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

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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 $FeCl_3/H_2O_2$ 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.

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 $FeCl_3/H_2O_2$ (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-thiophenacetic 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.

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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 ($FeCl_3$, Aldrich Co., USA) and a 30% aqueous solution of hydrogen peroxide (H_2O_2) (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 N_2 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 N_2 bubbling. H_2O_2 (0.87 mol, 98.73 g, 30% aq.) was then added to the reactant mixture solution. After 10 min, $FeCl_3$ (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 PTTA 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% H_2SO_4: 61% HNO_3: H_2O = 1.00: 0.17: 0.13 v/v) prior to GPC analysis. An excess amount of the mixed acids was added to the PTTA nanoparticles, and the mixture was stirred for 4 h at 40 °C. After cooling to room temperature, the mixture was poured into cold DDI water. The nitrated polymer was collected by filtration, washed with DDI water, and then dried in vacuo [13,14]. In addition, the analytical data of S/O molar ratio was obtained by elemental analysis. All samples were purified by centrifugation and subsequently analyzed by elemental analysis after freeze drying. Analytical data of PThTA-30s, PThTA-60s, PThTA-180s and PThTA-300s gave an S/O molar ratio of (13.8/32.1)/(11.6/16) = 1.19S/2O corresponding to about $[Th]_1[TA\text{-}salt]_5$, (14.1/32.1)/(10.8/16) = 1.3S/2O corresponding to about $[Th]_1[TA\text{-}salt]_3$, (17.5/32.1)/(9.3/16) = 1.88S/2O corresponding to about $[Th]_1[TA\text{-}salt]_1$, and (24.6/32.1)/(0.7.7/16) = 3.2S/2O corresponding to about $[Th]_2[TA\text{-}salt]_1$, respectively. Thus, polymerized [Th] unit was dramatically increased from 119% to 320%. Ultimately, Th and TA-salt unit were changed 1:5, 1:3, 1:1, and 2:1, respectively (Table 1).

2.4. Characterization of the PTTA 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 spectrofluorophotometer (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 $UV_{365\ nm}$ were captured by UV itec STX-20.M. For the UV and PL spectra analysis, the concentration of the PThTA nanoparticle emulsion was fixed at 3.89×10^{-5} M. Quinine sulfate (1.0×10^{-5} M) in a 0.1 M H_2SO_4 solution was used as a reference for calculating the quantum efficiency. The quantum efficiency of the sample was calculated using the following equation [15]:

$$\phi_{unk} = \phi_{std}\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2$$

where ϕ corresponds to the quantum yields, I to the integrated PL emission intensity excited at the maximum wavelength of the UV absorbance, A to the absorbance at the excitation wavelength at the same concentration, and η to the refractive index of the solvents used. The subscripts unk and std correspond to the unknown and the standard, respectively. Their values in this study were ϕ_{std} (0.54), I_{unk} (39.24), I_{std} (150.46), A_{unk} (0.23), A_{std} (0.028), η_{unk} (1.33), and η_{std} (1.33), respectively.

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

Sample	$[Th]_m[TA\text{-}salt]_n$	S	O	Degree of S ratio
PThTA-30s	$[Th]_1[TA\text{-}salt]_5$	13.8	11.6	1.19
PThTA-60s	$[Th]_1[TA\text{-}salt]_3$	14.1	10.8	1.3
PThTA-180s	$[Th]_1[TA\text{-}salt]_1$	17.5	9.3	1.88
PThTA-300s	$[Th]_2[TA\text{-}salt]_1$	24.6	7.7	3.2

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

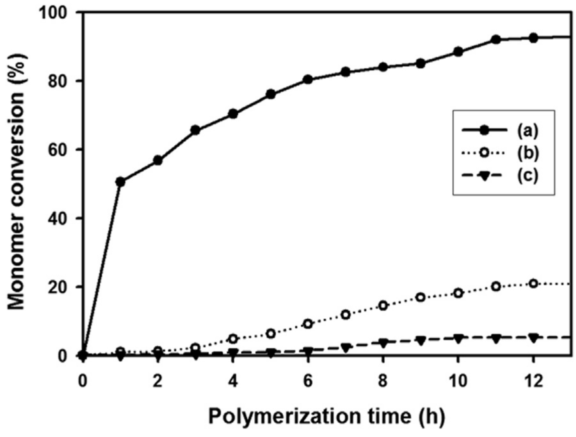

Fig. 1. Time–conversion curves for the PThTA nanoparticles prepared with different oxidants in the absence of a surfactant: (a) combinational $FeCl_3/H_2O_2$ system, $FeCl_3$ was 3.1×10^{-4} mol, 45.0 mg and H_2O_2 was 0.87 mol, 98.73 g 30% aq, (b) H_2O_2 was 0.87 mol, 98.73 g 30% aq and (c) $FeCl_3$ was 3.1×10^{-4} mol, 45.0 mg.