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Thermal decomposition study of some polyimide-polydimethylsiloxane copolymers

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ABSTRACT

This study presents the evaluation of thermal and thermo-oxidative stability of some polyimide-polydimethylsiloxane (PI-PDMS) copolymers and establishes the thermal degradation mechanism by simultaneous mass spectrometry and Fourier transform infrared spectroscopy of gas products from thermogravimetric analyzer (TG/MS/FTIR) in two working atmospheres: air and He. The thermal stability and the start mechanism of thermal degradation were correlated with the chemical structure of PI-PDMS and the working atmosphere. The main thermal decomposition products were determined in both oxidative and inert atmosphere.

1. Introduction

Aromatic polyimides represent one of the most important classes of high performance polymers due to their exceptional thermal and thermo-oxidative stability, good mechanical and electrical characteristics. These polymers are used in many important areas, such as aerospace, automotive, electronics or electrical industry [1,2]. However, in many cases, they have the main disadvantage of being insoluble and infusible, making them difficult to be processed. It is well known that the introduction of flexible bonds or segments such as ether linkages or aliphatic groups into the macromolecular chains of the polyimides increases their solubility in organic solvents and decreases the glass transition temperature [3,4]. Also, the incorporation of flexible polydimethylsiloxane (PDMS) segments in the chemical structure of polyimides led to a new class of imidic copolymers, polyimide-polydimethylsiloxanes (PI-PDMS) having improved processability and special properties conferred by the nature of these segments [5–19]. The PDMS segments enhance the adhesion of the polymeric material to various substrates, decrease the water absorption and dielectric constant, increase the impact resistance and fire resistance, improve the separation properties of a gas or liquid polymer membranes and maintain good thermal stability. By introducing PDMS-segment with $M_n > 1000\ g\ mol^{-1}$, a second phase transition and other properties determined by the presence of both polyimide and PDMS segments appear [5].

The thermal decomposition behavior of a series of fluorinated PI-PDMS was studied by using thermogravimetric analysis in air, at several heating rates [6]. The kinetic processing data were carried out using the Flynn-Wall-Ozawa and Kissinger methods. It was found that the presence of PDMS segments decreased the thermal stability and glass transition temperature. The increase of PDMS content reduced the initial decomposition temperature of polyimides and decreased the apparent activation energy of thermal degradation. The thermal degradation of these polymers begins with the decomposition of *n*-propyl segments of PDMS oligomers [7,8]. A substantial increase of carbonaceous residue at high temperature (700–800 °C) to form a silicate-containing surface was observed after thermal decomposition of PDMS segments. The generation of silicate-containing char limits the production of smoke and the polymer is isolated from the space in which combustion occurs [5,7,9]. Due to the formation of these products, PI-PDMS show improved fire resistance, making them important candidates for applications in areas such as spacecraft and satellite systems.

The study of the thermal degradation mechanism and the determination of the decomposition products are very important both theoretically and practically. The establishment of the mechanism for the initiation of the thermal degradation in both inert and oxidative atmosphere and the determination of the resulting products from thermal degradation is of particular importance in order to estimate their influence on the environment in case of fire. Previously, thermal degradation of some heterocyclic polyethers and polyimides was studied by our group and the degradation mechanisms in oxidative and inert atmosphere were proposed [20,21].

The degradation products were determined in correlation with the working atmosphere and the polymer structures. Herein, some PI-PDMS

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copolymers were prepared and characterized mainly by using TG/MS-FTIR analyses. For comparison purpose, an aromatic polyimide not containing PDMS segments was synthesized. The mechanisms of their thermal decomposition were proposed and the products which occur after the initiation process of degradation were determined.

2. Experimental

2.1. Preparation of polyimide *PI-1* and *PI-PDMS* copolymers

Aromatic polyimide **PI-1** was prepared by solution polycondensation reaction of 4,4′-(1,4-phenylenediisopropylidene)bisaniline and 4,4′-oxydiphthalic anhydride, following a method previously described [7]. PI-PDMS copolymers **PI-2**, **PI-3**, **PI-4** and **PI-5** were prepared by solution polycondensation reactions of 4,4′-oxydiphthalic anhydride or 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) with mixtures of polydimethylsiloxane, bis(3-aminopropyl) terminated (M_n = 2500 g mol^{-1}) and an aromatic diamine, such as 4,4′-oxydianiline or 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole, using a procedure previously reported [7,9]. The ratio between aromatic diamine and polydimethylsiloxane, bis(3-aminopropyl) terminated was adjusted in order to have a final content of polydimethylsiloxane (PDMS) segments of 20 wt%. The structures of the studied polymers are shown in Fig. 1.

2.1.1. PI-1

FTIR (KBr, cm^{-1}): 3061, 2967, 2932, 2663, 1775, 1733, 1600, 1510, 1372, 1260, 1237, 740. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.91 (2H, d), 7.46 (2H, s), 7.42 (2H, d), 7.29 (4H, d), 7.22 (4H, d), 7.12 (4H, m), 1.67 (12H, s).

2.1.2. PI-2

FTIR (KBr, cm^{-1}): 3060, 2961, 2922, 2866, 1774, 1730, 1600, 1500, 1374, 1260, 1234, 1085, 801, 740. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.91 (2H, d), 7.46 (2H, s), 7.42 (2H, d), 7.29 (4H, d), 7.20 (4H, d), 7.12 (4H, m), 3.65 (4H, m), 1.67 (12H, s), 1.62 (4H, s), 0.57 (4H, m), 0.07 (Si-CH_3).

2.1.3. PI-3

FTIR (KBr, cm^{-1}): 3097, 3095, 3065, 2961, 2913, 2852, 1780, 1725, 1601, 1505, 1373, 1265, 1234, 1081, 818, 743. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01 (2H, t), 7.56 (2H, m), 7.48 (2H, d), 7.44 (4H, d), 7.20 (4H, d), 3.65 (4H, m), 1.62 (4H, s), 0.57 (4H, m), 0.07 (Si-CH_3).

2.1.4. PI-4

FTIR (KBr, cm^{-1}): 3065, 2963, 2913, 2852, 1777, 1722, 1598, 1501, 1379, 1262, 1241, 1080, 799, 744. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.91 (2H, d), 7.43 (2H, s), 7.39 (2H, d), 7.34 (8H, d), 7.17 (4H, d), 7.04 (4H, d), 3.65 (4H, m), 1.75 (6H, s), 1.62 (4H, s), 0.57 (4H, m),

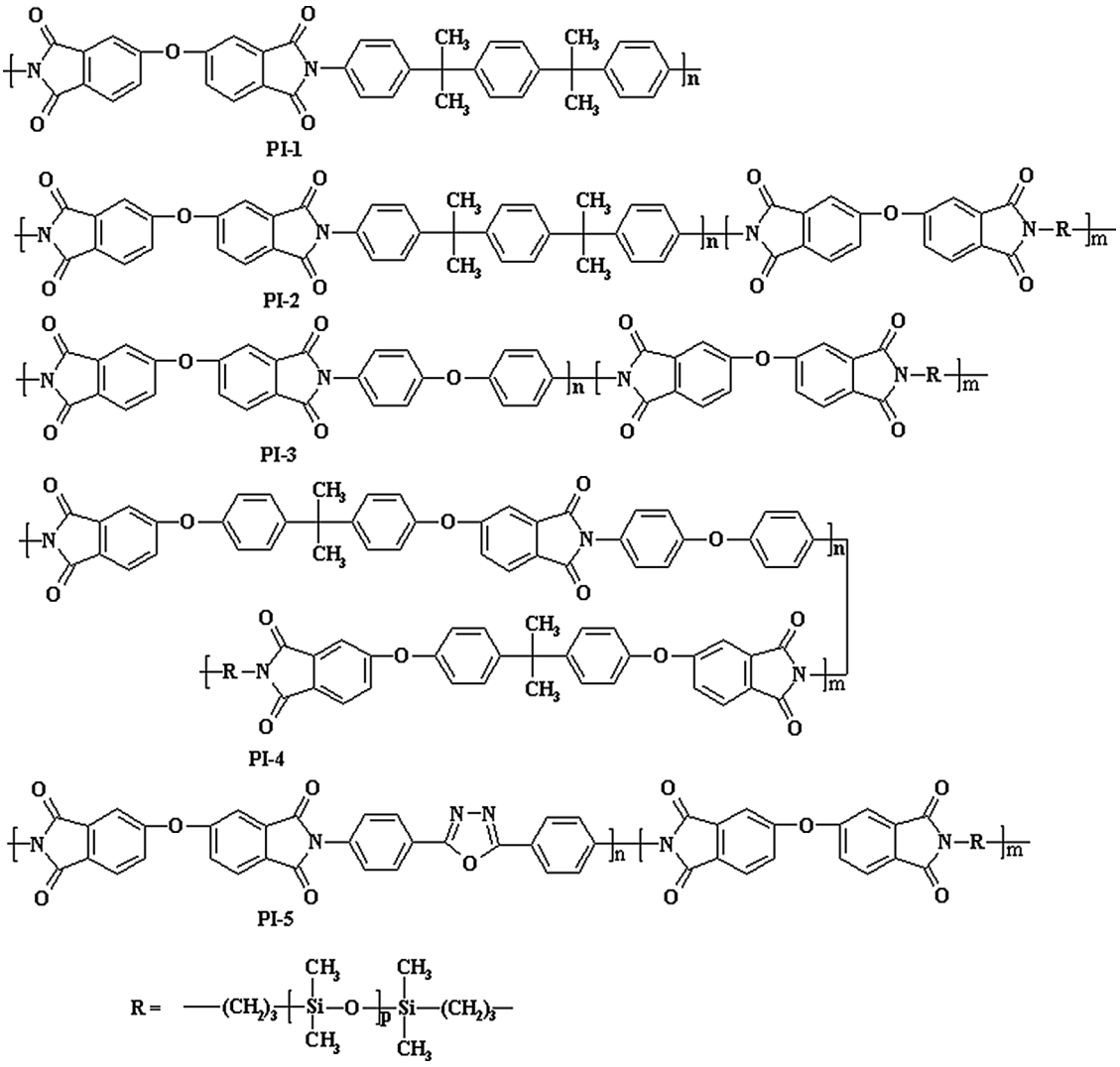

Fig. 1. Chemical structure of the copolymers.