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THERMAL DEGRADATION STUDY OF POLYMERIZATION OF MONOMERIC REACTANTS (PMR) POLYIMIDES

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Abstract

A novel PMR polyimides (TMBZ-15) based on substituted benzidines is examined and compared to state-of-the-art PMR-15. The mechanism for the thermal decomposition of two specific PMR polyimides is obtained using TG/FTIR/MS techniques. In order to verify the pathway of polyimide degradation, a pyrolysis/GC-MS technique was employed to evaluate the organic degradation products, particularly the larger components that are destroyed in traditional TG/MS. A proposed degradation mechanism involves two main stages of decomposition, each of which produce a variety of products. The first group includes aromatic hydrocarbons, aromatic amines and nitriles, which correspond to partial fragments of polymer chains. The second group consists largely of fluorene, naphthalene and phenanthrene, which are attributed to the isomerization, rearrangements and cyclizations of the aforementioned pyrolyzates at high temperature.

Keywords: degradation, polyimide, thermal analysis

Introduction

Polyimides comprise one of the most stable and environmentally resistant polymer systems. They are attractive in high temperature applications as matrix resins, due to their excellent thermo-oxidative stability and mechanical properties. As composite materials for aerospace applications, they possess certain unique characteristics such as toughness, resistance to temperature and solvents as well as high tensile strength and modulus. A novel PMR polyimides (TMBZ-15) based on substituted benzidines is examined and compared to state-of-the-art PMR-15, their structures were illustrated in Fig. 1.

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. EGA technique involves the analysis of gaseous species evolved during combustion and/or pyrolysis in which a series of chemical reactions as a function of temperature are analyzed using thermal analytical techniques and/or multiple techniques. It is nor-

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mally used to evaluate the chemical pathway of the degradation reaction through identifying the composition of the decomposition products from materials examined.

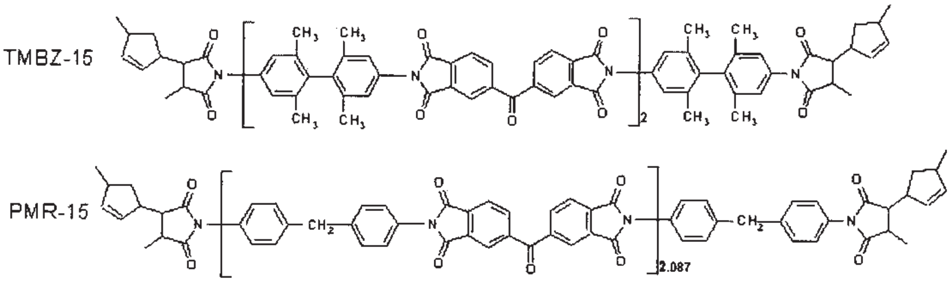

Fig. 1 Structure of TMBZ-15 and PMR-15

In the previous study [2] it is known that pendant groups on the biphenyl rings creates steric hindrance which increases the rotational barrier for PMR polyimides based on substituted benzidines which thus resulting in higher T_g's. However, the effect of pendant groups on the decomposition process is still unclear. Therefore, the objective of this study is to examine the degradation mechanism of PMR polyimides. The thermal degradation products of PMR polyimides are evaluated by EGA techniques, including TG/FTIR/MS and Pyrolysis/GC-MS. The degradation mechanism is proposed based on the information of decomposition products.

Experimental

Preparation of PMR polyimide resins

TMBZ polyimides is formulated from 3,3',4,4'-benzophenone tetracarboxylic acid dimethyl esters and nadic ester as the endcap with diamines, 2,2',6,6,'-tetramethylbenzidine (TMBZ), in 50% methanol solution. The monomer solution was concentrated to syrup by heating, and then staged at 204°C for 2 h and 260°C for 30 min to afford imidized resin powders. The PMR polyimide oligomers are generally insoluble even in polar aprotic solvents such as N-methyl-2-pyrrolidinone (NMP); therefore, the molecular mass can not be determined by GPC. The formulated molecular mass for PMR polyimides are listed as follows: PMR-15=1500, TMBZ=1584 g mol^{-1}. The resin discs were processed from the imidized powders by compression molding at 315°C at 1500 psi for 2 h. The structures of two PMR polyimides are shown in Fig. 1.

TG/MS technique

The non-postcured samples of PMR polyimides were placed in a ceramic pan and analyzed on a TA SDT2960 interfaced to a Fisions VG Thermolab mass spectrometer by means of a heated capillary transfer line (220°C). The Fisions unit is based on quadrupole design with a 1–300 atomic mass units(amu) mass range. The sample gas from the interface was ionized at 70 eV. The system operates at a pressure of $1\cdot10^{-6}$ torr. The samples were heated at 1°C min^{-1} from room temperature to 950°C in dynamic nitrogen atmosphere, the flow rate used in the experiments was 50 ml min^{-1}. A NST library database was used for MS analysis.

TG/FTIR technique

The sample was placed in the ceramic boat, and was heated in the DuPont TG 951 at 1°C min^{-1} from ambient temperature to 950°C, under a flowing (50 mol min^{-1}) nitrogen (UHP grade). The 951 TG interfaced to a Perkin Elmer 1600 series FTIR with a permanent silicon transfer line (length 1 inch). The purge gas carries the decomposition products from the TG through a 70 ml sample-cell with KBr crystal windows. For detection of the decomposition products, the cell was placed in the IR scanning path and kept at 150°C by wrapped heating tape to prevent possible condensation. The IR detection range was 450 to 4500 cm^{-1}.

Pyrolysis/GC-MS technique

The Pyrolysis/GC-MS system consists of Pegasus II GC/MS system and the ThermEx$^{\text{TM}}$ inlet system. The Pegasus II GC/MS system includes a time-of-flight mass spectrometer and a high speed gas chromatography. The advantage of time-of-flight mass spectrometry is its potential for tremendously fast acquisition rates. By combining TOF technology, LECO's Pegasus II GC/MS achieves the fastest acquision rate without a loss of data integrity. The TherEx$^{\text{TM}}$ inlet system is designed to heat small quantities of solid samples in a quartz Pyrocell$^{\text{TM}}$ and transfer the volatilised sample components to a heated capillary GC injection port. The carrier gas connections and seals have been designed to provide a leak free system for operation with GC-MS system. The associated gas chromatograph have 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 by maintaining the GC oven at ambient or cryogenic temperature. Once the sample has been heated to the desired temperature and all out-gassed components condensed the GC oven are temperature programmed.

Results and discussion

Thermogravimetric analysis (TG)

The mass loss curves are plotted in Fig. 2 for the samples. Based on DTG curves, both sample PMR-15 and TMBZ-15 show a two-stage degradation process, with the TMBZ one being more slightly resolved than that observed with the PMR-15. It can be clearly seen that for TG analysis in nitrogen the order of stability is PMR-15>TMBZ-15, based on the peak of the first stage reaction of DTG.

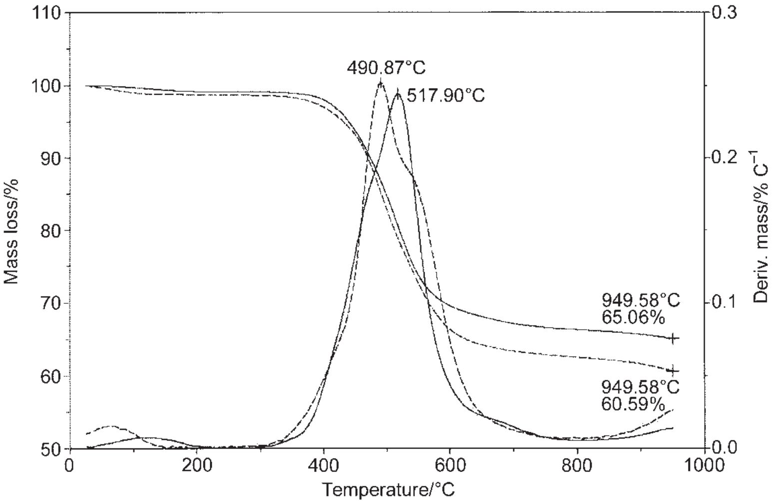

Fig. 2 TG results of TMBZ-15 and PMR-15

The previous study [2] indicates that the pendant groups on the biphenyl rings play an important role in the thermal stability of the corresponding resins. PMR-15, containing methylene dianiline, exhibits highest thermal stability, due to the presence of reactive benzylic hydrogens that are believed to form free radical upon cleavage of C–H bond, thus promoting additional crosslinking instead of degradation [3]. The methyl substituents in TMBZ-15 cleave off before the backbone ruptures, which was confirmed by TG/FTIR/MS experiments shown below.

Thermal degradation mechanisms of polyimides

TG-MS, TG-FTIR and pyrolysis/GC-MS are very useful techniques employed in examining the detailed thermal degradation mechanism [4, 5]. During TG/MS/FTIR experiments, the releasing products from samples studied are simultaneously and continuously monitored by MS and FTIR. As shown in Figs 3 and 4, the major products from decomposition of sample TMBZ-15 include water, CO, CO_2, CH_4 and NH_3 and some aromatic derivatives which are identified as phenyl isocyanates [5] which overlaps with CO_2 near 2358 cm^{-1}. Water is evolved at all temperature from very low temperature about 100°C to the very high temperature 950°C, this indicates that at least part of it 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 480°C for TMBZ-15.

As for PMR-15 shown in Figs 5 and 6, the generation of CH_4 at 521°C is derived from –CH_2–group of methylene dianiline. As an indication of the main chain degradation, NH_3 is observed at maximum intensity at temperature 557°C for TMBZ-15, and 514°C for PMR-15, respectively. CO_2 is released in two stages: the first maximum rate of

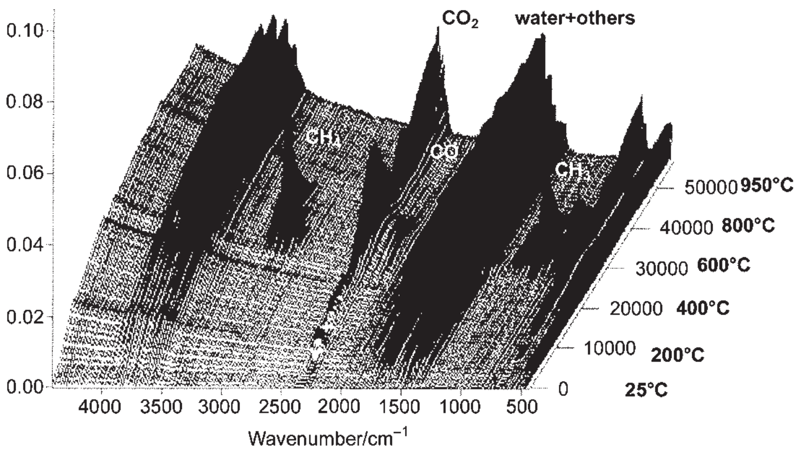

Fig. 3 TG/FTIR results of TMBZ-15

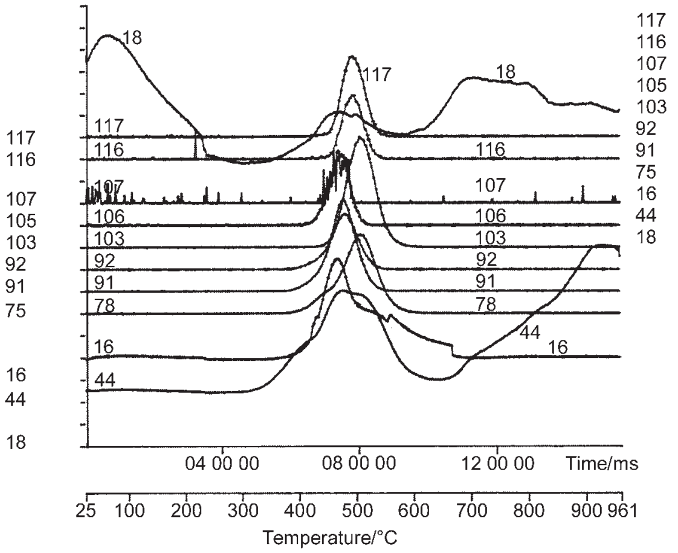

Fig. 4 TG/MS results of TMBZ-15

evolving CO_2 is around 485°C, and the second maximum rate is about 900°C. Although the evolution of CO_2 is even detected before CO under ultra-high purity (UHP) N_2 atmosphere, which seems to indicate that both CO_2 and CO are the direct products from the decomposition of sample TMBZ-15. However, by examining MS results, the spontaneous conversion of CO directly to CO_2 can occur at temperatures over 400°C [5]. The results illustrate that the degradation of the pendant groups has maximum intensity at

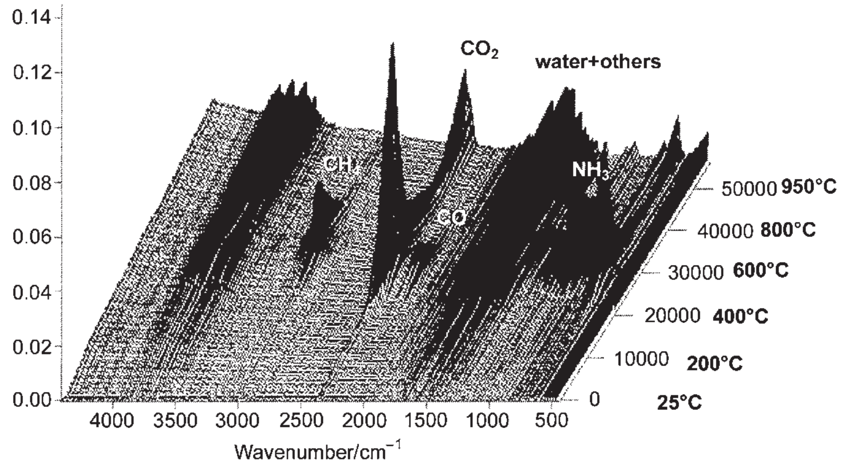

Fig. 5 TG/FTIR results of PMR-15

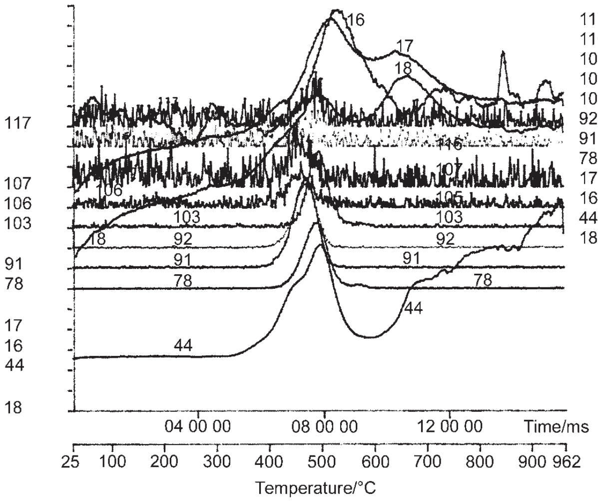

Fig. 6 TG/MS results of PMR-15

522°C, as indicated by the evolution of CH_4. At higher temperature around 600°C, the main chain starts to decompose and the product NH_3 is observed.

Two-step decomposition of sample TMBZ-15 concluded from 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 either fluorinated products or CH_4. And then the main chain of polyimide undergoes thermal degradation while releasing NH_3, CO and CO_2. Compared the pathway of CO which directly arises from the imide ring, the pathway of CO_2 is more complicated. Several mechanisms were suggested previously [4]:

1. amic acids which may form either from incomplete imidization or hydrolysis of imide

rings; 2. decomposition of the isoimides derived from the rearrangement of imides 3) unreacted anhydrides. It is difficult to explain the rearrangement of imides to isoimides during the TG-FTIR experiment. However, TG/MS could identify other aromatic fragments including phenyl isocyanates which overlapped with the very strong CO_2 absorption, and benzonitrile (*m*/*e*=103), toluene (*m*/*e*=91.92) as shown in Figs 4 and 6. Similar degradation products have been verified recently by high resolution pyrolysis GC-MS [6] on thermoplastic polyimides with identical backbones. The detection of benzonitrile by pyrolysis/GC-MS strongly confirmed the cleavage of carbonyl group (C=O) in the imide rings into oxygen radicals which could be combined with CO to form CO_2. Therefore, the most reasonable explanation for the source of CO_2 is from the pyrolysis of hydrocarbon polymers which produced CO_2 and water.

Table 1 Pyrolysis products of TMBZ-15 at different temperatures

No.	Pyrolysis products	*T*/500°C	*T*/600°C	*T*/740°C
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-Isoindole-1,3-(2H)-dione	×	×	×
11	Naphthalene Naphthalene, -methyl-	× ×	× ×	× ×
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	Benzenacetonitrile, α-phenyl			×
18	1(3H)-Isobenzofuranone			×
19	Benzophenone		×	×
20	Acridine			×
21	4H-Cyclopenta[def]phenanthrene		×	×

Table 2 Pyrolysis products of PMR-15 at different temperatures

No.	Pyrolysis product	*T*/500°C	*T*/600°C	*T*/740°C
1	Benzene, 1,2-dimethyl-	×	×	×
2	Benzaldehyde			
3	Diphenylmethane	×	×	×
4	Phenol	×	×	×
5	Benzonitrile	×	×	×
	Benzonitrile, -methyl-		×	×
6	Benzenamine, -methyl-	×	×	×
7	1,3-Benzenedicarbonitrile	×	×	×
8	Biphenyl, -methyl-			×
	Biphenyl	×	×	×
9	1H-Isoindole-1,3-(2H)-dione	×	×	×
10	Naphthalene	×	×	×
	Naphthalene, -methyl-	×	×	×
11	1H-Pyrrole-2,5-dione, 1-(4-methylphenyl)	×	×	×
12	1,2-Benzenedicarboxaldehyde	×	×	×
13	9H-Fluorene	×	×	×
14	Diphenylamine			×
15	1(3H)-Isobenzofuranone			×
16	Benzophenone		×	×
17	Acridine		×	×
	Phenanthridine		×	×
18	Benzenamine, 2-(phenylmethyl)-	×	×	×

Examining decomposition products of two polymer samples as presented in Tables 1 and 2, it is noted that these products can be classified into several groups: 1) small, light molecular mass compounds such as water, CO, CO_2; 2) the fragments cleavage from polymer chains, including aromatic hydrocarbons, aromatic amines, aromatic nitriles; 3) rearrangement and condensation products, such as naphthalene, fluorene, anthracene, 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 bond. The chain transfer, rearrangement, and condensation reactions are then followed at high temperature. The detailed degradation mechanism is proposed as shown in Fig. 7.

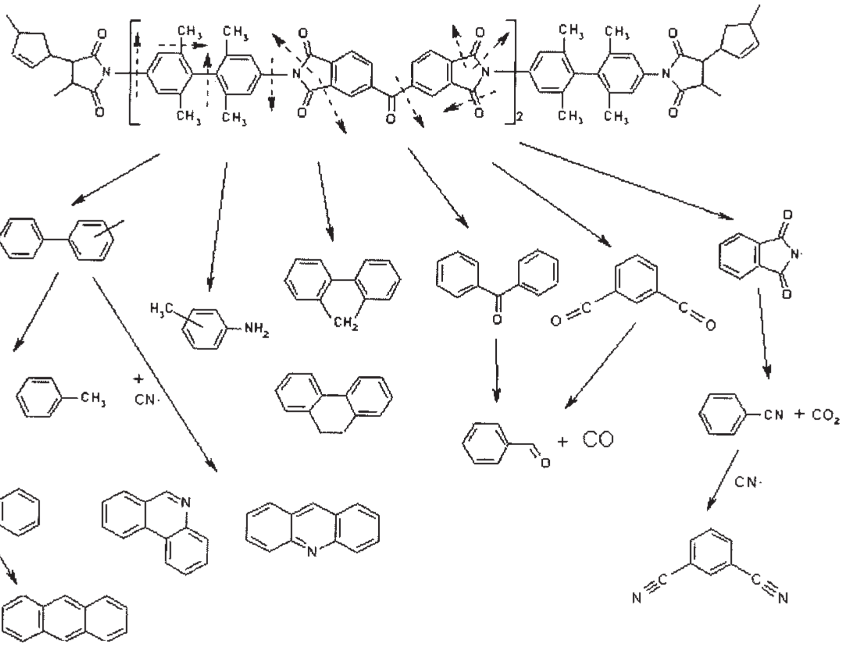

Fig. 7 Proposed thermal degradation pathway of TMBZ-15

Conclusions

1. Carbon monoxide (CO) is the direct degradation products from imide rings and carbon dioxide (CO_2) is produced through the further combination of CO with oxygen radicals during pyrolysis of hydrocarbon polymers.
2. Both polymers have the similar degradation products based on pyrolysis/GC-MS experiments. The first group includes aromatic hydrocarbons, aromatic amines and nitriles, which correspond to partial fragments of polymer chains. The second group consists largely of fluorene, naphthalene and phenanthrene, which are attributed to the isomerization, rearrangements and cyclizations of the aforementioned pyrolyzates at high temperature.

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