Thermal Degradation Mechanism of Poly(ether imide) by Stepwise Py–GC/MS

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ABSTRACT: The thermal degradation of poly(ether imide) (PEI) was studied through a combination of thermogravimetric analysis and stepwise pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) techniques with consecutive heating of the samples at fixed temperature intervals to achieve narrow temperature pyrolysis conditions. The individual mass chromatograms of various pyrolysates were correlated with pyrolysis temperatures to determine the pyrolysis mechanism. The major mechanisms were two-stage pyrolysis, involving main-chain random scission, and carbonization. In the first stage, the scission of hydrolyzed imide groups, ether groups, and isopropylidene groups produced $CO+CO_2$ and phenol as the major products and was accompanied by chain transfer of carbonization to form partially carbonized solid residue. In the second pyrolysis stage, the decomposition of the partially carbonized solid residue and remaining imide groups formed $CO+CO_2$ as the major product along with benzene and a small amount of benzonitrile. The yield of $CO+CO_2$ was the largest fraction in the total ion chromatogram of the evolved gas mixtures. Hence, the thermal stability of the imide group was identical to the maximum thermogravimetry loss rates in the two-stage pyrolysis regions. Afterward, carbonization dominated the decomposition of the solid residue at high temperatures. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1151–1161, 2001

Key words: thermal degradation of poly(ether imide); stepwise Py–GC/MS; main-chain random scission; carbonization

INTRODUCTION

Poly(ether imide) (PEI) is an amorphous plastic with high thermal durability that is useful in engineering. It also resists organic solvents, chemical corrosion, and ignition and can be easily adapted for processing. This is the reason it was evaluated recently as a replacement for conventional thermally durable materials and components used for packaging and automobiles. This means that more research and further evalua-

tions are required; its pyrolysis behavior and mechanism are of paramount importance.

The thermal degradation of polymers not only has been used for the identification of materials, structural determination, and thermal resistance but also has guided improvements in their backbone structures bringing higher thermal durability. There are numerous studies of the degradation behavior of polyimide in the literature. Zurakowska-Orszagh et al.[1] used IR spectroscopy and ^{13}C NMR to analyze the thermal degradation mechanism of polyimides with isoimide cycles. Hu et al.[2] pyrolyzed polyimide thin films over 500 °C. Stump and Snyder[3] analyzed the dynamic and isothermal kinetics of polyimide with thermo-

gravimetry (TG). Jacab et al.[4] observed the pyrolysis mechanism and pyrolysates of aryl-alicyclic polyimides studied with TG/MS and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS). Montaudo et al.[5] investigated the pyrolysis mechanism of copolyimides with Py–MS around 400–470 °C. Kuroda et al.[6,7] used gel permeation chromatography and thermomechanical analysis to analyze the cracking mechanism of polyimide and PEI between 300 and 400 °C. Huang et al.[8] analyzed the pyrolysates with TG, Py–GC/MS, and IR to evaluate the pyrolysis mechanism and kinetic parameters of PEI. Hummel et al.[9] compared the pyrolysis mechanism, pyrolysates, and solid residue of poly(1,4-phenylene terephthalimide) and PEI with Py–MS and Fourier transform infrared at temperatures between 30 and 680 °C. However, the relationships between the detailed mechanisms and kinetics of PEI pyrolysis are not fully clear because of the complexity of the pyrogram. In addition, traditional flash pyrolysis, such as Py–GC/MS under various temperatures for the pyrolysis of polymers, is unable to differentiate the major pyrolysis mechanism and evolved product distribution at specific temperature regions.[10,11] Recently, I used multistage or stepwise pyrolysis to study the pyrolysis of poly(ether ether ketone) and poly(arylene sulfone)s by Py–GC/MS with consecutive heating of the sample at fixed temperature intervals to achieve narrow temperature ($\sim$100 °C) pyrolysis conditions.[12,13] This method revealed the temperature dependence of individual pyrolysate formations, and the dominant pyrolysis mechanisms in different temperature regions were obtained. In this work, Py–GC/MS was also used to analyze the pyrolysis behaviors of PEI to identify the pyrolysates and mechanisms.

EXPERIMENTAL

Materials

PEI, obtained from General Electric Co., Ltd. (ULTEM®) as commercial-grade films ($\sim$0.09 mm thick) was used in this research. The number-average molecular weight was about 3.4×10^4 g/mol.

TG

The TG experiments were carried out with high-resolution TG (DuPont TA 2950 thermogravimetric analyzer) and a data acquisition module (TA 2100 thermal analyzer). The TG oven tempera-ture was programmed from ambient to 900 °C at 10 °C/min with helium gas purging at a flow rate of 100 mL/min.

Py–GC/MS Analysis

The Py–GC/MS experiments were carried out with a CDS-2000 Pyroprobe pyrolyzer (Chemical Data System Co.) coupled to an HP 5890 gas chromatograph linking to an HP 5972 quadruple mass spectrometer. The Pyroprobes were calibrated by the manufacturer to ensure temperature accuracy. Sample aliquots ($\sim$1.00 mg) were pyrolyzed in a quartz capillary sample holder with a platinum coil attachment with a 5/16-in. inner diameter (ID). The pyrolysis, under helium carrier gas at a flow rate of 50 mL/min, and the interface of Py–GC at 250 °C was used for flash pyrolysis up to 850 °C at a heating rate of 5 °C/ms for identifying pyrolysates from PEI and also for stepwise pyrolysis. The GC column was an HP-5MS (30 m $\times$ 0.25 mm i.d. with a coated film thickness of 0.25 μm). The GC oven temperature was initially held at 40 °C for 2 min, was programmed to 250 °C at 10 °C/min and held for 5 min, and then was programmed to 260 °C at 10 °C/min and held for 10 min. The temperature of the GC/MS interface was set at 280 °C. Mass spectra were recorded under an electron impact ionization energy of 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 analyses were performed with an HP Chem Station G1034 (version 3.00) to match the NIST Mass Spectra Library.

Stepwise Pyrolysis in Py–GC/MS

The stepwise pyrolysis[12] involved a series of interrupted pyrolyses of a sample exposed to a known series of programmed temperatures for a certain period in each step. A fresh sample ($\sim$1.00 mg) was placed in the quartz capillary sample holder at the beginning of each series of analyses and was used throughout the series. The pyrolyzer was initially set at 80 °C for 1 min and then was programmed to 450 °C at a heating rate of 5 °C/ms and held for 30 s. After the pyrogram was obtained, the temperature was programmed to the next higher temperature of 550 °C under similar conditions. The programs were repeated for 650, 750, 850, 950, and 1050 °C, with a total time of around 4 h for the series. The same procedure was repeated three times to ensure the reproduc-
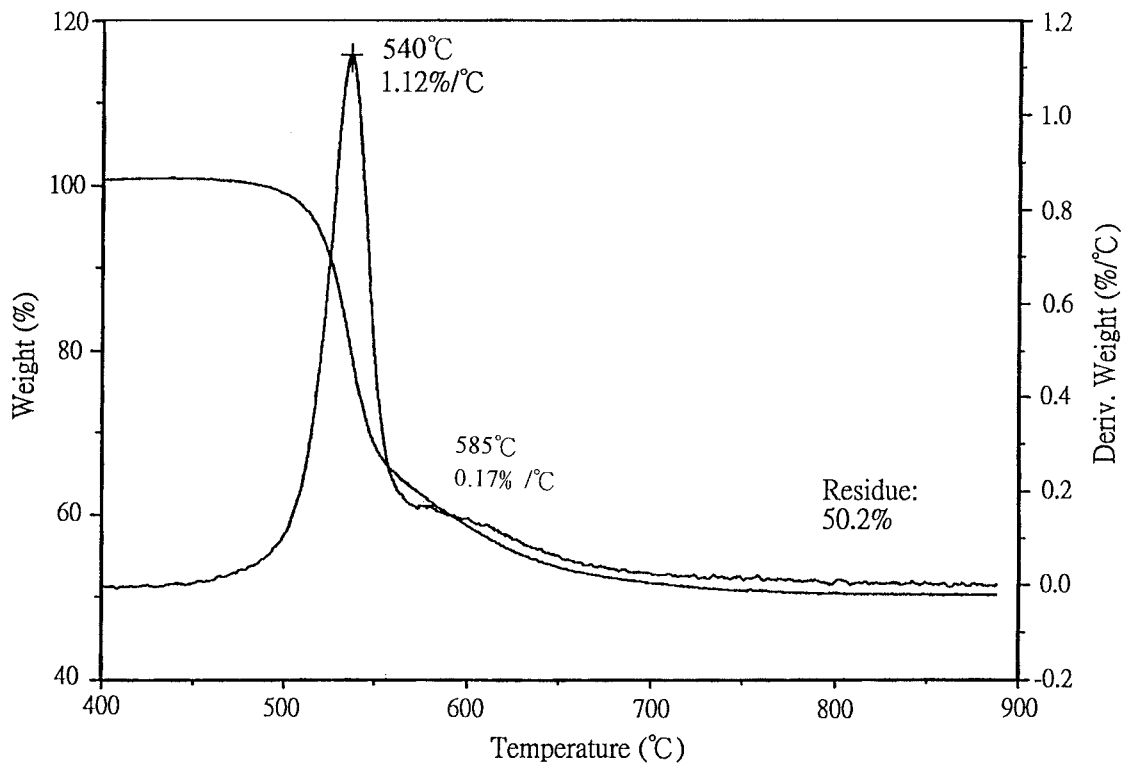
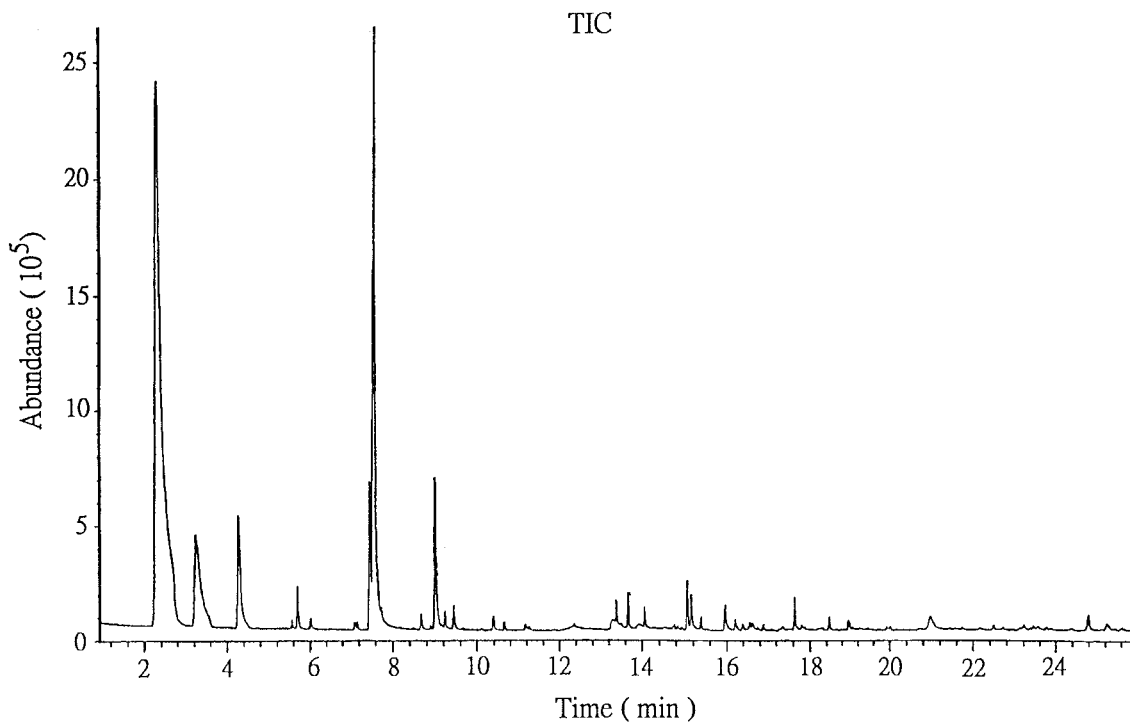**Figure 1**   TG/Differential TG curves of PEI in He at 10 °C/min.

Figure 2   Chromatogram of the flash pyrolysis products of PEI in He at 850 °C.

**Table I Identification of the Products in Flash Py–GC/MS of PEI up to 850°C in He**
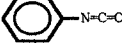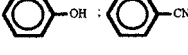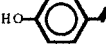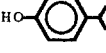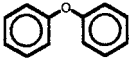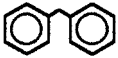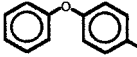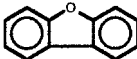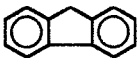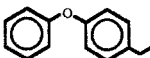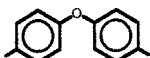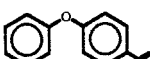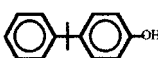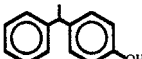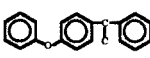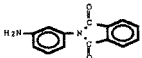
	Compound	Retention Time (min)	Molecular Weight	Major Mass Fragments
	$CO + CO_2$	2.4	28 & 44	28, 44
	Benzene	3.3	78	78, 52, 51, 50, 77
	Methyl-benzene	4.3	92	91, 92, 65, 63, 51
	Ethylbenzene	5.6	106	91, 106, 107, 65
	p-Xylene	5.7	106	91, 106, 105
	Styrene	6.1	104	104, 103, 78, 51, 77
	Isocyanatobenzene	7.0	119	119, 91, 64
	Aniline	7.4	93	93, 66
	Phenol(+)benzonitrile	7.5	94 & 103	94, 66, 65, 55, 95, 50, 51, 38, 103, 76
	2-Methylphenol	8.7	108	108, 107, 79, 77, 90
	4-Methylphenol	9.1	108	107, 108, 77, 79, 90
	4-Methylbenzonitrile	9.2	117	117, 116, 90, 89
	4-Ethylphenol	10.4	122	107, 122, 77
	Naphthalene	10.7	128	128, 127, 51, 129, 102, 126
	p-Vinylphenol	11.1	120	120, 91, 119, 65
	4-(p-Isopropenyl)phenol	11.2	136	121, 136
	2-Vinylnaphthalene	13.4	154	154, 153, 151

Table I *Continued*

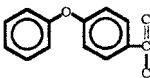| Compound	Retention Time (min)	Molecular Weight	Major Mass Fragments
Diphenylether	13.7	170	170, 141, 51, 142, 77, 169
Diphenylmethane	14.1	168	168, 167, 152, 153
1-Methyl-4-phenoxybenzene	15.1	184	184, 91, 77, 141, 155
Dibenzofuran	15.2	168	168, 139, 169, 63, 84, 140
Fluorene	16.0	166	166, 165, 82, 139, 69
4-Ethyl-1-phenoxybenzene	16.2	198	183, 198, 77, 105, 155
1,1′-Oxybis-4-methylbenzene	16.4	198	198, 91, 155, 97
4-Vinyl-1-phenoxybenzene	16.6	196	196, 181, 182, 167
4-(1-Methyl-1-phenylethyl)phenol	16.9	212	197, 212, 119, 77
4-(1-Methylvinyl)-1-phenoxybenzene	17.7	210	210, 195, 181, 211, 77
4-(1-Phenylethyl)-phenol	20.5	198	121, 198, 77, 93
4-(Phenoxy)-1-(1-phenylethyl)-benzene	24.8	274	197, 274, 77, 181
N-(4-Amino-phenyl)-phthalimide	25.2	238	238, 91, 76, 239

ibility of the resultant data presented later in Figure 3, and these data were normalized to moles of volatile product per mole of polymer subjected to pyrolysis (without a correction for the weight pyrolyzed). The method was based on a report by Day et al.[14]

RESULTS AND DISCUSSION

Outline of the Pyrolysis Behavior of PEI

The TG and differential TG curves in a helium atmosphere at a heating rate of 10 °C/min from
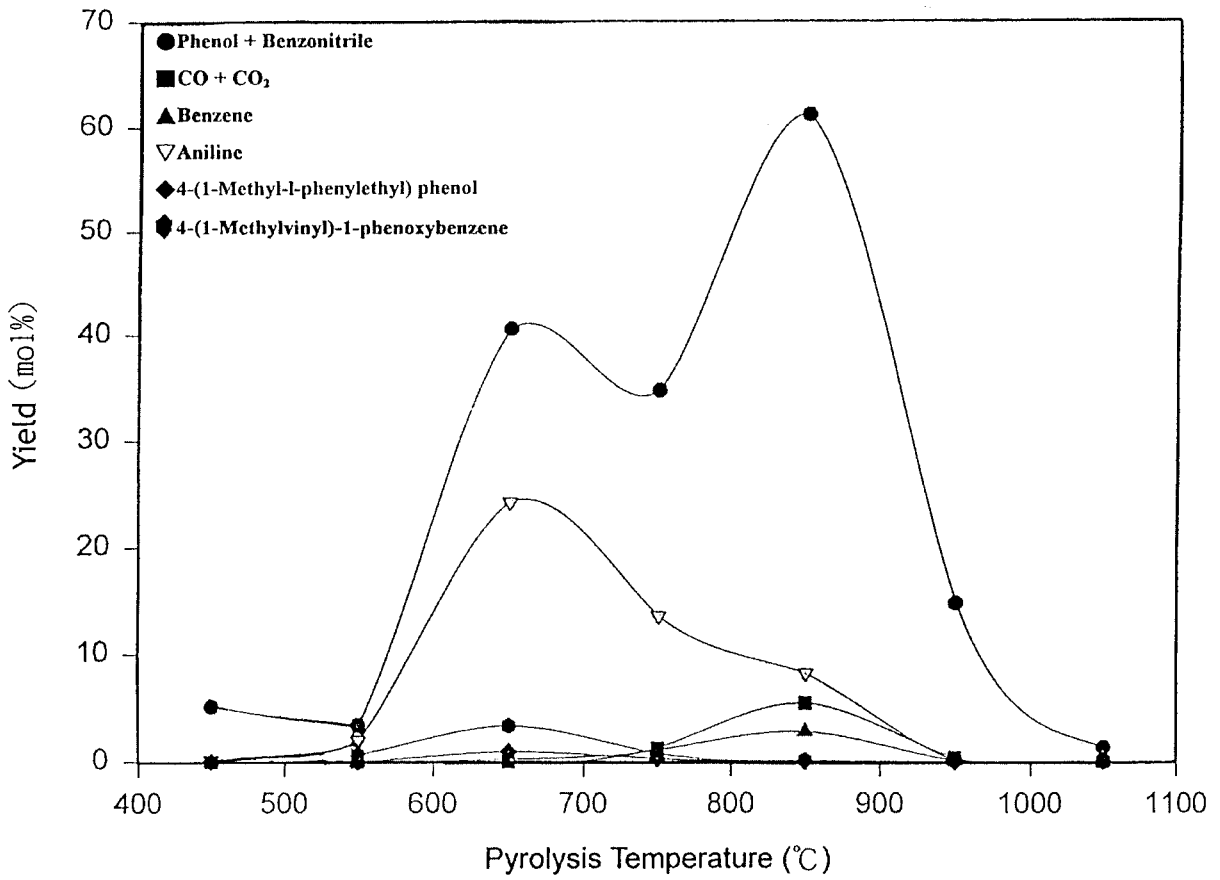
(a)
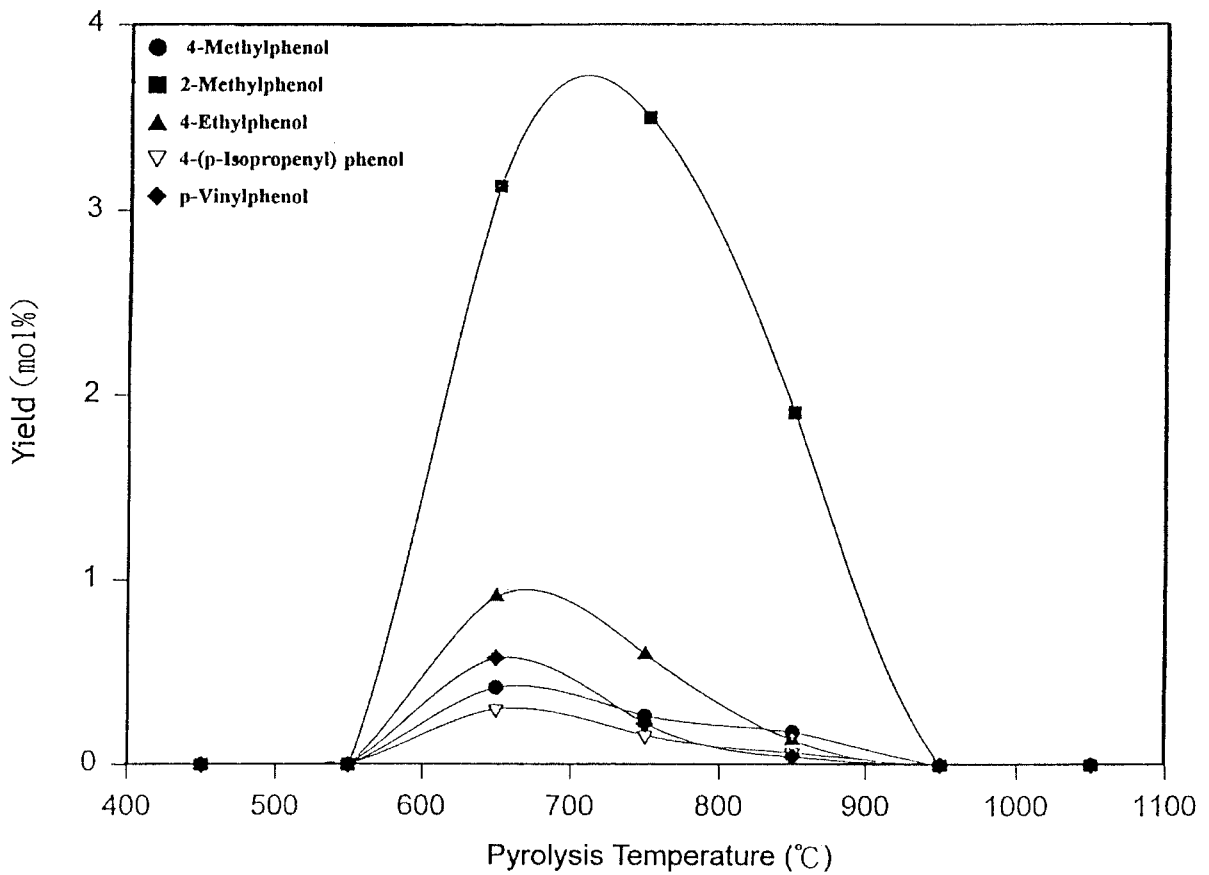
(b)

Figure 3
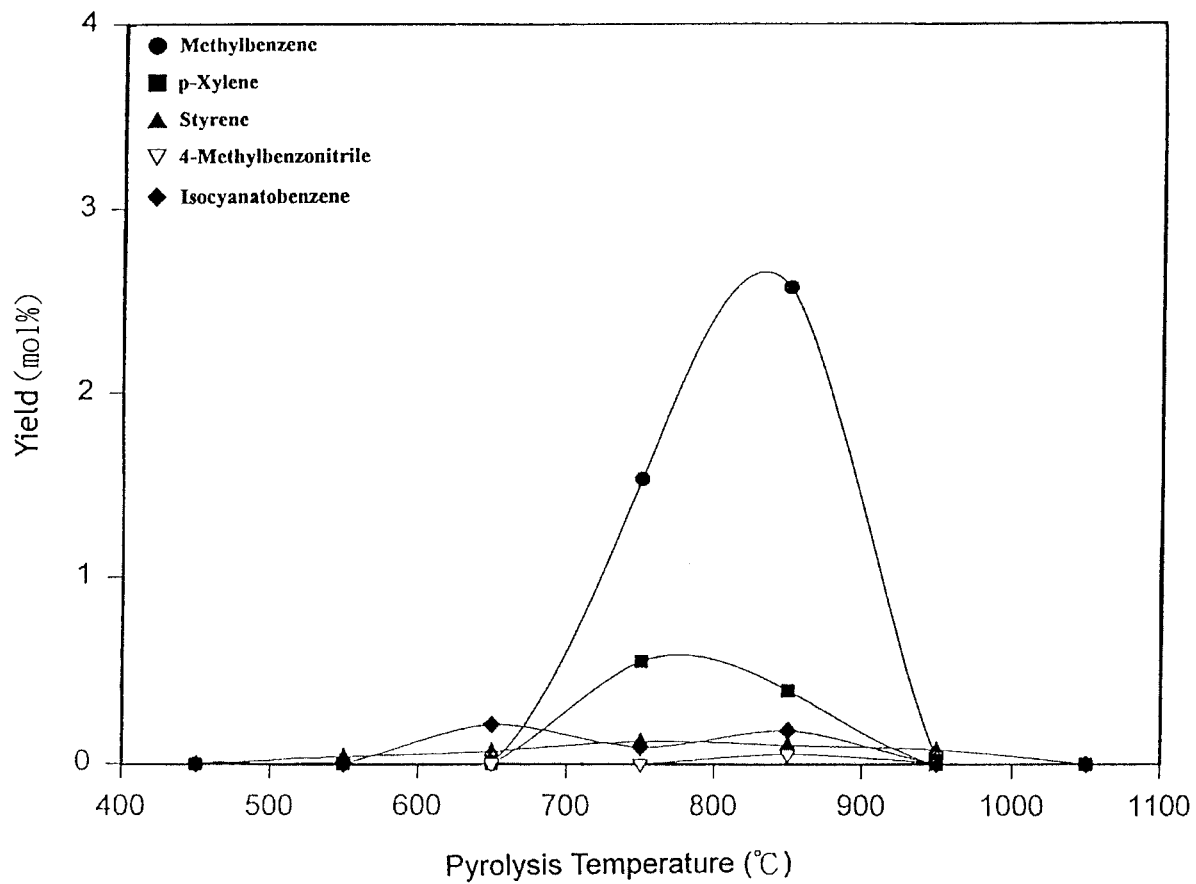
(c)
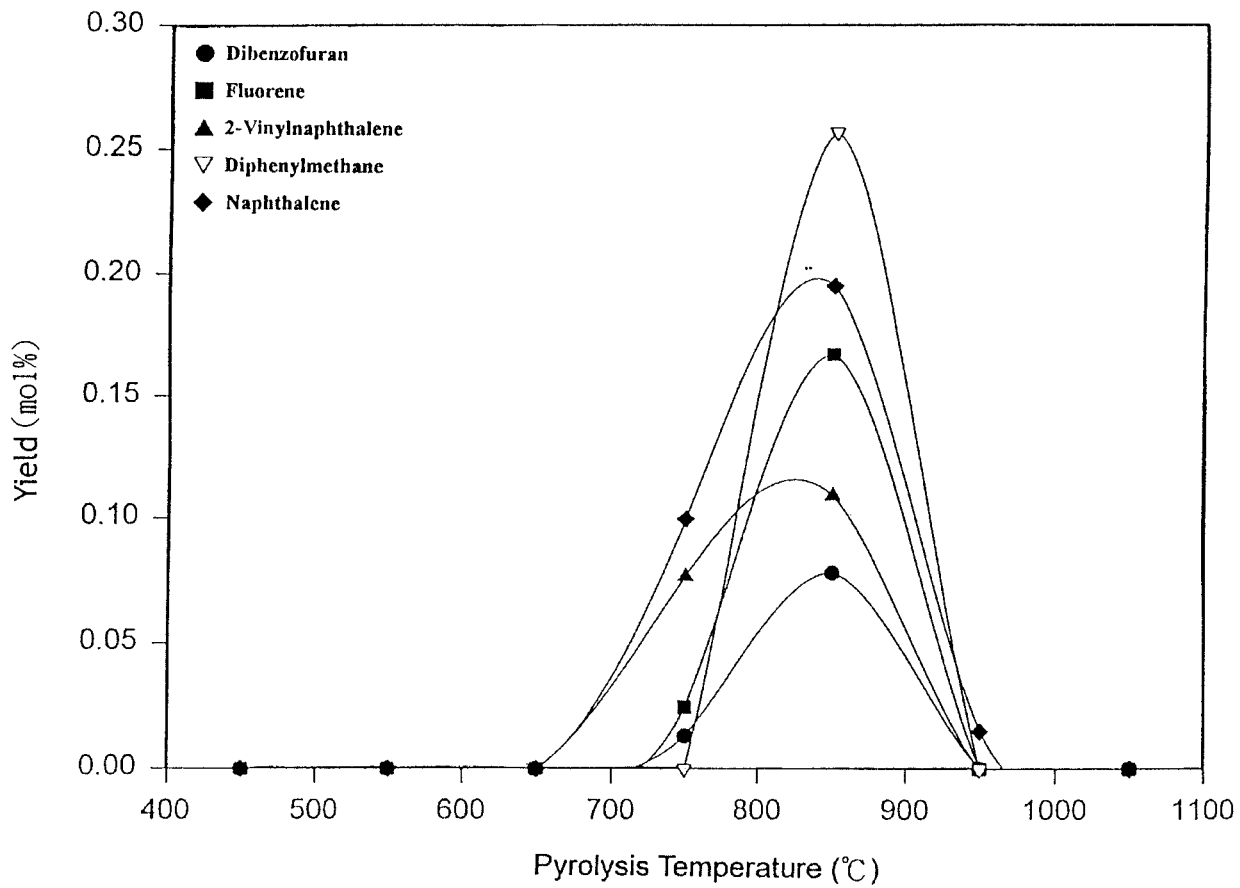
(d)

Figure 3 (*Continued from the previous page*)
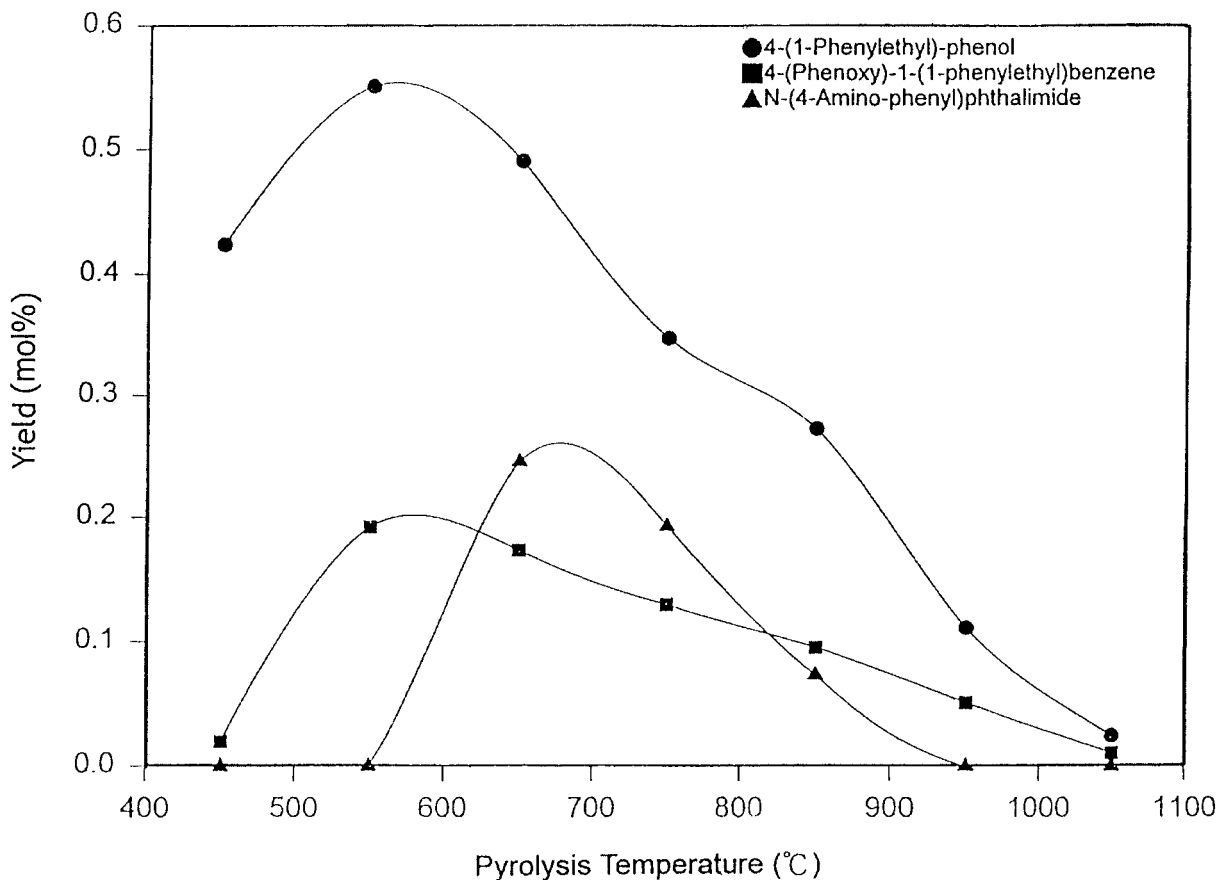
(e)

Figure 3 (*Continued from the previous page*) Change in the PEI pyrolysis products in stepwise Py–GC/MS: (a) phenol+benzonitrile, $CO+CO_2$, benzene, aniline, 4-(1-methyl-1-phenylethyl)phenol, and 4-(1-methylvinyl)-1-phenoxybenzene; (b) 4-methylphenol, 2-methylphenol, 4-ethylphenol, 4-(p-isopropenyl)phenol, and p-vinylphenol; (c) methyl-benzene, p-xylene, styrene, 4-methylbenzonitrile, and isocyanatobenzene; (d) dibenzo-furan, fluorene, 2-vinylnaphthalene, diphenylmethane, and naphthalene; and (e) 4-(1-phenylethyl)-phenol, 4-(phenoxy)-1-(1-phenylethyl)benzene, and n-(4-amino-phenyl)-phthalimide.

room temperature to 900 °C are shown in Figure 1. An apparent weight loss occurred when the temperature was raised over 400 °C, and this phenomenon matched what was found by Huang et al.[8] The maximum pyrolysis temperatures (T_{max}) and rates (r_{max}) in the two-stage pyrolysis were 540 °C (T_{max1}) and 1.12%/°C (r_{max1}) for the first stage and 585 °C (T_{max2}) and 0.17%/°C (r_{max2}) for the second stage, respectively. The residual weight appeared to remain constant above 700 °C with a char yield of about 50 wt %, indicating that the carbonization played an important role in the solid-phase pyrolytic mechanism. On the basis of the results of the TG analysis, the temperatures of the PEI pyrolysis in stepwise Py–GC/MS were

programmed at 450, 550, 650, 750, 850, 950, and 1050 °C to obtain GC and MS curves.

A typical pyrogram (the total ion chromatogram of the pyrolysates) by flash pyrolysis at 850 °C is shown in Figure 2. The major pyrolysates are listed in the order of increasing retention times. The pyrolysates were identified by mass spectra and confirmed through a comparison of their retention times to those reported in the literature.[8,9] Table I lists 30 identified evolved gaseous products from PEI pyrolysis.

Stepwise Pyrolysis

Figure 3(a) shows the major evolution profiles of phenol+benzonitrile, $CO+CO_2$, benzene, aniline,
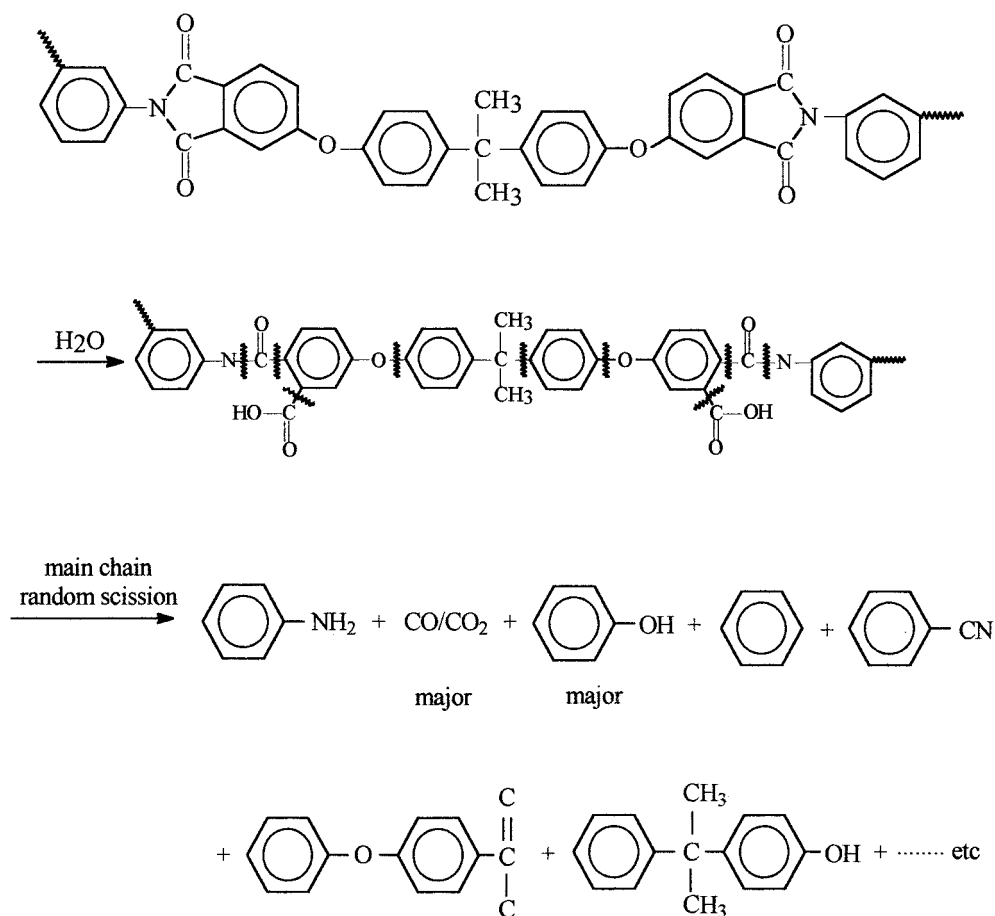
Scheme 1

4-(1-methyl-1-phenylethyl)-phenol, and 4-(1-methylvinyl)-1-phenoxybenzene as a function of the peak temperature. The phenol and benzonitrile and CO and CO_2 that adhered under the operating GC conditions are hereafter presented as phenol+benzonitrile and $CO+CO_2$. The yield of $CO+CO_2$ was the largest fraction in the total ion chromatogram of the evolved gas mixture shown in Figure 3. The major product began to evolve in a small amount around 450 °C and reached maxima around 650 and 850 °C, indicating that it had first evolved from partially hydrolyzed imide groups in the lower temperature region[8] and then had evolved from imide groups in the higher temperature region. These results also indicated that the thermal stability of the imide group was identical to the maximum TG loss rates of the two-stage pyrolysis regions. Phenol+benzonitrile began to evolve around 550 °C, reached the maximum amount around 650 °C, and decreased to trace amounts around 900 °C, indicating that the ether groups, similar to the hydrolyzed imide groups, were also pyrolyzed in the first-stage

pyrolysis region. The initial evolving temperature was higher than $CO+CO_2$, indicating that the hydrolysis of imide groups was induced by a trace of water that existed in the sample[8] and then caused their scission to reduce the initial thermal stability of PEI (see Fig. 1). 4-(1-Methyl-1-phenylethyl)-phenol and 4-(1-methylvinyl)-1-phenoxybenzene began to evolve around 550 °C, reached the maximum amount around 650 °C, and then decreased to a trace amount around 950 °C, indicating that the isopropylidene group was pyrolyzed in the first-stage pyrolysis region. Benzene and aniline began to evolve around 650 °C and reached the maximum amount around 850 °C, indicating that benzene and aniline were formed in the second-stage pyrolysis region. In addition to water existing in the sample, the scission of the ether and isopropylidene groups in the first-stage region also evolved water to catalyze the hydrolysis of imide groups.

Figure 3(b) shows the evolution profiles of the ether/isopropylidene-derivative pyrolysates such as 4-methylphenol, 2-methylphenol, 4-ethylphe-
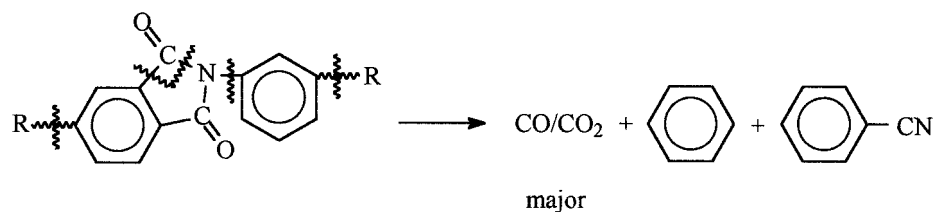
Scheme 2

nol, 4-(*p*-isopropenyl) phenol, and *p*-vinylphenol as a function of the peak temperature. The evolution profiles of these products began to evolve around 550 °C, reached the maximum amount around 650 °C, and then nearly vanished after 950 °C, indicating that these pyrolysates were formed along with the scission of the ether and isopropylidene groups. Diphenylether, 1-methyl--4-phenoxylbenzene, 4-ethyl-1-phenoxybenzene, 1,1′-oxybis-4-methylbezene, and 4-vinyl-1-phenoxbenzene behaved similarly to the pyrolysates in Figure 3(b). The evolution profiles of methylbenzene, *p*-xylene, styrene, 4-methylbenzonitrile, and isocyanatobenzene are shown in Figure 3(c). That the first four pyrolysates reached maxima between 650 and 850 °C indicated that they were forming after the scission of the ether, isopropylidene, and hydrolyzed imide groups. Isocyanatobenzene started only after 750 °C and reached the maximum amount around 850 °C. The evolution profiles of 4-methylbenzonitrile and isocyanatobenzene implied that the scission of imide groups occurred in low- and high-temperature pyrolysis regions, respectively. Figure 3(d) shows the evolution profiles of pyrolysates containing two aryl groups. Dibenzofuran, fluorene, 2-vinylnaphthalene, diphenylmethane, and naphthalene began to evolve around 750 °C, reached maxima around 850 °C, and then rapidly vanished around 950 °C. The evolution profiles of these pyrolysates indicated the recyclization of free radicals from main-chain scission in the higher temperature pyrolysis region. Figure 3(e) shows the evolution profiles of pyrolysates with higher mass. 4-(1-Phenylethyl)-phenol and 4-phenoxy-1-(1-phenylethyl)-benzene began to evolve around 450 °C similarly to $CO+CO_2$, but their amount around 450 °C was smaller than that of $CO+CO_2$ and they reached the maximum amount around 550 °C and continued to form at a higher temperature. The formation of $CO+CO_2$, 4-(1-phenylethyl)-phenol, and 4-phenoxy-1-(1-phenylethyl)-benzene at the initial temperature (~450 °C) indicated the instability of the hydrolyzed imide groups induced by water existing in the polymer sample, chain ends,

and chain branches. *N*-(4-Amino-phenyl)-phthalimide began to evolve around 650 °C, reached the maximum amount around 750 °C, and gradually decreased, indicating that the high-temperature environment could favor the scission of PEI to form the imide-containing products.

Thermal Degradation Mechanisms

The pyrolytic mechanisms of PEI with two-stage pyrolysis regions were postulated from the results in this study. In the first-stage reaction, main-chain random scission was the primary mechanism, including the scission of the ether and isopropylene groups with the evolution of a small amount of water that caused hydrolysis of the imide groups. The formation of $CO+CO_2$ and phenol as major products along with benzene, aniline, isopropylidene derivatives, and lesser amounts of benzonitrile are shown in Scheme 1.

The initial hydrolysis reaction of the imide groups was induced by a trace of water that always existed in the polymer sample.[8] This phenomenon resulted in the initial evolving temperature of $CO+CO_2$ being lower than that of the other pyrolysates. Besides, the main-chain random scission accompanying the chain transfer of carbonization formed partially carbonized solid residue in this pyrolysis region. In the second-stage region above 560 °C, the major mechanism was the decomposition of the remaining imide groups to form $CO+CO_2$ as the major product along with benzene and a lesser amount of benzonitrile, as shown in Scheme 2.

CONCLUSIONS

The process of PEI pyrolysis with two-stage reaction regions was initialized first by the scission of the hydrolyzed imide groups induced by water existing in the sample, and then the scission of the ether and isopropylene groups also evolved a small amount of water to hydrolyze part of the imide groups. Hence, the factor of the imide group hydro-

lysis reduced the initial thermal stability of PEI. In the first-stage pyrolysis reaction, the evolution of $CO+CO_2$ and phenol as the major products along with the chain transfer of carbonization formed partially carbonized solid residue. In the second pyrolysis region, the decomposition of the partially carbonized solid residue and remaining imide groups formed $CO+CO_2$ as the major product along with benzene and a lesser amount of benzonitrile. Thus, the major mechanisms in this two-stage pyrolysis reaction consisted of main-chain random scission followed by carbonization.

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