

THERMAL DECOMPOSITIONS OF SOME TRANSITION METAL POLYACRYLATES

*J. Skupińska, H. Wilczura and H. Boniuk**

DEPARTMENT OF CHEMISTRY, WARSAW UNIVERSITY,
02-093 WARSZAWA, UL. PASTEURA 1, POLAND

*DEPARTMENT OF CHEMISTRY, TECHNICAL UNIVERSITY,
00 662 WARSZAWA, UL. KOSZYKOWA 75, POLAND

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Polyacrylates of Fe, Cr, Ni, Co and Mn were synthesized by the reaction of poly(sodium)acrylate with metal halides. The salts obtained were investigated by thermal analysis. During heating in argon or air, all the salts behaved in a similar way. The initial decomposition temperature of the investigated salts increased in the following sequence: Fe < Cr < Ni < Co < Mn. The solid residues of the decompositions of the salts were also analysed.

Polymers containing metals are known as semiconductors, and thermal and chemical resistance materials. Therefore, one type of such polymers containing COOH groups are intensively investigated and the thermal behaviour of some divalent metal polyacrylates [1], alkali metal polyacrylates [2] and metal polyesters [3] has been reported. In this paper we present results on the thermal decompositions of iron(III), chromium(III), nickel(II), cobalt(II) and manganese(II) polyacrylates.

Experimental

The Fe, Cr, Ni, Co and Mn polyacrylates were prepared by reacting the metal halides with poly(sodium)acrylate as follows. Polyacrylic acid (PAA) was prepared by the general method described in [4]. About 2.5 g of PAA was dissolved in 200 ml of H₂O. During vigorous mixing, an equivalent amount of sodium hydroxide was added in 100 ml of H₂O. After 1 hr, when sodium salt formation was finished, the appropriate metal halide solution (2-fold excess relative to the carboxylic groups) was introduced and a coloured precipitate was deposited. The precipitates were next washed three times with water, dried under vacuum (1 Torr) and stored over P₂O₅.

Thermal analysis

TG, DTG and DTA curves were recorded simultaneously with a derivatograph (MOM, Budapest). 100 mg of powdered sample was heated in a ceramic crucible in the temperature range 20 to 900° at a constant heating rate of 10 deg/min in air or argon (15 l/h).

IR spectra

IR spectra were recorded with a SPECORD-75 (Carl Zeiss, Jena) spectrophotometer, using KBr pellets.

XRD

X-ray diffraction investigations were performed on a DRON-2 (USSR) diffractometer, using FeK_α radiation.

Results and discussion

The compositions of the metal polymers obtained were determined by elemental analysis and via the TG curves. The solid residues remaining after thermal decomposition were also analysed for every sample. Besides determination of the percentages of carbon and hydrogen, these results allowed calculation of the ratios of carboxylic groups to metal and of water to metal. The results are presented in Table 1. The amounts of carbon were determined by elemental analysis and from the TG curves. The values found by the two methods agreed for the Ni, Co and Mn

Table 1 Elementary analysis of polyacrylates

Compound	Found (calcd.), %		mmol COOH	mmol H ₂ O
	C	H	mmol M	mmol M
Pa Fe	26.56 (34.64)	3.83	2.8	2.1
PA Cr	31.91 (34.93)	4.69	3.7	3.4
PA Ni	27.94 (28.40)	5.3	2.5	4.2
PA Co	29.47 (28.36)	5.02	2.6	4.8
PA Mn	31.48 (32.17)	4.34	2.9	3.7

salts. For the Fe and Cr samples, the carbon content determined by TG was greater than that determined by elemental analysis. The COOH/metal ratio varied from 2.6 to 3.7 and was always larger than the real metal valency. This means that not all the carboxylic groups of PAA had reacted with metal. The H₂O/metal ratio varied from 2.1 for the Fe salt to 4.8 for the Co salt (3.4, 4.2 and 3.7 for the Cr, Ni and Mn salts, respectively).

IR spectra

Powdered metal polyacrylates pressed in KBr pellets were investigated by IR. The bands in the region 2000–1100 cm⁻¹ of the obtained spectra are presented in Table 2. The bands in the range 1440–1390 cm⁻¹ belong to asymmetric stretches of the O—C—O grouping, and the bands at 1700 cm⁻¹ to stretches of the carboxylic groups of pure PAA [5]. By analogy with the ruthenium salts [6], the bands at 1535–1545 cm⁻¹ and 1600–1610 cm⁻¹ may be attributed to complexed and free carbonyl groups, respectively, in the polyacid salts. The band at 1700 cm⁻¹ in all spectra indicates that about 20% of the carboxylic groups of the investigated polymers are unreacted. This supports the conclusion drawn from the elemental analysis and TG curves. The band at 1545 cm⁻¹ in all the IR spectra indicates that in all these polymers the metal ions are bonded to the polymer via the oxygen anions and the carbonyl oxygen of the carboxylic groups. However, the bands at ~1600 cm⁻¹ (characteristic of uncomplexed carbonyls of salt groupings) in the spectra of the Ni, Co and Mn polyacrylates reveal that some of the carboxylic groups are bonded only via the oxygen anion in these polymers. The most probable structures for the Fe and Cr polyacrylates are octahedra in which the metal ions are surrounded by three [7] carboxylic groups. Three sites are occupied by oxygen anions and three by carbonyl oxygens of the carboxylic groups. Such a situation is to be expected for the Fe and Cr polyacrylates, as their IR spectra do not contain the 1610 cm⁻¹ bands.

Table 2 IR bands at the range 2000–1200 cm⁻¹ of polyacrylates

Compound	C=O acid, cm ⁻¹	C=O salt, cm ⁻¹	OCO cm ⁻¹
PA Cr	1700w	1545s	1445w 1410m
PA Ni	1700w	1610m 1545s	1445w 1400m
PA Fe	1700w	1540s	1445w 1395m
PA Co	1700w	1600m 1540s	1440w 1390m
PA Mn	1700w	1600m 1535s	1445w 1390m

s = strong, m = middle, w = weak

For the Ni, Co and Mn polyacrylates, where the $H_2O/metal$ ratio is higher, at ~ 4 , the IR spectra show the bands of uncomplexed carbonyls. Besides the structures mentioned for the Cr and Fe polyacrylates it may be presumed that a large proportion of complexes are present where the metal ions are bonded to the polymer chains only via the oxygen anions of the carboxylic groups, the remaining sites being occupied by water molecules. This explains the higher $H_2O/metal$ ratio for these polysalts. The bands of the carboxylic groups of the salt at $\sim 1600\text{ cm}^{-1}$, and mainly the bands at $\sim 1540\text{ cm}^{-1}$ relating to complexed carbonyls, exhibit the following wavelength sequence: $Cr = Ni < Fe = Co < Mn$; this is connected with the increasing strenght of the metal ion—oxygen bonds. In the investigated polyacrylates, this bond is strongest for the manganese system.

Thermal behaviour of metal polyacrylates

The TG, DTG and DTA curves of the investigated polymers were recorded in the range $20\text{--}900^\circ$ in argon and air. The results are presented in Tables 3 and 4 in Figs 1 and 2. During heating, all these polyacrylates gave almost the same weight changes and DTA curves. This proves that the transformations occurring during heating are

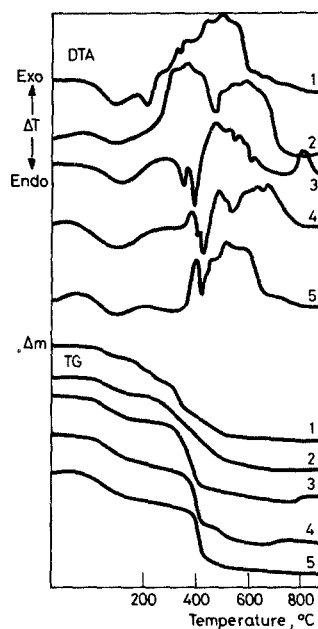


Fig. 1 DTA and TG curves of poly(Fe acrylate)-1, poly(Cr acrylate)-2, poly(Ni acrylate)-3, poly(Co acrylate)-4, poly(Mn acrylate)-5 in air

Table 3 DTA, DTG, TG of the polyacrylates decomposition in air

Compound	I step*				II step				III step				Total wt. loss, %
	Temp. range, °C	Wt. loss, %	Peak DTA, °C	Peak DTG, °C	Temp. range, °C	Wt. loss, %	Peak DTA, °C	Peak DTG, °C	Temp. range, °C	Wt. loss, %	Peak DTA, °C	Peak DTG, °C	
PA Fe	80-215	13.3	140	120	215-400	36.7	250	235	630-860	1.0	—	—	72.9
							300	293					
							377	376					
PA Cr	70-280 (70-220)	21.1 (17.6)	140	120	400-630	22.9	546	475					80.0
							398	305	700-860	—	—	—	
							505	470					
PA Ni	70-340 (70-240)	27.0 (24.0)	150	120	340-480	42.0	395	395	820-860	+3.4	860	855	78.0
							432	423					
							535	—					
PA Co	50-370 (50-200)	26.0 (26.0)	140	120	370-490	42.0	428	—	720-860	+3.5	750	750	79.6
							460	449					
							530	—					
PA Mn	60-370 (60-220)	27.1 (20.1)	150	127	380-480	38.3	420	—	660-860	2.0	—	—	77.7
							440	439					
							523	—					
					595	—							

* in brackets the temperature range and wt.% loss connected with water evolution is given.

Table 4 DTA, DTG, TG of the polyacrylates decomposition in argon

Compound	I step*			II step			III step			Total wt. loss, %	
	Temp. range, °C	Wt. loss, %	Peak DTA, °C	Peak DTG, °C	Temp. range, °C	Wt. loss, %	Peak DTA, °C	Peak DTG, °C	Temp. range, °C		Wt. loss, %
PA Fe	80-210	12.5	160	140	220-360	16.7	260	240	720-860	3.7	67.9
								300			
					360-420	21.4	395	410			
					420-720	13.0	705	660			
PA Cr	70-320 (70-210)	19.0 (16.0)	140	120	320-560	43.0	415	400	560-860	4.0	66.0
							500	460			
							560	—			
PA Ni	50-340 (50-210)	24.0 (21.0)	140	110	340-520	44.0	395	388	520-860	2.0	70.0
							426	414			
							520	—			
PA Co	75-350 (75-210)	26.6 (20.0)	130	110	350-480	42.5	450	450	520-860	3.0	76.0
					480-520	5.0	520	520			
PA Mn	50-360 (50-210)	21.0 (20.0)	110	100	360-470	44.0	435	435	620-860	4.0	75.0
					470-620	6.0	519	—			

* in brackets the temperature range and wt.% loss connected with water evolution is given.

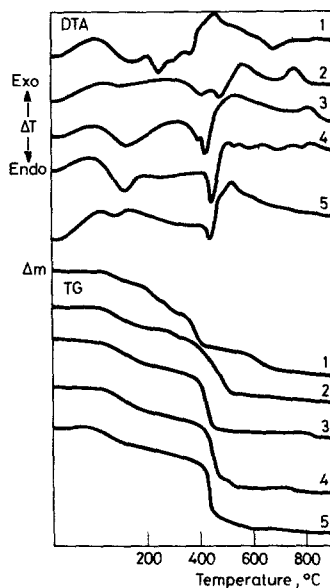


Fig. 2 DTA and TG curves of poly(Fe acrylate)-1, poly(Cr acrylate)-2, poly(Ni acrylate)-3, poly(Co acrylate)-4, poly(Mn acrylate)-5 in argon

very similar for all these polyacrylates. All the TG and DTA curves show steps and peaks of decomposition. They are located in the same range of temperature for each of the polyacrylates. The first step, at 70–370°, is mainly connected with water evolution. This process lasts from 50° to 220° and the rate maximum is reached in the range 120–160°. Above 220°, a small weight loss is also observed and may be caused by partial salt decomposition or, more probably, by the dehydration of unreacted carboxylic groups. The dehydration of pure PAA is observed in the temperature range 250–260° [8].

The second, main step, which occurs in the temperature range 220–700°, is connected with the violent decomposition of the investigated salts. It is accompanied by a great loss in weight. For the Fe and Cr polyacrylates it proceeds through several steps in a wider range of temperature than for the Ni, Co and Mn salts. The initial decomposition temperature is different for each of the salts; it increases in the sequence Fe < Cr < Ni < Co < Mn, irrespectively of whether the heating is carried out in air or argon. The lowest decomposition temperatures are observed for poly(Fe acrylates), 215° in air and 220° in argon, and the highest for poly(Mn acrylate), 370° in air and 360° in argon. The decomposition process is accompanied by strong heat effects.

Figure 2 shows the TG and DTA plots for the decomposition processes in argon atmosphere. In the second step, involving the fast, greatest weight loss, mainly an

endothermic effect is observed, followed by a strong exothermic one. The endothermic effect is probably caused by polymer chain decomposition and the exothermic one by metal oxide formation. The DTA curves of the processes in air are presented in Fig. 1. They show the strong exothermic effect in a very wide temperature range. At the point where the greatest weight loss is observed, the endothermic effect is added to this broad exothermic one.

In the third step, which occurs in the temperature range 520–860°, a small and steady weight loss is observed. However, poly(Ni acrylate) and poly(Co acrylate) exhibit a weight increase at 855 and 750°, respectively, on heating in air. The weight increase for the Ni and Co salts is proved by the presence of NiO and Co₃O₄, respectively, as detected by X-ray diffraction.

The solid residue after thermal decomposition of the investigated polysalts comprises 20–30% of the initial weight. The residue composition was analysed by X-ray diffraction, using the patterns presented in the ASTM tables [9]. The solid products of thermal decomposition are the metal oxides (Table 5). The composition of the solid product is more uniform for all polysalts when the reaction is carried out in air rather than in argon. The products of decomposition in air are oxides containing the metals in higher oxidation states, while those in argon additionally include metals and some unidentified compounds.

Table 5 Solid products of polyacrylates decomposition*

Compound	Argon	Air
PA Fe	<i>α-Fe_{met}</i> , Fe ₃ O ₄ , Fe ₃ C	<i>α-Fe₂O₃</i> , Fe ₃ O ₄ -traces
PA Cr	<i>Cr₂O₃</i> , Cr ₃ C ₃ -traces	Cr ₂ O ₃
PA Ni	<i>Ni_{met}</i> , NiO	<i>Ni_{met}</i> , NiO
PA Co	<i>CoO</i> , Co ₂ O ₃ , Co _{met}	<i>Co₃O₄</i> , CoO
PA Mn	<i>MnO</i> , Mn ₃ O ₄ , Mn _{met}	<i>Mn₃O₄</i> , MnO

* Main products are in italics.

Conclusions

These polyacrylic salts have lower decomposition temperatures than that of pure PAA [8]. The transition metal cations in the polymers may be considered as elementary catalysts of thermal destruction. They caused a decrease in the decomposition temperature. The thermal resistance of the polysalts increases, depending on the transition metal ion present, in the sequence: Fe < Cr < Ni < Co < Mn. The manganese salt is the most resistant and shows the greatest shift of the carbonyl group band in the IR spectra relative to this band for

the free carboxylic group. Divalent metal cations are more stable than trivalent ones. Trivalent ions bonded by three carboxylic groups probably form more rigid structures, causing greater tensions in the polymer chain, which would result in a decreased polymer persistence.

References

- 1 A. Gronowski and Z. Wojtczak, *J. Thermal Anal.*, 26 (1983) 233.
- 2 J. Hepter, W. Balcerowiak and J. Bereś, *J. Thermal Anal.*, 20 (1981) 345.
- 3 I. Vancsó-Szmrecsányi and Á. Szilágyi, *J. Thermal Anal.*, 18 (1980) 235.
- 4 G. R. Barrett, *Pat. USA 2 904 541* (1959).
- 5 *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.
- 6 G. Valentini, G. Sbrana and G. Braca, *J. Mol. Cat.*, 11 (1981) 387.
- 7 J. Żurakowska-Orszagh, J. Skupińska and K. Suchan, *Polimery* in press.
- 8 D. H. Grant and N. Grassie, *Polymer* 1 (1960) 125.
- 9 American Society for Testing Materials: *Diffraction Data Cards and Alphabetical and Grouped Numerical Index of X-ray Diffraction Data*.

Zusammenfassung — Polyacrylate von Fe, Cr, Ni, Co und Mn wurden durch Reaktion von Natriumpolyacrylat mit den entsprechenden Metallhaliden synthetisiert. Die erhaltenen Salze wurden thermoanalytisch untersucht. Beim Aufheizen in Argon und Luft verhalten sich alle Salze ähnlich. Die Temperatur, bei der die Zersetzung einsetzt, steigt in folgender Reihenfolge an: Fe < Cr < Ni < Co < Mn. Die festen Rückstände der Zersetzung der Salze wurden ebenfalls analysiert.

Резюме — Полиакрилаты железа, хрома, никеля, кобальта и марганца были получены реакцией натрия полиакрилата с галогенидами соответствующих металлов. Термический анализ солей, проведенный в атмосфере воздуха и аргона, показал их одинаковое поведение. Начальные температуры разложения исследованных солей располагаются в ряду Fe < Cr < Ni < Co < Mn. Проведен анализ конечных продуктов разложения.