



Chemical and electrochemical grafting of polypyrrole onto thiophene-functionalized polystyrene macromonomer



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ABSTRACT

In this paper, chemical and electrochemical graft copolymerization of pyrrole onto thiophene-functionalized polystyrene multicenter macromonomer (ThPStM) is described. The polystyrene-g-polypyrrole (PSt-g-PPy) obtained was characterized by means of Fourier transform infrared (FTIR) spectroscopy, and its electroactivity behavior was verified under cyclic voltammetric conditions in acetonitrile (ACN)–tetraethylammonium tetrafluoroborate (TEAFB) solvent–electrolyte couple and compared with electroactivity behavior of pure polypyrrole. Electrical conductivities of the samples were measured using samples in which the conductive materials were sandwiched between two Ni electrodes at room temperature. The chemical composition and molecular weight of the PSt-g-PPy graft copolymer were determined by means of elemental analysis, and gel permeation chromatography (GPC), respectively. Moreover, thermal behaviors of the synthesized polymers were investigated by means of differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

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1. Introduction

It is a decisive fact that intrinsically conductive polymers (ICPs) have stimulated great interest on the basis of their importance in basic scientific research and potential industrial applications, due to their unique semiconducting and optoelectronic properties [1–5]. On the other hand, since the introduction of doped polyacetylene as a conducting polymer in 1977 [6], it has been found that only a few polymers are stable enough under normal processing conditions to be incorporated in various practical and technological applications. Among leading candidates are polythiophene (PTh),

polyaniline (PANI), and polypyrrole (PPy) [7–12]. Among these important conducting polymers, polypyrrole presents additional features such as good mechanical and electrical properties, reversible redox ability, excellent environmental stability, and easy synthesis [13–16]. Polypyrrole can be prepared by chemical [17,18], and electrochemical [19,20] methods in various organic solvents and/or in aqueous media. The electrochemical process is more advantageous since film properties such as thickness and conductivity can be controlled by the synthesis parameters, including the current density, substrate, pH, nature and concentration of electrolyte [10,20]. Chemical approaches mainly include condensation polymerization or addition polymerization. Chemical synthesis, allows the scale-up synthesis of PPy, which is currently impossible with the electrochemical method. Another important advantage of chemical method is post-functionalization of PPy backbone [10,21].

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Polypyrrole has been applied in a number of applications, such as bio/chemical sensors [22–24], rechargeable batteries [25,26], switchable membranes [27,28], electrochromic devices (ECDs) [29,30], microwave shielding and corrosion protection [31–33]. In addition, PPy can be used as conducting filler in insulating polymer matrices in preparation of electrically conducting composites [34,35].

However, the main drawback of unsubstituted polypyrrole is limited in practical use due to very fragile structure and insolubility, which gives rise to processing difficulties [36–38]. In order to overcome these major deficiencies, well-established techniques are: (i) modification of the monomer structure (e.g., 3-substituted and *N*-substituted pyrroles) [39,40], and (ii) synthesis of polypyrrole copolymers with conventional thermoplastics [41,42].

In previous studies, the synthesis and characterization of a PSt-g-PTh by a combination of nitroxide-mediated polymerization and Kumada cross-coupling reaction has been investigated [43]. Following this work; we report here our preliminary investigations on the chemical and electrochemical graft copolymerization of pyrrole onto thiophene-functionalized polystyrene multicenter macromonomer (ThPStM). The synthesized graft copolymer (PSt-g-PPy) was characterized by means of FTIR, elemental analysis, GPC, DSC, and TGA. Moreover, its electroactivity behavior was verified under cyclic voltammetric conditions in acetonitrile (ACN)–tetraethylammonium tetrafluoroborate (TEAFB) solvent–electrolyte couple, and compared with electroactivity behavior of pure polypyrrole.

2. Experimental

2.1. Materials

Pyrrole monomer was supplied by Merck (Darmstadt, Germany) and was distilled under vacuum before use. Thiophene-functionalized polystyrene multicenter macromonomer (ThPStM) was synthesized in our laboratory [43]. Anhydrous ferric chloride (FeCl_3), and tetraethylammonium tetrafluoroborate (TEAFB), were supplied by Merck and used as received. Tetrahydrofuran (THF) from Merck was dried by refluxing over sodium and distilled under argon prior to use. Acetonitrile (CH_3CN) was dried by calcium hydride and was distilled before use. All other reagents were purchased from Merck and purified according to standard methods.

2.2. Graft copolymerization of pyrrole onto thiophene-functionalized polystyrene via chemical oxidation polymerization

In a two-necked round-bottom flask equipped with condenser, gas inlet/outlet, and a magnetic stirrer, 1 g (9 mmol) of macromonomer (ThPStM), and pyrrole monomer (0.42 mL, 6 mmol) were dissolved in 60 mL of dried tetrahydrofuran (THF). The solution was de-aerated by bubbling highly pure argon for 10 min and was stirred vigorously for 30 min under an argon atmosphere. Subsequently, the oxidant (FeCl_3 , 2.9 g, 18 mmol) was added into the above solution and further stirred for 3 h at room temperature under inert atmosphere. The reaction was stopped by pouring the contents of the flask

into a large amount of methanol. The crude product was filtered and washed several times with methanol (Scheme 1).

The crude product was extracted with cyclohexane in a Soxhlet apparatus for 24 h in order to remove any residual ungrafted polystyrene chains. The synthesized PSt-g-PPy is not soluble in cyclohexane, while the ungrafted polystyrene is completely soluble in cyclohexane. Moreover, the product was extracted with tetrahydrofuran (THF) for three times, in order to remove pure polypyrrole. The pure polypyrrole is not soluble in THF (Table 2); while the PSt-g-PPy grafts copolymer is completely soluble in THF (Table 2). The polymer solution was filtered, precipitated into excess methanol, and the black solid obtained was dried in vacuum at room temperature.

2.3. Synthesis of pure polypyrrole via chemical oxidation polymerization

In a two-necked round-bottom flask equipped with condenser, gas inlet/outlet, and a magnetic stirrer, pyrrole monomer (0.42 mL, 6 mmol) was dissolved in 60 mL of dried tetrahydrofuran (THF). The solution was de-aerated by bubbling highly pure argon for 10 min, and was stirred vigorously for 30 min under an argon atmosphere. Subsequently, the oxidant (FeCl_3 , 2.9 g, 18 mmol) was added into the above solution and further stirred for 3 h at room temperature under inert atmosphere. The precipitate was filtered off and washed with distilled water several times. The final black polypyrrole powder was obtained after drying at room temperature for 24 h under reduced pressure (Scheme 2).

2.4. Electrochemical system

The electrochemical measurements were performed using Auto-Lab equipment (ECO Chemie, Utrecht, The Netherlands) equipped with a three-electrode cell assembly. A platinum microelectrode (with a surface area of 0.03 cm^2), a platinum rod, and an Ag/AgCl electrode were used as working, counter, and reference electrodes, respectively. Prior to each use, the surface of the working electrode (Pt) was polished with 1.0 and $0.5 \mu\text{m}$ alumina powder on a polish pad, and then ultrasonicated in acetone and Milli-Q water, respectively for 5 min. The electrochemical measurements were accomplished in the acetonitrile (ACN)–tetraethylammonium tetrafluoroborate (TEAFB) solvent–electrolyte couple (0.1 mol L^{-1}). All experimental solutions were de-aerated by bubbling highly pure argon for 10 min, and an argon atmosphere was kept over the solutions during the measurements.

2.5. Graft copolymerization of pyrrole onto thiophene-functionalized polystyrene via electrochemical polymerization

Synthesis of PSt-g-PPy graft copolymer was performed via constant potential electrolysis by using potentiostat and a three-compartment cell. A 2% (w/v) solution of insulating thiophene-functionalized polystyrene multicenter macromonomer (ThPStM) was dissolved in chloroform and both sides of working electrode (Pt) were coated with ThPStM by drop-coating, and used as the working electrode. The electrolysis

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