

SYNTHESIS AND THERMAL STUDIES OF QUINAZOLINE POLYMER COMPLEXES WITH $UO_2(II)$, $Fe(III)$ and $Zn(II)$

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ABSTRACT

Poly Quinazoline (2-acrolyl-phthalizinone-carboxyl) homopolymer (PAPNH) and polymer complexes of phthalizinone with Fe^{3+} , UO_2^{2+} and Zn^{2+} metals have been prepared and characterized using spectral (1H -NMR, IR and Uv-vis) and magnetic measurements. The data suggest that the Fe^{3+} , UO_2^{2+} and Zn^{2+} polymer complexes are octahedral dimer. The thermal stabilities of (PAPNH) homopolymer and polymer complexes of (APNH) with metal chlorides were studied thermogravimetrically. The rates of polymerization of (PAPNH) in the absence and in presence of metal chlorides were studied. The activation energies of the degradation of the homopolymer and polymer complexes were calculated using Arrhenius equation.

Key words: Homopolymer, polymer complexes, IR, Uv-vis, 1H -NMR, Thermogravimetrically (TGA, DTA)

INTRODUCTION

Metal complexes of polymers are of interest for a variety of reasons¹. We have been interested in the chelating properties of polymers containing mixed donor atom sets. Increasing interest in synthesis and reactivity of polymeric metal complexes of poly (5-vinylsalicylidene-2-benzothiazoline) (PVSBH₂) arises due to their use against many diseases, antifungal activity and employment in industry². It has recently been observed that some drugs have increased activity administered as polymeric metal complexes, new heterocyclic azo compounds synthesized during the past few years have proved valuable for the rarer elements. In particular, pyridylazo and thiazolylazo derivatives have attracted much attention. Because their complexation behaviour (the color reaction complex) is often peculiar³.

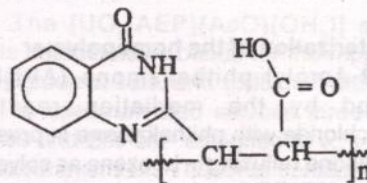
In this paper, polymer complexes of 5-vinyl-salicylidene-2-benzothiazoline with some transition metal salts were prepared and characterized. Also, polymer sensitized by polymerization cations. The analytical characteristics of the color reaction are given and the nature of the interaction is given and the nature of interactions of the chelate is discussed.

EXPERIMENTAL

Phthalizinone (2-acrolyl-phthalizinone) was prepared as reported previously, and stored over anhydrous Na_2SO_4 and 2,2-azobisisobutyronitrile (AIBN, Eastman Kodak) was purified by recrystallization from EtOH⁴.

2- Acrolyl-Phthalizinone (Quinazoline)

(APNH) monomer was prepared as reported, equimolar amounts of phthalizinone and acrylic acid in EtOH were stirred for 24 h to give 2-acrolyl-phthalizinone monomer molecular formula $C_{11}H_8N_2O_3$: (M. wt. 216) [Calcd. (found) C, 61.4 (61.11); H, 6.06 (6.02); N, 21.5 (21.21); O, 36.36 (36.60) %].



Polymer complexes

Polymer complexes of APNH $UO_2(II)$, $Fe(III)$ and $Zn(II)$ were prepared by dissolving⁵ equimolar

amounts of APNH and the metal salt in DMF with 0.1 w/v AIBN (AIBN = 2,2-azobisisobutyronitrile) as initiator. The mixture was boiled under reflux for 6h and the resulting polymer complexes precipitated by pouring into a large excess of distilled H₂O containing dilute HCl to remove contaminating metal salts. The polymer complexes were filtered off, washed with H₂O and dried in vacuo at 40°C for several days. The homopolymer and its metal polymer complexes were analyzed for C, H, N and S by microanalytical techniques at King Abdul-Aziz University, Saudi Arabia. Metal contents in the polymer complexes were estimated by standard methods⁴.

Measurements

Microanalysis of all the samples was carried out at Cairo University Analytical Centre, and the metal contents of the polymer complexes were calculated by a standard technique⁵ (Table 1). ¹H NMR spectra were obtained with a Jeol Fx 90 Fourier transform spectrometer with DMSO-d₆ as solvent and TMS as the internal standard. IR spectra were recorded on a Perkin-Elmer 1340 spectrophotometer, and UV-Vis spectra (nujol mull) on Shimadzu spectrophotometer.

Thermal analysis

Thermogravimetric (TG) measurements were made using a Du Pont 950 thermobalance. Samples (10 mg) were heated at 10°C min⁻¹ in a dynamic nitrogen atmosphere (70 ml min⁻¹), in a boat-shaped sample holder, 10 x 5 x 2.5 mm deep. The temperature-measuring thermocouple was placed within 1 mm of the holder. TG was also used for the determination of the rate constant of the degradation of (PAEPH) homopolymer and the polymer complexes. Activation energies were obtained from TG and DTA curves, using the method of Pilojan and Novikova¹⁶.

RESULTS AND DISCUSSION

Characterization of the homopolymer

2-Acrolyl phthalizinone (APNH) was prepared by the mediation reaction of acryloylchloride with phthalizinone in presence of hydroquinone refluxing in benzene as solvent⁷. The monomer (APNH) has been characterized in the experimental section. This monomer was then polymerized by radical polymerization initiated by 2,2-azoisobutyronitrile (AIBN). The homopolymer has been characterized by various techniques⁸.

Both IR and ¹H-NMR spectroscopy were used to characterize the (PAPNH) homopolymer. The IR spectrum of the new ligand Table 2 exhibits absorptions in common, due to the pyridine ring, imino, CO, phenyl ring and the -CH₂-CH₂- bridge. The vibrations of interest in PAPNH are the four $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$ bands between 1595 and 1425 cm⁻¹, the C-H in plane deformations in the region 1225-1045 cm⁻¹, the ring breathing at 995 and 1005 cm⁻¹, the out-of-plane C-H deformation vibrations between 775 and 750 cm⁻¹ and the C-C out-of-plane deformation at 400 ± 5 cm⁻¹.

The strong bands at 1595, 1560, 1475 and 1425 cm⁻¹ in the PAPNH spectrum are due to C=C and C=N symmetric and antisymmetric vibrations¹². The donation of electrons by the nitrogen atom of pyridine will increase the double bond character of C=C bonds because of the pull of electrons from hydrogen to C=C and C=N bonds. A medium to strong band at 630cm⁻¹ is due to an in-plane pyridine ring deformation, and a weak to medium band in the region 415-405 cm⁻¹ is attributed to an out-of-plane pyridine ring deformation⁹.

In PAPNH an intense band in the region 3160-3170 cm⁻¹ is attributed to the intramolecularly hydrogen bonded $\nu(\text{N-H})$ vibration. The ligands show strong multiple absorption centered at 1540 cm⁻¹, probably a major contributor being a combination of a CN stretch coupled with a N-H deformation mode. The ortho-substituted pyridine ring exhibits three characteristic bands around 1290, 1135 and 1040 cm⁻¹.

The ¹H-NMR spectrum of PAPNH showed the expected peaked $\delta(\text{DMSO-d}_6)$ at 11.1 (H, NH), 2.85 (4H, 2CH₂) and 8.56-7.06 ppm (4H, C₅H₄), which are downfield from TMS. The first signal disappeared on adding D₂O; the other signals were still observed.

The NMR spectrum of APNH monomer showed the expected peaks and pattern of the vinyl group (CH₂-CH), i.e. $\delta(\text{DMSO-d}_6)$ 6.25 for the vinyl CH proton and proton δ 5.12 ppm for the vinyl CH₂ protons, respectively. These peaks disappeared on polymerization while a triplet at δ 1.86 and a doublet at δ 1.80 ppm appeared. This indicates that the polymerization of APN monomer occurs on the vinyl group¹⁰. It is worth noting that the rest of the proton spectrum of the monomer and polymer remain almost without change.

Characterization of the polymer complexes

The stoichiometries of the complexes have been deduced from their elemental analyses. These indicate that the metal-polymer complexes

fall into two distinct categories, namely 1:1 and 1:2 (ligand:metal). PAPNH is mononucleating and hence requires one metal ion for coordination. All the products were found to be only partially soluble in common organic solvents. Because of this, it was not possible to characterize them in terms of their molecular weights. On the basis of elemental analysis (Table 1) the compositions of the complexes agree well with their structural formulae. The conductances of these polymer complexes were too low to indicate any dissociation.

The deprotonation is confirmed by the effervescence resulting from the formation of HCl gas and the evolution of ethanoic acid during complex formation, and has been assessed quantitatively by both pH measurement and a spot-test technique, as well as by detection of a characteristic odour.

These reactions are quite facile and the resulting isolated polymer complexes were air-stable, coloured, non-hygroscopic solids, which decomposed at high temperatures. The reactions appear to proceed only up to a 1:2 molar ratio. Even on prolonged refluxing (~ 32h) of 1:3 or 1:4 reaction mixtures, replacement of a third chloride group by the homopolymer was not observed. This is probably due to steric factors.

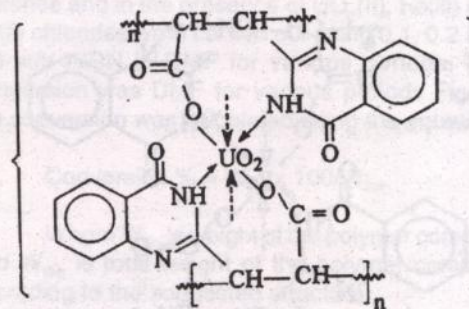
IR spectra

Table 2 gives diagnostic IR and for IR bands. In the $\nu(\text{O-H})_{\text{water}}$ region, the spectrum of compound shows two strong, sharp bands at 3430cm^{-1} attributed to the presence of coordinated water¹¹. The presence of coordinated water is further confirmed by the appearance of a non-ligand band in the region $830\text{-}840\text{cm}^{-1}$, non-ligand band in the region $830\text{-}840\text{cm}^{-1}$, assignable to the rocking mode of water. The spectrum of polymer exhibits, in addition to the bands of coordinated water, a broad continuous absorption at $3510\text{-}3100\text{cm}^{-1}$, which is apparently due to the presence of both coordinated and crystal water in this compound. In all the other compounds, a strong and broad absorption at $3480\text{-}3150\text{cm}^{-1}$ indicates that lattice water is present.

On examination of IR spectra of homopolymer and polymer complexes, it is observed that there is no significant change in C=O , but there is strong multiple absorption centered at 1530cm^{-1} in the homopolymer, probably a major contribution being a combination of a CN stretch coupled with a N-H deformation mode. This disappears in most complexes, which is evidence of the loss of the N-H proton on complexation. The

vibrations due to $\nu(\text{C=C})$ and $\nu(\text{C=N})$ are shifted to higher regions. This indicates participation of pyridine nitrogen during chelation, which is also confirmed by an upward shift of the pyridine ring breathing modes to about 1015cm^{-1} and ring deformation modes to the 630 and 430cm^{-1} regions. The Fe (III) polymer complexes show $\nu(\text{Fe-Cl})$ frequencies that seem too low for terminal Fe-Cl bonds and correspond to bridging chlorine ($340\text{-}225\text{cm}^{-1}$) groups. However, bands in the region $350\text{-}390\text{cm}^{-1}$ may be attributed to terminal Fe-Cl groups, to which there are no corresponding ligand bands. These assignments are in good agreement with the assignment given by Woodward and Taylor¹⁵.

The $\nu(\text{M-N}_{\text{homop}})$ and $\nu(\text{M-N}_{\text{ring}})$ assignments are in agreement with literature data¹² that metal-nitrogen stretching vibrations are often coupled with other normal modes of vibration of the same symmetry, especially ring vibrations. Thus, the proposed assignments in Table 2 must be regarded as approximate descriptions of the vibrations. The absence of a $\nu(\text{M-Cl})$ band in the appropriate region in compounds, and the appearance of a new weak to medium band at 395cm^{-1} , is assigned to $\nu(\text{M-O})$ in compound.



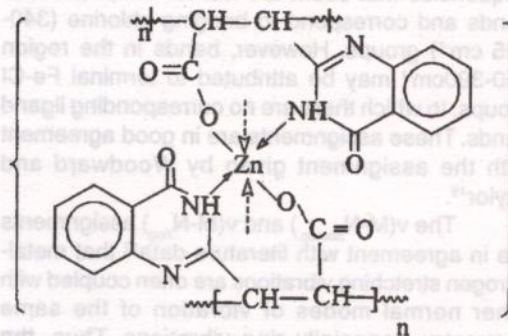
Where : \longrightarrow represents H_2O molecule

The $[\text{UO}_2(\text{AEP})(\text{AcO})(\text{OH}_2)]$ spectrum exhibits characteristic bands for the monodentate acetate group at 1620 and 1395cm^{-1} with $\Delta\nu = 235\text{cm}^{-1}$. The spectrum also exhibits three bands at 907 , 799 and 275cm^{-1} assigned to ν_3 , ν_1 and ν_2 of the dioxouranium ion. The force constant, f , for the $\nu(\text{U=O})$ vibration was calculated according to the method of McGlynn¹³ and was found to be 6.793mdynes/\AA . The U—O bond distance was calculated using the following equation :

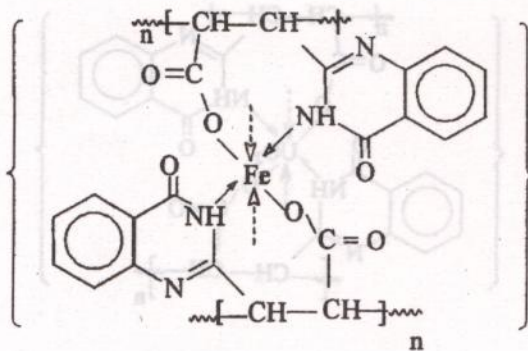
$$R_{\text{U-O}} = 1.08 f^{-1/3} + 1.7$$

The U—O bond distance is around 1.740 Å, which lies in the usual range (1.60-1.92 Å) observed for the majority of dioxouranium (VI) complexes.

The UV spectrum of the uranyl complex exhibits a band at 219 100 cm⁻¹ assigned to the E_g⁺¹ → ³π_g transition¹⁴.



All these observations taken together with the wide range of coordination numbers ranging from 4 to 8 suggest that in these complexes Fe(III) complexes, it may be suggested that these complexes may exist as trigonal bipyramidal structures.



Thermal methods of analysis

Thermal studies have been carried out on the polymer complexes. The thermal decomposition of the polymer complexes was studied using TGA/DTA techniques. The TG curves of all complexes show a first mass-loss between 55 and 120°C which corresponds very well to the release of the water content. (The relatively low temperature of water loss shows that this is lattice held). Polymer complex releases water in two steps, from 35 to 215°C indicates that stable hydrated intermediates cannot be formed. A clear TG plateau after complete dehydration is reached for all complexes, up to 165°C. In complex decomposition of the anhydrous species starts almost immediately after dehydration¹⁵.

The curves for all polymer complexes have similar patterns. After three stages of weight loss, the mass of the samples becomes constant above 530-700 °C. The DTA curves exhibit several endothermic peaks, I (130-145 °C), II (250-285 °C) and III (395-420 °C), and also two exothermic peaks, I (350-365 °C) and II (430-475°C). The compositions of the intermediate compounds formed at various stages of the thermal decomposition were evaluated by calculation from weight loss measurements (TG curves). The PAPNH homopolymer degrades in two stages, initially at 100 °C with 35% weight loss. Followed by a second stage at 155°C with 40% weight loss. There are three degradation stages in all the polymer complexes. The first stage is probably due to the loss of water molecules in the structure. TG studies showed that all the compounds decomposed in a first step at around 130-385 °C, losing the greater part of the ligand atoms. In a second step the halogens and/or halide heterocyclic base and the remaining part of the ligand were lost. The straight chain in homopolymer

Table-1: Analytical data for the polymer complexes

Polymer complex	Found (Calcd.) %					Metal	Molar ratio
	C	H	N	O	Cl		
[Fe(ANP) ₂ .2H ₂ O] _n	50.48 (49.90)	3.82 (3.60)	10.71 (9.97)	24.74 (24.60)	-	10.52 (10.04)	1:2
[UO ₂ (ANP) ₂ .2H ₂ O] _n	35.77 (35.20)	2.71 (2.55)	7.59 (6.75)	17.34 (16.95)	-	36.59 (37.30)	1:2
[Zn(ANP) ₂ Cl ₂ .H ₂ O] _n	43.21 (42.80)	2.95 (2.75)	9.17 (8.96)	18.33 (17.95)	11.46 (10.90)	14.89 (15.30)	1:2

Table-2: IR spectra of (PANPH) and its polymer complex

Polymer complex	$\gamma_{C=C}$	γ_{NH}	$\gamma_{C=N}$	δ_{CH}	γ_{CH}	$\gamma_{(M-N)}$	$\gamma_{(M-O)}$	$\gamma_{C=O}$	γ_{C-O}
PANPH	1560	3160	1565,1425	890,480	770,745	-	-	1750	1150
[Fe(ANP) ₂ .2H ₂ O] _n	1610	-	1572,1440	985,968	775,750	477	531	1680	1570
[UO ₂ (ANP) ₂ .2H ₂ O] _n	1615	-	1578,1440	980,960	795,780	540	460	1740	1302
[Zn(ANP) ₂ Cl ₂ .H ₂ O] _n	1610	-	1585,1433	954,873	795,780	335	525	1675	1340

Table-3: Apparent activation energy of polymerization of (APN) homopolymer and polymer complexes of APN with FeCl₃

Polymer	AIBN w/v	E _a (KJ mol ⁻¹)
PAPN	0.1	108:67
APN-FeCl ₃	0.1	98:25
PAPN	0.2	103:54
APN-FeCl ₃	0.2	65:40
PAPN	0.3	95:38
APN-FeCl ₃	0.3	35:60

and polymer complexes gave higher values of weight loss during the first decomposition step. Only small differences were observed in the characteristic temperatures corresponding to the second and third steps, which can be accounted for by the formation of a common decomposition product at the end of the first step.

The final details in the TG curves occasionally indicate two- or three- stage degradation, without any well defined plateau, all the compounds attained constant weight at 530-700 °C. Weight loss continued without interruption up to around 500 °C, at which temperature the weight of the residue (metal oxides) was in good agreement with those calculated from the metal content.

Finally, the halogeno complexes are most stable. It is evident that differences in the initial decomposition temperature of step 2 for the polymer complexes are due to the influence of the anion. The dehydration energy calculated for these effects varied between 40.0 and 29.0 kJ mol⁻¹, while $\Delta H = 52.0$ kJ mol⁻¹ (per H₂O released) for compound.

Kinetic of polymerization

The polymerization of (PAPNH) in the

absence and in the presence of UO₂(II), Fe(III) and Zn(II) chlorides were carried out using 0.1, 0.2 and 0.3 w/v AIBN in DMF for various periods. The conversion was DMF for various periods Fig. 1, the conversion was calculated using the equation:

$$\text{Conversion \%} = W_{PC} \times 100/W_{TPC}$$

Where W_{PC} is weight of the polymer complex and W_{TPC} is total weight of the polymer complex according to the suggested structure.

The conversion increases with increasing concentration of AIBN. The rate of polymerization increases as a result of addition of metal chlorides in the order APN-UO₂Cl₂ > APN-ZnCl₂ > APN-FeCl₃.

The polymerization of APNH in the presence of FeCl₃ was carried out with different concentrations of initiator for various periods. Show the conversion percentage in the absence and in the presence of FeCl₃ at different concentration of initiator. The role of polymerization increases with rising temperature, the apparent activation energies (E_a) were determined⁵ plots of log (initial rate) versus 1/T were linear Fig. 2.

Table 3 gives the activation energies in the presence of FeCl₃. The activation energies for PANP are higher than for ANP-FeCl₃ polymer

complexes and decrease with increasing AIBN initiator concentration Fig. 3.

The synthesis of thermally stable polychelates and their thermal decomposition now promises an interesting area in the chemistry of heat-resistant polymers. Some of the polymers containing metal ion linked by chelate rings derived from organic backbone units are much more stable than aliphatic rings, and have significantly higher

melting temperatures.

The greater stabilities of the polymer complexes compared with homopolymer may be due to the formation of six-membered ring structures in the homopolymer complexes.

The values of energy of activation (E_a) for dehydration of the polymer complexes were determined from TG and DTA curves, using the methods of Pilojan and Novikova.

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