

## THERMAL DECOMPOSITION OF METAL POLYACRYLATES

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Results of thermal and pyrolysis-GC/MS analyses of Na, Ca and Mg polyacrylates are presented. It was confirmed that the main decomposition reactions of the Na salt take place in the temperature range 420–470° and those of the other two polymers in the range 450–490°. It was found that the solid residue after decomposition was the metal carbonate or oxide, while the volatile products consisted of H<sub>2</sub>, CO, CO<sub>2</sub>, saturated and unsaturated hydrocarbons (including cycloolefins and aromatic hydrocarbons) and aliphatic ketones. This suggests that the thermal decomposition of the metal polyacrylates proceeds via side-chain splitting and breaking of the main chain of the polymer, without retropolymerization.

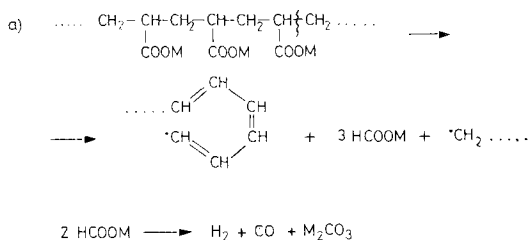
Metal salts of polyacrylic acid may be treated as inorganic-type solids as well as vinyl polymers. This double-meaning structure has to be pointed out in consideration of the thermal behaviours of these compounds.

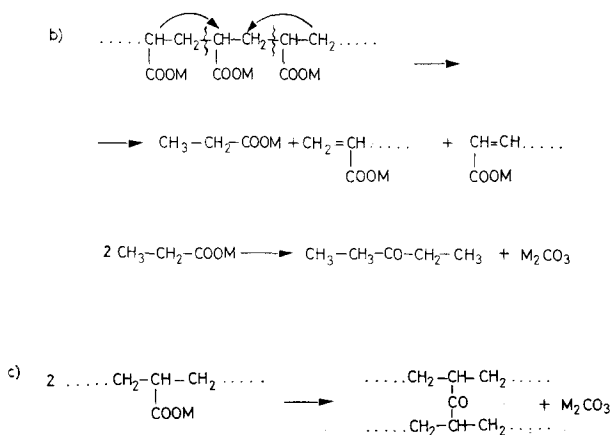
The thermal decomposition of simple carboxylic acid salts leads mainly to the respective ketones and inorganic solids [1–3]:



although hydrocarbons, H<sub>2</sub> and CO<sub>2</sub> are formed too. The solid residue after the decomposition is the metal carbonate or oxide, with a small amount of crack carbon.

On the other hand, the thermal reactions of organic polymers are dependent on the stability of the main or side-chain bonds, the reactivity of the radicals formed by chain fragmentation, the presence of reactive atoms in a molecule, and the interaction of neighbouring bonds [4, 5]. The typical thermal reactions of vinyl polymers are:





- statistical chain break (for example polyethylene);
- retopolymerization (polystyrene);
- side-chain splitting followed by aromatization of the fragments formed (polyvinylchloride).

It is difficult to predict the nature of the thermal decomposition of metal polyacrylates without experiments. The results of the present work, where thermal and pyrolysis-GC/MS analyses were used to investigate the thermal decompositions of Na, Ca and Mg polyacrylates, throw light on this question.

## Experimental

### Preparation of polyacrylates

Na, Ca and Mg acrylates were obtained in the reaction of freshly-distilled acrylic acid (99% purity) with sodium hydroxide, calcium oxide or magnesium oxide, respectively. The prepared salts were polymerized in ca. 20% aqueous solutions in the presence of the initiator system ammonium persulphate – sodium pyrosulphate. The gels obtained were dried at 120–130° to constant weight and powdered.

### Thermal analysis

The thermal analysis curves (TG and DTG) were obtained with a Mettler TA-2 thermal analyser. 50 mg sample in a 0.9 cm<sup>3</sup> Pt crucible was heated over the temperature range 25–600° at a heating rate of 2° per minute, in a flowing argon atmosphere.

### Pyrolysis-GC/MS analysis

A Curie point Pye Unicam pyrolyser coupled with the LKB GC/MS 2091 system was used. The pyrolysis was carried out at 610, 770 and 980°, the sample

being heated for 5 sec. The gas chromatographic separation of pyrolysis products was made on a  $2\text{ m} \times 4\text{ mm}$  column packed with 15% LB 550X (Perkin-Elmer) on 60/80 mesh Chromosorb P at  $120^\circ$ . Helium flowing at a rate of  $30\text{ cm}^3/\text{min}$  was used as the carrier gas in all systems.

Mass spectra of the separated compounds were obtained at 70 eV ionizing energy and 3.5 kV accelerating voltage. The temperature of the ion source was  $250^\circ$ .

### Results and discussion

TG and DTG curves of the investigated polyacrylates are given in Fig. 1. It can be distinguished that the temperature corresponding to the maximum in the decomposition rate is lower for Na than for Mg and Ca polyacrylates ( $430$ ,  $460$  and  $485^\circ$ , respectively). The higher thermal stability of Ca and Mg polyacrylates may be associated with their setting structure in contradistinction to the Na polymer.

In the solid residues after decomposition of the Na and Ca salts (at about  $600^\circ$ ) carbonates were found, whereas Mg polyacrylate decomposed to MgO because of carbonate instability at this temperature. In all cases a small amount of crack carbon was present.

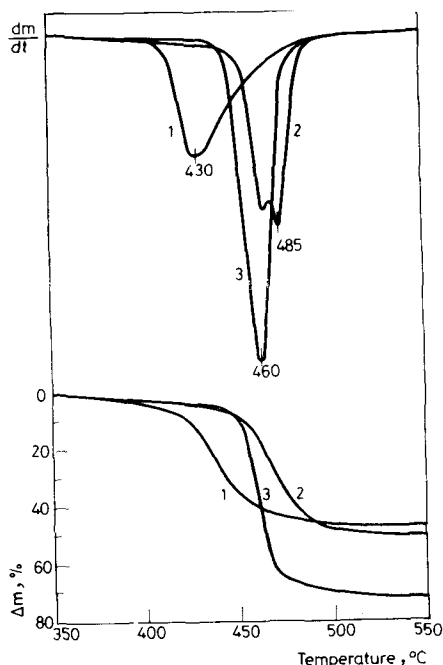


Fig. 1. TG and DTG curves of investigated polyacrylates: 1 — Na, 2 — Ca, 3 — Mg

To obtain a sufficient amount of volatile products of thermal decomposition in the pyrolysis-GC/MS system, high heating element temperatures had to be attained. Pyrolysis temperatures in the range 600–900° are usually convenient for organic polymers.

A typical chromatogram of the volatile pyrolysis products of Na polyacrylate heated to 770° is shown in Fig. 2. The compounds identified by comparison of their mass spectra with catalogue data [6, 7] are listed in Table 1.

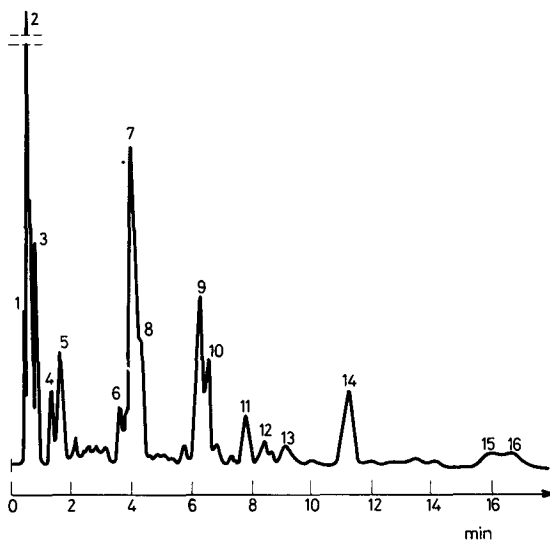


Fig. 2. Chromatogram of volatile pyrolysis products of sodium polyacrylate

Table 1  
Volatile products of pyrolysis of sodium polyacrylate at 770°

Peak No (Fig. 2)	Compounds
1	CH <sub>4</sub> , CO
2	C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , CO <sub>2</sub>
3	hydrocarbons C <sub>3</sub>
4, 5	hydrocarbons C <sub>4</sub>
6	dienes and cycloolefins C <sub>5</sub>
7	acetone
8	cyclopentadiene
9	butanone-2
10	cyclohexadiene
11	benzene
12	pentanone-2
13	methylcyclohexadiene
14	toluene
15	ethylbenzene
16	xylene

The compounds found may be considered in three groups:

- (1) gases:  $H_2$ , CO,  $CO_2$  and hydrocarbons  $C_1 - C_4$ ;
- (2) unsaturated hydrocarbons  $C_5 - C_8$ , including cycloolefins and aromatic hydrocarbons;
- (3) aliphatic ketones.

The presence of cycloolefins and aromatic hydrocarbons among the volatile decomposition products testifies to side-chain splitting and cyclizing of cleaned fragments of the stripped main chain. CO may be a decomposition product of metal formate formed as an instable intermediate (Scheme 1a).

The formation of aliphatic ketones is a result of the main chain breaking. There are two possible ways:

(1) formation of carboxylic acid salts (mainly acetates and propionates) and their secondary reactions (Scheme 1b);

(2) reaction of the carboxylate groups of the polymer, leading to formation of C=O bridges between polymer chains (Scheme 1c) followed by breaking of C-C bonds in the main chains.

It was confirmed that neither the temperature of the ferromagnetic wire of the pyrolyser (in the range 610–980°) nor the nature of the metal in the polyacrylate influences the qualitative composition of the pyrolysate. Only differences in the concentrations of the components are observed. The higher the pyrolysis temperature, the larger the percentages of gases and aromatic hydrocarbons present in the pyrolysate.

The absence of divinyl ketone from the pyrolysis products suggests that the retropolymerization process is not probable.

### References

1. I. C. MC NEILL and D. NEILL, *Thermal Analysis*, Acad. Press, New York, 1969, p. 353.
2. T. MEISEL and Z. HALMOS, *Thermal Analysis Proc. III-rd ICTA Congr.*, Davos, Vol. 3, 1971, p. 43.
3. T. MEISEL, I. LANYI and P. FRANZOSINI, *J. Thermal Anal.*, 17 (1979) 529.
4. D. O. HUMMEL, H. J. DÜSSEL and K. RÜBENACKER, *Macromol. Chem.*, 145 (1971) 267.
5. D. O. HUMMEL, H.-D. SCHÜDDEMAGE and K. RÜBENACKER, *Polymer Spectroscopy* (ed. D. O. Hummel), Verlag Chemie, Weinheim, 1974.
6. *Eight Peak Index of Mass Spectra*, Mass Spectrometry Data Centre, Awre 1974.
7. E. STENHAGEN, S. ABRAHAMSSON and F. W. MC. LAFFERTY, *Atlas of Mass Spectral Data*, Interscience, New York, 1969.

RÉSUMÉ — On présente les résultats des analyses thermiques et des produits de décomposition pyrolytique par chromatographie en phase gazeuse et spectrométrie de masse (GC/MS) des polyacrylates de Na, Ca et Mg. On confirme que la réaction de décomposition principale du sel de sodium a lieu entre 420° et 470° et celle des deux autres polymères entre 450 et 490°. On trouve que le résidu solide après décomposition est le carbonate ou l'oxyde du métal, tandis que les produits volatils consistent en  $N_2$ , CO,  $CO_2$ , en hydrocarbures saturés et non-saturés (y compris les cyclooléfines et hydrocarbures aromatiques) et en cétones aliphatiques. Cela per-

met de supposer que la décomposition thermique des polyacrylates métalliques s'effectue par coupure de la chaîne latérale et par rupture de la chaîne principale du polymère, sans rétropoly-mérisation.

ZUSAMMENFASSUNG — Die Ergebnisse der Thermo- und Pyrolyse-GC/MS-Analysen von Na-, Ca- und Mg-Polyacrylaten werden beschrieben. Es wurde bestätigt, dass die Hauptzersetzungsreaktionen des Natriumsalzes im Temperaturbereich von 420 bis 470°, jene der anderen zwei Polymeren im Bereich von 450 bis 490° ablaufen. Es wurde nach der Zersetzung ein fester Rückstand von Metallkarbonat oder -oxid gefunden, während die flüchtigen Produkte aus N<sub>2</sub>, CO, CO<sub>2</sub>, gesättigten und ungesättigten Kohlenwasserstoffen (darunter Zyклоolefinen und aromatischen Kohlenwasserstoffen) und aliphatischen Ketonen bestanden. Dies lässt darauf schliessen, dass sich die thermische Zersetzung der Metallpolyacrylate über die Abspaltung der Seitenkette und der Spaltung der Hauptkette des Polymers ohne Retropolymerisation vollzieht.

Резюме — Представлены результаты термического и комбинированного метода анализа пиролиз-газ-хроматография-масс-спектрометрия полиакрилатов Na, Ca и Mg. Подтверждено, что основные реакции разложения натриевой соли имеют место в области температур 420—470°, в то время как для двух других полимеров — в области 450—490°. Установлено, что твердый остаток после разложения представляет собой карбонат или окись соответствующего металла. Летучие продукты состояли из H<sub>2</sub>, CO, CO<sub>2</sub>, насыщенных и ненасыщенных углеводородов, включая циклоолефины и ароматические углеводороды, и алифатических кетонов. Это подтверждает, что термическое разложение металлполиакрилатов протекает через стадии расщепления боковой цепи и разрыва главной цепи полимера без обратной реакции полимеризации.