Chemical synthesis of some Schiff base-type polymers containing pyrrole units

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Summary

The synthesis of three Schiff-base type monomers containing pyrrole units was performed. Their polymerization was carried out by chemical oxidation with (NH₄)₂S₂O₈. Some preliminary thermal and electrical properties were determined.

Introduction

Electrically conductive polymers have received considerable attention in recent years due to both theoretical aspects and practical applications [1,2]. Among these polymers a great deal of work was devoted to polyheterocycles, i.e., polypyrrole and polythiophene, prepared by chemical and electrochemical polymerization because they present an increased environmental and thermal stability in both conductive and neutral states. Unfortunately, important disadvantages of conducting polymers such as infusibility and insolubility in all known organic solvents are preserved in the case of polypyrrole and polythiophene. Therefore a variety of pyrrole and thiophene derivatives along with polymers derived from them have been synthesized in order to improve both the physical and electronic properties and solution and melt processability.

The introduction of bulky substituents in β-position of the five-membered heterocycle was the most adequate method to achieve a molecular control of the properties of conducting polymers [3]. A less used direction was to obtain modified structures based on heterocycles by copolymerization. Thus, Hartel et.al [4] prepared polythiophenediylvinilene via a Wittig polycondensation reaction and Tanaka et. al [5] synthesized copolymers of thiophene and acetylene by electrochemical polycondensation of α,ω-dithienylpolyenes. Finally, Kossmehl and Grezmel have prepared poly(1,2-di(2-furyl)ethylene) by chemical oxidation of trans-1,2-di(2-furyl)ethylene with several inorganic oxidants [6].

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Copolymers containing thiophene and diacetylene units were synthesized using the Glesser coupling reaction from thiophene-based diethynyl monomers [7].

Fully aromatic polyazomethines have been known as an important class of thermally stable and highly conjugated materials. They were obtained by the conventional solution polycondensation of aromatic diamines with aromatic dialdehydes and their electrical conductivity varies between $10^{-12}$ $\Omega^{-1}$ cm$^{-1}$ (neutral state) and $10^{-7}$ $\Omega^{-1}$ cm$^{-1}$ (oxidized state) [8,9].

In this paper we report some results concerning the synthesis and characterization of polymers that combine the functionalities of pyrrole and Schiff bases containing alternating 2,2'-bipyrrrole-diyl rings and azometine units in the main chain. Formally, the polymer structure could be obtained by polycondensation of 5,5'-diformyl 2,2'-bipyrrrole with hydrazine, 1,4-diaminobenzene and 4,4'-diaminobiphenyl. Experimentally, the polymers were synthesized by oxidative coupling of monomers obtained by condensation of pyrrole 2-carboxaldehyde with the corresponding diamines.

**Experimental**

**Materials**

The chemicals used in the synthesis of the monomers were used as received or purified as described below. Pyrrole-2-carboxaldehyde (Aldrich, 99%), pyrrole (Carlo Erba, 98%) p-toluenesulfonic acid (Aldrich, 99%), hydrazine monohydrate (Fluka AG, 98%), 4,4'-diaminobiphenyl (Flucka AG, p.a.) and ammonium peroxidisulfate (Merck, p.a.) were used as received. p-Phenylenediamine (Schuchardt Munchen, p.a.) was twice recrystallized from methanol. Toluene was distilled from sodium before use.

**Instrumentation**

The melting points reported were determined on a Boetius Microscope. Infrared spectra were obtained on a Perkin Elmer 577 infrared spectrometer. Proton NMR spectral analyses were performed on a JNM-C60HL, 60MHz apparatus, at 20°C using DMSO-d$_6$ as solvent and tetramethysilane, TMS, was used as an internal standard and chemical shifts (8) are recorded in ppm from TMS. Thermogravimetric data were recorded with a Paulik-Paulik-Erdey (Budapest) apparatus, heating rate: 12°C/min. The UV spectra were registered using a Specord M80 Carl Zeiss Jena spectrophotometer. The conductivity measurements were performed on disc-shaped samples (13 mm diameter) prepared by pressing the polymer powder in mould under a pressure of $10^5$ N/cm$^2$. The discs were provided with vacuum evaporated silver electrodes of circular form. In order to remove current leakages on the surface, the electrodes had a diameter of