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STUDY OF THE THERMAL BEHAVIOUR OF SEVERAL METAL ACRYLATES AND METHACRYLATES

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The thermal behaviour of several metal acrylates and methacrylates was investigated and the temperature characteristics were determined. The main decomposition of the monomer was preceded by thermal polymerization. The values of the peak temperatures of this effect do not correlate either with the thermal stabilities or with the *Q* values of the Alfrey-Price scheme of the monomers. The thermal resistance of the salts depends on the type of cations present, but there is no simple relationship. Divalent metal acrylates are thermally more stable than the corresponding methacrylates.

In recent years, metal-containing monomers and polymers have been studied intensively. This is due to a number of valuable properties exhibited by coordination polymers and ionomers. The area of application of such polymers is continually becoming broader, and their characteristic features include chemical resistance and thermal stability. Metal derivatives of polymers containing COOH grups are a subject of great interest.

The results of thermal and gas-chromatographic analyses revealed the higher stabilities of sodium methacrylate and polymethacrylate than those of the corresponding potassium salts [1]. The activation energies of the processes of thermal destruction were calculated.

Polymers of lithium, sodium, potassium and caesium salts of methacrylic acid [2] were stable to ca. 350° under programmed heating at 10 deg/min in vacuo. The principal decomposition products were analyzed and identified, and a mechanism was proposed for the degradation.

The thermal behaviour of Na, Ca, Mg and Zn acrylates was investigated [3] in air and argon. It was found that the anhydrous acrylates were subject to thermal polymerization, which preceded the main decomposition. Metal

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carbonates or oxides made up the bulk of the residue obtained after the decomposition.

Thermal volatilization analysis, TG and degradation product analysis were used to compare [4] the thermal degradation behaviour of the Mg, Ca, Sr and Ba salts of poly(methacrylic acid) with that of the corresponding metal acetates and alkali metal methacrylate polymers. The sequence of thermal stability of the metal salt polymers increased with the increase in size of the metal ion.

The thermal decompositions of zinc, cobalt, nickel and copper acrylates and their polymers were investigated [5]. The following thermal stability sequence was observed for the compounds under study: Zn>Co>Ni>Cu. The reaction orders and activation energies of decomposition of the monomers and the polymers were calculated and the differences were discussed. Some other transition metal polyacrylates were also investigated by thermal analysis [6].

Although the thermal characteristics of certain salts employed in the present study have been published previously, they are either not complete or not suitable for comparative purposes. The aim of the present investigation is a comparison of the thermal behaviour and thermal stabilities of several metal acrylates and methacrylates subjected to decomposition in nitrogen.

Experimental

Preparation of metal acrylates and methacrylates

Alkali metal and alkaline earth metal salts were prepared by the reaction of the appropriate hydroxides in methanol with acrylic or methacrylic acid in a 10% stoichiometric excess. Calcium acrylate was the only salt prepared form the metal oxide. The reaction mixtures were stirred and the temperature was maintained at ca. 10°. The salts were precipitated in acetone (or petroleum ether in the case of Mg methacrylate), filtered off, washed with acetone or petroleum ether to remove the acid, and vacuum-dried at room temperature to constant weight.

The compositions of the monomers were characterized by the determination of metal, double-bonds and water contents.

Thermal analysis

TG, DTG and DTA curves were recorded simultaneously with a Paulik-Paulik-Erdey derivatograph (MOM, Budapest). 100 mg of powdered sample was heated in a Pt crucible over the temperature range 25–800^0 at a constant heating rate of 4 deg/min. A controlled dynamic atmosphere of nitrogen (20 l/h) was used in the furnace.

From the thermoanalytical curves, the following characteristics were determined: T_P = peak temperature of thermal polymerization, *IDT* = initial decomposition temperature, and T_S = temperature where the rate of decomposition is highest.

Results and discussion

Figure 1 shows the TG, DTG and DTA curves of the prepared calcium methacrylate.

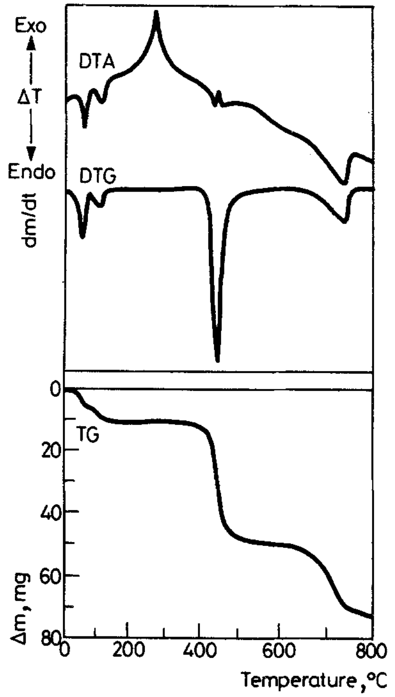

Fig. 1 Thermoanalytical curves of the thermal destruction of calcium methacrylate in nitrogen

The curves of the other metal acrylates and methacrylates are similar, but they differ in some features. More detailed data concerning the thermal behaviour of the salts under study are given in Table 1.

Table 1 Thermal parameters of decomposition of metal acrylates and methacrylates in nitrogen

Salt	Dehydration		T_p,	IDT,	T_s,
	°C	H_2O mole	°C	°C	°C
ALi	-	-	265	400	460
ANa	-	-	290	410	485
AK	-	-	290	400	455
MeLi	-	-	230	380	455
MeNa	-	-	335	410	502
MeK	-	-	340	415	474
A_2Mg	40-140	1	230	410	477
A_2Ca	50-140	0.5	285	425	498
A_2Sr	-	-	230	425	510
A_2Ba	-	-	215	420	492
Me_2Mg	75-125	2	280	393	430
Me_2Ca	50-75 75-125	0.65 0.45	275	400	442
Me_2Sr	60-90 90-180	0.2 0.7	190	400	487
Me_2Ba	80-90	0.2	250	410	480
A_2Zn	-	-	220	330	436
A_2Co	140-180	0.7	270	360	425
A_2Ni	40-110 10-200	0.3 0.4	290	280	327
A_2Cu	-	-	237	180	235 263

A = acrylate
Me = methacylate

The following main thermal processes can be distinguished: a) dehydration (in the case of hydrates), b) thermal polymerization, c) decomposition, and d) final decomposition of an inorganic residue. These processes will be discussed in sequence.

a) Dehydration

Alkali metal salts were obtained in anhydrous form, but some divalent metal salts contained various amounts of water. It is seen from Table 1 that in some cases water is liberated form a molecule of salt in a one-step process, but for calcium methacrylate and strontium methacrylate two dehydration steps are observed.

b) Thermal polymerization

The main decomposition of the monomer was preceded by thermal polymerization. The lowest temperature of this effect was observed for strontium methacrylate (190°) and the highest for potassium methacrylate (340°). A comparison of the data from Table 1 with the literature data [3] reveals the same T_p value for magnesium acrylate monohydrate and minor differences of the order of 10 and 20 deg for the respective T_p values of anhydrous zinc acrylate and sodium acrylate. However, a large difference is observed in the case of calcium acrylate semihydrate ($T_p = 285°$) and calcium acrylate dihydrate [3] ($T_p = 180°$).

The values of the peak temperatures of thermal polymerization do not coincide either with the thermal stabilities of the salts from Table 1 or with the Q values [7-9] of the Alfrey-Price scheme [10], describing the reactivity of the vinyl groups of the monomers in free-radical polymerization. Although polymerization in the solid state is considered [11] to be of radical type factors other than the inherent monomer reactivity are also operative. Polymerization may be controlled by the monomer mobility [12, 13], the lattice geometry [14], the nature of defects [12-14] (some of which may be introduced during the dehydration processes [12]) and the particle size [15].

c) Decomposition

The main decomposition tendency of the investigated salts on heating in nitrogen is an endothermic one-step process at 400-550°. In some cases, the presence of small exothermic effects is also seen, possibly arising from a momentary ignition of gaseous decomposition products.

The *IDT* and T_s values depend on the type of cation present in the salts. The sodium salts are the most stable of the alkali metal acrylates and methacrylates. The monomers containing strontium ions are thermally the most resistant of the divalent metal salts, while those containing magnesium ions are the least resistant. Though a correlation between the thermal stability and the size of the metal ion has been found for some polysalts [1, 2, 4], it does not seem to be of general significance for metal-containing compounds. There is no universal thermal stability sequence for both the acrylates and the methacrylates of the same series of metal ions from

Table 1, which indicates the role of the acid moiety. All the divalent metal acrylates have higher values of *IDT* and T_S than those of the corresponding methacrylates, but this tendency is not observed for the alkali metal salts. The data relating to some transition metal acrylates [5], given in Table 1 for comparative purposes, reveal that the thermal resistance of that group of acrylates is the least. The transition metal cations in the compound may be considered to be elementary catalysts of thermal destruction [5, 6].

d) Final decomposition of the inorganic residue

The solid residues remaining after thermal decomposition were not analyzed. However, the experimental and theoretical weight losses for the investigated salts were compared. This indicated that the alkali metal and alkaline earth metal acrylates and methacrylates decomposed to the respective metal carbonates, with the exception of the magnesium salts, which formed magnesium oxide. In each case, a small amount of crack-carbon was observed, too. The decomposition residues remained stable in the temperature range investigated, except for calcium acrylate and methacrylate, where the decomposition of $CaCO_3$ was observed as an endothermic process at about 680-800°.

The results obtained show that the thermal behaviour of some metal acrylates and methacrylates depends on both the acid moiety and the type of cations present, but there is no simple relationship. Further studies of the thermal processes of these salts are in progress.

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Zusammenfassung — Es wurde das thermische Verhalten verschiedener Metallacrylate und -methacrylate untersucht und die entsprechenden Temperatur charakteristiken bestimmt. Der eigentlichen Zersetzung des Monomers geht eine thermische Polymerisierung voraus. Die Werte für die Peak-Temperaturen dieses Effektes korrelieren für die Monomere weder mit der thermischen Stabilität noch mit dem Q-Wert im Alfrey-Price-Schema. Der Wärmewiderstand der Salze hängt von der Art des Kations ab, es existiert jedoch kein einfacher Zusammenhang. Bivalente Metallacrylate zeigen thermisch gesehen eine größere Stabilität als die entsprechenden Methacrylate.