

## The Thermal and Mechanical Properties of High Performance Polyimide Fibers

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**ABSTRACT:** Two organo-soluble aromatic polyimides have been synthesized by introducing pendant groups of trifluoromethyl or methyl onto the 2- and 2'-positions of a biphenyl diamine: 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) or 2,2'-dimethyl-4,4'-diaminobiphenyl (DMB) and reacting each of them with biphenyltetracarboxylic dianhydride (BPDA). These two polyimides, BPDA-PFMB and BPDA-DMB, are prepared *via* a one-step polycondensation method, and they can be fabricated into fibers, films, and other application forms. Our research shows that in fiber applications, these two fibers exhibit excellent mechanical properties and outstanding thermal and thermo-oxidative stability. Their long term mechanical tensile performance at high temperatures is found to be critically associated with the type of side pendant groups at the 2- and 2'-positions of the diamines. High resolution pyrolysis-gas chromatography/mass spectrometry results show that the pyrograms of these two polyimides possess more than sixteen pyrolyzates. Based on the compositions and distributions of the pyrolyzates at different temperatures, the thermal degradation mechanism for both of the polyimides are found to be the same.

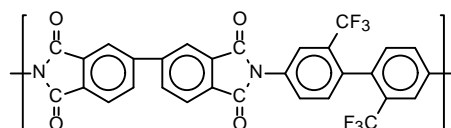
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## INTRODUCTION

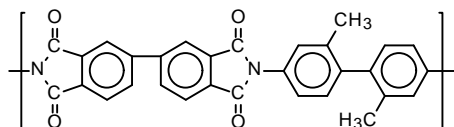
The choice of polyimide materials to develop high-performance structural materials for applications in the aerospace industry is based on the fact that this family of polymers possesses not only better mechanical and dielectrical properties, but also higher thermal and thermo-oxidative stability with a higher oxygen index and char yield in comparison with other polymeric materials such as phenolics, epoxies, polyesters and polyamides. We have focused on the fire resistant properties of aromatic polyimide fibers, coatings and thermoplastics. These materials have specific molecular designs with controlled architectures in order to achieve the desired properties needed for identified applications. Generally speaking, aromatic polyimides are impossible to fabricate in the melt and insoluble in common organic solvents. Therefore, they traditionally must be processed in the form of their soluble poly(amic acid) precursors, which are subsequently imidized in place (a so-called two-step polymerization) (Harris, 1989). There are several drawbacks to this approach such as creating strength-weakening voids and the occurrence of depolymerization during imidization. A considerable amount of research has been carried out aimed at the development of aromatic polyimides that are melt and/or solution processable in the imide form.

A general approach towards synthesizing organo-soluble aromatic polyimides is to structurally modify the aromatic polyimides to attain processability while not degrading their excellent mechanical properties and their thermal and thermo-oxidative stability. The overall goal of this ongoing research is to molecularly engineer the chemical structure to control solubility in common organic solvents without decreasing the rigidity of their backbones. For this purpose, new diamines with different pendant side groups at the 2- and 2'-positions of the biphenyl moieties have been prepared. For instance, trifluoromethyl or methyl pendant side groups at the 2- and 2'-positions of the biphenyl diamines cause significant steric hindrance which forces the two phenylenes to twist nearly 90° apart from each other, breaking the coplanar  $\pi$  bonds between the two phenylene groups (Harris and Hsu, 1989). This type of repulsion due to the side pendant groups also affects chain packing and the macroscopic responses to specific environments such as solubility, crystallinity, dielectric and optical properties (Cheng et al, 1991; Arnold <sub>a</sub>1992; <sub>b</sub>1993; <sub>c</sub>1993; <sub>d</sub>1994).

In this publication, we report two organo-soluble aromatic polyimides which can be fabricated into high-performance fibers. These two polyimides are based on the synthesis of 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA) and 2,2'-disubstituted-4,4'-diaminobiphenyl (either trifluoromethyl, PFMB or methyl DMB) using a one-step polymerization (Harris, 1989; Harris and Hsu, 1989). These fibers show excellent tensile properties which are equivalent to Kevlar® fibers (Cheng et al, <sub>b</sub>1991; Eashoo et al, <sub>a</sub>1993; Eashoo et al, <sub>b</sub>1994; Shen et al, 1994). In addition, these polyimides exhibit compressive strengths two times higher than that of Kevlar® fibers (Li et al, <sub>a</sub>1996, Li et al, <sub>b</sub>1997), and more importantly, their thermal and thermo-oxidative stability are 50 °C to 100 °C higher (Cheng et al, <sub>b</sub>1991; Eashoo et al, <sub>a</sub>1993; Eashoo et al, <sub>b</sub>1994; Shen et al, 1994). The chemical structure of BPDA-PFMB is



and BPDA-DMB is



Quite different from most of the thermal degradation studies of polyimides reported before (Ehlers et al, 1970; Stenzenberger, 1976; Zurakowska-Orszagh and Chreptowicz, 1981; Hatori et al, 1996), we specifically chose two polyimides with the same chemical backbone structure and added two different side pendant groups with different electron polarizabilities to investigate their effect on thermal and thermo-oxidative stability.

## Experimental Section

**Materials and fiber samples.** Over the past eight years, a family of organo-soluble aromatic polyimides have been designed and synthesized in our laboratory (Harris, 1989; Harris et al, 1996; Lin et al, 1998). Among them two polyimides were specifically synthesized by reacting 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) or 2,2'-dimethyl-4,4'-diaminobiphenyl (DMB) with biphenyltetracarboxylic dianhydride (BPDA), BPDA-PFMB and BPDA-DMB, in refluxing *m*-cresol (for BPDA-PFMB) and *p*-chlorophenol (for BPDA-DMB) at 200 °C through the one-step route. In this synthesis process, the intermediate poly(amic acid)s were not isolated (Harris, 1989; Harris and Hsu, 1989; Harris et al, 1996; Lin et al, 1998). The molecular weights of these two polyimides can be estimated *via* intrinsic viscosities which exceed 5.0 and 10.0 dL/g, respectively. This indicates that both polymers possess high molecular weights in comparison with other soluble aromatic polyimides whose absolute molecular weights have been determined by light scattering and gel permeation chromatography experiments (Kwan et al, 1997; Savitski E. P.).

Fibers were spun from the isotropic solution *via* a dry jet-wet fiber spinning method in the laboratory at The University of Akron. This procedure involves a spinning head, spinneret, coagulation bath and winder. A zone annealing process was utilized to thermally treat the fibers. Draw ratios were controlled by zone drawing in air between 380 °C - 420 °C. As-spun fibers could be drawn up to ten times. Detailed descriptions of the fiber spinning and annealing processes can be found in references (Cheng et al, 1991).

**Equipment and experiments.** BPDA-PFMB and BPDA-DMB fibers were wound on a stainless steel frame. The fibers were isothermally aged in an air circulating oven under 1 atmosphere pressure at 205 °C for 100, 250, 500, 750, 1000, 1500, 2000 and 2500 hours. Tensile strength, elongation to break and initial modulus were measured on a Rheometrics RSA II. Single filaments were mounted on the instrument with a gage length of 1.0 inch. The reported mechanical data was obtained by averaging 30 independent filament measurements. The typical standard deviation was around  $\pm 15\%$ . All samples were elongated at a constant rate of 6% per minute until the sample was broken.

Thermal gravimetry (TG) measurements were conducted in a TA TGA 2950. Non-isothermal experiments were carried out at a heating rate of 10 °C/min under dry nitrogen or air atmospheres. An isothermal mode was also adopted in order to obtain weight loss activation energy of the polymers. The temperature range was 380 °C - 470 °C. Weight losses *versus* time was recorded at different isothermal temperatures. A typical sample weight of 3 mg was used.

High resolution pyrolysis-gas chromatography/mass spectrometry (HR Py-GC/MS) was used to study the thermal degradation mechanism of the two polyimides. The pyrolysis

temperatures used in this study were 764 °C, 920 °C and 1040 °C. Samples with weights ranging from 0.3 mg to 0.5 mg were degraded in a JHP-3 Curie Point Pyrolyzer (Japan Anal. Ind. Corp.). The pyrolysis time was 5 seconds. The separation and identification of the fragments generated during degradation were carried out through the connection of a QP-5000 GC-MS (Shimadzu). The GC fused silica capillary column, CBP5 (0.25 mm i.d. x 25 m), was held at 50 °C for 5 minutes and then temperature-programmed at a heating rate of 5 °C/min to 250 °C. Helium gas was used as the carrier gas, with a total flow of 13 mL/min and a split ratio of 10:1. The electron impact source in the MS was operated at 70 eV and 250 °C.

## Results and Discussion

**Thermal degradation activation energies.** Non-isothermal TG experiments of the two polyimides under both dry nitrogen and air atmospheres are shown in Figures 1 and 2. These

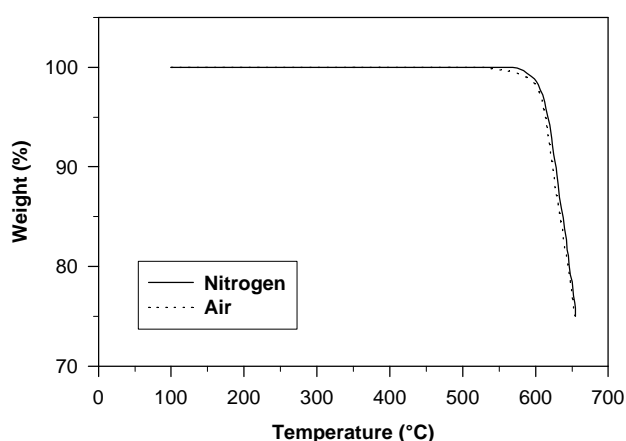


Figure 1. Non-isothermal TG experiments for BPDA-PFMB in dry nitrogen and air atmospheres.

plots may be used as rough examinations of the weight losses of these materials due to thermal degradation under dry nitrogen and air. Both polyimides exhibit excellent thermal and thermo-oxidative stability. The 5% weight loss temperatures of these materials are above 500 °C for BPDA-DMB and close to 600 °C for BPDA-PFMB. In particular, the 5% weight loss behaviors of BPDA-PFMB show little difference under dry nitrogen or air, while in BPRA-DMB, the 5% weight loss in air is substantially lower than that under dry nitrogen (about 30 °C difference). This indicates that the thermal and thermo-oxidative stability of these two polyimides, both of which possess the same backbone chemical structure, is critically determined by the oxidative resistance of the pedant side groups. Note that the trifluoromethyl group is strongly electron negative (withdrawing) and the methyl group is electron positive (donating). Therefore, the methyl group is relatively easily subject to attack by oxygen. However, the types of experiments shown in Figures 1 and 2 do not reflect the true thermal degradation routes of these polyimides. A more precise measurement of this phenomena requires study of the weight loss kinetics, which have been carried out under isothermal conditions in TG experiments. Figures 3 and 4 show changes in percentages of weight loss with time at different isothermal temperatures for BPDA- PFMB in dry nitrogen and air, respectively. In Figure 3, only a 1% weight loss is detected at

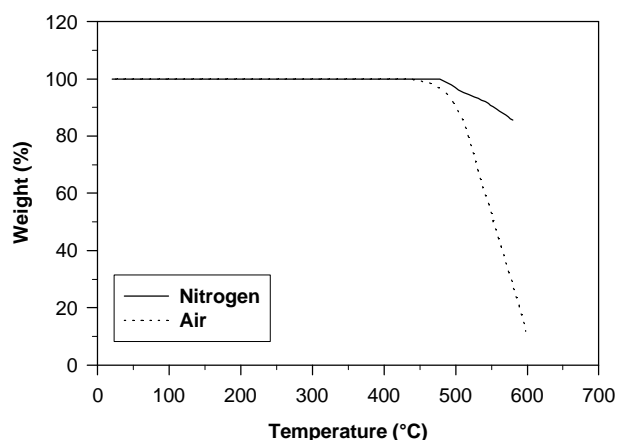


Figure 2. Non-isothermal TG experiments for BPDA-DMB in dry nitrogen and air atmospheres

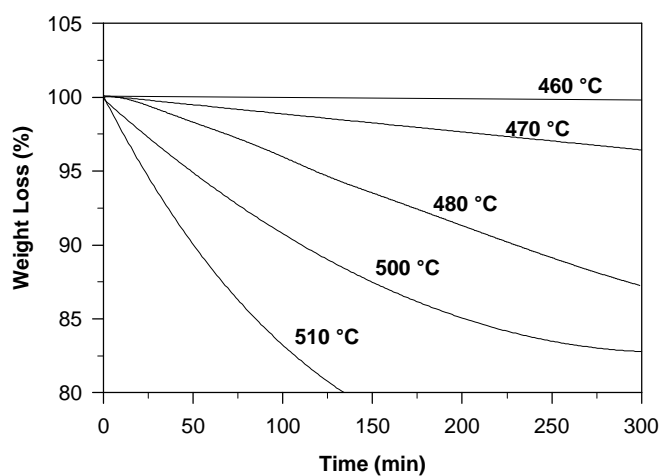


Figure 3. Isothermal TG experiments for BPDA-PFMB in dry nitrogen at different temperatures

460°C after 5 hours, indicating the excellent thermal stability of BPDA-PFMB in nitrogen. However, in air, a 1% weight loss is observed at 400 °C in the same period of time. This difference of more than 60 °C reveals the effect of thermo-oxidation reactions due to the presence of oxygen. Based on the kinetics model proposed by Flynn (Flynn, 1970), weight loss activation energies of BPDA-PFMB can be calculated using the following equation:

$$\ln(t) = \ln[g(\alpha)] - \ln A + E_a/(RT) \quad (1)$$

where  $t$  is the isothermal time,  $g(\alpha)$  is the integral of the rate of weight loss,  $A$  is the pre-exponential factor,  $R$  is the gas constant, and  $E_a$  is the weight loss activation energy. The slope

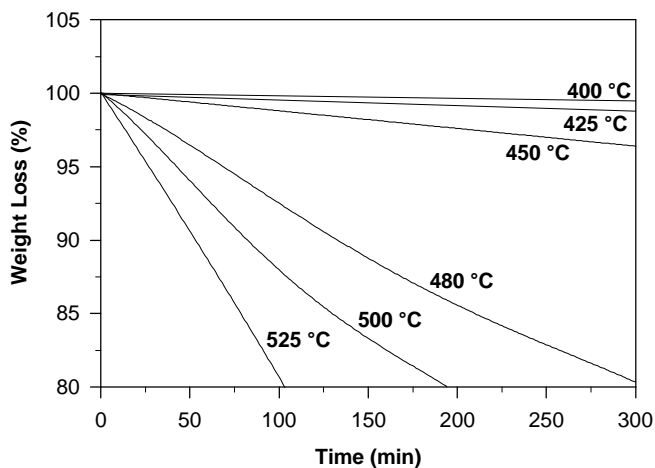


Figure 4. Isothermal TG experiments for BPDA-PFMB in air at different temperatures.

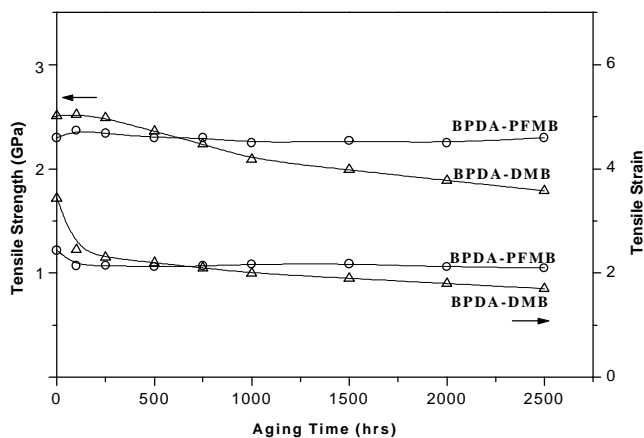


Figure 5. The tensile strength and strain changes of BPDA-PFMB and BPDA-DMB fibers after aging at different intervals in circulating air at 205 °C.

of a plot between  $\ln(t)$  and  $1/T$  at constant weight fraction loss  $g(\mathbf{a})$  yields  $E_a$ . The weight loss activation energies under dry nitrogen and air atmospheres were calculated as 300 kJ/mol and 200 kJ/mol for BPDA-PFMB. Based on previous data obtained in our laboratory, these activation energies are substantially higher than other known fibers in the same temperature region. For example, the activation energy calculated for Kevlar® 49 fibers in air is 100 kJ/mol. This experimental procedure can also be applied to BPDA-DMB fibers. For BPDA-DMB fibers isothermally heated under both dry nitrogen and air, the activation energies were calculated as 200 kJ/mol and 135 kJ/mol, respectively, which are still better than Kevlar® 49 fibers.

**Changes of tensile properties during isothermal aging.** The most reliable test of the thermal and thermo-oxidative stability of a fiber for practical applications can be obtained from the study of changes in its physical, and in particular, mechanical (such as tensile) properties upon

prolonged isothermal aging times at elevated temperatures. Figure 5 illustrates the tensile strength and strain changes of BPDA-PFMB and BPDA-DMB fibers after aging for different times at 205 °C in circulating air. It is evident that for BPDA-PFMB fibers, the tensile strength at around 2.6 GPa does not exhibit change within the aging time period, although a minor increase in strength can be seen in the first one hundred hours of aging. This is most likely attributed to a further crystallization and annealing process. The tensile strength of BPDA-DMB in Figure 5 shows only a slight decrease from 3.0 GPa in the first 250 hours at a rate of 0.004%/hour. The strength decrease accelerates between 250 and 1000 hours where its decreasing rate becomes 0.022%/hour. From 1000 hours up to 2500 hours, this decreasing rate is 0.011%/hour. The final tensile strength at 2500 hours of aging decreases to about 2.2 GPa. On the other hand, the relationships between the strains of these two fibers and aging times show that the tensile strain of BPDA-PFMB fiber decreases about 12% in the first one hundred hours of aging, after which the strain stays almost constant, while BPDA-DMB fiber shows a greater decrease of the strain in the first one hundred hours of aging (almost 30%), after which a gradual decrease of the tensile strain can be found (Figure 5).

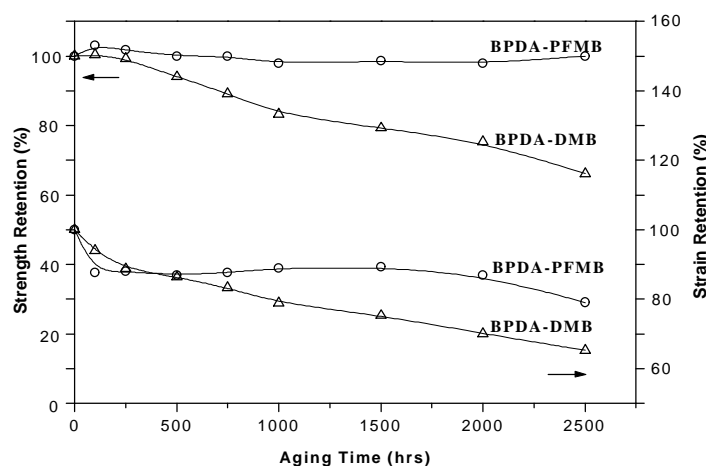


Figure 6. Plot of percent strength and strain retention of BPDA-PFMB and BPDA-DMB fibers *versus* isothermal aging time in circulating air at 205 °C.

Figure 6 is a plot of percent strength and strain retention *versus* the isothermal aging time in circulating air. It is obvious, as shown in Figure 6, that the both strength retention increase slightly or keep almost constant in the first 100 hours, while the strain retention in both of the fibers possess clear decreases. After the initial stage of 100 hours, the strength and strain retention of BPDA-PFMB fibers are only slightly decreased. However, in the case of BPDA-DMB fibers, both retention show gradual but greater decreases. At 2500 hours of aging at 205 °C, the strength retention changes of BPDA-PFMB and BPDA-DMB fibers are 100% and 73%, respectively. It is important to note that the difference of the two  $\text{CF}_3$  groups in the BPDA-PFMB diamines, as compared to the two  $\text{CH}_3$  groups in the BPDA-DMB diamines, contributes to the difference in the thermal and thermo-oxidative stability of these fiber materials. This may again be attributed to the electron withdrawing nature of the  $\text{CF}_3$  *versus* the electron donating tendency of the  $\text{CH}_3$ .

During isothermal aging in air, it is speculated that macroscopic mechanical property changes in fibers, particularly in their tensile properties, may be caused by chemical structure changes including scission of polymer chains, completion of cyclization, and crosslinking *via* chemical reactions. Secondary parameters such as crystallization, crystal perfection and orientation changes in the fibers may also affect macroscopic properties. However, the main effect is speculated to be the scission of the macromolecules as a result of thermal degradation. This process should be more prevalent in the case of BPDA-DMB fibers compared with BPDA-PFMB fibers.

***Mechanism of decomposition.*** High resolution Py-GC-MS can provide useful information on the mechanism of thermal degradation in polymers. BPDA-PFMB and BPDA-DMB fibers were pyrolyzed under the same conditions in order to compare their degradation mechanisms. The total ion current (TIC) pyrograms shown in Figures 7 and 8 were

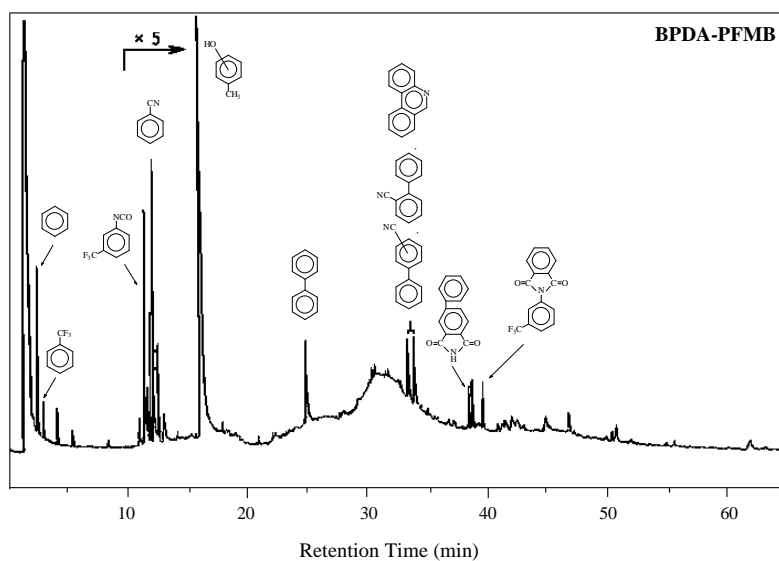


Figure 7. High resolution TIC pyrograms of BPDA-PFMB at a pyrolysis temperature of 920 °C.

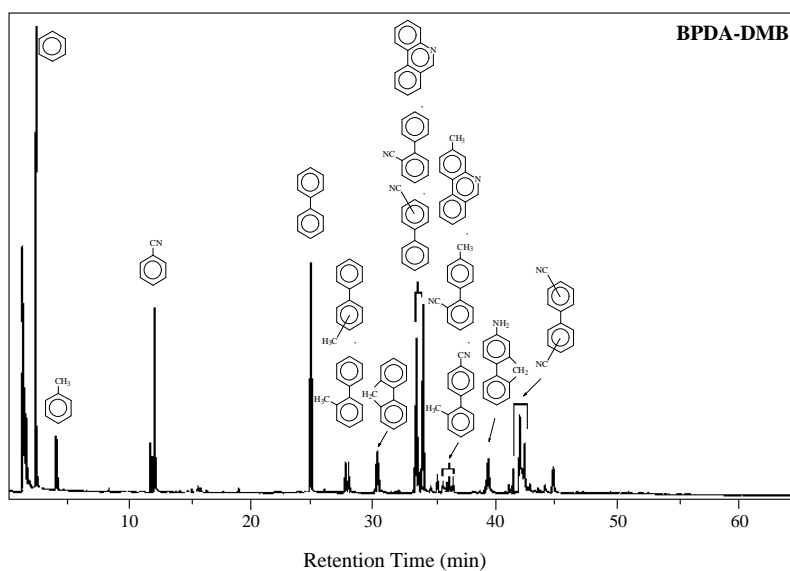

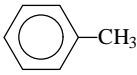
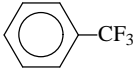
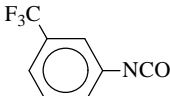
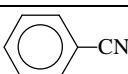
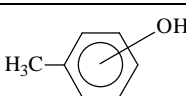
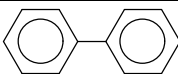


Figure 8. High resolution TIC pyrograms of BPDA-DMB at a pyrolysis temperature of 920 °C.



obtained at a pyrolysis temperature of 920 °C for 5 seconds, and the primary products summarized in Table 1 and 2 were separated by a capillary column, and identified by the on-line MS. It is noted that these products can be divided into four pyrolyzate groups: (1) 3-methylphenol, which may originate from residual solvent in the samples (*m*-cresol); (2) low boiling point products such as carbon monoxide (this compound cannot be distinguished in the GC condition used), carbon dioxide and hydrogen cyanide (this compound can not be distinguished in the GC condition used) which can form from the imide ring *via* carbon-carbon bond and carbon-nitrogen bond scissions as well as from the rearrangement of imide free radicals; (3) aromatic hydrocarbons, aromatic amines, nitriles, imides and isocyanate, all of which correspond to partial fragments of polymer chains. For BPDA-DMB, the characteristic pyrolyzates include toluene, 2- carbonitrile biphenyl, 2-methyl-4'-carbonitrile biphenyl and 2-carbonitrile-4'-methyl biphenyl, while trifluoromethyl benzene, 3-trifluoromethyl phenyl isocyanate, 4-phenyl phthalimide and N-(3-trifluoromethyl phenyl) phthalimide reflect the fragments in BPDA-PFMB; (4) fluorene, 2-amino fluorene, phenathridine and 3-methyl phenathridine which are attributed to the isomerizations, rearrangements and cyclizations of the aforementioned pyrolyzates at high temperatures.

Table 1. The pyrolyzates of BPDA-DMB and BPDA-PFMB identified by PyGC-MS

No.	Structure	Name	MW	BPDA-DMB	BPDA-PFMB
1	CO <sub>2</sub>	carbon dioxide	44	+	+
2		benzene	78	+	+
3		toluene	92	+	-
4		trifluoromethyl benzene	146	-	+
5		3-trifluoromethyl phenyl isocyanate	187	-	+
6		phenyl carbonitrile	103	+	+
7		3-methyl phenol	108	-	+
8		biphenyl	154	+	+

+, observed; -, not observed.

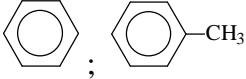
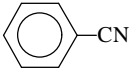
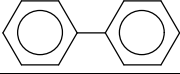
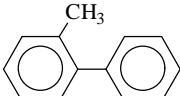
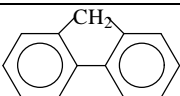
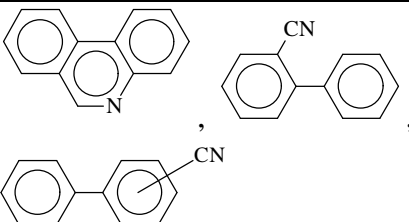
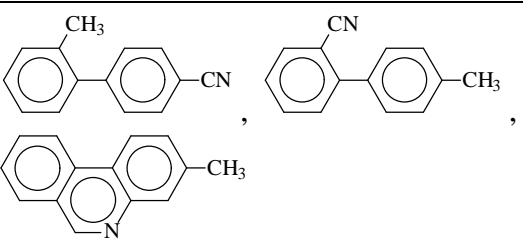
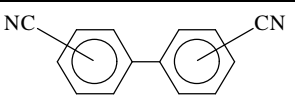
Table 2. The pyrolyzates of BPDA-DMB and BPDA-PFMB identified by PyGC-MS

9		2-methyl biphenyl	168	+	-
10		fluorene	166	+	-
11		phenanthridine  2-carbonitrile biphenyl	179	+	+
12		2-methyl-4'-carbonitrile biphenyl  2-carbonitrile-4'-methyl biphenyl  3-methyl phenanthridine	193	+	-
13		2-amino fluorene	181	+	-
14		4-phenyl phthalimide	223	-	+
15		N-(3-trifluoromethyl phenyl) phthalimide	291	+	-
16		2-carbonitrile-4'-carbonitrile biphenyl	204	+	-

+, observed; -, not observed.

The effect of pyrolysis temperature on the thermal degradation of BPDA-PFMB and BPDA-DMB has been investigated by comparing the distribution of the major pyrolyzates. Pyrolysis of BPDA-DMB and BPDA-PFMB is carried out at temperatures of 764 °C, 920 °C and


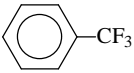
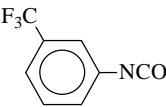
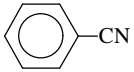
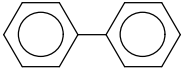
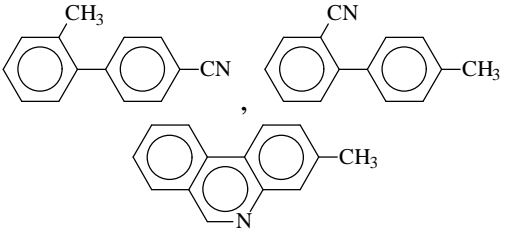
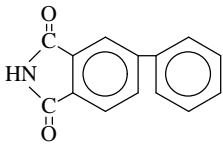
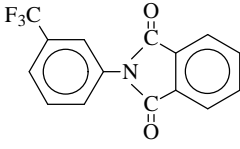
Table 3. Pyrolyzate yields of BPDA-DMB at different pyrolysis temperatures (calculated in peak area, %)

Pyrolyzate		Pyrolysis Temperature		
No.	Structure	764°C	920°C	1040°C
2, 3		30.3	27.8	30.7
6		5.7	10.7	10.2
8		27.4	18.6	18.8
9		2.7	2.1	1.8
10		2.5	1.9	2.0
11		16.6	27.6	22.3
12		4.9	5.2	4.7
16		9.9	9.1	9.6

1040 °C, respectively. The composition distributions of major pyrolyzates of these two polyimides at the varying pyrolysis temperatures are listed in Tables 3 and 4. It is noted that there is a maximum for some characteristic pyrolyzates (such as carbonitrile biphenyl and phenanthridine at 920 °C) in the temperature range of 764 °C - 1040 °C. It appears that the temperature of 920 °C is more beneficial towards the production of these pyrolyzates. The relative yields of the biphenyl decreases with increasing pyrolysis temperatures, especially for BPDA-PFMB. Comparing the data in Table 3 with that in Table 4, it is found that the yields of carbonitrile biphenyls and biphenyl in BPDA-DMB are higher than that in BPDA-PFMB at the same pyrolysis temperature. This is due to the different electron states of the substituting groups (-CH<sub>3</sub> and -CF<sub>3</sub>) for the two polymers. For BPDA-DMB, the electron donating nature of the

Table 4. Pyrolyzate yields of BPDA-PFMB at different pyrolysis temperatures

(calculated in peak area, %)

No.	Pyrolyrate Structure	Pyrolysis Temperature		
		764°C	920°C	1040°C
2		29.3	50.3	36.9
4		10.9	12.7	10.9
5		11.3	4.1	21.6
6		18.6	9.4	9.7
8		10.8	6.8	2.2
11		11.0	13.7	4.4
14		4.5	1.6	9.9
15		3.7	1.4	4.4

pendant methyl groups causes the carbon-carbon bonds linking the two phenylenes to strengthen, which in turn hampers the bond scission. Therefore, several pyrolyzates, such as 2-methyl biphenyl, fluorene, 2-methyl-4'-carbonitrile biphenyl, and 2-aminofluorene from BPDA-DMB are associated with the biphenyl fragments attached to the methyl groups. On the other hand, in the case of BPDA-PFMB the electron withdrawing nature of the trifluoromethyl groups strengthens the thermal and thermo-oxidative stability of the connection between the pendant groups and the backbones, but weakens the carbon-carbon bonds connecting these two phenylenes in the backbone diamines, and the carbon-carbon bonds may be cleaved relatively easily. This results in the formation of pyrolyzates such as 3-trifluoromethyl benzene, 3-trifluoromethyl phenyl isocyanate, and N-(3-trifluoromethyl phenyl) phthalimide containing a phenylene with a trifluoromethyl group rather than biphenyl fragments substituted by the methyl groups which would be seen in BPDA-DMB. However, it should be noted that BPDA-PFMB possesses an overall better thermal and thermo-oxidative stability compared with BPDA-DMB.

In summary, the composition and distribution of the pyrolysis products implies the thermal degradation of BPDA-PFMB and BPDA-DMB undergoes the same mechanism, which is initiated by random homolytic cleavage of the carbon-nitrogen, carbon-carbon bonds in the imide rings and carbon-nitrogen bonds in the main chains. These cleavages give rise to chain free radicals and carbon monoxide. The following steps consist of depropagation and chain transfer involving C-H and N-H hydrogen transfer processes leading to aromatic hydrocarbons, aromatic amines, nitrile and imides. Other pyrolyzates, such as phenanthridine and 2-aminofluorene, may result from rearrangements, cyclizations and secondary reactions. The detailed degradation mechanisms of BPDA-PFMB and BPDA-DMB are in the first time given in Figures 9 and 10.

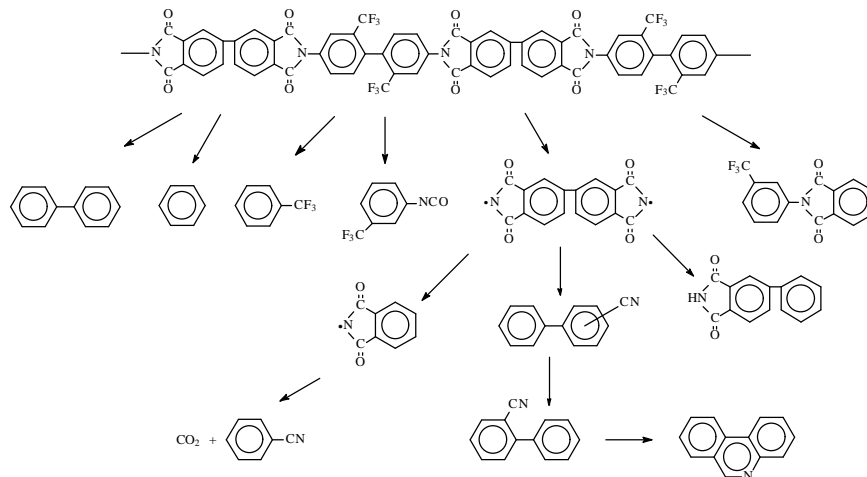


Figure 9. The thermal degradation mechanism of BPDA-PFMB.

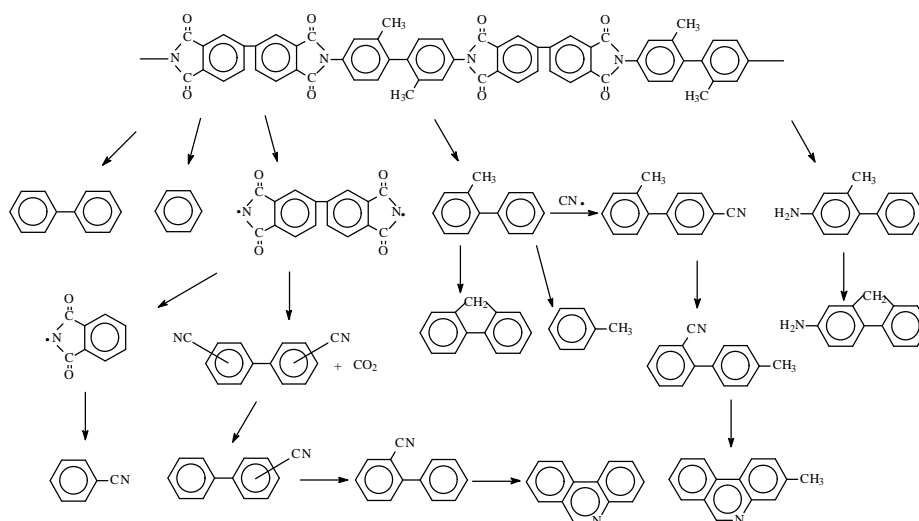


Figure 10. The thermal degradation mechanism of BPDA-DMB.

## Conclusion

It has been shown that both polyimide fibers studied possess excellent thermal and thermo-oxidative stability. Their weight loss activation energies have been determined using TG experiments. The long term thermal aging experiments of these two fibers have indicated that they exhibit outstanding mechanical property retention. In particular, the BPDA-PFMB fiber is thermally more stable and thus exhibits more retention of its mechanical tensile properties than the BPDA-DMB fibers. Since both polyimides have the same chain backbone structures, this difference is attributed to the electron states of the side pendant trifluoromethyl and methyl groups: the former is an electron withdrawing group and the latter is an electron donating one. Based on the composition and distribution of the pyrolysis product results obtained using high resolution PyGC-MS, one finds that the thermal degradation of BPDA-PFMB and BPDA-DMB fibers undergoes the same mechanism.

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