

THE THERMAL DECOMPOSITIONS OF SOME TRANSITION METAL ACRYLATES AND POLYACRYLATES

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The thermal behaviours of zinc, cobalt, nickel and copper acrylates and their polymers were investigated. It was found that the decompositions of these compounds are complex processes. The main decomposition of the monomer was preceded by thermal polymerization. The thermal effect of this reaction was greater for zinc acrylate than for the other salts. The reaction orders and activation energies of decomposition of the monomers and the polymers were calculated and the differences discussed.

In recent years metal-containing monomers and polymers have been subject to increasing interest. This is due to a number of valuable properties shown by coordination polymers and ionomers. The area of applications of such polymers is very broad and among their characteristic features are chemical resistance and thermal stability. Metal derivatives of polymers containing COOH groups are among the best known.

The thermal behaviours of some monovalent and divalent metal acrylates have been reported [1]. Monomers containing divalent transition metals may be especially interesting for the preparation of coordination polymers and ionomers. In the present paper, therefore the thermal decompositions of zinc(II), cobalt(II), nickel(II) and copper(II) acrylates and of their polymers were investigated and the results compared.

Experimental

Preparation of metal acrylates

Metal acrylates were prepared by the reaction of acrylic acid (5–10 wt.% stoichiometric excess) with zinc oxide, basic cobalt carbonate, basic nickel carbonate and cupric hydroxide, respectively, in toluene suspensions at 40–50°. The reactions were carried out for 5 h, with gradual addition of the reactants and with constant stirring. The evaporated toluene lost from the reaction vessel was constantly replaced. Water formed in the reactions was removed as an azeotropic mixture with toluene.

Zinc, copper and cobalt acrylates were washed with toluene and then dried in a vacuum drier at 40–50°.

Nickel acrylate, after a preliminary drying, was ground, washed with acetone and finally vacuum-dried like the other monomers.

The purities of Zn acrylate and Cu acrylate, determined by the contents of metal and of double bonds, were 99–100%, and those of Co acrylate and Ni acrylate were 94–95%.

Preparation of metal polyacrylates

Metal acrylates were polymerized in methanol solution at 60° under nitrogen with α,α' -azoisobutyronitrile (AIBN) as initiator. The reactions were performed in a four-neck flask, equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet. The processes were stopped by pouring the contents of the reaction flask into a 10-fold excess of cold methanol. The reaction products were washed several times with fresh portions of methanol and then dried in vacuum drier at 40–50°.

The physico-chemical properties, other than thermal ones, of the prepared metal acrylates and polyacrylates are the subject of a separate publication [2].

Thermal analysis

TG, DTG and DTA curves were recorded simultaneously using a Paulik-Paulik-Erdely derivatograph (Type OD-102, MOM, Budapest). 100 mg of powdered sample was heated in a Pt crucible (diameter = 9 mm) over the temperature range 25 to 500° at a constant heating rate of 3 deg/min. Controlled dynamic atmospheres of nitrogen or air (20 l/hr) were used in the furnace. Cu acrylate and poly(Cu acrylate) investigated in air atmosphere were diluted with Al_2O_3 (1:2).

Determination of reaction orders and activation energies of decomposition

The order of reaction, n was evaluated according to the Horowitz-Metzger method [3]. Then, the activation energy of decomposition for a given compound was determined by applying the appropriate H-M equation. For $n = 1$ a plot of $\log \log \frac{W_o - W_f}{W - W_f}$ against θ resulted in a straight line. The activation energy E was calculated from its slope, which was equal to $E/2.303 RT_s^2$. For $n \neq 1$ a plot of

$\log \left[\frac{1 - \left(\frac{W - W_f}{W_o - W_f} \right)^{1-n}}{1-n} \right]$ vs. θ was drawn and a straight line of the same slope as in the previous case was obtained.

The reaction order determined by the H-M method was also used in the treatment of the same data by the Coats-Redfern method [4]. In all cases straight lines were obtained, thus confirming the correctness of n . For $n = 1$ a straight line with slope

$E/2.303 R$ was obtained from a plot of $-\log \left[\frac{-\ln \frac{W-W_f}{W_o-W_f}}{T^2} \right]$ vs. $1/T$. For $n \neq 1$ a

plot of $-\log \left[\frac{1 - \left(\frac{W-W_f}{W_o-W_f} \right)^{1-n}}{(1-n) T^2} \right]$ vs. $1/T$ resulted in a straight line of the same slope,

from which the activation energy E was calculated.

Results and discussion

Thermal behaviour of metal acrylates

Figure 1 shows the thermal curves of zinc acrylate and copper acrylate as examples of the four investigated metal acrylates. Characteristic features of the thermal behaviour of the monomers are given in Table 1.

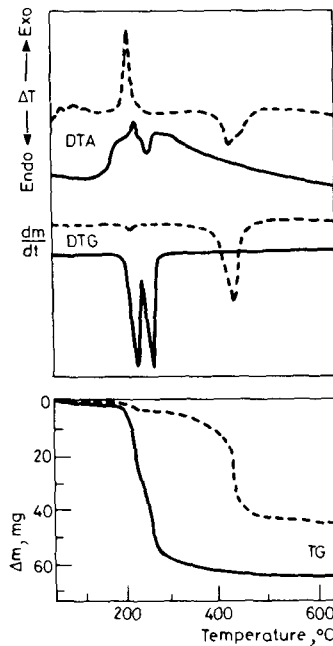


Fig. 1 TG, DTG and DTA curves of Zn acrylate (---) and Cu acrylate (—) in nitrogen

Table 1 Thermal behaviour data for Zn, Co, Ni and Cu acrylates in nitrogen

Compound	DTG		TG		DTA		Process
	Peak temp., °C	Temp. range, °C	Wt.% loss for a given stage*	Total wt.% loss in the range 25–500 °C	Peak temp., °C	Temp. range, °C	
Zn acrylate		<180	0.5				
	218	185–250	2.5	42	220	180–265	polymn. decomp.
	436	310–500	38		433	380–490	
Co acrylate		<130	1.0				
	163	130–180	6.0	55.5	165	135–175	dehydr.
	42				270	230–320	polymn.
Ni acrylate		<110	3.0				
	155	100–190	3.5	57.5	140	100–180	dehydr.
	327	260–400	48.5		290	250–320	polymn.
Cu acrylate		<180	0.5				
	235	180–243	28.5	61.5	237	205–242	dec. + polymn. decomp.
	263	243–275	25.5		265	242–275	

*The wt.% loss for a given stage of decomposition corresponds to range of temperatures read off the DTG curve.

The TG, DTG and DTA curves show the occurrence of three processes: dehydration, thermal polymerization and decomposition.

Zn acrylate and Cu acrylate lose 0.5% of their weight in the range 25–180°, which indicates the presence of only trace amounts of water. In the same temperature range Co and Ni acrylates lose ca. 6–7% of their weight. This is equivalent to 2/3 mole of water per mole of salt. These results agree very well with the purity determinations as well as with the IR spectra [2] of the compounds. Co acrylate loses water in essentially one step, whereas Ni acrylate does so in a two-stage process.

Exothermic peaks in the DTA curves show that the thermal polymerization of Zn, Co, Ni and Cu acrylates takes place at ca. 220, 270, 290 and 235°, respectively. The heights and widths of the peaks suggest that Co, Ni and Cu acrylates polymerize less easily than Zn acrylate. Both thermal and free-radical polymerizations of the monomers in methanol solutions in fact demonstrated the higher reactivity of the carbon-carbon double bonds in Zn acrylate than in Co and Ni acrylates, and a very poor reactivity of Cu acrylate [2].

The exothermic peak at 235^o, assigned to the polymerization of Cu acrylate, coincides with the first step of decomposition. This exothermic effect may therefore result from the overlapping of complex exothermic and endothermic processes.

The second decomposition step for Cu acrylate, at 265^o, is accompanied by an endothermic effect, as in the decompositions of the other three monomers.

Decomposition residues

The final products of decomposition were not identified, but considerable amounts of carbon were observed in the residues. The formation of crack-carbon often takes place when thermal decomposition is performed in a non-oxidizing atmosphere [5-7] and sometimes even in air [1].

It follows from the literature [5,8,9] that Zn acrylate in nitrogen decomposes to zinc oxide, and the other three acrylates to the metals. The stream of nitrogen passing through the furnace favours [9] the formation of only one final product, the metal or the metal oxide, and not their mixture.

Table 2 gives the molar ratios of stable residues to carbon, calculated from experimental and theoretical weight losses for the investigated acrylates.

Table 2 Decomposition residues calculated from experimental weight losses for assumed final stable products

Compound	Assumed final stable residue	Experimental total weight loss at 500 ^o for 100 mg sample, mg	Theoretical weight loss on complete decomp. of 100 mg sample to metal oxide or metal, mg	Molar ratio of stable decomp. residue to carbon in decomposed acrylates
Zn acrylate	ZnO	42.0	60.8	ZnO:3.25C
Co acrylate · $\frac{2}{3}$ H ₂ O	Co	55.5	72.3	Co:2.98C
Ni acrylate · $\frac{2}{3}$ H ₂ O	Ni	57.5	72.4	Ni:2.64C
Cu acrylate	Cu	61.5	69.1	Cu:1.30C

Thermal behaviour of metal polyacrylates

The DTA curves of the polymers do not exhibit exothermic effects assigned to thermal polymerization of the respective acrylates. The TG, DTG and DTA curves (Fig. 2) show the very similar nature of the thermal decompositions of poly(Zn acrylate), poly(Co acrylate) and poly(Ni acrylate). In Table 3 the changes observed in the curves are interpreted.

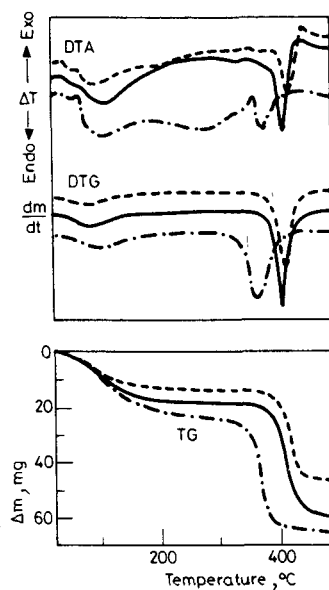


Fig. 2 TG, DTG and DTA curves of poly(Zn acrylate) (---), poly(Co acrylate) (—) and poly(Ni acrylate) (-.-.-) in nitrogen

Table 3 Thermal decomposition data on poly(Zn acrylate), poly(Co acrylate) and poly(Ni acrylate) in nitrogen

Compound	Process	DTG		TG		DTA	
		Peak temp., °C	Temp. range, °C	Wt.% loss for a given stage*	Total wt.% loss in the range 25–500 °C	Peak temp., °C	Temp. range, °C
poly(Zn acr.)	loss of CH ₃ OH decomp.	84	<210	14.5	51.5	90	<210
		418	360–460	35.0		416	397–440
poly(Co acr.)	loss of CH ₃ OH decomp.	96	<210	18.0	60.5	110	<210
		410	370–480	39.4		413	403–450
poly(Ni acr.)	loss of CH ₃ OH decomp.	93	<210	22.0	65.5	102	<210
		368	300–415	40.0		374	360–415

*The wt.% loss for a given stage of decomposition corresponds to the range of temperatures read off the DTG curve.

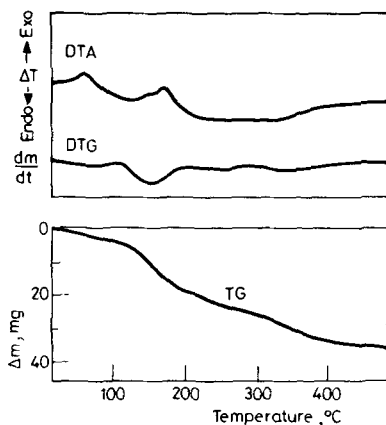


Fig. 3 TG, DTG and DTA curves of poly(Cu acrylate) in nitrogen

The first endothermic peak and a weight loss up to ca. 210^o are attributed to the removal of methanol occluded in the polymers. The second endothermic peak and a weight loss at ca. 400^o are related to the essential decomposition of the polysalts.

The molar ratios of the stable residues and carbon calculated for the three polyacrylates are ZnO:2.99C, Co:3.07C and Ni:2.51C, which are very similar to those obtained for the monomers.

Figure 3 reveals that poly(Cu acrylate) decomposes in a complex multi-step manner, differently than the other three polysalts. The decomposition extends over a wide temperature range, with relatively small weight losses for successive stages. Only in the range 130–180^o does a pronounced weight loss occur (14.5 wt.%). The total weight loss of poly(Cu acrylate) at 500^o (42 wt.%) is the lowest observed for the investigated polysalts, and contrasts with the highest weight loss for Cu acrylate among the monomers.

Thermal decompositions of Cu acrylate and poly(Cu acrylate) in air

In order to gain additional information concerning the thermal behaviour of the cupric compounds, their decomposition patterns were also studied in air.

The TG curve (Fig. 4) shows that Cu acrylate heated in air decomposes in the range 180–265^o, with a maximum at 215^o. The weight loss in this exothermic stage (62 wt.%) indicates almost complete decomposition of the sample to CuO. The DTA and DTG curves show the complex nature of the decomposition process.

The exothermic decomposition of poly(Cu acrylate) takes place in two major steps (Fig. 4). The first is observed at 170–240^o with a maximum at 200^o and a weight loss of 17 wt.%, and the second at 280–355^o with a maximum at 310^o and a weight loss

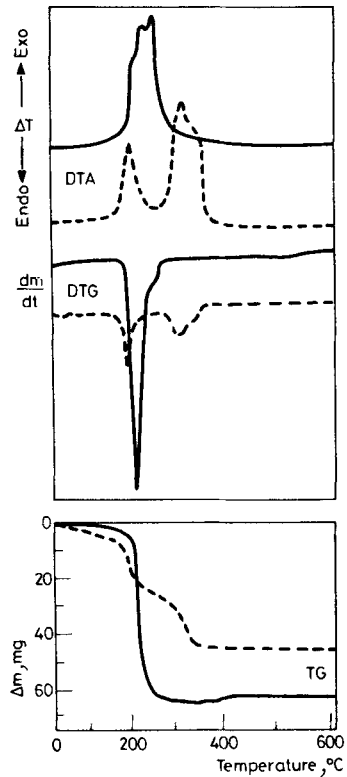


Fig. 4 TG, DTG and DTA curves of Cu acrylate (—) and poly(Cu acrylate) (- - -) in air (100 mg sample diluted with 200 mg Al_2O_3)

of 17 wt.%. The total weight loss in the range 25–500° is 45 wt.%. In comparison with Cu acrylate, a wider range of decomposition temperature and a smaller total weight loss of poly(Cu acrylate) are observed, similarly as in a nitrogen atmosphere.

Thermal stability sequence of metal acrylates and polyacrylates

The values of the peak temperatures of the decomposition processes show that the investigated metal acrylates and polyacrylates follow the following thermal stability sequence: $\text{Zn} > \text{Co} > \text{Ni} > \text{Cu}$. This is similar to the thermal stability sequence for the oxalates [10,11] and formates [11] of the same metals, but just opposite to the general stability sequence for divalent metal chelates, the Irving-Williams series [12]. The poor thermal stability of some other copper compounds has also been found [5,11,13,14].

The cations present in the salts were considered as elementary catalysts of the thermal decomposition processes. Their catalytic efficiencies related to the heat of cation formation give a sequence just the reverse of that for the thermal stabilities [11].

The thermal stability of complex compounds has been discussed in terms of the modification exerted by coordinate bonds on the electronic structure of the neighbouring bonds, with resulting changes in their stability [15,16]. The results of thermal stability studies on polyesters cross-linked with various metal ions [17] are in agreement with this conception.

Kinetics of decomposition

The data in Tables 1 and 3 show that the main decomposition processes of Zn, Co and Ni polyacrylates begin at temperatures several tens of degrees higher, and occur over narrower ranges of temperatures, than those for the respective monomers. This may indicate that the decomposition of these polysalts is connected with an increase in the activation energies.

For quantitative comparisons, the reaction orders and activation energies of decomposition of the compounds were calculated. Typical plots showing the application of the Horowitz-Metzger and Coats-Redfern equations are given in Figs 5 and 6, respectively. From the slopes of the straight lines the values of E were calculated and the results are given in Table 4. The specific character of the decomposition of poly(Cu acrylate) in nitrogen precluded the calculations for this compound.

The activation energies determined by the Horowitz-Metzger method are always higher than those obtained by the Coats-Redfern method for the same initial data. However, the results agree within the limits of error.

It is seen from Table 4 that the activation energy of the main decomposition is in almost all cases higher for the polymer than for the monomer acrylates, while the reaction order does not change. The observed differences are especially distinct for the zinc and cobalt compounds. It would seem that the loss of ca. 15–20 wt.% caused by the evaporation of methanol, anticipating the degradation of the polymers, cannot in itself explain such an appreciable and systematic increase in the E values of the polymers in comparison with those of the corresponding monomers.

It was found that the samples of poly(Zn acrylate), poly(Co acrylate) and poly(Ni acrylate) contained 9%, 15% and 27% of unreacted double bonds, respectively. This means that during the polymerization reactions of these divinyl monomers, in almost all cases both their double bonds reacted, leading to the formation of cross-linked, three-dimensional products. This is supported by the insolubility of the obtained polyacrylates in water and methanol, which are solvents for the monomers. Besides these cross-links, an additional cross-linking effect may result from ionic interactions between metal cations and carboxylate anions of different polymeric chains. The cross-linking densities of these three polysalts should change in the order: poly(Zn acrylate) > poly(Co acrylate) > poly(Ni acrylate), the reverse of their content of

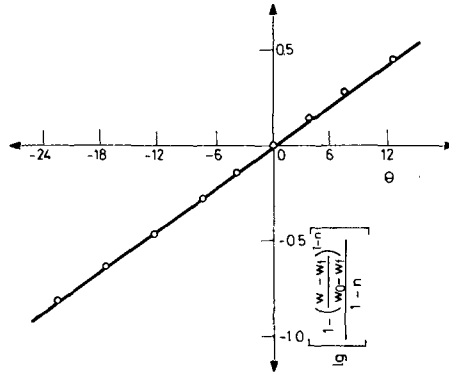


Fig. 5 Horowitz-Metzger plot for poly(Ni acrylate)

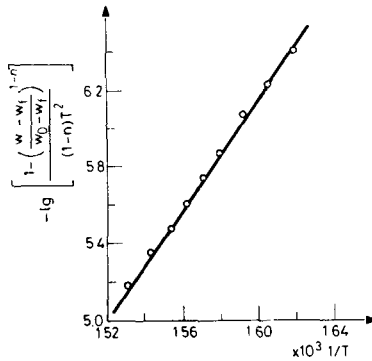


Fig. 6 Coats-Redfern plot for poly(Ni acrylate)

unreacted double bonds. The very low polymerizability of Cu acrylate and the lack of a marked loss of occluded methanol from the sample of poly(Cu acrylate) may suggest the lowest cross-linking density in that polysalt. Thus, the increase of E in these polymers correlates with the cross-linking density of the samples. A high cross-linking density can hinder the diffusion of the gaseous decomposition products out of the solid, which may be the rate-determining step of the reaction. This relates the structural features of the samples with the kinetics of decomposition. The calculated E values, higher than the energy of random rupture of carbon-carbon bonds (277 kJ/mole) [18], confirm the influence of factors other than the strength of the bonds to be broken.

Both the activation energy and the temperature of decomposition of poly(Cu acrylate) in air are lower than those for Cu acrylate. However, the sequence of

Table 4 Reaction orders and activation energies of thermal decomposition of the compounds in nitrogen

Compound	Stage of decomp.	Order of reaction	Energy of activation, kJ/mol	
			Horowitz-Metzger method	Coats-Redfern method
Zn acrylate	main	1	242	236
Co acrylate main	main	3/2	210	201
Ni acrylate	main	3/2	245	242
Cu acrylate	1	1/3	212	209
	2	1/2	289	284
Cu acrylate*	main	3	397	391
poly(Zn acr.)	main	1	390	377
poly(Co acr.)	main	3/2	356	345
poly(Ni acr.)	main	3/2	287	280
poly(Cu acr.)*	1	3/2	141	137
	2	3	287	284

*in air

increasing E values for all the investigated compounds does not correlate with their thermal stability sequence. The temperature sequence of increasing thermal stability may not coincide with the sequence of increasing activation energy values, since it can also depend on the value of the activation entropy [19]. The lack of such a correlation has been observed in the dehydration reactions of EDTA chelates of a number of metal ions [19], and also in the dehydration and decomposition reactions of mixtures of zinc and copper oxalates [20].

Conclusions

The TG, DTG and DTA curves of Zn acrylate and Cu acrylate show the occurrence of thermal polymerization and decomposition reactions, while those of Co acrylate and Ni acrylate additionally reveal dehydration processes.

The exothermic effect of thermal polymerization for Zn acrylate is the most distinct.

The polymerization of Cu acrylate coincides with the first step of decomposition.

The activation energies of decomposition for the polymers containing Zn, Co and Ni are higher than those for the respective monomers. For the cupric compounds it is the other way round.

The E values of the polysalts correlate with the probable cross-linking densities of the samples.

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Zusammenfassung — Das thermische Verhalten der Acrylate von Zink, Kobalt, Nickel und Kupfer und das der entsprechenden Polymere wurde untersucht. Es wurde festgestellt, dass die Zersetzung dieser Verbindungen komplexe Prozesse sind. Der Zersetzung der Monomeren ging eine thermische Polymerisation voraus. Der thermische Effekt dieser Reaktion war im Falle des Zinkacrylats grösser als bei den anderen Salzen. Die Reaktionsordnungen und Aktivierungsenergien der Zersetzung der Monomeren und Polymeren wurden berechnet und die Unterschiede diskutiert.

Резюме — Исследовано термическое поведение акрилатов цинка, кобальта, никеля и меди, а также их полимеров. Установлено, что разложение этих соединений представляет собой сложный процесс. Разложению мономеров предшествует термическая полимеризация. Термический эффект этой реакции для акрилата цинка был больше, чем для других солей. Были вычислены порядок реакции и энергии активации реакции разложения мономеров и полимеров и обсуждены их различия.