

Dielectric relaxation and electrical transport studies of polypyrrole nanostructures and swift heavy ion irradiation effects

Abstract

Conducting polymers with extended π -conjugation structure are organic conductors with advantage of flexible chemical functionalization that can replace the traditional metallic conductors. Due to high electrical conductivity, ease of synthesis, excellent optical properties, good environmental stability and biocompatibility, thermal stability, solubility, flexibility, low toxicity, reversible redox property and processibility, conducting polymers cover wide range of potential applications including sensors (gas and biosensors), actuators, drug delivery devices, corrosion protection, polymeric rechargeable batteries, artificial muscles, functional membranes, electro-chromic windows and displays etc. Recently, conducting polymer nanostructures such as nanoparticles, nanofibers, nanotubes, nanorods, nanoneedles etc. have drawn considerable attention owing to their improved physico-chemical properties, which results from their high electrical conductivity and large surface to volume ratio. Conducting polymer nanostructures can be used as promising functional materials for futuristic applications in molecular electronics, molecular wires and devices. Among the family of conducting polymers, polypyrrole (PPy) and its nanostructures have received extensive interest due to their wide potential applications. Polypyrrole nanostructures have been synthesized using different synthesis methods such as the template method, micro-emulsion polymerization, self-assembly method, interfacial polymerization, rapid mixing polymerization, seeding method etc. Depending on the type of nanostructures, one may choose a particular synthesis method. Different nanostructures of polypyrrole viz. nanoparticles, nanofibers and nanotubes have been studied extensively in the present thesis as these nanostructures of π -conjugated PPy are expected to give rise to better physico-chemical properties as compared to their bulk counterparts. The understanding of dielectric relaxation and electrical transport in conducting polymers is crucial from the fundamental and application viewpoint.

Swift heavy ion (SHI) irradiation is a special technique that can induce irreversible changes in the macroscopic properties of the polymeric materials such as

their electrical, morphological, mechanical, optical and thermal properties due to the change in the microscopic events such as the electronic excitation, ionization, chains scission and cross-linking as well as mass loss associated with the ion-polymer interaction. The materials modification by SHI irradiation has potential applications in electronics, medical and energy storage devices etc. The modification of polymer structure and properties induced by SHI irradiation are caused by the energy deposition when the irradiated ions pass through the material. The energetic heavy ions lose their energy mainly through the electronic process and the energy is deposited in a very small cylindrical region around the ion trajectory. The phenomena of cross-linking and chain-scissioning during SHI irradiation in materials depend on the ion source and ion energy used as well as on structure of the target material. The cross-linking results in increasing the molecular weight while the chain scission leads to decreasing molecular weight. Both the effects change the polymer phase, chemical structure, crystallinity and molecular weight.

The present thesis systematically describes a number of experiments in the field of conducting polymer nanostructures, particularly on the polypyrrole nanostructures. Three different nanostructures viz. nanoparticles, nanofibers and nanotubes of conducting PPy have been synthesized using different synthesis methods. The PPy nanoparticles have been synthesized using the micro-emulsion polymerization method at different molar concentration of sodium dodecylsulfate (SDS), which behaves both as dopant cum surfactant. The PPy nanofibers have been synthesized by the interfacial polymerization method using different alkylbenzenesulfonic acids (ABSA) as dopants in presence of ammonium persulfate (APS) as oxidant at a fixed molar ratio of Py (monomer)/APS (oxidant). The PPy nanotubes have been synthesized using the self-assembly polymerization method at different molar ratios of camphorsulfonic acid (CSA) to pyrrole (Py) monomer in presence of ammonium persulfate (APS) as oxidant.

The synthesized nanostructures of PPy have been characterized by High resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Fourier transform infra red spectroscopy (FTIR), Ultra-violet visible (UV-Vis) absorption spectroscopy and Thermogravimetric analysis (TGA). The dielectric relaxation and charge transport mechanism in PPy nanostructures have been investigated using the dielectric spectroscopy and ac conductivity studies. Swift heavy ion irradiation (SHI) on different nanostructures of polypyrrole has been carried out with 160 MeV Nickel ions (Ni^{12+}) at irradiation fluence of 10^{10} , 5×10^{10} , 10^{11} , 5×10^{11}

and 10^{12} ions/cm² with a view to study the SHI irradiation induced effects on different physico-chemical properties of PPy nanostructures.

The thesis contains seven chapters, each of which is again divided into several sections and sub-sections. **Chapter I** reviews the background of the exciting and emerging field of conducting polymers along with their potential applications and different nanostructures. Different types of doping in conducting polymers have been discussed. This chapter also focuses the mechanism of electrical transport in conduction polymers with special emphasis on polypyrrole as a promising conducting polymer. Different synthesis methods for different nanostructures of conducting polymers have been discussed in details. This chapter also emphasises the literature related to swift heavy ion irradiation induced modifications in different conducting polymers. At the end of this chapter, scope of the thesis along with the statement of the thesis problem has been spelt out.

Various theoretical models to account for the charge transport mechanisms and dielectric relaxations in conducting polymers and their nanostructures have been reviewed in **Chapter II**. Theories for explaining stopping power of materials and ion-solid interactions have also been discussed in this chapter.

The materials and methods used for the synthesis and characterization of different nanostructures of polypyrrole have been discussed in **Chapter III**. Working principles of various characterization techniques such as TEM, XRD, FTIR, UV-vis spectroscopy, TGA along with the measurement methods of ac conductivity and dielectric spectroscopy employed in the present work have also been explained.

Chapter IV describes the dielectric relaxation and electrical transport studies of PPy nanoparticles and swift heavy ion irradiation effects. The PPy nanoparticles have been synthesized using the micro-emulsion polymerization method at different molar concentration of sodium dodecylsulfate (SDS), which behaves both as dopant and surfactant. HRTEM microscopy studies depict that average diameter of PPy nanoparticles decreases with increasing SDS concentration. XRD studies reveal increase in crystallinity (ordering) of polymer chains and decrease in d-spacing in PPy nanoparticles with increasing SDS concentration. FTIR studies exhibit enhancement in “effective conjugation length” with increasing the SDS concentration. TGA studies indicate that thermal stability of PPy nanoparticles increases with increasing SDS concentration. Dielectric relaxation and ac conductivity in PPy nanoparticles have been investigated in the frequency range of 42Hz-5MHz. Higher value of dielectric

permittivity (ϵ') at lower frequencies is due to the electrode polarization effect. The shifting of the relaxation peak towards higher frequencies in the imaginary part of modulus (M'') with increasing SDS dopant concentration suggest the smaller relaxation times of the charge carriers motion. Moreover, the charge carriers in PPy nanoparticles follow the correlated barrier hopping (CBH) as the dominated transport mechanism. The same characterizations and measurements have been repeated for the 160 MeV Ni¹²⁺ swift heavy ion irradiated PPy nanoparticles to systematic examine of the irradiation induced enhancements in different physico-chemical properties. HRTEM micrographs of SHI irradiated PPy nanoparticles depict that upon SHI irradiation, there is no change in the spherical shape of PPy nanoparticles, but average diameter of nanoparticles increases with increasing the irradiation fluence. FTIR spectra of irradiated PPy nanopartilces show that the IR active vibrational bands have different cross sections for SHI irradiation and the N-H vibrational band at 3695 cm⁻¹ is most sensitive to SHI irradiation with formation cross section of 5.77×10^{-13} cm² and effective radius of 7.58 nm.

Chapter V explains the dielectric relaxation and electrical transport studies of PPy nanofibers and swift heavy ion irradiation effects on them. The PPy nanofibers have been synthesized by interfacial polymerization method using different alkylbenzenesulfonic acids (ABSA) as dopants in presence of ammonium persulfate (APS) as oxidant. HRTEM microscopy studies of PPy nanofibers confirm that the short alkyl chain ABSA doped PPy nanofibers have smaller average diameter as compared to the long alkyl chain ABSA doped PPy nanofibers. XRD studies reveal that PPy nanofibers doped with short alkyl chain ABSA dopant have higher ordering of the polymer chains. Also, from the FTIR studies it is observed that the “effective conjugation length” in short alkyl chain ABSA doped PPy nanofibers are higher than that in the other ABSA doped PPy nanofibers. The UV-vis absorption spectra studies show smaller optical band gap energy in short alky chain ABSA doped PPy nanofibers. The thermogravimetric studies depict that the thermal stability of different PPy nanofibers increases in order of PPy-(DBSA)<PPy-(OBSA)<PPy-(CSA)<PPy-(*p*-TSA). Dielectric relaxation and ac conductivity studies have been performed for different ABSA doped PPy nanofibers and at different temperatures in the frequency range of 42Hz-5MHz. For the purpose of systematic understanding of 160 MeV Ni¹²⁺ swift heavy ion irradiation induced modifications in PPy nanofibers, all the characterizations and measurements carried out on unirradiated samples have also been performed for the

irradiated samples. Upon SHI irradiation, degradation temperature at a given weight loss increases with increasing ion fluence from 1×10^{10} ions/cm² to 1×10^{12} ions/cm², which is a direct evidence of enhancement of thermal stability in the SHI irradiated PPy nanofibers over the pristine sample. Scaling of M'' spectra at different irradiation fluence suggests that the relaxation dynamics of charge carriers in SHI irradiated PPy nanofibers is independent of irradiation fluence. The scaling of ac conductivity at different irradiation fluence suggests that conductivity relaxation in irradiated PPy nanofibers is independent of the irradiation fluence.

Chapter VI embodies the dielectric relaxation and electrical transport studies of PPy nanotubes and swift heavy ion irradiation effects thereon. The PPy nanotubes have been synthesized using the self-assembly polymerization method at different molar ratios of camphorsulfonic acid (CSA) to pyrrole (Py) monomer in presence of ammonium persulfate (APS) as oxidant. HRTEM microscopy studies show that the average diameter of PPy nanotubes increases with increasing CSA/Py molar ratio. The crystallinity or ordering of PPy nanotubes chains increases with increasing CSA/Py ratio as revealed by the XRD studies. FTIR spectra confirm the enhancement in “effective conjugation length” of PPy nanotubes chains with increasing CSA/Py molar ratio. UV-vis absorption spectroscopy studies confirm that the optical band gap energy of PPy nanotubes decreases with increasing dopant/monomer ratio. Thermogravimetric analysis suggests that the thermal stability of PPy nanotubes increases with increasing CSA/Py ratio. Dielectric relaxation and ac conductivity in PPy nanotubes have been analyzed in the frequency range of 42Hz-5MHz with increasing dopant/monomer molar ratios and temperatures. The total conductivity in PPy nanotubes increases with increasing the CSA/Py ratio. The scaling of ac conductivity spectra suggests that the charge carriers in PPy nanoparticles follow the same conductivity mechanism at different dopant/monomer ratio. Different characterizations and measurements have been repeated to study the 160 MeV Ni¹²⁺ swift heavy ion irradiation induced modifications on various physico-chemical properties of PPy nanotubes with increasing irradiation fluence. Upon SHI irradiation, PPy nanotubes irradiated at the ion fluence of 5×10^{11} ions/cm² become more align and denser as compared to the pristine PPy nanotubes. However, PPy nanotubes irradiated at the highest irradiation fluence of 10^{12} ions/cm², degradation of the PPy nanotubes occurs. Upon SHI irradiation, both the direct and indirect band gap energies of irradiated PPy nanotubes decrease with increasing ion fluence from 1×10^{10} ions/cm² to 5×10^{10} ions/cm², however at the highest

ion fluence of 1×10^{12} ions/cm², both direct and indirect band gap energies decrease to a value smaller than that of pristine PPy nanotubes. Also, the value of indirect band gap energy is found to be lower than its corresponding direct band gap energy. The scaling behavior of M'' spectra at different irradiation fluence suggests that the conductivity relaxation dynamics in the irradiated PPy nanotubes is independent of the irradiation fluence.

Chapter VII summarizes the major conclusions drawn from the work presented in the thesis. The limitations and future scope of research in the field of conducting polymer nanostructures and swift heavy ion irradiation effects thereon also have been mentioned briefly.