ABSTRACT

Poly(2-hydroxy carbonyl meth(acrylamide)s) azo ligand, were prepared by reacting 4-(meth)acrylamidebenzenediazonium chloride with 2-hydroxy carbonyl compounds.

The DMF solution of the polymers containing a few drops of ammonium hydroxide on treatment with aqueous solution of Cu(II)/Ni(II) ions gave the corresponding metal complexes: poly(2-hydroxy-4-azo benzaldehyde phenyl acrylamide) poly(2H4ABPA)-Cu(II)/Ni(II), poly(2-hydroxy-4-azo benzaldehyde phenyl methacrylamide) poly(2H4ABPM)-Cu(II)/Ni(II), poly(2-hydroxy-4-azo acetophenone phenyl acrylamide), poly(2H4AAPA)-Cu(II)/Ni(II), poly(2-hydroxy-4-azo acetophenone phenyl methacrylamide) poly(2H4AAPM)-Cu(II)/Ni(II), poly(2-hydroxy-4-azo benzophenone phenyl acrylamide) poly(2H4ABPA)-Cu(II)/Ni(II), poly(2-hydroxy-4-azo benzophenone phenyl methacrylamide) poly(2H4ABPM)-Cu(II)/Ni(II). Characterization of the polymers and polymer-metal complexes were carried out.

The polymers were soluble in THF, DMF, DMAc, DMSO, acetone and methanol whereas insoluble in common organic solvents like benzene, toluene, chloroform and carbon tetrachloride. GPC data reveals that the molecular weight (MW) of the polymers is moderately high of the order of 3.01x10^4 - 3.81x10^4. Elemental analysis values and 1H-NMR signals are in good agreement with expected structure of the polymers.
The polymers exhibit strong bands around 1650-1600 cm\(^{-1}\) due to -N=N group of azo. The strong band at 1600-1550 cm\(^{-1}\) may be ascribed to ketonic groups (C=O). The medium intensity band at 1200 cm\(^{-1}\) in the spectrum of the polymer is due to hydrogen bonded ring system of the ligand. The broad absorption in the region around 3400-3000 cm\(^{-1}\) is due to intramolecular hydrogen bonded -OH stretching. The presence of weak band at 3050 cm\(^{-1}\) indicates the presence of –NH bridge in Cu(II) polychelate whereas this band seems to be merged with very broad band of phenolic hydroxyl group in polymer and Ni(II) polychelate. This band, therefore has to be due to water molecules taking part along with Ni(II) ions during coordination. The band around 625 cm\(^{-1}\) and 550 cm\(^{-1}\) corresponds to metal-oxygen vibration and metal-nitrogen vibrations respectively.

The X-ray diffraction and DSC studies indicate the polymers to be amorphous, while their metal complexes crystalline. From thermo gravimetric analysis, it is observed that the initial decomposition (10\%) for polymers is around 130\(^{\circ}\)C and the metal complexes around 320\(^{\circ}\)C, indicating superior thermal stability of the latter to the former.

1:2 ratio of metal ion to polymeric ligands is observed from elemental analysis. Further evidence for the above is provided by magnetic moment measurements 1.66 and 3.95 BM as also EPR data of \(g_{\parallel} = 2.39\) and \(g_{\perp} = 2.13\). It is to be noted that the above results go hand in hand with the FT-IR data already discussed pertaining to the structure of the complexes.
The metal ion uptake studies for all the polymers were carried out at different pH and with different electrolytes. All the polymers exhibited good metal ion uptake properties.

Taking poly(2H4ABPA)-Cu(II)/Ni(II) complexes as model, application studies were carried out. Both Cu(II) and Ni(II) complexes catalyze hydrolysis of ethyl acetate to ethanol and acetic acid as well as initiate the polymerization of N-vinyl pyrrolidone.

The antibacterial activities of polymer and its metal complexes against various microorganisms were also investigated using agar well diffusion method. This investigation revealed that the antimicrobial activity of the compounds increased after metal chelation. The fairly good antibacterial and antifungal activities exhibited by these polychelates may help them find potential application as effective antibacterial coating materials.

Cu(II) polymer-metal complex catalyze the oxidation of cyclohexanol to cyclohexanone in the presence of $\text{H}_2\text{O}_2$. Ni(II) polymer-metal complex gave negative result in this aspect. Cu(II) and Ni(II) were treated with 7M HCl. These results in dechelation giving the parent polymers without any degradation. The regenerated polymer on treatment with the metal ions forms the complexes. More than 97% of the adsorbed metal ions were removed using 7M HCl. The reproducibility of the above was established by repeating the sequence several times. Thus polymer/metal complex recyclability is ascertained along with the stability of the polymers in acidic conditions.