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Synthesis and properties of novel fluorinated ester substituted polythiophenes

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Abstract

The electronic properties of the conjugated backbone of polythiophene can be tailored by the incorporation of perfluoroalkyl ester substituents. A polythiophene substituted with two different kinds of semifluoro and perfluoroalkyl esters were prepared by $FeCl_3$ oxidative polymerization. Both polymers were found to be highly soluble in common organic solvents, such as $CHCl_3$, THF and acetone. The influence of bulky fluoroalkyl substitutions on electrical conductivity, electronic absorption, fluorescence and surface properties of polymer films were investigated, and the properties were compared with poly(3-octylthiophene) synthesized under similar experimental conditions.

Keywords: Polythiophenes; Conjugated polymer; Fluoroalkyl

1. Introduction

The incorporation of fluorine into polymers has been extensively studied due to the resultant low surface energies, remarkable chemical and oxidative resistance, hydrophobicity, rigidity, thermal stability and self-organization of perfluoro alkyl chains [1]. The combination of the unique characteristics of fluorine and the electronic characteristics of conjugated polymers (CPs) has led to the development of new materials that are of interest to the scientific and industrial communities. Among numerous CPs studied, polythiophene (PTh) derivatives have been the focus of extensive research due to the unique combination of electronic properties, including electrochemical stability, electrochromism and structural versatility [2]. Roncali and co-workers reported the synthesis of PTh possessing perfluorinated alkyl side chains containing 50 wt.% fluorine that had conductivities similar to those of poly(3-alkylthiophene) analogs [3]. Besides side chain organization of simple poly(3-alkylthiophene)s, a number of semifluoro and perfluoroalkyl substituted polythiophenes and their copolymers with alkyl substituted PThs [4] have been prepared with the aim of controlling molecular architecture and improving environmental stability. Alternating units of polythiophenes bearing hydrocarbon and fluorocarbon side chains gave rise to amphiphilic polymers that self-assembled into a lamellar structure. This suggests that fluoroalkyl substituted PThs may prove valuable in the development of liquid crystal based on PThs [5]. Lasing technology is another interesting application of these materials; a copolymer of 3-(methoxyethoxyethoxymethyl)thiophene and 3-(perfluoroalkyl)thiophene was found to be fluorescent and displayed minimum absorption and emission spectra overlap [6]. More recently, Ong et al. fabricated solution processable thin film transistors (TFTs) with different fluoroalkyl substituted polythiophene copolymers [7]. Reynolds and co-workers shown an elctrochromic device with relatively low oxidation potential and high visible contrast with perfluoroalkanate substituted poly(3,4-ethylenedioxythiophene) [8]. Furthermore, the fluoroalkyl substitution also presents the opportunity to prepare conjugated polymers that are soluble in supercritical carbon dioxide ($scCO_2$), an environmentally benign solvent explored for use in numerous reactions, polymer processing and nanomaterial synthesis [9]. In the light of the above facts, we have

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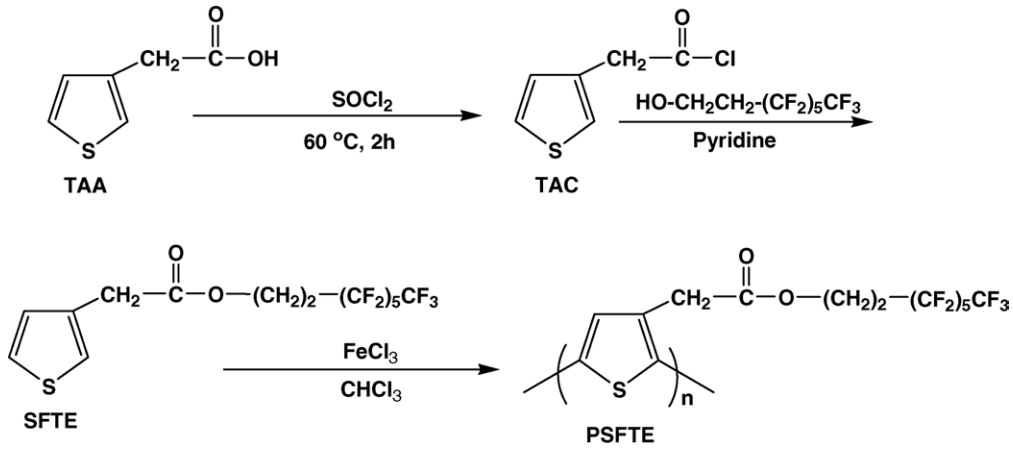


Scheme 1. Synthesis of semifluoroalkyl ester substituted polythiophene.

designed and synthesized two different kinds of 3-substituted semifluoroalkyl ester and perfluoroalkyl ester polythiophenes. In addition, the properties of the polymers and the influence of the substitutions on electrical conductivity, electronic absorption, fluorescence and surface properties of polymers were investigated.

2. Experimental

2.1. Materials

2-(3-Thienyl)ethanol, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol, heptafluorobutyryl chloride and ferric chloride (Aldrich) were used as received. Thiophene-3-acetic acid (TAA) (Aldrich) was recrystallized in 1:1 mixture of ethyl ether and hexane. Thionyl chloride (Junsei) was purified by distillation. Pyridine and dichloromethane (Junsei) were distilled from calcium hydride prior to use.

2.2. Characterization

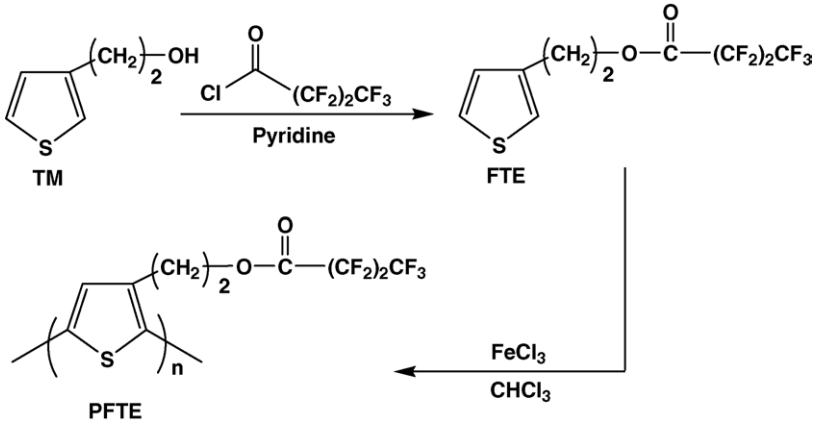
Size exclusion chromatography (SEC) was carried out with a HP1100 apparatus equipped with a set of four columns (10^5–10^4–10^3–10^2 Å: polymer standards service) with THF as the eluent. Polystyrene samples were used as standards to construct the calibration curve. ^{1}H NMR spectra were recorded using a JNM-ECP 400 (JEOL). UV–vis absorption spectra of polymer solutions in $CHCl_3$ at constant concentration of 10^{-5} M were recorded with a Perkin-Elmer Lambda 19 spectrometer. Fluorescence spectra were collected with a Hitachi-1681 spectrometer.

2.3. Synthesis of monomers

Synthetic routes of monomers and polymers are shown in Schemes 1 and 2. Thiophene-3-acetyl chloride (TAC) was synthesized according the literature procedure [10]. Monomers were synthesized by the esterification of corresponding acid chlorides with alcohols.

2.3.1. 2-(3-Thienyl) acetyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanate (SFTE)

SFTE was synthesized by the esterification reaction in the presence of pyridine base. TAC (2 g, 12.5 mmol) was added drop wise to a mixture of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (4.5 g, 12.5 mmol) and an excess of pyridine (2.7 g, 34.0 mmol) in dichloromethane (20.0 ml). The reaction mixture was refluxed for 2 h at 60 °C, cooled and filtered. The filtrate was



Scheme 2. Synthesis of perfluoroalkyl ester substituted polythiophene.