

## Synthesis, Characterization, and Conductivity Studies of Polypyrrole/Copper Sulfide Nanocomposites

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**ABSTRACT:** Nanocomposites of polypyrrole (PPy) containing copper sulfide (CuS) were synthesized by an *in situ* chemical oxidative polymerization. The nanocomposites were characterized by FTIR, SEM, XRD, DSC, TGA, and conductivity studies. The FTIR spectra ascertained the chemical interlinking of polypyrrole with metal sulfide nanoparticles. Morphological analysis showed that the nanoparticles were uniformly covering the entire substrate. The XRD pattern reveals that the nanoparticle incorporated polypyrrole showed a crystalline nature and the crystallinity of the polymer increases with increase in concentration of CuS nanoparticles. From DSC, an increase in glass transition temperature shows the increased orderness in the polymer composite than in the pure polypyrrole. Thermal analysis (TGA) of the composite showed a progressive increase in the thermal stability with increase in content of CuS. The frequency dependent electrical properties (a.c. conductivity) of the nanocomposites were higher than that of polypyrrole. The d.c. electrical conductivity increased with increase in amount of nanoparticles in the polymer matrix. The results obtained for these composites have greater scientific and technological interest. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polypyrroles; nanocomposites; conducting polymers; thermal properties; thermogravimetric analysis (TGA)

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### INTRODUCTION

In recent years, synthesis and characterization of electrically conducting polymers have become an important areas of research in polymer science and engineering owing to their excellent electro-active behavior. Among the conducting polymers, polypyrrole (PPy) has been regarded as one of the most promising functional materials; many scientists have extensively investigated its synthesis and applications.<sup>1–3</sup> Because of high electrical conductivity of conducting polymers, they have attracted lots of research interest and become popular basic materials for advanced applications such as batteries, light emitting diodes, EMI shields, electro chromic devices, gas separation membranes, smart windows, and sensors.<sup>4–11</sup> The understanding of electrical properties, morphology, and crystal structure of polypyrrole composites may be useful in improving the stability characteristics of these materials which are the key factors in governing the device performance. The electrical transport in polymeric materials has become an area of increasing interest in research because these materials possess a great potential for solid state devices.<sup>12,13</sup> The most important application of conducting polymer is as an antistatic material. Conductivities for antistatic applications need not to be high and the range  $10^{-6}$ – $10^{-5}$  S/cm is sufficient.

Polymeric systems containing metal particles are attractive systems because they are expected to exhibit properties that are of scientific as well as practical interests.<sup>14</sup> The composites of conducting polymers and inorganic materials have attracted the interest of researchers recently,<sup>15,16</sup> because the composites properties were improved and some new synergistic properties were found that could not be attained from individual materials. It has been found that such composites can exhibit some novel properties. Research in the field of such polymers aims mainly at some suitable modifications of existing polymers so that their applicability can further be improved. Some of these modifications involve preparing hybrid materials in which organic materials and inorganic oxides or salts of different metals, viz. SnO<sub>2</sub>, MnO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, fly ash composites, Fe<sub>3</sub>O<sub>4</sub>, ZrO<sub>2</sub>, etc. combine in some special fashion with the conducting polymers to give rise to the composites.<sup>17–23</sup> In almost all the cases some specific nature of association between the two components has been observed.

The typical polypyrrole, which is infusible, exhibits poor processability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researchers on the synthesis of polypyrrole by both the chemical and electrochemical routes. One way of making these composites involves

synthesizing the conducting polymer inside the matrices of conventional polymers using chemical<sup>24</sup> or electrochemical polymerization.<sup>25</sup> But for application of conducting polymers, knowing how these conducting polymer composites will affect the behavior in an electric field is a long-standing problem and is of great importance. Hence, my aim is to produce hybrid materials where the organic and inorganic components are truly dispersed at a molecular level. Therefore this article is focused on the chemical synthesis of polypyrrole/CuS hybrid as well as their corresponding characterization (FTIR, SEM, XRD, DSC, and TGA) and finally their conductivity studies.

## EXPERIMENTAL

### Materials

Pyrrole (Fluka) was purified by double distillation under reduced pressure. The oxidant, ammonium persulfate (APS), copper acetate monohydrate, thioacetamide, cetyl trimethyl ammonium bromide (CTAB), and methanol were chemicals used for the study. Deionized water was used as solvent in all synthesis.

### Preparation of Nano Copper Sulfide Solution

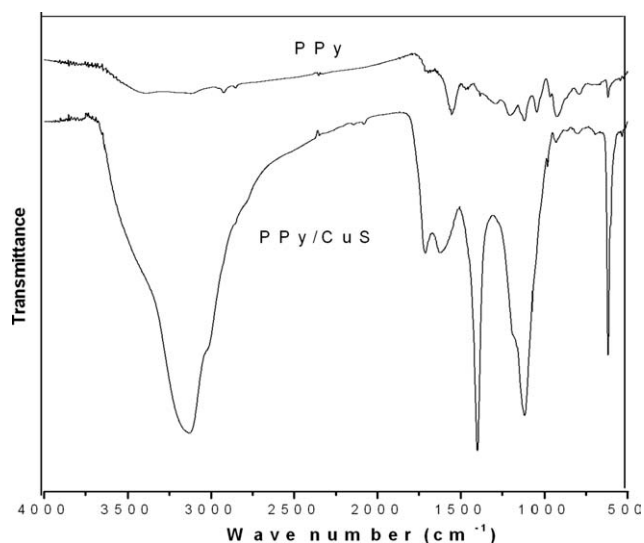
Copper sulfide nanoparticles (50, 100, 200, and 300 mmol) was prepared by a simple and environmentally benign technique involving the reaction of copper acetate with thioacetamide.<sup>26</sup> In a typical procedure, copper acetate monohydrate (appropriate amount) was dissolved in 10 mL deionized water. In another container, thioacetamide (appropriate amount) and 0.2 g of cetyl trimethylammonium bromide (CTAB) were dissolved in 10 mL deionized water. The copper acetate monohydrate solution was added to the thioacetamide solution dropwise at 30°C with continuous stirring over a period of 20 min. The solution turned golden brown as soon as the first drop of copper acetate monohydrate solution was added and the color deepened with more addition. The brown solution turned green over a period of 12 h. Thus CTAB trapped nanocrystals were formed.

### Synthesis of Polypyrrole/Copper Sulfide Nanocomposite

The PPy/CuS nanocomposite was synthesized via *in situ* chemical oxidative polymerization by using ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] in aqueous medium. Copper sulfide nanoparticle solutions (50, 100, 200, and 300 mmol) were dispersed with 0.03M pyrrole in 50 mL distilled water and ultrasonicated over a period of 30 min. Then 0.06M ammonium persulfate was added to the sulfide particle dispersion and stirred the solution at 10°C, it turned to a characteristic black color, indicating that the organic polymerization reaction began immediately. The polymerization was then carried out at room temperature for 8 h with constant mechanical stirring. The precipitated PPy/CuS nanocomposite was filtered and rinsed several times with distilled water and methanol. The fabricated powder was dried at 60°C for 24 h.

### Characterization

The IR spectra of the samples were recorded on a JASCO (model 4100) Fourier transform infrared spectrophotometer in the region 400–4000 cm<sup>-1</sup>. The surface structure of the composite was investigated by using Field Emission Scanning Electron Microscopy (FESCA)—Hitachi, SU 6600 FESEM). The



**Figure 1.** FTIR spectra of polypyrrole and polypyrrole/copper sulfide nano composite.

X-ray diffraction pattern of the sample was recorded on Philips X-ray diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The diffractogram was recorded in terms of  $2\theta$  in the range 20–80°. DSC studies of the nanocomposite were carried out by V2 6D TA instrument model DSC 2010. Initial scan was taken from 50 to 100°C to remove the thermal history effects and then cooled to room temperature. The samples were heated at a rate of 10°C/min (atmosphere N<sub>2</sub>; flow 40 mL/min) in wide temperature range suitable for given sample. Thermal stability of the resulting composites was investigated by a Perkin Elmer thermo gravimetric analyzer with pure nitrogen gas at a heating rate of 20°C min<sup>-1</sup>. The electrical resistivity of the samples was measured using Hewlett–Packard LCR Meter, fully automatic system in a frequency range 10<sup>2</sup>–10<sup>6</sup> Hz at room temperature. DC conductivities at room temperature were measured by using a standard four-probe method with a Keithley 2400 system digital electrometer. The samples for electrical conductivity measurements were prepared by a pressed pellet method.

## RESULTS AND DISCUSSION

### FTIR Characterization

The FTIR spectra of polypyrrole and polypyrrole-CuS nanocomposite are given in Figure 1. The peaks at 1551 and 1468 cm<sup>-1</sup> could be attributed to C–N and C–C asymmetric and symmetric ring-stretching, respectively.<sup>27,28</sup> The NH and CH stretching vibration of polypyrrole appeared at 3429 and 2928 cm<sup>-1</sup> respectively. The IR peak obtained at 1045 and 925 cm<sup>-1</sup> are due to the =CH out of plane vibration indicating the polymerization of pyrrole.<sup>29</sup> However, the spectra of CuS/PPy nanocomposite, contain the characteristic strong peak of CuS at about 611 cm<sup>-1</sup>. The IR absorption below 2000 cm<sup>-1</sup> was strongly influenced by the copper sulfide nanoparticles. The appearance of new frequencies, shifting of absorption frequencies and band broadening in these nanocomposites may be due to the interaction of polypyrrole with the inorganic part of the hybrid. From the results it can be inferred that the polymerization was

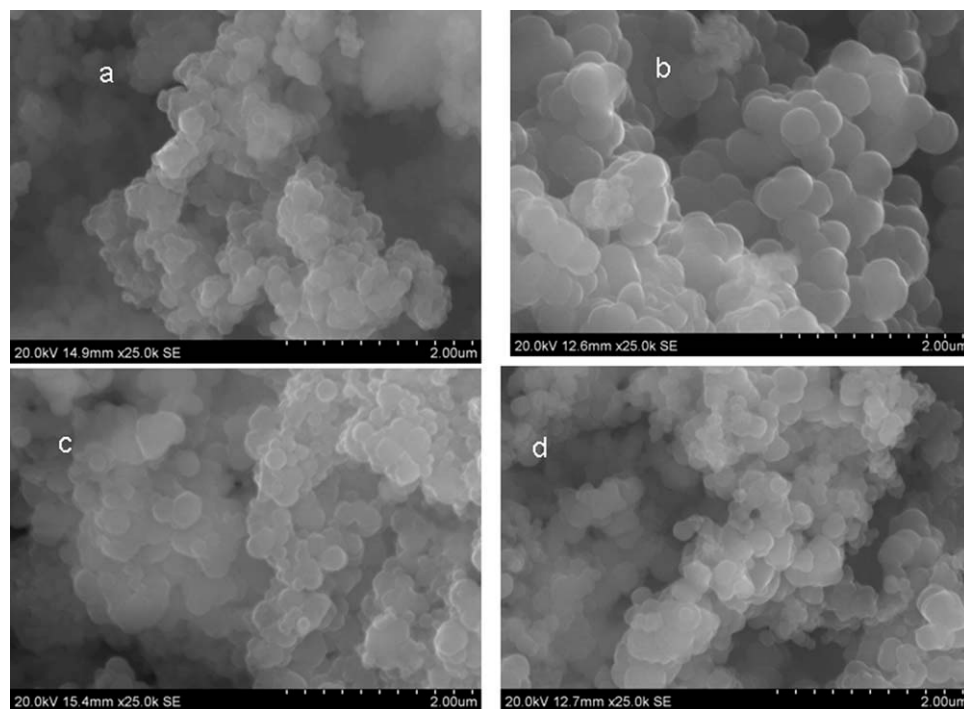


Figure 2. SEM images of (a) PPy, (b) 100 mmol, (c) 200 mmol, and (d) 300 mmol of CuS containing nanocomposite.

successfully carried out and the CuS nanoparticles are incorporated in the polymer matrices.

### Morphology Observations

The morphology of polypyrrole and different molar concentration of copper sulfide nanoparticle incorporated polypyrrole, synthesized by in situ chemical oxidative polymerization has studied by scanning electron microscope (SEM) are shown in Figure 2. The micrograph of polypyrrole [Figure 2(a)] reveals the presence of globular particles. The particles formed are irregular in nature. Figure 2(b) represents the morphology of the PPy/100 mmol CuS nanocomposite, indicates nanostructures with spherical shape with very good uniformity and adhesiveness. This is due to the coordination interaction between vacant orbitals available in the valence shell of Cu atoms in CuS and the lone-pair electrons of nitrogen atoms of PPy molecules. This type of ligand to metal charge transfer transitions are responsible for the formation of the global morphology<sup>30</sup>. It is also evident from the figure that 200 mmol of CuS/PPy composite shows better porous, granular and globular surface morphology. As the concentration of filler increased further, it is necessary to point out that the morphologies of the nanocomposites remarkably changed from the spherical structure into hemispherical structure. Based on the above analysis, it can be concluded that the interaction between the CuS nanoparticles and the polymeric chain prevent sedimentation and agglomeration of CuS nanoparticles in the polymeric system.

### X-Ray Diffraction Analysis

The XRD curves of PPy, CuS, and CuS/PPy are depicted in Figure 3. Crystalline peaks of CuS appeared<sup>26</sup> at  $2\theta = 27.9^\circ, 29.3^\circ, 32.3^\circ, 32.9^\circ, \text{ and } 48.2^\circ$ . A broad peak about  $2\theta = 23^\circ$ , a charac-

teristic peak of amorphous polypyrrole.<sup>31</sup> The XRD curve of CuS/ polypyrrole exhibit some of the characteristic peak of CuS with low intensities. The crystalline nature of the nanocomposite is due to the incorporation of CuS may be explained by the fact that because of *in situ* polymerization of pyrrole within the matrix, the interaction of PPy material and the metal sulfide layers, leads to a closely packed chain. The diffraction peaks are more intense in 300 mmol CuS/PPy composite as compared to those of 100 mmol of CuS containing polypyrrole. The increase in the degree of crystallinity with the addition of CuS nanoparticles

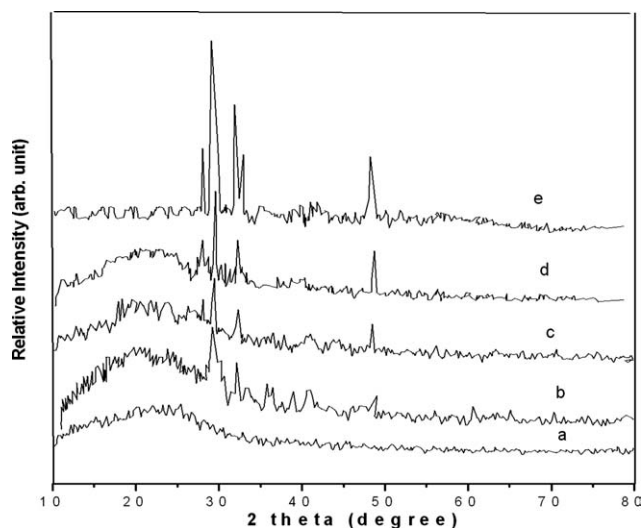
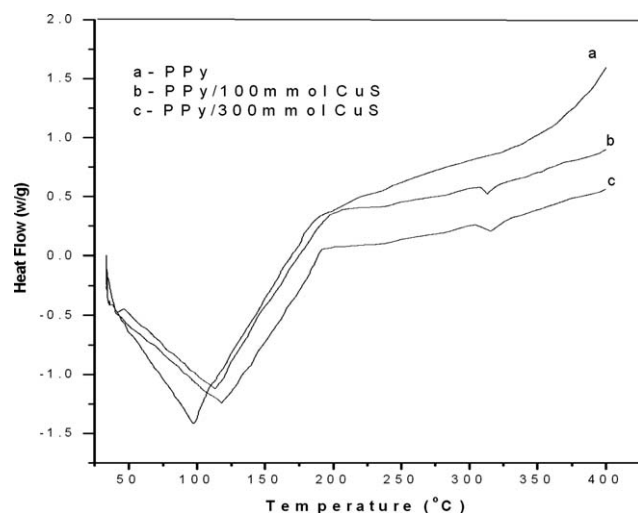


Figure 3. XRD pattern of (a) PPy, (b) 100 mmol, (c) 200 mmol, (d) 300 mmol of CuS containing nanocomposite, and (e) CuS.



**Figure 4.** DSC thermograms of (a) PPy (b) 100 mmol, and (c) 300 mmol of CuS containing nanocomposite.

indicates that the structure of PPy is strongly influenced by the concentration of the nanoparticles. Thus XRD pattern provides an additional evidence of the interaction between polymer and the nanoparticles. The average crystal grain size of these materials can be calculated according to Scherrer's formula:

$$D = K\lambda/\beta \cos \theta$$

where the X-ray wavelength of Cu K $\alpha$  radiation,  $\lambda$ , is 1.54 Å, and  $K$  is the shape factor, which can be assigned a value of 0.89 if the shape is unknown,  $\cos \theta$  is the cosine of the Bragg angle and  $\beta$  is the half height of diffraction angles in radians. When the reflecting peaks at  $2\theta = 28.08^\circ$ ,  $29.36^\circ$ ,  $32.34^\circ$ , and  $48.28^\circ$  were chosen to calculate the average diameter, the average size of the CuS nanoparticle was about 16 nm.

### Differential Scanning Calorimetry

DSC makes it possible to characterize the physical changes of states in a sample, in particular the glass transition. All measurements are carried out on samples of mass between 2.5 and 8 mg. Figure 4 shows the DSC thermogram of PPy and CuS incorporated PPy in the temperature range from 30 to 400°C. The DSC plot of pure PPy, had a broad endothermic dip at 98°C, is the glass transition temperature of the polymer. In case of nanocomposite, there is a corresponding steep dip at higher temperature viz. at 111°C and 117°C, for lower and higher concentrations of CuS in PPy respectively. It also contains an inflection point at 315°C may be due to the melting of PPy chain. There is no observable shoulder in the pure PPy as compared with the composite, indicating less orderness of the polymer molecules in the absence of metal sulfide in the polymer. So they can attain the maximum vibration of molecules at equilibrium at higher temperature (i.e., glass transition temperature in the case of composite) in case of composite. Increase in the glass transition temperature with increase in weight % of CuS is due to the more ordered arrangement of the polymer and the metal sulfide. It can be concluded that thermal parameters such

as glass transition temperature depends on the concentrations of CuS in polypyrrole.

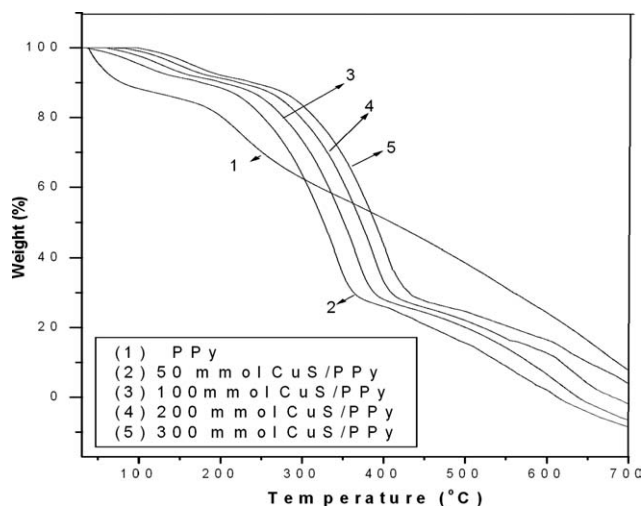
### Thermal Analysis

The TGA thermograms of PPy and PPy with different content of CuS are shown in Figure 5. From the figure it can be observed that, the initial weight loss is just below 100°C for pure PPy, which is due to the volatilization of water molecule and oligomers as well as unreacted monomer elimination. However, the CuS fabricated PPy shows a negligible weight loss throughout the temperature range indicating its higher thermal stability. It can be seen that, polypyrrole start its second decomposition at temperature of 204°C while PPy with low concentration of CuS composite decomposed at a higher temperature at about 226°C. The thermal stability of any polymer and its nanocomposite is an important property for designing the materials for a particular use in a specific field. In such cases the dispersion of nanoparticle in the polymer matrix plays a significant role in changing the thermal behavior. It can be distinctly observed that, there is increase in the thermal stability with increase in CuS nanoparticles in CuS/PPy nanocomposite. The improvement in thermal stability with the % loading of CuS nanoparticles can also be attributed to the increase in the orderedliness of polypyrrole chain around the nanoparticle supported by the analysis of XRD and SEM.

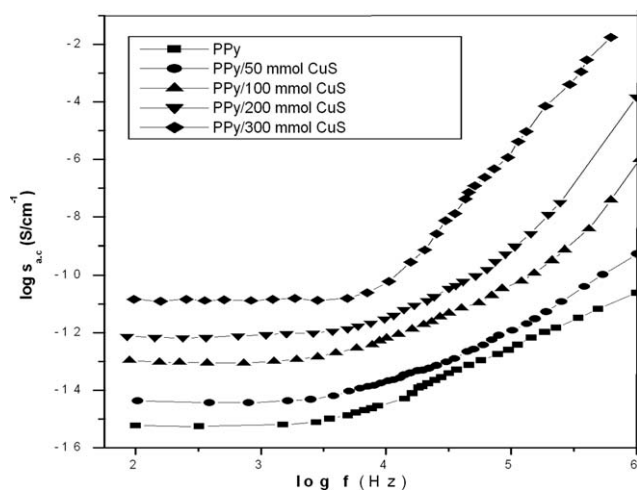
### Conductivity Studies

**A.C. Electrical Conductivity.** Figure 6 depicts the ac electrical conductivity of PPy, and the composite having various concentrations of copper sulfide at different frequencies. It is clear from the figure that ac conductivity of all the composites is significantly higher than the bare polymer. It is found that conductivity increased not only with increase in frequency but also with the increase in concentration of nanoparticles.

Further almost all the composites show similar behavior up to  $10^4$  Hz, viz. that there was not much variation in the conductivity with frequency during this range. The total conductivity of the composite depends on the microscopic and macroscopic



**Figure 5.** TGA curve of (1) PPy, (2) 50 mmol, (3) 100 mmol, (4) 200 mmol, and (5) 300 mmol of CuS containing nanocomposite.



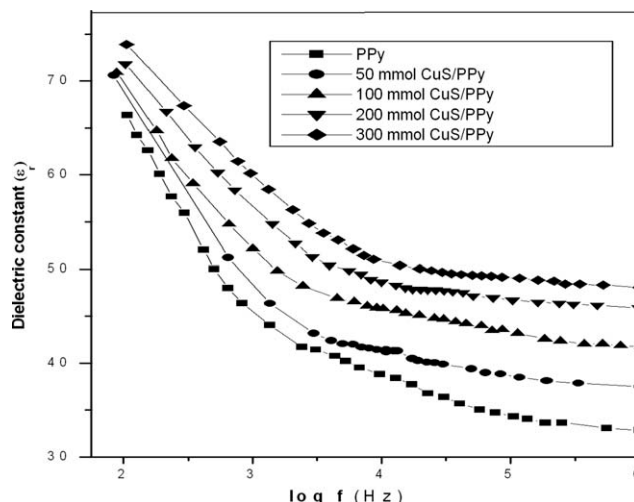
**Figure 6.** Variation of ac conductivity with frequency of PPy and different concentrations of CuS/PPy composites.

conductivities. The microscopic conductivity depends upon the interaction of molecules, conjugation length, or chain length etc., whereas the macroscopic conductivity depends on the homogeneities in the composites, compactness of pellets, orientation of microparticles, etc. The CuS/PPy composite is homogeneous due to the dispersion of CuS nanoparticles in the polymer composites. In this study, composites are synthesized in identical conditions by *in situ* polymerization of pyrrole in the presence of CuS nanoparticles. So the microscopic conductivities remain almost the same but the physical (macroscopic) properties viz. compactness and molecular orientations, may significantly vary due to the variation in the concentration of CuS in the composites. Microcrystalline nature of sulfide particles may give rise to increase in the orderness in the composites, which was confirmed from XRD and DSC. This orderness increases the compactness and molecular orientations leading to an increase in macroscopic conductivity.

The presence of copper sulfide in the composites helps to acquire a granular shape, which leads to an improvement in the compactness of the composite material. As the concentration of CuS in the polymer increased, the change in compactness becomes more significant as a result of increasingly improved links between the grains and coupling through the grain boundaries becomes stronger, which ultimately results in the improvement in the macroscopic conductivity. Therefore, the conductivity of CuS/PPy composites is higher than the pure polypyrrole. Hernandez et al.<sup>32</sup> accounted for the frequency dependent conductivity behavior due to two mechanisms expressed as

$$\sigma(\omega) = \sigma_{ac}(\omega) + \sigma_{dc}$$

This equation represents the total conductivity in the context of the theory of relaxation processes in dielectric materials,<sup>33</sup> which was a classical way of studying ac conductivity in conducting polymers. The total measured conductivity at a given frequency is separated into  $\sigma_{ac}(\omega)$  and  $\sigma_{dc}$  which was simply the limit of  $\sigma_{ac}(\omega)$  when  $\omega \rightarrow 0$ .



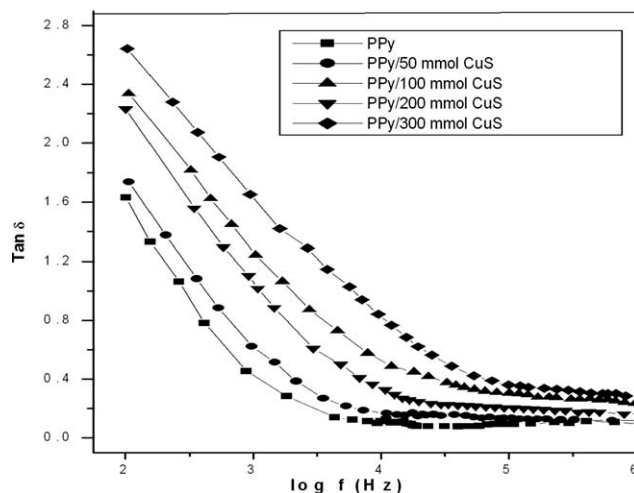
**Figure 7.** Frequency dependence of dielectric constant of PPy and PPy with various concentrations of CuS nanoparticles.

### Dielectric Behavior

Figure 7 shows the variation of dielectric constant  $\epsilon_r$  with frequency at room temperature for PPy and its nanocomposite. The dielectric constant continuously decreases with increasing frequency and reaches a constant value at high frequency. This might be attributed to the tendency of dipoles in macromolecules to orient themselves in the direction of the applied field in the low-frequency range. Meanwhile, in the high-frequency range the dipoles would hardly be able to orient themselves in the direction of the applied field and hence the value of the dielectric constant is nearly constant.<sup>34</sup>

### Dielectric Loss

Dependence of dielectric loss as a function of frequency ranging from  $10^2$ – $10^6$  Hz at room temperature for the pure PPy and its composites is plotted in Figure 8. It can be revealed that the dielectric loss also decreases steeply as frequency increases. It was interesting to note that higher dielectric loss is observed for 300 mmol of CuS nanoparticles, which might be due to increase



**Figure 8.** Dielectric loss versus frequency plot for PPy and PPy/CuS nanocomposite.

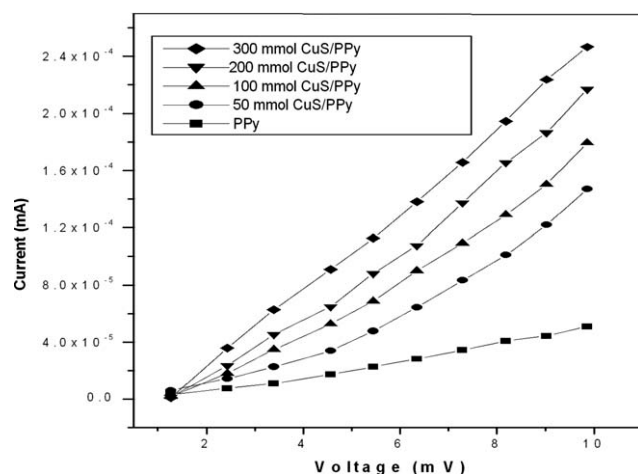


Figure 9. *I-V* Characteristics of polypyrrole and its nanocomposites.

in interaction which leads to higher crystallinity (also good agreement with the XRD data). As a result orderliness increases the interfacial interactions between the polymer chain and CuS lead to maximum space charge polarization. The coordination interaction between vacant orbitals in the valence shell of Cu atoms in CuS and the lone-pair electrons of nitrogen atom of PPy molecules gives local displacement of electrons in the direction of an applied electric field, which induces polarization in polymers.<sup>35</sup> In dielectric nanostructured samples, interface with large volume fraction contain a large number of defects, such as dangling bond, vacancies and vacancy clusters which can cause a change of positive and negative space charge distribution in interfaces. When subjected to an electric field, these space charge move. When they are trapped by defects, lot of dipole moments is formed. At low frequency region these dipole moments are easy to follow the change of the electric field.<sup>36,37</sup> So the dielectric loss and dielectric constant show a large value at low frequency. In an overlapped potential well, at least a few holes executing interwell hopping reverse the direction of motion when the electric field direction reverses. Hence, interwell hopping contributes to dielectric relaxation at low frequencies.

#### Room Temperature D.C. Conductivity Studies

Current-voltage (*I-V*) characteristics of polypyrrole with different concentrations of CuS are recorded at room temperature and are found to be linear as shown in Figure 9. The linear variation shows that incorporation of nanoparticle in the polymer exhibits ohmic conduction. The conductivity of the nanocomposite increased with increase in the molar concentration of CuS nanoparticle. Under the influence of applied external field the localized (short range) motions of the trapped charges in the sample serve as effective electric dipole.<sup>38</sup>

#### CONCLUSIONS

Polypyrrole-copper sulfide nanocomposite have successfully synthesized by an *in situ* chemical oxidative polymerization method. The FTIR spectrum confirms the presence of CuS nanoparticles in the polymer nanocomposites. Structural and morphological analysis showed that the fabricated 100 mmol

CuS/PPy nanocomposites has better porous, granular, and globular surface morphology with very good uniformity and adhesiveness. X-ray diffraction pattern showed that PPy is amorphous polymer do not show any sharp and highly intense peaks whereas the CuS nanoparticle incorporated PPy show sharp and highly intensified peaks indicating the crystallinity in polymer. An increase in glass transition temperature  $T_g$  with the CuS concentration reveals the increased orderliness in the polymer composite than in the pure polypyrrole TGA results indicate that the nanocomposite attain a better thermal stability than original PPy due to the interactions amongst CuS and polymer component. The increase in the ac electrical conductivity of the CuS/PPy composites over pure PPy is due to increased orderliness in the composites. Increase in the values of the dielectric behavior may be due to interface between the CuS and the polymer increases the orderliness and the packing. Dielectric loss arises due to the localized motion of the charge carriers. Highest dielectric behavior is possible for application in conductive paints, rechargeable batteries, sensors, and actuators, etc. D.C. conductivity of CuS/PPy is higher than PPy and the conductivity increase with the increase in concentration of CuS suggested that increase in filler content, increases the effective free volume in the polymer matrix and facilitates the mobility of either ions or molecules in it.

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