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Synthesis of Poly[(pyrrole-2,5-diyl)-co-(4-hydroxylbenzylidene)] Catalysed by Maghnite– H^+

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ABSTRACT

Rapid synthesis of poly[(pyrrole-2,5-diyl)-co-(4-hydroxylbenzylidene)] was achieve via the condensation of pyrrole and 4-hydroxylbenzylidene in dichloromethane using acid exchanged montmorillonite clay called Maghnite– H^+ (Mag–H^+) as an efficient catalyst The conjugated polymer was characterized by means of ^1H-NMR, UV-visible, FT-IR spectroscopy and TGA.

Key words: Maghnite-H^+, pyrrole-2,5-diyl,4-hydroxylbenzylidene, polymerization, conjugate polymer.

INTRODUCTION

Among conducting electroactive polymers, polypyrrole and its derivatives have received a great deal of attention due to its high electrical conductivity, good environmental stability, relative ease of synthesis and good redox reversibility. These properties are favourable to its applications in the areas of secondary batteries, electrocatalysis, electrochromic display devices, light-emitting devices, chemical sensors and biosensors[1-5]. However, polypyrrole and other conducting electroactive polymers are limited in practical use due to their very fragile structure and insolubility, which give rise to processing difficulties[6,7]. Several approaches have been taken to improve processability of conducting polymers[8-11]. One effective method is to introduce insulating polymeric matrices into them due to the excellent processability of classical insulating polymers[12-18]. This can be achieved by blending, composite formation or copolymerization. Copolymerization could be a desirable way because the chemical linkage between the insulating matrix and the conjugated polymer can improve the chemical stability of the polymer[17-19]. The resulting copolymers with new functional groups showed different properties from polypyrrole homopolymer, which probably widen the application of conducting polymer. Several kinds of copolymers containing pyrrole and other insulating units, such as styrene, tetrahydrofuran, methyl methacrylate, μ-caprolactone, acryloyl chloride, etc., have been prepared and studied[20-24]. All results showed the success in improving the mechanical and physical properties of polypyrrole. However, these synthetic methods contained many steps and strict condition, leading to limited application of these copolymers. A simple and alternative way is direct electrochemical copolymerization of monomers present in the mixture in proper solution[25-28].

Recently, an Algerian proton exchanged montmorillonite clay called Maghnite–H$^+$ (Mag–H$^+$), a new non toxic cationic initiator, was used as a catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers[29-32]. In the present work, we present a new approach to design poly[(pyrrole-2,5-diyl)-co-(4-hydroxylbenzylidene)] (PPHB) in one shot, namely by the condensation of pyrrole and 4-hydroxybenzaldehyde catalyzed by Mag–H$^+$ (Figure 1). In contrast to most of the other conductive polymers, PPHB is a soluble polymer in common organic solvents. The catalyst can be easily separated from the polymer product and regenerated by heating at a temperature above 0°C[15]. The effects of different synthesis parameters, such as the amount of Mag–H$^+$, monomer, pyrrole, and 4-hydroxybenzaldehyde are discussed.

EXPERIMENTAL

Materials

Pyrrole was purchased from Aldrich Chemical Co. and distilled under reduced pressure. Dichloromethane and 4-hydroxybenzaldehyde were used as received. MEB imaging was performed on Hitachi S 2500. The molecular structure of the polymer was characterized by FT-IR spectroscopy (Perkin-Elmer System). UV spectra were obtained by an OPTIZEN 2120 UV-Vis spectrometer using the dichloromethane solution of polymers with a concentration of 0,00125 mg/ml. ^{1}H-nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm in DMSO Tetramethylsilane (TMS) was used as the internal standard in these cases.

Polymer synthesis

In a 50 ml beaker, pyrrole (8 mmol) and 4-hydroxybenzaldehyde (8 mmol) were dissolved in 10 ml of dichloromethane and a chosen amount of Maghnite–H$^+$ was added. The weight ratio (Maghnite– H$^+$/Pyrrole; 4-hydroxybenzylidene) was kept constant (at the desired value) in all flask. The reactions were stirred by a magnetic stirring bar, At the end of the reaction, the resulting mixture was filtered to remove the clay and then slowly added to methanol with stirring and then the polymer was dried under vacuum at room temperature for 24 h.

RESULTS AND DISCUSSION

Most of the PPHB were found to be soluble in organic solvents such as tetrahydrofuran (THF), 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 of 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 (Φ) link and also to the low molecular weight to some extent.

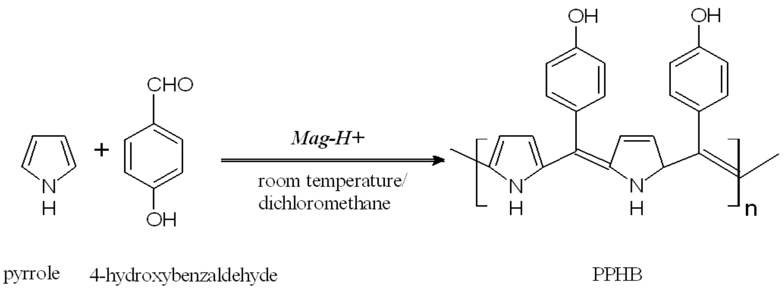

Fig. 1: The synthetic route of poly[(pyrrole-2,5-diyl)- co-(4-hydroxybenzylidene)] (PPHB) by Mag–H$^+$ catalyst

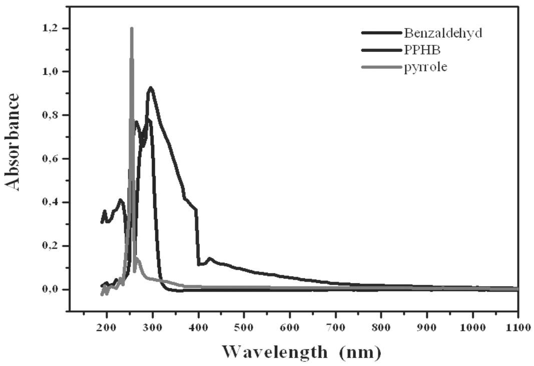

Fig. 2: Spectre UV-visible de PPHB (in CH_2Cl_2)

The UV-Vis absorption was recorded with an OPTIZEN 2120 spectrometer. Figure 2 shows the optical absorption spectra of polymers PPHB in CH_2Cl_2 solution. The colours of the polymer solution were brown or almost black. The absorption spectra in Figure 2 shows the band in the range of (300–350) nm assigned to the π-π^* transition of the aromatic heterocycles since it corresponds to the same band as its precursor, and the band in the range of (400–430) nm is assigned to the π-π^* transition.

The ^{1}H-NMR spectra of PPHB were obtained to further investigate and confirm the proposed structure. Figure 3 shows the ^{1}H-NMR spectrum of PPHB in DMSO, The resonance at 10.45 ppm is assigned to the proton resonance of hydroxyl group in the benzene ring. The resonance at 9.14 ppm is assigned to the proton resonance of hydrogen in pyrrole .we observe a new proton resonance of 6.64–6.93 ppm was observed, indicating the formation of the quinoid rings in the polymer backbone, x and y are impurities. The polymers so obtained are readily soluble in common organic solvents, such as chloroform, dichloromethane, THF.

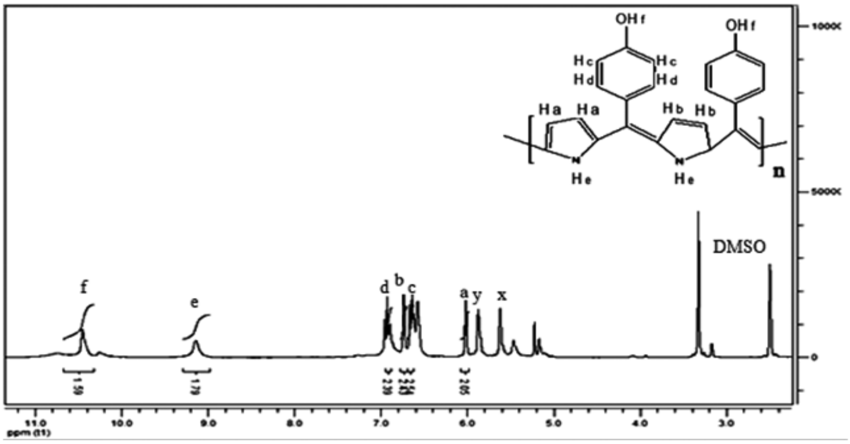

Fig. 3: ^{1}H-NMR spectrum (300 MHz) of PPHB in DMSO

Fig. 4 shows the FT-IR absorption spectra of PPHB. A distinct peak at 772 cm^{-1} of PPHB is due to the Cb–H the out-of plan vibration, characteristic of α-linkage in pyrrole ring. The peak at 1685 cm^{-1} of Fig. 4 is assigned to the C=C and the stretching vibration of aromatic in phenylene , this assignments is based on the FT-IR spectrum of pyrrole. The broad band at 3303 cm^{-1} is N–H stretching vibration of pyrrole ring and O–H vibration of hydroxyl on benzene ring in the side chain.

Fig. 5 show the TGA curves of PPHB obtained in a helium atmosphere at a heating rate of 100 ^{0}C/min. This polymer show bad thermal stability. For example, the intrinsic PPHB has an onset of thermal decomposition of 100 ^{0}C attributed to OH, the second at 114 ^{0}C is assigned to carbon bridge, so the PPHB is little stable at high temperature.

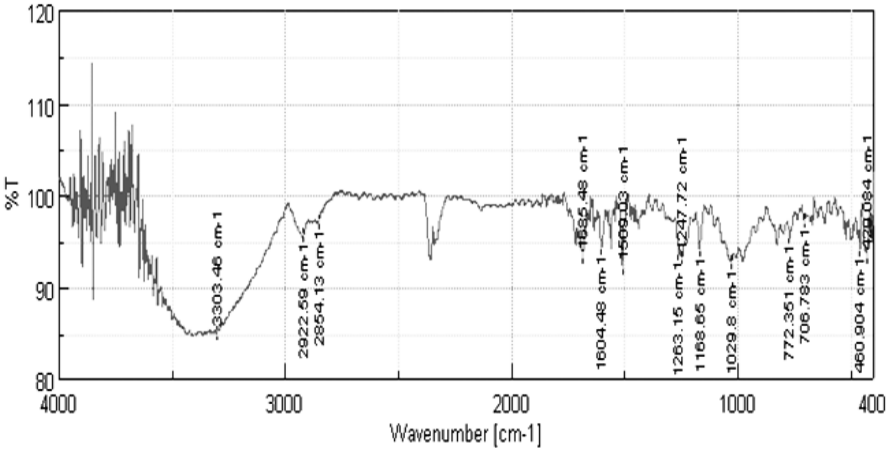

Fig. 4: FT-IR spectrum of PPHB

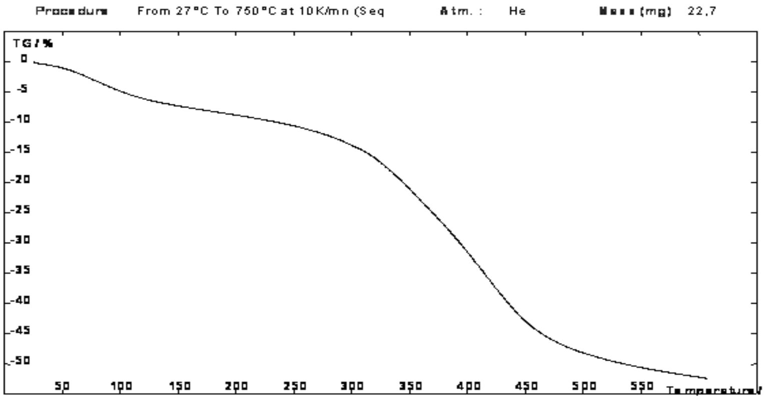

Fig. 5: TGA spectra of PPHB

CONCLUSIONS

Maghnite–H$^+$, proton exchanged montmorillonite clay is an effective initiator for the copolymerization of 4-hydroxybenzaldehyde with pyrrole.

A novel polymer, poly[(pyrrole-2,5-diyl)-co-(4-hydroxybenzylidene)], which has a π-conjugated chain was synthesized by using Maghnite–H+ as catalyse. The resultant polymer showed good solubility in common organic solvents and good film formability. Such results may serve primarily to illustrate a new strategy to increase the solubility of low band gap polymers through the arrangement of different aromatic heterocycles in conjugated polymer backbones.

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