Electric modulus based relaxation dynamics and ac conductivity scaling of polypyrrole nanotubes

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ABSTRACT

The relaxation mechanism and ac conductivity of camphorsulfonic acid (CSA) doped polypyrrole (PPy) nanotubes synthesized by self-assembly polymerization method at different molar ratio of dopant/ monomer (CSA/pyrrole) have been studied over a wide frequency range of 42 Hz–5 MHz in the temperature range of 303–373 K. The dielectric permittivity (ε') shows saturation at higher frequencies and a strong dispersion at lower frequencies. Higher (ε') at lower frequencies is attributed to the interfacial or electrode polarization effects. The dielectric loss (ε'') decreases almost linearly with increasing frequency due to the presence of dc conductivity. The frequency dependence of imaginary part of modulus (M'') shows a non-Debye conductivity relaxation peak which has been explained using the Kohlrausch–Williams–Watts (KWW) stretched exponential function. The relaxation time (τ) for charge carriers' motion decreases with increasing both temperature and dopant/monomer ratio. The scaling behavior of (M'') spectra suggests that the relaxation dynamics is independent of both the dopant/ monomer ratio and temperature. The frequency dependence of ac conductivity follows a power law, $\sigma_{ac}(\omega) = A\omega^s$ with $0 < s < 1$. The temperature dependence studies of frequency exponent (s) reveal that charge carriers in PPy nanotubes follow the correlated barrier hopping (CBH) model. The scaling behavior of conductivity spectra indicates the temperature independent electrical conduction in PPy nanotubes. The activation energy for the relaxation has been evaluated and is found to be almost same as that of dc conduction.

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1. Introduction

In the last few decades, π-conjugated conducting polymers have been a subject of great interest in research and industry due to their extensive use as materials for the different potential applications such as in compact capacitors, corrosion protection, antistatic coating, electromagnetic shielding, smart windows etc. [1,2]. Polypyrrole (PPy) deserves much attention due to its high electrical conductivity, good environmental and thermal stability, ease of synthesis, biocompatible and excellent optical properties although it suffers certain limitations such as insolubility in common solvents and poor mechanical strength [3]. Different conducting polymer nanostructures such as nanoparticles, nano-fibers, nanotubes, nanorods etc. show their improved physico-chemical properties over their bulk polymers due to their high surface to volume ratio and quantum confinement effects. Attempts have been made to synthesize PPy nanotubes using

different dopants such as from the family of sulfonic acid to improve its processability. In particular, dopants containing long alkyl groups are interesting because their effect is to produce doped PPy.

The understanding of the charge transport mechanism and other electrical properties in conducting polymers are crucial in improving device performance and designing novel devices. Till date, the mechanism of charge transports in conducting polymers is poorly understood because of their highly inhomogeneous structure. The dielectric techniques are useful to probe the charge transport mechanism and charge polarization in disordered materials. The dielectric properties can be studied using the different formalisms, for instance, a comparison of the complex dielectric permittivity (ε^*) and complex dielectric modulus (M^*) representations allow us to distinguish the local dielectric relation. More information can be extracted about the relaxation dynamics of charge carriers by representing the dielectric data in the modulus formalism introduced by Macedo et al. [4]. Thus evaluation of the dielectric modulus as a function of frequency permits the detection of the relaxation processes in the dielectric materials. In case of conducting polymers, the conductivity is

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largely affected by their synthesis conditions such as type of dopant used, dopant to monomer ratio, temperature etc. The doping in conducting polymers generates polarons and/or bipolarons, which contribute to the conduction process between the electronically localized states [5]. The bulk electrical conductivity and dielectric properties in conjugated polymers depend upon several factors such as structure, nature and number of charge carriers, their transport along and between the polymer chains, and across the morphological barriers [6–9].

In this context, the present work is taken to explore the charge transport dynamics in PPy nanotubes synthesized at different molar ratio of CSA/pyrrole using the analysis of frequency dependent ac conductivity obtained from the complex impedance measurements. The complex impedance data have been analyzed by means of complex permittivity and complex modulus formalisms to investigate the relaxation processes.

2. Experimental

2.1. Materials

Pyrrrole (Py) as monomer and ammonium persulfate ($(NH_4)_2S_2O_8$, APS) as oxidant were purchased from Sigma–Aldrich. Camphorsulfonic acid (CSA) as dopant was purchased from Merck. Pyrrole was distilled under reduced pressure before it was used. Other chemicals were used without further purifications.

2.2. Synthesis of PPy nanotubes

The PPy nanotubes were synthesized using the chemical oxidative self-assembly polymerization method in presence of ammonium persulfate ($(NH4)_2S_2O_8$, APS) as oxidant and camphorsulfonic acid (CSA) as dopant. In a typical synthesis method, 0.15 M pyrrole and 0.075 M CSA were mixed in 40 ml double distilled water and stirred for 30 min. The monomer–dopant mixed solution was cooled in an ice bath up to 0–5 °C before oxidative polymerization proceeds. A pre-cooled aqueous solution of APS (0.15 M in 20 ml double distilled water) was added drop-wise to the cooled monomer–dopant mixed solution and then the mixture was allowed to react for 15 h at room temperature. After complete polymerization, the black precipitate was filtered off and washed several times with methanol, acetone followed by double distilled water and finally dried at room temperature for 72 h. Four samples of PPy nanotubes were synthesized at different molar ratio of CSA/Py (such as 0.1:1, 0.5:1, 1:1 and 2:1) under the same molar concentration (0.15 M) of Py monomer.

2.3. Experimental

For the electrical conductivity and dielectric studies, the finely grounded powder samples of PPy nanotubes were pressed into pellets of 1 cm diameter and 2 mm thickness using a hydraulic press. The pressed pellets were mounted between two silver electrodes in a four probe conductivity set up connected to a computerised programmable Hioki LCR meter. The data for ac conductivity and dielectric properties were measured in the frequency range of 42 Hz–5 MHz and in the temperature range of 303–373 K.

3. Results and discussion

3.1. Dielectric studies

The complex dielectric permittivity (ε^*) of disordered materials can be calculated from the measured complex impedance $Z^*(\omega)$ data as follows:

$$\varepsilon^*(\omega) = \frac{1}{j\omega C_0 Z^*(\omega)} = \varepsilon'(\omega) - j\varepsilon''(\omega) \tag{1}$$

where the real part $\varepsilon'(\omega)$ implies the dielectric permittivity that corresponds to the energy storage and the imaginary part $\varepsilon''(\omega)$ implies the dielectric loss that corresponds to the energy loss in each cycle of electric field, $C_0 = \varepsilon_0 A/d$ is the capacitance of free space between the electrodes, ω is the angular frequency, A is the area of the electrode, d is the thickness of the sample and ε_0 is the permittivity in free space ($\varepsilon_0 = 8.854 \times 10^{-12}$ Nm^{-1}). The dielectric permittivity $\varepsilon'(\omega)$ and dielectric loss $\varepsilon''(\omega)$ can be calculated using the following relations [10]:

$$\varepsilon'(\omega) = -\frac{1}{C_0\omega}\left[\frac{Z''(\omega)}{Z'^2(\omega) + Z''^2(\omega)}\right], \tag{2}$$

$$\varepsilon''(\omega) = \frac{1}{C_0\omega}\left[\frac{Z'(\omega)}{Z'^2(\omega) + Z''^2(\omega)}\right] \tag{3}$$

where $Z'(\omega)$ is the real part of complex impedance (Z^*) that represents the current through the contact resistor, and $Z''(\omega)$ is the imaginary part of Z^* that represents the current through the capacitor.

To determine the nature of each of the relaxation, a least square fit of the experimental data to the Havriliak–Nigami (HN) function giving the complex dielectric permittivity for a single relaxation process is used [11],

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha_{HN}}]^{\gamma_{HN}}}, \tag{4}$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric relaxation strength, ε_s and ε_∞ are the dielectric constant at very low and high frequencies, respectively and τ is the average relaxation time, α_{HN} and γ_{HN} are the symmetrical and asymmetrical distribution parameters for the relaxation peak, which can assume values such that $0 \leq \alpha_{HN}\gamma_{HN} \leq 1$. This expression reduces to Cole–Cole (CC) function for $\gamma_{HN} = 1$, Davison–Cole (DC) for $\alpha_{HN} = 1$ and ideal Debye type for $\alpha_{HN} = \gamma_{HN} = 1$. From Eq. (4), the real part of permittivity $\varepsilon'(\omega)$ is given by:

$$\varepsilon'(\omega) = \varepsilon_\infty + \text{Re}\left\{\frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha_{HN}}]^{\gamma_{HN}}}\right\}, \tag{5}$$

The room temperature (303 K) frequency dependence of ε' for PPy nanotubes at different CSA/Py molar ratio is depicted in Fig. 1. As observed from Fig. 1, in lower frequencies, ε' shows stronger frequency dispersion and in higher frequencies, it follows nearly frequency-independent behavior. At lower frequencies, the response of the charge carriers to the externally applied electric field is faster resulting in the higher value of ε', which corresponds to ε_s (static value of dielectric permittivity). At higher frequencies, the applied electric field changes so rapidly that the charge carriers are unable to follow the ac electric field resulting lower value of ε' that corresponds to ε_∞ (value of dielectric permittivity at infinite frequencies). The higher value of ε' at lower frequencies can be attributed to the accumulation of charges at the interfaces within bulk of the sample (interfacial polarization phenomena) and/or at the interface between the sample and the electrodes (electrode or space charge polarization phenomena) [12]. To extract information about the dielectric relaxation, the experimental permittivity data in Fig. 1 have been fitted using Eq. (5) by the non linear curve fitting method. The solid line represents the best fitted curve for the