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THERMAL DEGRADATION OF IRON POLYMETHACRYLATE

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Abstract

Iron polymethacrylate was synthesized by free radical solution polymerization of methacrylic acid, followed by replacement of the carboxylic proton with iron. Thermal volatilization analysis and thermogravimetry were used to study its thermal stability from ambient temperature up to 500oC. The results reveal that ferric oxide is left as residue at the end of the thermal degradation experiments.

Keywords: degradation, ionic polymers, polymethacrylates

Introduction

The salts of poly(methacrylic acid) [PMAA] constitute an important group of ionic polymers, in which each carbonyl group has been neutralized to give the salt structure. The foremost studies on the salts of PMAA were initiated by Furukawa and others [1–3], who investigated the thermal degradations of calcium and barium polymethacrylates. McNeill and Zulfiqar studied the degradation of alkali metal [4] and alkaline earth metal [5] polymethacrylates by employing thermal volatilization analysis (TVA). Zulfiqar *et al.* recently reported a detailed comparative study of the thermal degradations of barium and lead polymethacrylates [6].

In the present work, the thermal degradation of iron polymethacrylate (FePMA) is reported and discussed in light of the results obtained from TVA and thermogravimetry (TG).

Experimental

Synthesis of FePMA

Freshly distilled methacrylic acid (MAA) supplied by E. Merck was polymerized in dried methanol (E. Merck) for 120 minutes, using 0.05% *w/v* azo bis isobutyronitrile (E. Merck) as a free radical initiator.

After dissolution in methanol, the PMAA was stirred with a methanolic solution of sodium hydroxide to obtain sodium polymethacrylate (NaPMA). Aqueous solutions of NaPMA and ferric chloride (E. Merck) were mixed in a 1:0.4 ratio to precipitate FePMA. The light-brown precipitate was separated following centrifuga-

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tion, washed copiously with deionized water and dried in a vacuum oven at 40°C for 24 h. The polymer was stored in a desiccator till use.

Characterization of FePMA

The infrared (IR) spectrum revealed the presence of symmetrical and antisymmetrical carbonyl peaks in the region 1600–1530 cm^{-1}. The peak at 1640 cm^{-1}, due to unsaturation, was absent from the polymer.

The metal content of the polymer was estimated by using atomic adsorption spectrophotometry, inductively coupled plasma spectrometry and potentiometry. The sample was digested in a mixture of perchloric acid and nitric acid before analysis. The metal content was found to be 17.7%, as compared with the envisaged value of 18.0% calculated on the basis of the molecular formula $[Fe(MAA)_3]_n$.

Analytical techniques

Thermal volatilization analysis (TVA)

The TVA trace of a 50 mg sample was recorded from ambient temperature up to 500°C at a heating rate of 10°C min^{-1} under normal TVA conditions on the equipment described by McNeill [7].

Thermogravimetry (TG)

The TG curve was recorded on a Stanton Redcroft (U.K.) 750B thermobalance. 10 mg of FePMA was heated up to 500°C at a heating rate of 10°C min^{-1} in dynamic nitrogen with a flow rate of 50 ml min^{-1}.

Results and discussion

The TVA curve for FePMA is presented in Fig. 1. It is discernible from the Figure that the polymer is stable below 180°C, beyond which it starts to decompose. The peaks indicating maximum evolution of volatiles appear at 239, 425°C (with a shoulder at 341°C) and 494°C. The appearance of these peaks during the in vacuo

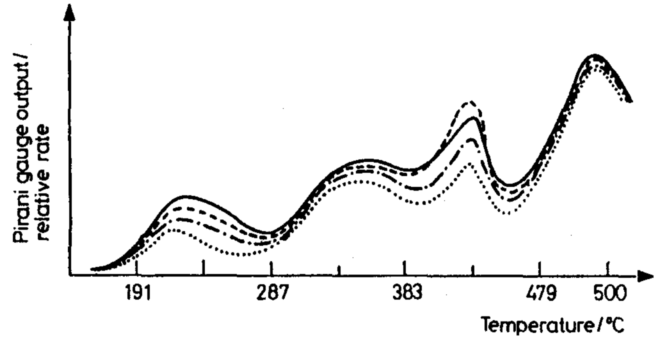

Fig. 1 TVA curves for iron polymethacrylate. — 0°C; — — –45°C; – · – –75°C and –100°C; · · · –196°C

degradation of FePMA can be ascribed to the decomposition of atactic, syndiotactic and cross-linked sequences in the polymer chain. It has been established by McNeill and Zulfiqar [5] that syndiotactic units decompose at temperatures higher than those required for atactic macromolecular units, because of their stable nature. The volatilization patterns for three temperature (–196, –45 and 0°C) traces are similar, i.e. all the traces are separated from each other after the onset of degradation, pointing to the evolution of volatiles in large quantities. The –75 and –100°C traces coincide. This indicates that the quantities of high-boiling products evolved at these temperatures are similar. A considerable amount of residue was left behind at the end of the TVA experiment, i.e. at 500°C.

The volatile degradation products (Table 1) were identified by subambient thermal volatilization analysis (SATVA). The constituents of the individual peaks were collected in miniature gas cells and examined by IR spectroscopy. The gaseous products were identified by comparison with reference spectra [8]. In the SATVA trace (Fig. 2), three fractions were collected, at –84.5, –63.0 and –11.0°C, respectively. Carbon dioxide (3820, 3800, 2980–2920 and 2320 cm^{-1}) and acetylenic

Table 1 Products identified in SATVA

Fraction No.	Products identified	IR data/cm^{-1}
I	carbon dioxide	3820; 3800; 2980–2920
	acetylene	732
II	carbon dioxide	3820; 3800; 2980–2920
	ketenes	2280–2260; 2120
III	ketenes	2280–2260; 2120
	ketones	1640–1620
	moisture	3400

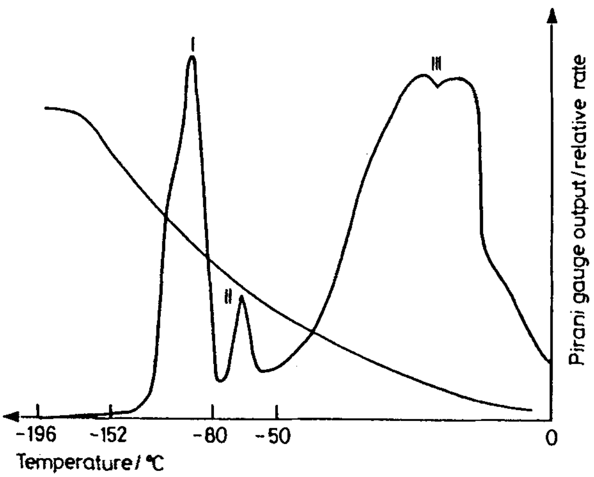

Fig. 2 SATVA curves for iron polymethacrylate

linkages (732 cm^{-1}) were detected in the first fraction. The second fraction comprised mainly carbon dioxide, together with ketenes (2280–2260 and 2120 cm^{-1}). The third fraction consisted of moisture, ketenes and ketones (1640–1620 cm^{-1}).

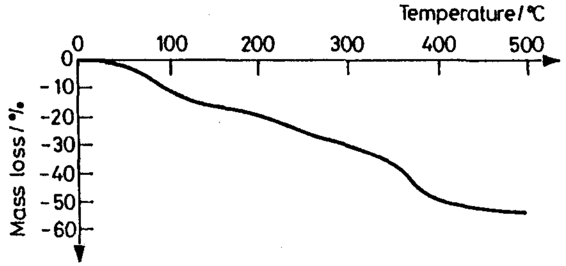

Fig. 3 TG curve for iron polymethacrylate

The TG curve reproduced in Fig. 3 shows three stages of degradation. The first stage, from ambient temperature up to 80°C, involves the removal of residual solvent/moisture entrapped in the polymer during synthesis. The second stage, in the temperature range from 80°C up to 400°C comprises incompletely resolved degradation steps. This can be attributed to the decomposition of moderately cross-linked units formed by the atactic and more stable syndiotactic units in the polymer. The third stage in the TG curve, involving a slow loss in mass starting from 400°C and lasting up to the end of the experiment, i.e. 500°C, points to the decomposition of highly cross-linked macromolecular units formed between the isotactically arranged metal methacrylate units. The presence of trivalent iron leads to the formation of interchain bonding via the metal atom, thereby producing cross-linking. The residue left at the end of the TG experiment amounts to 48.5% of the original sample. This corresponds to the calculated value of 51.45% for Fe_2O_3, which is known to be stable up to 1565°C [9]. The residue on analysis yielded 69.2% iron as major constituent, in agreement with the calculated value of 70% for ferric oxide.

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The authors dedicate this paper to the memory of the late Dr. Mohammad Zulfiqar of Quaid i Azam University, Islamabad, Pakistan.

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