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

The alkali metal salts (Li–, Na–, K–) and the alkaline earth metal salts (Mg–, Ca–, Ba–) of poly(itaconic acid) (PIA) were prepared by treating an aqueous solution of the polyacid with the corresponding metal hydroxide. The resulting polysalts were analyzed 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 but somewhat more complexly that the corresponding poly(methacrylic acid) salts.

Ion–containing polymers are characterized by a variety of properties, resulting from the interactions of the ions carried by the organic macromolecules [1–3]. By changing the amount and, in some cases, the position of the ions in the polymer chain, the physical and the rheological properties of the parent polymer are profoundly affected [4]. Ionic polymers are used as ion exchange resins, catalysts, semiconductors, microencapsulating agents, selectively permeable membranes, shielding materials for high–energy radiation, thermally and chemically resistant materials etc.

Metal salts of poly(methacrylic–) (PMA) [5–8] and poly(acrylic acid) (PAA) [9–11] are two important groups of ionic polymers: every second carbon atom in the backbone chain contains one ionic linkage, the high concentrations of ionic bonds being responsible for the unusual and useful properties. The alkali metal salts and the alkaline earth metal salts of PIA, with a twofold higher ion concentration compared to the closely related PMA and PAA polysalts, were prepared and their behavior during non–oxidative thermal degradation examined, as there is not much information available in the literature [11].

EXPERIMENTAL

The simplest route to prepare a polyacid salt is to neutralize the polyacid in an aqueous solution with the corresponding base. However, there is always the possibility that the reaction is not completed, especially when the obtained polysalt is insoluble [12]. A more satisfactory method is to prepare the salt of the monomer and polymerize it, but some serious difficulties arise when one tries to polymerize metal salts of itaconic acid, most probably due to steric reasons.

Poly(itaconic acid) was obtained by radical polymerization initiated with $K_2S_2O_8$, in an aqueous solution, as described earlier [13]. The alkali metal salts (Li–, Na–, K–) of PIA were prepared by reacting a 0.3 M aqueous solution of PIA with an equivalent amount of the corresponding alkali metal hydroxide during a potentiometric titration (pH=10.2). The polysalts obtained were repeatedly precipitated using 2–propanol, then washed with methanol, dried under vacuum at ambient temperature for several days and stored over anhydrous $CaCl_2$.

The alkaline earth metal salts (Mg–, Ca–, Ba–) of PIA were obtained by reacting a 0.75 M aqueous solution of PIA with an equivalent amount of the metal oxide (Mg–) or hydroxide (Ca–, Ba–). Since the alkaline earth metal oxides/hydroxides are poorly soluble in water [14] they were powdered and added to the PIA solution in small portions, under intensive and continuous stirring. The precipitated polysalts were repeatedly washed with water, dried under vacuum and stored over anhydrous $CaCl_2$.

The polysalts obtained are white powders insoluble in organic solvents. The alkali metal PIA salts are water soluble, while the alkaline earth metal polysalts are not. They degrade when heated before melting is observed. The polysalts were characterized by FTIR spectroscopy (Nikolet 800, KBr pellets). The metal contents were determined by flame photometry (Instrument model B6, Lange, Germany).

The thermal behavior of the polysalts was studied applying non isothermal thermogravimetry (TG) with a dry nitrogen flow (26 cm^3/min), at a heating rate of 10 $^{\circ}C$/min, in the temperature range 25–600$^{\circ}C$. The differential TG curves were also recorded. The alkali metal PIA polysalt samples were heated for 15 min at 90$^{\circ}C$ before the mass was adjusted to 100%. A Perkin–Elmer TGS–2 system was used.

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RESULTS AND DISCUSION

The analysis of all the polysalts shows that they are highly hygroscopic as are the corresponding 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, 11.0% for KPIA, 29,0% for MgPIA, 18.5% for CaPIA and 13.0 for BaPIA. The calculated values of the metal content for Li–, Na– and KPIA are 9.78, 26.44 and 37.86%, respectively. The observed contents were 26.60% for NaPIA and 36.30% for KPIA; the instrument used could not detect Li. In the alkaline earth metal polysalt series, the observed metal contents were lower than the calculated ones: 13.71% instead of 15.95% for MgPIA, 20.10% instead of 23.83% for CaPIA and 42.03% instead of 54.74 for BaPIA. The reason for these discrepancies lies in the insolubility of the polysalts obtained in water, since they are likely to precipitate before the neutralization is complete [12].

The FTIR spectroscopic data for PIA show the characteristic C=0 absorption band at about 1700 cm^{-1}, ascribed to free acid groups. In the polysalts this band is replaced by a band near 1560 cm^{-1}, attributed to complexed C=0 groups [5,6,10]. In the alkali metal PIA salts the band at 1700 cm was absent, while in the alkaline earth metal polysalts a weak absorption band is evident, indicating that some carboxylic groups have not reacted during the neutralization of PIA. This is the main objection for the preparation of polysalts from the polyacids, but some serious difficulties arose when attempts were made to polymerize the alkaline earth metal salts of PIA, most probably because of steric reasons.

The results of TG analyses indicate that the alkali metal PIA salts, as well as the alkaline earth metal polysalts, undergo similar transformations during heating under a dynamic nitrogen atmosphere. The first mass loss, up to 200°C, is related to the evolution of water of hydration. The second, major degradation step from about 200°C to 500°C in the alkali metal PIA salts proceeds via at least two reaction steps, as the DTG traces show. The first one corresponds to the partial formation of metal carbonates (and some volatile products formation) [15], the nature of the second reaction step is still unknown. On the other hand, the alkaline earth metal PIA salts decompose via one reaction step, corresponding to volatile products evolution and the simultaneous formation of metal carbonates. Above 500°C, mass losses of not more than 2% in the case of the alkali metal polysalts were observed and no mass loss in the alkaline earth metal polysalts series (Table 1, Table 2). A rather large amount of solid residue, probably consisting of metal carbonate (oxide for Mg–polysalt) [16], was obtained in each case. The theoretical metal carbonate/oxide contents and the observed solid residues are given in Table 3.

Table 1. The thermal degradation of MPIA. Non–isothermal TG, N_2 (26 cm^3 min^{-1}) ; HR = $10^{\circ}C$ 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			

Table 2. The thermal degradation of MPIA. Non–isothermal TG, N_2 (26 cm^3 min^{-1}) ; HR = $10^{\circ}C$ 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, %
MgPIA	50–160	29.0	98	270–500	53.5	450	500–600	0	82.5
CaPIA	50–150	18.5	100	320–500	33.6	440	500–600	0	52.1
BaPIA	60–170	13.0	105	370–500	21.5	420	500–600	0	34.5

Table 3. Theoretical metal carbonate contents and observed solid residues of the alkali–and alkaline carth metal PIA salts

Polymer	Metal carbonate (oxide for MgPIA), % (calc)	Solid residue, % (dry basis)
LiPIA	52.0	74.0
NaPIA	60.9	71.6
KPIA	67.0	70.2
MgPIA	26.4	24.6
CaPIA	59.5	58.7
BaPIA	74.3	75.3

In the alkali metal polysalts series the amount of solid residue is higher than the expected amount of metal carbonate indicating the presence of other solid products, such as a carbonaceous residue. In the alkaline earth metal salts series somewhat lower values of the solid residues, in spite of the presence of carbonaceous products, are due to the incomplete neutralization of PIA and, consequently, the lower then theoretical metal content in the polymer samples.

The alkali metal PIA salts, as well as the alkaline earth metal PIA salts, show considerably higher thermal stability than the parent PIA [15,16], their threshold temperature ranging from 200°C (for alkali metal salts) to 370°C (for BaPIA) while PIA decomposition begins at 140°C [15]. In the divalent metal series of polysalts strong ionic cross–links are feasible and it is possible that intramolecular salt formation provides the bases for the increased stability of the polymeric salts [17]. The same behavior was reported earlier for the alkaline earth metal salts of PMA [12]. The increase in stability with increasing cation size was also reported with the PMA alkali– and alkaline earth metal salts [12], the PIA salts of both series being characterized by the same phenomenon.

CONCLUSION

The alkali– and the alkaline earth metal salts of PIA show increased stability compared to PIA, probably caused by the reduced possibility of a dehydration reaction and crosslinking via the divalent cations. The similarities in the degradation of PIA– and PMA metal polysalts are obvious, the degradation of the PIA polysalts being more complex.

REFERENCES

[1] L. Holiday, "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, H.J. Proser, "Developments in ionic polymers", I, Appl. Sci. Publ., London 1983.

[4] R.A. Weis, W.J. McKnight in "Coulombic interactions in macromolecular system". A. Eisenberg, F.E. Bailey (Eds.), ASC Symp. Series 302, Am. Chem. Soc., Washington DC 1986.

[5] I. McNeill, M. Zulfikar, J. Polym. Sci., Polym. Chem. Ed., **16** (1978) 201, ibid, **16** (1978) 2465.

[6] I. McNeil, M. Zulfiqar, Polym. Degrad. Stabil., **1** (1979) 89.

[7] M. Zulfiqar, R. Hussain, ibid., **41** (1993) 45.

[8] A.K. Farid, M.M. Pasha, ibid, **42** (1993) 81.

[9] J. Hepter, W. Balcerowiak and J. Beres, J.Thermal Anal., **20** (1981) 345.

[10] J. Skupinska, H. Wilezura, H Boniuk, ibid., **31** (1986) 1017.

[11] J.M.G. Cowie, Z. Haq, British Polym. J., September 1977, 264.

[12] I.C. McNiell in "Developments in Polymer Degradation", VII, N. Grassie (Ed.), Elsevier Appl. Sci., London 1987, p. 4

[13] J. Veličković, J. Filipović, D. Petrović–Djakov, Polym. Bull., **32** (1994) 169

[14] R.C. West, CRC Handbook of Chemistry and Physick, 57th Ed., CRC Press Inc., Cleveland 1976–77, pp. B93, 99, 128

[15] J.M. Filipović, L. Katsikas, I.G. Popović, S.J. Veličković, T.A. Djakov, D.M. Petrović–Djakov, J. Thermal Anal., **49** (1997) 335

[16] D.M. Petrović–Djakov, J.M. Filipović, ibid, **56** (1999) 1087

[17] B.N. Hendy in "Speciality Polymers", R.W. Dyson (Ed.), Chapman and Hall, N.Y. 1986

IZVOD

TERMIJSKA RAZGRADNJA SOLI POLI(ITAKONSKE KISELINE)

(Naučni rad)

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Soli poli(itakonske kiseline) i alkalnih (Li, Na, K), odnosno zemnoalkalnih metala (Mg, Ca, Ba) dobijene su neutralizacijom vodenog rastvora polikiseline odgovarajućim hidroksidima. Polimerne soli su bezbojne, praškaste supstance, nerastvorne u organskim rastvaračima. Soli alkalnih metali i poli(itakonske kiseline) su vodorastvorne, dok se soli zemnoalkalnih metala u vodi ne rastvaraju. Infracrveni spektri pokazuju da se reakcija neutralizacije hidroksidima zemnoalkalnih metala ne odigrava u potpunosti. Rezultati neoksidativne termijske analize uzoraka ukazuju na povećanu termijsku stabilnost ovih polimernih soli u poređenju sa polaznom polikiselinom. Polimerne soli zemnoalkalnih metala su znatno stabilnije od soli alkalnih metala. Termijska razgradnja soli poli(itakonske kiseline) se odigrava na sličan način, ali nešto složenije od razgradnje strukturno srodnih soli poli(metakrilne kiseline). U slučaju alkalnih soli, koje sadrže jednovalentne katjone, povećanje stabilnosti se objašnjava smanjenom mogućnošću izdvajanja vode iz poli(itakonske kiseline) uz stvaranje polianhidrida, dok u prisustvu dvovalentnih katjona postoji verovatnoća umrežavanja polimernih lanaca.

Ključne reči: alkalne soli poli(itakonske kiseline) • zemnoalkalne soli poli(itakonske kiseline) • termijska razgradnja •
Key words: Alkali metal salts of poly(itaconic acid) • Alkaline earth • Metal salts of poly(itaconic acid) • Thermal degradation •