Synthesis and Thermal Studies of Poly(N-acryloyl,N'-cyanoacetohydrazide) Complexes with Co(II), Fe(III), and UO$_2$(II) Ions

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ABSTRACT: Polymer complexes with uranium, cobalt, and iron chlorides were synthesized and investigated by elemental analysis, electronic (uv–visible), IR vibration, and magnetic moment measurements. The thermal stabilities of N-acryloyl,N'-cyanoacetohydrazide (ACAH) homopolymers and polymer complexes of poly(ACAH) (PACAH) with metal chlorides were studied thermogravimetrically. The rates of polymerization of PACAH in the absence and presence of metal chlorides were studied. The activation energies of the degradation of the homopolymer and polymer complexes were calculated using the Arrhenius equation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3354–3358, 2003

Key words: synthesis; poly(N-acryloyl,N'-cyanoacetohydrazide); thermal analysis

INTRODUCTION

N-Acryloyl,N'-cyanoacetohydrazide (ACAH) has been synthesized as a new water-soluble chelating monomer. Its structure has been elucidated by both elemental and spectral analyses. This new monomer readily undergoes free-radical polymerization in both aqueous and nonaqueous media.[1]

Uranium has great importance in the nuclear field, because it represents the trivalent lanthanides and transuranic elements that are found in fusion products and cobalt and iron transition elements. They are also produced as corrosion products in nuclear fuel treatment. Ion exchange techniques are used to separate uranium from acidic nitrate solutions using phosphoric acid resins.

It was found that this resin showed better extraction for europium than sulfonic resins[2] and a mechanism proposed for stabilization of poly(vinyl chlroide) (PVC) using organometallic stabilizers. However, attempts to demonstrate the addition of ligands from the stabilizer to PVC molecules were not successful at first, and the theory did not find wide acceptance. Although recent evidence has been reported suggesting the presence of weak links in other polymers as in radical polymerization polystyrene, these bonds appear to be in the backbone chain. Poly(5-vinyl salicylidene)-2-aminophenol hompolymer and polymer complexes of 5-vinylsalicylidene-2-aminophenol with transition metal acetates have been prepared and characterized[3,4] by elemental analysis, IR and electronic spectroscopic, and magnetic moment measurements. The thermal stabilities of the polymer complexes were compared with the homopolymer, and the activation energies of degradation were calculated. Polymer metal complexes may have catalytic activities[1,3] and offer an excellent model for metalloenzymes.[11] Thermal analysis is a powerful tool, which is frequently used to evaluate the thermal stability of polymeric materials,[5] whereas spectral analyses (IR, NMR) can be useful to follow the thermal degradation reactions.

In the present work of homopolymer and polymer complexes of iron chlorides were characterized by elemental analysis, uv–visible (Uv–vis), IR, and magnetic moments measurements. The thermal stabilities of homopolymer and polymer complexes with metal salts were studied by means of thermogravimetric analysis (TGA). The activation energies of the degradation of the homopolymer and polymer complexes were calculated.

Consequently, it is of interest to investigate the thermal characteristics of poly(ACAA) (PACAH) as a new chelating polymer. Moreover, a comparison of the thermal behavior of PACAH with that of its metal complexes will certainly clarify the effect of the incorporation of metal ions in the polymeric chains on their thermal stability.

EXPERIMENTAL

Materials

The preparation of ACAH was as follows: N-cyanoacclohydrazide (Aldrich) was recrystallized from etha-

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nol (mp 99°C), dissolved in the smallest possible amount of distilled water, and cooled in an ice-salt bath to 3°C. A cold, equivalent portion of acryloyl chloride (Aldrich) was then added dropwise with stirring while maintaining the temperature below 5°C. A continuous stream of nitrogen gas was bubbled through the reaction medium. After complete addition of the acid chloride, the mixture was kept at 5°C for 30 min with occasional stirring until complete precipitation of the ACAH crystals,[1] which have the following structure:
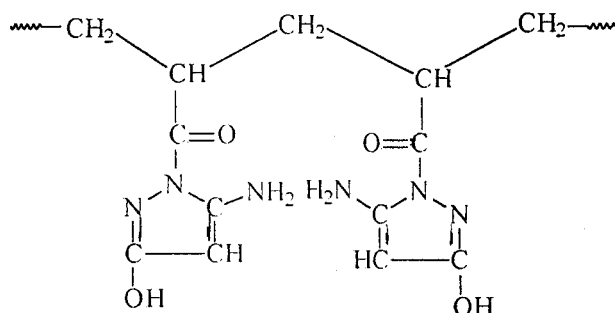
The fine white crystals of the monomer that were formed were filtered with a Buchner funnel, recrystallized from methanol, rinsed with diethyl ether, and dried in air (mp 195–197°C). The obtained product was confirmed as the monomer by ^{1}H-NMR (200 MHz, Varian), which can be interpreted only in terms of the suggested structure and FTR spectra (FT/IR-3 spectrometer, Nikon Bunko, Tokyo), which confirmed the proposed structure. Elemental analysis was also carried out in the central Microanalytical Unit, Cairo University. Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use (mp 104°C). Dimethylformamide (DMF, British Drug House) was purified by vacuum distillation just before use. Potassium persulfate, bisulfite, and the metal halides British Drug House were used without further purification.

Measurements

The UV spectral analysis was carried out using a Perkin–Elmer Lambda 3 spectrophotometer equipped with thermostatted cells. Viscosity measurements were carried out in an Ubbelohde suspended level dilution viscometer in DMF at 30°C. Thermal analyses were performed under nitrogen at a heating rate of 10°C/min. Differential thermal analysis and TGA data were obtained by using a DT-30 B thermal analyzer equipped with a MDM-20 (Shimadzu) sample container (Seisa Kusho Co., Kyoto, Japan).

ACAH homopolymer was prepared by reflux using DMF as a solvent and 0.1 (w/v) AIBN as an initiator for 6 h. The polymer was precipitated by pouring it in distilled water. The ACAH–UO_2Cl_2, ACAH–$CoCl_2$,

and ACAH–$FeCl_3$ polymer complexes were prepared by dissolving equimolecular amounts of the metal salts in DMF as a solvent and 0.1 (w/v) AIBN as an initiator.

The mixture was refluxed for 6 h and the resulting polymer complexes of metal salts were precipitated by pouring them into a large excess of distilled water containing diluted hydrochlroic acid to remove the metal salts incorporated in the polymer complexes. The polymer complexes were filtered, washed with water, dried in a vacuum oven at 40°C for several days, and weighed to determine the rate of polymerization. The metal contents were determined gravimetrically by complexometric titration of the metals with ethylenediaminetetraacetic acid (EDTA).

The IR spectra were recorded with a Perkin–Elmer model 257 spectrometer. The polymer samples were examined as KBr disks. Uv–vis spectroscopy, magnetic susceptibility measurements, and TGA are described.[6] TGA was also used for the determination of the rates of degradation of the homopolymer and polymer complexes in the initial stages of decomposition. The activation energies were obtained by application of the Arrhenius equation.[7]

RESULTS AND DISCUSSION

All the polymer complexes are intensely colored and air stable. The IR spectrum of the homopolymer shows a broad band at 3430–3500 cm^{-1} that is due to the stretching frequency of the phenolic and carbonyl, but a strong band at 1700 cm^{-1} is assigned to $\nu_{C=O}$ of the carbonyl group, beside additional absorption bands at 1410 and 1240 cm^{-1} that are due to the coupled ν_{C-O} and δ_{OH} in the plane frequency.[8] The strong band at 1620 cm^{-1} is due to $\nu_{C=N}$. The IR spectra of the polymer complexes show the presence of some new bands and shifts of the characteristic modes. The IR spectrum of ACAH uranyl chloride shows a change in the position of azomethine nitrogen and carboylate ion groups, indicating the involvement in coordination. The new bands at 909 and 820 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the uranyl entity.[9,10] In the electronic spectrum of the ACAH uranyl chloride polymer complex, there are bands at 390 and 450 nm that seem to be overlapped by the fairly strong homopolymer to metal charge transfer bands. This charge transfer transition probably occurs from the π orbitals of the homopolymer to the f orbitals of the uranyl.[11–14] Elemental analysis (Table I) and IR reveal that ACAH reacts with $UO_2(II)$ to form the following structure:
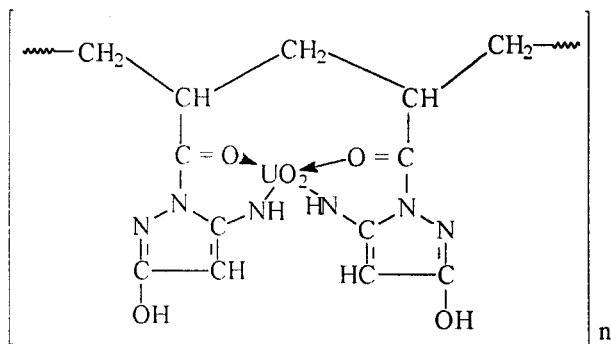
In the Co(II) polymer complex, the IR spectrum shows that the $\nu_{C=N}$ stretching vibration is located at 1595 cm^{-1} and the decrease in this frequency upon coordination indicates that the imino nitrogen is taking part in Co—N bond formation.[15,16] However, the reduction in this frequency is not large because of conjugation with the pyrazol ring.[8] The $\nu_{C=O}$ of the carboxylic group appears at 1650 cm^{-1} and the carbonyl band is located at 3330 cm^{-1}. The disappearance of ν_{NH2} and the appearance of ν_{sym} phenolic (C—O) at 1280 cm^{-1} indicate the involvement of phenolic oxygen in the bonding to the metal. The electronic spectrum of the Co(II) polymer complex shows bands at 640 and 430 nm that are due to $^3A_{2g} \rightarrow {}^3l_{1g}$ (f) and $^3A_{2g} \rightarrow {}^3l_{1g}$ (P) transitions, respectively. These data together with the magnetic moment listed in Table I indicate the square planar structure.[17–20] From the IR and elemental analysis, the possible structure of the product of the reaction of ACAH with CoCl$_2$ is as follows:
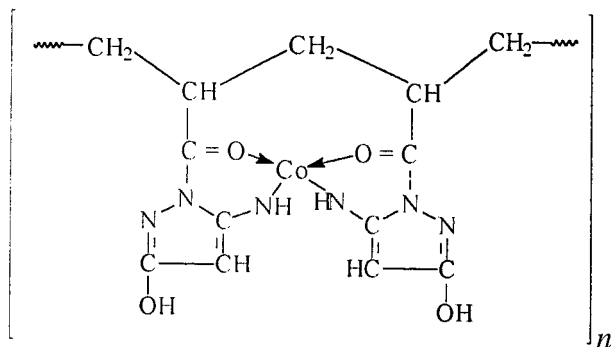
The IR spectrum of the ACAH–FeCl$_3$ polymer complex shows the disappearance of amino NH$_2$ groups. There is a shift in the CO frequency as observed at 1587 cm^{-1}. The spectral feature of the ACAH–FeCl$_3$ polymer complex indicates the involvement of phenolic oxygen, carbonyl, and azomethine groups in coordination. There is a new broad band that appears at 3500 cm^{-1} that is due to water molecules. The electronic spectrum of the ACAH–FeCl$_3$ polymer complex reveals two weak bands at 760 and 915 nm, which could be attributed to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. These spectral data are simi-

lar to those reported for square planar Fe(III) chelates.[21–23] The effective magnetic moment measured at room temperature was found to be 1.81 BM (Table I). The IR electronic spectral data and the elemental analysis indicate that FeCl$_3$ reacts with ACAH in a 1:1 metal–ligand molar ratio and the polychelates are of the following type:
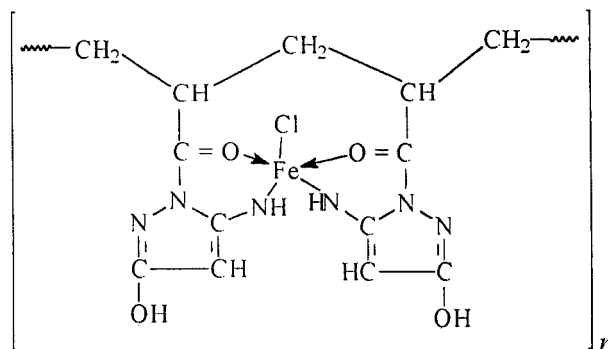
Thermal methods of analysis

The TG curves of ACAH–homopolymer and of polymer complexes of ACAH with UO$_2$(II), Fe(III), and Co(II) chlorides were determined. The results are similar to those obtained recently,[24,25] with the polychelates from poly(acrylamido-4-aminoantipyrinyl), poly-(2-acrylamido-benzoic acid), and poly(ethylene glycol), respectively. The stabilities of the polymer complexes increase in the order ACAH–UO$_2$Cl$_3$ > FeCl$_3$ > ACAH–CoCl$_3$ > ACAH–homopolymer. The greater stabilities of all the polymer complexes compared with the ACAH–homopolymer may be due to the formation of 6-membered ring structures. The ACAH–homopolymer degrades in two stages. The first starts at ~90°C with a weight loss of ~47% and

TABLE I
Microanalytical and Magnetic Data of PACAH Homopolymer and Polymer Complexes of ACAH with FeCl$_3$, CoCl$_3$, and UO$_2$Cl$_2$

| Polymer complex | Analysis (%) | | | | | μ_{eff} (BM) |
	C	H	N	Metal	MO[a]	
PACAH						
Calcd	71.91	4.87	5.24	—	—	—
Found	71.70	4.59	5.10			
ACAH–FeCl$_3$						
Calcd	55.47	3.75	4.04	18.34	22.91	1.81
Found	55.55	3.55	4.14	18.09		
ACAH–CoCl$_3$						
Calcd	44.47	3.24	3.24	13.60	16.92	0.37
Found	44.35	3.09	3.31	13.30		
ACAH–UO$_2$Cl$_2$						
Calcd	47.88	2.99	29.68	29.68	65.35	0.00
Found	47.59	2.86	30.96	30.96		

[a] From TGA.
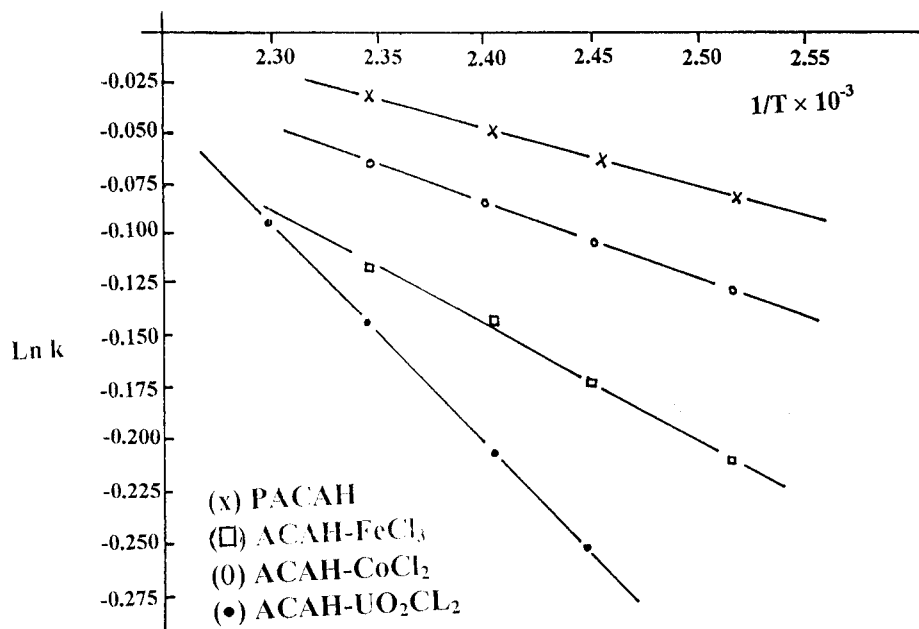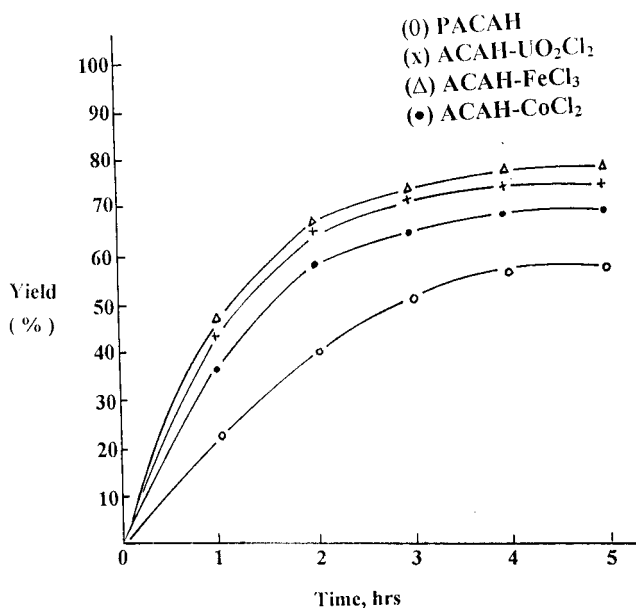
Figure 1 Arrhenius plots for the degradation of PACAH homopolymer and polymer complexes of ACAH with $FeCl_3$, $CoCl_2$, and UO_2Cl_2.

the second starts at ~150°C with a weight loss of 45%. In ACAH–$FeCl_3$ and ACAH–UO_2Cl_3 polymer complexes, there are two degradation steps. The first stage is at ~110, 120, and 150°C, respectively. There are three TG degradation stages for the ACAH–$CoCl_2$ polymer complex. The first, at ~105°C, is due to the loss of water molecules in the outer coordinated structure. The percentage weight losses and the maximum rate of weight loss of the polymer complexes were shown by derivative equipment associated with the TG apparatus. The final weight residue, which can be considered as metal oxides, are in good agreement with those calculated from the metal content using EDTA. Table I shows the residual weight percentage at 1000°C.

The effective activation energies[10] of the thermal degradation of the PACAH–homopolymer and the polymer complexes were determined from the temperature dependence of the rate of degradation. The activation energies are presented in Figure 1. It is clear that the activation energies are in same order as the stabilities.

Kinetics of polymerization

The polymerization of ACAH in the absence and presence of Fe(III) and UO_2(II) chlorides were carried out using 0.1, 0.2, and 0.3 (w/v) AIBN in DMF for various

Figure 2 The yield percentage versus the time of PACAH using 0.1 (w/v) AIBN in the absence and presence of metal chlorides.

TABLE II
Activation Energies of Thermal Degradation of PACAH Homopolymer and Polymer Complexes of ACAH with $FeCl_3$, $CoCl_2$, and UO_2Cl_2

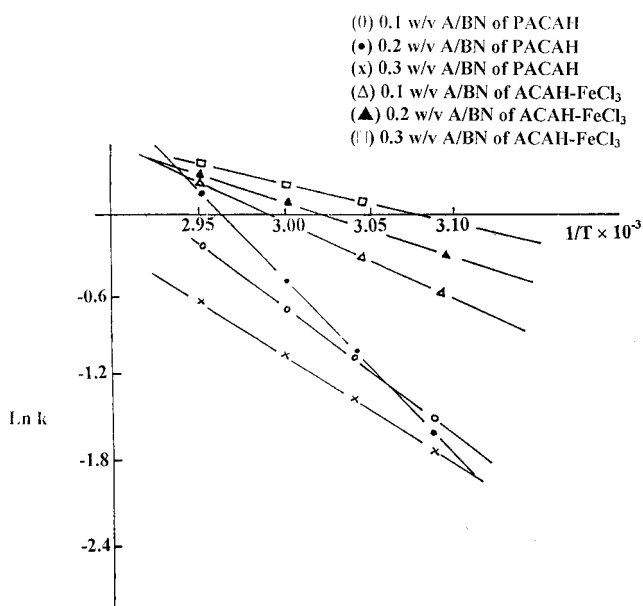| Polymer Complex	E_a (kJ mol^{-1})
PACAH	3.0
ACAH–$FeCl_3$	8.1
ACAH–$CoCl_2$	5.3
ACAH–UO_2Cl_2	18.8

periods. The conversion was calculated using the equation[26]

$$\text{conversion (\%)} = \frac{W_{PC} \times 100}{W_{TPC}}$$

where W_{PC} is the weight of the polymer complex and W_{TPC} is the total weight of the polymer complex according to the suggested structure. Figure 2 shows the conversion percentage of polymerization of ACAH in the absence and presence of metal chlorides using 0.1, 0.2, and 0.3 (w/v) AIBN initiator, respectively. The conversion increases with the increasing concentration of AIBN. The rate of polymerization increases as a result of the addition of metal chlorides in the order ACAH–UO$_2$Cl$_2$ > ACAH–CoCl$_2$ polymer complexes > PACAH–homopolymer. It seems that the addition products that are formed in the polymerization were active in increasing the rate of polymerization of ACAH in the presence of UO$_2$Cl$_2$, and FeCl$_3$.

To study the kinetics of polymerization in detail, the polymerization of ACAH in the presence of FeCl$_3$ was carried out at various temperatures (50, 55, 60, and 65°C) with different concentrations of initiator for various periods. The conversion percentage in the absence and presence of FeCl$_3$ at different concentrations of initiator was ascertained. The rate of polymerization increases with rising temperature. The apparent activation energies (E_a) were determined.[7] Plots of log (initial rate) versus $1/T$ were linear (Fig. 3). Table III gives the activa-

TABLE III
Apparent Activation Energy of Polymerization of (ACAH) Homopolymer and Polymer Complexes of ACAH with FeCl$_3$

Polymer	AIBN (w/v)	E_a (kJ mol^{-1})
PACAH	0.1	112.83
ACAH–FeCl$_3$	0.1	66.64
PACAH	0.2	105.67
ACAH–FeCl$_3$	0.2	45.69
PACAH	0.3	99.67
ACAH–FeCl$_3$	0.3	38.17

tion energies in the absence and presence of FeCl$_3$. The activation energies for PACAH are higher than for ACAH–FeCl$_3$ polymer complexes and decrease with increasing AIBN initiator concentrations.

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(□) 0.1 w/v A/BN of PACAH
(●) 0.2 w/v A/BN of PACAH
(x) 0.3 w/v A/BN of PACAH
(△) 0.1 w/v A/BN of ACAH-FeCl$_3$
(▲) 0.2 w/v A/BN of ACAH-FeCl$_3$
(○) 0.3 w/v A/BN of ACAH-FeCl$_3$

Figure 3 An Arrhenius plot of the polymerization rate constant of PACAH homopolymer and ACAH with FeCl$_3$ polymer complexes.