Synthesis of Highly Fluorescent Polythiophene with Polystyrene Branches Using ATRP

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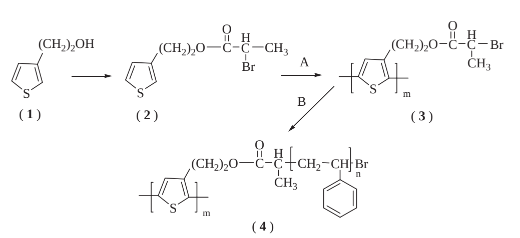
(Received August 8, 2005; CL-051023)

The graft copolymer containing a polythiophene (PT) backbone and polystyrene branches with superior solubility and processability was obtained by the atom transfer radical polymerization (ATRP) of styrene from the initiating sites on the PT backbone. The grafted PS branches could separate the PT chains and form a PS matrix for effectively trapping the PT in a solution conformation, which was advantageous to the improvement of fluorescent efficiency in the solid state.

The conjugated polythiophenes (PTs), the most promising members of the conjugated polymer family, have drawn considerable attention because of their interesting electronic properties and high thermal, chemical stability.[1] As the unsubstituted conjugated PT suffers from processability limitations due to its poor solubility in common solvents, a variety of PTs with alkyl constituents or dentric moiety have been synthesized showing good solubility and processability. Besides, the comb-like soluble PT copolymers have been prepared.[2] In most of these attempts, however, the backbone was prepared by a free radical polymerization of monomers with thiophene moiety, then oxidatively polymerized with $FeCl_3$ from the backbone. In these approaches, it is difficult to control the molecular weight distribution and the structure of copolymers. Probably, these copolymers show poor fluorescent ability due to the severe stacking of PT chains.

In this letter, we demonstrated the preparation of PT with soluble well-designed polystyrene (PS) branch on almost all repeat thiophene units rather than only a few units per backbone. To obtain branch with narrow molecular weight distribution, controlled atom transfer radical polymerization (ATRP)[3] was employed. Our procedure developed in this research can be briefly described in Scheme 1.

The typical synthesis conditions of **2**: 3-(2-hydroxyethyl)-thiophene (5.00 g, 39 mmol) was dissolved in CH_2Cl_2 (50 mL) in a flask and placed in an ice bath. 2-Bromopropionyl bromide (10.70 g, 50 mmol) and triethylamine (7 mL, 50 mmol) were added dropwise to the flask. After stirring for 30 min, the cooling bath was removed. The solution was stirred for 12 h at room temperature, and then washed with water (100 mL), extracted with CH_2Cl_2 (3×50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and then the solvent was removed, and the crude product was purified by column chromatography (silica gel, CH_2Cl_2). The product **2** was isolated as colorless oil (9.22 g, 90% yield).



Conditions: (A) $FeCl_3$, CH_3NO_2/CCl_4; (B) ATRP conditions

Scheme 1. Synthetic route of graft copolymer synthesis.

Polymer **3** was prepared by an oxidative coupling with $FeCl_3$ in CH_3NO_2/CCl_4. Morgera and co-workers proposed that the microcrystal form of $FeCl_3$ in its solvent/nonsolvent mixed system can provide a wider surface for polymerization to begin and lead to the formation of a more chloroform-soluble polymer with low dispersion.[4] Monomer **2** (1.57 g, 6 mmol) was placed in a three-necked round-bottom flask under nitrogen and dissolved in 45 mL of CH_3NO_2, with solid $FeCl_3$ (3.90 g, 24 mmol) under stirring. The mixture was allowed to react under stirring for 1 h. CCl_4 (180 mL) was then added to the system, and the mixture was kept under stirring for an additional 3 h. The reaction mixture was then precipitated by methanol, followed by subsequent Soxhlet extractions (methanol, chloroform) to recover a red powder **3** (0.79 g, 52% yield) from the chloroform soluble fraction. The glass transition temperature (T_g) determined from DSC thermogram was 58 °C. The M_n of **3**, obtained by GPC measurement (using PS as standards and THF as an eluent), was 25,000 (PDI: 5.33). Indeed, we also tried the oxidative polymerization using the traditional $CHCl_3$ as the solvent, and the M_n was 24,500 (PDI: 7.18) with a slightly lower yield of 48% as insoluble gel parts increased. The polymerization of **2** could be clearly confirmed by the comparison of the intensities of ^1H NMR signals from protons for thiophene units to those of methylene groups adjacent to the oxygen and methyl group. The change of the signal ratio in **3** supported the disappearance of protons on the 2 and 5 position of thiophene after the polymerization of **2**. From the intensity ratio of two signals (3.0 and 3.2 ppm), the regioregular part in 3 (head-to-tail configuration) can also be determined as 66%.[5]

Copolymer **4** was obtained by grafting styrene via ATRP from the initiating sites on the **3** backbone. CuBr (54.7 mg, 0.38 mmol), $CuBr_2$ (9 mg, 0.038 mmol), styrene (15.8 g, 152 mmol), anisole (4 mL), *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethyltriamine (66 mg, 0.38 mmol) and a stir bar were placed into a 50-mL round-bottom flask. After the evacuation followed with backfilling of N_2, the solution of polymer **3** (0.2 g, 0.77 mmol Br) in 8 mL of anisole was then transferred to flask dropwise. The reaction mixture was stirred at 95 °C for 2 h and then precipitated in methanol, filtered, dried to recover an orange powder **4** (1.27 g, 8% yield, based on styrene). GPC measurement revealed that the M_n of **4** was 43,000 (PDI: 4.81). Copolymer **4** exhibited the glass transition at 81 °C.

The increase of M_n of **4** indicated that the PS branches were successfully introduced to the PT backbone. The increased signals in aromatic region in ^1H NMR spectrum, which related to the protons on the benzene ring from PS branches, could confirm the grafting of PS. Besides, the increase of T_g value from 58 °C

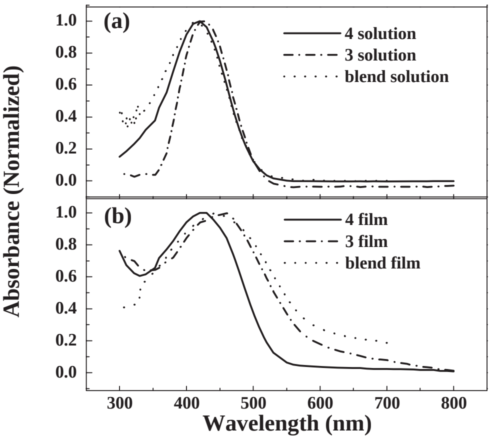


Figure 1. UV–vis spectra of polymer **3**, copolymer **4**, and polymer **3** (8.3 wt %) and PS (91.7 wt %) blend system in solution (a) and film (b): measurements were conducted on JASCO UV/vis/NIR spectrophotometer. Chloroform solutions (≈0.01 mg/mL) and thin films dropcast from solution (≈0.1 mg/mL) onto glass slides.

(polymer **3**) to 81 °C (copolymer **4**) also evidenced the grafting of the PS branches onto the PT backbone. Only one T_g observed in the graft copolymer **4** indicated that there was no phase separation in this case, and the T_g of copolymer **4** was resulted from the cooperative contribution of PT backbone and PS branches. Moreover, from the ^{1}H NMR signal intensities for phenyl rings and methylene group adjacent to the oxygen, the number of repeating unit of the PS branch could be calculated as 29 which was much higher compared with that obtained from GPC analysis. It is well-known that the GPC analysis of star, branch and graft copolymers underestimate their actual values because their hydrodynamic volume were much smaller than the linear polymer with the same molecular weight as the result of the grafting density.[6]

By isolating the PT backbone in PS matrix, interesting optical and electric properties emerged. UV–vis absorption spectra, from which one could qualitatively determine the effective conjugation length of PT, were recorded with JASCO UV/vis/NIR spectrophotometer. As shown in Figure 1a, **3** and **4** showed similar absorption spectra in solution characterized by maximum absorption at around 420 nm, resulting from the π–π^* transition of the conjugated main chain. However, in their solid states, the polymers behaved differently. The spectrum of **4** film had almost the same $\lambda_{\max}$ as its solution spectrum, while that of **3** film had a red-shifted $\lambda_{\max}$ at 460 nm. The red-shifted $\lambda_{\max}$ of **3** film resulted from PT–PT π-stacking interactions caused by the aggregation of polymer chains. The fact that **4** film showed absorption at the same wavelength as well-solvated PT could be explained by the contribution of grafted PS branches, which separated the PT chains and formed a PS matrix for effectively trapping the PT in a solution conformation. To further make our explanation reasonable, the blend system consisting of polymer **3** and PS ($M_n = 2.67 \times 10^3$, PDI $= 1.05$) was also characterized. As shown in Figure 1, the UV–vis spectrum for blend system was similar to that of **3** in a solid state. It indicated that polythiophene aggregated in the blend system.

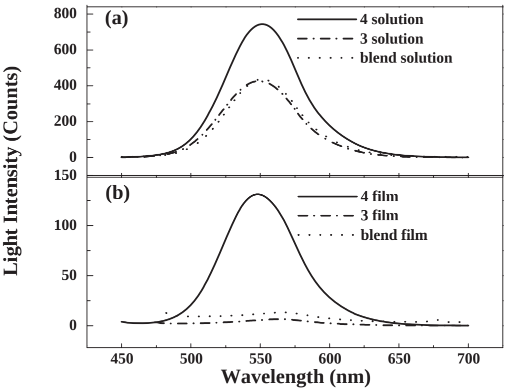


Figure 2. Fluorescence spectra of polymer **3**, copolymer **4**, and polymer **3** (8.3 wt %) and PS (91.7 wt %) blend system in (a) and (b) respectively: Fluorescence analysis was conducted on a JASCO FP-6500 spectrofluorometer. Dilute solutions in $CHCl_3$ were analyzed at an excitation wavelength of 420 nm. Thin films were dropcasted from solution (≈0.1 mg/mL) onto glass slides and the excitation wavelengths used were 445, 420, and 445 nm, respectively.

Fluorescence studies clearly indicate that PT chain is isolated each other by PS branches (Figure 2). In solution, all samples fluoresced at the same magnitude (Figure 2a). In the solid state, **3** as well as blend system films showed minimal fluorescence, whereas **4** film afforded a blue-shifted fluorescence spectrum with approximately 20 times greater intensity (Figure 2b). As we know, the π-stacking interactions could induce fluorescence quenching. Therefore, consistent with the discussion of UV–vis absorption spectra results, the PS branches could well separate the PT backbones and inhibit any aggregation, which improves the fluorescent capabilities.

In summary, we successfully prepared the graft copolymer containing a polythiophene backbone with polystyrene branches. The results of UV–vis and fluorescence spectroscopy showed that the grafted PS branches could separate the PT chains and form a PS matrix for effectively trapping the PT in a solution conformation. It was also found that the fluorescent capability of the polymer film is improved almost 20-fold through grafting PS branches on its backbone.

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Published on the web (Advance View) December 5, 2005; DOI 10.1246/cl.2005.1616