

An in depth study of solvent effects on yield and average molecular weight in poly(3-hexylthiophene)



Jennifer Gadiant, Rebecca Groch, Cora Lind*

Department of Chemistry & Biochemistry, The University of Toledo, 2801 W. Bancroft Street, Toledo, OH 43606, USA

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ABSTRACT

Poly(3-hexylthiophene) was synthesized by chemical oxidation using FeCl_3 in chloroform, dichloromethane, acetonitrile, nitromethane, nitrobenzene and mixtures of these solvents. Comparative reactions for 1 day at room temperature were carried out to investigate solvent effects. Polymer samples and the remaining reaction solutions were analyzed by MALDI-MS and LDI-MS to determine M_w and reaction completeness, respectively. Solubilities of FeCl_3 , FeCl_2 , and P3HT in each pure solvent were measured and correlated to the results. Open circuit potentials of FeCl_3 and mixtures of FeCl_3 and FeCl_2 in pure solvents were measured and compared to the experimentally determined oxidation potential of 3-hexylthiophene. An optimized solvent system for reproducible synthesis of high M_w P3HT with quantitative yields is proposed based on MS analysis results.

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1. Introduction

Conductive polymers have a broad range of applications, including but not limited to flexible electronics, LEDs [1], solar cell components [2] [3], sensors [4] and biosensors [5]. Polythiophenes are of particular interest due to their high conductivity when doped, and environmental stability compared to other conducting polymers. However, polythiophene is difficult to process, which limits its possible applications [6]. Modifications to the thiophene ring such as alkyl chains, fused rings or pendant groups have been employed to make these polymers more soluble in common organic solvents and easier to process while maintaining the inherent electrical properties.

Poly(3-hexylthiophene) (P3HT) [7] is a commonly studied polythiophene that can be synthesized by electrochemical polymerization, Grignard metathesis (GRIM), and oxidative chemical polymerization with iron (III) chloride (Fig. 1), with the latter being the most commonly used and most easily scalable method [6].

During oxidative polymerization of 3 H T, it is interesting to note that longer chains require lower oxidation potentials than the monomer or shorter chains, allowing for continued chain growth even after a reduction in solution potential [8–10]. While the iron

(III) chloride method is not as regioselective at ambient conditions as the GRIM method, it is attractive because the precursors are less expensive, less moisture sensitive, and the product yields are typically higher [11,12]. Both regioregularity and chain length have direct effects on the bandgap and charge transport properties [13]. During chemical oxidation, both can be improved at the expense of decreased overall yield by decreasing the reaction temperature [14,15]. These trends were observed in the solvents chloroform, acetonitrile, and dichloromethane by Fukumoto et al., with chloroform giving the highest yields at each temperature, and dichloromethane and acetonitrile resulting in comparable yields ranging from 45% up to 70%, with reactions at room temperature giving the highest yields in all solvents. Samples synthesized from acetonitrile had low polydispersities (1.5), while the other solvents gave broader distributions (PDI = 4.0 to 5.7). The average molecular weights determined by GPC were lower for CF ($M_n = 22,000$ g/mol) than for the other solvents ($M_n = 34,000$ g/mol) at room temperature [14]. Based on these observations, temperature can be used to control regioregularity through tuning of kinetics, while the solvent choice can affect the yield, polymer chain lengths and polydispersity, which are controlled by both the reaction mixtures' oxidation potentials and product and reactant solubilities. In particular, the solubilities of FeCl_3 , FeCl_2 , and higher molecular weight polymers in the common reaction solvents have direct effects on the final polymer product.

Addition of a second solvent to the polymerization reaction has

* Corresponding author.

E-mail address: cora.lind@utoledo.edu (C. Lind).

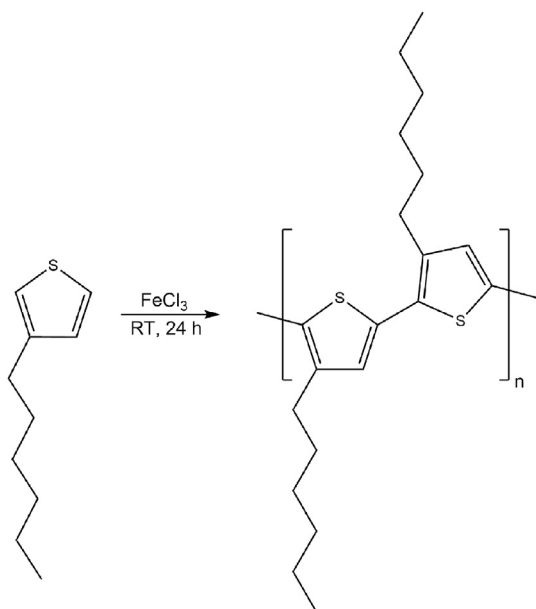


Fig. 1. Synthesis of P3HT using FeCl_3 .

successfully been employed to optimize the solubilities of both FeCl_3 and polymer to increase the yield and degree of polymerization, particularly for modified 3 H T monomers in chloroform and carbon tetrachloride [16–18]. However, each study used different reaction conditions and different analysis methods, making comparison between solvent mixtures and pure solvent results, as well as between many pure solvents, impossible. The two most commonly used analysis methods included gel permeation chromatography (GPC), which is known to overestimate chain lengths for P3HT, and matrix assisted laser desorption ionization mass spectrometry (MALDI-MS), which can underestimate chain lengths due to more facile ionization of shorter chains [19]. This paper presents a comprehensive study of the influence of solvent choice on yield, polymer chain lengths and polydispersity under identical reaction conditions using five common solvents for poly(3-hexylthiophene) synthesis, namely chloroform [20–22], acetonitrile [23,24], dichloromethane [23], nitrobenzene [25], and nitromethane [17,18]. Analysis of molecular weight and polydispersity was carried out using MALDI-MS on all samples. This allows for direct observation of molecular weights, and can give insights into various end groups that could be generated in different solvents. Absolute average molecular weight values may not be representative of the true average molecular weights of the samples due to the ion suppression effect observed for longer chains, where longer chains do not ionize as well in the mass spectrometer, leading to reduced intensity at the detector. However, sample to sample comparison remains meaningful as long as all samples are prepared and measured in the same way.

2. Experimental

2.1. Monomer synthesis

The monomer 3-hexylthiophene was synthesized through the addition of 50 mmol of magnesium bromohexane to a solution of 53 mmol of 3-bromothiophene and 0.43 mmol of dichloro(1,3-bis(diphenylphosphino)propane)nickel ($\text{Ni}(\text{dppp})\text{Cl}_2$) catalyst in 18 mL of dry diethyl ether via addition funnel. The reaction was allowed to progress overnight at room temperature under Ar

atmosphere and constant stirring. It was quenched by the addition of 50 mL of 0.5 M HCl, and the organic layer was washed with water three times and isolated. Solvents were removed under reduced pressure, and the product was distilled under reduced pressure at 140 °C to yield a clear liquid. The identity of the isolated sample, which was recovered with a yield of 7.20 g (85.6%) was confirmed by $^1\text{H-NMR}$ spectroscopy (CDCl_3 , δ , ppm: 0.89 (t, 3H), 1.30–1.36 (m, 6H), 1.62 (m, 2H), 2.63 (t, 2H), 6.94 (m, 2H), 7.23 (d, 1H).

2.2. Polymer synthesis

Poly(3-hexylthiophene) was synthesized through oxidative polymerization using FeCl_3 as the oxidant. Nitromethane (NM) packaged under argon, nitrobenzene (NB) packaged under argon, distilled chloroform (CF), distilled dichloromethane (DCM), non-distilled DCM (nd-DCM), distilled acetonitrile (AN) and binary mixtures of these were used as solvents¹ For the discussion section of this paper, pure solvent samples will be named “solvent-20”, and binary mixtures of 5 mL:15 mL, 10 mL:10 mL and 15 mL: 5 mL will be referred to as “solvent1-solvent2-5-15” etc.²

In a glovebox, 4.5 mmol (0.73 g) of FeCl_3 were added to a reaction flask and dissolved in 20 mL of total solvent volume, giving an FeCl_3 solution with a maximum concentration of 0.225 M.³ Outside the glovebox, 1.1 mmol (0.2 mL) of 3-hexylthiophene (3 H T) were quickly injected into the solution under argon atmosphere. The quantities of FeCl_3 (4.5 mmol) and 3 H T (1.1 mmol) were identical for every solvent system tested. After the addition of monomer, all reactions were stirred for approximately 24 h at room temperature under argon atmosphere. P3HT was precipitated by addition of methanol. The product was recovered by vacuum filtration and washed with copious amounts of MeOH followed by distilled water. For several samples, the initial solvent wash was retained for mass spec analysis. Washing was repeated until the filtrate came off clear to remove as much of the residual iron chloride and shorter oligomer chains from the sample as possible. Samples were allowed to air dry overnight, and then vacuum dried in a desiccator until the weight remained constant (approximately 45 min) to remove any residual solvent before weighing to determine crude yields. The amount of residual iron in the samples was determined through a burn off procedure where 10–20 mg of sample were heated to 700 °C for 12 h. The residual solid was weighed and identified using powder x-ray diffraction. Solubilities of FeCl_3 , FeCl_2 , and two chosen samples of P3HT in each pure solvent were determined experimentally by dissolving each compound until each solution reached saturation.

2.3. Analysis

Matrix assisted laser desorption ionization-mass spectrometry (MALDI-MS) and laser desorption ionization-mass spectrometry (LDI-MS) were used to determine polymer chain lengths and end groups using a Bruker Daltonics ultrafleXtreme MALDI-TOF/TOF mass spectrometer with a Nd/YAG laser at 355 nm wavelength in positive ion mode for both linear mode detection and reflectron mode detection. Solid polymer samples were dissolved in an excess of tetrahydrofuran (THF). *Trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as matrix at a concentration of 40 mg/mL in chloroform. The polymer solution was cospotted with the DCTB matrix using the dry droplet method. MALDI-MS analysis on each sample was carried out in

¹ In binary solutions, only distilled DCM was used.

² Binary mixtures of NM and NB were not attempted.

³ None of the solutions completely dissolved the added FeCl_3 .

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