Physica B 481 (2016) 268–279

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Studies of structural, optical, dielectric relaxation and ac conductivity of different alkylbenzenesulfonic acids doped polypyrrole nanofibers

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ARTICLE INFO

Article history:
Received 10 September 2015
Received in revised form
24 October 2015
Accepted 18 November 2015
Available online 1 December 2015

Keywords:
Polypyrrole nanofibers
HRTEM
XRD
dielectric relaxation
ac conductivity

ABSTRACT

Polypyrrole (PPy) nanofibers doped with alkylbenzenesulfonic acids (ABSA) have been synthesized using interfacial polymerization method. HRTEM studies confirm the formation of PPy nanofibers with average diameter ranging from 13 nm to 25 nm. Broad X-ray diffraction peak in 2θ range 20–23.46° reveals amorphous structure of PPy nanofibers. The ordering or crystallinity of polymer chains increases, while their interplanar spacing (d) and interchain separation (R) decreases for short alkyl chain ABSA doped PPy nanofibers. FTIR studies reveal that short alkyl chain ABSA doped PPy nanofibers show higher value of "effective conjugation length". PPy nanofibers doped with short alkyl chain ABSA dopant exhibit smaller optical band gap. TGA studies show enhanced thermal stability of short alkyl chain ABSA doped PPy nanofibers. Decrease in dielectric permittivity $\varepsilon'(\omega)$ with increasing frequency suggests presence of electrode polarization effects. Linear decrease in dielectric loss $\varepsilon''(\omega)$ with increasing frequency suggests dominant effect of dc conductivity process. Low value of non-exponential exponent $\beta\ (<1)$ reveals non-Debye relaxation of charge carriers. Scaling of imaginary modulus (M'') reveals that the charge carriers follow the same relaxation mechanism. Moreover, the charge carriers in PPy nanofibers follow the correlated barrier hopping (CBH) transport mechanism.

1. Introduction

Conducting polymers are class of functional polymers having alternating single and double carbon–carbon bonds along the main chain. A wide range of conducting polymers such as polyacetylene (PA), polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh) etc. are well known for their excellent electronic and optical properties with conductivity ranging from insulator to metallic regimes along with additional properties of retaining lightweight, flexible, biocompatible, good mechanical properties and processing advantages [1]. The pictorial representation of mostly studied conducting polymers is depicted in Fig. 1. PPy has been studied most extensively owing to its excellent potential applications in sensors, actuators, drugs delivery devices, advanced polymeric batteries, electro-chromic windows and displays, corrosion protection etc. [2] due to their easy fabrication processes, good environmental stability, biocompatibility, flexibility, low toxicity, reversible redox property, controllable electrical and optical properties [3–5]. The nanostructures of conducting polymers display the unique properties that further increase the merit of conducting polymers in designing and making of novel devices [6]. Recently, synthesis of one dimensional (1-D) nanostructures of conducting PPy has brought considerable attention due to their application as molecular wires [7]. Various methods such as template method [8], interfacial polymerization [9], seeding polymerization [10] etc. have been developed for synthesis of PPy nanofibers. However, each method has its own advantages and disadvantages. Template guided synthesis method uses structural directing agents and surfactants as templates [11,2] and needs post polymerization step to remove externally applied templates, which limits their application due to lower yield with less reproducibility. Good quality nanofibers can be produced using the electrospinning, but the production scale is very limited [12]. A relatively new method, the interfacial polymerization [13,14] has been widely used for synthesis of conducting polymer nanofibers as one of the most effective alternative chemical route. This interfacial polymerization occurs at the interface of two immiscible aqueous-organic biphasic medium and resulting products diffuse away from the interface to the aqueous solution because of their hydrophilic nature. This approach needs equal volume of organic solvent to the aqueous water. However, the organic solvents immiscible to water are very toxic to the environment and also make the synthesis costly. Therefore it is crucial to find out a novel, reliable, cost effective, less toxic synthesis method for fabrication of conducting polymer nanofibers. Synthesis of π-conjugated polymers with different dopants influences on their

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http://dx.doi.org/10.1016/j.physb.2015.11.023
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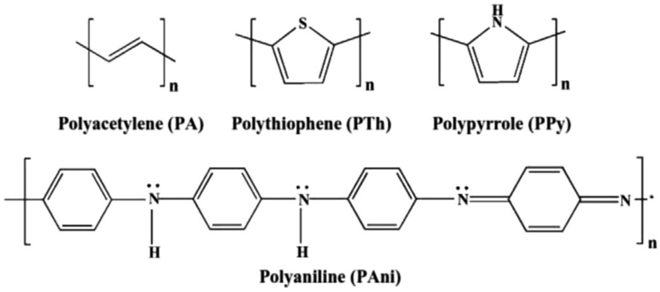

Fig. 1. Pictorial representation of different conducting polymers.

electrical, dielectric, optical and structural properties [15,16]. Doping in conducting polymers generates charge carriers viz. solitons, polarons and bipolarons into the conjugated chains [17]. Furthermore, the properties of doped conducting polymers depend on the type and molecular size of the dopant [18].

In recent studies, the charge transport mechanism in conducting polymers has been investigated using dielectric spectroscopy [19,20]. The frequency dependent conductivity provides information on the relaxation of charge carriers in conducting polymers. The dielectric properties of conducting polymers depend on the choice of dopant, chain structure, doping level [21] and synthesis method [22]. The charge carriers generated upon doping follow the hopping and tunneling transport mechanisms in such disordered systems [23]. Although previous reports are available on polypyrrole doped with different dopants [24], their dielectric and conductivity relaxation mechanism is not fully understood. Moreover, work has been mostly done on bulk polypyrrole.

In the present work, synthesis of PPy nanofibers doped with different alkylbenzenesulfonic acids (ABSA) by interfacial polymerization method have been reported and the effects of their alkyl chain lengths on structural, optical and thermal properties have been discussed. Moreover, the dielectric spectroscopy and ac conductivity have been studied to elucidate their dielectric relaxation and charge transport mechanism.

2. Experimental

2.1. Materials

Pyrrole (Py) was purchased from Sigma Aldrich and was distilled under vacuum before use. Dopants such as *p*-toluenesulfonic acid (*p*-TSA), camphorsulfonic acid (CSA), dodecylbenzenesulfonic acid (DBSA) and octylbenzenesulfonic acid (OBSA) and oxidant, ammonium persulfate (APS) were purchased from Merck and were used as received.

2.2. Interfacial synthesis of PPy nanofibers

The typical synthesis method of PPy nanofibers by interfacial approach was as follows [25]: at the initial stage 0.5 M Py was dissolved in 1 ml xylene and the solution was added drop wise into the aqueous solution of 1 M of each of dopant (*p*-TSA, CSA, DBSA and OBSA) containing 0.5 M of APS oxidant. The mixture was allowed to react under constant stirring for 12 h at room temperature. The molar ratio of Py (monomer) to APS (oxidant) was kept at 1:1 and total volume of the mixture was kept at 100 ml. After complete polymerization, black precipitate was collected and washed off several times with ethanol, methanol, acetone and double distilled water to remove the impurities and then dried under vacuum at room temperature for 72 h.

2.3. Characterizations

High resolution transmission electron microscope (HRTEM) Jeol, JEM-2100 model was used to study the formation and morphology of different ABSA doped PPy nanofibers. Structural characterization was carried out by recording X-ray diffraction (XRD) patterns using a Rigaku Miniflex X-ray diffractometer with CuK$_\alpha$ radiation (wavelength, $\lambda = 1.5406$ Å) in the 2θ range of 5–50° at a scan speed of 5° min^{-1}. Fourier transform infrared (FTIR) spectra of ABSA doped PPy nanofibers were recorded using a Nicolet Impact 410 spectrophotometer in the wavenumber regions of 500–4000 cm^{-1}. UV-vis absorption spectra of ABSA doped PPy nanofibers were recorded by using a Lambda Perkin Elmer spectrophotometer in the wavelength region of 300–800 nm. The UV–vis spectra of the powder samples of different ABSA doped PPy nanofibers were recorded by dispersing them into MilliQ water and keeping the solution in a quartz cuvette of 1 cm path length in the chamber of a UV–vis spectrophotometer [26]. Thermal stability of different ABSA doped PPy nanofibers were measured by using a thermo-gravimetric analyzer (TGA), model STA-6000 in the temperature range of 50–700 °C at a constant heating rate of 30° min^{-1} under nitrogen environment. Measurements of dielectric parameters and ac conductivity were carried out by interesting pressed pellets kept between two silver electrodes in a four probe conductivity set up connected to a computerized programmable Hioki LCR meter in the frequency range of 42 Hz–5 MHz and temperature range of 303–373 K.

3. Results and discussion

3.1. Formation mechanism of PPy nanofibers

The formation mechanism of PPy nanofibers by novel interfacial polymerization method can be understood as analogous to formation mechanism of nanofibers by interfacial polymerization method. The interfacial polymerization takes place at the interface between the organic (monomer and organic solvent mixture) and aqueous (dopant and oxidant solution) biphasic medium. On addition of dopant into the aqueous solution, the dopant anions can self-assemble at the aqueous-organic interface due to their amphiphilic characters. At the interface, the cations of monomer and the dopant anions form a double layer and free monomer cations can diffuse into the hydrophobic part of the dopant to form inclusion supermolecular complex. The supermolecular complex can act as the template in formation of sulfonic acid doped PPy nanofibers. The resulting nanofibers grow up from the organic phase to the aqueous phase because of their hydrophilic nature. In analogous, the same formation mechanism can also be applied to the formation of PPy nanofibers by novel interfacial method. For high molar concentration of dopant and pyrrole (keeping the molar ratio of [Py]/[APS] at 1:1), some elliptical organic phase consisting of pyrrole doped with sulfonic acid can form inside the aqueous water. As APS is added, these elliptical organic cores are surrounded by aqueous phase containing APS oxidant, resulting in PPy-(ABSA) doped nanofibers as precipitates. Just from the time of polymerization begins; the PPy-(ABSA) nanofibers grow from the elliptical organic cores to the aqueous phase.

3.2. High resolution transmission electron microscopy

The HRTEM micrographs of different ABSA doped PPy nanofibers are depicted in Fig. 2. It is observed that uniform PPy nanofibers result with average diameter ranging from 13 nm to 25 nm and length of nanofibers are in micrometer scale. The morphology and diameter of ABSA doped PPy nanofibers are strongly affected by