AROMATIC POLYIMIDES CONTAINING METHYLENE UNITS. THERMAL BEHAVIOUR

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The thermal behaviour of two series of aromatic polyimides in air and nitrogen atmosphere have been investigated. The results indicated that the polymers were easier to decompose in air than in nitrogen, with 52-58% residue remaining in nitrogen versus 3-5% in air, at 900°C. The presence of methyl substituents on phenyl ring, in the diamine component, led to slightly lower decomposition temperature and higher glass transitions.

INTRODUCTION

Aromatic polyimides, owing to their good thermal stability, chemical resistance, and good mechanical and low dielectric constants, have been extensively applied in microelectronic, aviation, liquid crystal displays, and optoelectronic and separation industries.[1-4] They are distinguished from other high performance polymers by the solubility of poly(amidic acid) precursor form, which can be cast into uniform films and quantitatively conversed to polyimide structure. However, most aromatic polyimides encounter processing difficulty due to their infusibilities and poor solubilities in organic solvents. Such difficulty is due to strong interchain forces, inherent macromolecular rigidity, or semicrystallinity.[5-9] Many studies have attempted to enhance their processabilities and solubilities either by introducing bulky groups or flexible chains, nonsymmetric, alicyclic or nonlinear moieties into the polymer backbones or by attaching bulky side groups.[10-14] In 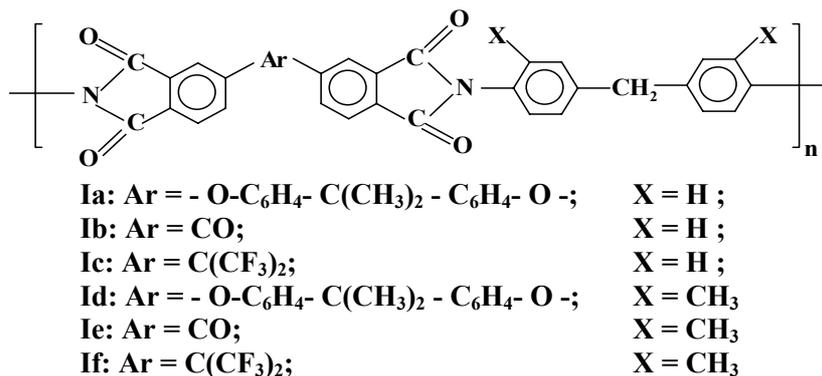general, polyimides are the most thermally stable polymers because of their high glass transition and high decomposition temperatures and are useful in long-term service temperatures. Therefore, studying the thermal behavior of polyimides is of both scientific significance and engineering applied importance.

This paper presents the thermal behaviour in air and in nitrogen of two series of polyimides derived from 4,4'-(4,4'-isopropylidenediphenoxy)bis (phthalic anhydride), benzophenotetracarboxylic dianhydride or hexafluoroisopropylidenediphthalic dianhydride and aromatic diamines containing flexible methylene bridges (4,4'-diaminodiphenylmethane or 3,3'-dimethyl-4,4'-diaminodiphenylmethane).

RESULTS AND DISCUSSION

The structure of the investigated polyimides is presented in Scheme 1. These polymers have been obtained by methods previously reported and the detailed descriptions have been presented elsewhere.[15]

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Ia: Ar = - O-C$_6$H$_4$- C(CH$_3$)$_2$ - C$_6$H$_4$- O -;   X = H ;
Ib: Ar = CO;   X = H ;
Ic: Ar = C(CF$_3$)$_2$;   X = H ;
Id: Ar = - O-C$_6$H$_4$- C(CH$_3$)$_2$ - C$_6$H$_4$- O -;   X = CH$_3$
Ie: Ar = CO;   X = CH$_3$
If: Ar = C(CF$_3$)$_2$;   X = CH$_3$

Scheme 1. The structure of the aromatic polyimides **I**.

The polyimide films were obtained by casting the polyamidic acid solution 10-14% in dimethylacetamide (DMA), onto glass plates and drying at 60°C over 4 h to evaporate the solvent. The subsequent heating of the precursor films at 100, 150, 200, and 250°C consecutively (for 1 h at each temperature) resulted in a final polyimide film.

The FTIR spectra of all polymers show characteristic absorption bands for: the carbonyl group of the imide ring at about 1770-1780 cm^{-1} and 1710-1720 cm^{-1}, the corresponding carbonyl bridge in benzophenone group at 1660-1670 cm^{-1} and the characteristic band for the C-N vibration at 1360-1375 cm^{-1} and 720-730 cm^{-1}.[16,17] In the polymers **Ic** and **If** the characteristic absorption bands of hexafluoroisopropylidene are present at 1260 cm^{-1} and 1210 cm^{-1}. The absorption peaks at 2940 cm^{-1} and 2870 cm^{-1} are characteristic for methyl and methylene groups. A typical FTIR spectrum is presented in Figure 1.
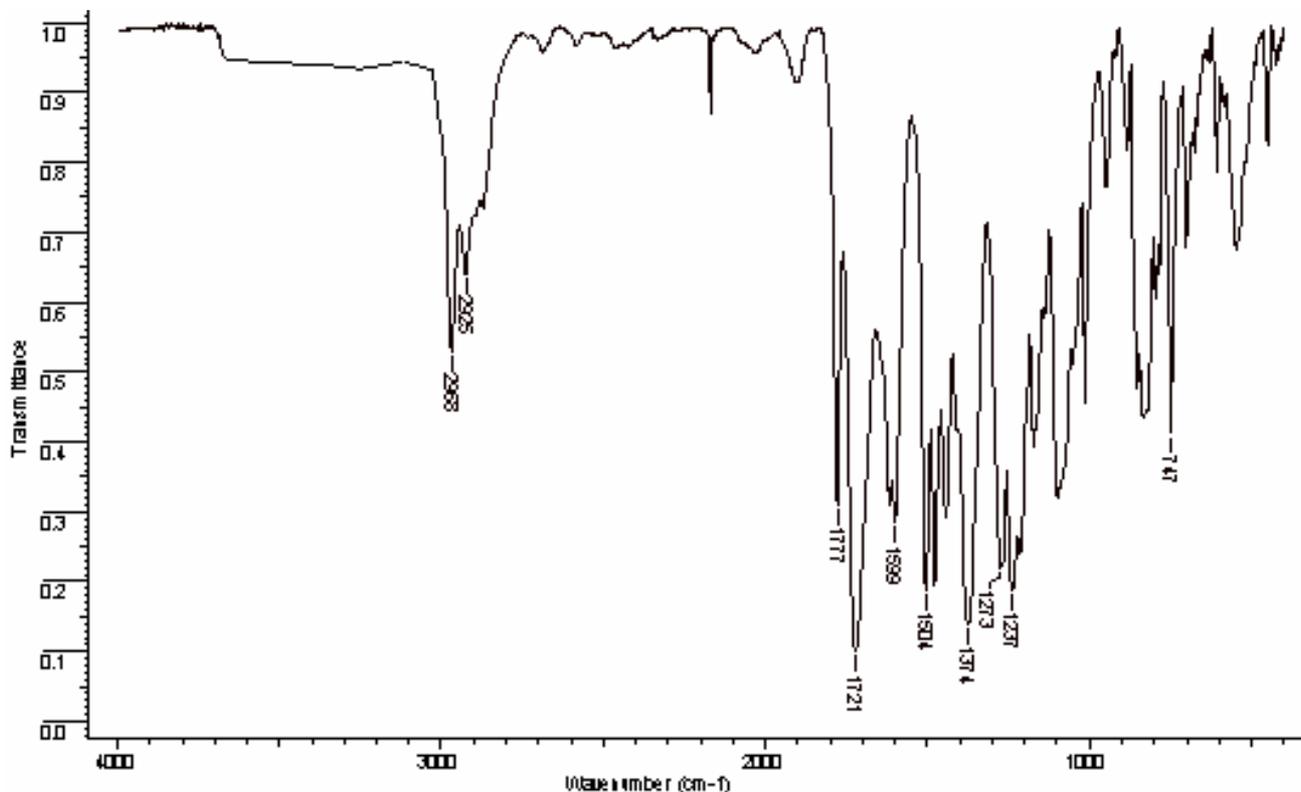

Fig. 1 – FTIR Spectrum of the polymer **Id**.

All the polymers are easily soluble in DMA, N-methylpyrrolidone (NMP), N,N'-dimethylforma-mide (DMF) and dimethylsulfoxide (DMSO). Their good solubility may be explained by the

presence of methyl groups or isopropylidene or hexafluoroisopropylidene units[18], which increase the free volume allowing for the small solvent molecules to penetrate more easily among the polymer chains. The incorporation of the two methyl groups on the diamine moiety leads to an increase in the free volume and a resultant decrease of the molecular packing. The steric hindrance from the methyl groups might also lead to a distortion of the packing of the polyimide backbones. For these reasons, the polyimides based on 3,3'-dimethyl-4,4'-diaminodiphenylmethane have a better solubility compared with polymers obtained from 4,4'-diaminodiphenylmethane.[18,19]

All these polyimides have a good film forming ability from solutions in DMA, except for **Ib.** The films with thickness of tens of microns were obtained by casting their DMA polyamidic acid solutions onto glass plates and they showed good adhesion to such substrates.

The thermal stability of the samples was evaluated by dynamic thermogravimetric analysis (TGA) in nitrogen and air, at a heating rate of 10°C/min. The TGA curves are presented in Figure 2.
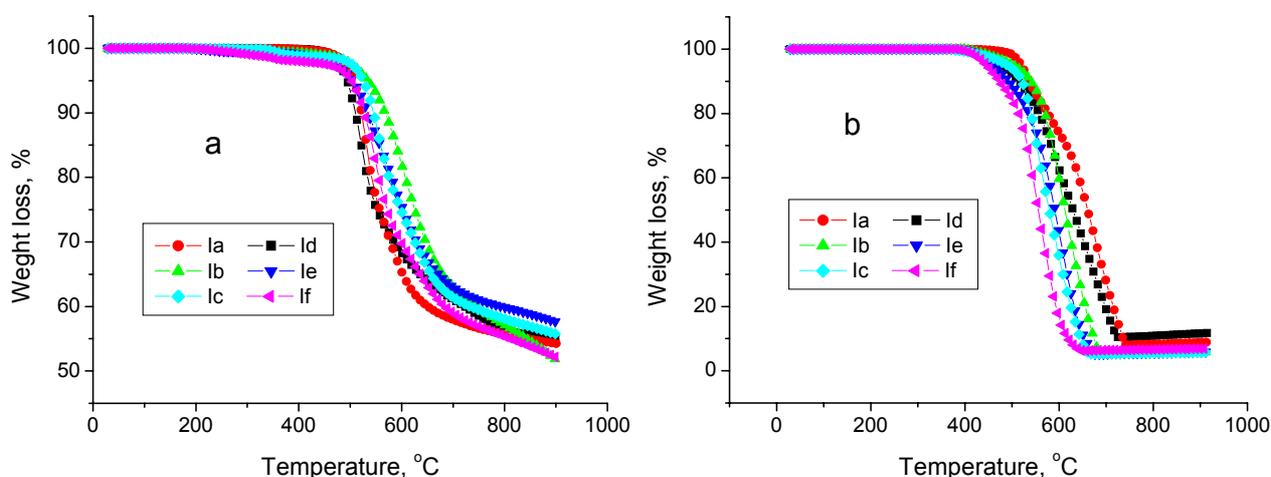

Fig. 2 – TGA curves of polyimide films in (a) nitrogen and (b) air.

Polyimides degrade faster in air than in nitrogen, with 52-58 % residue in nitrogen versus 3-5% in air, at 900°C. The temperature corresponding to the maximum rate of decomposition (T_{max}) of the polyimides determined from DTG curves is in the range of 523-610°C in nitrogen and in the range of 534-600°C in air, respectively. The starting decomposition temperature (5% weight loss) of the polyimides is lower in air than in nitrogen being in the range of 495-530°C in nitrogen and in the range of 445-503 °C in air, respectively (Table 1). It is worthy of note that the polymers which contain methyl substituents showed lower decomposition temperature than the other polymers, in nitrogen as well as in air atmosphere. As it was mentioned above, polyimides degrade faster in air than in inert atmosphere because the surrounding water vapors can lead to scission and decarboxylation of

the imide ring and increases the rate of the degradation process. In the same time, the imide ring can be oxidized to polymer peroxide or phenyl radical by oxygen in air. The decomposition reaction of polyimides is speeded up by water and oxygen in air. Therefore, the 5% weight loss temperature of the polyimides is lower in air than in nitrogen. In air, the oxygen and water can accelerate degradation of polyimides until complete decomposition as primary decomposition products CO, CO_2 and H_2O.[20] Therefore the residual mass is so low in air (3-5%). In nitrogen decomposition reaction rate of polyimides decrease at the higher temperatures due to carbonization.[20]

The differential weight loss, DTG curves, recorded under the same experimental conditions (in air and nitrogen atmosphere), are presented in Figures 3-5.

Table 1

Thermal properties of aromatic polyimides **Ia-f**

Polymer	[a]$T_{5\%}$ (°C)		[b]T_{max} (°C)		Weight loss at T_{max} (%)		[c] Char yield (%)		[d]Tg (°C)
	In nitrogen	In air	In nitrogen	In air	In nitrogen	In air	In nitrogen	In air	
Ia	516	503	530	534	14	20	54	4.35	200
Ib	530	497	610	600	15	30	52	3.15	260
Ic	523	487	557	554	14	30	56	3.20	275
Id	495	475	523	591	16.5	33.5	55	4.81	228
Ie	503	461	565	599	16.6	56	58	4.02	278
If	503	445	548	553	17	48	52	3.14	287

[a] Temperature of 5% weight loss of polymers; [b]Maximum decomposition temperature; [c]Residual weight at 900°C; [d]Glass transition temperature determined in the second heating scan, at a heating rate of 10°C/min.
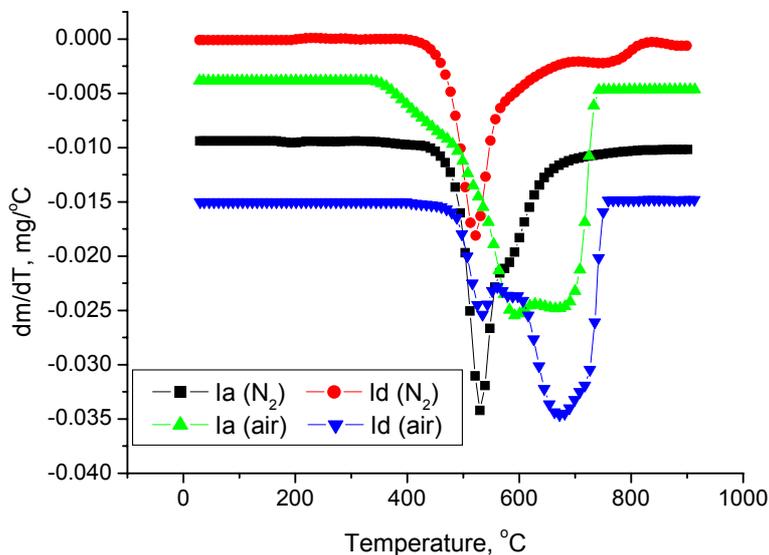
Fig. 3 – DTG curves of the samples **Ia** and **Id**.
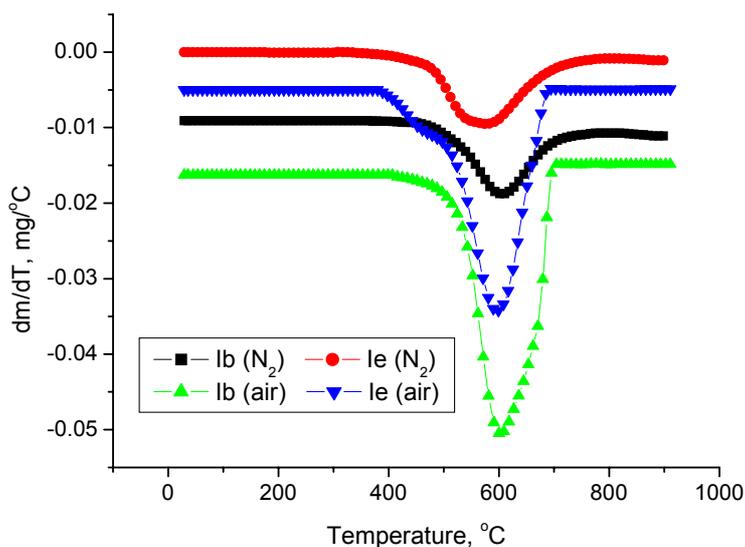
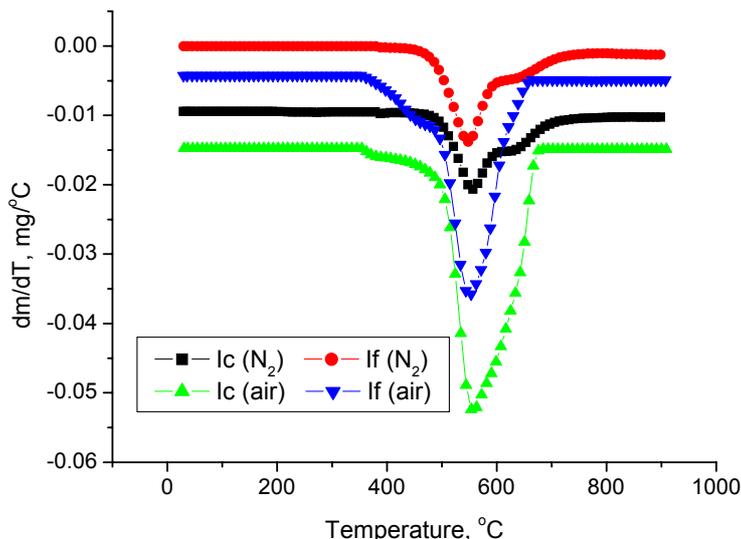Fig. 4 – DTG curves of the samples **Ib** and **Ie**.

Fig. 5 – DTG curves of the samples **Ic** and **If**.

As can be seen from these curves the decomposition of the polyimides is faster in air than in nitrogen. The weight loss at maximum rate of decomposition temperature is in the range of 14-21% in nitrogen and in the range of 20-56% in air, respectively. The sample **Ia** and **Id** exhibited two steps of degradation having the maximum rate of decomposition temperature of 530°C and 523°C in nitrogen, and 534°C and 591°C in air, respectively (Figure 3). The other polymers exhibited one step of degradation having the maximum rate of decomposition temperature of 610°C and 565°C in nitrogen, and 600°C and 599°C in air, respectively, for polymers **Ib** and **Ie** (Figure 4). The polymers **Ic** and **If** exhibited the maximum rate of decomposition temperature of 557°C and 548°C in nitrogen and 554°C and 553°C in air, respectively (Figure 5).

All the polymers showed a glass transition temperature, in the range of 200-287°C, with higher values for polyimides containing hexafluoroisopropylidene units (Table 1). The introduction of isopropylidene groups together with ether linkages brings much more flexibility to the macromolecular chain and decreases the glass transition of the polymers **Ia** and **Id**. In the same time, the presence of methyl substituents into the diamine segment increased the glass transition of the corresponding polyimides **Id, Ie** and **If,** due to the steric effect of the these substituents.[19]
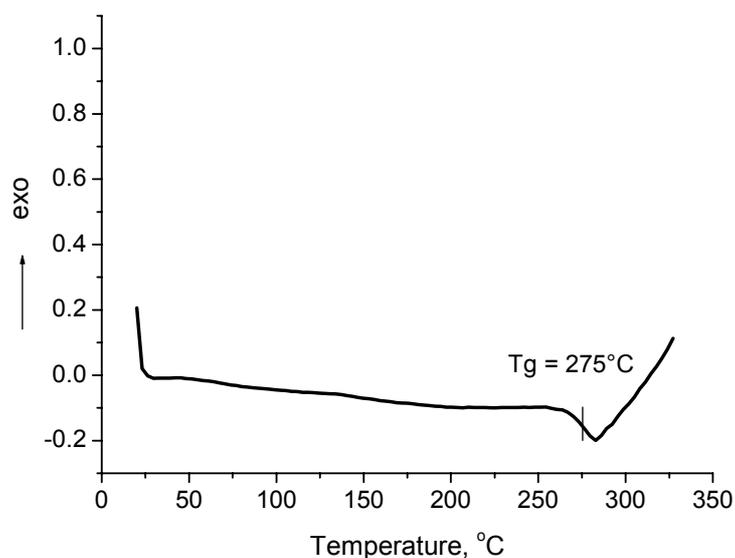
A typical DSC curve is shown in Figure 6.

Fig. 6 – DSC curve of polymer **Ic**.

Flexible free-standing films were prepared by casting the DMA solutions of polymers. These films were subjected to tensile tests and the results are listed in Table 3. These polyimides showed a tensile strength of 27-87 MPa and an elongation at break in the range of 2.3 – 8.8%, proving good mechanical properties.

Table 3

Mechanical properties of the polymers

Polymer	Strain, %	Stress, MPa
Ia	8.8	79.5
Ib	4.2	87.4
Ic	-	-
Id	4.4	62.4
Ie	4.4	81.5
If	2.3	19.7

EXPERIMENTAL

FTIR spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm^{-1}.

Thermogravimetric analysis (TGA) was performed in air and nitrogen flow (20 cm^{3}min^{-1}) atmosphere at a heating rate of 10°C/min from 25 to 900°C with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was 3-5 mg.

Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland) operating with version 9.1 of STAR^e software in the range of 25-350°C. The samples (2–4 mg) were encapsulated in aluminium pans having pierced lids to allow escape of volatiles. The heating rates of 10 °C min^{-1} and nitrogen purge at 100 mL min^{-1} were employed. The mid-point of the inflection curve resulting from the typical second heating cycle was assigned as the T_g of polymers.

The mechanical properties of the polymer films were determined by stress-strain measurements at room temperature on an Instron Single Colomn Systems tensile testing machine (model 3345) equipped with a 5 kN load cell and activate grips, which prevented the slippage of the sample before break. The cross head speed was 50 mm min^{-1}.

CONCLUSIONS

The thermal behaviour of two series of aromatic polyimides containing methylene bridge and/or methyl groups was investigated. The polyimides show high thermal stability with decomposition temperature being above 445°C in air and 495ºC under nitrogen atmosphere and glass transition in the range of 200-287°C. The maximum rate of decomposition temperature is in the range of 523-610°C in nitrogen and in the range of 534-600°C in air, respectively. The polymers based on 4,4'-diaminodiphenyl methane showed slightly higher decomposition temperature than those based on 3,3'-dimethyl-4,4'-diaminodiphenyl methane, while their Tg are slightly lower. The free standing films having the thickness of tens of micrometers exhibit good mechanical properties.

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