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Thermal and thermo-oxidative stability and probable degradation mechanism of some polyetherimides

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ABSTRACT

This study assesses the thermal and thermo-oxidative stability and establishes the degradation mechanism for five aromatic polyetherimides, by simultaneous mass spectrometry and Fourier transform infrared spectroscopy of off-gases from thermogravimetric analyzer in two working atmospheres: air and helium. Aromatic polyetherimides were synthesized starting from 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) and five aromatic diamines, three of them containing 1,3,4-oxadiazole ring. The study establishes the influence of the structure and of the working atmosphere on the thermal stability and the start mechanism of thermal degradation. Moreover, it determines the main decomposition products both in inert atmosphere (helium) and in air.

1. Introduction

Aromatic polyimides can be considered some of the most thermally and environmentally stable polymers. They are widely used in the aerospatial and electronic industry because of their outstanding high thermal stability, good insulating properties with low dielectric constant, and good adhesion to substrates.

These polymers can also be used as adhesives, gas separation membranes, composite matrix, coatings and foams [1–3]. However these applications are limited in many fields because most of them are normally insoluble and intractable being thus difficult to be processed. To overcome these problems, much research effort has been focused on the synthesis of soluble polyimides in fully imidized form, without deterioration of their own excellent properties. For this purpose chemical modifications of polyimides have been done, such as the introduction of flexible linkages in their backbone or incorporation of bulky side groups [4,5]. The aromatic ether linkages inserted into the aromatic main chains of the polyimides provide them with a significantly lower energy of internal rotation and lead to lower glass transition temperature as well as significant improvement in solubility and other characteristics of the polymers without greatly sacrificing other advantageous polymer properties [5,6].

Polyetherimides are manufactured by the reaction of bis(ether anhydride)s and aromatic diamines. These polymers were developped as high performance engineering thermoplatics that combine the excellent thermal and oxidation stability of aromatic polyimides with the procesability of polyethers. They can provide a compromise between high thermal stability and processability when compared with fully aromatic polyimides [6,7]. Their advantage over other wholly aromatic polyimides is that they are melt processable, so they can be molded or extruded into a variety of shapes, parts, and films. Polyetherimides exhibit high thermo-oxidative stability, high strength and stiffness, chemical resistance, and fire resistant characteristics [8]. They can be structurally modified with the aim to meet the requirements for new applications. Chemical modification is performed by incorporation of diferent groups into the main or side chain of polyetherimides using appropriate monomers, in principal aromatic diamines and bis(ether anhydride)s containing performed groups, to give polymers having desired properties.

Aromatic polymers having 1,3,4-oxadiazole rings in the main chain or side chain are well known for their thermal resistance in oxidative atmosphere, good hydrolytic stability, low dielectric constant and good mechanical properties. 1,3,4-Oxadiazole derivatives present special interest due to their physico-chemical properties and their potential use as electron transporting materials in organic light emiting diodes [9–11]. However, fully aromatic poly(1,3,4-oxadiazole)s are completely infusible and insoluble in organic solvents and show extremely high glass transition

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temperature which makes their fabrication very difficult [12]. Therefore, much effort has been made to develop structurally modified polyoxadiazoles having increased solubility and lower glass transition temperature in order to improve their processability while maintaining the good thermal stability. The intoduction of 1,3,4-oxadiazole rings into the macromolecular chains of polyetherimides leads to polymers with caracteristic properties of 1,3,4-oxadiazole rings having in the same time good processability. For example, the introduction of 2,5-disubstituted 1,3,4-oxadiazole groups into polyetherimides chains lead to polymers that emit light in blue region and exhibit in the same time good solubility in organic solvents [13].

The materials demanding service at high temperature must exhibit good thermal and oxidative stability and the retention of their physical properties at heating. They can be subjected to drastic thermal conditions during their use. Thermo-oxidative stability is also a crucial factor to determine the processing and application of materials. Thermal degradation study of the polymers was used not only for the evalution of thermal resistance but also for the determination of toxicity of volatile components evolved during decomposition. The thermal degradation mechanism of (poly[2,2′-bis(3,4-dicarboxyphenoxy) phenylpropane-2-phenylenediimide]) was investigated by thermogravimetry and by pyrolysis mass spectrometry. The pyrolysis mechanism of polyetherimides consisted of main chain random scission followed by chain transfer of carbonization [14–16]. Previously we investigated by TG/MS/FTIR technique (Simultaneous mass spectrometry and Fourier transform infrared spectroscopy analyser) aromatic polyethers containing phenylquinoxaline and/or oxadiazole rings. The influence of these heterocycles on the polymer thermodegradation behavior was investigated in air and helium atmosphere. It was evidenced the chemical modification appearing at the beginning of thermal decomposition and a mechanism of decomposition [17]. Herein, we present the evaluation of thermal and thermo-oxidative stability of some aromatic polyetherimides, three of them containing 1,3,4-oxadiazole ring, by TG/MS/FTIR. The main decomposition products were determined both in inert atmosphere (helium) and in air. The degradation mechanism was established. The influence of imide and 1,3,4-oxadiazole rings and of the working atmosphere on the thermo-degradation behavior of the polymers was discussed.

2. Experimental

2.1. Materials

Aromatic polyetherimides were prepared by solution polycondensation reaction of different aromatic diamines, such as 2,2-bis[4-(4-aminophenoxy) phenyl]propane, 4,4′-diaminodiphenyl ether, 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole, 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole, and 4,4′-diamino-4″-[2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole)]triphenylmethane with a bis(ether anhydride), namely 4,4′-(4,4′-isopropylidenediphenoxy) bis(phthalic anhydride) (**6HDA**) (Scheme 1). 2,2-Bis[4-(4-aminophenoxy) phenyl]propane, 4,4′-diaminodiphenyl ether and **6HDA** were provided from Aldrich and used as received. 2,5-Bis(4-aminophenyl)-1,3,4-oxadiazole was prepared by the reaction of 4-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid [18]. 2-(4-Dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole was synthesized by a multistep procedure, starting from 4-(dimethylamino) benzohydrazide and 3,5-dinitrobenzoyl chloride, according to a published method [19]. 4,4′-Diamino-4″-[2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole)]triphenylmethane was prepared by a nucleophilic substitution reaction of a fluorinated compound 2-(4-dimethylaminophenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole with 4,4′-diamino-4″-hydroxytriphenylmethane, as it was previously reported [20]. The fluorinated compound was obtained by reacting 4-(dimethylamino) benzohydrazide with *p*-fluorobenzoyl chloride, and cyclodehydration of the resulting product with $POCl_3$. Aromatic polyetherimides were prepared in two steps, in one pot. In the first step poly(amic acid)s were synthesized by the reaction of an aromatic diamine with **6HDA**, at room temperature, in *N*-methyl-2-pyrrolidone (NMP) as solvent (Scheme 1). The concentration of the reaction mixture was adjusted to 15% w/w. In the second step the resulting solutions of poly(amic acid)s were heated, under a nitrogen stream, at 180–185 °C, for 6 h. The water of imidization was evacuated by a slow stream of nitrogen which was used as inert medium, at the same time. All the polymers were soluble in NMP at the end of the reaction.

PEI-1

FTIR (KBr, cm^{-1}): 3053, 2966, 2931, 2871, 1777, 1723, 1593, 1500, 1376, 1239, 744. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.87 (2H, d) 7.46 (2H, s), 7.33 (10H, m), 7.24 (4H, d) 7.10 (4H, d), 7.04 (4H, d), 6.98 (4H, d), 1.73 (12H, d).

PEI-2

FTIR (KBr, cm^{-1}): 3054, 2966, 2932, 2871, 1777, 1723, 1598, 1500, 1376, 1241, 744. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.87 (2H, d), 7.42 (2H, s), 7.39 (4H, d), 7.34 (6H, m), 7.17 (4H, d), 7.03 (4H, d), 1.75 (6H, s)

PEI-3

FTIR (KBr, cm^{-1}): 3097, 3064, 2966, 2932, 2871, 1779, 1726, 1599, 1499, 1363, 1239, 1014, 950, 748. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.26 (2H,d), 7.91 (4H, m), 7.46 (2H, s) 7.33 (8H, m) 7.03 (4H, d), 1.76 (6H, s)

PEI-4

FTIR (KBr, cm^{-1}): 3067, 2967, 2932, 2871, 1778, 1727, 1611, 1500, 1363, 1237, 1014, 980, 748. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.25 (2H, d), 8.04 (1H, s), 7.85 (6H, m), 7.46 (2H, s), 7.35 (4H, m), 7.01 (4H, m), 6.80 (2H, d), 3.03 (6H, s), 1.74 (6H, s).

PEI-5

FTIR (KBr, cm^{-1}): 3062, 2966, 2931, 2870, 1778, 1728, 1619, 1513, 1367, 1245, 1014, 980, 748. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.26 (2H, d), 7.93 (6H, m), 7.72 (2H, d), 7.41–7.15 (12H, m), 7.03 (10H,d), 6,70 (2H, d), 5.37 (1H, s), 3.03 (6H,s), 1.76 (6H, s).

The structures of the polymers were evidenced by FTIR and ^{1}H NMR spectroscopy. In the FTIR spectra of all the polymers (Figs. S1(a) and S2(a) of the Supporting information show typical FTIR spectra of **PEI-2** and **PEI-5**, respectively) strong bands appearing at around 1780–1775 and 1730–1720 cm^{-1} were attributed to asymmetrical and symmetrical stretching vibrations of carbonyl groups of imide rings, and absorption band at around 740 cm^{-1} was due to imide ring deformation. The polyetherimides containing 1,3,4-oxadiazole cycles present in their FTIR spectra absorption bands at 1014 and 950 cm^{-1} characteristic of =C — O — C = stretching vibration in 1,3,4-oxadiazole rings. The absorption band for ether linkages appeared at around 1240 cm^{-1}. The complete conversion of *o*-carboxy-amide groups to the imide rings was confirmed by the disappearance of the absorption bands at 1660–1670 and 2500–3000 cm^{-1}. The imidization of the poly(amic acid)s was also confirmed by the fact that ^{1}H NMR spectra of polyetherimides showed no residual resonance in the region 9–11 ppm indicating the absence of amide NH protons. Fig. S3 of the Supporting information illustrates the ^{1}H NMR spectrum of **PEI-1** with the assignment of all the protons, as an example.

The polymers were easily soluble in polar organic solvents, such as NMP, *N,N*-dimethylformamide (DMF), as well as in certain low boiling-point organic solvents such chloroform. They were less soluble in tetrahydrofurane and dimethylsulfoxide. The