

## **THERMAL CHARACTERIZATION OF MATERIALS USING EVOLVED GAS ANALYSIS**

*W. Xie and W.-P. Pan*

Thermal Analysis Laboratory, Materials Characterization Center, Department of Chemistry,  
Western Kentucky University, Bowling Green, KY 42101, USA

(Received April 27, 2001)

### **Abstract**

Thermal analysis combined with evolved gas analysis has been used for some time. Thermogravimetry (TG) coupled with Fourier transform infrared (FTIR) spectroscopy (TG/FTIR), Thermogravimetry (TG) coupled with mass spectrometry (TG/MS), and Thermogravimetry (TG) coupled with GC/MS offers structural identification of compounds evolving during thermal processes. These evolved gas analysis (EGA) techniques allow to evaluate the chemical pathway of the degradation reaction by determining the decomposition products. In this paper the TG/FTIR, TG/MS, and Pyrolysis/GC-MS systems will be described and their applications in the study of several materials will be discussed, including the analysis of the degradation mechanisms of organically modified clays, polymers, and coal blends.

**Keywords:** Pyrolysis/GC-MS, TG/FTIR, TG/MS, thermal analysis

### **Introduction**

Evolved gas analysis (EGA) [1] is a technique to determine the nature and amount of a volatile product or products formed during the thermal degradation of materials. EGA technique involves the analysis of gaseous species evolved during combustion and/or pyrolysis in which a series of chemical reactions occur as a function of temperature and are analyzed using thermal analytical methods and/or multiple techniques. EGA is normally used to evaluate the chemical pathway of degradation reactions by determining the composition of the decomposition products from various materials.

Two approaches are generally used for EGA, simultaneous analysis and combined analysis. In the simultaneous analysis approach two methods are employed to examine the materials at the same time, such as TG/FTIR and TG/MS on-line analysis, in which decomposition products that evolve from pyrolyzed materials can be monitored simultaneously. The combined analysis technique, on the other hand, employs more than one sample for each instrument, and real time analysis is not possible.

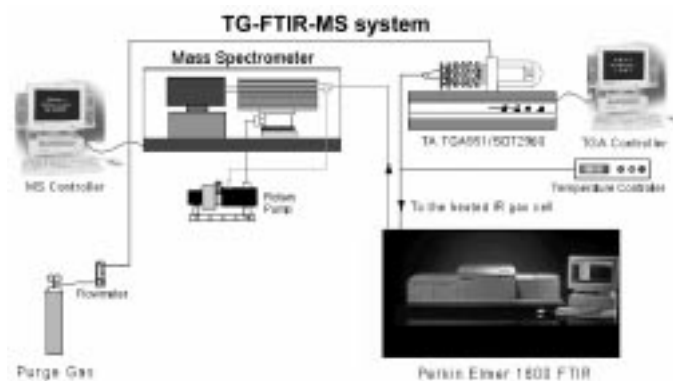
With regard to simultaneous and combined analysis, there are two major forms of sampling procedures which can be used to semi-quantitatively and qualitatively de-

termine the decomposition products, which are continuous mode and intermittent mode. Continuous mode involves introducing the gaseous products directly into the detector system using an interface coupling [2–4], such as TG/FTIR, and TG/MS. In this case, the products can be continuously and simultaneously examined by the detector. Intermittent or batch mode refers to trapping evolved gaseous species at a low temperature or in an absorption chamber [5, 6] and the trapped products are then introduced into a detector for identification, such as a TG/GC-MS or Pyrolysis/GC-MS system. The intermittent mode allows the investigator to optimize the detector parameters to make the best choice for different samples. The detector system does not have to be extensively modified for the intermittent mode. The main advantage of the continuous mode is the ability to conduct simultaneous and continuous real time analysis.

The ability to measure the simultaneous and continuous mass loss of materials and monitor the gaseous products responsible for the mass loss allows TG/FTIR and TG/MS techniques to be widely employed in the material science field, including the study of coal pyrolysis and combustion, polymer degradation, evaluation of hazardous materials, thermal stability of materials, and formation of pharmaceuticals [7]. Considerable work [8–13] on characterizing materials, determining kinetic parameters, and quantitative analysis of degradation products has been performed with TG/FTIR. TG/MS had also been widely employed in the characterization of materials. The development of this instrumentation and its application has been discussed in several excellent reviews [14–17]. However, the fact that one cannot distinguish between all the evolved gases due to overlapping either in FTIR spectra (similar wavelengths) or MS spectrum (identical masses) is an obvious disadvantage of these techniques. Diatomic molecules that do not possess a permanent dipole moment are not infrared active, and therefore cannot be detected using infrared absorption. Also, overlapping peaks, such as the O–H stretching vibration in water and carboxylic acids, presents a problem in the analysis of mixtures. On the other hand, the mass spectrometer is very sensitive and can identify the mass range of the species in a sample. Also, it has a faster response time than an FTIR system. The detection limit of the MS system is usually less than 1 ppm, which is more sensitive than an FTIR system having a general detection limit of approximately 10 ppm. However, the MS system has a relatively high cost and since it measures only mass-to-charge ratios, it does not have the ability to determine isomers. Another major disadvantage of TG/FTIR and TG/MS techniques is their inability to detect high molecular mass compounds. TG/GC-MS or Pyrolysis/GC-MS techniques, however, are capable of identifying high molecular mass compounds released from materials during the pyrolysis/combustion process, although they cannot provide the time- and/or temperature-dependent gas evolution profiles that can be obtained from TG/FTIR and TG/MS techniques. Therefore, the combination of TG/FTIR/MS/GC-MS techniques makes it possible to determine the composition and distribution of almost all the gaseous products evolved from materials, and then evaluate the decomposition mechanisms of the materials.

*TG/FTIR/MS and Pyrolysis/GC-MS systems*

Schematic diagrams of the TG/FTIR/MS and Pyrolysis/GC-MS systems at Western Kentucky University are shown in Fig. 1.



**Fig. 1** A schematic diagram of TG/MS/FTIR at Western Kentucky University

**TG/FTIR system**

The Western Kentucky University TG/FTIR system consists of a DuPont Instruments Model 951 Thermogravimetric Analyzer interfaced with a Perkin Elmer 1650, or 2000, Fourier Transform Infrared Spectrometer. The Model 951 system has a horizontal quartz tube furnace which allows large samples to be used. A ball joint connection allows easy access for introducing samples. A custom-made connector prevents condensation of decomposition products. The ball and socket joints and Teflon connector are wrapped with a heating coil which is controlled by a variable autotransformer. The samples are heated at a given heating rate from room temperature to the desired temperature in either an inert gas such as ultra-purity nitrogen or oxidizing gas such as air or oxygen. The purge gas ( $50 \text{ mL min}^{-1}$ ) flow carries the decomposition products from the TGA through a 70 mL sample cell with KBr crystal windows. The cell is placed in the IR scanning path for detection of the decomposition products and is kept at  $150^\circ\text{C}$  by a wrapped heating tape to prevent possible condensation. IR detection range used is between  $450$  and  $4500 \text{ cm}^{-1}$ .

**TG/MS system**

The Western Kentucky University TG/MS system consists of either a DuPont Instruments Model 951 Thermogravimetric Analyzer or a TA Instruments 2960 TGA/DTA interfaced with a Fisons VG Thermolab Mass Spectrometer using a heated capillary transfer line. The sample is heated from ambient temperature to the desired temperature, under flowing ( $50 \text{ mL min}^{-1}$ ) nitrogen (UHP grade) or air. The capillary transfer line is heated to  $220^\circ\text{C}$ , and the inlet port on the mass spectrometer is heated to  $150^\circ\text{C}$ . The capillary inlet (1.8 m) is constructed from fused silicon encased within a stainless-steel sheath. It is then covered with Teflon and then with a red fiber glass

sheathing. Such a construction allows for good mechanical strength and means to resistively heat the long capillary line. Another major advantage of this interface is that it produces a partial pressure in the MS ion source proportional to that in the gas sample at atmospheric pressure at the inlet probe. The Fisons unit is based on quadrupole design with a 1–300 atomic mass units (amu) mass range and the sample gas from the interface is ionized at 70 eV. The system is operated at a pressure of  $1 \cdot 10^{-6}$  torr and this MS system is equipped with an NIST library database for MS analysis.

#### *Pyrolysis/GC-MS system*

The Western Kentucky University Pyrolysis/GC-MS system consists of a LECO Pegasus II GC/MS system and a ThermEx<sup>TM</sup> Inlet System. Pegasus II GC/MS system includes a time-of-flight mass spectrometer and a high speed gas chromatograph. The advantage of time-of-flight (TOF) mass spectrometry is its potential for tremendously fast acquisition rates. By combining TOF technology, LECO's Pegasus II GC/MS achieves the fastest acquisition rate without loss of data integrity. The ThermEx<sup>TM</sup> Inlet System is designed to heat small quantities of solid samples in a quartz Pyrocell<sup>TM</sup> and transfer the volatilized sample components to a heated capillary GC injection port. The carrier gas connections and seals are designed to provide a leak free system for operation with a GC-MS system. The associated gas chromatograph has a capillary injector capable of operating in the split mode and an oven configured with a cryogenic option (liquid nitrogen). During the sample-heating period, extracted volatiles are condensed at the column head at ambient or cryogenic temperature. Once the sample has been heated to the desired temperature in the ThermEx<sup>TM</sup> system and all out-gassed components condensed at the column head, the cryogenic system is very rapidly heated to vaporize the components and inject them onto the GC column for analysis.

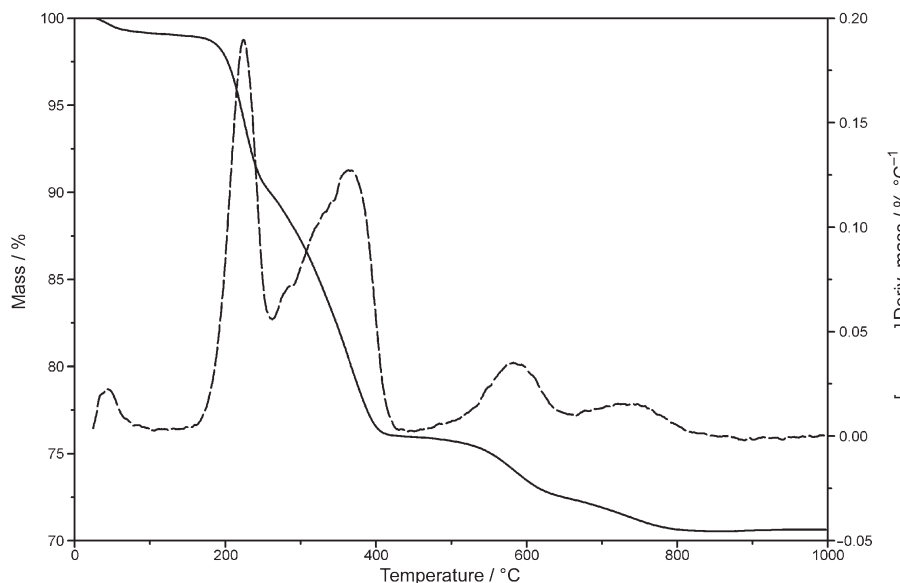
## **Applications of evolved gas analysis techniques**

#### *Thermal characterization of organically modified montmorillonite*

Polymer/organically modified layered silicate (OLS) nanocomposites are a new class of filled polymers with ultrafine phase dimensions. They offer an outstanding combination of stiffness, strength and mass that is difficult to attain separately from the individual components. These nanocomposites are synthesized by blending organically modified layered silicates (OLS) into the melt polymer. Thus, understanding the relationship between the molecular structure and the thermal stability (decomposition temperature, rate, and degradation products) of the OLS is critical. TG/FTIR, TG/MS and Pyrolysis/GC-MS techniques were used to evaluate the thermal decomposition mechanisms and the degradation products of OLS.

Montmorillonite exchanged with trimethyloctadecyl, quaternary ammonium chloride was used in the study. The TG/DTG curve shown in Fig. 2 for OLS can be considered in four parts: 1. water region at temperatures below 200°C; 2. the region

from 200–500°C where organic substances evolve; 3. the structural water region in the temperature range from 500–800°C; 4. and the region from 800–1000°C where metal species within the aluminosilicate potentially catalyzes a reaction between the carbonaceous residue and the oxygen in the crystal structure of the dehydroxylated montmorillonite yielding CO<sub>2</sub>.



**Fig. 2** TG curve of trimethyl octadecyl quaternary ammonium montmorillonites

As shown in Figs 3 and 4, the decomposition products of OLS are mixtures of alkanes and alkenes, and other light gases, including water and CO<sub>2</sub>. The release of alkanes and alkenes can be identified from MS spectra of the investigated materials ( $m/z=41, 55, 69, 73, 87, 101, 115, 139$ , and  $m/z=43, 57, 71, 85, 99, 113, 127, 141$ ). H<sub>2</sub>O and CO<sub>2</sub> can be identified from FTIR results. Based on the TG curve shown in Fig. 2, the decomposition of organic compounds intercalated into montmorillonite is a two-step process. In order to identify the degradation products over the temperature range of 200 to 500°C, the Pyrolysis/GC-MS technique was employed to examine the products evolved at 200 and 300°C. For comparison, the pure trimethyloctadecyl, quaternary ammonium chloride (TMO) was also examined by Pyrolysis/GC-MS using the same program employed for OLS samples. The decomposition products of the samples are listed in Table 1. Degradation of TMO yields long chain tertiary amines, long chain alpha-olefins and 1-chloro alkanes. GC-MS analysis at the beginning (200°C), at maximum mass loss (250°C) and completion (300°C) of the decomposition process indicated that the same type of fragments (tertiary amines, alpha-olefins and 1-chloro alkanes) are present throughout, with an increased number of shorter chain fragments at the higher temperatures. Decomposition of ammonium salts generally proceeds by a Hoffmann elimination mechanism in which a basic anion, such as hydroxide, extracts a hydrogen from the  $\beta$ -carbon yielding

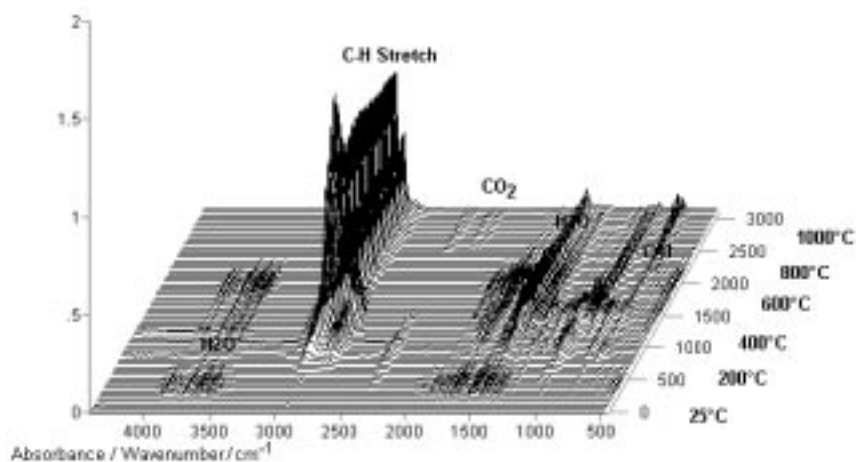


Fig. 3 3D FTIR results of trimethyloctadecyl quaternary ammonium montmorillonite

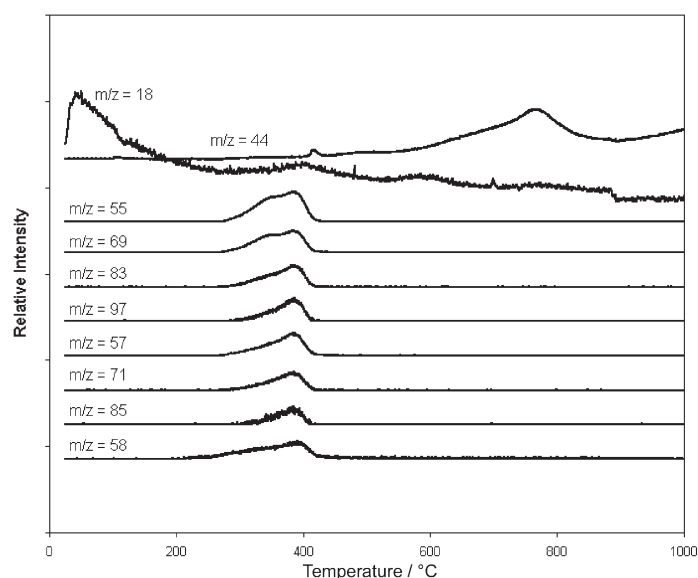


Fig. 4 MS results for the evolution products for trimethyloctadecyl quaternary ammonium montmorillonite

an olefinic and tertiary amino group [18]. For chloride salts the subsequent production of HCl along with the olefinic and amino groups will produce the observed species through secondary reactions.

During high temperature decomposition events of OLS sample, long chain tertiary amines are observed along with shorter chain olefins, branched olefins and aldehydes. After the initial decomposition step, the evolved products are confined in-

**Table 1** Representative organic species evolved from TMO exchanged montmorillonite and trimethyloctadecyl quaternary ammonium chloride during Pyrolysis/GC-MS

Sample	Type of organic compounds	200°C	400°C
2048	alkane, linear 1-chloro branched alkane	C <sub>16</sub> H <sub>33</sub> Cl, C <sub>18</sub> H <sub>37</sub> Cl tridecane, 3-methyl-, C <sub>14</sub> H <sub>30</sub>	
	tertiary amine, N,N-dimethyl- primary amine, linear	C <sub>15</sub> H <sub>33</sub> N, C <sub>17</sub> H <sub>37</sub> N	C <sub>15</sub> H <sub>33</sub> N, C <sub>17</sub> H <sub>37</sub> N C <sub>18</sub> H <sub>39</sub> N
	linear alkene, 1- linear alkene, n-	C <sub>16</sub> H <sub>32</sub> , C <sub>17</sub> H <sub>34</sub>	C <sub>9</sub> H <sub>18</sub> , C <sub>10</sub> H <sub>20</sub> , C <sub>14</sub> H <sub>26</sub> , C <sub>17</sub> H <sub>34</sub> 3-nonene, (E)- [C <sub>9</sub> H <sub>18</sub> ], 2-decene, (Z)- [C <sub>10</sub> H <sub>20</sub> ], 3-undecene, (E)- [C <sub>11</sub> H <sub>22</sub> ], 5-dodecene, (Z)- [C <sub>12</sub> H <sub>24</sub> ], 3-tridecene, (Z)- [C <sub>13</sub> H <sub>26</sub> ], 6-tridecene [C <sub>13</sub> H <sub>26</sub> ], 3-octadecene, (E)- [C <sub>18</sub> H <sub>36</sub> ], 3-octadecene, (E)- [C <sub>18</sub> H <sub>36</sub> ]
	branched alkene		1-octene, 3-methyl- [C <sub>9</sub> H <sub>18</sub> ], 3-heptene, 2,6-dimethyl- [C <sub>9</sub> H <sub>18</sub> ], 4-nonene, 2-methyl [C <sub>10</sub> H <sub>20</sub> ], 1-octene, 3,7-dimethyl-, [C <sub>10</sub> H <sub>20</sub> ], 4-undecene, 10-methyl, (E)- [C <sub>12</sub> H <sub>24</sub> ] C <sub>14</sub> H <sub>28</sub> O, C <sub>15</sub> H <sub>30</sub> O, C <sub>16</sub> H <sub>32</sub> O E-15-hepadecenal [C <sub>17</sub> H <sub>32</sub> O]
TMO	alkane, linear 1-chloro tertiary amine, N,N-dimethyl- linear alkene, 1-	C <sub>13</sub> H <sub>29</sub> Cl, C <sub>16</sub> H <sub>33</sub> Cl, C <sub>18</sub> H <sub>37</sub> Cl C <sub>9</sub> H <sub>21</sub> N, C <sub>10</sub> H <sub>23</sub> N, C <sub>15</sub> H <sub>33</sub> N, C <sub>17</sub> H <sub>37</sub> N C <sub>10</sub> H <sub>20</sub> , C <sub>12</sub> H <sub>24</sub>	

side montmorillonite's lamellar crystal structure and undergo additional and successive secondary reactions. For example, the presence of oxygen and metals in the structure of montmorillonite serve as catalysts to enable the oxidative cleavage of alkenes to produce aldehydes at elevated temperatures. Analysis of the kinetics in TG results [19] from the decomposition of trimethyl alkyl montmorillonites indicated that the activation energy for the first event is 156–162 kJ mol<sup>-1</sup>. The activation energy for the second series of events is 50–100 kJ mol<sup>-1</sup> higher, mirroring the GC-MS results where alkyl scission and condensation occur.

In summary, evolved gas analysis allows to have a better understanding of the thermal degradation mechanism of organically modified clays, and provides fundamental data on how the organic intercalated substances affect the thermal stability of OLS. The details of thermal degradation of organically modified clays have been presented elsewhere [20].

#### *Thermal characterization of PMR polymer*

Polyimides make up one of the most stable and environmentally resistant polymer systems. PMR polyimides (most noticeably PMR-15), prepared by Polymerization of Monomeric Reactants, are high temperature polymers used as the matrix resins in fiber-reinforced composites for a variety of advanced aerospace applications [21, 22]. As composite materials, they possess certain unique characteristics such as toughness, resistance to temperature and solvents as well as high tensile strength and modulus. PMR polyimide, TMBZ-15, which is formulated from 2,3', 4,4'-benzo-

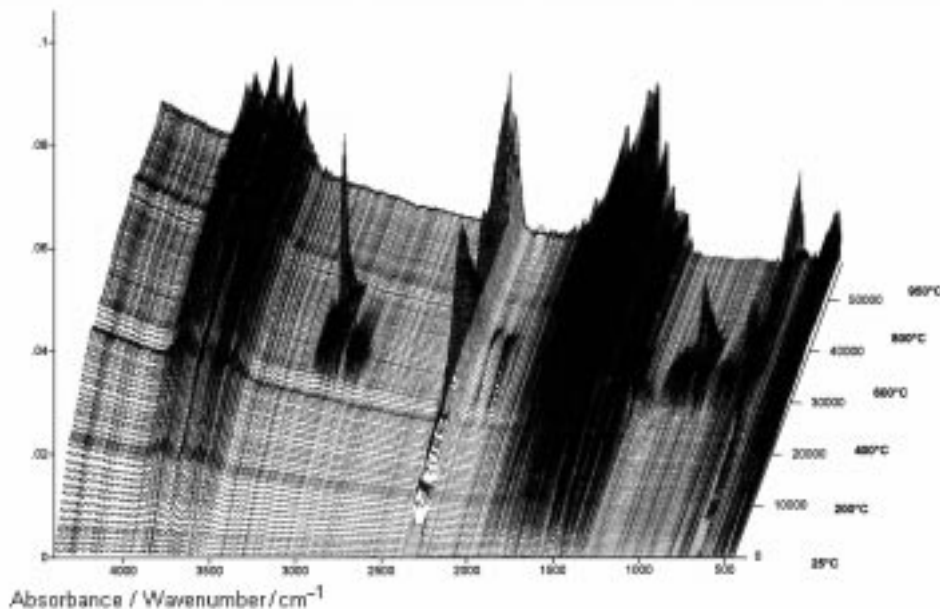


Fig. 5 3D FTIR results of the decomposition of TMBZ-15 polyimide



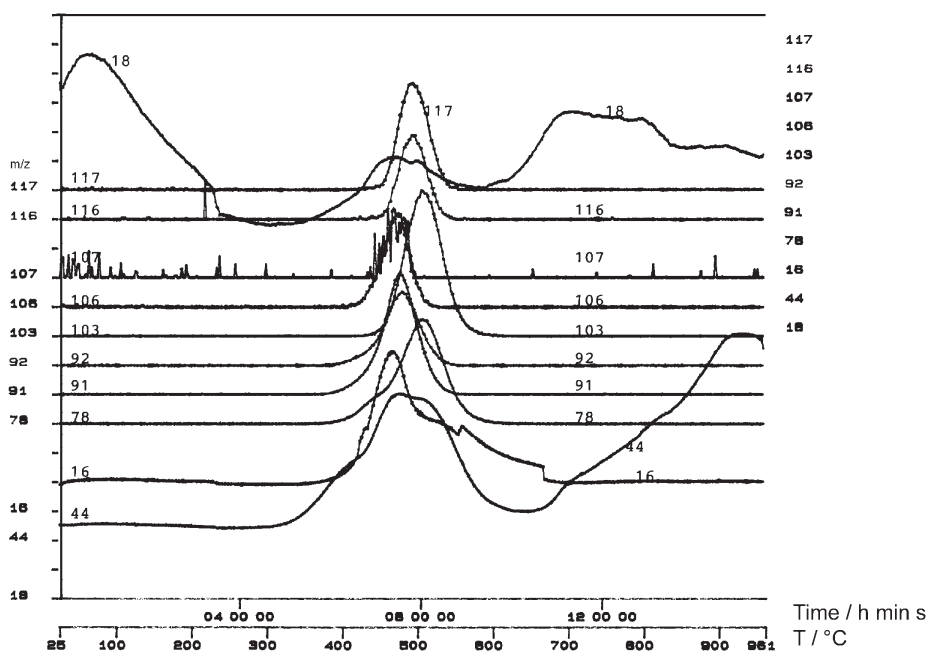


Fig. 6 MS results of the evolution products for TMBZ-15 polyimide

phenone tetracarboxylic acid, dimethyl ester and nadic ester as the endcap with 2,2', 6,6'-tetramethylbenzidine (TMBZ), was examined.

The major products from the decomposition of sample TMBZ-15 include  $H_2O$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $NH_3$ , and some aromatic derivatives identified a phenyl isocyanate [23], the FTIR spectra of which overlaps with that of  $CO_2$  near  $2358\text{ cm}^{-1}$ , as shown in Figs 5 and 6. Water is evolved at all temperatures from around  $100^\circ\text{C}$  to the very high temperature of  $950^\circ\text{C}$ . This indicates that at least part of the water must be a genuine degradation product and not just adventitious moisture. The pendant methyl groups in TMBZ-15 are released as  $CH_4$ , which reaches the maximum intensity at  $479^\circ\text{C}$ . As an indication of main chain degradation,  $NH_3$  is observed and reaches its maximum intensity at  $557^\circ\text{C}$  to TMBZ-15. Therefore, both TG/FTIR and TG/MS techniques provide the time- and/or temperature-dependent evolved gas information, which, in turn, helps one understand the degradation mechanism of polyimides.

A two-step decomposition of sample TMBZ-15 can be proposed from the TG/FTIR/MS/GC-MS data. In the first step, the end groups and side groups are broken from the main chain to produce  $CO$ ,  $CO_2$ , water, and fluorinated products or  $CH_4$ . And then the main chain of polyimide undergoes thermal degradation while releasing  $NH_3$ ,  $CO$  and  $CO_2$ . Compared to the pathway for  $CO$ , which rises directly from the imide ring, the pathway for  $CO_2$  is more complicated. Several mechanisms have been suggested previously [24]. 1. from amic acids, which may form either from incomplete imidization or hydrolysis of imide rings; 2. from decomposition of the isoimides

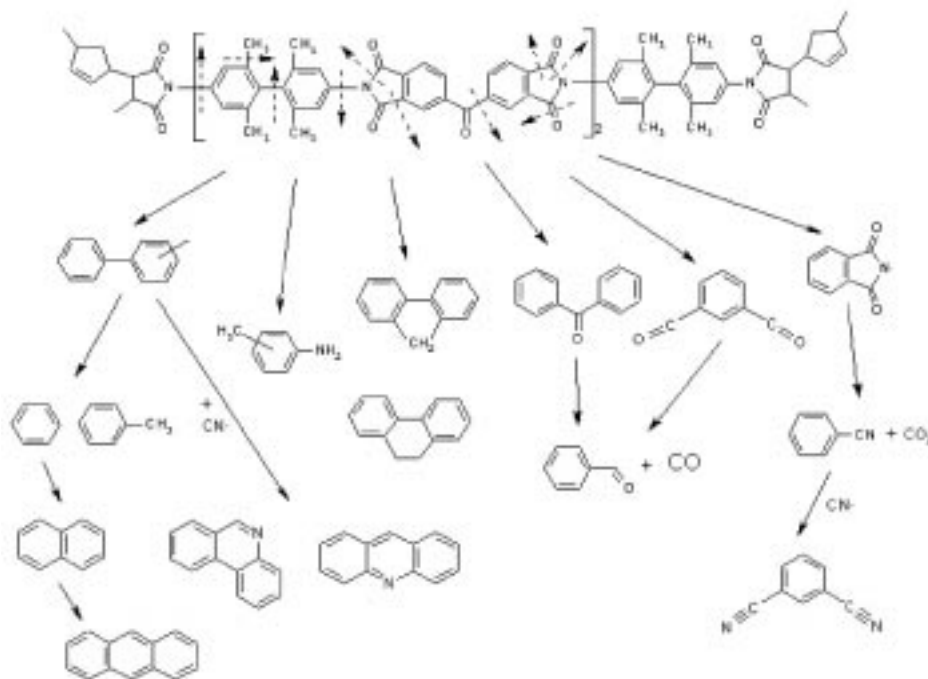
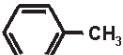
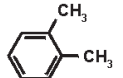
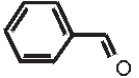
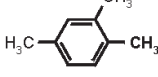
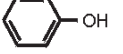
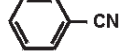


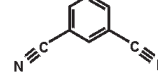
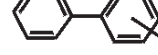
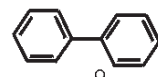
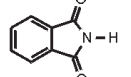
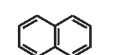
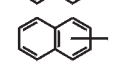


Fig. 7 The degradation mechanism of TMBZ-15 polyimide

derived from the rearrangement of imides; or 3. from unreacted anhydrides. It is difficult to explain the rearrangement of imides to isoimides during TG/FTIR experiment. However, in TG/MS experiments other aromatic fragments including phenyl isocyanates, the spectra of which overlap with the very strong CO<sub>2</sub> absorption, benzonitrile ( $m/e=103$ ), and toluene ( $m/e=91,92$ ) were identified as shown in Figs 5 and 6. Similar degradation products have been verified recently by high resolution Pyrolysis GC-MS [25] on thermoplastic polyimides with identical backbones. The detection of benzonitrile by Pyrolysis/GC-MS strongly confirmed the cleavage of the carbonyl group (C=O) in the imide rings into oxygen radicals which could be combined with CO to form CO<sub>2</sub>. Therefore, the most reasonable explanation for the source of CO<sub>2</sub> is from the pyrolysis of hydrocarbon polymers which produced CO<sub>2</sub> and water. Upon examination of the decomposition products of TMBZ-15, as presented in Table 2, it can be noted that these products can be classified into three groups: 1. small, light molecular mass compounds such as water, CO, CO<sub>2</sub>; 2. the fragments cleaved from polymer chains, including aromatic hydrocarbons, aromatic amines, aromatic nitriles; and 3. rearrangement and condensation products, such as naphthalene, fluorene, anthracene, and acridine. In summary, based on the composition of pyrolysis products of polymer samples, it can be understood that the degradation reaction is initiated from the cleavage of the carbon-nitrogen and carbon-carbon bonds. The chain transfer, rearrangement, and condensation reactions then follow at higher tempera-

tures. The degradation steps then can be proposed as shown in Fig. 7. The detailed degradation mechanisms have been discussed elsewhere [26, 27].

**Table 2** Pyrolysis products of TMBZ-15 at different temperatures

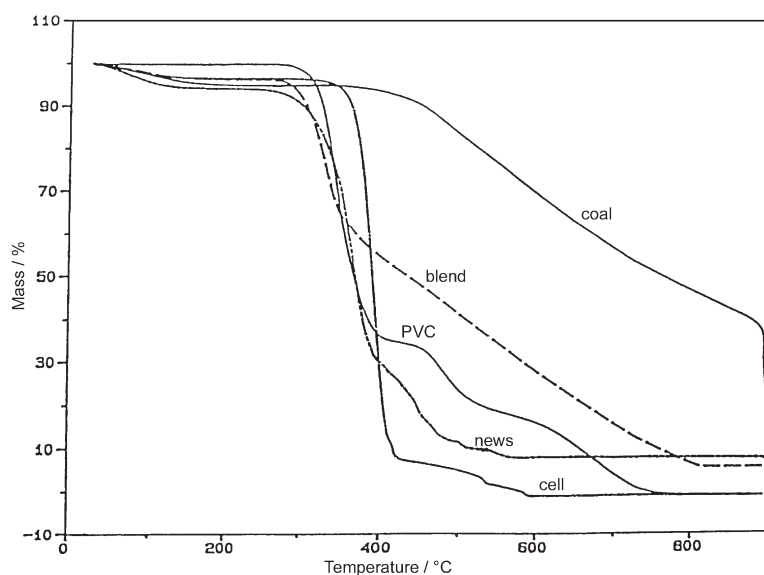
No.	Structure	Name	Temperature/°C		
			500	600	740
1		toluene	×	×	×
2		benzene, 1,2-dimethyl-	×	×	×
3		benzaldehyde	×	×	×
4		benzene, 1,2,4-trimethyl-	×		
5		phenol	×	×	×
6		benzonitrile	×	×	×
		benzonitrile, -methyl-	×	×	×
7		benzenamine, -methyl-	×	×	×
8		1,3-benzenedicarbonitrile		×	×
9		biphenyl, -methyl-	×	×	×
		biphenyl	×	×	×
10		1H-indole-1,3(2H)-dione	×	×	×
11		naphthalene	×	×	×
		naphthalene, -methyl-	×	×	×

**Table 2** Continued

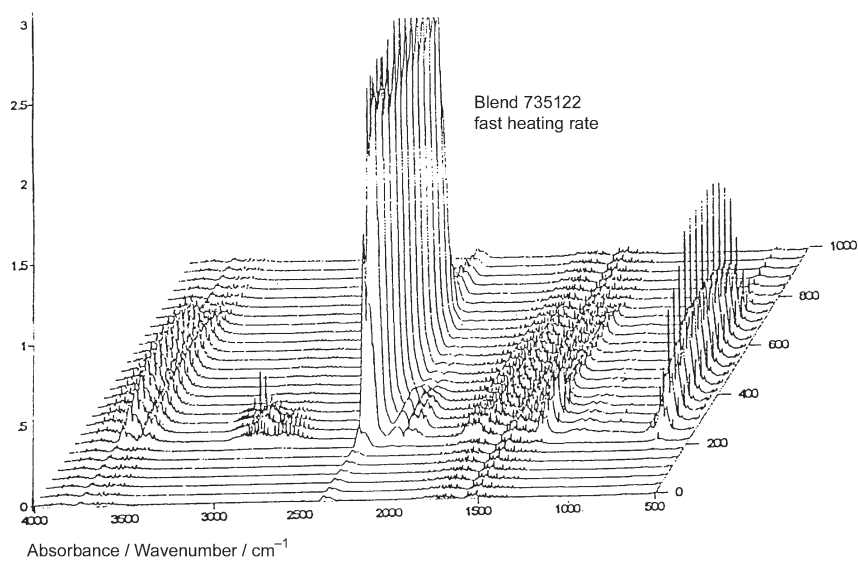
No.	Structure	Name	Temperature/°C		
			500	600	740
12		1,1'-biphenyl, 3,4-diethyl-	×	×	×
13		1,2-benzenedicarboxaldehyde			×
14		phenanthrene, 9, 10-dihydro-1-methyl-	×	×	×
15		9H-fluorene	×	×	×
16		anthracene		×	×
		phenanthrene		×	×
17		benzeneacetonitrile, $\alpha$ -phenyl-			×
18		1(3H)-isobenzofuranone			×
19		benzophenone		×	×
20		acridine			×
21		4H-cyclopenta[def]phenanthrene		×	×

#### *Thermal characterization of coal/RDF combustion products*

The reaction pathways for formation of gaseous products such as chlorinated organic compounds during the combustion of mixtures of high sulfur and/or high chlorine coals and municipal solid waste (MSW) can be evaluated using TG/FTIR/MS/GC-MS techniques. Several kinds of coals and the major combustible components of MSW, including PVC, newspaper, and cellulose, were tested in this study. Coals with a wide range of sulfur and chlorine contents were used. TG/MS/FTIR/GC-MS analyses were performed on the raw materials and their blends. Complete details of the results have been presented elsewhere [28].



**Fig. 8** TG curves for the mixture of coal and MSW



**Fig. 9** 3D FTIR results of a coal/MSW blend

Figure 8 presents the TG curve of a fuel blend and its individual components. The TG curve was obtained with a heating rate of  $100^{\circ}\text{C min}^{-1}$ . It is obvious that there are some mutual chemical interactions among the individual components in the blend during the combustion process. Three mass losses can be observed from the TG

curve. Figure 9 shows 3D FTIR plot for the fuel blend 735122. The combustion process can be illustrated by following the emission of  $\text{CO}_2$  ( $2230$  and  $670\text{ cm}^{-1}$ ), and  $\text{H}_2\text{O}$  ( $3851$  and  $1652\text{ cm}^{-1}$ ), which correspond to the second mass loss in the TG curve. Organic and inorganic species, such as  $\text{HCl}$  ( $2600\text{--}3000\text{ cm}^{-1}$ ), water, hydrocarbons, organic acids and alcohols, are released during the decomposition stage, which corresponds to the third mass loss in the TG curve for the blend samples. From the analysis of single materials, it is known that the evolution of  $\text{HCl}$  is due primarily to the decomposition of PVC. The organic acids and alcohols are mainly from the combustion of newspaper and cellulose. The sulfur dioxide peaks appear around  $280^\circ\text{C}$  and reach their maximum at about  $340^\circ\text{C}$ . This indicates that the coal starts to decompose rapidly at this temperature, and reaches another combustion maximum at about  $420^\circ\text{C}$ , which is the third mass loss in the TG curve. This is supported by the presence of peaks for  $\text{CO}$ ,  $\text{CO}_2$  and methane in FTIR spectra.

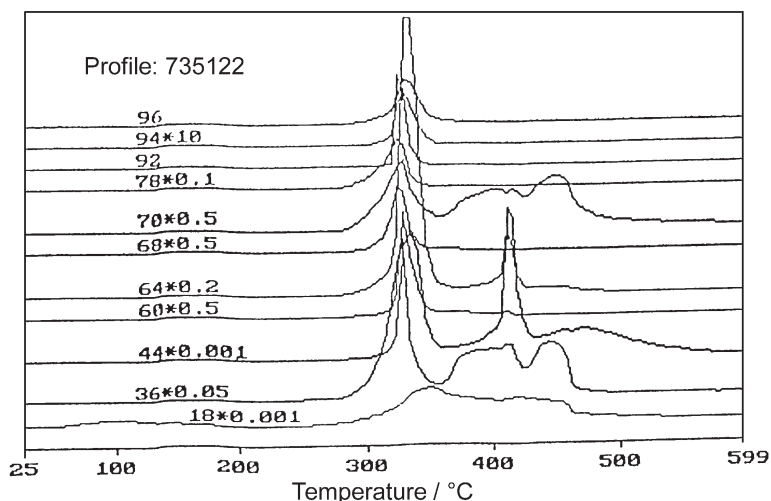


Fig. 10 MS results of the evolution products for a coal/MSW blend

Figure 10 illustrates some mass profiles from the combustion of fuel blend 735122. Clearly, only moisture ( $m/z=18$ ) evolves from the fuels around  $100^\circ\text{C}$ . When the temperature reaches  $300^\circ\text{C}$ , the fuels start decomposing and releasing as combustion products small organic and inorganic molecules such as  $\text{HCl}$ , benzene and toluene ( $m/z=92$ ) from PVC, acetic acid and/or carbonyl sulfide ( $m/z=60$ ), furan ( $m/z=68$ ), phenol ( $m/z=94$ ), and furfural ( $m/z=96$ ) from newspaper and cellulose, while carbonyl sulfide ( $m/z=60$ ) and sulfur dioxide ( $m/z=64$ ) are released from coal. The decomposition reactions reach their maximum rate at  $300^\circ\text{C}$  and finish around  $370^\circ\text{C}$ . This corresponds to the second mass loss in the TG curve. After then, only a few peaks such as  $m/z=18$ , 36, 44, 64 and 70 appear in the mass spectra. The absorption bands for carbon dioxide and sulfur dioxide display their maximum around  $420^\circ\text{C}$ , which is consistent with the third mass loss around  $420^\circ\text{C}$  in the TG curve.

**Table 3** Pyrolysis/GC-MS results of products of fuel blend 735122

No.	Name	Formula	Molecular mass
1	methylbenzothiophene	C <sub>9</sub> H <sub>8</sub> S	148
2	phthalic anhydride	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	148
3	dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	147
4	chlorophenol	C <sub>6</sub> H <sub>5</sub> ClO	129
5	di-chlorophenol	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> O	163
6	tri-chlorophenol	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> O	197
7	methyltetrahydronaphthalene	C <sub>11</sub> H <sub>14</sub>	146
8	naphthalene, 2-methyl-	C <sub>11</sub> H <sub>10</sub>	142
9	<i>p</i> -chlorobenzaldehyde	C <sub>7</sub> H <sub>5</sub> ClO	140
10	naphthalene	C <sub>10</sub> H <sub>8</sub>	128
11	trimethylcyclohexane	C <sub>9</sub> H <sub>18</sub>	126
12	1,4-benzodioxin	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	134
13	propylbenzene	C <sub>9</sub> H <sub>12</sub>	120
14	acetophenone	C <sub>8</sub> H <sub>8</sub> O	120
15	methylbenzaldehyde	C <sub>8</sub> H <sub>8</sub> O	121
16	trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120
17	chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	113
18	<i>p</i> -xylene	C <sub>8</sub> H <sub>10</sub>	106
19	benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	106
20	ethylbenzene	C <sub>8</sub> H <sub>10</sub>	106
21	methylthiophene	C <sub>5</sub> H <sub>6</sub> S	98
22	furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96
23	toluene	C <sub>7</sub> H <sub>8</sub>	92
24	hexene	C <sub>6</sub> H <sub>12</sub>	84
25	thiophene	C <sub>4</sub> H <sub>4</sub> S	84
26	benzene	C <sub>6</sub> H <sub>6</sub>	78
27	furan	C <sub>4</sub> H <sub>4</sub> O	68

An important finding in this work using TG/FTIR/MS techniques is that molecular chlorine, phenol, furan and other hydrocarbon species are released in the same temperature range. This indicates there is the possibility of producing chlorinated organic compounds at this temperature. In order to confirm MS results above, Pyrolysis/GC-MS techniques were used to identify the evolution of organic products, which are listed in Table 3. Several kinds of chlorinated organics such as chlorophenol, di-chlorophenol, tri-chlorophenol, dichlorobenzene, *p*-chlorobenzaldehyde and chlorobenzene were identified [29]. Again, the low molecular mass compounds had been confirmed by GC-MS, and the high molecular mass compounds were identified by

the GC-MS system. It is clear, therefore, the Pyrolysis/GC-MS system cannot only confirm the results from TG/FTIR and TG/MS, but also provide more information about high molecular mass compounds evolved or formed during pyrolysis/combustion processes.

## Conclusions

- The combination of the complementary TG/FTIR, TG/MS and Pyrolysis/GC-MS techniques provides a versatile and complete analytical system for the detection and identification of gases evolved during thermal decomposition processes.
- TG/FTIR/MS/GC-MS system makes it feasible to study reaction pathways for the formation of gaseous products and the degradation mechanisms of materials during pyrolysis and combustion.
- TG/FTIR and TG/MS techniques can provide precise time- and/or temperature-dependent gas evolution information. On the other hand, Pyrolysis/GC-MS technique can provide more accurate information on the composition and distribution of pyrolysis/combustion products.
- TG/FTIR/MS technique is limited in the detection of high molecular mass compounds. Pyrolysis/GC-MS, however, has a great ability to identify these high molecular mass compounds.

## References

- 1 W. W. Wendlandt, *Thermal Analysis*, 3<sup>rd</sup> Ed., John Wiley & Sons, New York, NY 1985, pp. 461–588.
- 2 J. Chiu, *Analytical Chemistry*, 40 (1968) 1516.
- 3 P. C. Uden, D. E. Henderson and R. J. Lloyd, In: *Proceedings of First European Symposium on Thermal Analysis*, D. Dollimore, Ed. Heyden, London 1976, p.29.
- 4 F. Zitomer, *Analytical Chemistry*, 40 (1968) 1091.
- 5 R. A. Flath, *Guide to Modern Methods of Instrumental Analysis*, T. H. Gouw, Ed., Wiley-Interscience, New York 1972, Chap. 9.
- 6 S. K. Freeman, *Ancillary Techniques of Gas Chromatography*, L. S. Ettre, W. H. McFadden, Eds, Wiley-Interscience, New York 1969, Chap. 6.
- 7 R. B. Prins, *New Techniques, News and Applications*, North American Thermal Analysis Society Notes, Winter Issue, 1987–1988, 19(4), pp. 48–51.
- 8 C. L. Putzing, M. A. Leugers, M. L. Mckelvy, G. E. Mitchell, R. A. Nyquist, R. R. Papenfuss and L. Yurga, *Analytical Chemistry*, 66(12) (1994) 51R.
- 9 A. Attar and F. Dupuis, *ACS Div. of Fuel Chem. Preprints*, 23 (1978) 44.
- 10 R. B. La Count, *Fuel*, 66 (1987) 873.
- 11 H. Juntgen and K. H. Van Heek, *Fuel Proc. Tech.*, 2 (1979) 261.
- 12 J. H. Campbell, *Fuel*, 57 (1978) 217.
- 13 R. M. Carangelo, P. R. Solomon and D. Gerson, *Fuel*, 66 (1987) 960.
- 14 H. L. Friedman, *Thermochim. Acta*, 1 (1970) 199.
- 15 D. Dollimore, G. A. Gamlen and T. J. Taylor, *Thermochim Acta*, 75 (1984) 59.



- 16 M. R. Holdiness, *Thermochim. Acta*, 75 (1984) 59.
- 17 G. Szekely, M. Nebuloni and L. F. Zerilli, *Thermochim. Acta*, ??? (1992) ???.
- 18 A. C. Cope and E. R. Trumbull, In: *Organic Reactions* 11, John Wiley and Sons, New York 1960, pp. 317–487.
- 19 Standard Test Method for Decomposition Kinetics by Thermogravimetry, ASTM E1641-99, Annual Book of ASTM Standards, American Society for Testing and Materials, West Conshohocken, PA, V14.02, published annually.
- 20 W. Xie, Z. Gao, W.-P. Pan, D. Hunter, A. Singh and R. Vaia, *Chem. Mater.*, submitted, 2001.
- 21 D. Wilson, *British Polymer Journal*, 20 (1988) 405.
- 22 A. S. Ansari, W. B. Alston, A. A. Frimer and D. A. Scheiman, In: *Proceedings of High Temperature Workshop XVII*, Feb. 10–13, Monterey, California 1997.
- 23 B. Crossland, G. J. Knight and W. W. Wright, *British Polymer Journal*, 19 (1987) 291.
- 24 F. Li, Z.-Q. Wu, E. P. Savitski, X. Jing, Q. Fu, F. W. Haris, S. Z. D. Cheng and R. E. Lyon, In: *Proceedings of 42<sup>nd</sup> International SAMPE Symposium*, B38(1–2) (1997) 107.
- 25 F. Li, F. L. Hwang, Y. Shi, X. Jin, Z. Wu, Z. Shen, K. Chuang, R. E. Lyon, F. W. Harris and S. Z. D. Cheng, *J. Macromol. Sci., Phys.*, B38(1–2) (1999) 107.
- 26 W. Xie, W.-P. Pan, K. C. Chuang, *Thermochim. Acta*, 367–368 (2001) 143.
- 27 W. Xie, W.-P. Pan, K. C. Chuang, In: *Proceedings of the 12<sup>th</sup> International Congress on Thermal Analysis and Calorimetry*, Copenhagen, Denmark, August 14–18, 2000, 259.
- 28 R. Lu, S. Purushothama, X. Yang, J. Hyatt, W.-P. Pan, J. T. Riley, W. Lloyd, *Fuel Processing Technology*, 59 (1999) 35.
- 29 X. Yang, MS Thesis, Western Kentucky University, 1996.