Thermal degradation behaviour of aromatic poly(ester–imide) investigated by pyrolysis–GC/MS

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Abstract The thermal degradation behaviours of a novel aromatic poly(ester–imide) (PEI) derived from pyromellitic dianhydride and 2,7-bis(4-aminobenzoyloxy)naphthalene have been investigated by thermogravimetric analysis (TGA) and by pyrolysis–gas chromatography/mass spectrometry (pyrolysis–GC/MS). The weight of PEI fell slightly in the temperature range of 350–450 °C in the TGA analysis, but the major weight loss occurred at 520 °C. Evolve gas analysis (EGA) of the PEI showed maximum release of pyrolyzates at 550 °C. The chemical structure of the volatile products resulted from the PEI pyrolysis at different temperatures was identified by pyrolysis–GC/MS. The cleavage of the ester linkage within the polymer chain initiated at 350 °C, and bond scission in the partially hydrolyzed pyromellitimide unit occurred in the temperature range of 450–500 °C. The bonds within the pyromellitimide unit started to cleave at 550 °C. The extensive decomposition of the pyromellitimide segment within the polymer backbone occurred at 600 °C. The possible thermal degradation pathways of this PEI are proposed on the basis of the pyrolysis products.

Keywords Poly(ester–imide) · Thermal degradation · TGA · Pyrolysis–GC/MS

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Introduction

Wholly aromatic polyimides have been categorized as high-performance polymeric materials with several useful properties such as outstanding thermal and oxidative stability, excellent mechanical strength, low flammability, good chemical and radiation resistance, and low dielectric constant [1–3]. However, one of the problems with most polyimides is their insolubility in most organic solvents and high glass-transition or softening temperatures caused by the high intermolecular interactions and rigidity of the polymer backbones. Thus, they are generally difficult to be cast into articles in the fully imidized form, and their applications are restricted in many fields. For this reason, various efforts have focused on the synthesis of soluble and/or thermoplastic polyimides without sacrificing their desired thermal and mechanical properties. Those efforts include the introduction of flexible links [4–8], asymmetric units [9–11], bulky pendant groups [12–16], and kinked or non-coplanar structures [17–22] into the polymer chain. These modifications have lowered the melting temperature and increased the solubility by reduction in crystallinity.

In connection with our interest in preparing easily processable high-performance polymers bearing naphthyl units, we have reported the synthesis of aromatic poly (ester–imide)s derived from polycondensation of 2,7-bis (4-aminobenzoyloxy)naphthalene with the corresponding aromatic dianhydrides [23]. These polymers with flexible ester groups exhibited an increased solubility and processability as compared with wholly aromatic polyimides and might find practical uses in some fields. Understanding of the thermal decomposition characteristic of a polymer is of crucial importance for practical application, and thermal degradation mechanisms of these polymers are still unclear due to the lack of direct experimental evidence.

The technique of pyrolysis has been employed for the identification of materials, analysis of compound structures, and the understanding of poisonous pyrolysates. There are many studies of pyrolysis in the literatures by using TGA/FTIR [24, 25], TGA/EGA/FTIR [26], TGA/GC/MS [27], and pyrolysis–GC/MS [28–31]. Recently, pyrolysis–GC/MS analysis has been successfully applied to the elucidation of the thermal degradation mechanisms of polymeric materials. In this work, we characterized the thermal degradation of the aromatic poly(ester–imide) (PEI) and identified the volatile products resulted from the polymer pyrolysis at different temperatures by pyrolysis–GC/MS. The structure of the pyrolysis products allowed a schematization of the thermal degradation pathways involved in the degradation of the investigated PEI.

Experimental section

Materials

Preparation of the aromatic poly(ester–imide) (PEI)

A naphthalene-ring-containing diesteramine, 2,7-bis(4-aminobenzoyloxy)naphthalene (**2**), was prepared by hydrogen Pd/C-catalyzed reduction of the dinitro compound **1** resulting from the condensation reaction of 2,7-naphthalenediol with 4-nitrobenzoyl chloride. The aromatic poly(ester–imide) (PEI) was synthesized from the diesteramine **2** and pyromellitic dianhydride (PMDA) via a conventional two-stage synthesis that included ring-opening polyaddition to give poly(amic-acid) followed by chemical imidization to polyimide, as shown in Scheme 1. The detailed synthetic procedures and characterization data of diesteramine **2** and the PEI have been described in our previous article [23].

Preparation of 4-cyanophthalimide and N-phenyl-4-cyanophthalimide

To a solution of DMF (11 ml) was added 4-bromophthalimide (0.0234 mol) and CuCN (0.0398 mol), and the mixture was heated to 150 °C for 12 h under nitrogen. The reaction mixture was then cooled to 100 °C, H_2O (20 ml) and NaCN (0.0743 mol) added, and the suspension was stirred for 2 h at ambient temperature and partitioned with ethyl acetate. The organic phase was washed with water (2×50 ml), dried with $MgSO_4$, and concentrated in vacuo to give the crude desired product. The crude product was purified by re-crystallization from ethanol to give the desired 4-cyanophthalimide in 75% yield. Physical data of 4-cyanophthalimide: mp. 231–232 °C; IR (KBr): ν (cm^{-1})= 3,189; 3,089; 2,236; 1,774; 1,660; 1,623; 1,474; 1,426; 1,356; 1,303; 1,168; 1,112; 1,074; 1,052; 934; 869; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.98 (d, J=7.6 Hz, 1H), 8.27 (d, J=7.6 Hz, 1H), 8.33 (s, 1H), 11.70 (s, 1H); MS, m/z 172 (M$^+$), 129, 128, 101, 75, 50.

N-Phenyl-4-cyanophthalimide was prepared from *N*-phenyl-4-bromophthalimide [32] by the similar procedure. *N*-Phenyl-4-cyanophthalimide is a known compound, and the physical data of the *N*-phenyl-4-cyanophthalimide synthesized herein were consistent with the published results [33].

Measurements

Thermogravimetric analysis (TGA) was conducted with a Perkin Elmer Pyris 1 TGA. The TGA experiment was run three times on a sample of approximately 5 mg for each time and was carried out in flowing nitrogen (40 cm^3/min) at a heating rate of 20 °C/min from 200 to 800 °C. Pyrolysis–GC/MS analyses were run in a Frontier Laboratories model PY-2020iD Double-Shot Pyrolyser coupled to a Hewlett Packard 6890 series Gas Chromatographer linking to a Hewlett Packard 5973 Mass Selective Detector. The pyrolysis temperatures were respectively set at 300, 350, 400, 450, 500, 550, 600, and 700 °C. The pyrolysis gases from the PEI were respectively introduced directly into the GC/MS analysis system. The pyrolyser is based on a technique in which a small deactivated stainless steel cup loaded with a sample is dropped into a small sized vertical furnace by gravitational free-fall with push button mechanism. This system is designed to provide precise temperature control and minimal condensation of pyrolysates in the system. A sample of 1 mg was placed in the small stainless steel cup and attached it to the pyrolyser. After the GC conditions were established and the pyrolysis furnace heated up to 300 °C at a heating rate of 20 °C/min, the sample cup was dropped into the pyrolysis furnace by manually pressing the sample drop button and introduced the sample cup to reach instantly the indicated pyrolysis temperature; the run was then immediately started. Once the system started to run, the sample controller stopped sampling after 0.5 min and the pyrolysis gases from the PEI sample were introduced directly into GC/MS analysis system. The operations were repeated at 350, 400, 450, 500, 550, 600, and 700 °C. Every procedure was repeated three times to ensure reproducibility.

The interface temperature of pyrolysis–GC/MS was set at 320 °C. The GC column is an F-Lab UA5-30M-0.25F metal capillary column (30 m×0.25 mm i.d. with a coated film thickness of 0.25 μm) which shows higher thermal resistance up to 380 °C and is more effective in analyses of pyrolysates. The flow of the helium carrier gas was 1.0 ml/min. The GC oven temperature was initially held at 40 °C for 2 min, and then was programmed to 300 °C at 20°C/min and held for 5 min. Total time of a sample run was 20 min. The GC
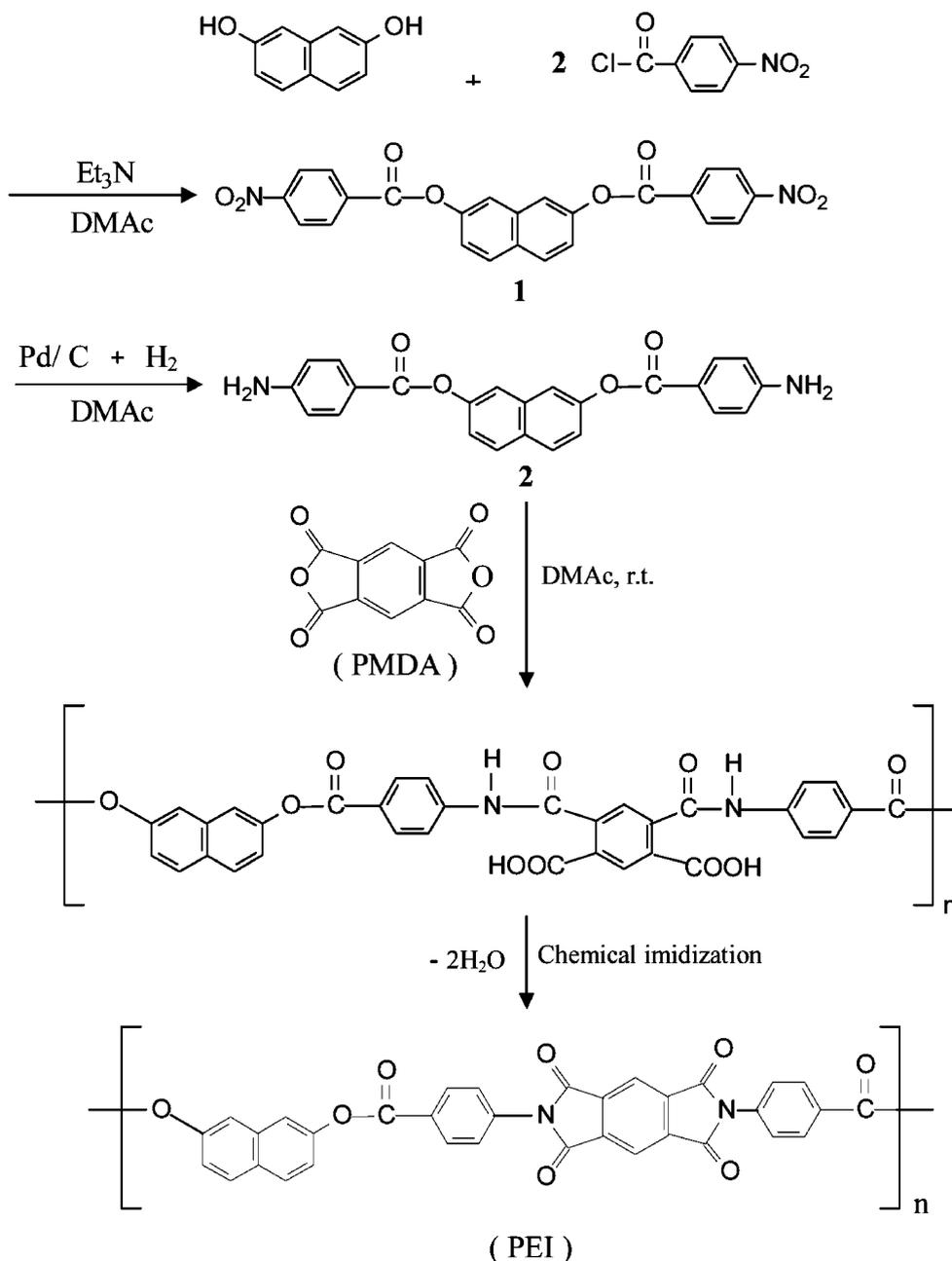
Scheme 1 Synthesis of the PEI

inlet temperature was 320 °C, pressure 7.1 psi, total flow 14.1 ml/min, split ratio 10/1, and split flow 10 ml/min. The temperature of the GC/MS interface was set at 280 °C. The MS detector was scanned from 29 to 550 m/z at a scan rate of 4.4 scans/s. Data analyses were searched by computer to match the database of Wiley275.L Mass Spectra Library.

The pyrolyser can also be operated in evolved gas analysis–mass spectrometry (EGA-MS) mode to provide total ions emission abundance versus temperature or time. The EGA-MS curves were generated by detecting evolved

gases obtained by continuously heating a sample at a heating rate of 20 °C/min from 50 to 700 °C and at 700 °C the sample was held for 10 min. Thus, the EGA-MS mode started to run, the sample controller was continuously sampling for 42.5 min. The evolved gases for EGA-MS mode were introduced directly into GC/MS analysis system through an F-Lab UADTM-2.5M deactivated metal capillary column (2.5 m×0.15 mm i.d. with a coated film thickness <0.01 μm). The GC column was only 2.5 m and coated film thickness <0.01 μm so that the evolved gases

for EGA-MS mode were detected without any chromatographic separation. The GC oven temperature was held at 300 °C for 42.5 min. Total time of a sample run was 42.5 min.

Results and discussion

Thermal degradation behaviour

In Fig. 1 are reported the TGA and DTG curves of PEI obtained under nitrogen, showing that this polymer starts decomposing in the temperature range of 250–450 °C and experiences the maximum rate of decomposition at about 520 °C. This maximum is followed by a less marked decomposition step in the 550–650 °C temperature range. At 800 °C about 50% of charred residue is left. In Fig. 2 is reported the EGA-MS curve for the total ions of the PEI, which displays a peak maximum at 550 °C with a shoulder at near 600 °C and can be attributed to the evolution of thermal decomposition products of the polymer.

Products from pyrolysis of PEI

To further identify the structure of the pyrolysis products of the PEI, pyrolysis–GC/MS was employed in this study. According to the DTG and EGA-MS data, the pyrolysis temperatures of PEI in pyrolysis–GC/MS were set at eight different temperature conditions, 300, 350, 400, 450, 500, 550, 600, and 700 °C. The chromatograms of PEI at flash pyrolysis temperatures between 350–500 °C and 550–700 °C are shown in Figs. 3 and 4, respectively.
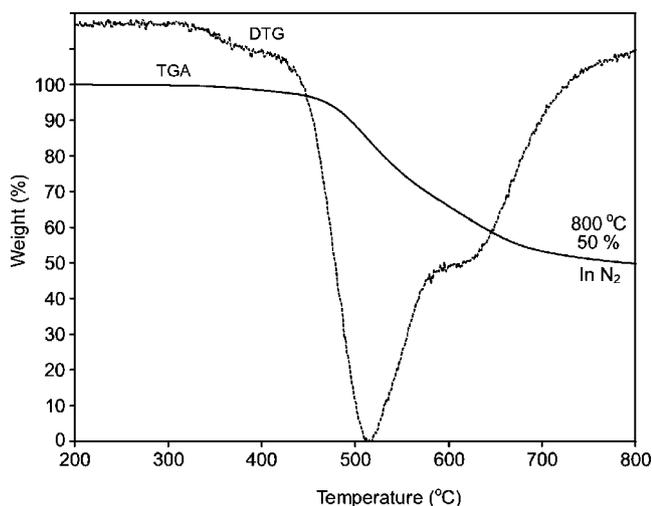

Fig. 1 The TGA and DTG curves of the PEI from 200 to 800 °C at a heating rate of 20 °C/min
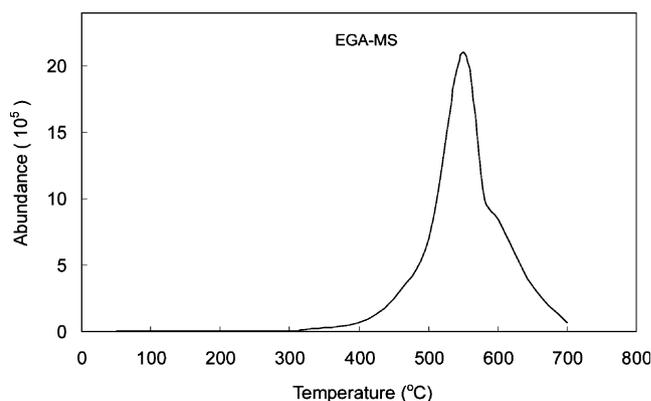

Fig. 2 The EGA-MS curve of total ions of the PEI from 50 to 700 °C at a heating rate of 20 °C/min

The assigned pyrolysates of PEI at 700 °C are listed with increasing retention time in Table 1. The most chemical structures of pyrolysates listed in Table 1 were identified by mass data bank, but two peaks, 13 and 16, with the molecular mass of 172 and 248 were not registered in our
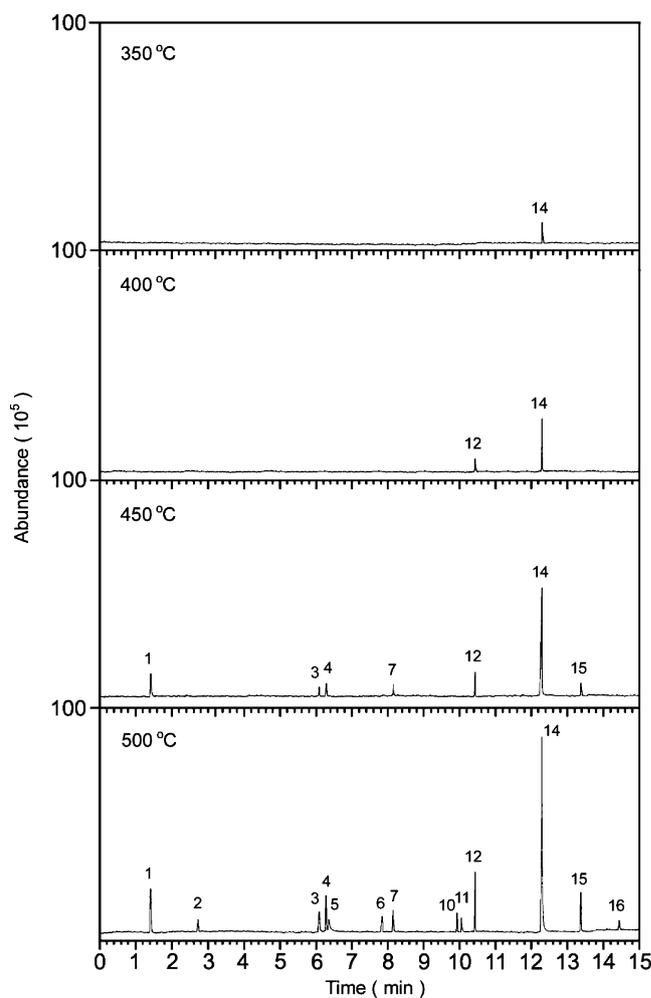
Fig. 3 The chromatograms of the pyrolysates of the PEI at 350–500 °C
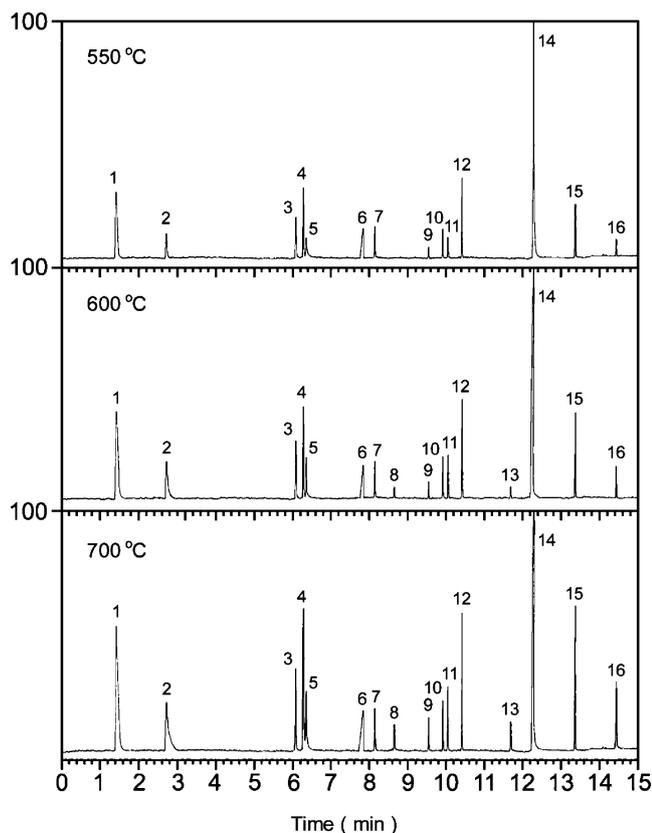
Fig. 4 The chromatograms of the pyrolysates of the PEI at 550, 600 and 700 °C

mass data bank for chemical structure identification. Judging from the structure of the polymers, we hypothesized that these two unexpected molecular mass peaks should have the chemical structures equivalent to the 4-cyanophthalimide and *N*-phenyl-4-cyanophthalimide. In order to confirm our hypothesis, we decided to synthesize these two compounds and analyzed them by GC-mass under the polymer pyrolysis condition. The one step synthesis of 4-cyanophthalimide and *N*-phenyl-4-cyanophthalimide was outlined in Scheme 2. The synthesized compounds 13 and 16 were separately subjected to pyrolysis using the condition similar to that used for the PEI, and the corresponding pyrolysates were analyzed by GC-MS. 4-Cyanophthalimide and *N*-phenyl-4-cyanophthalimide yielded the GC peaks with retention time of 11.69 and 14.43 min, respectively. The molecular masses corresponding to these two peaks were 172 and 248, and their mass fragmentation patterns were identical to the peak 13 and 16 generated from pyrolysis of PEI at 700 °C. These results indicated that 4-cyanophthalimide and *N*-phenyl-4-cyanophthalimide were evolved during the pyrolysis of PEI.

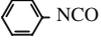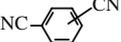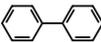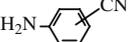Two major groups of the pyrolysates were categorized in Table 1. Most pyrolysates were directly formed from polymer backbone degradation, but the only one exception was the observed biphenyl which was the secondary reaction product. In order to characterize the initial pyrolysis reactions of the PEI, the temperature dependence of product formation was studied, and the results are summarized in Table 2. No pyrolysis product of this PEI was detected at 300 °C. The 2,7-naphthalenediol was the initial degradatio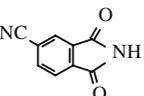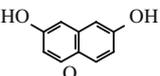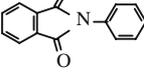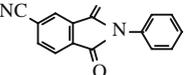n product of the PEI at 350 °C as shown in Table 2. 2-Naphthol started to evolve along with 2,7-naphthalenediol at about 400 °C, and the amount of these two products increased appreciably between 400 and 550 °C. A number of other pyrolysis compounds including naphthalene, aniline, carbon dioxide, phenylisocyanate, and *N*-phenylphthalimide were detected at 450 °C, and their concentration showed a steady increase up to 700 °C. The next set of released products observed at 500 °C was phthalimide, benzonitrile, benzoic acid, benzene, *N*-phenyl-4-cyanophthalimide and inseparable mixture of 3- and 4-aminobenzonitrile. The evolution of the secondary product, biphenyl, was observed at 550 °C. The release of 4-cyanophthalimide and inseparable mixture of 1,3- and 1,4-dicyanobenzenes occurred at 600 °C, and their peak intensity increased obviously at 700 °C.
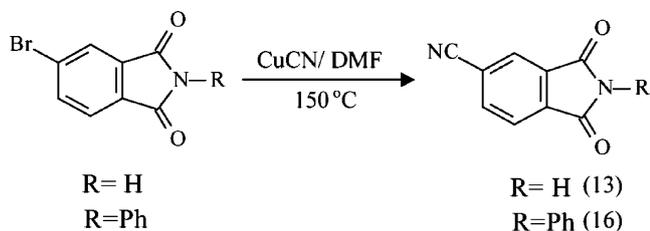
As shown in Table 2, we found the release of phthalimide, *N*-phenylphthalimide and *N*-phenyl-4-cyanophthalimide at the temperature below 500 °C. This result is somewhat surprising since there has been reported in the literatures that imide ring cleavage mainly occurred at 500–600 °C [34]. The temperature-resolved evolution profiles of these phthalimides are shown in Fig. 5. Phthalimide began to evolve in small amount in the temperature range of 450–500 °C and peaked at near 600 °C as shown in Fig. 5a. Two stages evolution were noticed for *N*-phenylphthalimide and *N*-phenyl-4-cyanophthalimide; the first stage occurred at temperature around 500 °C, and the second stage centered at 580 °C as shown in Fig. 5b and c. From these results, we proposed that the initial release of these phthalimides at the lower temperature (≤500 °C) was originated from bond cleavage of the partially hydrolyzed pyromellitimide moieties of PEI [28, 35]. The later stage of release was attributed to the direct bond scission at the intact pyromellitimide moieties of PEI.

Thermal degradation mechanisms

On the basis of pyrolysis–GC/MS results, the proposed pyrolysis mechanisms of PEI are depicted in Scheme 3. The release of 2,7-naphthalenediol at 350 °C and 2-naphthol at 400 °C indicated that the initial degradation reactions occurred mainly at ester linkage. With the 2,7-naphthalenediol appeared to be the largest peak in all chromatograms, this result suggested that 2,7-naphthalenediol was the major pyrolytic product. The release of 2,7-naphthalenediol from

Table 1 Identification of the pyrolysates in pyrolysis–GC/MS of the PEI at 700 °C

Peak code		Compound	Retention time (min)	Molecular weight
1	CO_2	Carbon dioxide	1.42	44
2		Benzene	2.72	78
3	NCO	Phenylisocyanate	6.08	119
4	NH$_2$	Aniline	6.28	93
5	CN	Benzonitrile	6.37	103
6	COOH	Benzoic acid	7.82	122
7		Naphthalene	8.15	128
8	NC—CN	1,3- and 1,4-Dicyanobenzene	8.64	128
9		Biphenyl	9.55	154
10	H$_2$N—CN	3- and 4-Aminobenzonitrile	9.92	118
11	NH	Phthalimide	10.04	147
12	OH	2-Naphthol	10.42	144
13	NC...NH	4-Cyanophthalimide	11.69	172
14	HO...OH	2,7-Naphthalenediol	12.29	160
15	N—Ph	N-Phenylphthalimide	13.38	223
16	NC...N—Ph	N-Phenyl-4-cyanophthalimide	14.43	248

Scheme 2 Synthesis of 4-cyanophthalimide (13) and N-phenyl-4-cyanophthalimide (16)
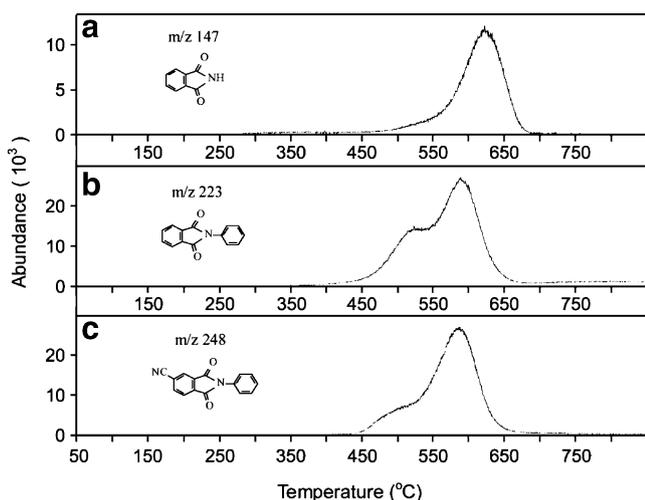
PEI could be the direct results of the hydrolysis of the ester linkage by the absorbed moisture. The release of 2-naphthol indicated that a homolytic breakage of the $C_{naphthyl}$–O bond (labeled as b in Scheme 3a) occurred at 400 °C for PEI. Naphthalene evolved from PEI at 450 °C was the result of a homolytic bond breaking of both $C_{naphthyl}$–O bonds (labeled as b and c in Scheme 3a) followed by hydrogen transfer reactions.

The other pyrolytic products such as aniline, phenyl-isocyanate, carbon dioxide, and N-phenylphthalimide were

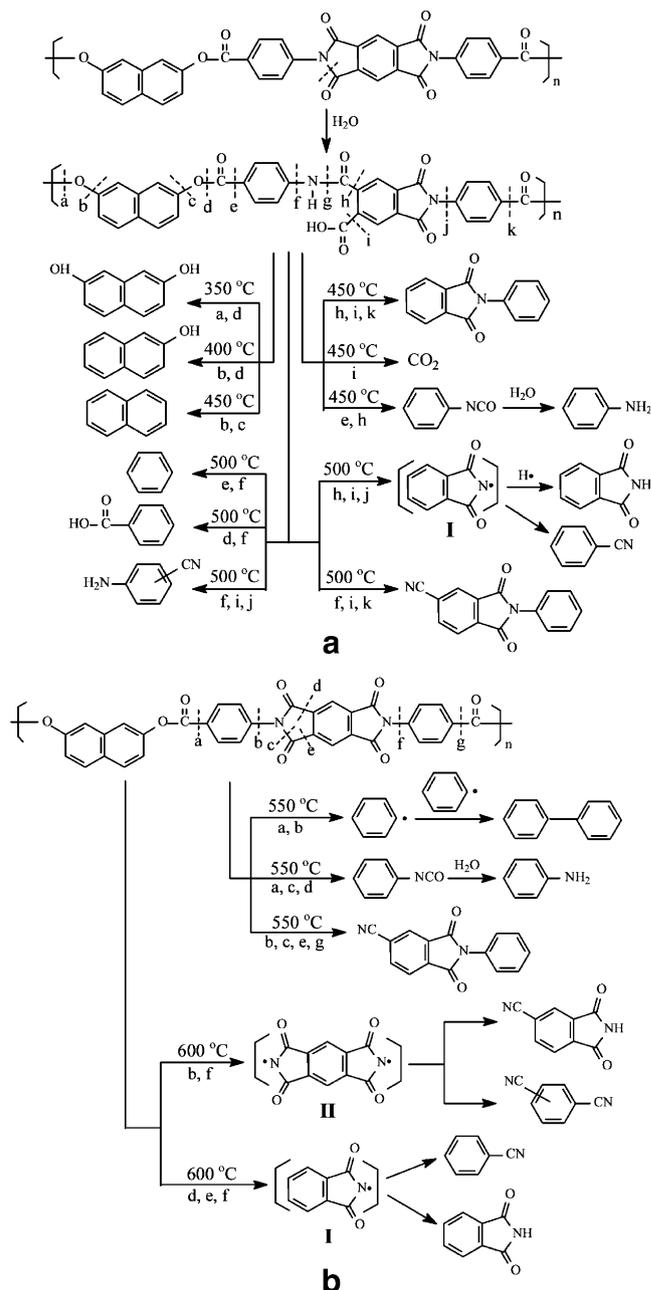**Table 2** Detection temperatures of the pyrolysates of the PEI

Temperature (°C)	PEI
350	2,7-Naphthalenediol
400	2-Naphthol
450	Naphthalene, N-phenylphthalimide, aniline, CO$_2$, phenylisocyanate
500	Benzoic acid, benzene, mixture of 3- and 4-aminobenzonitrile, phthalimide, benzonitrile, N-phenyl-4-cyanophthalimide
550	Biphenyl
600	Mixture of 1,3- and 1,4-dicyanobenzene, 4-cyanophthalimide

Benzoic acid, benzene, phthalimide, benzonitrile, N-phenyl-4-cyanophthalimide and mixture of 3- and 4-amino-benzonitrile were the pyrolytic products from partially hydrolyzed PEI at 500 °C. The ester hydrolysis of the main chain followed by the homolytic scission of the C_{phenyl}–N bond (labeled as d and f in Scheme 3a) gave benzoic acid. Benzene was the product of the homolytic cleavage of $C_{carbonyl}$–C_{phenyl} and C_{phenyl}–N bonds (labeled as e and f in Scheme 3a) followed by hydrogen abstraction. N-Phenyl-4-cyanophthalimide was released from the partially hydrolyzed pyromellitimide moiety by homolytic

also detected at 450 °C, and this result correlated with the above indication which chemical bond disconnected within the partially hydrolyzed pyromellitimide moiety at this temperature. As shown in Scheme 3a, N-phenylphthalimide and phenylisocyanate were released from homolytic bond cleavage at ester linkage and amide linkage, but the phthalimide ring was remained intact. The presence of N-phenylphthalimide was the result of the homolytic cleavage of three $C_{carbonyl}$–C_{phenyl} bonds (labeled as h, i and k in Scheme 3a) with subsequent hydrogen abstraction reactions. At 450 °C, the evolution of phenylisocyanate might be the result of the homolytic cleavage of $C_{carbonyl}$–C_{phenyl} bond on the amide linkage (labeled as e and h in Scheme 3a) followed by hydrogen radical elimination. The observed aniline at 450 °C was believed as the secondary product from hydrolysis of phenylisocyanate. Thermal decarboxylation on polymer backbone occurred at 450 °C to release the carbon dioxide.

Fig. 5 EGA curves of the individual ions at m/z 147 (**a**), 223 (**b**), and 248 (**c**) of the poly(ester–imide) when it was heated from 50 to 700 °C at a heating rate of 20 °C/min

Scheme 3 The pyrolysis mechanisms of the PEI at **a** 350–500 °C and **b** 550–600 °C

cleavage of C_{phenyl}–N and $C_{carbonyl}$–C_{phenyl} bonds (labeled as f, i and k in Scheme 3a) with subsequent hydrogen abstraction and dehydration. Small amount of phthalimide, benzonitrile and inseparable 3- and 4-aminobenzonitrile released at 500 °C might also be the result of bond scission from the partially hydrolyzed pyromellitimide linkage as shown in Scheme 3a. The observed phthalimide at 500 °C also suggested that cleavage of C–N bond connecting the imide ring with diester section occurred at this temperature. Phthalimide radical I, formed by homolytic cleavage of the $C_{carbonyl}$–C_{phenyl} bonds and N–C_{phenyl} bond (labeled as h, i and j in Scheme 3a) with partial hydrogen abstraction, might further abstracts a hydrogen atom to give phthalimide. The formation of benzonitrile most likely takes place from a high temperature secondary pyrolysis process of phthalimide, which involves the formation of a thermal labile isocyanate intermediate that decomposes generating nitriles and carbon dioxide [30]. Mixture of 3- and 4-aminobenzonitriles may be the results of initial homolytic scission of C_{phenyl}–$C_{carbonyl}$, C_{phenyl}–N_{amide} and C_{phenyl}–N_{imide} bonds (labeled as f, i and j in Scheme 3a), the radicals generated on the imide ring and terminal amide moiety further rearrange to the corresponding cyano group and amino group.

At 550 °C, phenyl radical formed by homolytic bond scission of $C_{carbonyl}$–C_{phenyl} and C_{phenyl}–N (labeled as a and b in Scheme 3b) combined to give biphenyl. Homolytic bond cleavage on pyromellitimide ring occurred at temperature ≥550 °C, was an alternative pathway to release various pyrolytic products. As shown in Scheme 3b, high amount of phenylisocyanate could be formed from the homolytic bond scission of C_{phenyl}–$C_{carbonyl}$ and $C_{carbonyl}$–N (labeled as a, c and d in Scheme 3b), since the peak intensity of phenylisocyanate and aniline increased significantly at temperature ≥550 °C. Similarly, the amount of N-phenyl-4-cyanophthalimide evolved from imide ring cleavage (labeled as b, c, e and g in Scheme 3b) of the pyromellitimide moiety also significantly increased at 550 °C.

At 600 °C, the observed pyrolytic products of 4-cyanophthalimide and inseparable mixture of 1,3- and 1,4-dicyanobenzene suggested homolytic scission of both N–C_{phenyl} bonds connecting the pyromellitimide moiety with diester sections occurred at this temperature. As shown in Scheme 3b, the diradical intermediate II generated on the pyromellitimide ring could either rearrange to give inseparable mixture of 1,3- and 1,4-dicyanobenzenes, or underwent hydrogen abstraction and radical rearrangement simultaneously to give 4-cyanophthalimide. Also shown in Scheme 3b, bond cleavage on pyromellitimide ring (labeled as d, e and f) might provide another route to generate radical intermediate I, which further abstracted a hydrogen atom to give phthalimide or rearranged and decarboxylated to give benzonitrile.

Conclusions

The thermal degradation behaviour of the poly(ester–imide) (PEI) was identified in this study. The TGA and DTG curves of the PEI showed a slight weight loss at the temperature range of 350–450 °C followed by a main decomposition around 520 °C. Results from pyrolysis–GC/MS suggested that the slight weight loss at the temperature range of 350–450 °C was the result of bond cleavage at ester linkage. A major weight loss at 520 °C was attributed to bond scission at the imide ring. The release of 2,7-naphthalenediol from PEI started at 350 °C and it was the major degradation product of the PEI. This result suggested that the ester bond in PEI was apparently the thermal weak points of the polymer chain, and this result was also concurred by the TGA experiments. Homolytic scission of the $C_{naphthyl}$–O bond began at 400 °C which resulted in the release of 2-naphthol. Pyrolysis products such as CO_2 and phthalimide derivatives were found in the temperature range of 450–500 °C; they were the results of bond scission at the partial hydrolyzed pyromellitimide moiety. Bond scission at the pyromellitimide linkage of PEI occurred at 550 °C and beyond. The degradation products, 4-cyanophthalimide and inseparable mixture of 1,3- and 1,4-dicyanobenzene were found at 600 °C. In this work, we identified 16 pyrolysates of the PEI at 700 °C.

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