). The enhancement effect of the colloid becomes more evident when poly(Py-*co*-Py-TDI-Tween20) was used.

It has been verified that the conductivity enhancement effect of the PPy colloidal particles does not come from their PEO pendant coils alone. Instead, the PPy core is an active component that improves the ionic conduction of the DMSO-LiBr electrolyte system. This particular behaviour of PPy particles may relate to the electrically positive surface on them due to the existence of protonic sites as well as cationic (doped) sites, anions (SO_4^{2-} in the present case that are from the oxidant) surrounding the positively charged core. In the resulting double layer, the negatively charged out-layer may contain not only SO_4^{2-} but also Br^-ions. The migration of Br^- ions toward the surface of colloidal particles is driven by the surplus positive charge, which is likely due to incomplete shielding of the positive charge by SO_4^{2-} diffusion layer. Accordingly, incoming of Br^- into the diffusion layer will enhance the dissociation of LiBr in DMSO. Following this logic, the larger extent of the enhancement of Li conductivity when the particle bearing Tween20 was used can be attributed to the bulky sorbitan unit and the hydrophobic dodecyl segment of Tween20 as shown in Scheme 1. These two structural features may lead to a more expanding anion diffusion layer, which favours the participation of Br^- ions into the diffusion layer and thus enhancing the ionic conductivity in the solution.

AC impedance measurement

As the DC measurement does not cause swift perturbation in the diffusion double layer of PPy colloidal particles, the method allows one to assess the involvement of Br^- ions into the diffusion layer. However, DC measurement cannot be employed to detect the charge transfer at the interface between the electrode and the solution. Frequency scanning in the AC impedance spectroscopy ($0.1\sim10^5$ Hz) can screen the diffusion layer's effect of PPy particles and study the mass transport of Li^+ ions at the interface between liquid electrolyte and cathode. Approximately, an electrolyte between two electrodes can be simulated by a RC



(a) (b)

Fig. 2 (a) The simplified equivalent circuit; (b) The plot of impedance in the complex plane of a simple electrochemical system.

equivalent circuit (Fig. 2a), where R_e stands for the resistance of the electrolyte between the two electrodes, R_{ct} the resistance of charge transfer between electrolyte and electrodes, and C_{dl} the capacitor of the double layer formed between electrolyte and the electrodes. The experimental impedance plot is always obtained as the plot shown in Fig. 2b. According to the impedance plot, one is able to work out the values of the resistance of the electrolyte (R_e) and the overall low frequency resistance (R_e+ R_{ct}). Table 3 shows that the AC conductivity (admittance) of electrolyte are almost the same in all the cases, while the conductivity based on (R_e+ R_{ct}) are apparently greater in the presence of the PPy colloids than in the absence of them. The results suggest that poly(Py-*co*-Py-TDI-PEG600) colloidal particles can facilitate the charge transfer in the double layer between electrodes and the electrolyte. This inference is actually similar as the report by Lindfors et al. [4], where a small amount of PAn could improve significantly the charge transfer at the substrate-membrane interface in a single-piece all-solid-state lithium-selective electrode.

Table 3 Effect of poly(Py-*co*-Py-TDI-PEG600) colloidal particles on the low frequency AC admittance for LiBr/DMSO electrochemical cell system

LiBr (wt %)	Colloid content (wt %)	Admittance of electrolyte[a] (S/cm)	Overall low frequency admittance[b] (S/cm)
0	0.1	1.6×10^{-5}	8.3×10^{-6}
0.42	0	1.3×10^{-3}	1.6×10^{-5}
	0.1	1.6×10^{-3}	7.2×10^{-5}
0.88	0	2.2×10^{-3}	1.6×10^{-5}
	0.1	2.3×10^{-3}	8.9×10^{-5}

a. Calculation based on R_e; *b*. Calculation based on $R_e + R_{ct}$

CONCLUSIONS

Nanoparticles of polypyrrole with grafted oxyethylene oligmer chains have been synthesized via an in-situ seed-blocked method. They are able to enhance Li ion transport in polar aprotic organic liquid and at the interface between the electrolyte and cathode as well.

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