Polythiophene Microspheres Synthesized by Transition Metal Mediated Oxidative Dispersion Polymerization

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INTRODUCTION

In the past two decades, significant achievements have been made in the synthesis of soluble polythiophene (PT) derivatives. The incorporation of various functional side chains enables PT to be easily processed by solution method and gifts many interesting bonus properties as well. Nonetheless, these procedures are usually complex and expensive, which generally require stringent conditions and sometimes toxic solvents. Furthermore, for photovoltaic applications, the material stability under continuous illumination has to be taken into account. The solubilizing side chains may be passive in terms of light harvesting and charge transport, and they may also make the materials soft and allow for diffusion of small molecules and constituents. Recently, Bjerring et al. prepared unsubstituted PT films by solution processing thermocleaving method in which the solubilizing side chains were removed after the formation of polymer film.

Dispersible PT micro/nanostructure has emerged as a promising alternative. One of the most convenient synthetic procedures is the heterogeneous oxidative polymerization of thiophene in organic solvents, traditionally with the aid of commercially available small molecule surfactants. Recently Li et al. made a detailed investigation on the polymerization of thiophene in acetonitrile with cetyltrimethylammonium bromide (CTAB) as surfactant. PT nanoparticles were successfully prepared, although some problems still remained. The shape of PT particles was not as regular as usually observed in conventional emulsion or dispersion polymerization, and agglomeration was usually observed. The authors stated that it was because CTAB failed to form stable micelles in acetonitrile. This could also explain why discrete PT particles could not be obtained in chloroform with all the three common types of small molecule surfactants (anionic, nonionic, and cationic). On the other hand, Lee et al. and recently our group managed to synthesize well dispersed PT nanoparticles in aqueous medium, where a typical small molecule surfactant sodium dodecyl sulfate (SDS) capable to form micelles was employed.

This article aims at overcoming the present difficulties in the preparation of well-dispersed PT microspheres in organic solvents. We postulate that the problem encountered in organic solvents can be solved by using macromolecular stabilizers instead of small molecule surfactants. The experimental results showed that, by using polyvinylpyrrolidone (PVP) as a macromolecular stablizers in the oxidative polymerization of thiophene, we obtained well-dispersed PT microspheres with tunable diameters ranging between 180 nm and 1.1 µm. To our best knowledge, this may be the first dispersion polymerization of thiophene in organic solvents.

RESULTS AND DISCUSSION

All the experimental results are summarized in Table 1. We first made a comparison between two oxidative polymerizations of thiophene with SDS in water and ethanol, respectively, to describe how our idea is generated. In aqueous medium, the initial state of reaction is similar to that of emulsion polymerization (although the chain wise kinetics is not followed). The solubilizing side chains may be passive in terms of light harvesting and charge transport, and they may also make the materials soft and allow for diffusion of small molecules and constituents. Therefore, micelle nucleation dominates, and the formation of stable colloid particles is straightforward. Similarly, well-dispersed PT particles can be obtained in aqueous medium with SDS as surfactant [run 1, Fig. 1(a)]. But when water is replaced by organic solvents (e.g., ethanol used here), the reaction begins as a homogeneous system because both thiophene and SDS are soluble. Thiophene oligomer chains generated in continuous phase will...
precipitate out, when the critical chain length for precipitation is reached. As there are no micelles to accommodate these insoluble oligomers, they form unstable particles and then coagulate. In this case, similar to conventional precipitation polymerization, it is difficult to obtain discrete PT particles [run 2, Fig. 1(b)]. But if appropriate macromolecular stabilizers with large excluded volume and good compatibility with oligomer chains are used, the coalescence of unstable particles will stop when there are enough stabilizer chains absorbed on the particle surface to provide steric stabilization.\textsuperscript{18,19} This procedure is similar to conventional dispersion polymerization.

Then, we performed the prototype dispersion polymerization of thiophene in ethanol. In the presence of 5 wt % PVP, well-dispersed PT particles with quite regular morphology were obtained [run 3, Fig. 2(a)]. The number-average particle diameter ($D_n$) is 181 nm with a quite narrow distribution ($D_w/D_n = 1.04$, $D_w$ represents the weight-average particle diameter). This result shows that PVP is an effective stabilizer for dispersion polymerization of thiophene in ethanol/H$_2$O$_2$ solution mixture. If the particle size could be controlled in the same way as in conventional dispersion polymerization, we next decreased the stabilizer concentration to 2.0 wt %. As expected, $D_n$ increased to 556 nm [run 4, Fig. 2(b)]. Because with lower stabilizer concentration, more unstabilized particles have to coalesce before sterically-stable particles can form.\textsuperscript{18} Although the particle size distribution is somewhat broad ($D_w/D_n = 1.09$), stable dispersed phase still manages to form with decreased PVP concentration. The dependence of particle size on monomer concentration was also checked. Figure 2(c) shows that when monomer mass was increased from 6 to 9 g, the particle size increased as expected (run 4, $D_n = 231$ nm). Nonetheless, particle size distribution also increased considerably ($D_w/D_n = 1.19$) and some agglomeration was observed.

Encouraged by the above results, we performed one extra polymerization run in acetone/H$_2$O$_2$ solution mixture to check if it was possible to extend current methodology to other organic solvents with quite different solvent power (run 6). Although PVP is not well soluble in pure acetone, it can be dissolved in acetone/H$_2$O$_2$ solution mixture under the current experimental condition. It should be noted that 1.5 g FeCl$_3$·6H$_2$O was used as oxidants in run 6 instead of Cu(NO$_3$)$_2$·3H$_2$O, because the rate of Cu(II) mediated polymerization in acetone was found slow (<15% yield after 24 h). Figure 3 shows that well dispersed PT microspheres can still be obtained by the same procedure. No agglomeration is observed, but the size of PT microspheres is much larger than those prepared in ethanol/H$_2$O$_2$ solution mixture.
It is well-known that one of the most important applications of dispersion polymerization is to prepare polymer microsphere, whose size (0.1–15 μm) falls in-between those of suspension polymerization (50–1000 μm) and emulsion polymerization (0.06–0.7 μm).\textsuperscript{18} Indeed, the results from Lee et al.’s and our research showed that the diameter of PT particles prepared by emulsion polymerization is generally smaller than 150 nm.\textsuperscript{14,15} In comparison, the dispersion polymerization of thiophene reported here is capable of generating PT microsphere sizing between 180 nm and 1.1 μm.

Owning to their unique properties, conducting polymer microspheres are expected to show significant potential in multiple fields especially for medical and electronic applications.\textsuperscript{20} Recently, high efficiency polymer solar cells based on unsubstituted PT has been reported, showing its capability for photovoltaic devices.\textsuperscript{3} In the production of photovoltaic devices, stable PT dispersion is especially suitable for the fabrication of polymer inks for spin-coating and roll-to-roll process.\textsuperscript{21} Although other conducting polymer microspheres (e.g., polyaniline and polypyrrole) have been synthesized successfully by dispersion polymerization, the realization that PT microsphere can also be prepared by this method may considerably expand their capability for practical applications.

Despite all these, several issues have to be noted. A high amount of metal salts is required compared with that in the oxidative emulsion polymerization,\textsuperscript{14,15} although it is still comparable with those in previous studies in organic solvents.\textsuperscript{12,13} The rate of polymerization in organic solvents is also lower than that in water. This is probably because metal salts may form some complex with solvents thus reducing its oxidative power, and similar phenomenon was observed in Fe (III) catalyzed oxidative polymerization of pyrrole in ethanol.\textsuperscript{22} The relatively low local monomer concentration compared with emulsion polymerization in water is also one of the factors which reduce the rate of polymerization. Additionally, the relatively broad particle size distribution on the increased monomer concentration indicates that the efficiency of stabilizer needs improvement. Regarding the

\begin{figure}
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\includegraphics[width=\textwidth]{figure2.png}
\caption{PT microspheres prepared in ethanol/H\textsubscript{2}O\textsubscript{2} solution mixture with PVP as surfactant. (a) run 3; (b) run 4; (c) run 5.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{PT microspheres prepared in acetone/H\textsubscript{2}O\textsubscript{2} solution mixture with PVP as surfactant (run 6).}
\end{figure}
previous studies on conventional dispersion polymerization,23–30 elaborate designed amphiphilic block copolymer stabilizers or reactive macromonomers may show higher stabilizing efficiency and allow better control on PT microspheres morphology. They may also be used for the preparation of conducting polymer composite microspheres and the surface functionalization of conducting polymer particles. The relevant research is underway in our laboratory.

EXPERIMENTAL

Materials
Thiophene (99% Lancaster) was stored in a refrigerator before use. PVP (Mw ~ 40,000), Sodium dodecyl sulfate (SDS), hydroxyl peroxide (H2O2, 30% solution), cupric nitrate trihydrate [Cu(NO3)2·3H2O], ferric chloride hexahydrate (FeCl3·6H2O), sodium chloride, dimethyl sulfoxide, N,N-dimethylformamide (DMF), tetrahydrofuran, acetone, ethanol, methanol, ethyl acetate, ethyl ether, toluene, and chloroform were all analytical grade reagents purchased from Shanghai Chemical Reagent Company and were used as received.

Oxidative Polymerization of Thiophene
The reaction was performed in a 250-mL three-necked flask equipped with a mechanical stirrer and a condenser at 50 °C. All the six polymerization runs were carried out in the same manner: given amounts of thiophene monomer and PVP were added into 47 g solvent (water for run 1; ethanol for run 2–5; and aceton for run 6), and the mixture was stirred at 255 rpm for 20 min. Then 10 g 30% H2O2 solution was introduced, and 1.5 g Cu(NO3)2·3H2O (run 1–5) or FeCl3·6H2O (run 6) dissolved in 3 g water was added in one portion. The reaction was allowed to proceed for 24 h.

Sample Purification
For run 1, the reaction mixture was diluted with 50 mL deionized water, and the polymer was precipitated by adding sodium chloride. After filtration, the precipitate was purified by five centrifuging–washing cycles. For the rest samples, the reaction mixture was added with 200 mL deionized water and purified by five centrifuging–washing cycles. Finally, all the samples were dried under vacuum at 50 °C for 48 h.

Characterization
Infrared absorption spectra of purified samples were obtained with a Bruker TENSOR 27 fourier transform infrared spectroscopy at room temperature. The morphology of PT samples was observed under a Zeiss Ultra 55 field emission scanning electron microscope, with an accelerating voltage of 5 kV and InLens observation mode. The samples were coated on a silicone wafer for scanning electron microscopy characterization. The number-average particle diameter and particle diameter distribution were evaluated by randomly measuring 100 individual particles with image analysis software. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 system, and the samples were prepared as dilute solution of DMF in quartz cells.

PT Dispersibility Test
Purified PT sample (5 mg) was added into a glass bottle and then 5 mL of given solvent was introduced with no agitation. Digital photos were taken by a SONY DSC-W5 camera after 24 h.

CONCLUSIONS
In summary, we found that by using PVP as macromolecular stabilizer rather than traditionally used small molecule surfactants, well-dispersed PT microspheres with tunable particle size could be facially synthesized by oxidative dispersion polymerization. In future research, we plan to explore the scope of this system, including the control of particle morphology and the decoration of particle surface with functional groups for the production of electroactive devices.

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REFERENCES AND NOTES
31 FTIR spectra, UV–vis spectra, and the results for dispersibility test can be found in Supporting Information.