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# THE THERMAL DEGRADATION OF ALKALINE EARTH METAL SALTS OF POLY(ITACONIC ACID)

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## Abstract

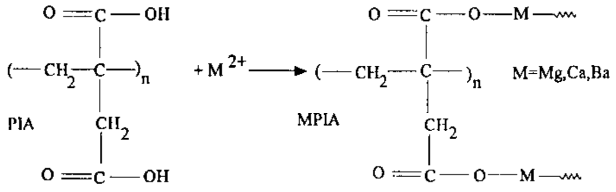
The Mg-, Ca- and Ba-salts of poly(itaconic acid) (PIA) were prepared by treating the aqueous solution of the polyacid with the corresponding metal oxide or hydroxide. The resulting polysalts were analysed by FTIR spectroscopy and thermogravimetry. The results indicate that the polysalts are thermally more stable than the parent PIA, they all degrade in a similar manner, the Ba-salt being the most stable.

**Keywords:** alkaline earth metals, poly(itaconic acid), polysalts, thermal degradation, thermogravimetry

## Introduction

Ionic polymers prossess unusual and often very useful properties, resulting from the interactions between ions carried by organic macromolecules. Their properties are tailored by changing the amount and, sometimes, the position of the ions in the polymer chain [1–4]. Depending on their structure and composition the ionic polymers are used as semiconductors, microencapsulating agents, ion exchange resins, catalysts, schielding materials for high energy radiation, thermally and chemically resistant materials, etc.

The synthesis, the dilute solution properties and the thermal degradation of several homologous series of poly(di-itaconates) as well as of poly(itaconic acid) have been studied systematically in this laboratory. The alkali metal salts [5] and some transition metal salts of poly(itaconic acid) [6] have been synthesized recently and their thermal degradation examined. The present paper deals with the synthesis of the alkaline earth metal salts of PIA (Mg-. Ca- and Ba-) and their behaviour during the nonoxidative thermal degradation, as in the literature there is no information available.



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## Experimental

The simplest route to prepare a polyacid salt is to neutralize the polyacid in an aqueous solution with the appropriate base. However, there is always a possibility that the reaction is not completed, especially when the product polymer is insoluble [7].

Poly(itaconic acid) was obtained by the radical precipitation polymerization of itaconic acid in dioxane at 34°C, using AIBN as an initiator, as described previously [8]. The alkaline earth metal salts (Mg-, Ca-, Ba-) of PIA ($M_w$~$10^5$ g $mol^{-1}$) were prepared by reacting a 0.75 M aqueous solution of PIA with an equivalent amount of the corresponding metal oxide (Mg-) or hydroxide (Ca-, Ba-). Since the alkaline metal oxides/hydoxides are poorely soluble in water [9] they were powdered and added to the PIA solution in small portions, applying intensive and continuous stirring. The precipitated polysalts were repeatedly washed with water, dried under vacuum at ambient temperature for several days and stored over anhydrous $CaCl_2$.

The obtained Mg-, Ca- and BaPIA are colorless powders, insoluble in water and organic solvents. As expected, they degrade when heated before melting is observed. The polysalts were characterized by FTIR spectroscopy (Nicolet 800, KBr pellets). The metal contents were determined by flame photometry (Instrument Model 6,B. Lange, Germany).

The thermal behaviour of the polysalts was studied applying non-isothermal thermogravimetry (TG) with a dry nitrogen flow (26 $cm^3$ $min^{-1}$), the heating rate was 10°C $min^{-1}$, the temperature range 25–600°C. Differential TG curves were recorded as well. A Perkin-Elmer TGS-2 system was used in all experiments.

## Results and discussion

The analysis of three alkaline earth PIA polysalts, MgPIA, CaPIA and BaPIA indicates that they are very hygroscopic, as reported earlier for poly(acrylic-) [10] poly(methacrylic-) [7] and poly(itaconic acid) salts [5, 6, 11]. The moisture contents (determined by TG) are as follows: 29.0% for MgPIA; 18.5% CaPIA and 13.0% for BaPIA. The calculated values for the metal contents of Mg-, Ca- and BaPIA are 15.95%, 23.83% and 51.74%, respectively. The observed metal contents are lower: 13.70 for MgPIA, 20.10 for CaPIA and 42.03% for BaPIA. The reason for these discrepancies is mentioned above.

The FTIR spectroscopic data, given in Table 1, show the characteristic C=O absorption band at 1700–1730 $cm^{-1}$ for PIA, ascribed to free acid groups. In the polysalts this band is weak and a new band appears near 1560 $cm^{-1}$, attributed to complexed C=O groups [5–7, 10].

The residual weak absorption bands at about 1700 $cm^{-1}$ in all three alkaline earth metal salts of PIA indicate that some carboxylic groups have not reacted during the neutralization of PIA and this is the main objection for the preparation of polysalts from polyacids. On the other hand, some serious difficulties arise when one tries to polymerize alkaline earth metal salts of itaconic acid (an alternative route for polysalt preparation), most probably because of the steric reasons.

**Table 1** Characteristic IR absorption bands

| Polymer sample | Characteristic bands/cm$^{-1}$ | |
|---|---|---|
| | C=O (acid) | C=O (salt) |
| PIA | 1720 (s) | none |
| MgPIA | 1720 (w) | 1558 (s) |
| CaPIA | 1716 (w) | 1558 (s) |
| BaPIA | 1700 (w) | 1560 (s) |

s – strong; w – weak

The TG analysis shows that all three polysalts undergo similar transformations during heating under dynamic $N_2$ atmosphere. The TG and DTG traces of MgPIA and BaPIA are presented in Fig. 1.

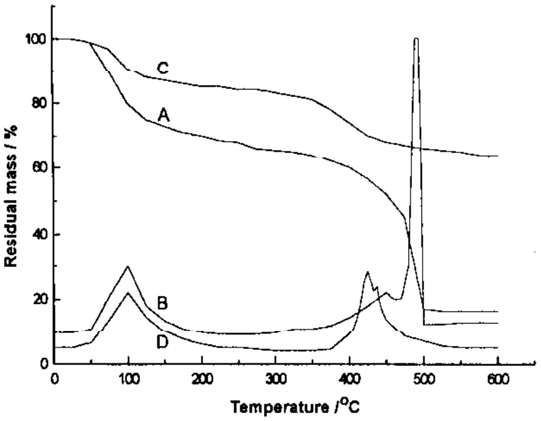

**Fig. 1** TG and DTG curves of MgPIA and BaPIA (*HR* 10°C min$^{-1}$, $N_2$ flow rate 26 cm$^3$ min$^{-1}$), MgPIA: A – TG; B – DTG. BaPIA: C – TG; D – DTG

The TG traces of the polysalts are characterized by the mass losses in the similar temperature intervals (Table 2).

The first mass loss, in the temperature range 50–170°C, is related to the evolution of water. The second, major degradation step, from 250–500°C, corresponds to volatile products evolution and the simultaneous formation of metal carbonates. All three polysalts decompose via one reaction step with the DTG maximum at about 450°C (420° for BaPIA). However, $MgCO_3$ formed during MgPIA thermal decomposition is thermally unstable at temperatures higher than 300°C and undergoes the decomposition reaction giving $CO_2$ and metal oxide. Since the reaction system is complex, the $MgCO_3$ decomposition begins at about 280°C achieving the maximum rate at about 480°C, with a very intensive and sharp peak in DTG curve. The solid residue

**Table 2** The thermal degradation of MPIA; non-isothermal TG, $N_2$: 26 $cm^3$ $min^{-1}$; $HR$=10°C $min^{-1}$; $T$=25–600°C

| Polysalt | I step | | | II step | | | III step | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta T$/ °C | mass loss/ % | $T_{max, DTG}$/ °C | $\Delta T$/ °C | mass loss/ % | $T_{max, DTG}$/ °C | $\Delta T$/ °C | mass loss/ % | total mass loss/ % |
| MgPIA | 50–160 | 29.0 | 98 | 270–500 | 53.5 | 450 | 500–600 | 0 | 82.5 |
| CaPIA | 50–150 | 18.5 | 100 | 320–500 | 33.5 | 440 | 500–600 | 0 | 47.9 |
| BaPIA | 60–170 | 13.0 | 105 | 370–500 | 21.5 | 420 | 500–600 | 0 | 34.5 |

observed corresponds to MgO (Table 3). The TG trace of CaPIA is quite similar to that of MgPIA, the DTG peak in temperature range 400–500°C ($T_{max}$=440°C) being somewhat more intensive than that of MgPIA.

The TG trace of BaPIA (Fig. 1) indicates that the decomposition begins at 370°C and proceeds, in one step, till 500°C, with DTG maximum at 420°C. Above 500°C no mass loss is observed in the PIA polysalts. The three polymers give solid residues consisting mainly of metal carbonate (CaPIA and BaPIA) and metal oxide (MgPIA). The calculated metal oxide and carbonate contents and the measured solid residues are given in Table 3. The corresponding values for alkaline earth metal salts of poly(methacrylic acid) [7] are given for comparison.

Somewhat lower values of the solid residues observed in PIA salts, in spite of the presence of some carbonaceous products, are caused by the incomplete neutralization of PIA and consequently, lower metal content in polymer samples. The alkaline earth metal salts of PIA show considerably higher stability than the parent PIA [5] their threshold temperatures ranging from 270 to 370°C while PIA decomposition begins at 140°C.

**Table 3** The theoretical metaloxide/carbonate contents and measured solid residues of alkaline earth metal salts of poly(itaconic acid)

| Polysalt | Metaloxide/carbonate/ % (calc.) | Solid residue/ % |
|---|---|---|
| MgPIA | 26.4 | 17.5 |
| CaPIA | 59.5 | 47.9 |
| BaPIA | 74.3 | 66.5 |
| MgPMA | 20.7 | 31.0 |
| CaPMA | 47.6 | 57.0 |
| BaPMA | 64.2 | 70.0 |

In the divalent metal series of polymers strong ionic cross links are feasible and it is possible that intramolecular salt formation provides the basis for the increased stability of polymer salts [12]. The same behaviour was reported earlier for alkaline earth metal salts of poly(methacrylic acid) (PMA) [7]. The increase of stability with the cation size increase was also reported in PMA alkali- and alkaline earth metal salts [7]. The PIA salts of both series mentioned are characterized by the same phenomenon.

## Conclusions

Alkaline earth metal salts (Mg-, Ca-, Ba-) of poly(itaconic acid) degrade thermally in the similar manner and show increased thermal stability compared to PIA probably caused by crosslinking via divalent cations. The similarities in the degradation of PIA and PMA metal salts are observed, but the degradation of PIA salts is more complex. The data, presented here, are of general nature and enable the further, detailed study of this class of ionic polymers.

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