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Synthesis and characterization of some modified acrylic polymers

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ABSTRAC T

Polymethylmethacrylate (PMMA) was modified with phenyl hydrazine (A) and hydrazine hydrate (B).The complexes of the modified polymers with copper (II) and nickel (II) ions (chlorides and acetates) were prepared. The modified polymers and complexes were characterized by elemental analysis and IR spectroscopy . Thermal stabilities of polymer metal complexes were studied using thermogravimetric analysis (TGA). found that the thermal stabilities of polymer complexes higher than the homopolymers.

Key words: Polymethylmethacrylate (PMMA) , IR , complexes and TGA.

INTRODUCTION

Bamford et al [(1)] were the first to notice and describe that radical polymerization of vinyl monomers is accelerated by addition of inorganic salt. According to the kinetic measurements the effect was ascribed to the increase in propagation rate constant and explained by the complexation of the nitrile groups of the radicals with lithium chloride.

Structural modification of polymers has been shown to be an effective method for stabilizing polymers against thermal degradation. Polymer complexes of poly(N-isopropylacrylamide) with poly(acrylic acid) and poly(methacrylic acid) partially neutralized have been isolated.. The obtained samples have been calorimetrically studied, all complexes present a single high Tg, while the blends present two Tgs, one of them also very high. Thermal behavior of complexes and blends have also been studied[2].

A series of new naphthyl acrylate polymers with good thermal stabilities were synthesized from substituted 1,5-naphthalene diol with acryloyl chloride. , and confirmed by elemental analysis, IR and NMR spectroscopies. Thermal decomposition temperatures of these newly prepared naphthyl acrylate polymers were studied by thermogravimetric analysis[3].

Poly (2-acrylamido phenol) (PAP) and its complexes with Cu(II), Ni(II), Co(II), Cd(II) chlorides and uranyl acetate were prepared and characterized by elemental analysis, infrared, electronic spectroscopy and thermal analysis[4].

Polymer complexes of 2-acrylamido-1,2-diaminobenzene (ADB) with Cu (II) , Ni (II) , Cd (II), Zn (II) chlorides and uranyl acetate have been prepared. The prepared complexes were characterized by elemental analysis, electronic and vibration spectroscopy[5].

Thermogravimetric studies of the sodium salt of poly(acrylic acid), its modified sodium salt and its various metal complexes were made. The metal-ion complexation of carboxylate ligands of linear poly(acrylic acid), optimization of the complexation conditions and infra-red and ultraviolet-visible spectrometric characterizations are also illustrated[6].

Copolymers (PMGI) containing iminodiacetic acid were obtained from copolymerization of methyl methacrylate and a chelating monomer, glycidyl methacrylate–iminodiacetic acid (GMA–IDA), with potassium persulfate as an initiator. Cu(II)–PMGI complexes were prepared by mixing PMGI and copper sulfate solution[7].

The thermal degradation behaviour of polyacrylate and its zinc oxide composites were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG) and Fourier transform infrared spectroscopy (FTIR)[8].

In this paper the modified polymers and prepared complexes were characterized by elemental analysis ,IR, and thermal analysis.

EXPERIMENTAL

Materials

Copper (II) acetate – hydrate (Fluka), nickel (II) acetate - 4 – hydrate (Fluka), copper (II) chloride -2 – hydrate (BDH) and nickel (II) chloride -6– hydrate (BDH) were used without purification. Methanol (BDH), dimethylsulfoxide (BDH) and toluene (LAB-Scan) were used as solvents. Poly methylmethacrylate (Aldrich-average M.W. 120000), Phenyl hydrazine (Fluka) and hydrazine (BDH) were used as received.

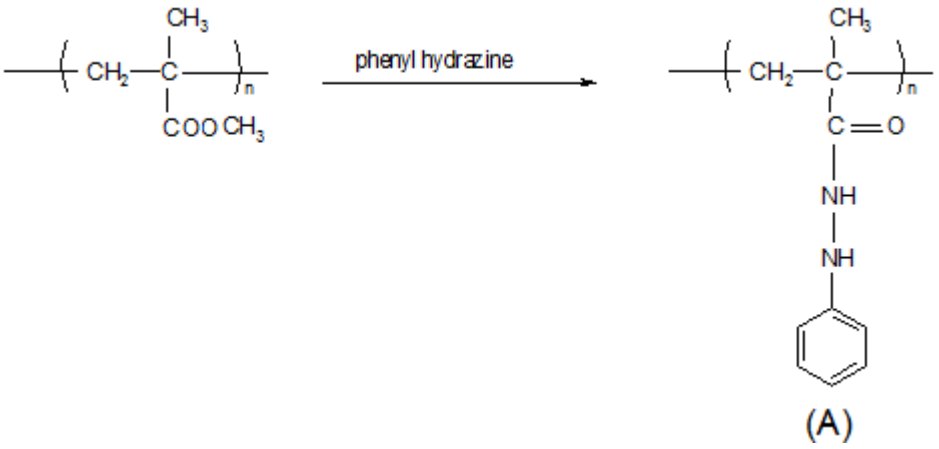
Preparation of poly[methacryloyl phenyl hydrazine] (A)

Polymethylmethacrylate (PMMA) (6.6 g) solution in dimethylsulfoxide (160 ml) was treated with phenyl hydrazine (60 ml) and boiled under reflux with constant stirring for 24 hours. The modified polymer was added with constant stirring to a large excess of distilled water (500 ml). The precipitated polymer was filtered and dried under vacuum for one week.

Preparation of poly[methacryloyl hydrazine] (B):

Polymethylmethacrylate (PMMA) (4.069g) solution in dimethyl- sulfoxide (160 ml) was treated with hydrazine hydrate (42 ml) and boiled under reflux with constant stirring for 24 hours. The modified polymer was added with constant stirring to a large excess of methanol (800 ml). The precipitated polymer was filtered and dried under vacuum for one week.

The obtained complexes have the following formula:



(A)

Preparation of the polymer complexes

Polymer complexes of polymer (A) or polymer (B) with copper and nickel acetates and chlorides were prepared. A solution of the polymer in methanol was treated with a solution of metal salt in methanol. The reaction mixture was boiled under reflux with constant stirring for 5 hours. The resulted complex was filtered, washed with methanol and dried under vacuum for five days.

Characterization of the polymers

IR spectra were recorded using Perkin Elmer infrared spectrophotometer. The samples were examined as KBr discs. Carbon, hydrogen and nitrogen content determination were performed at the Microanalytical unit.

TGA measurements were recorded with Perkin Elmer TGA7, thermal analysis system. Samples were heated from 30 to 700 °C in a platinum pan with a heating rate 20 °C / min in air 25 ml /min. The analytical data for the prepared polymer (A) and (B) and their complexes are shown in Table 1 and 2 respectively.

Table - 1: Microanalytical data for polymer (A) and its corresponding metal complexes

Compound	Analysis (Calculated) / Measured %C	%H	%N
Polymer(A)	(68.16)68.32	(6.86)7.01	(15.90)16.12
A-$CuCl_2$ complex	(52.9)52.12	(5.62)5.80	(12.34)12.68
A-$NiCl_2$ complex	(53.28)53.72	(5.66)5.42	(12.43)12.12
A-$Cu(OAc)_2$ complex	(56.07)56.58	(6.09)6.21	(11.54)11.80
A-$Ni(OAc)_2$ complex	(56.45)56.92	(6.13)6.30	(11.62)11.91

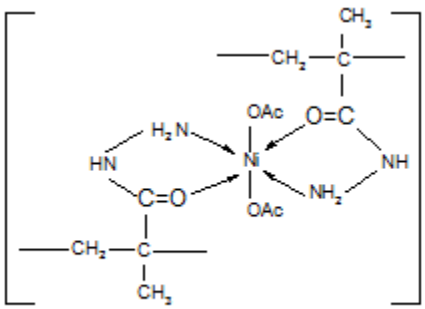
Table - 2: Microanalytical data for polymer (B) and its corresponding metal complexes

Compound	Analysis (Calculated) / Measured %C	%H	%N
Polymer(B)	(47.99)48.4	(8.05)7.9	(27.9)28.3
B-$CuCl_2$ complex	(20.48)20.7	(3.44)3.6	(11.94)12.3
B-$NiCl_2$ complex	(34.10)33.7	(5.01)5.20	(9.94)9.7
B-$Cu(OAc)_2$ complex	(26.26)25.97	(5.51)5.4	(15.31)15.5
B-$Ni(OAc)_2$ complex	(38.23)38.62	(5.88)5.71	(14.86)14.65

RESULT AND DISSCUTION

All polymer complexes are intensely colored, stable in air . The IR spectrum of homopolymer (A) shows a broad band at 3324 cm^{-1} is due to the secondary amide $\nu_{(N-H)}$. The band at 1687 cm^{-1} is characteristic to the amide (I) ν(c=o).

Copper (chloride and acetate) complexes and Nickel (chloride and acetate) complexes there is significant shift of NH band to high frequency in comparison with homopolymer, indicating the involvement of this group in the coordination. The IR absorption of amide (I) ν(c=o) appeared at 1686 cm^{-1}, the position of this band is unaltered in comparison with the homopolymer so the carbonyl group is not involved in the coordination.



polymer (B)-Ni(II) acetate complex

The IR spectrum of homopolymer (B) show a broad band at 3432 cm^{-1} is due to the secondary amide $\nu_{(N-H)}$. The ν(c=o) of amide (I) appeared at 1629 cm^{-1}.

Comparison of IR spectrum of Copper (chloride and acetate) complexes , Nickel (chloride and acetate) complexes and homopolymer shows a shift in the position of NH band to lower frequency, suggesting coordination of homopolymer to metal ions via (NH) nitrogen atom.

The band of ν(c=o) of amide (I) occurred at 1603 cm^{-1}. There is a change in the absorption of this group to lower frequency in the polymer complex, indicating the involvement of oxygen of (C=O) group in bonding with the metal ions[9,10].

Elemental analysis and IR revealed that polymer (A) reacted with copper (II) and nickel chlorides and acetates in 1:3 (metal: ligand) molar ratio. Polymer (B) reacted with copper (II) chloride and acetate in 1:1 (metal: ligand) molar ratio and with nickel (II) chloride and acetate in 1:2 (metal: ligand) molar ratio.

The homopolymer(A) degraded in three stages, Fig. -1 .The first stage started at 125 °C with 3.0 % weight loss, and the second stage started at 200 °C with weight loss 85.0 %. The third stage observed between 475 ° C and 615 °C with weight loss 12.0 %.

TGA curves and thermoanalytical results of polymer (A)-$CuCl_2$ and polymer (A)-$Cu(OAc)_2$ complexes shows three stages of decomposition. The first stage occurred in the temperature range 165 - 195 °C with 2.6 % weight loss. The second stage appeared at 195 - 440 °C with weight loss 79.0 % and the third stage started at 440 °C and continued up to 580 °C (15.0 % weight loss).

Two stages of decomposition was observed for polymer(A)-$Cu(OAc)_2$ complex ,the first stage started at 122 °C and continued up to 265 °C with 4.4% weight loss. And the second stage started at 265 °C and continued up to 520 °C with 69.3% weight loss.

TGA curves and thermoanalytical results of polymer(A)-$NiCl_2$ and polymer(A)- Ni $(OAc)_2$ complexes shows three degradation steps for polymer(A)-$NiCl_2$ and polymer(A)-Ni $(OAc)_2$ complexes. The first stage appeared in the temperature range 175 - 240 °C and 145 - 185 °C with 3.9% and 2.7 % weight losses for polymer(A)-$NiCl_2$ and polymer(A)- Ni $(OAc)_2$ complexes . The second stage observed at 240 - 495 ° C and 185 - 480 °C with 70.2 % and 62.0 % weight losses for polymer(A)- $NiCl_2$ and Ni $(OAc)_2$ complexes respectively. The third stage started at 495°C and continued up to 620°C (21.0 % weight loss) for polymer(A)- $NiCl_2$ complex ,and started at 480 °C and ended at 665 °C (25.0 % weight loss)for polymer(A)- Ni $(OAc)_2$ complex .

The prepared poly[methacryloyl hydrazine] (B) degraded in three stages,figure(1) ,

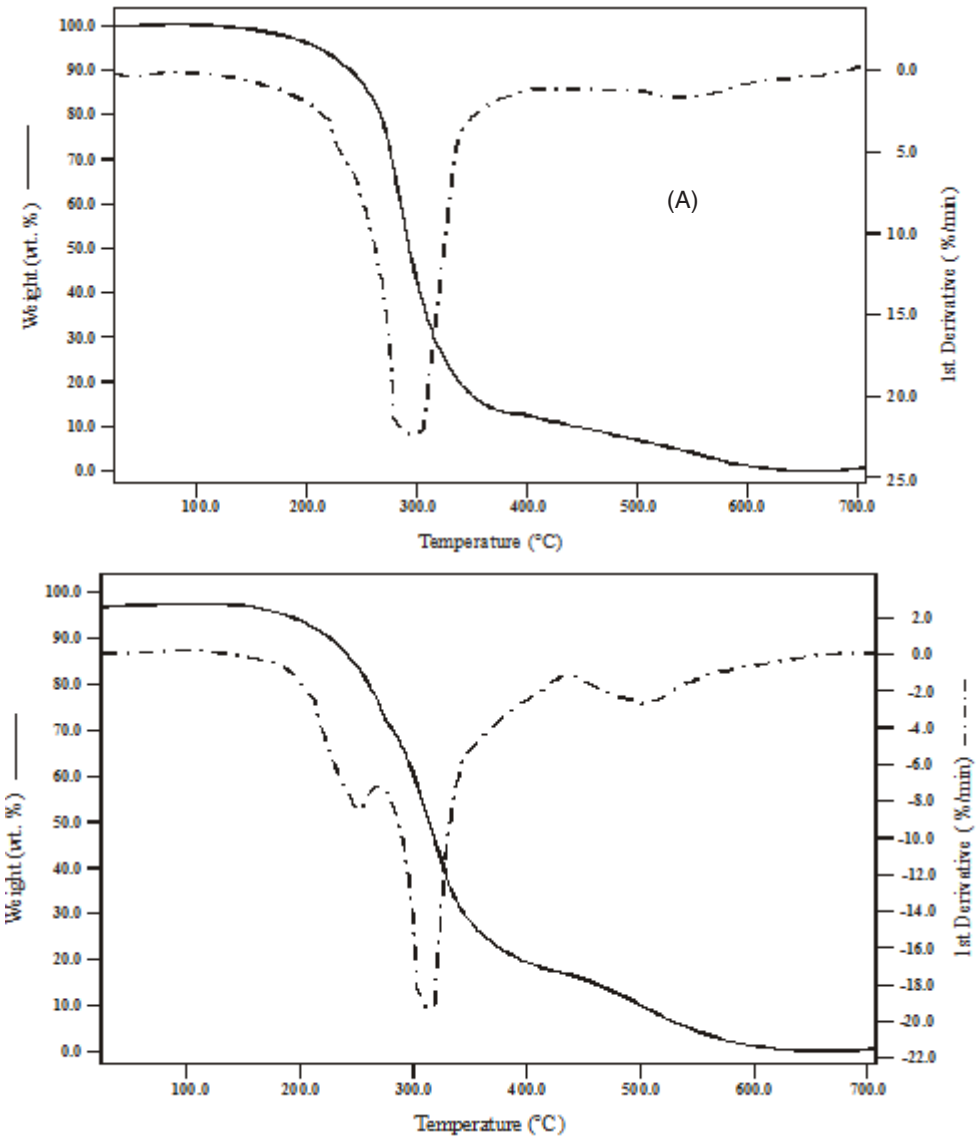


Fig. - 1: TGA curves for polymer(A) and polymer(B)

the first stage started at 115 °C with weight loss 1.2 % . The second stage started at 190 °C with weight loss 78.5 %. The third stage started at 410 ° C and ended at 660 °C with weight loss 20.3 %.

Two stages of decomposition were observed for polymer (B)-$Cu(OAc)_2$ complex and for polymer (B)-$CuCl_2$ complex. The first stage occurred in the temperature range 245 - 500 °C and 216 - 300 °C with 52.0 % and 21.1 % weight losses for polymer (B)-$Cu(OAc)_2$ and polymer (B)- $CuCl_2$ complexes respectively .The last stage for polymer (B)-$Cu(OAc)_2$ complex and for polymer (B)-$CuCl_2$ complex occurred in the temperature range 500 - 700 °C and 300 - 505 °C with weight losses 22.8% and 67.7% respectively.

There are three degradation steps for polymer (B)-$NiCl_2$ and polymer (B)-Ni $(OAc)_2$ complexes . The first stage appeared in the temperature range 120 - 197 °C and 145 - 235 °C with 5.3 % and 6.0 % weight losses for polymer

(B)-$NiCl_2$ and Ni $(OAc)_2$ complexes respectively. The second stage observed at 197 - 510 ° C and 235 - 505 °C with 67.0 % and 42.0 % weight losses for polymer (B)- $NiCl_2$ and polymer (B)-Ni $(OAc)_2$ complexes respectively. The third stage started at 510°C and continued up to 700 °C (21.0 % weight loss) for polymer (B)- $NiCl_2$ complex and started at 505 °C and ended at 642 °C (23.5 % weight loss) for polymer (B)- Ni $(OAc)_2$ complex. Finally, it was found that the thermal stabilities of polymer complexes are higher than the homopolymer. And that poly [methacroyloyl phenyl hydrazine] (A) is slightly more stable than poly[methacroyloyl hydrazine] (B).

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