Sakarya University Journal of Science, 22 (6), 1571-1575, 2018.

SAKARYA ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ
SAKARYA UNIVERSITY JOURNAL OF SCIENCE

e-ISSN: 2147-835X
Dergi sayfası:http://www.saujs.sakarya.edu.tr

Received
06-12-2016
Accepted
26-02-2018

Doi
10.16984/saufenbilder.273829

Synthesis of Nano Poly(2-thiophenecarboxaldehyde) and Characterization of Structure

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ABSTRACT

This article describes a chemical oxidative polymerization for the preparation of nano polymeric thiophene by using $FeCl_3$ as oxidant. 2-thiophenecarboxaldehyde (2-THCA) compound was used as a monomer at this polymerization process. The structure of synthesized nano polymeric thiophene was confirmed by scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), raman spectroscopy, and elemental analysis of C, H, O and S. SEM images showed that the poly(2-thiophenecarboxaldehyde) (PTHCA) was synthesized in nanoscale and had a homogeneous and smooth structure. The size of the synthesized nano particles was not more than 35 nm. Thermal analysis of nano polymeric thiophene showed that the polymer is thermally stable up to 450-460 ºC. When elemental analysis results of PTHCA were examined, it was seen that the obtained data after the synthesis of nano polymeric thiophene and the theoretically determined data were agree with each other.

Keywords: 2-thiophenecarboxaldehyde, nano polymer, characterization

1. INTRODUCTION

Over the last few decades, extensive researches have been focused on the development of new functional organic materials for optics, electronics and other industrial applications. The most used organic materials for these applications were conductive polymers (ICPs) [1] such as polyaniline, polypyrrole (PPy) [2-4] and polythiophene (PTH) [5]. Among these polymers, polythiophene (PTH) has considerable attention due to the some characteristic properties such as high electrical [6] conductivity, environmental and thermal stability [7], oxidation and/or reduction levels, electrical and optical properties, high energy density, easy and low cost synthesis or potential application in various fields such as electromagnetic interference (EMI), polymer rechargeable batteries, DNA detection, organic light emitting diodes (OLEDs), photovoltaic cells [8], electrical memory performance, separation membranes, sensors [9], biomedical fields and so on [10-20].

Two techniques for polymerization of thiophene have been reported in the literature. The first one is electrochemical polymerization and the second one is chemical oxidative polymerization [21]. In electrochemical polymerization some potential is applied through a solution of monomer. The

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chemical oxidants or cross-coupling catalysts are used in chemical polymerization process. The chemical method for the synthesis of polythiophenes offers two advantages when compared to electrochemical method, larger monomer selection and ability to synthesize polythiophenes nanoparticles using appropriate catalysts [22-25].

In the present work, we synthesized PTHCA by chemical polymerization method. In the polymerization process, $FeCl_3$ was used as an oxidant and 2-THCA was used as a monomer for the polymerization of thiophene. The synthesized nano polymeric thiophene was characterized by different techniques such as scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), raman spectroscopy, and elemental analysis of C, H, O and S.

2. EXPERIMENTAL: MATERIAL AND METHODS

2.1. Material and Methods

2-thiophenecarboxaldehyde, anhydrous ferric(III) chloride, chloroform and methanol were all purchased from Merck KGaA, Darmstadt, Germany.

Fourier transform infrared (FTIR) spectra of the polythiophene were recorded by Perkin Elmer Spectrum FTIR in the range of 4000–400 cm^{-1} with ATR technique. Thermal properties of the PTHCA were investigated using thermogravimetric analyzer Schimadzu DTG-60H instruments. The thermogravimetric experiments were conducted under nitrogen atmosphere in a temperature range of 25–1200 °C with a heating rate of 10 °C/min. The morphology of polythiophene was analyzed by using FEI Quanta FEG 250 scanning electron microscopy (SEM). Raman spectroscopic studies were carried out by a Renishaw Invia Raman Microscope. The polythiophene composition was determined by elemental analysis using Thermo Scientific Flash 2000 elemental analyzer.

2.2. Synthesis of poly 2-thiophene carboxaldehyde

4.7 mL of 0.05 mol of 2-THCA was mixed with 350 mL of chloroform in a two-necked round-bottom flask containing a magnetic stir bar. 0.15 mol of anhydrous $FeCl_3$ was dissolved in 150 mL chloroform. Anhydrous $FeCl_3$ solution was put in a dropping funnel and it was added drop by drop to the stirred thiophene solution. The polymerization was continued at room temperature for 24 hours. Dark brown precipitate was filtered and washed first with $CHCl_3$ and then washed with methanol several times to remove the oxidant. The consisted PTHCA powder was dried at 50 ºC for 24 h. The reaction for the synthesis of PTHCA was presented in Figure 1. Reaction mechanism was occurred (i); head-to-tail-head-to-tail (ii) head-to-head-head-to-tail (iii) head-to-tail-tail-to-tail and (iv) head-to-head-tail-to-tail as shown in the literature [24, 26]. Since the polymerization yield is about 20%, the soluble fraction is too weak to determine the average molecular weight and NMR analysis [24, 26-27].

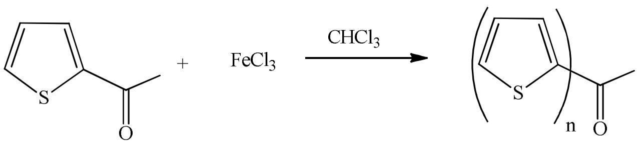

Figure 1. Synthesis of PTHCA

3. RESULTS

3.1. FTIR Spectroscopy Analysis

The chemical structures of PTHCA and 2-THCA were elucidated by FTIR spectroscopy and the spectra were demonstrated in Figure 2. The FTIR spectrum of THCA (Figure 2a) showed that a broad –OH stretching absorption band was between 3500 and 3100 cm^{-1} and the aliphatic C–H stretching band was between 2990 and 2850 cm^{-1}. As the –OH stretching band and the aliphatic C–H stretching band were aligned, they appeared as a broad band from 3089 to 2837 cm^{-1} in the spectrum. When the FTIR spectrum of PTHCA (Figure 2b) was examined, the major peaks observed at 1629 cm^{-1} and 1423 cm^{-1} assigned for C=C asymmetric and symmetric stretching vibration of thiophene ring. The other peaks at 1313 cm^{-1}, 1055 cm^{-1} and 1029 cm^{-1} were due to deformation of C-H bending and CH in-plane of vibrations. The peak at 891 cm^{-1} and at 661 cm^{-1} was assigned for C-S bending vibration and C-S-C ring deformation stretching of PTHCA, respectively. These peaks proved that the polymerization process was successfully carried out and the PTHCA was synthesized.

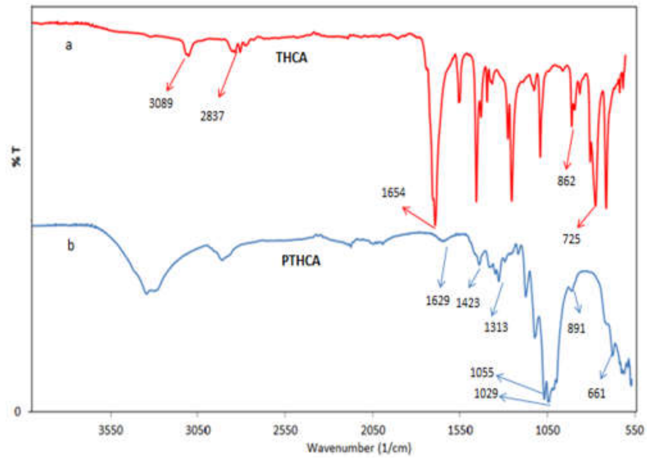

Figure 2. FTIR spectra of (a) 2-THCA and (b) PTHCA

3.2. Raman Spectroscopy Analysis

The Raman spectrum peak exhibited a peak at 1641 cm^{-1} showed dispersion with increasing polymer chain length [28]. The most significant peaks at 1584 cm^{-1} and 1462 cm^{-1} accredited with the C=C ring stretching of the PTHCA. The peak at about 1354 cm^{-1} was C–C ring stretching. The peaks at 1147 cm^{-1} and 1027 cm^{-1} assigned to the ring symmetric bending vibration and the in-plane C-H bending mode, respectively. The peak at 779 cm^{-1} was attributed to the ring deformation C–S–C. Raman spectrum of PTHCA was described in Figure 3.

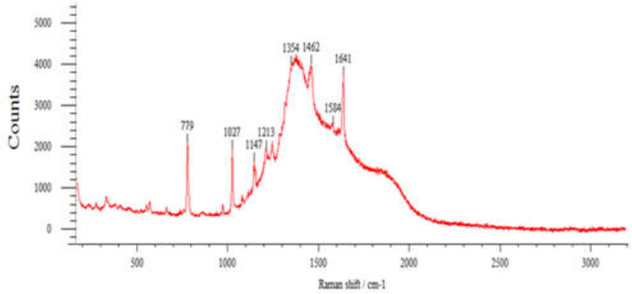

Figure 3. Raman spectrum of PTHCA

3.3. Scanning Electron Microscopy Analysis

The scanning electron microscope (SEM) in Figure 4 exhibited the surface morphology of PTHCA. These SEM images clearly indicated that the formed particles were uniform and homogeneous. Their dimensions were no more than 35 nm. This means that the synthesized PTHCA was nano-sized. Smooth surface of polythiophene indicates that the synthesized PTHCA has a better conductivity than other rough polythiophene compounds [20].

3.4. Thermogravimetric analysis

As shown in Figure 5, TGA study of the PTHCA indicates that there were two weight loss areas and the initial decomposition occurred at about 50–150 °C due to the loss of solvent and water. The second weight loss started at 512 °C was due to thermal decomposition of polythiophene. The TGA curve showed that the first and second weight loss areas of the polythiophene were 12 and 78 wt %, respectively. The DTA curve showed as small exothermic peak at about 100 °C related with the loss of solvent and water from polythiophene and an exothermic peak at 600 °C conformed to thermal degradation of polythiophene. Thermal analysis of nano polymeric thiophene showed that the polymer is thermally stable up to 450-460 °C.

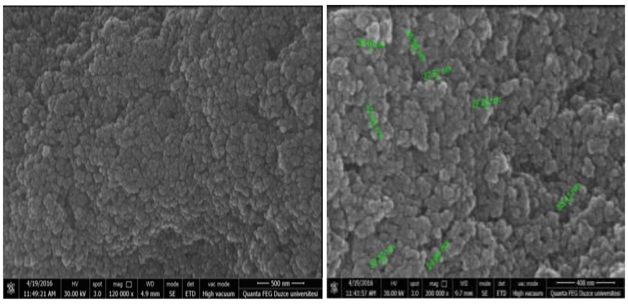

Figure 4. SEM images of PTHCA

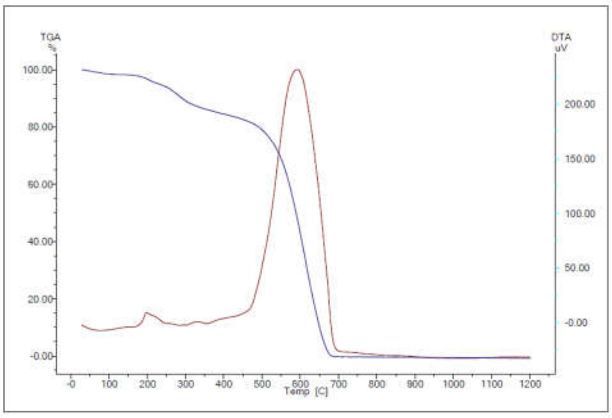

Figure 5. TGA and DTA spectra of PTHCA

3.5. Elemental analysis

Elemental analysis was performed to determine the elemental composition of the synthesized PTHCA. Theoretical and experimental results of PTHCA were presented at Table 1. The results presented in Table 1 proved that the experimental data were compatible with theoretical ones for the synthesized polythiophene.

Table 1. Elemental analysis of polythiophene

PTHCA	Theoretical	Experimental
% C	57.11	54.48
% H	4.79	4.31
% S	25.41	27.02
% O	12.68	10.67

4. CONCLUSION

The nano polythiophene particles were successfully synthesized by chemical oxidative polymerization method. The structure of nano polythiophene was characterized by FTIR, TGA, Raman Spectroscopy and Elemental Analysis techniques. The surface morphology of nano poly(2-thiophenecarboxaldehyde) was also examined with SEM. The sizes of the synthesized nano particles were not more than 35 nm. The TGA studies showed that the PTHCA was thermally stable up to 512 ºC.

Acknowledgments

This work was supported by the Duzce University Research Fund with Project Number 2014-05-03-259 and 2015-05-03-354.

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