

LAYER BY LAYER SELF-ASSEMBLY OF POLYTHIOPHENE

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Introduction

The high conductivity, stability and processibility of head-to-tail polythiophene have stimulated a lot of interests in the utilization of this fascinating material as active electronic or optical elements in various thin film devices and sensors.¹ The multilayer structure of polythiophene will provide the control over the molecular and supermolecular organization of the film. Decher et al has reported an easy way to fabricate layer by layer structure which involves the alternate deposition or adsorption of absorbed layers of oppositely charged polyelectrolytes from dilute solutions has emerged.² This approach provides molecular-level control over the thickness and architecture of multilayer thin films. This paper will demonstrate that this process can also be applied to polythiophene with polyanion and polycation side chains.

Experimental

Synthesis of 3-Bromohexylthiophene. HPLC grade hexane was dried over CaH₂, and dried THF were used as solvents. 3-Bromothiophene (30g, 0.18mol) was dissolved in hexanes (250mL), and the solution is cooled down to -40°C. BuLi was added dropwise at this temperature. Stirring for 10 min, THF was added dropwise (about 15-20 mL) until the lithium thiophene salt precipitate. The solution was stirred for 1 hour and warmed up to -10°C, 5-10mL of dried THF was added to the solution and dibromohexane (110mL, 0.72mol) was added. This solution was stirred for 2 hours at room temperature, then extracted with ether and washed with water (3 times). The organic layer was dried over anhydrous MgSO₄ and the solvent was removed.

Synthesis of 2-Bromo-3-bromohexylthiophene. 3-bromohexylthiophene (27.39g, 0.11mol) was dissolved in mixture solvents of THF and Acetic acid (135mL: 135mL). NBS (23.66g, 0.13mol) was added to the solution and stirred for 1 hour. Washed with water, NaHCO₃ saturated aqueous solution and extracted with ethyl ether. The organic layer was dried anhydrous MgSO₄ and removed the solvent. Distillation at 120°C under 0.05mmHg gave 25.2g colorless 2-bromo-3-bromohexylthiophene.

Synthesis of HT-poly(3-bromohexylthiophene). 1.6mL (12mmol) dry diisopropylamine and 25mL freshly distilled THF were placed into a dry round-bottom flask. The solution was cooled down to -70°C. 4.0mL of 2.5M n-butyllithium (10mmol) was added and the mixture was warmed to 0°C and stirred for 5 minutes. The reaction mixture containing LDA was then cooled down to -70°C, and 3.26g 2-bromo-3-hexylbromothiophene (10mmol) was added. The mixture was stirred for 40min at -55°C. The mixture was then cooled to -70°C, 1.37 g ZnCl₂ (10 mmol) was added and the reaction was stirred until ZnCl₂ dissolved. The mixture was warmed up to -5°C and 20mg Ni(dppp)Cl₂ (0.2mmol) was added. The mixture was allowed to warm to room temperature, stirred for 20min and quenched with methanol. The solid polymer was washed with methanol by using a Soxhelt extractor. The polymer then was dissolved in chloroform, the chloroform was removed, and the residue was dried under vacuum to yield 1.51g of 98% head-to-tail coupled poly(3-bromohexylthiophene) with 61% yield.

Synthesis of 2,5-Poly(3-(2(4,4-dimethyloxazolin-2-yl)heptyl)thiophene). 2.55mL freshly dried 2,4,4-trimethyloxazoline (20 mmol) was dissolved in 30ml dry THF and cooled to -70°C. 7.2mL 2.5M BuLi (18mmol) was added dropwise to the solution at -65°C. Stirred for 2 hours. 490mg poly(3-bromohexylthiophene) (2 mmol) was dissolved in 30 mL dry THF. The polymer solution was transferred to oxazoline lithium salt solution quickly and then cooling bath was removed. The mixture solution was allowed to stir for 1 hour and quenched in hexane. The solid polymer was washed with hexane by using a Soxhelt extractor.

Synthesis of HT-2,5-poly(3-octanic acid thiophene). A sample of 7 (200 mg) was dissolved in 3N HCl (60 ml) and heated to reflux for 12 hr. The solution consisted of a dark purple suspension at this point. The solid was filtered, rinsed with H₂O, and dried to recover the product in 86% yield.

Synthesis of HT-2,5-poly(3-hexylazide thiophene). 490mg poly(3-bromohexyl)- thiophene) (2 mmol) was dissolved in 30 ml DMF. 1.3g

(20mmol) sodium azide was added and the mixture was stirred overnight at reflux temperature of DMF. The reaction was quenched in methanol. The solid polymer was washed with methanol by using a Soxhelt extractor.

Synthesis of HT-2,5-poly(3-hexylammonium thiophene). 470mg poly(3-hexylazide- thiophene) (2 mmol) was dissolved in 30 ml dry THF. 4ml 1M lithium (4 mmol) aluminum hydride in THF solution was injected and the solution was stirred for 30 min. followed by working up with acid solution.

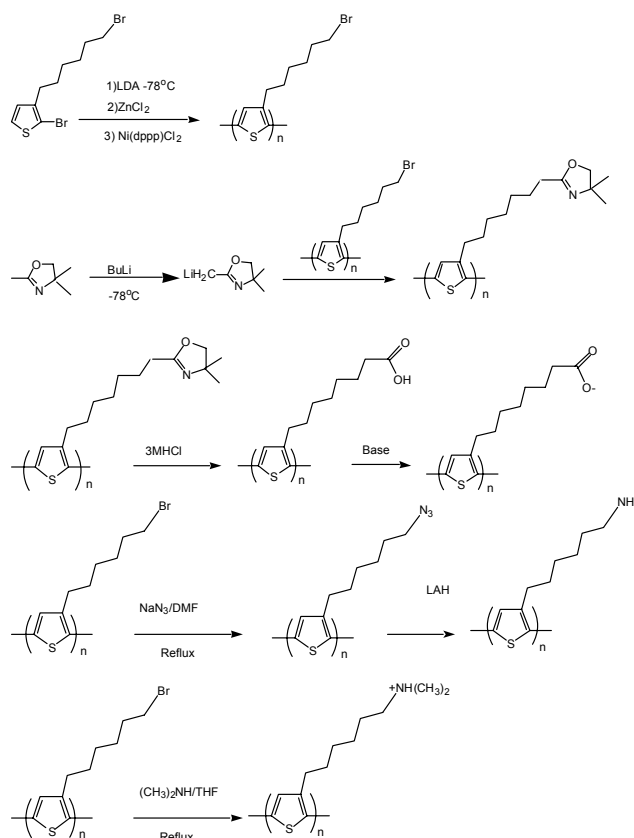
Synthesis of HT-2,5-poly(3-(6-N,N-dimethylhexylammonium thiophene). 490mg poly(3-bromohexyl)- thiophene) (2 mmol) was dissolved in 30 ml dry THF. 15ml 2M (30mmol) trimethylamine in THF solution was added and the mixture was stirred at 60°C overnight. The mixture was dissolved in methanol/water and extracted with chloroform.

Substrate Preparation. The glass slides were cleaned with a solution of 3 volumes of H₂SO₄ and 1 volume of 30% H₂O₂ for 30 min followed by treated with 5% (v/v) (3-aminopropyl)trimethoxy- silane(Acros) in anhydrous octane at 105°C for 1 hour.

Multilayer Deposition. 44mg poly(3-octanic acid thiophene) was dissolved in 20ml DMF and 42mg poly(3-hexyl ammonium thiophene) was dissolved in 1/1(DMF/water) to make 0.01M solutions. The glass slide was dipped into polyanion solution for 30 min, rinsed with DMF and dried with air. The slide was then dipped into polycation solution for 30 min. followed by washing and drying. Multilayer thin films were prepared by simply repeating this basic bilayer deposition process.

Results and Discussion

Polythiophene bearing acid, primary amine and tertiary amine were employed to fabricate the layer-by-layer assembly. These polymers were synthesized by post polymerization functionalization method as shown in Scheme 1.



Scheme 1. Synthesis of polythiophene derivatives by PPF

Layer-by-layer assembly was constructed using poly(3-octanic acid thiophene)-poly(hexylammonium thiophene) system and poly(3-octanic acid thiophene)-poly(3-(6-N,N-dimethylhexyl ammonium thiophene) system. The Uv-vis absorption spectra generated during the fabrication of multilayer thin films of these polythiophene derivatives indicated that the deposition process was completely reproducible. **(Figure 1)** The linear relationship of the plot clearly indicated that each layer deposited contributes an equal amount of material to the thin film. It also demonstrated that high molecular weight polythiophene ($M_n = 14K$ from GPC) could be readily manipulated into multilayer thin films. The Uv-vis absorption of poly(3-octanic acid thiophene)-poly(hexylammonium thiophene) system (Figure 1) and poly(3-octanic acid thiophene)-poly(3-(6-N,N-dimethylhexyl ammonium thiophene) system (**Figure 2**) suggested that different polycation system could be used to build layer-by-layer assembly. It is also found that the conjugation of the polymer layers was determined by the distribution of functional groups on glass slides. The polymer layers will be ordered if the functional groups on glass slides are uniformly distributed.

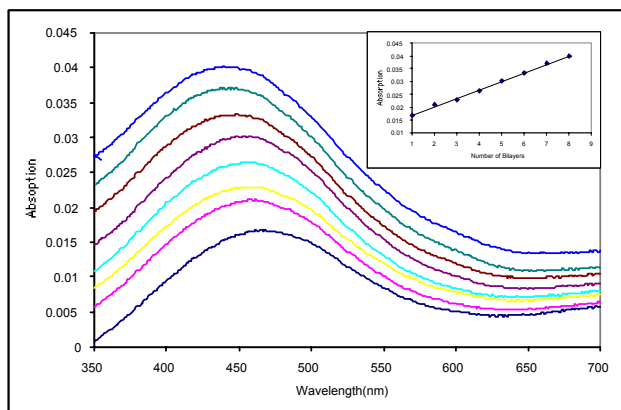


Figure 1. Optical adsorption vs. number of bilayers deposited for poly(3-octanic acid)thiophene-poly(3-hexyl ammonium)thiophene

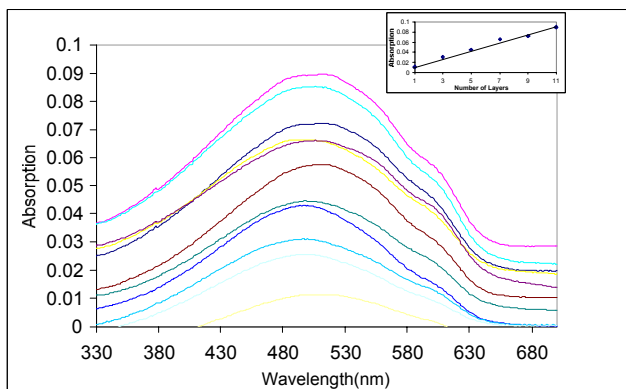


Figure 2. Optical adsorption vs. number of monolayers deposited for poly(3-octanic acid thiophene)-poly(3-(6-N,N-dimethyl hexyl thiophene)

Conclusions

Layer-by-layer deposition of polythiophene was successfully carried out using only polyanion and polycation dilute solution of polythiophene. This investigation provides basic tools for the construction and the exploration of organized polythiophene structures on electrodes.

References

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