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POLYMER COMPLEXES. XVI[1]
Thermal stability of poly(5-vinylsalicylidene) aniline homopolymer and polymer complexes of 5-vinylsalicylidene aniline with some transition metal salts

M. A. Diab, A. Z. El-Sonbatil, A. A. El-Bindary and *A. A. Aggour*

UNIVERSITY OF MANSOURA,FACULTY OF SCIENCE, CHEMISTRY DEPARTMENT,
DEMIATTA, EGYPT

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Polymer complexes of 5-vinylsalicylidene aniline with some transition metal salts were prepared and characterised by elemental analyses, IR, electronic spectroscopy and magnetic moment measurements. Thermal stabilities of the polymer complexes were compared with poly(5-vinylsalicylidene) aniline homopolymer, and the order of stabilities of the complexes was given. The activation energies of the polymer complexes were calculated.

Polymer complexes have been given a great deal of attention in the last few years [1-3]; their structures and thermal stability have been of particular interest [4-6]. Recently, we dealt with polymer complexes derived from 5-vinyl salicylaldehyde and 5-vinyl salicylidene anthranilic acid with some transition metal salts [7, 8]. In the present investigation, polymer complexes of 5-vinylsalicylidene aniline with some transition metal salts were prepared and characterized. The thermal stabilities of the formed polymer complexes were studied and the activation energies of the degradation were calculated.

Experimental

Materials

Salicylaldehyde (Alderich Chemical Co., Inc.) was degassed and twice

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distilled on a vacuum line, dried over anhydrous sodium sulphate. Paraformaldehyde and aniline (Merck Chemical Co., Inc.) were used without further purification and 2,2'-azobisisobutyronitrile (AIBN) (Estman Kodak) was purified by dissolving in hot ethanol and filtering [9].

Preparation of 5-vinylsalicylidene aniline (VSA)

The monomeric VSA was prepared by chloromethylation of salicylaldehyde followed by formation of phosphenium salt which then reacts with aqueous formaldehyde to give 5-vinyl salicylaldehyde as described in our previous paper [7]. Equimolecular amount of 5-vinyl salicylaldehyde and aniline in ethanol was stirred for 24 hrs to give 5-vinylsalicylidene aniline monomer, (M. W. 223.26) (Cal., C, 80.72; H, 5.83; N, 6.28; Found, C, 80.63; H, 5.75, N, 6.18).

Preparation of the polymer complexes

Poly(5-vinylsalicylidene) aniline (PVSA) was prepared by reflux using dimethylformamide (DMF) as solvent and 0.1% w/v AIBN as initiator for 6 hrs. The polymer was precipitated by pouring in distilled water. Polymer complexes of VSA with copper chloride, copper bromide, copper acetate, nickel chloride, cobalt chloride, cadmium chloride, uranyl acetate and uranyl nitrate were prepared by dissolving equimolecular amounts of VSA and the metal salts in DMF as a solvent and 0.1% w/v AIBN as initiator. The mixture was refluxed for 6 hrs and the resulting polymer complexes of VSA-metal salt were precipitated by pouring them into a large excess of distilled water containing dilute hydrochloric acid to remove the metal salts incorporated in the polymer complexes. The polymer complexes were filtered, washed with water and dried in a vacuum oven at 40°C for several days. Metal contents in the polymer complexes were determined by complexometric titration after decomposition by aqua-ragia using ethylenediaminetetraacetic acid (EDTA) [10].

Characterization of the polymer complexes

Infra-red spectroscopy (IR)

Spectra were recorded using a Pye Unicam SP 2000 spectrophotometer in Nujol mull.

Visible-ultraviolet spectroscopy

Polymer samples were carried out in Nujol mull and the spectra were recorded using Varian 634 spectrophotometer.

The magnetic moments measurements were carried out at Alexandria University using Gouy balance and Hg[Co(SCN)]$_4$ as a calibrant.

Carbon, hydrogen and nitrogen content determination were performed by the Microanalytical Unit of Cairo University. The uranium content of the polymer complexes were determined by igniting a measured mass of the sample at 1000°C and weighing the residue as U_3O_8 [11].

Thermal methods of analysis

Thermogravimetry

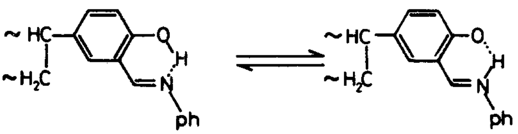
TG measurements were made with a Du Pont 950 thermobalance. 10 mg of the samples were heated at 10 deg/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10 mm x 5 mm x 2.5 mm deep, the temperature measuring thermocouple was placed within 1 mm of the holder .

TG was also used for the determination of 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.

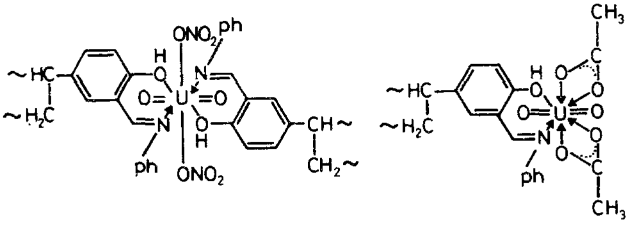
Results and discussion

Characterization of the polymer complexes

All the polymer complexes are intensely coloured and air stable. The IR spectrum of PVSA homopolymer shows a weak and broad band at 3200 cm^{-1} which may be assigned to hydrogen bonded OH or NH. The C = N stretching appears at 1620 cm^{-1}, while the phenolic C-O stretching vibration appears at 1290 cm^{-1}. It seems that PVSA could be presented on the following:

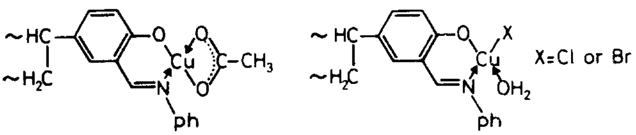


The IR spectra of VSA-uranyl acetate and VSA-uranyl nitrate polymer complexes show a broad bands in the region 3360-3350 cm^{-1} assignable to the absorption of ν_{OH} or ν_{NH} groups. The C = N stretching vibration shows shift indicating the involvement in the coordination. The band due to C-O stretching vibration was found at 1305 cm^{-1} suggesting that the hydroxyl group of the homopolymer has been taking part in complexes formation. The IR absorption due to UO_2 group for uranyl acetate and nitrate with VSA polymer complexes are observed at 930, 830 and 920, 855 cm^{-1} as sharp bands corresponding to the asymmetric stretching frequency ν_{asy} (U-O) and symmetric stretching frequency ν_{sym} (U-O), respectively. These observations indicate that the UO_2 moiety is virtually linear [12, 13]. The VSA-uranyl nitrate polymer complex show no strong absorption band near 1380 cm^{-1} indicating the absence of uncoordinated nitrate ion, but exhibit strong bands around 1525 and 1290 cm^{-1} assignable to the ν_1 (NO_2 symmetric stretching) and ν_4 (NO_2 asymmetric stretching) vibrations, respectively [14, 15]. Hence the nitrato group is coordinated as a unidentate [16]. In the VSA-uranyl acetate polymer complex, the two COO^- stretching bands, ν_{asy} and ν_{sym} were observed at about 1545 and 1405 cm^{-1} respectively, indicating that the acetate group is bidentate in the polymer complex [17]. The electronic spectra of VSA with uranyl acetate and uranyl nitrate polymer complexes exhibit a new band around 22222-24641 cm^{-1} assignable to UO_2^{2+} group which seems to be overlapped by the polymer to metal charge transfer bands [18, 19]. This charge transfer transition probably occurs from the π-orbital of the polymer to the f-orbital of the uranium. From IR, electronic spectra and the analytical data listed in Table 1, VSA reacts with uranyl nitrate in a 2:1 ratio and with uranyl acetate in a 1:1 ratio to form the following structures:



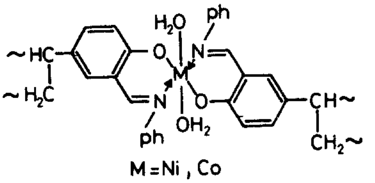
The IR spectra of VSA-$CuCl_2$, VSA-$CuBr_2$ and VSA-Cu acetate polymer complexes show formation of a strong broad band at 3250-3400 cm^{-1} which is attributable to the coordinated water. The phenolic C-O has been shifted of the order 5-15 cm^{-1} indicating its involvement in the complexation. The azomethine group has been shifted to a higher frequency in the polymer complexes and this may be ascribed to the increase in the bond order of the carbon to nitrogen link [20, 21]. The observation of two bands at 1590 and

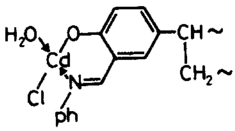
1440 cm^{-1} in VSA-Cu acetate polymer complex attributed to ν_{asy} and ν_{sym} of the acetate group. The great difference between those two bands indicates a bidentate nature for the acetate group. Bands at 445, 395 and 265 cm^{-1} are assigned to $\nu_{(M-O)}$ [22], ν_{M-N} [23] and ν_{M-Cl} [24] modes, respectively. The electronic spectra of VSA-Cu salts polymer complexes are characterized by broad bands with maxima in the 14400-13600 cm^{-1} range due to the $^2B_{1g} \rightarrow {}^2A_{ag}$ transition and a shoulder in the 21400-21600 cm^{-1} range, in a square planar configuration [25]. The band in the 25300-24850 cm^{-1} range may be due to a charge transfer, probably d-π^* [26]. The magnetic moment values listed in Table 1 can be taken as additional evidence of square planar configuration [27]. The IR, electronic spectra and elemental analyses data indicate that Cu(II) salts reacts with VSA monomer in a 1:1 molar ratio and the polychelate are of the types:



The IR spectra of VSA-NiCl$_2$, VSA-CoCl$_2$ and VSA-CdCl$_2$ polymer complexes have the characteristic features of coordination between the nitrogen atom of the azomethine since the band of this group is observed at 1635 cm^{-1} and the oxygen atom of the hydroxyl group. The disappearance of ν_{OH} and the appearance of ν_{C-O} at around 1330 cm^{-1} suggesting that the O-hydroxyl group has entered into the bond formation with the metals. Furthermore, the presence of an additional band in the region 860-635 cm^{-1} is assignable to coordinated water. The new bands in the region 460-445, 430-395 and at 275 cm^{-1} are attributed to $\nu_{(M-O)}$, $\nu_{(M-N)}$, and $\nu_{(M-Cl)}$ modes, respectively [22-24]. The electronic spectrum of VSA-NiCl$_2$ polymer complex shows two main absorption bands at 16260 and 10416 cm^{-1}, which are generally observed in high spin octahedral Ni(II) polymer complex and are assigned to the transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ respectively. Also, a weak band observed at 13513 cm^{-1} attributed to the spin-forbidden transition $^3A_{2g} \rightarrow {}^1E_g(D)$ [28]. The transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in the polymer complex is observed at 23255 cm^{-1}. Three bands are observed at 10256, 16390 and 18518 cm^{-1} in the electronic spectrum of VSA-CoCl$_2$ polymer complex and are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and

$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transition respectively, assuming octahedral coordinatin around Co ion [29]. The magnetic moments of VSA-$NiCl_2$ and VSA-$CoCl_2$ polymer complexes were found to be 3.5 and 5.2 B.M. supporting the octahedral structure. From IR, electronic spectra and elemental analyses presented in Table 1, VSA reacts with $NiCl_2$ and $CoCl_2$ in a 2:1 ratio and with $CdCl_2$ in a 1:1 ratio. The possible structure of VSA-$NiCl_2$, VSA-$CoCl_2$ and VSA-$CdCl_2$ polymer complexes are as follows:





Thermal analysis

TG curves of PVSA homopolymer and of polymer complexes of VSA with $CuCl_2$, $CuBr_2$, and Cu acetate are shown in Fig. 1 and with $NiCl_2$, $CoCl_2$, $CdCl_2$, uranyl acetate and uranyl nitrate are shown in Fig. 2. The

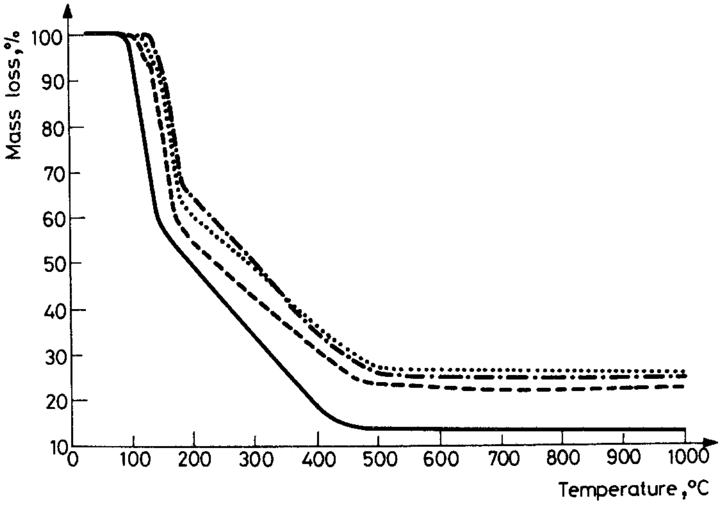


Fig. 1 TG curves of PVSA homopolymer and polymer complexes of VSA with $CuCl_2$, $CuBr_2$ and Cu acetate. (——) PVSA, (····) VSA-$CuCl_2$, (– – –) VSA-$CuBr_2$ and (–•–) VSA-Cu acetate

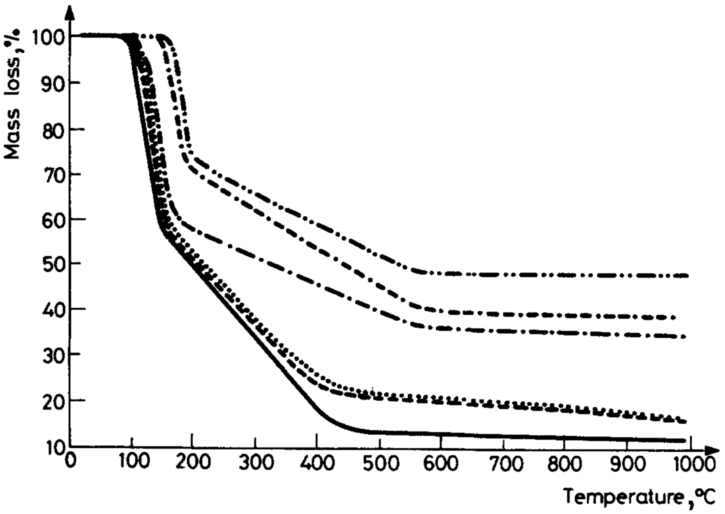


Fig. 2 TG curves of PVSA homopolymer and polymer complexes of VSA with $NiCl_2$, $CoCl_2$, $CdCl_2$, uranyl acetate and uranyl nitrate (——) PVSA, (– – –) VSA-$NiCl_2$, (·····) VSA-$CoCl_2$, (—·—) VSA-$CdCl_2$, (–·–·) VSA-uranyl acetate and (—··—) VSA-uranylnitrate

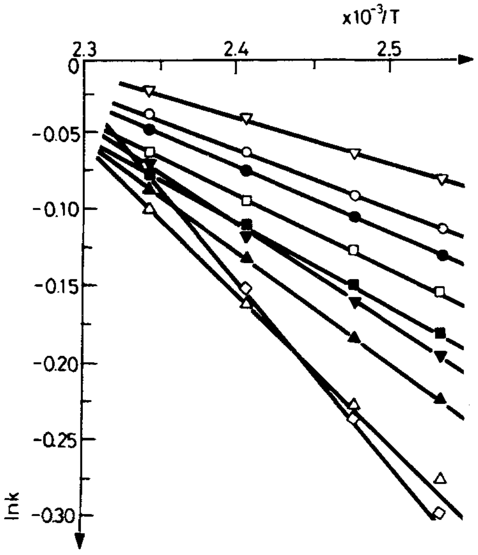


Fig. 3 Arrhenius plot of the thermal degradation rate constant of PVSA homopolymer and polymer complexes of VSA with $CuCl_2$, $CuBr_2$, Cu acetate, $NiCl_2$, $CoCl_2$, $CdCl_2$, uranyl acetate and uranyl nitrate (◇) PVSA, (△) VSA-$CuCl_2$, (▲) VSA-$CuBr_2$, (▼) VSA-Cu acetate, (■) VSA-$NiCl_2$, (□) VSA-$CoCl_2$, (●) VSA-$CdCl_2$, (○) VSA-uranyl acetate and (▽) VSA-uranyl nitrate polymer complexes

Table 1 Elemental analyses and magnetic moment of PVSA homopolymer and polymer complexes of VSA with $CuCl_2$, $CuBr_2$, Cu acetate, $CoCl_2$, $NiCl_2$, $CdCl_2$, uranyl acetate and uranyl nitrate

Polymer complex	Calculated/found, % C	H	N	X	M	MO*	μ_{eff}, B.M.
PVSA	80.72	5.83	6.28	–	–	–	–
	80.63	5.75	6.18				
VSA-$CuCl_2$	53.09	4.13	4.13	10.47	18.74		
	52.89	4.00	3.98	10.50	18.76	23.50	1.97
VSA-$CuBr_2$	46.93	3.65	3.65	20.86	16.57		
	46.86	3.55	3.56	20.89	16.59	20.74	1.80
VSA-Cu acetate	59.21	4.35	4.06	–	18.44		
	59.12	4.29	4.16		18.56	23.08	1.86
VSA-$NiCl_2$	66.82	5.20	5.20	–	10.90		
	66.68	5.11	5.22		10.82	13.90	3.50
VSA-$CoCl_2$	66.80	5.20	5.20	–	10.93		
	66.78	5.25	5.10		10.99	13.90	5.20
VSA-$CdCl_2$	46.40	3.61	3.61	–	28.98		
	46.32	3.55	3.65		28.79	33.11	0.00
VSA-uranyl acetate	37.32	3.11	2.29	–	38.95		
	37.22	3.00	2.31		39.01	45.93	0.00
VSA-uranyl nitrate	42.86	3.10	6.67	–	28.33		
	42.81	2.90	6.72		29.09	33.41	0.00

M = Metal, X = Cl or Br

* Residual weight percentage of the polymer complexes at 1000°C

Table 2 Weight loss percentage of PVSA homopolymer and polymer complexes of VSA with $CuCl_2$, $CuBr_2$, Cu acetate, $NiCl_2$, $CoCl_2$, $CdCl_2$, uranyl acetate and uranyl nitrate

Polymer complex	Volatilization	First stage		Second stage		Third stage	
	T, °C	T_{max}, °C	Wt. loss, %	T_{max}, °C	Wt. loss, %	T_{max}, °C	Wt. loss, %
PVSA	100	125	41	284	43	–	–
VSA-$CuCl_2$	130	135	7	195	33	355	35
VSA-$CuBr_2$	115	125	6	185	37	300	34
VSA-Cu acetate	145	180	32	320	53	–	–
VSA-$NiCl_2$	108	112	6	164	36	290	44
VSA-$CoCl_2$	110	114	6	169	37	296	43
VSA-$CdCl_2$	112	115	7	173	32	340	30
VSA-uranyl acetate	190	203	30	376	34	–	–
VSA-uranyl nitrate	195	210	26	398	26	–	–

polymer complexes are more stable than PVSA homopolymer. This is similar to the results obtained by Diab *et al.* [7, 8] with polymer complexes derived from 5-vinylsalicylaldehyde and 5-vinyl salicylidene anthranilic acid with some transition metal salts. The stabilities of the polymer complexes of VSA increase in the order uranyl nitrate > uranyl acetate > Cu acetate > $CuCl_2$ > $CuBr_2$ > $CdCl_2$ > $CoCl_2$ > $NiCl_2$ > PVSA homopolymer. The greater stabilities of the polymer complexes compared with PVSA homopolymer may be due to the formation of 6-membered ring structures. PVSA homopolymer degrades in two stages. The first starts at ~ 100° with a weight loss of ~ 41% and the second stage at ~160° with a weight loss of ~43%. There are three TG degradation stages for VSA-$NiCl_2$, VSA-$CoCl_2$, VSA-$CdCl_2$, VSA-$CuBr_2$ and VSA-$CuCl_2$ polymer complexes. The first stage is probably due to the loss of water molecules in the coordinated structures. In VSA-Cu acetate, VSA-uranyl acetate and VSA-uranyl nitrate polymer complexes, there are two degradation steps. Table 2 presents the percentage weight losses for each polymer complex and the maximum rate of weight loss shown by the derivative equipment associated with the TG apparatus. The final weight of residues, which can be considered as metal oxides, are in good agreement with those calculated from the metal content using EDTA. Table 2 shows the residual weight percentages at 1000°. The effective activation energies of the thermal degradation of PVSA and the polymer complexes were determined from the temperature dependence of the rate of degradation as shown in Fig. 3.

Table 3 Activation energies of the thermal dagradation of PVSA homopolymer and polymer complexes of VSA with $CuCl_2$, $CuBr_2$, Cu acetate, $NiCl_2$, $CoCl_2$, $CdCl_2$, uranyl acetate and uranil nitrate

Polymer complex	E_a, kJ mol^{-1}
PVSA	3.6
VSA-$CuCl_2$	12.2
VSA-$CuBr_2$	10.5
VSA-Cu acetate	16.2
VSA-$NiCl_2$	5.9
VSA-$CoCl_2$	7.8
VSA-$CdCl_2$	9.1
VSA-uranyl acetate	22.2
VSA-uranyl nitrate	26.5

The activation energies are presented in Table 3. It is that the activation energies are in the same order as the stabilities.

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Zusammenfassung — Polymerkomplexe von 5-Vinylsalizylidenanilin mit einigen Übergangsmetallsalzen wurden dargestellt und mittels Elementaranalyse, IR, Elektronenspektroskopie und magnetischen Momentmessungen charakterisiert. Die thermische Stabilität der Polymerkomplexe wurde mit der des Homopolymers Poly(5-Vinylsalizyliden)-anilin verglichen. Die Aktivierungsenergien der Polymerkomplexe wurden berechnet.