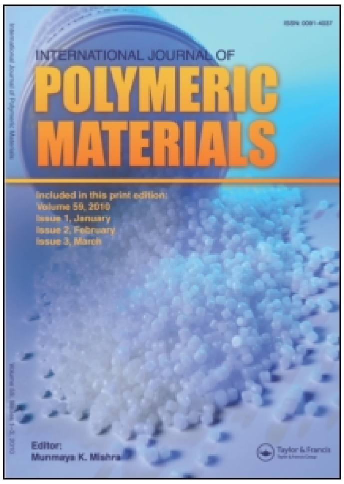

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Analysis Characterization and Some Properties of Polyacrylamide Copper Complexes

H. Dweik[a]; W. Sultan[a]; M. Sowwan[a]; S. Makharza[a]
[a] Faculty of Science and Technology, Department of Chemistry and Chemical Technology, Al-Quds University, East Jerusalem, Palestine

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Analysis Characterization and Some Properties of Polyacrylamide Copper Complexes

H. Dweik
W. Sultan
M. Sowwan
S. Makharza
Faculty of Science and Technology, Department of Chemistry and Chemical Technology, Al-Quds University, East Jerusalem, Palestine

The complexation of polyacrylamide (PAam) with Cu^{+2} metal ions was investigated. The metal complexes were characterized by FTIR, UV-Vis and DSC analysis. The Fourier transform infrared spectroscopy was used to study the characteristic shifts in the maximum absorbance bands of N-H amide C=O and $N\text{-}H_2$ absorption bands. UV-Vis spectroscopy was also used to follow the complex formation of PAam-Cu^{+2}. UV-Vis spectroscopy shows the appearance of a new band that was absent both in the polymer and its salt solutions.

Thermal analysis of PAam-Cu^{+2} complexes was studied using DSC. The shifts in Tg values could be attributed to the improvement in the rigidity of PAam in the presence of Cu^{+2} associated with the polymer chain. Pure polyacrylamide polymer is electrically insular. The electrical conductivity improved by several orders of magnitude after the complexation process.

AFM was used to image the surface features of PAam and PAam-Cu^{+2}complex films. The association of polyacrylamide with Cu^{+2} metal ions at 2.5% (w/w) concentration, showed the formation of large grains with roughness 0.5 μm. *Increasing the concentration of PAam-Cu^{+2} complex up to 25% (w/w), showed different and surprising results: instead of film with large grains, rods 1* μm *in diameter were formed.*

Keywords: copper complex, conductivity, morphology, polyacrylamide

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Address correspondence to H. Dweik, Faculty of Science and Technology, Department of Chemistry and Chemical Technology, Al-Quds University, East Jerusalem, Palestine. E-mail: hdweik@planet.edu

INTRODUCTION

Polyacrylamide (PAam) is a water-soluble polymer [1]. PAam has a hydrophobic main chain and a hydrophilic side group. It may be considered as polyethylene main chain with $-CONH_2$ side groups [2]. The amide group of polyacrylamide and carbonyl group can undergo reactions such as hydrolysis and dehydration [3]. Polyacrylamide undergoes hydrolysis under acidic conditions to produce poly (acrylamide-coacrylic acid). Forcing conditions of low pH and long reaction times can provide complete hydrolysis of all the amide groups [4]. Polyacrylamides (PAam) are among the most widely used synthetic polymers, often used in different fields such as water treatment, papermaking, petroleum recovery, mineral processing and soil conditioning [5]. PAam interacts with many metal cations in hydrous solutions. Gels and polymer salts can be obtained by desiccation of these solutions [4].

The thermal parameters of a polymer, such as glass transition temperature (Tg) melting point (Tm) and crystallization point (Tc) can be determined using a differential scanning calorimeter (DSC) [61. The glass transition temperature is the most important characteristic of the amorphous state in the polymer during its transition from solid to liquid [7].

The glass transition temperature of polymer thin films has important consequences because of the importance of thermal properties in the technological applications of thin films [8]. The association of metal ions in polymer matrices generates charge carrier ions and increases the rigidity of the polymer chain up to moderately high metal salt concentration, resulting in a higher Tg [9].

Metal complexation is a process by which certain transition metal ions coordinate with organic functional groups like carbonyl, amine groups through ionic bonds, coordination bonds, and ion dipole interactions to form what we call complexes, having many interesting properties and applications. Metal complexation polymers are used in wastewater treatment for selective removal of toxic metal ions [10–13] and to improve the thermal properties of polymers [14–16]. An important application of polymer-metal complexes is in the area of catalysis. Catalytically active organic polymers can be obtained through the coordination of certain transition metal ions with functional group on polymer [17].

Yet, the winners of the 2000 Nobel Prize in Chemistry, Alan Heeger, Alan G. MacDiarmid and Hideki Shirakawa, were rewarded for their revolutionary discovery that plastic can be made electrically conductivey after certain modifications [18].

The formation of metal-polymer complexes opens a unique opportunity for creating a new material with advanced properties [19]. As a result of the considerable interest in this field, the present work was devoted to study the complexation of PAam with Cu^{+2} metal ions.

EXPERIMENTAL

Chemicals

Polyacrylamide (Aldrich.PAam, Mwt 5000,000), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), Hydrochloric acid 32% by weight, and sodium hydroxide of analytical grade and were purchased from Sigma-Aldrich Co. and used as received. All solutions were prepared in deionized water.

Instruments

1. Fourier transform infrared spectrophotometer (Testscan shimadzu FT-IR 8000 series).
2. A Perkin-Elmer lambda 5 UV-visible spectrophotometer.
3. Differential Scanning Calorimeter, DSC 2920 modulated DSC (TA instruments).
4. Two point probe system.
5. Atomic Force Microscope (AFM).

Procedure

Preparation of Polyacrylamide Film

To prepare PAam film, 0.7104 g of PAam was dissolved in 25 ml deionized water. The solution was then poured into a petri dish placed in an oven at 35°C for 24 h. Transparent film was obtained after evaporation of water.

Preparation of Polyacrylamide–Cu^{+2} Film Complexes

To prepare PAam-Metal complexes, 0.7104 g of PAam was dissolved in 25 ml of deionized water. By gradual addition of metal salt solution on obtains the adequate concentrations of polyacrylamide $-Cu^{+2}$ metal complexes. Then the solutions were poured in petridishes and placed in an oven at 35°C for 24 h. Transparent films were obtained. Different concentrations of PAam-Cu^{+2} complexes were used to form 2.5, 5, 7.5, 10, and 25% (w/w) concentrations.

Preparation of PAam-Cu^{+2} Complexes for FTIR

About 5 µL Polyacrylamide-Cu^{+2} complex solution was spread onto silicon window. Then the window was placed in the oven at 35°C for 24 h. Water was completely evaporated to constant weight. Film of a few µm thicknesses was obtained.

Preparation of PAam-Cu^{+2} Complexes for Conductivity Measurements

To prepare the film of PAam-Cu^{+2}, 5 µL of the complex was deposited on a mica surface and inserted in an oven for 24 h at 35°C to evaporate the water.

Preparation of PAam-Metal Complexes at Different pHs

To prepare film of PAam at different pHs, 0.7104 g of PAam was dissolved in 25 ml of deionized water. Then the pH was adjusted by the gradual addition of standard 0.1 M NaOH and 0.1 M HC1 using Jenway pH meter (3310) in the presence of a buffer. Solutions of various pH (1.7–10.0) were prepared.

RESULTS AND DISCUSSIONS

Analysis and Characterization of PAam and Complexes using FTIR Spectroscopy

The characteristic peaks of polyacrylamide are: υ_{sym} N-H symmetrical stretching mode is situated at 3201.6 cm^{-1}, and υ_{asym} N-H antisymmetric stretching mode at 3348.2 cm^{-1}. The NH_2 groups are involved in intra-inter-chain hydrogen bonds of the N-H…O=C type [20].

The peaks at 1662.5 and 1620.1 cm^{-1} are the two strong peaks which are the characteristic bands of the C=O stretching (ν), and N-H bending (δ) respectively (Figure 1).

Polyacrylamide–Cu^{+2} Complexes

The carbonyl group(C=O) stretching band of pure PAam is shifted by 3.9 cm^{-1} in the presence of Cu^{+2} ions. While the amine group (NH_2) is shifted by 3.9 cm^{-1} at 5, 7.5, and 10% concentration, This peak shift indicates that the complexation occurs from both the carbonyl and amine group. However, at 2.5 and 25% concentration, the amine group shows no change, which indicates that the coordination is to carboxyl groups as a monodentate one (Table 1). Figures 2–6 give the FTIR spectrum of the PAam-Cu^{+2} complexes. It should be noticed that

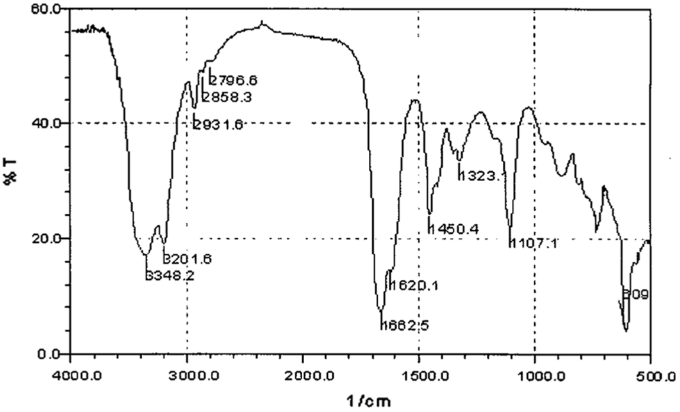

FIGURE 1 FTIR spectrum of pure PAam.

Cu^{+2} ions form a complex with PAam from C=O side at 2.5, 25% concentration and from both C=O and NH_2 at 5 and 10%.

Complexation of PAam–Metal in Acidic and Basic Conditions

The hydrolysis of polyacrylamide in acidic and basic conditions occurs randomly, and complete hydrolysis occurs under specific conditions, especially at high temperature and normal pH [4]. In Figures 7 and 8 FTIR show the hydrolysis of PAam under acidic (pH 1.7) and basic (pH 10) conditions, respectively, to produce randomly polyacrylamide-co-acrylic acid. The amine group in the polymer chain was reduced to hydroxyl group during hydrolysis, this behavior occurs because the absorbances of amine and carbonyl groups still show no significant change. We expected that the complete hydrolysis of polyacrylamide to acrylic acid occurs under specific pH and temperature conditions.

TABLE 1 Characteristic Peaks of PAam–Cu^{+2} Complexes

Complexes	υ_{as} NH_2	υ_{s} NH_2	υ_{s} CH_2	υ_{as} CH_2	υ CH	υ (C=O)	N-H bending
Polyacrylamide	3348.2	3201.6	2931.6	2858.3	2796.6	1662.5	1620.1
P–Cu (2.5%)	3348.2	3201.6	2935.5	2862.2	2792.7	1666.4	1616.2
P–Cu (5%)	3352.1	3201.1	2939.3	2866.0	2796.6	1666.4	1616.2
P–Cu (7.5%)	3352.1	3197.8	2939.3	2804.3	–	1666.4	1616.2
P–Cu (10%)	3352.1	3201.6	2947.0	–	–	1666.4	1616.2
P–Cu (25%)	3348.2	3201.6	2950.9	–	–	1666.4	1612.4

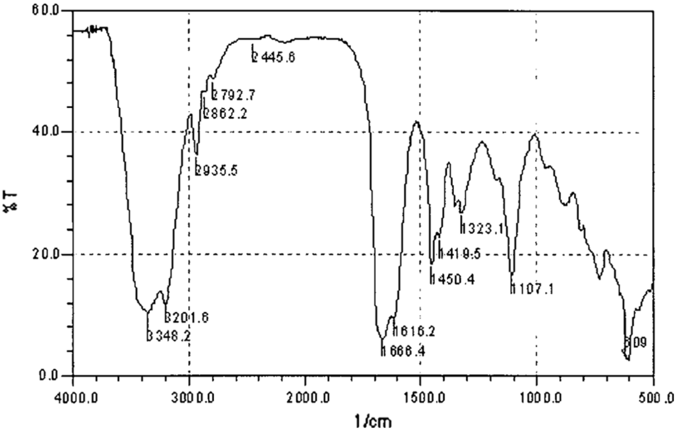

FIGURE 2 FTIR spectrum of PAam-Cu^{+2} at 2.5% concentration.

Analysis and Characterization of PAam and Complexes using DSC

DSC 2920 modulated DSC (TA instruments) was used for our study. Sealed aluminum cells were used with a sample mass of 10 mg and an empty aluminum cell was used as a reference. The experiments were carried out in a dry nitrogen atmosphere, with a 40 ml/min flux. After an initial temperature jump to −15°C, we used a special heating and cooling program at a heating rate of 10°C/ min as given in Table 2.

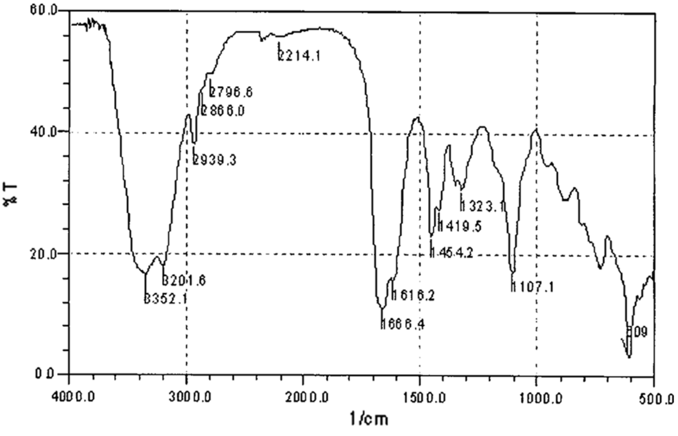

FIGURE 3 FTIR spectrum of PAam-Cu^{+2} at 5% concentration.

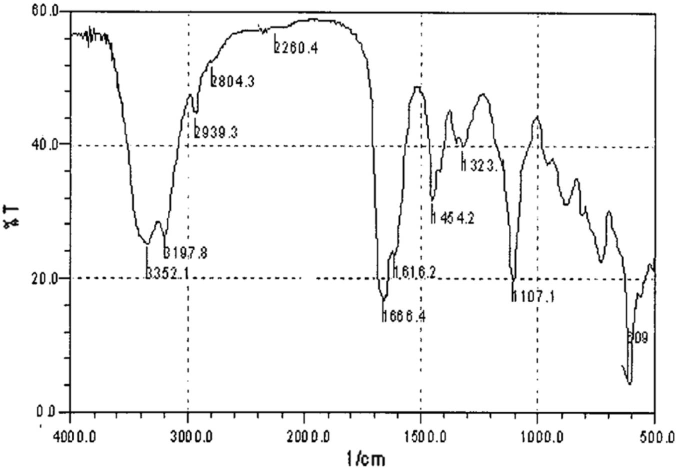

FIGURE 4 FTIR spectrum of PAam-Cu^{+2} at 7.5% concentration.

The study was devoted to measure the variation of the glass transition temperature of the polymer and polymer-metal complexes thin films.

Analysis of PAam

The thermogram of pure PAam is shown in Figure 9, the glass transition temperature and melting point of PAam and 161.4°C, 237°C respectively.

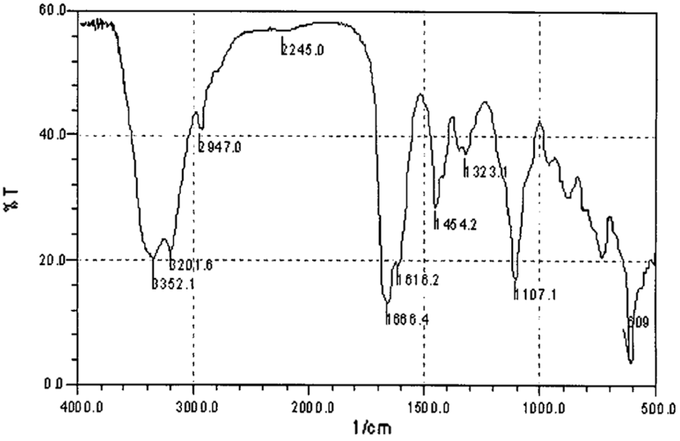

FIGURE 5 FTIR spectrum of PAam-Cu^{+2} at 10% concentration.

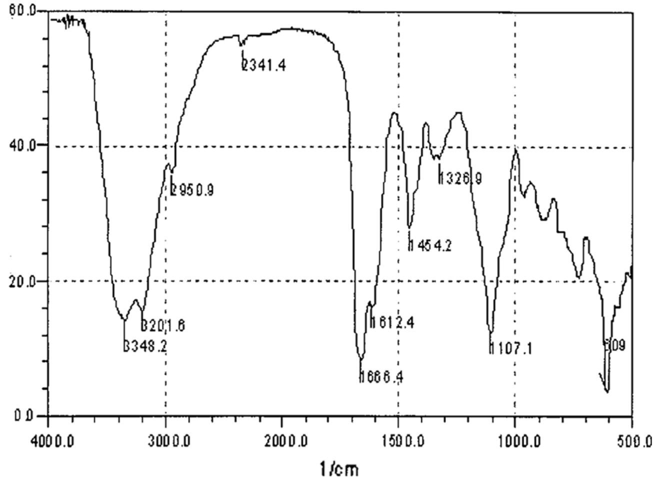

FIGURE 6 FTIR spectrum of PAam-Cu^{+2} at 25% concentration.

Analysis of PAam-Cu^{+2} 5% Concentration

The thermal behavior of the complex PAam-Cu^{+2} at (5%) is shown in Figure 10. The glass transition temperature and melting temperature of this complex appear at 168.8°C and 248.5°C respectively. These two transitions are shifted from the transitions of polyacrylamide which are caused by a decrease in flexibility of the chain segments caused by complexation.

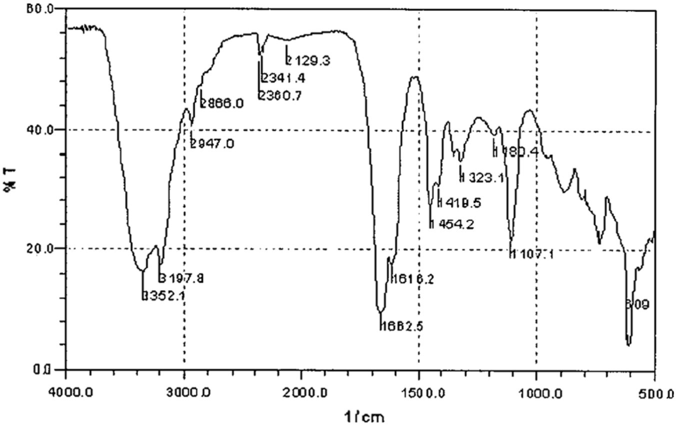

FIGURE 7 FTIR spectrum of PAam in acidic condition (pH = 1.7).

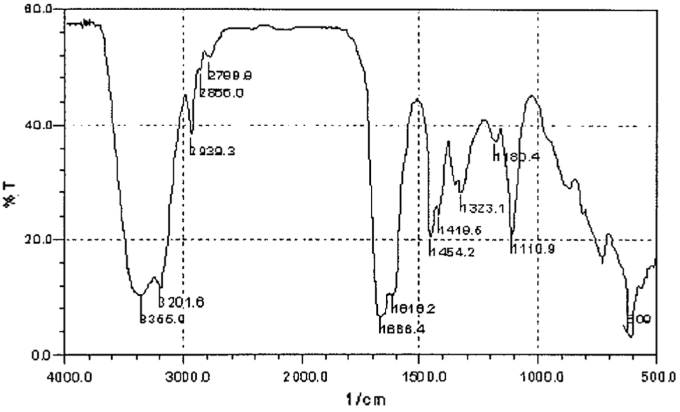

FIGURE 8 FTIR spectrum of PAam in basic condition (pH = 10.0).

Analysis of Polyacrylamide and Complexes using UV-visible Spectroscopy

The UV-visible spectroscopy study of all films was obtained at 70−80 μm film thickness. The wavelength was measured in the range of 200–800 mm. In order to investigate the PAam-Cu^{+2} complexation by UV-visible spectroscopy, UV-vis spectra of PAam and free ions was obtained for comparison.

The spectrum of free Cu^{+2} ions solution is presented in Figures 11. The main band appears at 197 mm. The characteristic band of PAam-Cu^{+2} (10%) is at 276 mm due to the complexation (Figure 12), This band is an important band which is not observed in either PAam (Figure 13), and Cu^{+2} ions solution spectra.

Electrical Conductivity of PAam and PAam-Cu^{+2} Complexe

The current-voltage (I-V) characteristic curves of PAam and PAam-Cu^{+2} were measured using a two-point probe system; the

TABLE 2 Special Program for Evaluating Tc

Ramp	20°C
Thermal equil.	1 mints
Jump	−40°C
Ramp	20°C to 250°C (1st heating)
Ramp	20°C to −40°C (cooling)
Ramp	To 250°C (2nd heating)

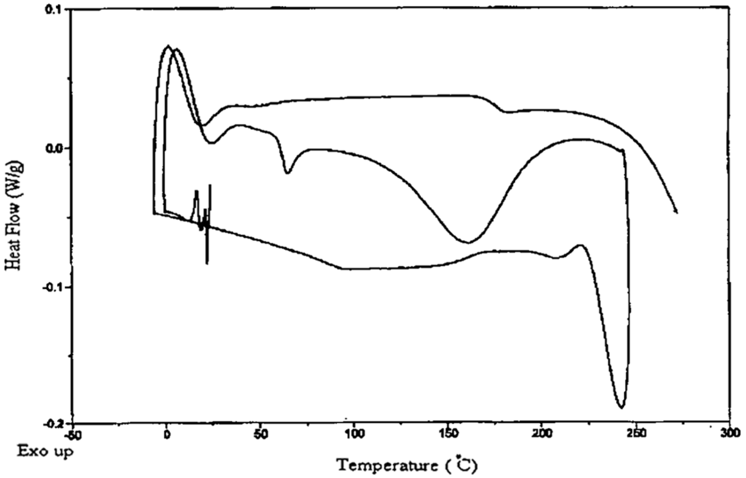

FIGURE 9 DSC thermogram of pure PAam.

probes were moved across the sample, applying a voltage across the surface, measuring the resultant current.

The (I-V) curve of polyacrylamide is shown in Figure 14, three dimensional films where formed. The surface conductivity was calculated depending on the relation:

$$\sigma = \mathrm{I}/2\pi \mathrm{sV}\ \mathrm{mhos\,cm}^{-1}$$

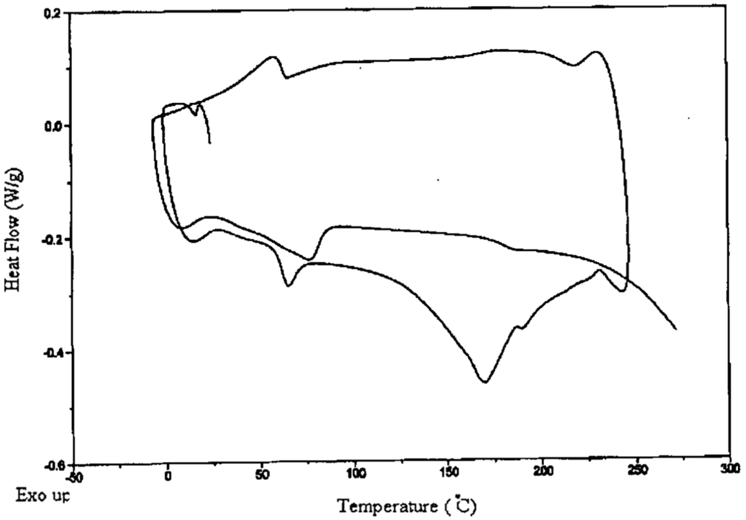

FIGURE 10 DSC thermogram of PAam-Cu^{+2} at 5% concentration.

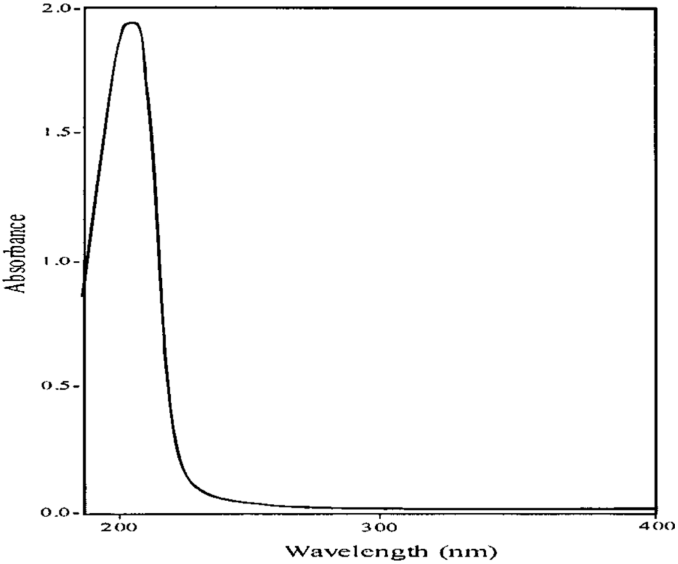

FIGURE 11 UV-spectrum of Cu^{+2}.

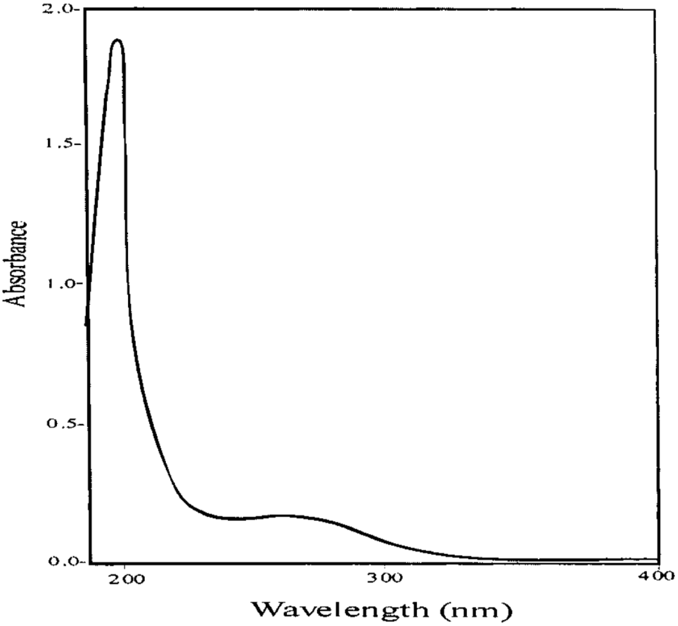

FIGURE 12 UV-spectrum of PAam-Cu^{+2} at 10% concentration.

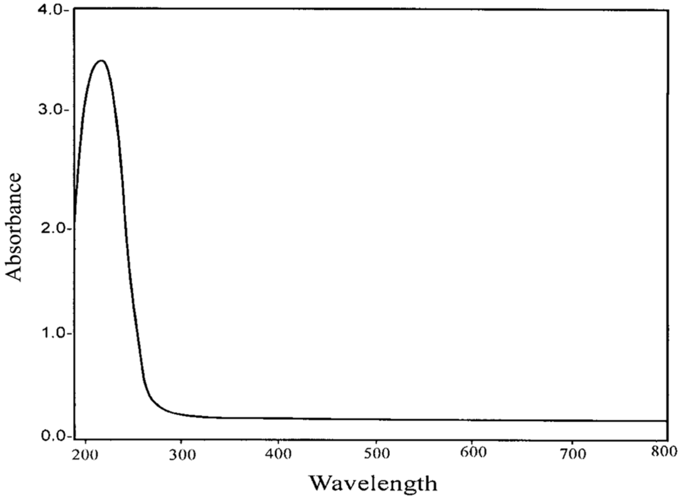

FIGURE 13 UV-spectrum of pure PAam.

where I is the resultant current; s is the distance between the electrodes (0.2 cm); σ is the surface conductivity; V is the voltage.

Surface conductivity (σ) = slope (I-V) curve/2πs = $5.278 \times 10^{-11}/2\pi$ 0.2 cm = 0.042 nS cm^{-1}. According to the calculation, polyacrylamide is classified as an insulator.

The current-voltage of PAam-Cu^{+2} 2.5% is shown in Figure 15. The surface conductivity of PAam was improved using Cu^{+2} at 2.5% concentration. For this case, the surface conductivity of PAam-Cu^{+2}

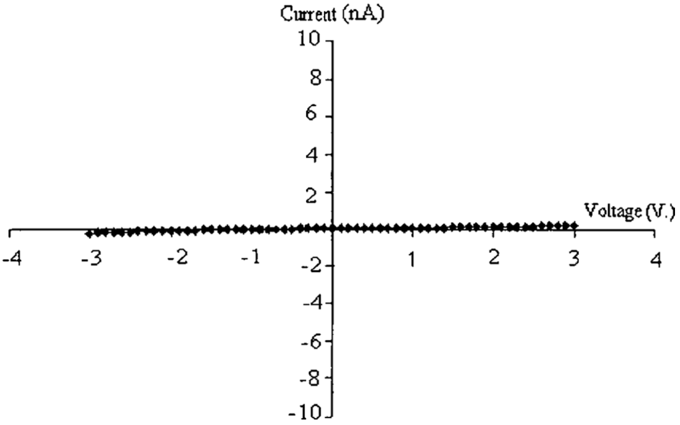

FIGURE 14 I vs. V of PAam.

(2.5%) was calculated according to relation $\sigma = I/2\pi sV$, and was increased significantly to 10.76 nS cm^{-1}.

The electrical resistivity of PAam-Cu^{+2} up to 25% concentration was calculated using the relation $R = \rho L/A$, since rods were formed. R is the resistance; ρ is the resistivity and L, A are the length (15 μm) and the cross-sectional area (r = 0.5 μm) of the rod formed, respectively. The current-voltage curve (Figure 16) show that the resistance (R) equals 0.73* $10^8\Omega$ and so by calculation, the resistivity (ρ) equals 0.6 Ω cm, and the electrical conductivity of PAam-Cu^{+2} complex (25%) equals to $1/\rho = 1/0.6 = 1.66$ S cm^{-1}. According to the calculation, the PAam-Cu^{+2} (25%) complex is classified as a semiconductor with a voltage gap of 0.5 JV.

Morphological Characterization of PAam and PAam-Cu^{+2} Complexes Using Atomic Force Microscopy

Atomic force microscopy (AFM) is an important technique due to its ability to image and characterize polymers. The images of AFM depend on the size, shape, and terminal functionality of the probe tips used for imaging [21]. AFM probes consist of microfabricated silicon nitride cantilevers with integrated pyramidal tips [22].

Major objectives of this study have been (i) to determine how metal ions (Cu^{+2}) affect the surface reactivity of PAam, and (ii) to characterize the morphology of the PAam surface. The main components of this effort are surface structure, surface chemistry, and surface electronic properties.

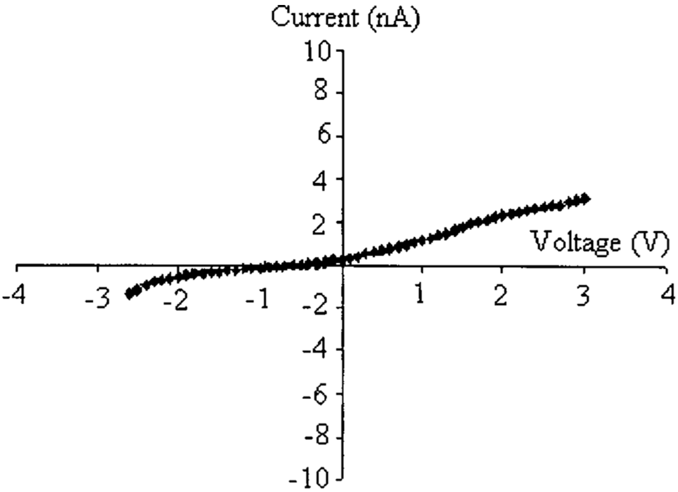

FIGURE 15 I vs. V of PAam-Cu^{+2} at 2.5% concentration.

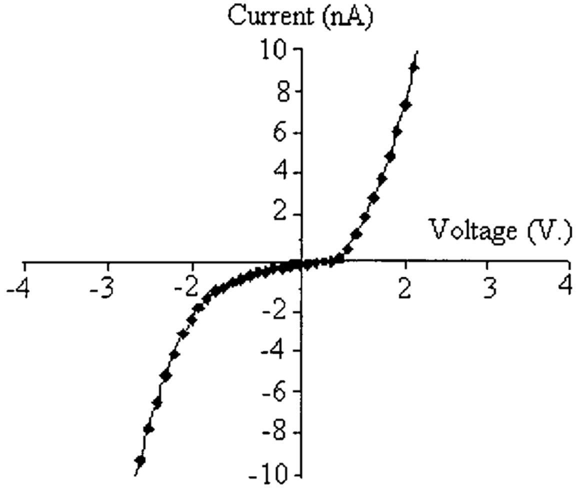

FIGURE 16 I vs. V of PAam-Cu^{+2} at 25% concentration.

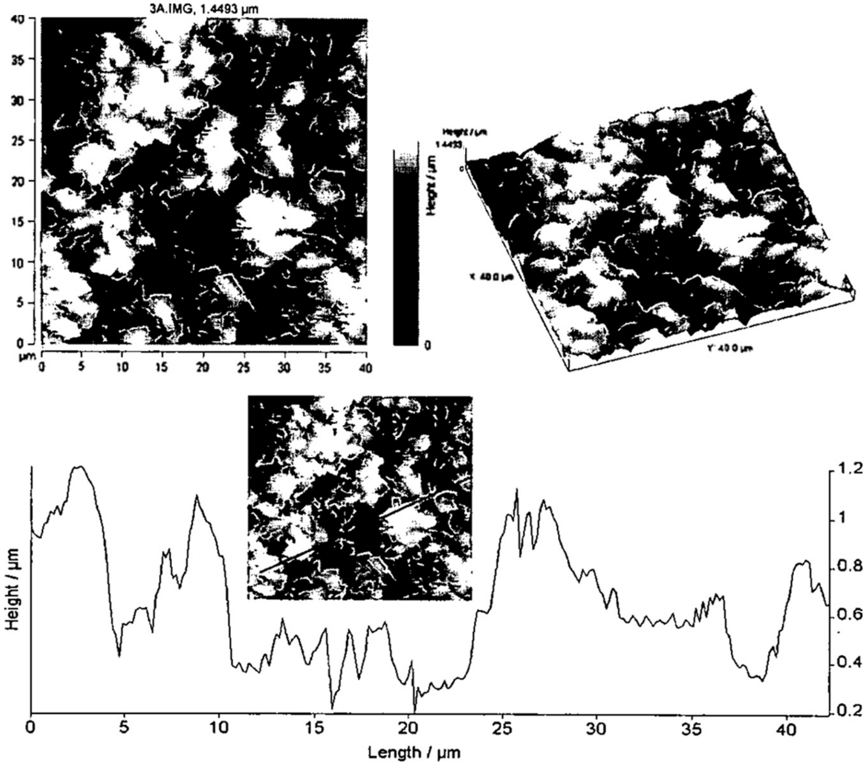

FIGURE 17 AFM image of PAam.

AFM was used to characterize the surface of the prepared samples. The AFM image of polyacrylamide is shown in Figure 17, from the cross section, we can see that the roughness is about 0.5 µm. The image of PAam-Cu^{+2} (2.5%) is shown in Figure 18, the roughness is 0 5 µm. Different and surprising results, instead of three dimensional Glorsules, one dimensional rods were formed when 25% PAam-Cu^{+2} complex was prepared as shown in Figure 19. The rods were about 1 µm in diameter and about 15 µm long.

CONCLUSION

We have investigated the complexation of the hydrophilic side-groups in PAam with metal ions using FTIR, UV-visible spectroscopy and DSC techniques. The PAam-Cu^{+2} complexes have specific transmittance that is completely different from the pure polymer, this behavior related to the metal ions association with the polymer chain. The UV-visible spectroscopy and DSC analysis characterized the association of Cu^{+2} at the backbone of PAam by showing different transitions at different concentration ratios.

Glass transition temperature Tg of PAam-Cu^{+2} and melting point Tm were determined using DSC. Tg of PAam appears at 161.4°C,

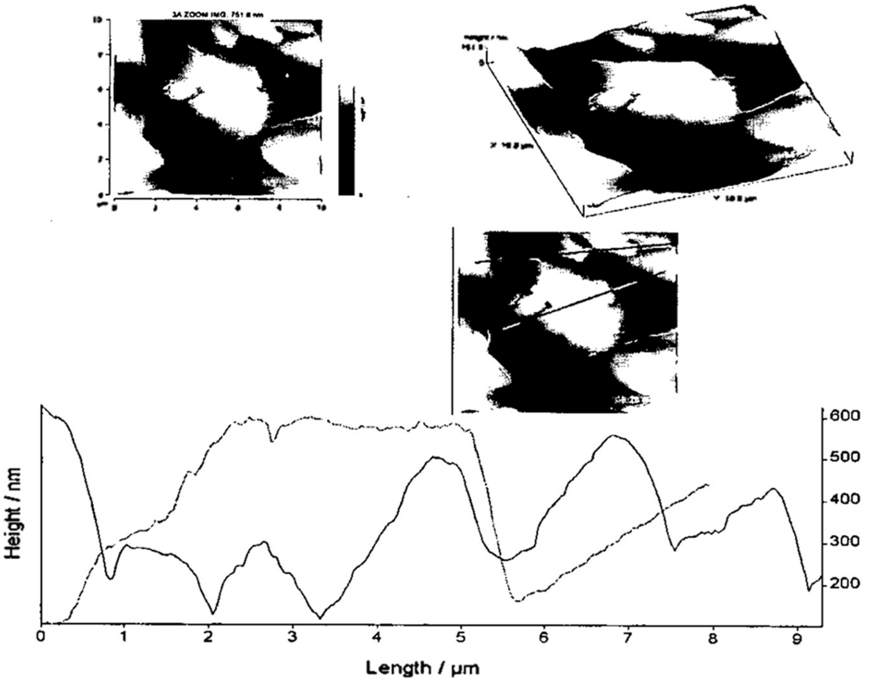

FIGURE 18 AFM image of PAam-Cu^{+2} (2.5%).

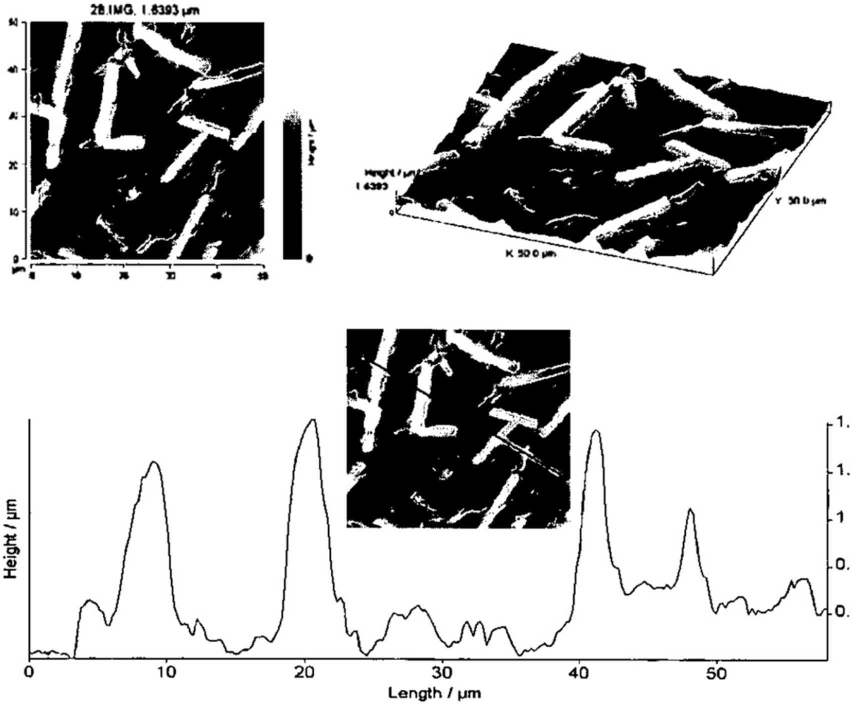

FIGURE 19 AFM image of PAam-Cu^{+2} (25%).

while the Tg of PAam-Cu^{+2} was observed at 168.8°C. This result indicates that the polymer became more rigid after complexation. The melting temperature (Tm) of PAam appear at 237°C. The melting temperature (Tm) of the complex was observed at 248.5°C.

The electrical conductivity of PAam improved in the presence of Cu^{+}. AFM images confirmed the formation of rods at high concentrations of the metal ions.

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