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Thermal decomposition of polyimides containing phosphine-oxide units

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ABSTRACT

This work details analyses of the thermal decomposition behaviour of three phosphine-oxide containing aromatic processable polyimides. The polymers exhibited high thermal stability with initial decomposition temperatures in the range of 473–483 °C and a char residue at 900 °C in the domain of 48.58–58.38%. The values of non-isothermal decomposition kinetic parameters were determined using the Friedman isoconversional method, as recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The data evidenced a complex decomposition process of the main chain, being probably initiated by the cleavage of the weaker P–C bonds, followed by the decomposition of the macromolecular backbone. The volatile products formed during the thermal decomposition of polyimides were analysed by TGA-FTIR. All spectra evidenced peaks associated with water, CO₂, CO and aliphatic and aromatic decomposition products predominant from 500° to 800 °C. By using Py-GC-MS studies the fragments originating from the thermal decomposition of the polyimides up to 600 °C were identified. Based on these data, it was suggested that the thermal decomposition pathways of the three polyimides undergoes the same mechanism. Additionally, an oversimplified decomposition mechanism for the polyimides was proposed. The morphology of the char residue obtained after TGA experiments showed a continuous and dense structure. The EDX mapping identified the C, N, O and P atoms uniformly dispersed in the residual char surface.

1. Introduction

Classical aromatic polyimides are well known for their excellent thermal and thermo-oxidative stability, good mechanical and dielectric properties, chemical and solvent resistance [1]. The excellent thermal resistance and physical strength are based on the conjugation of the aromatic rings and to the presence of strong intermolecular forces, which are mediated by the imide bonds [2]. Compared to other polymeric materials such as phenols, epoxies, polyesters and polyamides, polyimides possess a higher oxygen index and char yield [3]. Therefore, the choice of polyimide to develop high-performance materials for various applications is based on these considerations. In order to avoid some drawbacks of classical aromatic polyimides such as low solubility, processability, transparency and high glass transition temperatures, the need to modify the main polyimide chain becomes imperative. The challenges consist in improving the overall processability while retaining the desirable and attractive properties e.g. by reducing the rigidity of polymer backbone or the interchain interactions.

The limitation of conventional polyimides in some applications may be overcome by introducing thermally stable flexible or asymmetric linkages, large polar or non-polar pendant substituents [4–8]. Depending on their structural characteristics such polyimides may be successfully used in different industrial segments. They have an important role in high technology applications such as aerospace, automotive, chemical and electronic industry [9–13]. Recently, aromatic polyimides have found a wide range of applications in the microelectronics and photoelectronics industries as alignment films in displays, circuit boards, photoresists and dielectric films [12,14–16]. Other domains include membranes for gas separation or filtration [17–19], aerogels/sponges or foams and matrices for high temperature applications [20–22].

The strategies to improve the processability of polyimides include the introduction of specific moieties in the chemical structure of the polyimides so as to obtain targeted properties. Thus, the introduction of phosphorus, either as a constituent part in the polymer chain or as an additive, can enhance its inherent flame retardant behaviour.

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Phosphorus-based compounds do not have problems associated with halogen-based flame retardants which increase the amount of smoke and toxic decomposition products evolved during polymer combustion [23]. Compared with other phosphorus groups, the use of phosphine oxide has several advantages, due to the hydrolytically stable P–C bonds (compared to phosphate) and the oxidatively stable P=O bonds (compared to trivalent phosphines) [24–27]. The incorporation of short bridges such as ether (–O–), carbonyl (–C=O–), hexafluoroisopropylidene (–C(CF₃)₂–) into polyimide backbones has led to an increase of solubility and a decrease in glass transition temperature, without a consistent compromise of useful properties [28–31].

The need of highly thermostable polyimides is demanded in modern applications. For example, in aerospace industry, the engine monitoring require that the sensor-containing polyimide films should be as close as possible to the engine, leading to their exposure at high temperatures [32,33]. Moreover, the exploration of new sources for clean energy, geothermal and electrical energy has significantly motivated the development of high temperature electronic materials [34]. High temperature sensors for structure health monitoring can ensure enhanced lifetime and reliability, less maintenance and downtime, and can thus reduce the cost of renewable energy sources [35]. Therefore, the search for new thermostable polymers exhibiting outstanding properties to fulfil the requirements of the industry is a continuous challenge.

The study of polymer thermal decomposition has been used not only for the evaluation of global kinetic parameters and of thermal resistance but also has guided improvements in their backbone chemistry [36]. There are numerous studies on the decomposition behaviour of polyimide in the literature [37–39]. It is evidenced that the pyrolysis pathway [40–42] and kinetics [43–46] of aromatic polyimides requires a temperature of more than 500 °C and produces a low value CO- and CO₂- rich gas as well as more than 50 wt% carbonized solid [2].

The present study aims a thorough investigation on the thermostability of a series of structurally comparable polyimides. The thermal and thermo-oxidative decomposition of the polymers was monitored by TGA. The global kinetic parameters were identified by using Friedman isoconversional method. Evolved gas analysis using coupled techniques such as TGA-FTIR and Py-GC-MS were performed in order to elucidate the decomposition mechanism of the polyimides. The residue obtained after TGA process was analyzed by SEM, EDX to establish the char structure and to identify the phosphorus species remaining in the solid.

2. Experimental

2.1. Materials

Aromatic polyimides were prepared by solution polycondensation reaction of an aromatic diamine, namely bis(3-aminophenyl) methyl phosphine oxide, with different aromatic dianhydrides containing various flexible units such as, 4,4'-oxydiphthalic anhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride or 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (Fig. 1). The reaction was performed in two steps using N-methyl-2-pyrrolidone (NMP) as solvent. The concentration of the reaction mixture was adjusted to 15% w/w. The water of imidization was evacuated by a slow stream of nitrogen which was used also as inert medium [47].

2.2. Measurements

Infrared spectra were recorded on FT-IR Bruker Vertex 70 analyzer, by using KBr pellets.

¹H-NMR and ³¹P-NMR were recorded on Bruker Avance400 NMR spectrometer (frequencies of 400.13 and 100.61 MHz, respectively) in DMSO-*d*₆ at 25 °C. Chemical shifts are reported in δ units (ppm) relative to the remaining resonances of the solvent at 2.49 ppm for ¹H-NMR. The ³¹P-NMR spectra are externally referenced to a sample of neat H₃PO₄ at 0.0 ppm.

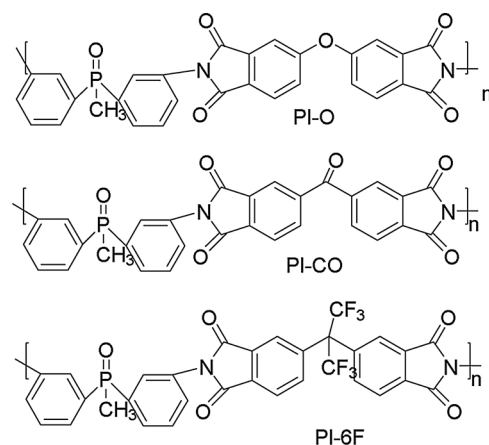


Fig. 1. Structure of the polyimides.

Thermogravimetric analysis (TGA) was performed on a NETZSCH TG209 F1 Iris instrument. The sample of around approx. 3 mg, was heated from 25 to 900 °C at a heating rate of 10 °C min⁻¹. The measurements were performed two times with a total gas flow of 50 mL min⁻¹. Non-isothermal kinetic measurements were performed on a STA 449F1 Jupiter device from Netzsch (Germany) by recording thermograms at three different heating rates (10, 20, 30 °C min⁻¹). The obtained data were processed with the “Thermokinetics 3” software supplied by Netzsch (Germany).

Evolved gases analysis of the polyimides was investigated with a TGA-FTIR technique using the Netzsch TG 209 F1 Iris[®] instrument coupled with the Bruker TENSOR-27 FTIR instrument. For these experiments, 10 mg of samples were heated from 50 to 800 °C at a rate of 10 °C min⁻¹ under nitrogen flow (50 mL min⁻¹). IR spectra were recorded in the spectral range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹.

Py-GC-MS measurements were performed with samples of 30–100 µg of the polymer which were placed in a quartz tube (1 mm internal diameter x 25 mm length). The polymers specimens were then loaded in the pyrolysis probe (Pyroprobe-5200 HP) and placed in the special inlet at the interface. The polymer specimens were pyrolyzed at 600 °C under helium atmosphere for 30 s. The volatiles were separated by a Hewlett-Packard 5890 Series II gas chromatograph and analyzed by a Hewlett-Packard 5989 Series mass spectrometer. GC column filled with cross-linked 5% PH-ME siloxane, 0.53 mm diameter and 30 m length, was employed. The GC oven was programmed to hold at 50 °C for 1 min. The oven was then heated from 50 to 250 °C at a heating rate of 10 °C min⁻¹ and held at 250 °C for 5 min. Masses were scanned from *m/z* 40–500.

The distributions of P atoms on the surface of polyimides char residue were measured by using scanning electron microscope SEM type Quanta 200 operating at 30 kV with secondary and backscattering electrons in high vacuum mode. The elemental analysis on the char residue surface was obtained by using coupled dispersive X-ray spectroscopy (EDX).

3. Results and discussions

3.1. Structural characterization of polyimides

The chemical structure of the polyimides was evidenced by FTIR, ¹H NMR and ³¹P NMR spectroscopy (Tables 1 and 2). Thus, in the FTIR spectra of all polymers strong bands of absorption which appeared in the range of 1785–1778 cm⁻¹ and 1723–1719 cm⁻¹ were attributed to asymmetrical and symmetrical stretching vibrations of carbonyl groups in the imide rings. The vibrations of C–N stretching and the ones corresponding to imide ring bending deformation were identified in the

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