Hyper Functionalized Nanoparticle Technology and Their Applications

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Introduction

During the last decade, polyaniline (PANI) and polythiophene (PT) have emerged as important conductive and luminescent polymers because of its good environmental stability, low cost, and high conductivity upon doping with acid. Due to π-conjugated carbon backbone, polythiophene exhibits a number of interesting electrochemical, electrochromic, luminescent, and shielding properties, and which provides a basis for various new technologies.[1,2] Thiophene derivatives can be oxidized chemically, photochemically or electrochemically and polymerized to corresponding oligo- or polythiophenes. And generally conductive polymers, PT and PANI in particular, however, are difficult to process because of their insolubility in common solvents. Thus, many works have been conducted to improve its processability[3]. Therefore, intensive efforts have been initiated to aim for the development of highly soluble and easily processible PTs by incorporating alkyl, aryl or alkysulfonyl groups, for organic solvents and carboxylic or sulfonic acids for water and PANIs by ring substituted PANIs[4] and N-substituted PANIs[5], respectively. Despite the progress achieved in these studies, the yield of PT was often low and the process itself can be expensive or requires the use of toxic solvents. Until now, the oxidative chemical polymerization of unsubstituted thiophene in aqueous medium has hardly been reported due to several critical problems, such as poor water-solubility of PTs, low oxidizing activity of catalysts, and extremely low conversion. However, preparation of PANI dispersions is one of the ways to tackle these problems, since colloidal dispersions may often be applied in place of true solutions. The PANI dispersions were prepared by an oxidative dispersion polymerization using dodecylbenzene sulfonic acid and poly (sodium 4-styrenesulfonate) as stabilizer and co-dopant[6].

An alternate route for preparing colloidal conductive polymers involves coated latex particles with a thin layer of conjugate polymer to form conductive composites with core-shell morphology[7]. Conductive polymer thin films coated onto the colloidal surfaces have been of particular interest, owing to the expected improvement of polymer processability and unique properties intrinsic in dispersed nanometer or micrometer-sized materials. Therefore, in this study, we proposed the formation of polythiophene nanoparticles via an Fe^{3+} catalyzed oxidative polymerization of unsubstituted thiophene inside nano-sized droplets of the thiophene monomer, i.e., nano-reactors, dispersed in the aqueous phase. This novel and facile method includes an $FeCl_3/H_2O_2$ (catalyst/oxidant) combination system and is different from the conventional oxidative polymerization of thiophene in chloroform. And, for core-shell morphology, we prepared 2 dimensional luminescent polymer film layer of ten nanometers in thickness onto monodisperse polystyrene nanoparticles surfaces. Furthermore, we prepared poly (SHEA) modified PSt latex particles of which shell have sulfonic acid-rich layer by using sulfonated N-(2-hydroxyethyl) aniline (SHEA). This sulfonic acid-rich layer from the poly (SHEA) can play an important role in the colloidal stability and conductivity. The poly (SHEA) and PANI-coated poly (SHEA) modified PSt (PSHEA-PANI-PSHEA-PSt) composite latex particles were also synthesized in the presence of sodium lauryl sulfate (SLS) by chemical oxidation polymerization, and extensively characterized.

Experimental

Materials

1. Preparation of polythiophene nanoparticles
Polythiophene nanoparticles were synthesized in a 100mL round bottomed flask, which was fitted with a reflux condenser, a nitrogen gas inlet, ingredient inlet, and a Teflon-magnetic stirrer. The reaction temperature was 50°C and maintained in a thermostat. The reaction procedure is as follows: dissolved DDI water was added to the reactor.

Thiophene monomer was dropped on the aqueous SDS solution and then several hydrogen peroxides were added to the reactant mixture solution. Anhydrous $FeCl_3$ in DDI water was added to the reactant mixture solution, and then this reactant mixture was stirred for 12 hrs at 50 °C. The yield of PT was ca. 99%.

2. Synthesis of Core-Shell Poly(Styrene/Thiophene) nanocomposite latexes
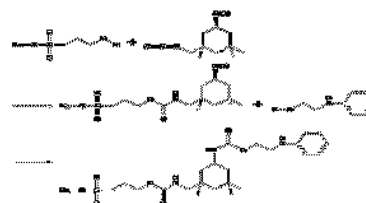Sodium *p*-styrene sulfonate and sodium bicarbonate were dissolved in DDI for 0.5hr under N_2 atmosphere. Styrene and thiophene were added to the mixture and heated to 80°C. After 0.5hr, KPS, $FeCl_3$, hydrogen peroxide were added to the mixture and kept at the same reaction conditions for 24hrs.

3. Synthesis of polyaniline-coated multi core-shell polystyrene latexes
3.1. Preparation of Sulfonated N-hydroxyethyl Aniline(SHEA)
Synthesis of the SHEA was shown in Scheme 1 and can be summarized as follows: 3-hydroxy-1-propanesulfonic acid, sodium salt (8.11g, 50mmol), was dissolved in 80 ml of DMSO and heated to 80℃ for 0.5 hrs under N_2 atmosphere. IPDI (11.17g, 50mmol) was added to the mixture and kept at the same temperature. The remaining isocyanate (NCO) concentration was monitored by *in-situ* FT-IR. When the NCO peak disappeared, the reaction was terminated. Then, the final SHEA product as brown powder was obtained after the removal of water. The yield of SHEA was ca. 95%.

Scheme 1. Sulfonated hydroxyethyl aniline(SHEA)

3.2. Synthesis of PSHEA-PSt Composite Particles
The PSt model colloid was prepared by emulsifier-free emulsion polymerization. All reactants (styrene, sodium *p*-styrene sulfonate, deionized water) were added in a round bottom flask equipped with condenser and mechanical stirrer. The PSt model colloid was cleaned by a serum replacement. The SHEA aqueous solutions were added into the PSt model colloid with different SHEA concentration. APS aqueous solutions were added into the mixture and the reaction mixture was stirred at 20℃ for 24 hrs. After polymerization, the APS and unreacted SHEA/or water-soluble low-molecular poly (SHEA) were removed using serum replacement for 12 days.

3.3. Synthesis of PSHEA-PANI-PSHEA-PSt Composite Particles
PANI-PSHEA-PSt composite latex was prepared by oxidation polymerization of Ani-HCl with APS after the protonation of PSHEA-PSt latex. Basic preparation protocol was as follows: The PSHEA-PSt and PSt model latexes were stabilized with SLS and followed by the addition of Ani-HCl. Afterwards, the latexes were stirred for 1 hr. Calculated amount of HCl was added to adjust total ionic strength (incl. HCl) of the all samples. In the case of 10wt% aniline based on the PSt polymer, no external acid was added. Oxidation polymerization of aniline was initiated by the addition of aqueous APS, equivalent to Ani-HCl, solution and the reaction was allowed to proceed for 6 hrs at 3℃. After 6 hrs, reaction temperature was elevated to 25℃ and allowed to proceed for another 18 hrs.

Results and discussion
1. Preparation of polythiophene nanoparticles
Fig. 1 shows the TEM micrograph and particle size distribution of the polythiophene nanoparticles. Fig. 1-(a) shows some aggregates of the polythiophene nanoparticles and the individual particle with raspberry-like morphology. The average particle size of individual particle is ca. 30 nm, and which is in good agreement with CHDF data in Fig. 1(b). Dispersion status shows that the polythiophene nanoparticles are well dispersed in many polar solvents except acetone, chloroform, hexane, and ethyl acetate. Hansen solubility parameters (δ) were introduced to interpret the dispersibility of polythiophene

nanoparticles for various organic solvents. The solubility parameter includes cohesive energy from dispersive force (δ_d), permanent dipole-dipole interaction (δ_p), and hydrogen bonding force (δ_h).
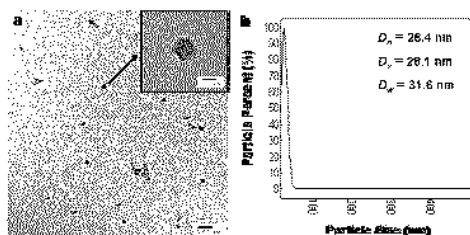

Fig. 1. The TEM images of 30nm unsubstituted polythiophene nanoparticles with spherical-shaped morphologies.

As shown in Table 1, the δ_h is one of the governing factors in the index of dispersions. Thiophene is a heterocyclic compound having one sulfur atom; therefore, hydrogen atoms from organic solvents are attracted to a lone-pair of electrons on the negatively polarized sulfur atom of thiophene to form a hydrogen bond. Dispersibility is affected by the δ_p. The sulfur atom of thiophene is more electronegative than hydrogen and has lone-pair electrons. The lone-pair orbital of the sulfur atoms in polythiophene stick out into space away from the positively charged nuclei, which gives rise to a considerable charge separation and large contribution to δ_p. As a result, the dispersibility of polythiophene nanoparticles in polar solvents, like as alcohol, DMSO, DMF and NMP, is better than in non-polar solvents.

Table 1. Hansen solubility parameters of various organic solvents at 25℃

2. Synthesis of Core-Shell Poly(Styrene/Thiophene) nanocomposite latexes

Core-shell poly(St/T) latex particles were prepared by oxidative polymerization of thiophene during emulsion polymerization of styrene using the different polymerization rates of each monomers. In general, polystyrene seed particles with 3wt% NaSS can be polymerized in 4hrs, but on the other hand polythiophene needs more time to be polymerized from monomers. Pre-matured growing polystyrene latex particles provide polymerization loci with hydrophobic domains for growing oligo-thiophene to polymerize with monomers or other oligomers. A high concentration of cationic radicals of thiophene around the vicinity of the pre-matured growing PS particles is expected due to the electrostatic attraction between sulfonate (SO$_3^-$) groups from the surface-rich NaSS and Fe^{3+} ions, which are drawn into the interface of the pre-matured growing PS particles from the water phase. Representative SEM images of core-shell poly(styrene/thiophene) latexes are shown in Fig. 2. The average particle size (D_n) of the latexes was from 200 nm to 600 nm. Surface morphology of the particles is rugged due to polythiophene in the shell of the latex. To confirm core-shell morphology of the resulting particles, they were exposed to a chloroform (CHCl$_3$) solution for 15-20 h to remove the polystyrene in core. As seen in Fig. 2-(b), crumpled polythiophene shell was observed.
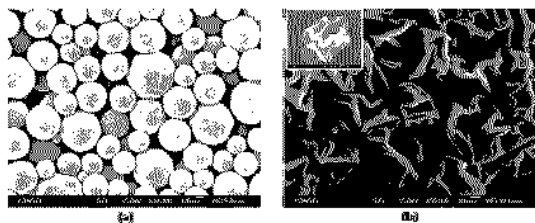

Fig. 2. SEM images of (a) core-shell poly(St/T) latex particles (b) crumpled polythiophene shell of poly(St/T) latex particles

3. Synthesis of polyaniline-coated multi core-shell polystyrene latexes

For the investigation of the role of poly (SHEA) in the composite latex formation and conductive property, the PSt model latexes were prepared and characterized. The poly (SHEA) modified PSt (PSHEA-PSt) particles prepared by APS showed higher ζ-potential compared to PSt model latexes due to the sulfonic acid sodium salt of SHEA, which implied that the poly (SHEA) polymerized by APS was successfully coated onto the PSt model colloids. Most of the SHEA molecules would rather adsorb onto the PSt model particles than form self-aggregates during the oxidation polymerization by APS since the amphiphilic structure of the SHEA. Prior to PANI coating onto the poly (SHEA)-modified PSt (PSHEA-PSt) composite particles, sodium salt in the SHEA was replaced. During these exchange process, APS was exchanged with hydrogen or removed. ζ-potential of the PSHEA-PANI-PSHEA-PSt composite particles, which were treated by post-addition of the SHEA and APS, was -21.8mV at pH 6.8. However, the ζ-potentitial of the PANI-PSt particles was 4.8 mV at pH 6.8 and this latex particle was coagulated during the cleaning process. These results can be explained by the fact that the PSHEA-PANI-PSHEA-PSt composite particles are well stabilized by anionic shells due to the poly (SHEA). On the contrary, the PANI-PSt particles show positive potential value due to the cationic nitrogen in the PANI. This result notes that stable and conductive polymer colloids can be prepared by multi-layered polymers of the poly (SHEA), PANI, and poly (SHEA), where the poly (SHEA) was used as a stabilizer, PANI, conductive materials, and the poly (SHEA), co-doping agent and stabilizer onto the PSt model colloids as shown in Fig. 3.
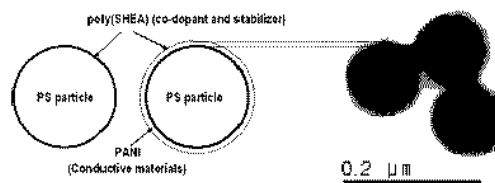

Fig. 3. Schematic presentation of PSHEA-PANI-PSHEA-PSt composite particles.

Conclusions

We have demonstrated that unsubstituted thiophene can be polymerized by oxidative polymerization. 99% monomer conversion was achieved by minimizing the amount of FeCl$_3$, which usually deteriorates the PL property of polythiophene nanoparticles. The fine dispersion state would be expected to increase the processibility of polythiophene in various electrical and electro-optical fields. In addition polydispersed core-shell poly(St/T) latex particles were successfully prepared by oxidative polymerization during emulsion polymerization. The resulting latex particles showed improved luminescence efficiency in solid state due to the polythiophene shell thickness below 20nm. Styrene and thiophene were polymerized independently and each composition was isolated with independent domain by the phase separation, which was corroborated by the SEM analysis. The PSHEA-PSt composite particles using PSt model colloids were prepared successfully by chemical oxidation polymerization using APS. The PSHEA-PANI-PSHEA-PSt composite particles were prepared by oxidation polymerization of aniline and SHEA in the seeded polymerization with PSHEA-PSt particles.

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