Direct synthetic route for water-dispersible polythiophene nanoparticles via surfactant-free oxidative polymerization

Hyun Woog Ryu a, Yong Seok Kim a, Jung Hyun Kim a,*, In Woo Cheong b,**

a Department of Chemical and Biomolecular Engineering, Yonsei University, 134 Shinchon-Dong, Sudaemoon-Gu, Seoul 120-749, Republic of Korea
b Department of Applied Chemistry, Kyungpook National University, 1370 Sankyuk-3-dong, Buk-gu, Daegu 702-701, Republic of Korea

ABSTRACT

Water-dispersible poly(thiophene-co-3-thiopheneacetic acid) (PThTA) nanoparticles were successfully prepared by Fe 3+-catalyzed oxidative polymerization in the absence of a surfactant. This facile method adopted the recyclable FeCl 3/H 2 O 2 initiator couple to yield a high conversion of approximately 97%, and the sodium salt of 3-thiopheneacetic acid (TA) was used for the colloidal stability of the PThTA nanoparticles. The particle formation and growth of PThTA were examined with photoluminescence (PL) spectroscopy and time-evolution variation of the particle number in the early period of polymerization. The final average particle size of PThTA was 320 nm, measured by dynamic light scattering (DLS). The number-average molecular weight of PThTA was about 2 × 10 4 g/mol. The light-emitting properties of the PThTA nanoparticles in an emulsion state were studied with UV−vis absorption and PL spectroscopy, and it was found that the quantum efficiency increased from 1.43 to 3.22 with the polymerization time at an excitation wavelength of 405 nm. Our results provide new insights on surfactant-free oxidative polymerization and may serve as guidelines for the preparation of new conjugated polymer emulsion systems for potential optoelectronic devices.

© 2014 The Authors. Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

1. Introduction

Polythiophene (PTh) and its derivatives have been studied extensively since the electrochemical synthesis of PTh was first reported in 1981 [1,2]. PTh polymers show good electrochemical, electrochromic, luminescent, and shielding properties, as the π-conjugated carbon backbone structures provide bases for a wide range of technologies, such as field-effect transistors [3,4], light-emitting diodes [5,6], and solar cells [7,8].

Unfortunately, PTh derivatives generally exhibit poor solvent solubility and processability, impeding their use in practical applications such as electroluminescent (EL) devices or conducting film because these applications require good solubility in polar solvent with binders (polyurethane or acrylic polymer). We previously reported the preparation of PTh nanoparticles in an aqueous phase via Fe 3+-catalyzed oxidative polymerization. This method includes a FeCl 3/H 2 O 2 (catalyst/oxidant) combination system [9], which can make roughly 30 nm PTh nanoparticles with only a trace of FeCl 3. A simple procedure for PTh nanoparticle synthesis with controllable particle size was also reported, in which sodium dodecyl sulfate (SDS) was used in an aqueous medium [10,11]. However, the addition of a surfactant can deteriorate the film properties of the PTh nanoparticles; thus, a purification step to remove the surfactant is needed [12]. Conjugated polymer nanoparticles prepared by surfactant-free oxidative polymerization can be directly utilized for the film application without any further purification process compared with surfactant system. In addition, enhanced photoluminescence property of polythiophene nanoparticles can be revealed because of high molecular weight of polythiophene nanoparticles via surfactant-free oxidative polymerization than emulsion oxidative polymerization in our previous study [9].

To overcome this drawback, we attempted to copolymerize unsubstituted thiophene (Th) and 3-thiopheneacetic acid (TA) to prepare water-dispersible PThTA nanoparticles in an aqueous medium by Fe 3+-catalyzed oxidative polymerization without any surfactants. This synthetic route requires no surfactant removal process and has the significant advantage of having both high purity and a simple process design. In this paper, the particle formation/growth mechanism as well as the photoluminescence (PL) and dispersibility of the PThTA nanoparticles are discussed.
2. Experimental

2.1. Materials

Thiophene monomer (Th, Acros Organics, USA) and 3-thiopheneacetic acid (TA, Aldrich Co, USA) were refrigerated at 5–8 °C until used. Anhydrous ferric chloride (FeCl3, Aldrich Co., USA) and a 30% aqueous solution of hydrogen peroxide (H2O2) (Junsei, Japan) were purchased. All chemicals were used as received without any further purification. Distilled/deionized (DDI) water was used throughout the experiments.

2.2. Preparation of the PThTA nanoparticles

PThTA nanoparticles were synthesized in a 300 mL double-jacketed glass reactor fitted with a reflux condenser, an N2 gas inlet, an ingredient inlet, and a Teflon-blade mechanical stirrer. The reaction temperature was maintained with a thermostat at 50 °C. The stirring rate was 600 rpm. Before the copolymerization, TA was deprotonated with NaOH aqueous solution in order to prepare the sodium salt form of TA for better electrostatic stabilization. The reaction procedure was as follows: Th (0.28 mol, 24.0 g) and TA salt (0.005 mol, 0.72 g) were added to 100 mL DDI water under N2 bubbling. H2O2 (0.87 mol, 98.73 g, 30% aq.) was then added to the reactant mixture solution. After 10 min, FeCl3 (3.1 × 10−4 mol, 45.0 mg) in 5 mL of DDI water was injected into the reactant mixture to initiate copolymerization, and the mixture was kept for 24 h.

2.3. Nitration of the PITA nanoparticles

The PThTA nanoparticles were nitrated for better solubility in THF as a GPC eluent. Owing to the poor solubility of PTh, nitration of the PTh nanoparticles was carried out with mixed acids (95% H2SO4: 61% HNO3:H 2O in the range of 600/32.1/16) corresponding to about [Th]1[TA-salt]3, (17.5/32.1)/(9.3/16) where [Th] and [TA-salt] ratio of the PThTA nanoparticles. An excess amount of the mixed acids was added to the PTTA corresponding to about [Th]1[TA-salt]3, (17.5/32.1)/(9.3/16) was then added to the reactant mixture solution. After 10 min. FeCl3 (3.1 × 10−4 mol, 45.0 mg) in 5 mL of DDI water was injected into the reactant mixture to initiate copolymerization, and the mixture was kept for 24 h.

2.4. Characterization of the PITA nanoparticles

The chemical structure of the Th, TA-salt, and PThTA was studied with Fourier transform infrared spectroscopy (FT-IR; TENSOR27, Bruker Optik GmbH, Germany) in the range of 600–4000 cm−1 at room temperature. The initial growth mechanism of the PThTA nanoparticles was confirmed by a spectrophotometer (RF-5301PC, Shimadzu, Japan) with a sample concentration of 1.6 × 10−3 M. The particle size and number of particles were measured by dynamic light scattering (DLS, Malvern, UK). For the DLS analysis, the sample was diluted 100 times with DDI water and measured at 25 °C. The particle distribution was examined by field-emission scanning electron microscopy (FESEM; JSM-600F, JEOL, Japan) and transmission electron microscopy (TEM; JEM-2000EXII, JEOL, Japan). The average molecular weights of the nitrated PThTA were measured with gel permeation chromatography (GPC, Waters Co., USA) equipped with a series of Waters columns (HR4, HR3, HR2, HR1), HPLC pump, RI detector, and data module at 40 °C. The molecular weights were determined from the refractive index data, which were analyzed with the Waters Breeze® System. Polystyrene standard samples were used for narrow peak calibration. The eluent was tetrahydrofuran (THF) with a flow rate of 1.0 mL/min. Elemental analysis was carried out with a LECO CHNS-932 analyzer and a Yanaco YS-10 SX-Elements microanalyzer. The photographic images of nanoparticles under UV365 nm were captured by UV itec STX-20.M.

Table 1 [Th] and [TA-salt] ratio of the PThTA nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Th][TA-salt]n</th>
<th>S</th>
<th>O</th>
<th>Degree of S ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PThTA-30s</td>
<td>13.8</td>
<td>11.6</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>PThTA-60s</td>
<td>14.1</td>
<td>10.8</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>PThTA-180s</td>
<td>17.5</td>
<td>9.3</td>
<td>1.88</td>
<td></td>
</tr>
<tr>
<td>PThTA-300s</td>
<td>24.6</td>
<td>7.7</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Conversion of the PThTA nanoparticles

The time–conversion curves under different initiation systems are shown in Fig. 1. For comparison of the initiation systems, the
amounts of Th monomer (0.28 mol, 24 g) and TA-salt (0.005 mol, 0.72 g) were fixed, and the oxidant amount was varied as follows: (a) FeCl$_3$ (3.1 × 10$^{-4}$ mol, 45.0 mg)/H$_2$O$_2$ (0.87 mol, 98.73 g), (b) H$_2$O$_2$ (0.87 mol, 98.73 g), and (c) FeCl$_3$ (3.1 × 10$^{-4}$ mol, 45.0 mg), respectively. The final conversion at 24 h was approx. 97% in the combinational FeCl$_3$/H$_2$O$_2$ system (a). However, about 21% and 5% of the final conversions were obtained in the cases for (b) and (c), respectively. The high monomer conversion with FeCl$_3$/H$_2$O$_2$ is attributed to the recyclical redox mechanism between the monomer and the FeCl$_3$/H$_2$O$_2$: Fe$^{3+}$ ions existing on the surface of the PThTA nanoparticles bringing about the oxidative polymerization of the Th and TA monomers, while the reduced Fe$^{2+}$ ions are oxidized by H$_2$O$_2$. This cyclic reaction happens mainly at the surface of growing particles due to the electrostatic attraction between the TA-salt and the ferric/ferrous ions [9,16].

3.2. Morphology of the PThTA nanoparticles

Fig. 2(a) shows the SEM and TEM (inset) images of the PThTA nanoparticles prepared after 24 h of polymerization. As seen in the images, the PThTA nanoparticles have a spherical shape with a smooth surface. The particle size distribution (PSD) of PThTA was measured by DLS and seems broad, as shown in Fig. 2(b). The number-average particle size ($D_n$) and the polydispersity index ($D_w/D_n$, where $D_n$ is the weight-average particle size) were 320 nm and 2.48, respectively. The solid content of the final PThTA emulsion determined by gravimetry was 10.8 wt%. The inset of Fig. 2(b) shows the emission of the PThTA nanoparticle emulsion under UV irradiation at 365 nm. The occurrence of protonation in the PThTA nanoparticles shifted the surface zeta potential from −50 ± 6 to −36 ± 4 mV because of the acidic condition during the oxidative polymerization.

3.3. Structural analysis of the PThTA nanoparticles

The FTIR spectrum of the PThTA nanoparticles was measured and is shown in Fig. 3(c). For comparison, the FTIR spectra of the Th monomer and TA-salt sodium salt are shown in Fig. 3(a) and (b), respectively. Fig. 3(a) shows the C=C stretching peaks of the thiophene aromatic rings at 1443–1523 cm$^{-1}$ [17,18], the C−H out-of-plane bands at 864–987 cm$^{-1}$ [19], and the C=S−C out-of-plane deformation at 758 cm$^{-1}$ [20,21]. Fig. 3(b) shows the symmetric and asymmetric stretching peaks of carboxylate (COO) at 1408 and 1562 cm$^{-1}$ [22]. Fig. 3(c) shows the CH$_2$ stretching peak at 1455 cm$^{-1}$ and the C−O stretching peak at 1265 cm$^{-1}$, respectively [22]. The COO of the TA sodium salt was bonded with sodium in salt form. However, the salt form of TA was completely dissolved in the mixture medium. Simultaneously, Fe$^{3+}$ ions were drawn to the COO of TA through the electrostatic attractions between the cationic Fe$^{3+}$ and the COO of TA. Under the acid condition, the COO functional group of the PThTA was protonated by rich of proton during oxidative polymerization [22−24]. The surface charge density and surface (zeta) potential are also related to the protonation of COO.

3.4. Formation and growth of the PThTA nanoparticles

Fig. 4 shows the SEM images of the PThTA nanoparticles captured at different polymerization times. As shown in Fig. 4(a−c), the PThTA nanoparticles in the early period of polymerization, from 10 min to 60 min, exhibit an irregular shape, seeming not yet solidified. After 120 min, the PThTA nanoparticles become larger and spherical due to the increase in monomer conversion. After 240–360 min, the PThTA nanoparticles become concrete and exhibit a discrete particle morphology.

The time-evolution particle number ($N_p$) of the PThTA nanoparticles was obtained from the DLS data and gravimetry [25]; the results are shown in Fig. 5. At the beginning of polymerization (after 15 min, ~11% monomer conversion), the $N_p$ was
approximately $2.5 \times 10^{21} \text{ cm}^{-3}$. After that, $N_p$ exponentially decayed until the conversion approached 60% and became invariant at about $0.3 \times 10^{21} \text{ cm}^{-3}$ [26,27]. This can be explained by the coagulation among the PThTA precursor particles during the early stage of polymerization. As coagulation proceeds, both the size and electrostatic stability of the PThTA precursor particles increase. From 120 to 240 min during the polymerization, the conversion increased from 60 to 80%, and, thereafter, the coagulation almost ceased and neither $N_p$ nor $D_n$ changed further. The results are in good agreement with the SEM images in Fig. 4.

To estimate the relative reactivity between the Th and TA sodium salt in the early stage of copolymerization, the PL emission spectra of the PThTA nanoparticles were recorded at a wavelength of 400 nm as a function of the polymerization time from 30 s to 10 min, with the results shown in Fig. 6. The PL spectra in Fig. 6 shed light on the initial growth mechanism of the PThTA precursors. After 30 s of polymerization, the intensity of the PL peak at 438 nm rapidly increased, compared to that before the polymerization (indicated as ‘TA salt monomer’ in the legend because of the low water-solubility of the Th monomer) [28]. The intensity increase at 438 nm is attributed to the TA salt-rich oligomers at the beginning of the copolymerization. In addition, Th does not exhibit any PL emission peak in the monomer state. As the polymerization proceeds from 60 to 600 s, the maximum emission wavelength shifts from 438 to 510 nm, which implies that the Th monomers are dominantly polymerized. As the polymerization continues, the PThTA oligomers become more hydrophobic and readily precipitate, forming precursor particles. These particles then coagulate until they can gain sufficient colloidal stability.

### 3.5. Formation mechanism of the PThTA nanoparticles

Fig. 7 shows a schematic diagram of the copolymerization between the Th and TA salt with FeCl$_3$/H$_2$O$_2$ in the water phase. Before polymerization, the Th monomer is dispersed in the water phase and exists as droplets due to high-shear mixing. On the other hand, TA salt monomers are oxidized first by Fe$^{3+}$ before the Th monomers due to their higher water-solubility. TA salt monomers form a dimer by oxidation, while the reduced Fe$^{2+}$ ion is oxidized by H$_2$O$_2$, which accompanies the Fenton reaction [29,30]. As the polymerization proceeds, the oligomers become more hydrophobic by adding Th monomers, that is, Th-rich oligomers. They then precipitate in a coil-up conformation and become PThTA precursor
particles because of their hydrophobicity. Coagulation of the hydrophobic precursor particles continues until the growing particle obtains sufficient electrostatic stability. Simultaneously, the Th monomers in the droplet phase diffuse into the growing PThTA particles through the aqueous phase, and oxidative polymerization continuously proceeds.

3.6. Dispersibility of the PThTA nanoparticles

Fig. 8 shows the dispersion state of the PThTA nanoparticles in various organic solvents. The photographic image suggests that the PThTA nanoparticles are well dispersed in polar solvents. For dispersibility of PThTA, both hydrogen bonding and dipole−dipole interaction are important factors governing the dispersion state. PThTA has a heterocyclic compound with one sulfur atom; thus, hydrogen atoms from the organic solvent are attracted to the lone-pair of electrons on the negatively polarized sulfur atom of PThTA to form a hydrogen bond. The sulfur atom of the thiophene structure is more electronegative than the hydrogen and has a lone-pair of electrons. The lone-pair orbital of the sulfur atoms in PTh projects into space away from the positively charged nuclei, causing a considerable charge separation and a large contribution to the dipole−dipole interaction component [9,31]. As a result, the PThTA nanoparticles have better dispersibility in polar solvents, such as alcohol, DMSO, DMF, and NMP, than in non-polar solvents [13].

3.7. PL emission properties of the PThTA nanoparticles

Fig. 9(a) shows the PL emission of the PThTA nanoparticle emulsions with different polymerization time under UV irradiation at 365 nm. The emission color of PTh is generally known to be red. However, the emission color of the PThTA nanoparticle emulsions after 1 and 3 h of polymerization seems bluish purple; after that, the color turns to scarlet. Enhanced luminescence quantum yields of the PThTA nanoparticles in an aqueous medium were estimated to be 3.22. In addition, the color change of the PThTA particles in an emulsion was closely related to the growth of the polymer chain length rather than the size effect. In this system, thiophene monomer was diffused onto the surface of SDS and polymerization was initiated by the surface dym C2þ through the electrostatic attractions. As the result, the oligomers are more easily oxidized than the monomer and turn into their cationic radical forms. And the molecular weight of polythiophene nanoparticles can be indicated a linear dependence on the conversion. However, COO− of TA-salt was used as a co-monomer and stabilizer to drive Fe3þ through the electrostatic attractions as mention in Answer 1. Consequently, an electron would be more easily transferred to the near neighbor conjugated molecules than previous study [9]. Fig. 9(b) shows the weight-average molecular weight of the PThTA nanoparticles as a function of monomer conversion, measured by GPC after the nitrination of PThTA [32,33]. Additionally, the amount of the nitrated final polythiophene nanoparticles was about 90 mg (approx. 90%). The degree of nitrination was calculated from the N/C molar ratio obtained in elemental analysis. The nitrated polythiophene analytical data was indicated an N/C molar ratio of (9.34/14.01)/(34.92/12.01) = 0.92N/4C, corresponding to a degree of nitration of 92%. As the polymerization proceeded, the molecular weight of PThTA increased simultaneously with the conversion.

In particular, the initial nucleation of a particle occurs by micelle formation with a sphere morphology in the case of the emulsification method. In this surfactant-free method, nucleation was started by aggregation of the initial random copolymer particles through a particle growth mechanism. The TA sodium salt plays a pivotal role in the growth of PTh to drive Fe3þ into the initial PThTA particles. Based on the results, it can be concluded that the molecular weight (or chain length) significantly affects the PL emission color of the PThTA nanoparticles rather than the particle size [34,35]. Until now, a couple of mechanisms have been proposed for size-dependent
Fig. 9. (a) Photographic image of the PL emission of the PThTA nanoparticle emulsions with varying polymerization time under UV irradiation at 365 nm. The concentration of PThTA was 2.3 × 10^{-5} M. (b) Average molecular weight of PThTA nitrate for CPC analysis as a function of monomer conversion.

spectroscopic properties in nanoscale particles: quantum confinement [36,37] and lattice softening [38,39]. Thus, the PThTA solution concentration was controlled at 1.6 × 10^{-3} M because of preventing an effect of quantum confinement. The interparticle interaction was occurred by the particle size below 30 nm, however, the size of PThTA nanoparticles in the surfactant free system was over 300 nm. As the result, the PThTA nanoparticle was not affected by both confinement effect and interparticle interaction.

4. Conclusion

We reported that PThTA nanoparticles were successfully prepared with Fe^{3+}-catalyzed oxidative polymerization and surfactant-free oxidative polymerization in an aqueous medium. A growth mechanism for the particle formation of the PThTA nanoparticles was suggested based on the initial PL spectroscopy and the number of particles in relation to the polymerization time. As the polymerization time increases, the emission color of the PThTA nanoparticles in the emulsion state changes from bluish purple to scarlet, with an estimated quantum yield of 3.22. Moreover, the maximum emission wavelength significantly shifted from 450 nm to 520 nm as the PThTA chain length, i.e. the molecular weight, increased as a function of monomer conversion. Our results provide new insights on surfactant-free oxidative polymerization and may serve as guidelines for the preparation of new conjugated polymer emulsion systems for potential optoelectronic devices. Future studies will be undertaken in new substituted polythiophene nanoparticles using surfactant free oxidative polymerization.

Acknowledgments

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0093823). This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2007-0056091) and a grant from the Industrial Technology Development program (K0006005) of the Ministry of Knowledge Economy (MKE) of Korea. This research was supported by the Nano Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2008-2002380/2012-0006227). This research was supported by the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT & Future Planning (2010-0019550). This research was also supported by the Converging Center Program through the Ministry of Education, Science and Technology (2010K001430).

References


de Souza JM, Pereira EC. Luminescence of poly (3-thiopheneacetic acid) in alcohols and aqueous solutions of poly (vinyl alcohol). Synth Met 2001;118:167–70.


Beri RG, Hacche LS, Martin CF. Gel permeation chromatography Hplc: practical and industrial applications; 1997. p. 245.


