Luminescent Polymer Latex Particles Prepared by Oxidative Polymerization in Emulsion Polymerization

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Summary: It was demonstrated that core-shell poly(styrene/thiophene) latex particles were successfully prepared by oxidative polymerization during emulsifier-free emulsion polymerization. This method provided a new fabrication route of core-shell type luminescent polymer particles with a thin shell layer. The core/shell structure of the resulting latex particles was proved by SEM analysis. It supported a strong evidence that each composition was isolated in independent domains, and which was corroborated by the TGA analysis. The resulting latex particles showed that luminescence efficiency in the solid state was better than that in the emulsion state due to the core-shell morphology with a thin shell structure. This new strategy is universal for the synthesis of many other materials or composite particles with controlled morphology. Such core-shell morphology controlled conjugated polymer composite particles may have potential practical applications in various electrical and electro-optical devices, especially in polymer light emitting diodes (PLEDs).

Keywords: core-shell; emulsifier-free emulsion polymerization; luminescence efficiency; luminescent polymers; oxidative polymerization

Introduction

Poly(thiophene)s are one of the most studied and important classes of linear conjugated polymers because they can easily produce a red color that is difficult to achieve in other conjugated polymers.[1] Unique electro-optical properties that can be widely tuned result in a tremendous amount of interest being focused on this class of conjugated polymers.[2] However, the luminescence efficiency of poly(thiophene)s in the solid state is relatively low. Whereas in solution the photoluminescence efficiency of poly(3-alkylthiophenes) is ~30–40%, for example, it drastically drops to 1–4% and lower in the solid state due to the increased contribution of non-radiative decay via interchain interactions and intersystem crossing caused by the heavy-atom effect of sulfur.[2,3] Thus, it becomes one of the most critical drawback for practical applications.[4] In this study, we have introduced shell layer of luminescent polymer, i.e., poly(thiophene)s with a film thickness below ca. 30nm onto the surface of monodisperse poly(styrene/sodium *p*-styrene sulfonate) (poly(St/NaSS)) latex particles to improve the photoluminescence efficiency of poly(thiophene)s in the solid state. In recent years, it has been reported to prepare colloidal conducting polymers, which involves coated latex particles with a thin shell layer of conjugated polymer to form conductive composites with core-shell morphology.[5] In contrast, few studies have dealt with luminescent core-shell latex particle composites with the thin layer of luminescent polymer. For the first time, we have successfully prepared the core-shell poly(styrene/thiophene) latex particles via oxidative polymerization during emulsifier-free emulsion polymerization.

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Experimental Part

Materials

Styrene monomer (St, Junsei Chemical, Japan) was purchased and purified using an inhibitor remover column (Aldrich Co., USA). The purified monomer was kept at $-5\,^\circ C$ until use. Sodium *p*-styrene sulfonate (NaSS, Aldrich Co., USA) was purchased and used as received. Potassium persulfate (KPS, Junsei Chemical, Japan), sodium bicarbonate ($NaHCO_3$, Aldrich, USA), thiophene (Aldrich, USA), iron chloride ($FeCl_3$, Kanto Chemical, Japan), and hydrogen peroxide (H_2O_2, Dong Yang Co., Korea) were analytical grades and used without further purification. Double-distilled and deionized (DDI) water was used throughout the experiment.

Synthesis of Core-Shell Poly(Styrene/Thiophene) Latex Particles

Sodium *p*-styrene sulfonate (NaSS) and sodium bicarbonate ($NaHCO_3$) were dissolved in DDI water for 0.5hr under N_2 atmosphere. Styrene and thiophene were added to the mixture and heated to $80\,^\circ C$. After 0.5hr, hydrogen peroxide, KPS, $FeCl_3$ were added to the mixture and kept at the same reaction conditions for 24hrs.

Characterization

The solid content of the final latex, as determined by a gravimetrical analysis method, was 7.94 wt%. The particle size and size distributions were measured by field-emission scanning electron microscopy (FE-SEM; JSM-6500F, JEOL). Photoluminescence spectra were recorded with a spectrofluorophotometer (RF-5301PC, Shimadzu). The solid content of the latex in the quartz cell was 0.1 wt%. The excitation was incident at an angle of 0° onto the front face of the sample, and the emission was recorded in reflection at an angle of 90° with respect to the surface normal.

Result and Discussion

Core-shell poly(styrene/thiophene) latex particles were prepared by the oxidative polymerization of thiophene monomers during the emulsifier-free emulsion polymerization of styrene monomers using the different polymerization rate of each monomer. In general, poly(St/NaSS) seed particles with 3 wt% NaSS (based on the styrene monomer) can be polymerized in 4hrs at $80\,^\circ C$, on the other hand, thiophene monomer (0.072 mol, 6.0 g) needs a longer time to polymerize (i.e., for 12 hrs, with using $FeCl_3$ (5.5×10^{-5} mol, 9.0 mg) and H_2O_2 (0.397 mol, 13.5 g) as oxidants at $80\,^\circ C$). Growing and pre-existing poly(St/NaSS) latex particles provide polymerization loci for the growing oligomers of thiophene to polymerize with monomers or other oligomers. The shell layer of poly(thiophene) is believed to be prepared by the Fe^{3+}-catalyzed oxidative polymerization of thiophene monomers onto the surface of the pre-existing poly(St/NaSS) particles.[6] This luminescent shell layer of core-shell type poly(-styrene/thiophene) particles resulted from the electrostatic attraction between sulfonate (SO_3^-) groups of the NaSS and Fe^{3+} ions, which are rich on the surface of latex particles, and different hydrophilicities of growing polymers. The high concentration of oligomeric cationic radicals of thiophene around the vicinity of the poly(St/NaSS) particles is expected due to the electrostatic attraction with the sulfonate (SO_3^-) groups of the NaSS-rich surface, which are drawn into the interface of the pre-matured poly (St/NaSS) particles from the water phase.

The representative SEM images of core-shell poly(styrene/thiophene) latexes are shown in Figure 1. The average particle size (D_n) of the latexes was from 200 nm to 600 nm. Rugged surface morphology of the particles was observed, as shown in Figure 1-(a). To confirm core-shell morphology of the resulting particles, they were exposed to a chloroform ($CHCl_3$) solution for 15–20 hrs to remove the polystyrene cores. As seen in Figure 1-(b), the image of crumpled poly(thiophene) shells corroborates the core-shell morphology of the resulting latex particles.

Figure 2 shows thermal degradation of poly(styrene), poly(thiophene) and core-

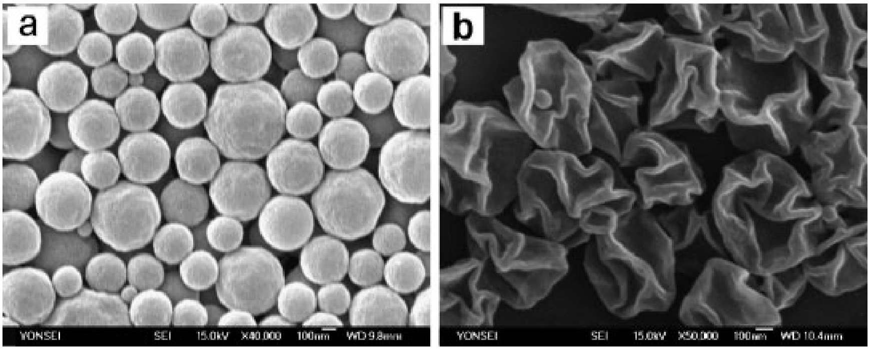

Figure 1.
SEM images of (a) core-shell poly(styrene/thiophene) latex particles (b) crumpled polythiophene shell layer of poly(styrene/thiophene) latex particles.

shell poly(styrene/thiophene) latexes. As seen in Figure 2-(a) and (b), the initial decomposition temperature of poly(styrene) and poly(thiophene) samples were 400 °C and 100 °C, respectively. As seen in Figure 2-(c), however, two onset points of decomposition were observed in the core-shell poly(styrene/thiophene) sample. This result provides more evidence on the core/shell structure of resulting latex particles. In addition, this result shows indirectly that each composition maintained independent domains.

Figure 3 represents the photographs and photoluminescence of core-shell poly(styrene/thiophene) latex particle in the emulsion and solid states under 365 nm UV light. As seen in Figure 3, core-shell poly(styrene/thiophene) latex (s.c. = 0.1wt%) in the emulsion state emitted orange-red light ($\lambda^{PL} = 570$ nm) under 365nm UV light. In the solid state, core-shell poly(styrene/thiophene) solid emitted the same color ($\lambda^{PL} = 571$ nm) under 365 nm UV light. From the PL spectra seen in Figure 3-(e and f), this emission colors are in good

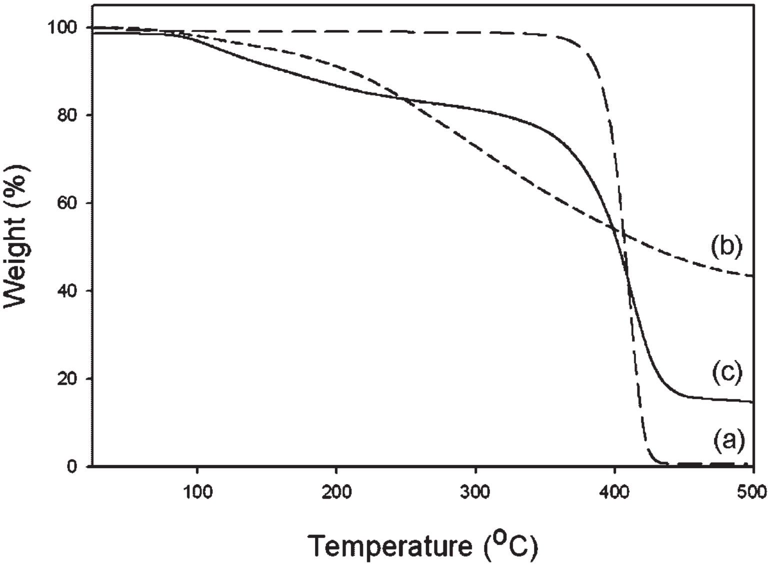

Figure 2.
TGA curves of (a) poly(styrene) (b) poly(thiophene) (c) core-shell poly (styrene/thiophene) latex particles.

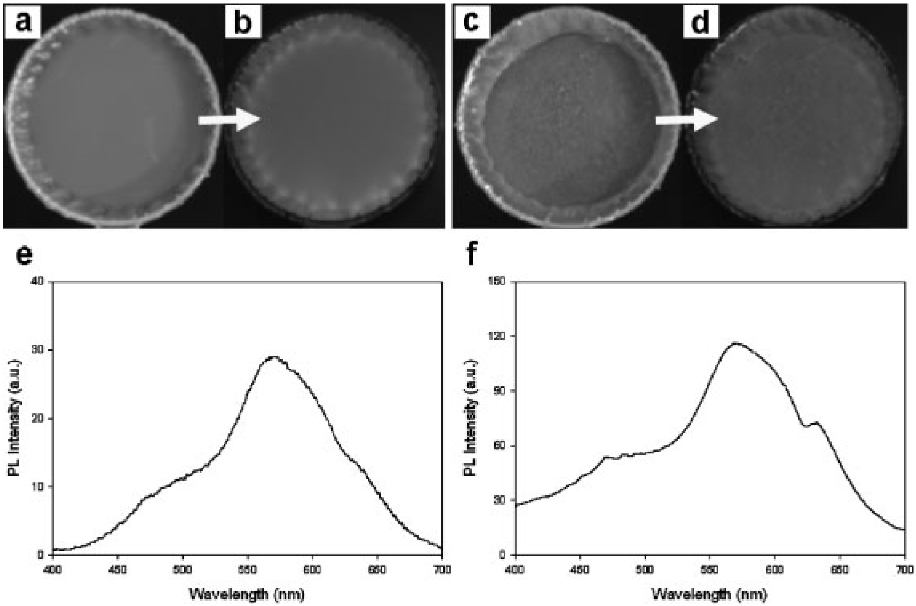

Figure 3.
Photographs and photoluminescence of core-shell poly(styrene/thiophene) latex particles. Emission of core-shell poly(styrene/thiophene) latex particles in the emulsion state under (a) white light and (b) 365 nm UV light and in the solid state under (c) white light and (d) 365nm UV light, respectively. PL spectra of core-shell poly(styrene/thiophene) latex particles in the (e) emulsion and (f) solid state, respectively. Reference peak: 469 nm (this peak resulted from H_2O and H_2O_2)

agreement with the PL data ($\lambda^{PL}_{Emulsion} = 570$ nm and $\lambda^{PL}_{Solid} = 571$ nm) in the emulsion and solid state, respectively. Moreover, PL intensities of core-shell poly(styrene/thiophene) latex in the emulsion state and solid state were ca. 30 and 120, respectively. Following the proportion of efficiency drop mentioned above, the PL intensity of core-shell poly (styrene/thiophene) latex in the solid state should have been ca. 25 considering the poly(thiophene) shell content (32.3 wt%) of resulting latex particles. However, it was ca. 120 in the same measuring conditions, thus luminescence efficiency increased 5 times, resulted from reducing the luminescence quenching in the solid state by suppressing the aggregation effect due to the thin shell layer. This result is particularly important when, for example, core-shell poly(styrene/thiophene) latex particles are desired for applications as emissive materials in LEDs. In addition, an increase in the PL intensity was observed at 632nm in the solid state, which resulted from the difference in effective conjugation chain length effect.[7]

Conclusions

In summary, we have demonstrated that core-shell poly(styrene/thiophene) latex particles were successfully prepared by oxidative polymerization during emulsifier-free emulsion polymerization. This method provides a new fabrication route of core-shell luminescent polymer composite particles with a thin shell layer, offering far greater control of core-shell morphology than techniques that involve stepwise reactions to modify the surface of seed particles chemically in order to coat core seed particles. From the SEM data, core/shell structure of resulting latex particles was proved and this provides key evidence that each composition was isolated with independent domains, and which was corroborated by the TGA analysis. The resulting latex particles showed that the luminescence efficiency in the solid state is better than that in the emulsion state due to the core-shell morphology with the thickness of shell layer below ca. 30nm. Moreover, this new strategy is universal for many materials beyond the poly(thiophene) illustrated in this paper, i.e., poly(pyrrole), poly(fluorene) and poly(aniline), etc. Such core-shell morphology controlled conjugated polymer composite particles may have potential practical applications in various electrical and electro-optical devices, for example, solar cells, and field-effect transistors, especially in polymer light emitting diodes (PLEDs).

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