Thermal Decomposition Characteristics of Poly(ether imide) by TG/MS

Li-Hsiang Perng

Department of Chemical Engineering, Ta Hwa Institute of Technology Chung-Lin, Hsinchu 30703, Taiwan

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Abstract: Thermal degradation of poly(ether imide) (PEI) was studied by the combination of pyrolysis/gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetric analysis/mass spectrometry (TG/MS) techniques. The composition of evolved gases was determined by Py-GC/MS and the real-time formation curves were obtained through TG/MS. The thermal degradation mechanisms of PEI were resolved through TG/MS methods. The major pyrolysis mechanisms with the two-stage reaction regions were main chain random scission and carbonization. In the first stage pyrolysis, the decomposition of the hydrolyzed-imide, ether and isopropylene groups caused the evolution of CO₂ and phenol as major products accompanied by a chain transfer of carbonization to form partially carbonized solid residue. In the second stage pyrolysis, the decomposition of partially carbonized solid residue and the remaining imide group produced CO₂ as a major product along with benzene and small a amount of benzonitrile. Afterward, the chain transfer of carbonization dominated the decomposition of solid residue in higher temperatures to produce a high char yield. A kinetic model was proposed from the calculation of two flat regions in the activation energy curve. The theoretical pyrolysis curve from the proposed model was calculated and compared with the experimental curve, which were quite well matched.

Keywords: Poly(ether imide) pyrolysis, Mechanism and kinetic model, Py-GC/MS, TG/MS.

Introduction

Poly (ether imide) (PEI) is an amorphous high-performance polymer with a high thermal durability used in engineering. It resists scratching, chemical corrosion and ignition so as to be easily adapted for processing. This is the reason why it has been evaluated recently for its possible replacement of conventional thermally durable materials and components used in aircraft, medical equipment and automobiles. Degradation studies of PEI are important since processing under high temperatures may produce changes that will affect ultimate performance. Therefore, studies of PEI pyrolysis behavior and mechanism will be of paramount importance for processing and performance evaluation.

The thermal degradation of polymers has been used not only for the identification of materials, the determination of structure and the calculation of thermal resistance, but also for the evaluation of the reaction with its influence on material strength and for the determination of toxicity of volatile components. The degradation behaviors of polyimide were previously studied by many different methods; Zurakowska-Orszagh et al. [1] used infrared spectroscopy (IR) and a 13C nuclear magnetic resonance spectrometer (13C NMR) to analyze the thermal degradation mechanisms of polyimides with isoimide cycles. Hu et al. [2] used X-ray photoelectron spectroscopy (XPS) to study the structural changes of polyimide thin films pyrolyzed above 500 °C. Stump et al. [3] analyzed the dynamic and isothermal kinetics of polyimide using thermogravimetric analysis (TG). Jaccob et al. [4] observed the pyrolysis mechanisms and pyrolysates of aryl-alicyclic polyimides studied by TG/MS and Py-GC/MS. Montaudo et al. [5] investigated the pyrolysis mechanisms of copolyimides using Py-MS at temperatures of 400~470 °C. Kuroda et al. [6,7] used gel permeation chromatography (GPC) and thermo-mechani-

*To whom all correspondence should be addressed.
Tel: 886-3-5923551; Fax: 886-3-5927310
E-mail: cephs@ctu.thir.edu.tw

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cal analysis (TMA) to analyze the cracking mechanisms of polyimide and PEI between 300 and 400 °C. Huang et al. [8] analyzed pyrolysates by TG, Py-GC/MS and IR to evaluate the pyrolysis mechanisms and kinetic parameters of PEI, indicating two-stage pyrolysis reactions. Hummel [9] et al. compared the pyrolysis mechanisms, pyrolysates and solid residues of both poly(1,4-phenylene terephthalimide) and PEI, using Py-MS and Fourier transform infrared spectroscopy (FTIR), respectively, at temperatures between 30 and 680 °C. However, the relationships between the detailed mechanisms and kinetics of PEI pyrolysis are not fully clear due to the complexity of the pyrogram.

Thermogravimetric analysis (TG) is an excellent tool for studying the kinetics of thermal degradation. It provides information on frequency factors, activation energy, and overall reaction order. Unfortunately, it does not provide clear information on thermal degradation mechanisms because of the insufficient capability of evolved gas mixture analysis. However, solid residue analysis is limited by the interference of cross-linking of functional groups in the polymer structure and is not ideal for interpretation. Thus, the direct analysis of gas compositions by continuous monitoring with a real-time TG/MS technique for the identification of gaseous products in the pyrolysis of polymers has gained more attention, particularly for mechanism studies. The development of TG/MS interface design has recently made a significant breakthrough in stability. Such a system has been used in studying the mechanisms of poly(ether ether ketone) [10], liquid crystalline polymers [11], polyimide [12] and fire-retardant additives in polystyrene [13]. The interface system has still not reached ideal status[14] and needs more improvement. TG/MS has been used mostly in the analysis of small-size molecules, such as CO, CO₂, water and phenol. The interface system had been modified in our previous study [15], which used a high sensitivity and low interference for real-time monitoring of major gas evolution curves in the thermal pyrolysis of polymers.

The real-time evolution curves were obtained by the combination of Py-GC/MS and TG/MS techniques in this study. The mechanisms and kinetic model were postulated; in addition, a theoretical pyrolysis curve was calculated from the proposed kinetic model. The correlation of the theoretical and experimental curves was also discussed.

**Experimental**

1. **Materials**

The commercial grade films (~0.09 mm in thickness) of PEI were used in this research were obtained from General Electric Co. Ltd. (USA) (trade name ULTEM®). The number average molecular weight (Mₐ) was ~ 3.4 × 10⁴ g/mol.

2. **Py-GC/MS Analysis**

The Py-GC/MS experiments were carried out using a CDS-2000 Pyroprobe pyrolyzer (Chemical Data System Co.), coupled to a HP 5890 gas chromatograph linking to a HP 5972 quadruple mass spectrometer. Sample aliquots (~1.00 mg) were pyrolyzed in a quartz capillary sample holder using the platinum coil attachment with 5/16” inner diameter (I.D.). The factory-calibrated pyro-probes were used to ensure the accuracy of the nominal setting temperature. Pyrolysis with helium carrier gas at a flow rate of 50 mL/min and an interface of Py-GC at 250 °C was used for flash pyrolysis up to 850 °C at a heating rate of 5 °C/msec for identifying pyrolysates from PEI pyrolysis. The GC column was a HP-5MS (30 m × 0.25 mm I.D. with coated film thickness of 0.25 μm). The oven temperature of the GC was initially held at 40 °C for two minutes, then programmed to 250 °C at 10 °C/min and held for 5 minutes; then programmed to 260 °C at 10 °C/min and held for 10 minutes. The GC/MS interface was set at 280 °C. Mass spectra were recorded under electron impact ionization energy at 70 eV and the flow rate was kept constant. The MS detector was scanned from 10 to 400 m/z at a scan rate of 1.8 scan/s. Data analysis was performed with a HP Chem Station G1034 (version 3.00) to match the NIST Mass Spectra Library by comparison.

3. **TG/MS Analysis**

The TG/MS experiments were performed with a TG/MS system [15] by coupling a Du Pont TA 2950 analyzer with modified CDS-3500 interface and HP 5972 quadruple mass spectrometer. The samples (~1.00 mg) were decomposed with TG and the evolved gases were introduced from the CDS 3500 interface to the HP 5972 mass spectrometer to obtain the generation curves of the pyrolysates. The interface was a splitter using two deactivated columns of 0.53 mm and 0.1 mm I.D. capillary tubing, respectively, with a length of 30 cm to split the evolved gases. The operating conditions were as following: purge gas, helium of 99.9995% purity; temperature setting of the interface, 300 °C; MS range, 10–500 a.m.u.; scan rate 1.2 scans/sec; and two computer systems were used to control the TG and MS respectively. For kinetic studies of PEI pyrolysis, the heating rates were set at 5, 10 and 15 °C/min from 30 to 900 °C in helium atmosphere.