Electronic Supplementary Information for

Synthesis and molecular weight control of poly(3-hexylthiophene) using electrochemical polymerization in a flow microreactor

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1. Instrumentation

Electrochemical polymerization was carried out with a Galvanostat (Hokuto Denko HABF-5001). HPLC and GPC analyses were performed with a LC pump (Shimadzu LC-20AD), a UV detector (Shimadzu SPD-20A), and columns (Kanto Kagaku Mightysil RP-18 GP 250-4.6 for HPLC analyses and Showa Denko GPC K-802.5 for GPC analyses). Both chromatograms were recorded by a LC workstation (Shimadzu LabSolutions DB).

2. Materials

All reagents were purchased from commercial supplier and used without further purification. 3-Hexylthiophene, tetrabutylammonium triflate (Bu_4NOTf), tetrabutylammonium perchlorate (Bu_4NClO_4), tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) were purchased from Tokyo Chemical Industry. Acetonitrile, dichloromethane, dimethylsulfoxide, nitromethane were purchased from Kanto Chemical Co..

3. Flow Microreactor

Figure S1 shows schematic illustration of the electrochemical flow microreactor. The reactor was constructed from stainless plate cathode (3 cm width, 3 cm length) and Pt plate, glassy carbon (GC) plate, glass plate coated with ITO, or graphite plate anode (3 cm width, 3 cm length). A spacer (80 μm thickness double faced adhesive tape) was used to leave a rectangular channel exposed, and the two electrodes were simply sandwiched together (area of the two electrodes: 1×3 cm^2). After connecting Teflon tubing to inlets and outlet, the reactor was sealed with epoxy resin (Figure S2).

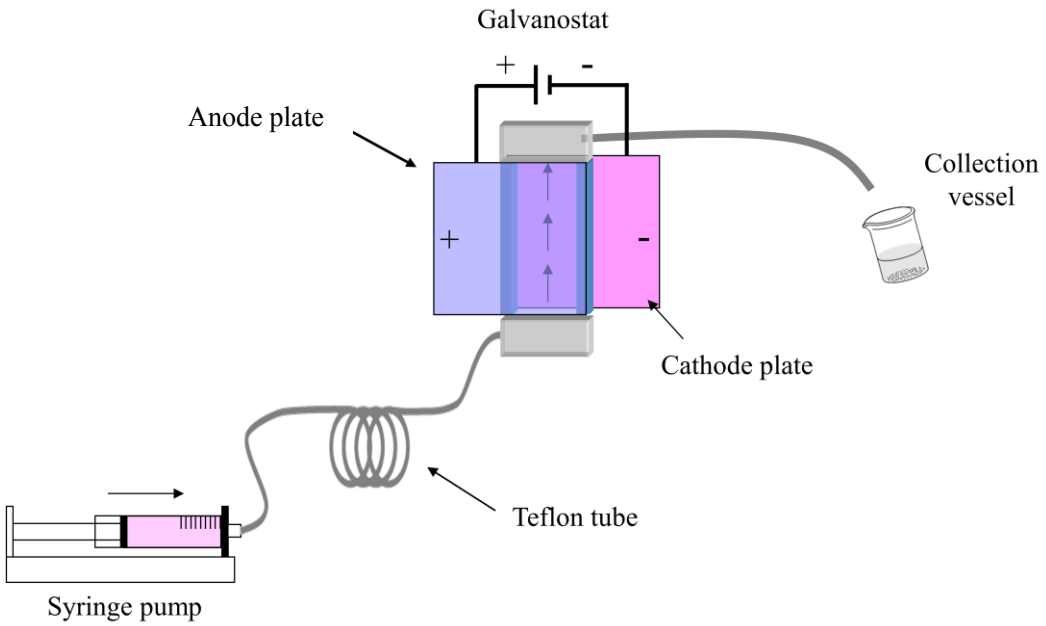

Figure S1. Schematic illustration of the electrochemical flow microreactor.

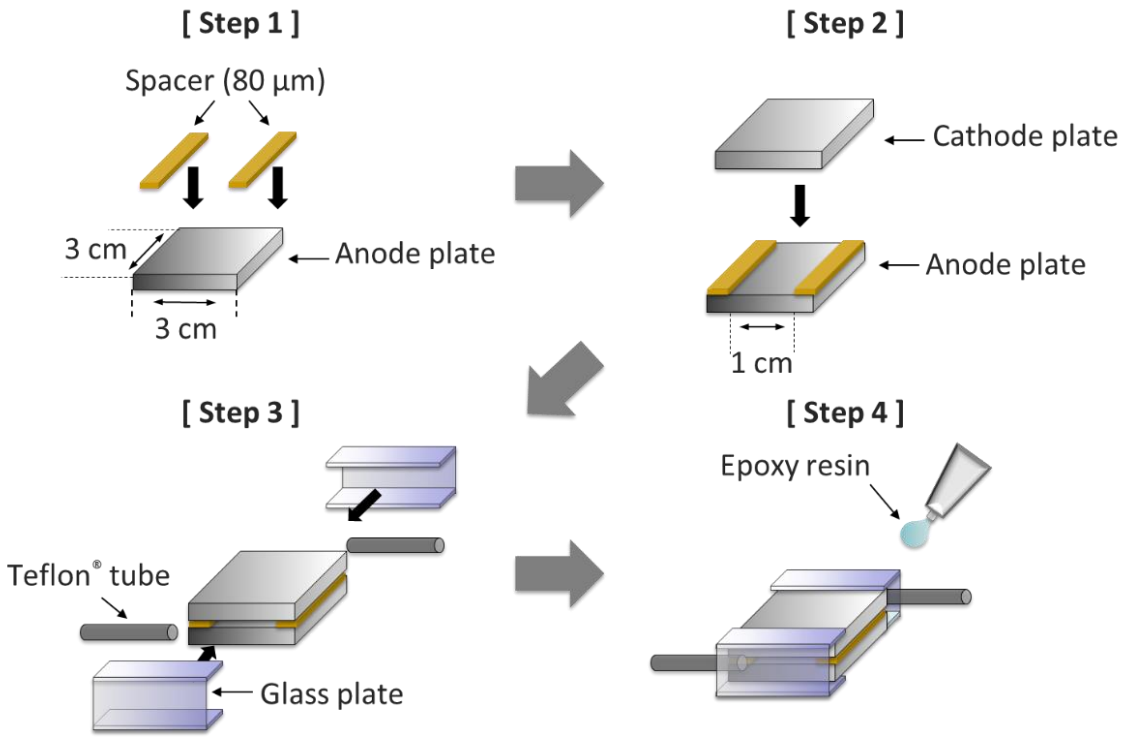

Figure S2. Schematic illustration of construction procedure for the electrochemical flow microreactor.

4. General Procedure for Electrochemical Polymerization of 3-Hexylthiophene Using a Flow Microreactor

KdScientific model 100 syringe pumps were used to pump the reaction solutions. The solution containing of 3-hexylthiophene (10 mM) in 50 mM supporting electrolyte/electrolytic solvent (10 mL) was introduced into the reactor. Constant current electrolyses (5 mA cm^{-2}) were performed using the electrochemical flow microreactors composed of various anode plates (1 × 3 cm^2) and stainless cathode plate (1×3 cm^2). The electrolytic solution ejected from the reactor was collected, and subjected to short column chromatography on silica gel in order to remove supporting electrolytes. Then, the resulting solution was analyzed using HPLC to determine the conversion of 3-hexylthiophene. The resulting solution was also analyzed using GPC to determine the number and weight average molecular weights and the molecular weight distribution. The average molecular weights were calibrated with a polystyrene standard.

5. General Procedure for Electrochemical Polymerization of 3-Hexylthiophene Using a Batch Type Reactor

Constant current electrolyses were conducted using a galvanostat (Hokuto Denko HABF-5001). Electrochemical polymerization of 3-hexylthiophene (10 mM) was performed using ITO plate anode (working electrode, 1 × 3 cm^2) and Pt plate cathode (counter electrode, 2 × 2 cm^2) in 50 mM Bu_4NClO_4/acetonitrile (10 mL). Electrolysis was conducted with a constant current mode (5 mA cm^{-2}) by passing 2 F mol^{-1} of electricity. After the electrolysis, the reaction mixture was subjected to short column chromatography on silica gel in order to remove supporting electrolytes, and then analyzed using HPLC to determine the conversion of 3-hexylthiophene. The resulting solution was also analyzed using GPC to determine the number and weight average molecular weights and the molecular weight distribution. The average molecular weights were calibrated with a polystyrene standard.