Journal of Thermal Analysis, Vol. 49 (1997) 335-341

THE THERMAL DEGRADATION OF SOME ALKALI METAL SALTS OF POLY(ITACONIC ACID)

J. M. Filipović, L. Katsikas, I. G. Popović, S. J. Veličković, T. A. Djakov and D. M. Petrović-Djakov

Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 494, 11001 Belgrade, Yugoslavia

Abstract

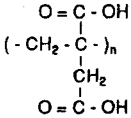
The Li-, Na- and K salts of poly(itaconic acid) (PIA) were prepared by treating the polyacid with the corresponding aqueous hydroxide.The resulting polysalts were analyzed by elemental analysis, FTIR spectroscopy and thermogravimetry. The results indicate that the polysalts are thermally more stable than the parent PIA, they all degrade in a similar manner and somewhat more complexly than the poly(methacrylic acid) salts.

Keywords: alkali metals, poly(itaconic acid), polysalts, thermal degradation, thermogravimetry

Introduction

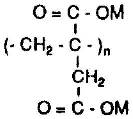
Polymers with ionic groups are characterized by a variety of properties and possible applications, resulting from the interactions between ions bound to organic macromolecules [1–3]. These interactions, tailored by changing the amount and, in some cases, the position of the ions in the polymer chain, affect the physical, as well as rheological properties of the parent polymer [4]. Depending on their composition and structure, ionic polymers are used as chemically and thermally resistant materials, semiconductors, selectively permeable membranes, microencapsulating agents, ion exchange resins, etc.

Salts of polymethacrylic [5–8] and polyacrylic acids [9, 10] form two important groups of ionic polymers, in which each carboxyl group in the polyacid has been neutralized – every two carbon atoms in the backbone chain contain one ionic linkage. The high concentration of ionic bonds is responsible for the unusual and useful properties.



$(-CH_2-\underset{\underset{O=C-OH}{CH_2}}{\overset{O=C-OH}{C}}-)_n$

(PIA)



$(-CH_2-\underset{\underset{O=C-OM}{CH_2}}{\overset{O=C-OM}{C}}-)_n$

(MPIA)

M = Li, K, Na

The synthesis and the dilute solution properties of several homologous series of poly(di-itaconates) as well as of poly(itaconic acid) [11] have been studied extensively in this laboratory. The present paper is an attempt to prepare and investigate

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

alkali metal salts of poly(itaconic acid), especially their behavior during non-oxidative thermal degradation, as there is not much information available in the literature [12].

Experimental

Poly(itaconic acid) was obtained by the $K_2S_2O_8$ initiated polymerization of itaconic acid in aqueous solution, as described previously [11]. The alkali metal salts (Li, Na, K) of PIA ($\overline{M}_w=1\times10^5$ g mol^{-1}) were synthesized by reacting a 0.3 *M* aqueous solution of PIA with an equivalent amount of the corresponding alkali metal hydroxide during potentiometric titration ($pH=10.2$). The polysalts were repeatedly precipitated from aqueous solution using isopropanol, then washed with methanol, dried under vacuum at ambient temperature for several days and stored over anhydrous $CaCl_2$.

The obtained polysalts are colorless powders, soluble in water, but insoluble in organic solvents. As expected, they degrade as they are heated before melting is observed. The salts were characterized by elemental analysis and FTIR spectroscopy, using a Nicolet 800 instrument and KBr pellets. The metal contents of Na- and KPIA were determined by flame photometry (instrument Model 6, B. Lange, Germany).

The thermal behaviour of the polysalts was studied by non-isothermal thermogravimetry (TG) under a N_2 atmosphere (26 cm^3 min^{-1}) at heating rates of 2.5, 10, 20 and 40°C min^{-1} in the temperature range 25–600°C. In all experiments a Perkin Elmer TGS-2 thermogravimetric system was used. The samples were prepared by heating for 15 min at 90°C; then the mass was adjusted to 100%. The activation energies of the processes during the thermal degradation of the samples were calculated according to the procedure of Flynn and Wall [13]. Differential TG curves were recorded at a heating rate of 10°C min^{-1}. DSC was performed on a Perkin Elmer DSC-2 instrument at a heating rate of 10°C min^{-1} in a dynamic N_2 atmosphere (50 cm^3 min^{-1}) from 50 to 350°C.

Results and discussion

The analysis of all three polysalts, LiPIA, NaPIA and KPIA, indicate that they are highly hygroscopic, as are poly(acrylic) and poly(methacrylic acid) salts [5, 6, 10]. The moisture contents determined by TG are as follows: 16.0% for LiPIA, 12.2% for NaPIA and 11.0% for KPIA. The calculated values for the metal contents of LiPIA, NaPIA and KPIA are 9.78, 26.44 and 37.86% respectively. The observed contents were 26.60% for NaPIA and 36.30% for KPIA. Li could not be detected by our instrument.

The reduced viscosities of dilute aqueous solutions of the polysalts increase with dilution. The results of the viscosity measurements, treated according to the method proposed by Fuoss [14], indicate that the limiting viscosity numbers (LVN) in water at 25°C for all three alkali metal salts of PIA and for the parent PIA as well, have the same value: LVN=0.55 m^3 kg^{-1}.

Table 1 Characteristic IR absorption bands

Polymer sample	Characteristic bands, cm $^{-1}$	
	C=O (acid)	C=O (salts)
PIA	1720 (s)	none
LiPIA	none	1564 (s)
NaPIA	none	1564 (s)
KPIA	none	1564 (s)

s=strong

The FTIR spectroscopic data, presented in Table 1, show the characteristic C=O absorption bands at 1720 cm^{-1} for PIA, ascribed to free acid groups. In the case of polysalts this band is replaced by a band at 1560 cm^{-1} attributed to complexed carboxyl groups in the polysalts [5, 6, 10].

The results of TG analysis (Fig. 1) indicate that the polysalts undergo similar transformations during heating under dynamic N_2 atmosphere. For the sake of clarity, only the TG curve of NaPIA is shown and compared to the TG curve of PIA.

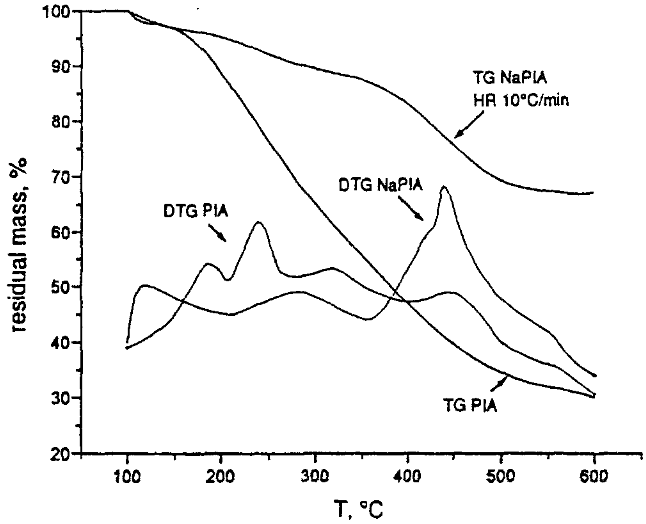


Fig. 1 TG and DTG curves of NaPIA and PIA (HR 10°C min^{-1}, N_2 flow rate 26 cm^3 min^{-1})

The TG curves of the polysalts show mass losses in the same temperature range. The first mass loss interval, from 100–220°C, is related to the evolution of water of hydration. The second, major degradation step, in the temperature interval from about 200 to about 500°C, is accompanied by mass losses of 22–26%. All three polysalts decompose via at least two reaction steps, the DTG traces having maxima at 280 and 415°C for LiPIA, at 265 and 438°C for NaPIA and at 243 and 430°C for KPIA. It is proposed that the first reaction taking place from 200–320°C is the partial formation of metal carbonates. MPIA samples degraded isothermally at 300°C for 30 min in an inert atmosphere are yellowish-gray and dissolve in water more readily than the untreated MPIA samples. The IR spectra of these partially degraded samples show absorption bands of medium intensity in the region of 880–860 cm^{-1} ascribed to metal carbonates [15], while anhydride structures are not detected.

The main decomposition takes place in the temperature interval from 320–500°C. The corresponding mass losses for Li, Na and KPIA are about 17% (Table 2). The nature of these processes is still unknown, but the thermal behaviour of the three metal salts is similar.

Above 500°C mass losses of not more than 2% are observed. All three polymers gave a large amount of solid residue, probably consisting mainly of metal carbonate. The calculated metal carbonate contents and the measured solid residues are given in Table 3. The corresponding values for alkali metal salts of poly(methacrylic acid) [5] are also shown in this table. In both series of polysalts the amount of solid residue is higher than the expected amount of metal carbonate indicating the existence of other products in the residue such as a carbonaceous residue.

Table 3 Theoretical metal carbonate contents and observed solid residues of alkali metal salts of poly(itaconic acid) and poly(methacrylic acid) [5]

Polymer sample	Metal carbonate/% (calc.)	Solid residue/%
LiPIA	52	67
NaPIA	61	67
KPIA	67	66
LiPMA	42	54
NaPMA	49	64
KPMA	56	66

In order to compare the effect of alkali metal ions in PIA salts on their thermal degradation, a TG curve for the parent PIA was recorded under the same experimental conditions (Fig. 1). In the temperature range from 120–270°C two well resolved peaks appear in the DTG curve, which have been assigned to the elimination of water and the formation of polyanhydride, followed by decarboxylation, from 270–400°C. The mass losses were 30% and 23%, respectively.

DSC analysis of the PIA sample was carried out in order to confirm the reaction of anhydride formation. In the temperature range from 120–250°C, an endothermic peak appeared with a heat effect corresponding to the enthalpy of reaction of itaconic acid to itaconic anhydride (IA) and water (76 kJ mol^{-1} calculated, 73 kJ mol^{-1} observed value). An additional endothermic peak followed in the range 250–340°C, with a slightly higher heat effect (+82 kJ mol^{-1} IA), probably corresponding to decarboxylation.

Table 2 The thermal degradation of MPIA and PIA. Sample preparation: 15 min at 90°C, mass adjusted to 100%. Non-isothermal TG, N_2 (26 cm^3 min^{-1}); HR=10°C min^{-1}, ΔT=25–600°C

Polysalt	I step			II step			III step		
	ΔT/°C	Mass loss/%	$T_{max,\ DTG}$/°C	ΔT/°C	Mass loss/%	$T_{max,\ DTG}$/°C	ΔT/°C	Mass loss/%	Total mass loss/%
LiPIA	100–225	9.5	140	225–325	4.5	280	520–600	2.0	33.0
				325–520	17.0	415			
NaPIA	100–215	6.5	130	215–330	7.0	265	520–600	2.0	33.0
				330–520	17.5	438			
KPIA	100–200	6.0	138	200–320	9.5	243	500–600	2.0	34.0
				320–500	16.5	430			
PIA				140–220	16.5	185			
				220–275	13.2	230			
				275–400	23.0	315			
				400–520	14.3	450	520–600	3.0	70.0

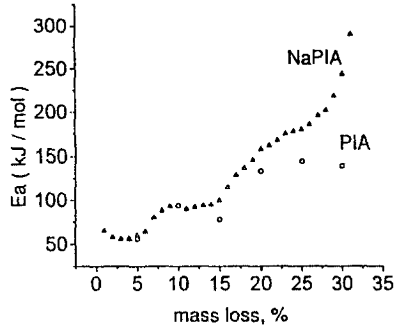


Fig. 2 Degradation activation energies of MPIA and PIA

The activation energies, E_a, of the processes occurring during the thermal degradation of the polysalts are very similar. Comparing the results one can conclude that, after water evolution, the E_a values are level in the range 10–15% mass loss at about 60 kJ mol^{-1}. As the mass loss increases the values of the E_a steadily increase to values higher than 200 kJ mol^{-1}. An example of this trend is shown in Fig. 2. The steady changes in the values of the E_a indicate a complex and continuously changing thermal degradation mechanism of, most probably, successive and parallel reactions, so E_a values can not be ascribed to specific thermolysis reactions. A detailed analysis of the volatile degradation products, which would assist in assigning the E_a values, is currently in progress. Comparison to the E_a trends of PIA indicate similarities in the initial stages of decomposition, which can be ascribed to water evolution and decarboxylation. At mass losses higher than 20%, the E_a values for PIA remain constant and can be related to decarboxylation, while the E_a values for the salts increase sharply.

Conclusion

Alkali metal salts of poly(itaconic acid) degrade thermally in the same manner and similarly to that of poly(methacrylic acid) alkali metal salts. The degradation of PIA salts, however, is more complex. The data presented here are of a general nature and enable the further, more detailed study of this class of ionic polymers.

* * *

The authors would like to acknowledge the financial support of the Ministry of Science and Technology of the Republic of Serbia.

References

1 L. Holliday, "Ionic Polymers", Appl. Sci. Publ., London 1975.
2 A. Eisenberg, "Ions in Polymers", Adv. Chem. Ser. 187, Am.Chem.Soc., Washington DC 1980.
3 A. D. Wilson and H. J. Proser, "Developments in Ionic Polymers", I. Appl. Sci. Publ., London 1983.

4 R. A. Weiss and W. J. McKnight in "Coulombic Interactions in Macromolecular Systems", A. Eisenberg, F. E. Bailey (Eds), ACS Symp. Series 302, Am. Chem. Soc., Washington DC 1986.
5 I. McNeill and M. Zulfiqar, J. Polym. Sci., Polym. Chem. Ed., 16 (1978) 201, ibid, 16 (1978) 2465.
6 I. McNeill and M. Zulfiqar, Polym. Degrad. Stabil., 1 (1979) 89.
7 M. Zulfiqar and R. Hussain, Polym. Degrad. Stabil., 41 (1993) 45.
8 A. K. Farid and M. M. Pasha, Polym. Degrad. Stabil., 42 (1993) 81.
9 J. Hepter, W. Balcerowiak and J. Beres, J. Thermal Anal., 20 (1981) 345.
10 J. Skupinska, H. Wilezura and H. Boniuk, J. Thermal Anal., 31 (1986) 1017.
11 J. Veličković, J. Filipović and D. Petrović-Djakov, Polym. Bull., 32 (1994) 169.
12 J. M. G. Cowie and Z. Haq, British Polym. J., September 1977, 264.
13 J. H. Flynn and L. A. Wall, Polym. Letters, 4 (1966) 329.
14 R. M. Fuoss, J. Polym. Sci., 3 (1948) 603.
15 A. D. Cross and A. Jones, "Practical Infra-Red Spectroscopy", Butterworths, London 1969.