

Preparation and characterization of electroconductive poly(thiophene-*co*-pyrrolylundecanoic acid) Langmuir–Blodgett films

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Abstract

An amphiphilic pyrrole derivative, 11-pyrrolylundecanoic acid (PUA) was synthesized and the Y-type multilayer Langmuir–Blodgett (LB) film was successfully fabricated by the conventional vertical dipping method. However, it was not possible to fabricate an electroconductive polymeric LB film from PUA. Well-ordered electroconductive Y-type poly(thiophene-*co*-PUA) LB film was successfully prepared by in situ copolymerization of thiophene and PUA at air–water interface by spreading the chloroform solution of thiophene and PUA with various feed ratio onto a subphase containing FeCl₃. The optimum condition for the preparation of poly(thiophene-*co*-PUA) LB film was at 17 °C and pH 5.3 under the surface pressure of 40 mN/m² with the feed mole ratio of 10:1 (thiophene/PUA). Poly(thiophene-*co*-PUA) LB multilayer film showed electrical conductivity of 7.15×10^{-5} S/cm and very smooth surface.

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1. Introduction

In recent years, Langmuir–Blodgett (LB) technique is widely employed for the preparation of ultra thin film of electrically conducting polymers [1–3]. LB technique is one of a few methods by which organic films of controlled thickness, uniform surface, and highly ordered structure can be deposited onto a substrate [4]. Therefore, LB processing of electrically conducting polymer is attractive not only because of the exploitation of the electrically conducting properties of the polymers but also because of the molecular control provided by LB technique. However, conducting

polymers have some limitations for LB processing because of poor processibility and lack of amphiphilicity. Some studies have been carried out in order to overcome these weak points and to fabricate the electrically conducting polymer films using LB technique [5]. These include a derivation of polymer backbone with long alkyl chain [6–9], co-deposition along with amphiphilic molecules to form mixed LB films [9,10] and use of soluble parent polymers [11–15]. Among the various conducting polymers, polythiophene and polypyrrole are widely studied because of their good conductivity and stability [16,17].

In this study, the effect of amphiphilic pyrrole derivative for the formation of thiophene-based LB film is reported. Synthesis of an amphiphilic pyrrole derivative, 11-pyrrolylundecanoic acid (PUA), was conducted by following the same method reported earlier [2]. The PUA is expected to have reactivity with thiophene and amphiphilicity for LB monolayer formation. The behavior of PUA at air–water interface was investigated in order to confirm the formability

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of LB film. Then, the conducting LB film of poly(thiophene-*co*-11-pyrrolylundecanoic acid) (poly(thiophene-*co*-PUA)) was fabricated by in situ copolymerization of thiophene and PUA by spreading the mixture solution onto a subphase containing FeCl₃. The structure–property relationships of poly(thiophene-*co*-PUA) LB films were investigated.

2. Experimental details

2.1. Materials

The pyrrole (98%, Aldrich) was purified by distillation under reduced pressure. Chloroform (Daejung Chemicals and Metals Co., extra pure reagent), tetrahydrofuran (THF; Daejung Chemicals and Metals Co., extra pure reagent) and benzene (Daejung Chemicals and Metals Co., extra pure reagent) were dried over calcium hydride (Aldrich, 99.9%) and distilled under argon atmosphere. Potassium hydride (30 wt.% dispersion in mineral oil, Aldrich) was washed several times with dry hexane to remove mineral oil before use. 11-Bromoundecanoic acid (99%, Aldrich), methyl iodide (99%, Aldrich), dichlorodimethylsilane (99%, Aldrich) and all other chemicals were used as received.

2.2. Synthesis and characterization of 11-pyrrolylundecanoic acid (PUA)

PUA was synthesized by following the procedure as shown in Fig. 1. First, potassium pyrrole salt was formed from the reaction of pyrrole with potassium hydride at room temperature under N₂ in THF for 4 h and then, the 11-bromoundecanoic acid (BUA) was transformed to 11-bromomethylundecanoate (BMU) by the reaction of BUA with methyl iodide in order to protect carboxylic acid group

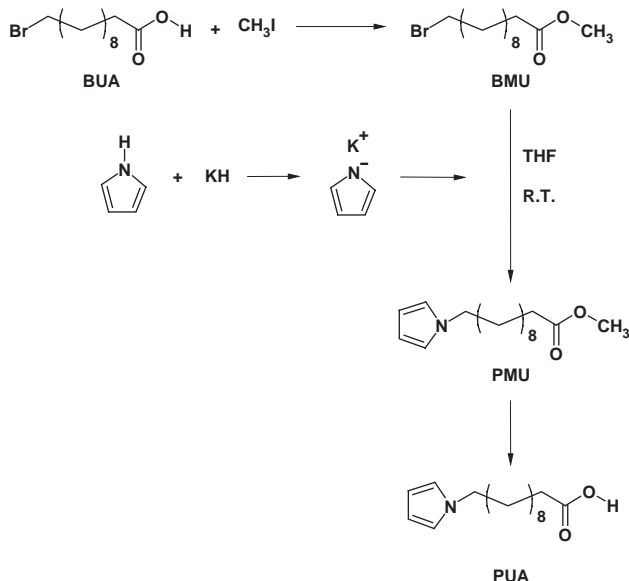


Fig. 1. Synthesis of 11-pyrrolylundecanoic acid (PUA).

of BUA. 11-Pyrrolyl methylundecanoate (PMU) was obtained by dropwise addition of BMU to a flask containing potassium pyrrole salt in THF and maintaining the reaction under constant stirring at room temperature for 6 h. PUA was finally obtained by hydrolyzing PMU with 35% hydrochloric acid in THF solution. All chemical structures were confirmed by FT-IR (Fourier Transform Infrared) and ¹H-NMR (Nuclear Magnetic Resonance) spectroscopy. FT-IR spectra of all synthesized monomers were taken with Perkin Elmer 2000 FT-IR Spectrometer and ¹H-NMR spectra were obtained by a 500-MHz ¹H-NMR spectrometer, where CDCl₃ and DMSO-*d*₆ were used as a solvent.

2.3. Preparation of LB films

LB films were prepared by using a trough apparatus of KSV 5000 System (Chang Yeon Co.). Deionized ultrapure millipore water (the resistivity=18.2 MΩ, pH 5.3) purified by using a Milli-Q system (Millipore) was used as subphase. The pH of subphase was adjusted by the addition of either 0.1 N KHCO₃ or NaOH aqueous solution. KRS-5 (TiBr/Ti) plate and the silicon wafer were used as the deposition substrates of LB film. In order to obtain the hydrophobic surface of the substrate, KRS-5 plate was treated with toluene in an ultrasonic bath for 4 h and then dried in an oven. In the case of silicon wafer, it was immersed in 3% solution of dichlorodimethylsilane in chloroform for 20 min, rinsed with chloroform, and then dried in an oven.

PUA solution of 1 mM in benzene was spread on the subphase with various pH using a microsyringe. After evaporation of the solvent, PUA monolayer was compressed at a speed of 1.3 Å²/(mole min) at 17 °C for the measurement of surface pressure (π)–area (A) isotherm. LB film of poly(thiophene-*co*-PUA) was prepared at the air–water interface of the LB trough by spreading the mixture solution of thiophene and PUA with various mole ratio in chloroform onto the subphase containing 1 wt.% of FeCl₃. The π–A isotherm of poly(thiophene-*co*-PUA) are measured at different subphase temperatures (13 °C, 15 °C, 17 °C, 21 °C) and at different pH of subphase (3.5, 5.3, 7.0) at 17 °C. LB multilayer films of poly(thiophene-*co*-PUA) were prepared by the normal vertical dipping technique at 17 °C and pH 5.3.

2.4. Characterization of the LB films

Deposition mode of LB film was determined by measuring the transfer ratio, which is defined as the ratio of the decreased area of the monolayer on the subphase to the moving area of the deposition substrate. UV/Visible absorption spectra were obtained using Perkin Elmer Lambda 19 UV/Vis/NIR (Ultra Violet/Visible/Near Infrared) spectrometer to investigate the electronic structure of the LB films. X-ray diffraction (XRD) measurements of LB films were carried out using a Rigaku Geigerflex (Cu Kα) to determine the structural order of the LB films. The surface morphology of the prepared copolymer LB film was

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