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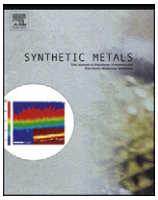

Chemical synthesis and characterization of a new soluble conducting polymer

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ABSTRACT

A new conjugated aromatic poly [(pyrrole-2, 5-diyl)-co-(4-nitrobenzylidene)] (PPNB) have been prepared by polycondensation of 4-nitrobenzaldehyde and pyrrole catalyzed by Maghnite-H$^+$ was reported. Maghnite-H$^+$ is a montmorillonite sheet silicate clay, which was exchanged with protons. The results reveal that the yield of PTTM increases with time and Mag-H amount. The conjugated polymer was characterized by means of FT-IR spectroscopy, UV–vis spectroscopy, matrix-assisted laser desorption/ionization time of-flight (MALDI-TOF) mass spectrometry, thermogravimetric analysis (TGA) and X-ray diffraction. The X-ray data showed the presence of a backbone form of the PPNB formed.

The new polymer is a useful precursors to small-bandgap polymers based on poly (heteroary1ene methines) and is also a useful model system for the investigation of the effects of π-conjugation length on the electronic and optical properties of the conjugated polymers. The electrical conductivity of the synthesized polymer was $\sigma = 0.02251\ \Omega\,\mathrm{cm}^{-1}$.

The results obtained by means of the optical measurements and analyzed by different models, show clearly that our material (PPNB) is a good semi-conductor, where the optical gap separating the extrema of the valence and the conduction band is estimated at 3.7 ± 0.2 eV. This result is in good agreement with those prepared with tetrahedral amorphous carbon.

1. Introduction

Conducting polymers (CPs) are an exciting new class of electronic materials, which have brought rapid and increasing interest since Shirakawa's report in 1977 [1].

Due to the fact that they have combined properties of metals and polymers, the CPs have found applications in the fields of battery materials [2], electrochromic devices [3,4], electromagnetic shielding [5], sensor technology [6], nonlinear optics [7], molecular electronics [8] and enzyme immobilization matrices [9,10]. Many unsubstituted conducting polymer systems have limited solubility as a result, they intractable and infusible. This is primarily due to the rigid rod nature of CPs, arising from their extended-delocalization. Several approaches have been considered to improve processability of conducting polymers [11]. The most effective one is the introduction of insulating polymeric matrices into them [12–18]. This can be achieved by blending, composite formation or copolymerization. Copolymerization could be an effective way because the chemical linkage between the insulating matrix and the conjugated polymer can improve the chemical stability of the polymer [17,18]. The resulting copolymers, with the new functional groups showed different properties from polypyrrole homopolymer, which probably widen the application of the conducting polymer.

Several kinds of copolymers containing pyrrole and other insulating units, such as, styrene, tetrahydrofuran, methyl methacrylate, ε-caprolactone, acryloyl chloride, etc., have already been prepared and studied [18–23]. All results revealed the success in improving the mechanical and physical properties of polypyrrole; however, these synthetic methods follow many steps under strict condition, limiting the application of these copolymers. One simple and alternative way is the direct electrochemical copolymerization of monomers present in the mixture in proper solution [24–26].

Recently, the Algerian proton exchanged montmorillonite clay, called Maghnite-H$^+$ (Mag-H$^+$), representing a new non toxic cationic initiator, was used as a catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers [27–30].

In this paper, we will present a new approach to design poly[(pyrrole-2,5-diyl)-co-(4-nitrobenzylidene)] (PPNB) in one shot, namely by the condensation of pyrrole and 4-nitrobenzaldehyde which is catalyzed by Mag-H. In contrast to most of other conductive polymers, PPNB is a soluble polymer in common organic solvents. The catalyst can be easily separated

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from the polymer product and then regenerated by heating at temperature above 0 °C [27]. The effect of the catalyst amount and time on the polymerization yield of the polymers was studied. These polymers can be dissolved in high polar solvents such as DMSO, DMF.

The conjugated polymer was characterized by means of FT-IR spectroscopy, UV–vis spectroscopy, matrix-assisted laser desorption/ionization time of-flight (MALDI-TOF) mass spectrometry, thermogravimetric analysis (TGA) and X-ray diffraction. The X-ray data showed the presence of a backbone form of the obtained poly [(pyrrole-2,5-diyl)-co-(4-nitrobenzylidene)].

2. Experimental

2.1. Materials

The pyrrole was purchased from Aldrich Chemical Co. and distilled under a reduced pressure. Dichloromethane and 4-nitrobenzaldehyde were used as received. The double bond content was obtained by UV spectroscopy (UV/visible OPTIZEN 2120 PC apparatus) in CH_2Cl_2. The molecular structure of the polymer was characterized by FT-IR spectroscopy (Perkin-Elmer System). The conductivity values were measured using a four-probe technique at room temperature. "The MALDI-TOF mass spectra (m.s.) were recorded on a Bruker Biflex III equipped with a nitrogen laser (l = 337 nm). All m.s. were recorded in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were prepared from THF or CH_2Cl_2 solutions with the dithranol as matrix and the NaI as dopant.

2.2. Polymer preparation

The condensation of 4-nitrobenzaldehyde with pyrrole in the presence of Mag-H$^+$ as a catalyst was carried out by condensation in solution under nitrogen during 6 h.

Each mixture was prepared with a weighted quantity of Mag-H$^+$, dried at 100 °C before use during 1 h. 4-Nitrobenzaldehyde (8 mmol) and pyrrole (8 mmol) were dissolved in 10 ml of 1,2-dichloroethane, and the same 10% by weight of the Mag-H$^+$ were added. The reaction was carried out at 25 °C during 6 h resulting by a mixture which was filtered to remove the clay, then it was slowly added to methanol with stirring, finally, the polymer was dried under vacuum at room temperature during 24 h. The yield was 93.86%.

3. Results and discussion

The search for organic conducting polymers started in the 1970s and up to date is largely focused on polyfuran [31], polythiophene [32], polypyrrole [33], polycarbazole [34], and their derivatives. In this study we report the synthesis of a new soluble obtained in a single step of polymerization through a very simple acid-catalyzed condensation of pyrrole and 4-nitrobenzaldehyde in the presence of an exchanged clay montmorillonite called Mag-H as catalyst.

Most of the PPNB are soluble in organic solvents such as CH_2C1_2, N, N-dimethylformamide (DMF), and sulfolane. Although polymers have highly conjugated chains due to the high degree of dehydrogenation, they were very soluble in organic solvents such as THF, giving grey solutions under high concentrations. The very good solubility of polymers in spite of their high degree of π-conjugation is due largely to the bulky side groups (ϕ) at the methane carbon = $C(\phi)$ link and to some extent to the low molecular weight.

3.1. Effect of the amount of Mag-H

The effect of the amount of Mag-H on the synthesized of PPNB was examined. Fig. 1 shows the effect of the amount of Mag-H, expressed by using various weight ratios Mag-H/monomer, on the polymerization rate. The polymerization was carried out in bulk. As shown in Fig. 1, a yield of 94 wt% was reached for 10 wt% of Mag-H. Similar results are obtained by Boutaleb et al. [35] in the polymerization of l'o-anisidine, aniline by Mag-H. This phenomenon is probably the result of the number of "initiating active sites" responsible of inducing polymerization, a number which is prorating to the catalyst amount used in the reaction.

3.2. Effect of time on condensation

Fig. 2 shows the yield of polymer versus time of polymerization of pyrrole with 4-nitrobenzaldehyde using the Mag-H as catalyst. Moreover, it shows that the polymerization in the presence of 10% of Mag-H takes place slowly and smoothly, reaching a yield of 91% after 6 h at 25 °C. The polymerization yield became constant at that time; this is probably the result of an increase in the medium viscosity.

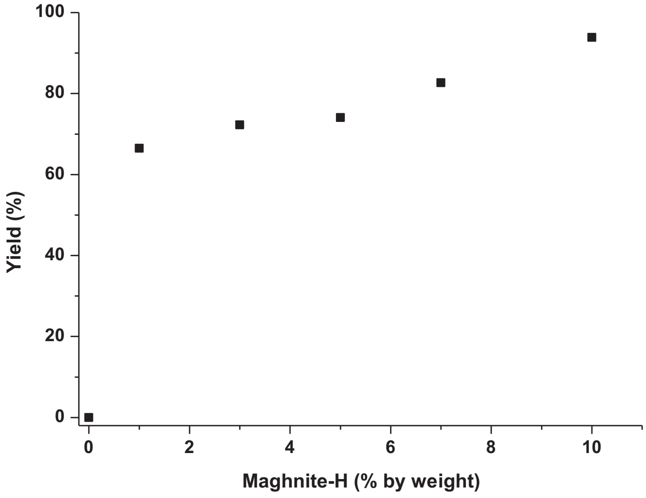

Fig. 1. Effect of the Mag-H amount on the yield of PPNB.

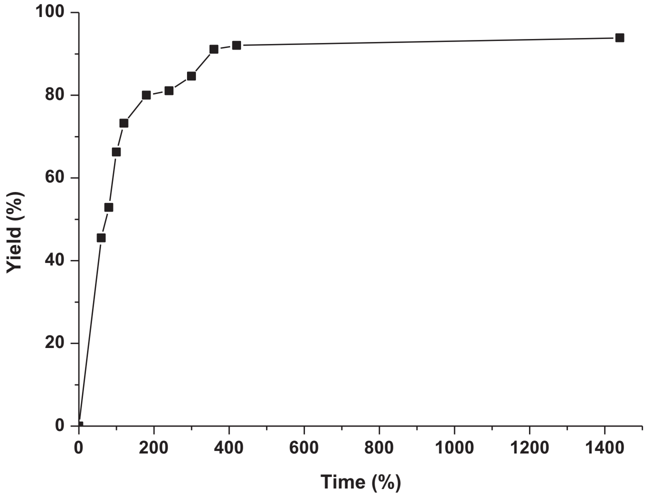

Fig. 2. Effect of polymerization duration on yield of PPNB in CH_3Cl at 20 °C and 10% of Mag-H$^+$.