Polymer 54 (2013) 5754–5761

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Pyrrole polymerization on polyimide surfaces creates conductive nano-domains

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ARTICLE INFO

Article history:
Received 19 July 2013
Received in revised form
12 August 2013
Accepted 15 August 2013
Available online 22 August 2013

Keywords:
Conducting polymers
Polypyrroles
NMR

ABSTRACT

Oxidative polymerization of pyrrole on the surface of polyimide (PI) films was demonstrated to generate uniform, adherent coatings consisting of polypyrrole (PPy) electro-active nano-domains. This polymerization was carried out in aqueous methanol solution with $FeCl_3$ as oxidant/dopant. Model kinetic reactions carried out by hydrogen Nuclear Magnetic Resonance (^1H NMR) spectroscopy using ammonium persulfate (APS) as oxidant found evidence for an increase in the polymerization rate of pyrrole in the presence of a molar excess of PI. Attempts to identify changes to the PI chemical structure during pyrrole polymerization were investigated by high-resolution carbon ^{13}C NMR spectroscopy and Infrared Attenuated Total Reflection (IR-ATR) spectroscopy. No differences were observed in concentrated D_2SO_4 solutions by NMR. However, IR-ATR noted a shift to lower wavenumbers of the PI carbonyl band and a higher wavenumber shift of the aromatic ether band. The morphology of PPy-coated PI films was analyzed by atomic force microscopy (AFM). The average size of PPy nanospheres was in the range of 20 nm with narrow distribution and was found to increase with reaction time.

1. Introduction

Most polymers are inherently electrical insulators. This property has been long exploited in applications where insulation and low electrical loss are important considerations. However, there is also interest in tailoring the electrical conductivity of polymers to make them useful in applications such as the dissipation of electrostatic charge from parts, electrostatic spray painting, and the shielding of electrical components to prevent transmission of electromagnetic waves.

Electrically conductive polymers such as polypyrrole (PPy) can be used to alter the insulating state of the surface of other polymers. PPy is typically obtained by chemical polymerization of pyrrole in the presence of strong chemical oxidants [1–11]. This polymerization occurs in the bulk of the solution, and the resulting conductive PPy precipitates as a solid that is insoluble in common solvents, infusible, and decomposes before melting. Therefore, it is not possible to obtain quality films from chemically polymerized PPy. Electrically conductive surfaces on insulating polymers are commonly obtained by mixing the polymer with PPy [12,13]. Although conductivity is required only on the surface of the insulating polymer film, in this approach the conductive PPy particles are present in the bulk of the mixture and have only random contribution to the surface conductivity. This leads to surfaces with non-uniform conductivity and a deterioration of mechanical properties of the polymer matrix due to the presence of conductive polymer particles as separated domains.

Previously, we reported on the electropolymerization of *N*-substituted PPy and its reactions with amino-substituted DNA sequences [14], and on *in-situ* polymerizations of pyrrole in water soluble polymer templates [15] that produced nanospheres. The polymerization of conductive polymer precursors onto different surfaces has been limited to a few investigations. For example, a solution based method was reported for growing transparent films of nanofibers of polyaniline, polythiophene and its derivatives on various substrates. [16] *In-situ* polymerization of pyrrole onto printed circuit boards using $FeCl_3$/5-sulfosalicylic acid oxidant complex was carried out and demonstrated the formation of uniform PPy films with good electrical conductivity [17].

The present investigation reports on the chemical polymerization of pyrrole on polyimide (PI) films in the presence of $FeCl_3$, as oxidant/dopant species, in aqueous methanol solutions. This

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http://dx.doi.org/10.1016/j.polymer.2013.08.034

chemical process includes both the polymerization of the monomer and grafting reactions of the growing conductive polymer chains, resulting in conductive PPy nanospheres that increase the electrical conductivity of the surface of the PI film.

A variety of analytical techniques including IR-ATR spectroscopy, solution NMR, and AFM were employed in an attempt to characterize the structure of PI surfaces at different reaction times. *In-situ* polymerization of pyrrole in the presence of PI film was followed by ^{1}H NMR experiments using ammonium persulfate (APS) as oxidant. These kinetic studies provided preliminary evidence for a decrease in the pyrrole polymerization rate at a high PI film/pyrrole ratio. The rate of polymerization of pyrrole was unaffected when instead of the PI film, a non-polar polypropylene (PP) film was used. In this case, no PPy domains were found to form on PP film surfaces which remained in an electrically insulating state. In contrast, the surfaces of PI films were uniformly coated with PPy nanospheres with a diameter of approximately 20 nm as indicated by the AFM examinations. The presence of PPy nanospheres led to the transformation of the PI film from insulator to conductive state without impacting film transparency.

2. Experimental

2.1. Materials

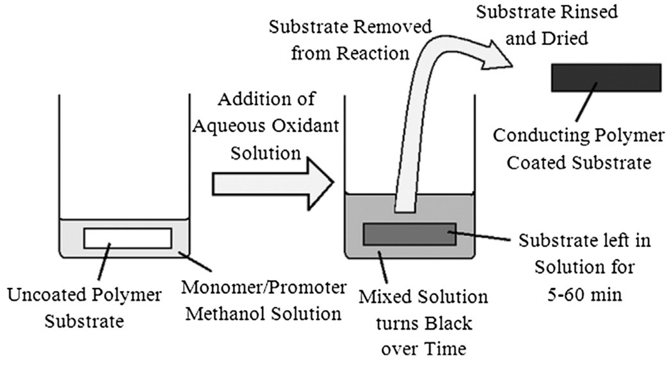
All reagents were obtained from Sigma–Aldrich Chemical Co. unless otherwise indicated. Pyrrole was distilled under vacuum immediately prior use. Ferric chloride ($FeCl_3 \bullet 6H_2O$) was used as received. Poly[(*N,N'*-(*p,p'*-oxydiphenylene)pyromellitimide] (PI) was obtained as a film (under trade name Kapton®) from DuPont Electronics & Communications (Circleville, OH), E. I. du Pont de Nemours and Company.

2.2. Methods

2.2.1. Polymerization of pyrrole in aqueous-methanol solution with $FeCl_3$

The set-up used in these reactions is shown in Scheme 1.

Typical polymerization reactions and purifications were carried out as follows. Pyrrole (0.3170 g, 0.00472 mol) and imidazole (0.0750 g, 0.0011 mol) were dissolved in methanol (50.0222 g) in a 400 mL beaker. A piece of PI film (6 cm × 6 cm) was fully submerged in the liquid with no bubbles present. $FeCl_3 \bullet 6H_2O$ (5.9711 g, 0.0223 mol) was dissolved in 50 g of deionized water (D_2O) and then added to the beaker. Care was taken to make sure no bubbles were present and that the PI film was fully submersed. The solution turned from yellow to black over approximately 30 s and was accompanied by a slight exotherm. The beaker was covered with paraffin film and left to stand for a specific reaction time. After that, the PI film was hung to dry for 30–60 min without washing or removing the PPy layer. Then, the PPy that had coated the film evenly was easily removed by rinsing with D_2O. Once dry, the film was wet briefly by re-immersion in the beaker. The film was then washed with water to remove any solid, not adhering PPy particles. The film had gained a black tinge, but was totally homogeneous. The film was rinsed thoroughly with acetone, and then rubbed with a tissue to remove the remaining PPy particles and dust. After an additional rinse with acetone and drying, the samples collected at different reaction times were submitted for AFM analysis.



Scheme 1. Experimental set-up for pyrrole polymerization on PI film.

The adhesion of the conductive PPy coatings was tested by "rub" and "tape tests". The "rub test" consisted of rubbing the upper half of the films with a tissue wipe, observing any conducting polymer removal, and then testing electrical resistance. The "tape test" consisted of applying a piece of Highland Invisible Tape (3M, St. Paul, MN) to the films, pulling off the tape, and noting whether any conducting polymer was removed. In all tests, no PPy coating was removed from the PI films.

2.2.2. Infrared Attenuated Total Reflection (IR-ATR) spectroscopy

IR-ATR was performed on the PPy coated polyimide in an attempt to investigate the PPy bonding chemistry to the polyimide surface. Infrared spectra were collected on a diamond single-bounce ATR apparatus mounted in a Nicolet Nexus FTIR instrument. This technique probes roughly to a depth of ~2.5 microns into the surface chemistry.

2.2.3. NMR data collection

NMR data were collected on either a Varian INOVA Spectrometer operating at 400 MHz equipped with an H/F, C/P quad probe and variable temperature controller, or a Bruker Advance Spectrometer operating at 500 MHz equipped with a carbon optimized cryoprobe.

^{1}H NMR Kinetics: ^{1}H NMR samples for kinetics were prepared from solutions in pre-cooled glassware, mixed, and transferred to a 5 mm NMR tube over dry ice, to minimize the reaction, prior to NMR analysis. The sample was quickly inserted in the NMR magnet, with the probe temperature set at −20 °C (calibrated from neat methanol NMR standard). Film strips were cut, weighed, and carefully slid into the NMR tube prior to adding solutions. The reactant solutions were 60:40 (by weight) D_2O:MeOD mixtures, at equivalent concentrations to the $FeCl_3$ oxidized polymerization reactions. Data for the initial ($t = 0$) spectrum were acquired from a single transient after minimal lock and shimming, with an acquisition time of 4 s, a 6400 Hz spectral window, and 52,000 data points. Data were zero-filled to 65,000. Kinetics data were collected as an arrayed 1D dataset, each spectrum had 1D water suppression (PRESAT), a 45° pulse width, a recycle time of 7 s, and 8 transients. Peak integrals *vs.* time were attained from processed data with auto integration routines using drift correction (DC) and automatic phase applied to each spectrum. The film recovered from the NMR tube following the kinetics run, was rinsed with D_2O to remove any PPy not adhered to the PI surface, then rinsed with methanol and dried at room temperature under N_2 purge for 30 min.

Solution ^{13}C NMR: Solutions for ^{13}C NMR analysis were prepared by dissolving PI film in concentrated D_2SO_4.

2.2.4. Optical microscopy

Optical microscopy evaluation was done with a Keyence Digital Optical Microscope VHX-500, Microscope head–VH-Z100, Light Source–CA-DO100.

2.2.5. Atomic force microscopy

AFM images were obtained using a D5000 Nanoscope V scanning probe microscope (Digital Instruments, Inc., Santa Barbara,