

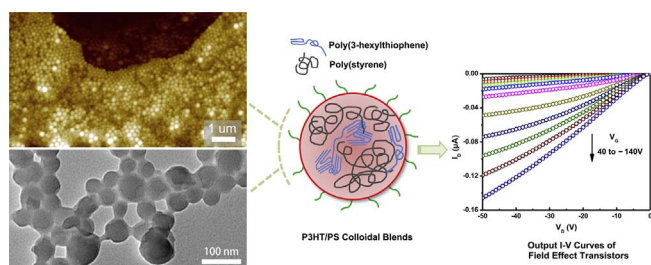
Poly(3-hexylthiophene)/poly(styrene) blended colloids: Exploiting the effects of composition and marginal solvent

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GRAPHICAL ABSTRACT



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ABSTRACT

Herein, aqueous suspensions of poly(3-hexylthiophene)/poly(styrene) (P3HT/PS) blended colloids with varied ratios were prepared using a miniemulsion process. The effects of composition and marginal solvent amount on the aggregates, optical and hole-transport properties of P3HT/PS blended colloids were investigated. Both PS and THF promoted P3HT chain aggregation and electronic coupling, resulting in a red-shift and increased absorbance intensity at the 0-0 and 0-1 vibronic peaks in aqueous suspensions. But, PS prevented further chain packing and aggregation during thermal annealing in solid-state of P3HT/PS blended colloid films, compared to pure P3HT colloids. The crystal lattice spacing in alkyl packing direction of P3HT was not affected by either PS or THF. Additionally, the hole mobility of FETs using pure P3HT colloids was $9.08 \times 10^{-5} \text{ cm}^2/\text{Vs}$, which decreased when P3HT/PS blended colloids were used. However, incorporation of THF enhanced the hole mobility of FETs using P3HT/PS(2/8) blended colloids, from $0.76 \times 10^{-5} \text{ cm}^2/\text{Vs}$ for FETs using blended colloids made from solvent without THF to $1.24 \times 10^{-5} \text{ cm}^2/\text{Vs}$ for FETs using blended colloids made from solvent mixture with 10 vol% THF. These performance improvements will enable greener, more industrially-relevant water-processing of polymers for emerging organic electronics.

1. Introduction

Poly(3-hexylthiophene) (P3HT) as a benchmark semiconducting polymer has been the subject of extensive investigations for various applications, including organic solar cells [1–3], organic light emitting diodes [4–6], and field-effect transistors (FETs) [7,8], attributed to its relatively high hole mobility, controllable regioregularity, tunable microstructure, light weight, flexibility and low-cost solution processing

[9–17]. However, high material cost and environmental instability of P3HT also limit its industrial applications and commercialization.

In recent years, P3HT/insulating polymer blends with majority insulating polymers have attracted increasing interest for reducing materials cost, enhancing mechanical characteristics and providing air stability [18–24]. These blends have showed high charge carrier mobility and excellent electronic performance, even exceeding the performance of pure semiconducting polymer [19,25]. Lu *et al.* showed

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that P3HT/polystyrene blend (0.05/0.95 ratio) FETs doped with F4-TCNQ (tetrafluoro-tetracyanoquinodimethane, 1.5 Å) submonolayer had hole mobility up to 0.1 – 0.5 cm²/Vs [19], Reichmanis *et al.* found that P3HT/insulating polymers (polystyrene, polyisobutylene or polydimethylsiloxane) blends pretreated with either ultraviolet (UV) irradiation or ultrasonication could achieve higher device performance than pure P3HT [20,21].

In addition to bulk P3HT, aqueous P3HT colloids have also presented an attractive alternative for manufacturing electronic devices, since they can decouple the manufacturing processing from final device performance and provide well-defined crystal packing structures [26–32]. Moreover, the morphology and microstructural properties of colloids can be tuned during the colloid formation stage before device manufacture [33]. Most importantly, it provides a greener route for device manufacturing, since it eliminates chlorinated solvents and only water vapor is emitted during device manufacturing.

Andersen *et al.* showed that solar cells with thickness-controlled colloidal active layers could be achieved using either roll-to-roll or screen printing method, where the highest power conversion efficiency of 0.55% was achieved when the film thickness was 500 nm [32]. Good hole mobility of P3HT colloid FETs on the order of 10⁻³ cm²/Vs was reported when a precipitation method was adopted to prepare colloids, and relatively lower hole mobility was reported when using a miniemulsion process to prepare colloids [27,34,35]. It is believed that the miniemulsion process produces lower hole mobility than the precipitation method, due to the charge-trapping effect of the surfactant, which can act as an insulator. However, our previous work showed that the miniemulsion process is still promising and worthy of further investigation, because it could provide a much higher concentration of colloids without coalescence in suspensions rather than precipitation process, which is beneficial to long-time storage, transportation and coating applications for industrial manufacturing. It demonstrated that the hole mobility was enhanced by increasing the number of conjugation groups in the surfactant, which improved the π - π coupling of P3HT colloids and improved FETs performance [36].

Disentanglement of semiconducting P3HT chains in a marginal solvent such as toluene was recently reported to lead to long-range ordering in P3HT aggregates, resulting in enhanced carrier transport properties [37]. A binary solvent mixture of methylene chloride and toluene was also found to improve the molecular ordering of P3HT thin-films [38]. The rationale for using tetrahydrofuran (THF) in our study as the marginal solvent, was its favorable Hansen solubility parameters, its polarity and miscibility with chloroform (CHCl₃) and it is a less toxic alternative to the previously reported on halogenated (methylene chloride) and non-halogenated non-polar (toluene) marginal solvents for P3HT.

Considering the advantages of both P3HT/insulating polymer blends and colloidal processing, it is interesting to explore a material system that utilizes polymer blended colloids. This research probes whether the blends in a colloidal state would have worse, retain a similar or even better performance than that in the bulk state? Thus, one objective of our study is to fundamentally explore the properties of P3HT/polystyrene (P3HT/PS) blended colloids. The other is to investigate the effect of pre-aging on P3HT/insulating polymer blended colloids, by using a marginal solvent for P3HT but good solvent for PS. The P3HT/PS blended colloids were prepared using a miniemulsion process followed by solvent-evaporation, and the morphology and electrical properties of these blended colloids as well as their FETs performance were investigated.

2. Experimental methods

2.1. Materials and sample preparation

Regioregular poly(3-hexylthiophene-2,5 diyl) (P3HT, $\geq 96\%$, $M_w = 71$ K, PDI = 1.7 ~ 1.9) was purchased from Rieke Metals, Inc.

(Lincoln, NE) and used as received. Polystyrene ($M_w = 105$ K, PDI: 2.37) was supplied by AmSty Styrenics Corporation. Technical grade sodium dodecylbenzenesulfonate (SDBS), chloroform (CHCl₃) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Deionized water (18.2 M Ω) was used for the synthesis of all the colloids.

P3HT and PS were dissolved separately in CHCl₃, both at a concentration of 10 mg/ml at 45 °C for 8 hours. Subsequently, P3HT/PS blends with varied weight ratio (2/8, 3/7, 5/5 and 10/0 P3HT/PS) were prepared and magnetically stirred at 700 rpm for 12 hours before usage. To investigate the effect of pre-aging, various concentrations of THF (0, 5, 10, 20 and 30 vol%) were mixed into P3HT/PS (2/8) dissolved in CHCl₃ and they were aged for 12 hours, with magnetic stirring at 700 rpm. P3HT/PS blended colloids in this study were prepared using a miniemulsion process followed by solvent-evaporation from a binary solvent mixture of CHCl₃ and THF. Briefly, P3HT/PS solution (1 ml) was injected into a pre-prepared aqueous solution (3 ml) of surfactant with SDBS at its critical micelle concentration (1.8 mM), and ultra-sonicated using a probe sonicator (Branson sonifier, model S – 450D) at 200 W for 5 min to produce a homogenous dispersion of the organic phase in water. Finally, the dispersion was heated up to 70 °C with gentle stirring for 20 min to remove CHCl₃ and THF. This process resulted in aqueous suspensions of P3HT/PS blended colloids, which were stable for several weeks and with a final concentration of 3.3 mg/ml.

2.2. Colloids characterizations

Atomic force microscopy (AFM) images were acquired using a Veeco atomic force microscope (PSIA 100, Park Systems) with a silicon cantilever in non-contact mode on samples drop casted on glass slides. Transmission electron microscopy (TEM, EM400, Philips) was performed at 10 kV accelerating voltage on samples prepared by drop-casting diluted colloidal suspensions onto carbon-coated copper grids and drying under vacuum for 15 min. Dynamic light scattering (DLS) was performed using a Malvern Zetasizer NANO ZS instrument (Malvern Instruments). UV-vis spectra of colloids were investigated using a PerkinElmer Spectrometer (Lambda 950, PerkinElmer), a quartz cuvette with 1 mm path length for colloidal suspensions and 1 mm thick glass slide for films were used. Wide angle X-ray diffraction (WAXD) was performed using a Scintag Pad wide angle X-ray diffractometer (Scintag XDS-2000 Powder) with Cu K α radiation on P3HT/PS blended colloid films directly cast from colloidal suspensions. These films were annealed at 150 °C for 30 min under nitrogen atmosphere before the WAXD test.

2.3. Field effect transistors

Bottom-gate, bottom-contact field effect transistors (FETs) with varying channel lengths ($L = 30, 40, 50, 60, 70, 80$ and $100 \mu\text{m}$) and a channel width of 4 mm were used to measure the electric properties of P3HT/PS blended colloid films. 100 nm thick source/drain (S/D) gold (Au) electrodes were deposited on 500 μm thick n-doped silicon substrates with 300 nm thick silicon dioxide as gate dielectric. The substrates were cleaned with acetone, isopropanol, DI water and oxygen plasma, and then passivated by grafting with a self-assembled monolayer of *n*-octadecyltrichlorosilane (OTS) before coating P3HT/PS blended colloid films. Colloid films were coated using a doctor blade coater at 1 mm/s on the OTS/SiO₂/Si substrates and then annealed at 150 °C for 30 min under nitrogen atmosphere. Current-voltage (I - V) characteristics were measured using Keithley 2612B dual SourceMeters in nitrogen atmosphere. The hole mobility was averaged from at least 12 FETs.

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