



Trade Science Inc.

Research & Reviews On Polymer

Full Paper

RRPL, 2(1), 2011 [34-38]

Synthesis and characterization by FTIR of polythiophene confined in a mesoporous material

Manuel F. Rubio-Arroyo¹, Lilia Ortega-Espinosa¹, M.A. Mora^{2*}, Tatiana Klimova³

¹Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510, Coyoacán, México D. F., (MÉXICO)

²Departamento de Química, Universidad Autónoma Metropolitana, Campus Iztapalapa, Av. Sn. Rafael Atlixco 186, 09340, México D. F., (MÉXICO)

³Facultad de Química, Departamento de Ingeniería Química, Universidad Nacional Autónoma de México, 04510, México D.F., (MÉXICO)

E-mail: mam@xanum.uam.mx

Received: 7th June, 2011 ; Accepted: 7th July, 2011

ABSTRACT

In this study, doped homopolymers of thiophene were synthesized by chemical oxidative polymerization. The polymerization was carried out inside a mesoporous material of the MCM-41 type avoiding the polymer instability after the doping. The polymer was characterized by FTIR spectroscopy and the conductivity of the doped polymer was determined.

© 2011 Trade Science Inc. - INDIA

KEYWORDS

Conducting polymers;
Polythiophene;
Mesoporous material;
Dopant.

INTRODUCTION

The study of polythiophenes, PTh's, has been intensified over the last decades. Between the properties of these materials, one of the most notable is the electric conductivity. However, conductivity is not the only interesting property resulting from electron delocalization. The optical properties of these materials respond to environmental stimuli, with dramatic color shifts in response to changes in solvent, temperature, applied potential, or binding to other molecules. A number of applications have been proposed for conducting PTh's. Potential applications include field-effect transistors^[1], electroluminescent devices, solar cells, photochemical-resists, nonlinear optic devices^[2], batteries, diodes, and chemical sensors^[3].

A variety of reagents have been used to dope

PTh's. Iodine and bromine produce high conductivities^[4], but are unstable and slowly evaporate from the material^[5]. Organic acids including trifluoroacetic acid, propionic acid, or sulfonic acids produce PTh's with lower conductivities than iodine, but with higher environmental stabilities^[5,6]. Oxidative polymerization with ferric chloride can result in doping by residual catalyst^[7]. Unsubstituted PTh's are conductive after doping, and have excellent environmental stability compared with some other conducting polymers such as polyacetylene, but are intractable and soluble only in solutions like mixtures of arsenic tri- or penta-fluoride^[8]. However, in 1987 examples of organic-soluble PTh's were reported^[9-19].

The practical application of the conducting polymers is limited mainly by problems in the synthesis process and their instability specially after the doping, which

means that a special process of synthesis is necessary, a process including the use of an inert atmosphere or vacuum. Because of these inconveniences we have decided to study the synthesis of polythiophene inside the channels of a porous material such as a mesoporous material (MM)^[20]. After the polymerization the silica channels are inundated with chains of polymer, the inorganic inert walls act as a protect case. In this way the polymer's tendency to disarrange is drastically reduced. This route brings the advantage that the materials can be stored and process in the presence of oxygen without the risk of the altering its properties.

The aim of this work was the synthesis and characterization of polythiophene doped with HCl or p-toluensulfonic acid supported on a mesoporous material, MM, previously impregnated with an oxidant. We tried to find a route of polymerization in which there was no an excessive wear of reagents. The obtained polymer was characterized by infrared spectroscopy and the conductivity of the doped polymer was determined.

EXPERIMENTAL

In order to obtain a supported conducting polythiophene the next steps were followed: synthesis of the support material (MM), impregnation of the support with an oxidant, synthesis of the polythiophene inside the support pores, characterization of the polymer and measurement of conductivity.

Support synthesis: The MM support of the MCM-41 type was synthesized mixing a solution of NH_4OH with a surfactant, hexadecyltrimethyl ammonia, and tetramethylorthosilicate under vigorous stirring. The solution was filtered, washed with distilled water, dried at room temperature for 24 h, and then calcined at 550 °C for 4 h. The obtained material was subjected to the nitrogen physisorption test. The determined surface area, pore volume and pore diameter were 1332 m^2/g , 0.973 cm^3/g and 29 Å, respectively. The N_2 adsorption-desorption isotherm and the X-ray powder diffraction data are shown in reference^[20], and the FTIR spectrum of MM is shown in Figure 1.

Impregnation: The support was transformed into a powder by crashing it in a mortar, and then it was spread on a watch glass. An aqueous solution of ferric chloride

was prepared and distributed with a syringe on the support. Then the sample was dried at room temperature for 24 h. Several samples with different amount of ferric chloride (from 10 to 22 wt. % of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were prepared, TABLE 1. Other series of samples were prepared using anhydrous FeCl_3 .

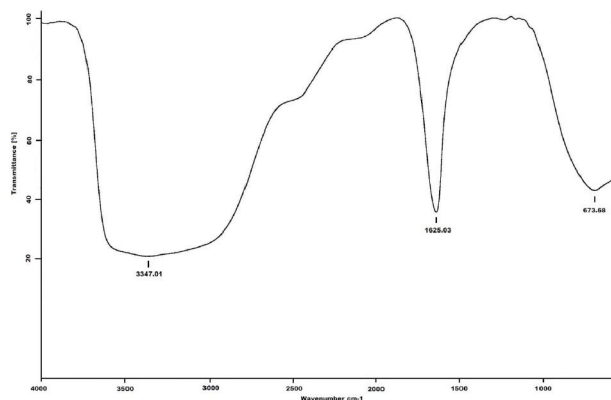


Figure 1 : FTIR spectrum of the mesoporous material MM.

TABLE 1 : Amount of ferric chloride hexahydrate used for the impregnation of the mesoporous material MM.

Oxidant content	
wt. %	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, g
10	0.5367
12	0.6587
15	0.8224
16.5	0.9545
18	1.0603
20	1.2076
22	1.3624

Synthesis of polythiophene

The FeCl_3 -containing MM support was mixed with chloroform in a reaction vessel containing a magnetic stirring bar. In other reaction vessel, thiophene was added to chloroform with constant stirring. Both solutions were mixed and the polymerization was carried out for 24 h in a nitrogen atmosphere. The obtained solution was filtered and the PT confined in the MM was dried in a vacuum drier for 24h. The obtained dry solid was characterized by FTIR spectroscopy.

Instrumental and materials

Fourier transformed infrared (FTIR) spectra were recorded in the 400-4000 cm^{-1} range on a Bruker-tenso 27 spectrophotometer. Electric conductivity of the PT-MM was measured with a Hanna Instruments

Full Paper

conductimeter microprocessor logging HI 933300. Aldrich supplied all reactants used.

RESULTS AND DISCUSSION

During the experimental development different tests of polymerizing were performed in the presence of anhydrous FeCl_3 or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, supported on a mesoporous material MM or without the support. The tests were performed by varying the rate of impregnation of the support. To measure the conductivity of the polymer the samples of the polymer were dissolved in deionized water.

Synthesis of PT-MM with anhydrous FeCl_3 in N_2 atmosphere

PT-MM synthesis was realized in nitrogen atmosphere using anhydrous ferric chloride impregnated on the MM support from chloroform solution. Two solid phases were obtained: a black color solid which corresponded to the unreacted ferric chloride and a brown solid which was the polythiophene and which infrared spectrum is shown in Figure 2. In the FTIR spectrum of the PT-MM sample the following signals can be appreciated: a band at 1435 cm^{-1} which is characteristic of carbon-carbon double bonds, the bands at 840 cm^{-1} and 581 cm^{-1} indicating the presence of C-S and C-S-C links, respectively.

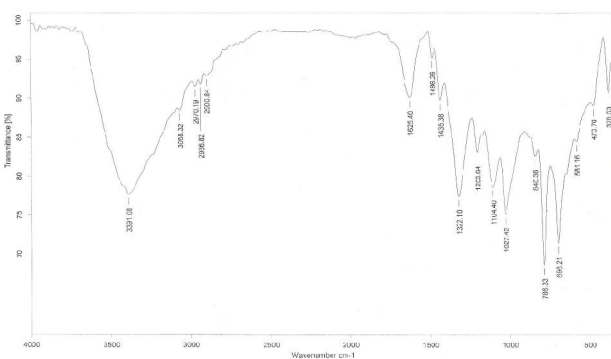


Figure 2 : Spectrum obtained from the brown material in the synthesis carried out with ferric chloride in a nitrogen atmosphere without the mesoporous material, you can see the band in 1600 cm^{-1} , characteristic of carbon - carbon double bonds, the bands at 840 cm^{-1} and 581 cm^{-1} indicates the existence of carbon-sulphur bonds.

Synthesis of PT-MM using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ supported on MM

This synthesis was performed several times with

different amounts of ferric chloride impregnated on the mesoporous material, TABLE 1. When the amount of ferric chloride was equal to 16.5 wt. %, an orange-brown color solid was obtained. This color is characteristic of a non-doped polythiophene state. In figure 3, the corresponding FTIR spectrum shows bands near 1400 cm^{-1} , 800 cm^{-1} and 560 cm^{-1} corresponding to thiophene. The displacement was attributed to the support.

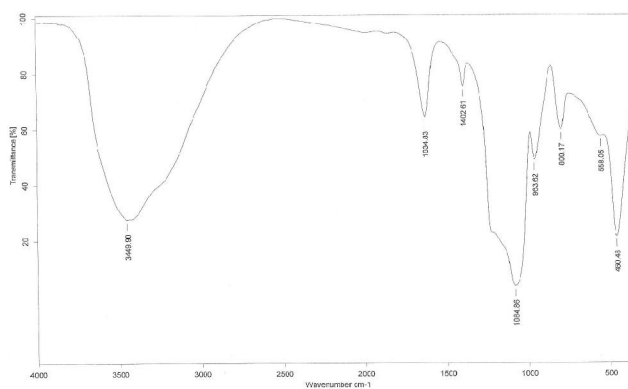


Figure 3 : Spectrum of the polymer synthesized in the presence of the mesoporous material impregnated with 16.5 wt. % of ferric chloride hexahydrate, the bands at 1600 cm^{-1} , 840 cm^{-1} and 560 cm^{-1} confirm the presence of polythiophene, the displacement is attributed to the support.

Synthesis of PT-MM using anhydrous FeCl_3 supported on MM

Several trials were conducted varying the amount of the anhydrous FeCl_3 on the support, TABLE 2. When the amount of the oxidant was equal to 12 wt. %, the obtained material had an orange color. The corresponding FTIR spectrum, Figure 4, showed the characteristic bands of polythiophene near 1400 cm^{-1} , 800 cm^{-1} , and 560 cm^{-1} . Samples prepared with other amounts of oxidant also showed these bands, but the coloration was more tenuous, besides that the absorbance was higher for the sample with 12 wt. % of FeCl_3 .

TABLE 2 : Amount of anhydrous ferric chloride used for the impregnation of the mesoporous material MM in nitrogen atmosphere.

wt. %	Oxidant content	
	Anhydrous FeCl_3 , g	
6	0.1848	
12	0.3949	
15	0.5111	

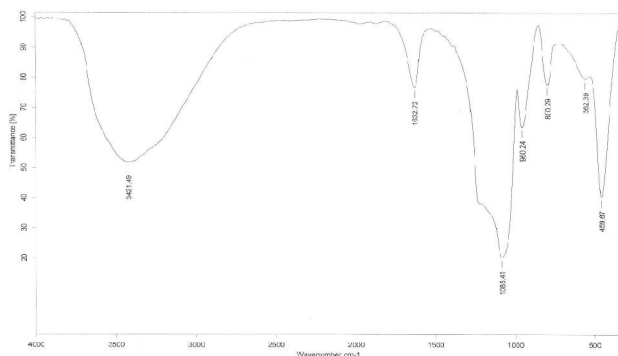


Figure 4 : Spectrum of the polymer synthesized in the presence of mesoporous material MM impregnated with 12 wt. % of anhydrous ferric chloride and in nitrogen atmosphere, note the bands at 1600 cm^{-1} , 840 cm^{-1} , and 560 cm^{-1} characteristic of the polythiophene, the displacement is attributed to the presence of the support.

CONDUCTIVITY

TABLE 3 shows results from the conductivity measurements for the polythiophenes obtained under different conditions.

TABLE 3 : Polymer conductivity values registered for PTh's obtained under different reaction pathway conditions.

Dopant a=P-toluensulfonic acid, dopant b = hidrochloric acid.

Sample	FeCl ₃ anhidro	FeCl ₃ 6H ₂ O	Dopant
PT pure	2.61×10^{-6}		-
PT a-doped	1.15×10^{-2}		a
PT b-doped	8.57×10^{-3}		b
PT supported on MM	1.076×10^{-7}	5.64×10^{-7}	-
PT a-doped, supported on MM	1.06×10^{-3}	8.11×10^{-4}	a
PT b-doped supported on MM	9.74×10^{-4}	2.56×10^{-4}	b
PT a-doped supported on MM. In the presence of solar light.	9.87×10^{-3}	9.63×10^{-4}	a

As it can be seen, the experiments can be separated into two groups, in the first one anhydrous FeCl₃ was used, and in the second one hydrated FeCl₃·6H₂O was employed, either with or without support. Furthermore, it can be noted that the samples doped with hydrochloric acid or p-toluenesulfonic acid showed better conductivity results than corresponding undoped references. The polymers obtained with anhydrous FeCl₃ in chloroform solution were always better conductor than the polymers obtained with hydrated FeCl₃·6H₂O. The polymer obtained with anhydrous ferric chloride supported on the mesoporous material MM and doped with p-toluensulfonic acid also had a high conductivity,

only slightly below the polymer obtained with the same catalyst and dopant but without the support. However, the advantage of the first is the stability of PT given by the support. This conductivity stability can be attributed to the support because it reduces the interaction between the polymer and the humidity from the atmosphere, avoiding the dedoping of the polymer as has been shown for poly(2-octylthiophene) in reference 21. Aavapiriyanont and coworkers^[22] have also shown that the presence of small amount of water affects the rate of growth and the polymer conductivity.

Also in TABLE 3 the conductivity values obtained for undoped polythiophenes are shown, these have a low electrical conductivity of around 10^{-7} , in agreement with the range of $10^{-10} - 10^{-8}$ S/cm known^[23] for undoped conjugated polymers.

CONCLUSIONS

Polythiophene was prepared inside the channels of a mesoporous material MM of the MCM-41 type. The sample with the highest conductivity, $1.15 \times 10^{-2}\text{ Scm}^{-1}$, was the sample prepared with 16.5 wt. % of oxidant (anhydrous FeCl₃) doped with p-toluensulfonic acid. Performance of the PT synthesis inside the MM-mesopore channels allowed us an increase in the stability of the obtained PT.

REFERENCES

- [1] F.Garnier; Electronic Materials: The Oligomer Approach, K.Müllen, G.Wegner, (Eds); Wiley-VCH, Weinheim, (1998).
- [2] M.G.Harrison, R.H.Friend; Electronic Materials: The Oligomer Approach, K.Müllen, G.Wegner, (Eds); Wiley-VCH, Weinheim, (1998).
- [3] V.Martina, K.Ionescu, L.Pigani, F.Terzi, A.Ulrici, C.Zanardi, R.Seeber; Anal.Bional.Chem., **387**, 2101 (2007).
- [4] R.D.McCullough, S.Tristram-Nagle, S.P.William, R.D.Lowe, M.Jayaraman; J.Amer.Chem.Soc., **115**, 4910 (1993).
- [5] M.Loponen, T.Taka, J.Laakso, K.Vakiparta, K.Suuronen, P.Valkeinen, J.Osterhlm; Synth.Met., **41**, 379 (1991).
- [6] J.J.Bartus; Macromol.Sci.Chem., **A28**, 917 (1991).
- [7] X.Qiao; Synth.Met., **122**, 449 (2001).

Full Paper

- [8] J.E.Fromer; *Acc.Chem.Res.*, **19**, 2 (1986).
- [9] R.Elsenbaumer, K.Jen, R.Oboodi; *Synth.Met.*, **15**, 169 (1986).
- [10] S.Hotta, S.D.D.V.Rughooputh, A.J.Heeger, F.Wudl; *Macromol.*, **20**, 212 (1987).
- [11] S.Hotta, M.Soga, N.Sonoda; *Synth.Met.*, **26**, 267 (1998).
- [12] S.Hotta; *Synth.Met.*, **22**, 103 (1987).
- [13] S.Hotta, S.Rughooputh, A.Heeger; *Synth.Met.*, **22**, 79 (1987).
- [14] S.D.D.V.Rughooputh, S.Hotta, A.J.Heeger, F.Wudl; *J.Polym.Sci.Phys.Ed.*, **25**, 1071 (1987).
- [15] A.O.Patil, Y.Ikenoue, F.Wudl, A.Heeger; *J.Amer.Chem.Soc.*, **109**, 1858 (1987).
- [16] P.Englebienne, M.Wiland; *Chem.Comm.*, **14**, 1651 (1996).
- [17] B.S.Kim, L.Chen, J.P.Gong, Y.Osada; *Macromol.*, **32**, 3964 (1999).
- [18] M.Anderson, P.O.Ekeblad, T.Hjerberg, O.Wennerstöm, O.Iganäs; *Polym.Commun.*, **32**, 546 (1991).
- [19] S.Jung; *Synth.Met.*, **98**, 107 (1998).
- [20] M.F.Rubio-Arroyo, M.A.Ayona-Argueta, M.Poisot, G.Ramírez-Galicia; *Energy & Fuels*, **23**, 2840 (2009).
- [21] T.Taka; *Synth.Met.*, **55**, 4985 (1993).
- [22] S.Aavapiriyanont, A.K.Chandler, G.A.Gunawardena, D.Pletcher; *J.Electroanal.Chem.*, **177**, 279 (1984).
- [23] G.Gordon Wallace, M.S.Geoffrey, L.A.P.Kane-Maguire, P.R.Teasdate; *Conductive Electroactive Polymers: Intelligent Polymer Systems, Third Edition*, CRC Press, Taylor & Francis Group, (2009).