

Synthesis and thermal kinetic studies of quinazolin polymer complexes

Polymer of 2-acrolyl-quinazolin-carboxyl and homopolymer (PAQNH) complexes with Mn^{2+} , UO_2^{2+} , Zr^{4+} and Nb^{5+} metals have been synthesized and characterized using different spectroscopic techniques (1H -NMR, IR and UV-Vis) and magnetic measurements. The results obtained suggest that the metal ions doping in dimer monomer forming octahedral complexes. The thermal stabilities of doping polymer complexes of AQNH with metal chlorides were studied thermally, The rates of polymerization of quinazoline acrolyl (PAQNH) in the absent and in presence of metal ions were studied. The activation parameters of the degradation of doping were discussed and calculated.

Key words: Quinazoline; Dopping, polymer complexes; IR, UV VIS 1H -NMR, (TGA, DTA).Activation parameters.

1. INTRODUCTION

We have been interested in the chelating properties of polymers containing mixed donor atom sets[1-3]. Increasing interest in synthesis and reactivity of polymeric metal complexes of poly (5-vinylsalicylidene-2-benzothiazoline) (PVSBH₂) arises due to their use against many Metal complexes of polymers are of interest for a variety of diseases, antifungal activity and employment in industry[2]. It has recently been observed that some drugs have increased activity administered as polymeric metal complexes [1], the azo-dyes form a very interesting class of reagents for the photometric determination of niobium [2,1]. New heterocyclic azo compounds synthesized during the post 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 peculiar [3, 4]. The azo-dyes form a very interesting class of reagents for the photometric determination of niobium, new heterocyclic azo compounds synthesized during the post few years have proved valuable for the rarer elements. In particular, pyridylazo and thiazolylazo derivatives have attracted much attention, because their complexation behavior (the colour reaction complex) is often peculiar [5,6]. In this paper, polymer complexes of 5-vinylsalicylidene-2-benzothiazoline with some transition metal salts were prepared, characterized and the nature of chelate is discussed.

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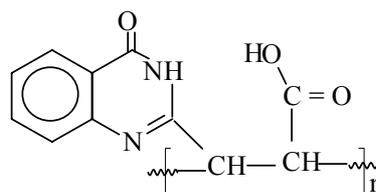
2. EXPERIMENTAL

Quinazolinone (2-acrolyl-quinazoline) was prepared as reported previously, and stored over anhydrous Na₂SO₄ and 2,2-azobisisobutyronitrile (AIBN, Eastman Kodak) was purified by recrystallization from EtOH [5].

2- Acrolyl-quinazoline

(AQNH) monomer was prepared firstly new monomer in this work but the method for preparation according to reported previously [1].

The homopolymer and its metal polymer complexes were analyzed for C, H, N and S by microanalytical techniques at Cairo University, Egypt. Metal contents in the polymer complexes were estimated by standard methods [8, 9].



Equimolar amounts of quinazoline and acrylic acid in Et OH were stirred for 24 h to give 2-acrolyl-quinazoline monomer molecular formula C₁₁H₈N₂O₃: (M. wt. 216) [Caled. (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 AQNH Mn(II), UO(II), Zr(IV) and Nb(V) were prepared by dissolving equimolar amounts of APNH and the metal salt in DMF with 0.1 w/v AIBN (AIBN=2,2-azobisi-

sobutyronitrile) as initiator. The mixture was boiled under reflux for 6 h 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.

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 technique[14] (Table 1). ¹H NMR spectra were obtained with a Jeol Fx 90 Fourier transform spectrometer with DMSO-d₆ as solvent after heating 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.

Table (1): Analytical data for the polymer complexes

Polymer complex	Found (Caled.) %					Metal	Molar ratio
	C	H	N	O	Cl		
[Mn(ANP) ₂ .2H ₂ O] _n	50.48	3.82	10.71	24.74	-	10.52	1 : 2
	(49.90)	(3.60)	(9.97)	(24.60)	-	(10.04)	
[UO ₂ (ANP) ₂ .2H ₂ O] _n	35.77	2.71	7.59	17.34	-	36.59	1 : 2
	(35.20)	(2.55)	(6.75)	(16.95)	-	(37.30)	
[Zn(ANP) ₂ Cl ₂ .H ₂ O] _n	43.21	2.95	9.17	18.33	11.46	14.89	1 : 2
	(42.80)	(2.75)	(8.96)	(17.95)	(10.90)	(15.30)	
[Nb(ANP) ₂ Cl ₃ .H ₂ O] _n	40.74	2.78	8.64	17.28	16.20	14.35	1 : 2
	(40.30)	(2.64)	(8.110)	(16.98)	(15.80)	(13.95)	

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, 10x5x2.5 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 Novikova [11].

3. RESULTS AND DISCUSSION

3.1. Characterization of the homopolymer

2-Acrolyl-quinazoline (AQNH) was prepared by the a mediation reaction of acrylic acid with quinazoline in presence of hydroquinone refluxing in benzene as solvent [12]. The monomer (AQNH) 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 techniques [10].

Both IR and ¹H-NMR spectroscopy were used to characterize the (PAQNH) 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 ν (C=C), ν(C=N) bands between 1595 and 1425 cm⁻¹, the C-H in plane deformations in the region 1225-1045cm⁻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 ± 5cm⁻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 vibrations[12]. 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 630 cm⁻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 deformation [12].

Table (2): IR Spectra of (PANQH) and its polymer complex.

Polymer complex	ν C=C	ν NH	ν C=N	δ CH	ν CH	ν (M-N)	ν (M-O)	ν C=O	γ C-O
PANQH	1560	3160	1565,1425	890,480	770,745	-	-	1750	1150
[Mn(ANQ) ₂ .2H ₂ O] _n	1610	-	1572,1440	985,968	775,750	477	531	1680	1570
[UO ₂ (ANQ) ₂ .2H ₂ O] _n	1615	-	1578,1440	980,960	795,780	540	460	1740	1302
[Zr(ANQ) ₂ Cl ₂ .H ₂ O] _n	1610	-	1585,1433	954,873	795,780	335	525	1675	1340
[Nb(ANQ) ₂ Cl ₃ .H ₂] _n	1616	-	1570,1480	950.875	783,772	296	510	1730	1300

In PAQNH an intense band in the region 3160-3170 cm^{-1} is attributed to the intramolecularly hydrogen bonded ν (N-H) vibration. The ligands show strong multiple absorption centred at 1540 cm^{-1} , probably a major contributor being a combination of a CN stretch coupled with a N-H deformation mode [12]. The ortho-substituted pyridine ring exhibits three characteristic bands around 1290, 1135 and 1040 cm^{-1} .

The ¹H-NMR spectrum of PAQNH showed the expected peaked δ (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 AQNH monomer showed the expected peaks and pattern of the vinyl group (CH₂-CH), i.e. δ (DMSO-*d*₆) 6.25 for the vinyl CH proton and proton δ 5.12ppm 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 AQN monomer occurs on the vinyl group [12]. It is worth nothing that the rest of the proton spectrum of the monomer and polymer remain almost without change.

3.2 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). PAQNH 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

3.3 IR spectra

Table 2 gives diagnostic IR and for IR bands. In the ν (O-H)_{water} region, the spectrum of compound shows two strong, sharp bands at 3430 cm^{-1} attributed to the presence of coordinated water^[14]. The presence of coordinated water is further confirmed by the appearance of a non-ligand band in the region 830-840 cm^{-1} , non-ligand band in the region 830-840 cm^{-1} , assignable to the rocking mode of water[14]. The spectrum of polymer exhibits, in addition to the bands of coordinated water, a broad continuous absorption at 3510-3100 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 3480-3150 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 1530 cm^{-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 ν (C=C) and ν (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 1015 cm^{-1} and ring deformation modes to the 630 and 430 cm^{-1} regions. The Zr (IV) polymer complexes show ν (Zr-Cl) frequencies that seem too low for terminal Zr-Cl bonds and correspond to bridging chlorine (225-340 cm^{-1}) groups. However, bands in the region 350-390 cm^{-1} may be attributed to terminal Zr-Cl groups, to which there are no corresponding ligand bands.

The ν (M-N_{homop.}) and ν (M-N_{ring}) assignments are in agreement with literature data^[16] It is well known^[12] 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 $\nu(\text{M}-\text{Cl})$ band in the appropriate region in compounds, and the appearance of a new weak to medium band at 395cm^{-1} , is assigned to $\nu(\text{M}-\text{O})$ [14] in compound.

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 $\nu(\text{U}=\text{O})$ vibration was calculated according to the method of McGlynn [17] and was found to be $6.793\text{mdynes}/\text{A}^\circ$. The $\text{U}-\text{O}$ bond distance was calculated using the following equation:

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

The $\text{U}-\text{O}$ bond distance is around 1.740A , which lies in the usual range ($1.60-1.92\text{A}$) observed for the majority of dioxouranium (VI) complexes.

The UV spectrum of the uranyl complex exhibits a band at 219100cm^{-1} assigned to the $\text{E}_g^{+1} \rightarrow {}^3\pi_4$ transition [17].

3.4 Stereochemistry

The polymer complexes are diamagnetic as expected for square planar d^8 metal ion complexes. The electronic spectra of square planar Mn^{2+} and Nb^{5+} polymer complexes are expected to show three d-d bands, ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ ($\sim 19400, 30040\text{cm}^{-1}$);

$${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g} (\sim 23500, 32\ 230\text{cm}^{-1});$$

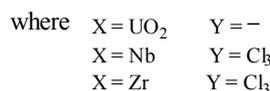
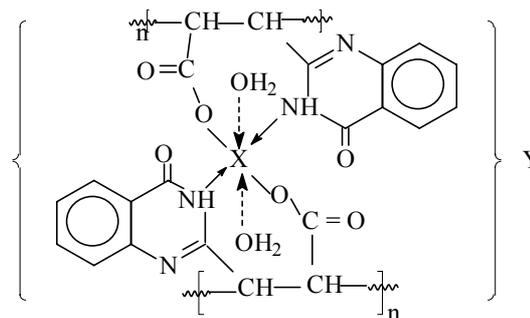
$$\text{and } {}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g (\sim 29\ 380, 39550\text{cm}^{-1}),$$

Table (3): Apparent activation energy of polymerization of (AQN) homopolymer and polymer complexes of AQN with NbCl_5

Polymer	AIBN w/v	E_a (KJ mol ⁻¹)
PAQN	0.1	108:67
AQN-NbCl ₅	0.1	98:25
PAQN	0.2	103:54
AQN-NbCl ₅	0.2	65:40
PAQN	0.3	95:38
AQN-NbCl ₅	0.3	35:60

In order of increasing energy (Table 3). The values of ligand field parameters, Δ_1 , Δ_2 and Δ_3 , were calculated [18] using various energy level

diagrams. These are consistent with the values reported earlier for such complexes [19]. The Δ_1 value for Nb^{5+} complex is much higher than that observed for Mn^{2+} complex but is in accordance with those required for Nb^{5+} square planar complexes. The values of Δ_1 lie between those observed for cyanide ($\sim 30000\text{cm}^{-1}$) and chloride complexes ($\sim 19000\text{cm}^{-1}$) and are consistent with intermediate ligand field strength [18].



All these observations taken together with the wide range of coordination numbers ranging from 4 to 8 suggest that in these complexes zirconium exhibits a coordination number of 5 or 6.

However, it is known from the available data [20] that complexes belonging to d^0 , d^8 and d^{10} systems have trigonal bipyramidal configuration, and only a few have square pyramidal configuration. In view of these findings for the zirconium complexes, it may be suggested that these complexes may exist as trigonal bipyramidal structures.

3.5. 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 that 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 , the decomposition of the anhydrous species starts almost immediately after dehydration. The curves for all polymer complexes have similar patterns. After three stages of weight loss, the mass of the samples becomes constant above $530-700^\circ\text{C}$. The DTA curves exhibit several endo-

thermic 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 PAQNH 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 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 kg mol⁻¹, while $\Delta H = 52.0 \text{ kg mol}^{-1}$ (per H₂O released) for compound.

3.6 Kinetic of polymerization

The polymerization of (PAQNH) in the absence and in the presence of Mn(II), UO₂(II), Zr(IV) and Nb(V) 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. The conversion was calculated using the equation [17]:

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

Where W_{PC} is weight of the polymer complex and W_{IPC} 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 AQN-UO₂

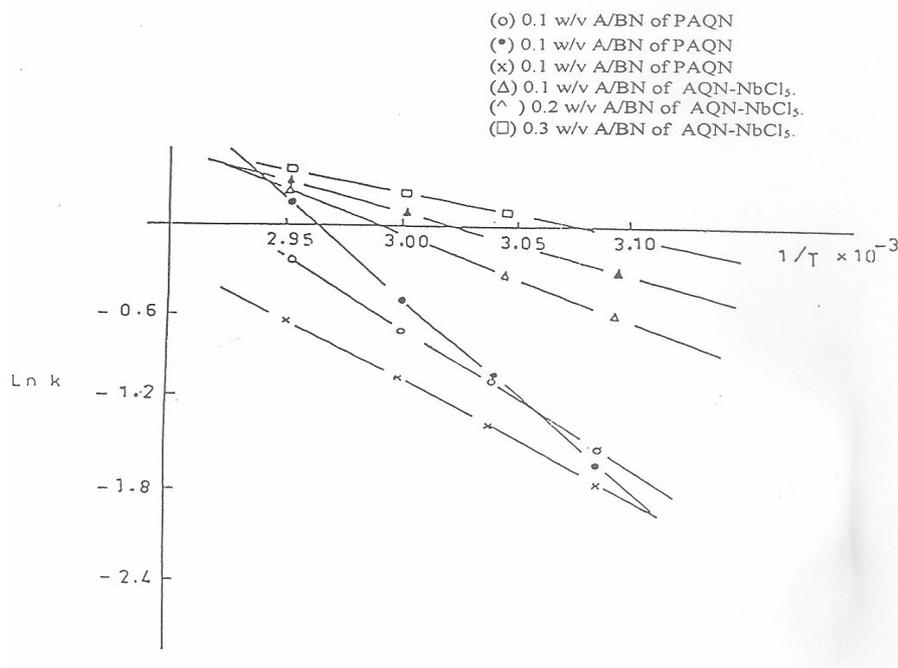


Figure 1. Arrhenius plot of the polymerization rate constant of PAQN homopolymer and AQN with NbCl₅ polymer complexes

The polymerization of AQNH in the presence of NbCl_5 was carried out at various temperature (60, 65, 70 and 75 °C) with different concentrations of initiator for various periods. Show the conversion percentage in the absence and in the presence of NbCl_5 at different concentration of initiator. The role of polymerization increases with rising temperature, the apparent activation energies (E_a) were determined [14] plots of \log (initial rate) versus $1/T$ were linear Fig. (1).

Table (3) gives the activation energies in the absence and in the presence of NbCl_5 . The activation energies for PANP are higher than for ANP- NbCl_5 polymer complexes and decrease with increasing AIBN initiator concentrations.

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 [17].

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