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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

SIMULTANEOUS PLASTICIZATION AND DOPING OF POLYANILINE STUDIED BY THERMAL ANALYSIS METHODS

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Abstract

The thermal behaviour of polyaniline plasticized by an oligoester of phosphoric acid was investigated by means of thermogravimetry, either alone or coupled with Fourier transform infrared spectroscopy, and differential scanning calorimetry. It was found that additional thermal transitions, resulting from the dopant, occur in the temperature range 200–250°C. The emission of volatile products, as evidenced by the Gram-Schmidt chromatograms, was suppressed by the plasticizer used. This stabilization was probably due to a decreased possibility of diffusion in the three-dimensional honeycomb polymer–plasticizer structure.

Keywords: conducting polymers, plasticization, polyaniline, thermal properties

Introduction

Polyaniline (PANI) is a conjugated polymer of current interest as an electronic, electrochemical and nonlinear optical material [1–4]. PANI has attracted considerable attention because of its relatively good environmental stability and the control of the electronic and optical properties via the level of oxidation and protonation. However, due to strong interchain interactions associated with a spatially extended π-bonding system, PANI, like all conjugated systems, is nearly insoluble and cannot be melted. Attempts have been made to overcome this serious technological drawback since the beginning of conducting polymer research, with the first successful attempts reported by Yen *et al.* [5] and Cao *et al.* [6]. The concept behind this counterion-induced processability is that, during the protonation of polyemeraldine base (a form of PANI with a degree of oxida-

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tion equal to 0.5) with an acid HA, the counterion A^- is incorporated into the polymer matrix. If A^- contains a hydrophobic tail, it should facilitate the dissolution of the polymer in solvents commonly used in polymer solution processing. An increase of the number of appropriate functional groups of the counterion should lead to the better processability of PANI. Among the best protonating agents which simultaneously act as plasticizers are phosphoric acid diesters, first introduced for this application by Proń *et al.* [7, 8]. It was found for a series of different diesters of phosphoric acid that the long and branched substituents facilitate plastification, but at higher temperatures partial degradation of the plasticized mixture occurs.

The aim of the present work is to investigate the thermal behaviour of PANI plasticized with an oligoester of phosphoric acid, a novel kind of additive introduced for processable systems of PANI.

Experimental

Materials

PANI was synthesized by chemical oxidation in an acidic medium following a previously described procedure [9]. Aniline (POCh Gliwice, Poland) was distilled under nitrogen prior to use; ammonium peroxydisulphate (POCh Gliwice, Poland) was used without further purification.

The oligoester of phosphoric acid (acidic number=324.5) was prepared according to a procedure described elsewhere [10], using ethylene glycol S-4 from ICSO, Kędzierzyn, Poland.

The samples are described in Table 1.

Table 1 Description of the samples

Sample No.	Oligoester content/mass %
1	0 (pristine PANI)
2	10
3	20
4	30

Techniques

Differential scanning calorimetry

For the DSC measurements, a Netzsch DSC 200, operating in dynamic mode, was employed. A sample of ~5 mass was placed in a sealed aluminium pan. A heating rate of 10 K min^{-1} was applied as the best choice to ensure the high resolution of the DSC curves. Prior to use, the calorimeter was calibrated with an indium standard; an empty aluminium pan was used as a reference.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a Netzsch TG-209 thermogravimetric analyser, operating in dynamic mode at a heating rate of 10 K min^{-1}. The conditions were: sample mass: ~5 mg, atmosphere: argon, flow rate: 30 cm^3 min^{-1}, temperature range: 30–450°C.

Thermogravimetric analysis coupled with Fourier transform infrared (FT-IR) spectroscopy

Thermogravimetric analysis coupled with FT-IR spectroscopy was carried out with a Perkin Elmer 7 thermogravimetric analyser (heating rate: 50 K min^{-1}, sample mass: ~5 mg, nitrogen flow: 50 cm^3 min^{-1}) and a Perkin-Elmer 1725X FT-IR spectrometer. The thermogravimetric analyser and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimize secondary reactions or condensation on the cell walls.

Results and discussion

DSC traces of samples 2–4, depicted in Fig. 1, show a similar character of the thermal events up to ca. 170°C.

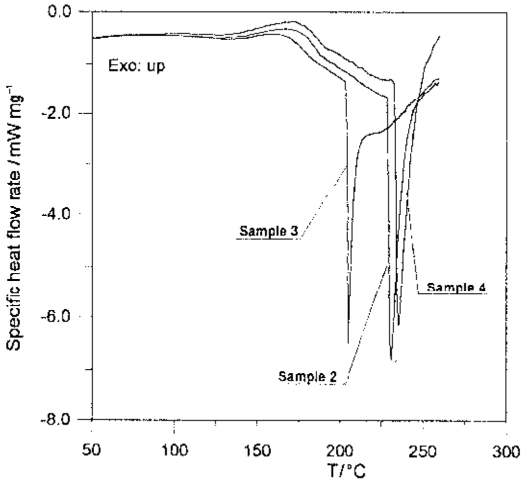

Fig. 1 DSC traces at 10 K min^{-1} for samples 2–4

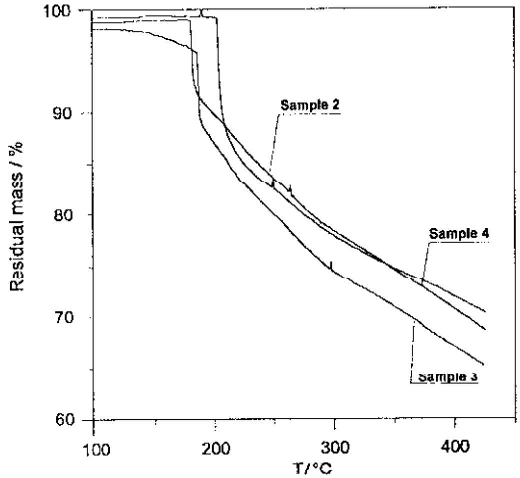

Fig. 2 TG curves at 10 K min^{-1} for samples 2–4

The broad exothermic peak in the range 120–180°C is probably due to plasticizer–polymer interactions, since for pristine PANI and its salts two forms of thermal behaviour have been reported in the literature [11–19], and none of these indicated an initial exothermic event. For the thermal behaviour described, a two-step mass loss process was one type, in which, initially, water escapes from the polymer chain (although the coevolution of other species such as free acids and oxidant cannot be ruled out), followed by thermal degradation of the polymer salt. In a three-step mass loss process, the thermal degradation of PANI commenced with the evolution of water, followed by loss of the acid dopant, and finally complete degradation of the skeletal PANI chain structure. A similar type of thermal behaviour was observed for other PANI based systems, such as

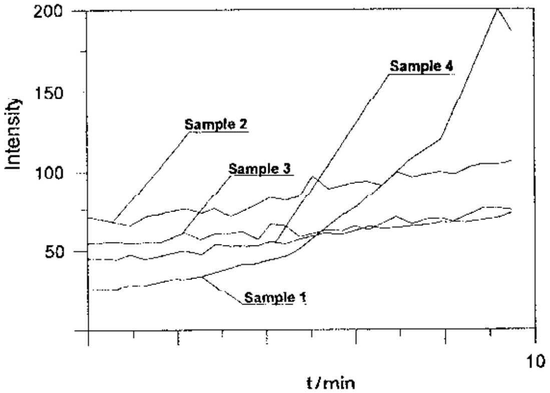

Fig. 3 Gram-Schmidt chromatograms for samples 1–4

poly(aniline-co-*o*-ethylaniline) [20], poly(*o*-chloroaniline) [21], and poly(N-ethylaniline) [22].

For the samples under investigation, a sharp endothermic transition was observed, which can be attributed to evaporation of the oligoester component from the polymer blend; the location of this thermal event depends on the local state of aggregation of the polymer–plasticizer system. Evolution of dopant is confirmed by the TG results, which show a rapid mass loss during the first stage of decomposition (Fig. 2).

The emission of volatile products can readily be followed by using the Gram-Schmidt orthogonalization method [23]. The comparison of the intensity of emission of gaseous products *vs.* time (temperature) for samples 1–4 in Fig. 3 shows that phosphoric ester decreases the evolution of volatiles.

This effect can be explained by the lubricity theory of plasticization, assuming that in an internal, three-dimensional honeycomb structure polymer–plasticizer bonds are preferred over polymer–polymer bonds. On the other hand, esters of phosphoric acid may stabilize residual water since they are able to form strong hydrogen-bonds [24]. In fact, volatile species containing –OH groups were detected by TG/FT-IR spectroscopy at the high-frequency end (Fig. 4).

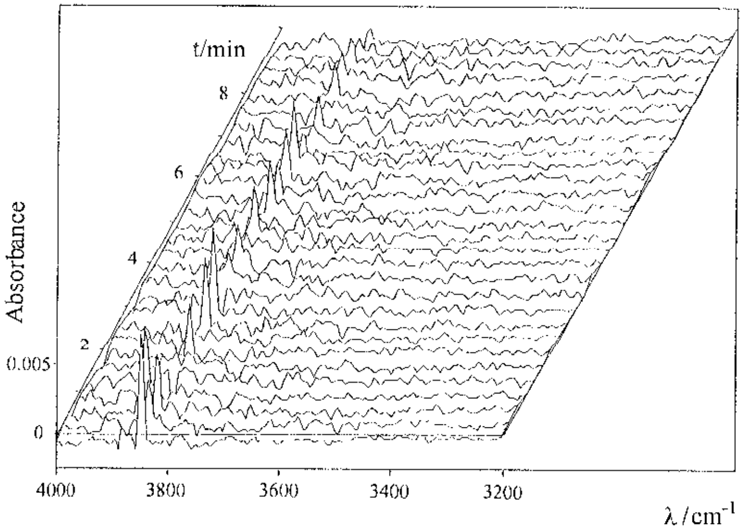

Fig. 4 Stacked plots of FT-IR spectra of sample 3 from 0 to 9.50 min

To summarize, the oligoester of phosphoric acid applied as plasticizer and doping agent for PANI improves its thermal properties by exerting stabilizing action on the emission of volatiles. More attention should be focused on the structure–property relationship for PANI-oligomers systems. Such studies are currently in progress.

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