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Comparative study of aromatic polyimides containing methylene units

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Abstract Two series of aromatic polyimides have been synthesized by solution polycondensation of certain aromatic dianhydrides with two aromatic diamines containing methylene groups; one of the diamines has also a methyl substituent on each benzene ring. These polymers have been studied with regard to their solubility, thermal stability, film forming ability, and mechanical properties of their films.

Keywords Aromatic polyimides · Methylene bridges · High thermal stability

Introduction

Aromatic polyimides have long been considered as one of the most useful super engineering plastics because of their excellent thermal stability, chemical resistance, mechanical properties, and low dielectric constant. 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. Thus, polyimides have been especially used in microelectronic, film, adhesive, and membrane industry due to these prior properties [1–4]. One of the most notable applications of polyimide thin films is as the interlayer dielectrics in multi level very-large-scale integrated circuits and as matrix resins in high-temperature composite structures [5–7]. Here, a dielectric material should possess a

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number of other high performance characteristics such as high thermal stability, good resistance to aggressive media, and good mechanical properties. From this point of view aromatic polyimides meet these requirements [8, 9]. However, fully aromatic polyimides are processed with great difficulties because they are insoluble and infusible, and do not show a glass transition before decomposition. One of the successful approaches to increase solubility and processability of polymers is by introduction of bulky lateral substituents, flexible linkages, nonsymmetric, alicyclic or nonlinear moieties [10–14]. Being known that the introduction of flexible linkages into the backbone of fully aromatic polymers can lead to soluble products, the synthesis of polyimides containing flexible isopropylidene (6H), hexafluoroisopropylidene (6F) groups or other groups is a promising way to easy processable compounds having high thermal stability.

This paper presents the synthesis and characterization of two series of polyimides containing flexible methylene bridges in the main chain. One series is based on 4,4′-diaminodiphenylmethane, and another one is based on 3,3′-dimethyl-4,4′-diaminodiphenylmethane, which reacted with the same dianhydrides: 4,4′-isopropylidene-diphenoxy)bis(phthalic anhydride), benzophenontetracarboxylic dianhydride or hexafluoroisopropylidendiphthalic dianhydride. The properties of these polyimides, such as solubility, thermal stability, glass transition temperature, and film forming ability were studied and compared.

Experimental

Starting materials

N, *N*′dimethylacetamide (DMA) (Merck) was used as received.

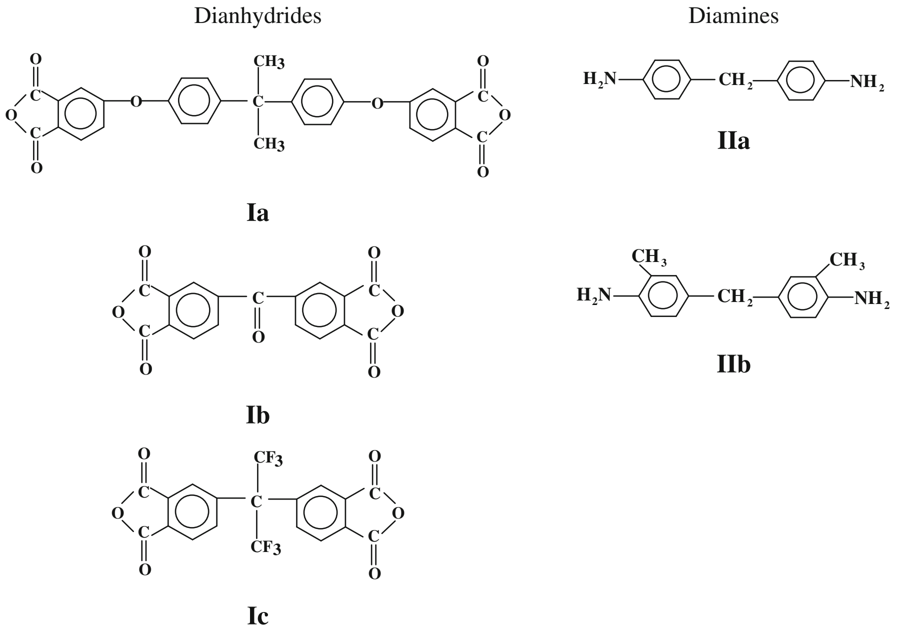
4,4′-Isopropylidene-diphenoxy-bis(phthalic anhydride) (6HDA), **Ia** and benzophenontetracarboxylic dianhydride (BTDA), **Ib**, from Aldrich were used as received. Hexafluoroisopropylidendiphthalic dianhydride (6FDA), **Ic**, from Hoechst–Celanese was purified in our laboratory by recrystallization from acetic anhydride. Melting point (m.p.) of 6HDA was 184–187 °C, m.p. of BTDA was 224–226 °C, and m. p. of 6FDA was 245–247 °C.

Aromatic diamines used in this study are: 4,4′-diaminodiphenylmethane (**IIa**) from Fluka, and 3,3′-dimethyl-4,4′-diaminodiphenylmethane, (**IIb**), obtained in our laboratory by a previously reported method [15, 16]. M.p **IIa**: 90–92 °C and m.p. **IIb**: 155–157 °C.

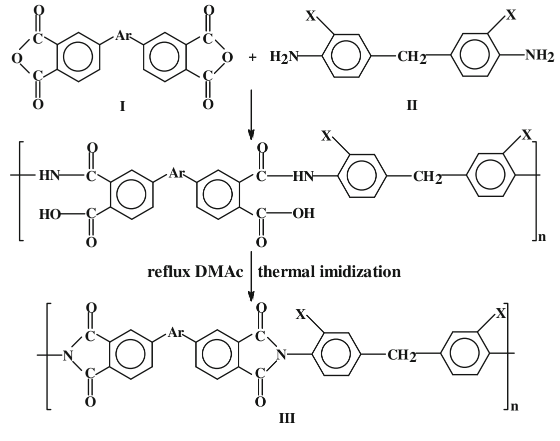
The structures of these monomers are shown in Scheme 1.

Polymer synthesis

The method of two steps polycondensation reaction has been used for the preparation of the polyimides. The first step of the polycondensation reaction was performed at room temperature with equimolar amounts of an aromatic dianhydride **I** and an aromatic diamine **II** in N,N-dimethylacetamide, at a total concentration of 10–14%, under inert atmosphere during 4–6 h (Scheme 2).



Scheme 1 Structure of aromatic monomers



Scheme 2 Synthesis of the aromatic polyimides **III**

IIIa: Ar = - O-C_6H_4- $C(CH_3)_2$ - C_6H_4- O -; X = H ;
IIIb: Ar = CO; X = H ;
IIIc: Ar = $C(CF_3)_2$; X = H ;
IIId: Ar = - O-C_6H_4- $C(CH_3)_2$ - C_6H_4- O -; X = CH_3
IIIe: Ar = CO; X = CH_3
IIIf: Ar = $C(CF_3)_2$; X = CH_3

The second step consists in thermal imidization of the obtained polyamidic solution in the same reaction flask by heating at reflux temperature for 3–4 h, under a slow stream of nitrogen to remove the water of imidization. The final product was precipitated in water, washed with water and then dried in a vacuum oven at 105 °C.

The polyimide films were obtained by casting the polyamidic acid solution 10–14% in 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.

Measurements

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 under nitrogen flow (20 cm^3 min^{-1}) 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. 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.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5 [17].

Weight-average molecular weights (M_w) and number-average molecular weights (M_n) were determined by means of gel permeation chromatography (GPC) using a Waters GPC apparatus, provided with Refraction and Photodiode array Detectors and Phenomenex-Phenogel MXN column. Measurements were carried out with polymer solutions having 0.2% concentration, using dimethylformamide as eluent. Polystyrene standards of known molecular weight were used for calibration.

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}.

Results and discussion

The FTIR spectra of all polymers show characteristic absorption bands for: the carbonyl group of the imide ring at about 1770–1780 and 1710–1720 cm^{-1}, the corresponding carbonyl group in the benzophenone group at 1660–1670 cm^{-1} and the characteristic band for the C–N vibration at 1360–1375 and 720–730 cm^{-1} [18]. In the polymers **IIIc** and **IIIf** the characteristic absorption bands of hexafluoroisopropylidene are present at 1260 and 1210 cm^{-1}. The absorption peaks at 2940 and 2870 cm^{-1} are characteristic for methyl and methylene groups. Figures 1 and 2 present the characteristic absorption bands of polyimides **IIId** and **IIIf**, respectively.

All the polymers, except for **IIIb**, are easily soluble in DMA, N-methylpyrrolidone (NMP), N,N′-dimethylformamide (DMF), and dimethylsulfoxide (DMSO). Their good solubility may be explained by the presence of methyl groups or

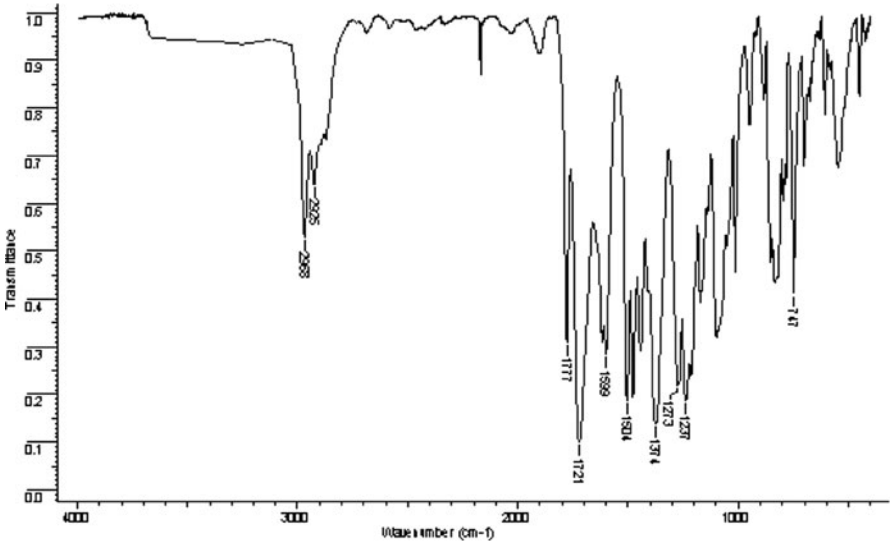


Fig. 1 FTIR Spectrum of the polymer **IIId**

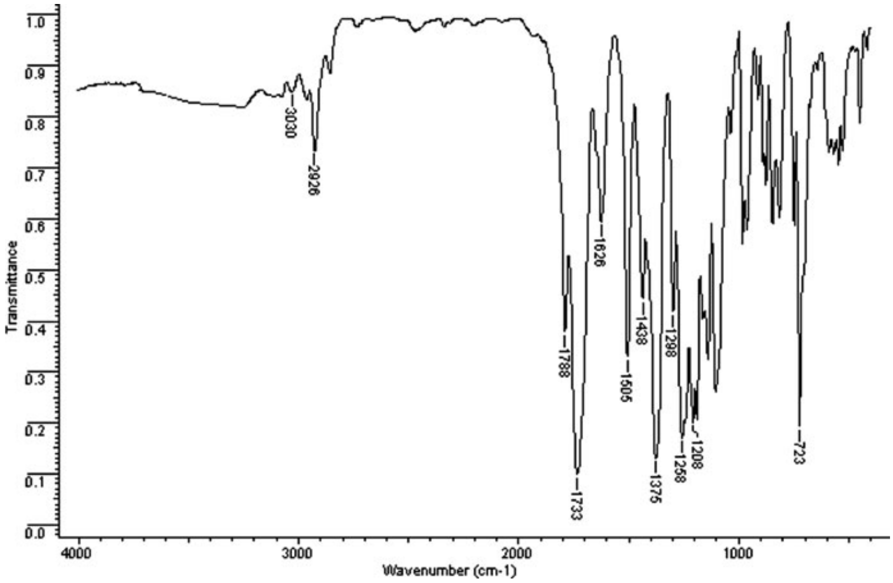


Fig. 2 FTIR Spectrum of the polymer **IIIf**

isopropylidene or hexafluoroisopropylidene units [19], 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 [15, 20]. This good solubility was also explained by using the molecular modeling: the shape of a macromolecular chain is far from a linear rigid-rod which is characteristic to wholly aromatic insoluble structures. Model molecules of polymer **IIIb** and **IIIe** are shown in Fig. 3. Due to such a shape, the dense packing of the chains is disturbed, the diffusion of small molecules of solvents between the polymer chains is facilitated and that leads to better solubility.

As can be seen from Fig. 3, in the case of polymer **IIIb**, the shape of the macromolecular chains tends to orient in the extended form (rigid-rod) in comparison with polymer **IIIe**, and as a consequence the solubilities are different. After imidization the polymer **IIIb** precipitated from solution (proving the above-mentioned supposition) while all the other polyimides were soluble.

Inherent viscosities of polyimides are in the range of 0.34–0.54 dL/g (Table 1).

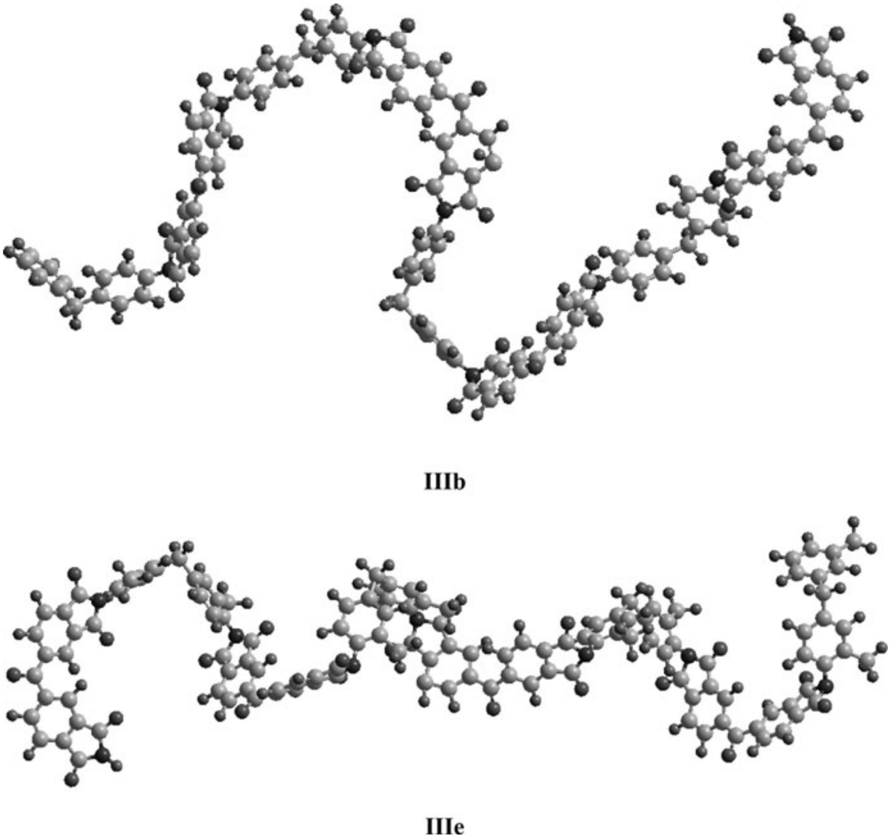


Fig. 3 Model molecules for polymers **IIIb** and **IIIe** (four repeating units)

Table 1 Inherent viscosities and molecular weights of polymers

Polymer	Inherent viscosity[a] (dL/g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
IIIa	0.54	35000	71000	2.03
IIIb[b]	–	–	–	–
IIIc	0.39	19500	41000	2.1
IIId	0.46	28000	54000	1.93
IIIe	0.44	25000	52000	2.08
IIIf	0.4	21000	42500	2.02

[a] Measured in DMA on 0.5 g/dL at 20 °C, [b] insoluble

The molecular weight of the polymers was determined by gel permeation chromatography (GPC). The weight-average molecular weight values M_w are in the range of 41000–71000 g/mol, the number-average molecular weight values M_n are in the range of 19500–35000 g/mol and the polydispersities M_w/M_n are in the range of 1.9–2.1 (Table 1). In any case these values have to be taken as indicative only, since calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the studied polymers deviate strongly from those of polystyrene.

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

The thermal stability of the samples was evaluated by dynamic thermogravimetric analysis in nitrogen and air, at a heating rate of 10 °C/min.

The summary of the important thermogravimetric characteristics of polyimides obtained from the thermograms is listed in Table 2. This table reveals the TGA data such as: T_i the initial temperatures thermal degradation, T_m the temperature corresponding to the maximum degradation rate, T_f the final temperature at which the degradation process for each stage ends, mass loss (W%), corresponding for each stage, and DTA characteristics (endo or exo).

These polymers did not show weight loss below 480 °C; they began to decompose in the range of 480–510 °C (Table 2), except for polymers **IIIe** and **IIIf** which decompose in air at a slightly lower temperature (450 and 430 °C, respectively). As can be seen from Table 1, the polyimides which contain methyl substituents in the diamine component showed slightly lower initial decomposition temperature for both conditions (nitrogen and air). For each sample, the degradation processes are not complete, the char yields at 900 °C in nitrogen atmosphere were in the range of 52–60% (Table 2).

It can be noticed that the polyimides **IIIa** and **IIId**, which contain isopropylidene units, showed the lowest decomposition temperatures in nitrogen atmosphere. This can be explained by the presence of $-C(CH_3)_2-$ linkages in the polyimides backbone, which are more sensitive to thermal degradation [21]. On the other hand in oxidative atmosphere, the polymers **IIIf** and **IIIe** showed the lowest initial decomposition temperature, than all the other polymers, being 432 and 451 °C, respectively.

Table 2 Thermal properties of aromatic polyimides **IIIa–f**

Polymer	Stage of thermal degradation	T_i N$_2$/Air (°C)	T_m N$_2$/Air (°C)	T_f N$_2$/Air (°C)	W% (N$_2$)	DTA characteristic data	T_g (°C)
IIIa	I	493/498	530/533	548/569	23.92	Exo	200
	II	548/569	595/579	656/625	22.44	Exo	
	Residue				53.64		
IIIb	I	509/525	606/599	693/684	47.72	Exo	260
	Residue				52.28		
IIIc	I	508/509	555/551	582/656	21.72	Exo	275
	II	582	640	695	22.30	Exo	
	Residue				55.98		
IIId	I	479/482	521/584	621/610	33.10	Exo	228
	II	621/610	768/684	801/721	12.13	Exo	
	Residue				54.77		
IIIe	I	498/451	558/598	710/672	41.75	Exo	278
	Residue				58.25		
IIIf	I	501/432	545/456	575/507	27.03	Exo	287
	II	575/507	682/546	702/637	20.76	Exo	
	Residue				52.21		

T_i temperature corresponding to the starting degradation step, T_m temperature corresponding to the maximum rate of the degradation process, T_f temperature corresponding to the end of the degradation step, residue material that remains in the crucible above 900 °C, W weight loss, T_g glass transition temperature

The differential weight loss DTG curves, recorded under the same experimental conditions, under nitrogen atmosphere, are presented in Figs. 4, 5, 6.

The samples **IIIe** and **IIIb** exhibited one step of degradation having the maximum polymer decomposition temperature 558 and 606 °C, respectively (Fig. 5). The other polymers exhibited two steps of degradation having the maximum polymer decomposition temperature of 530 and 521 °C for polymers **IIIa** and **IIId** (Fig. 4) and 555 and 545 °C for polymers **IIIc** and **IIIf** (Fig. 6).

Using as thermal stability criteria the onset temperatures (T_i) for the first stage or the temperature corresponding to the maximum degradation rate (T_m), the thermal stability of the polymers containing methyl substituents is lower than that of the samples which do not contain such substituents

$$\mathbf{IIId} < \mathbf{IIIa};\ \mathbf{IIIe} < \mathbf{IIIb};\ \mathbf{IIIf} < \mathbf{IIIc}$$

For the first stage the thermogravimetrical values were processed by differential methods Freeman–Carroll and the results are presented in Table 3.

The overall rate of polymer degradation is commonly described by Eq. 1.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) F(\alpha) \qquad (1)$$

where α is a normalized fractional conversion and is defined as:

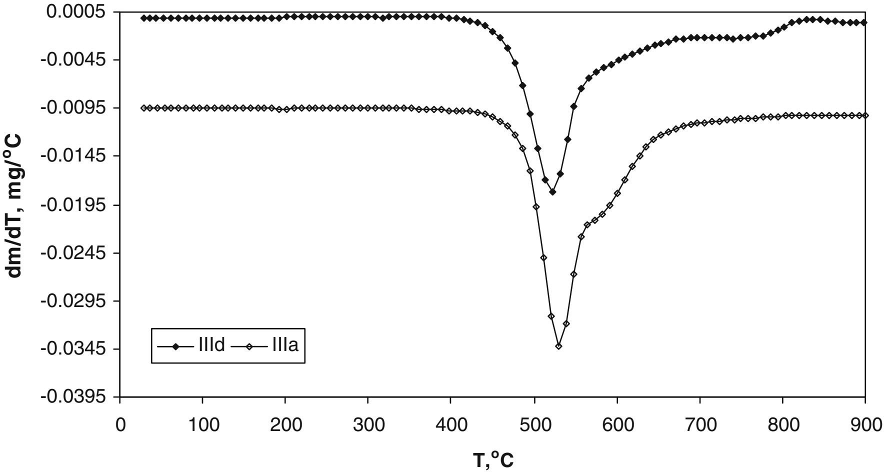


Fig. 4 DTG curves of the samples **IIIa** and **IIId**

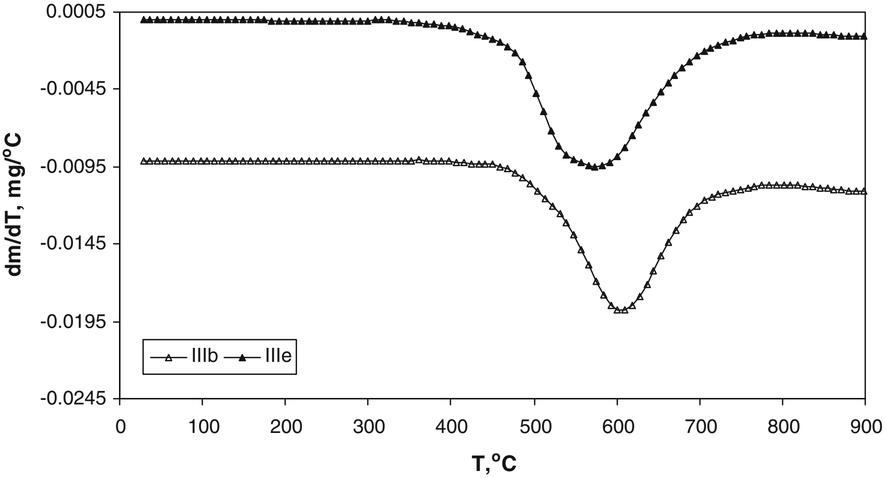


Fig. 5 DTG curves of the samples **IIIb** and **IIIe**

$$\alpha = \frac{m_{\mathrm{i}} - m(t)}{m_{\mathrm{i}} - m_{\mathrm{f}}} \tag{2}$$

$m(t)$ is the weight at any time t, and m_{i} and m_{f}, respectively, are the initial and final sample weights; A is pre-exponential factor; E_{a} is activation energy; R is universal constant of gases; T is absolute temperature in K and $F(\alpha)$ is the reaction model [22].

The Freeman and Carroll [23] method assumes $F(\alpha) = (1-\alpha)^n$ and considers incremental differences in $(\mathrm{d}\alpha/\mathrm{d}T)$, $(1-\alpha)$, and $(1/T)$ which lead to the expression:

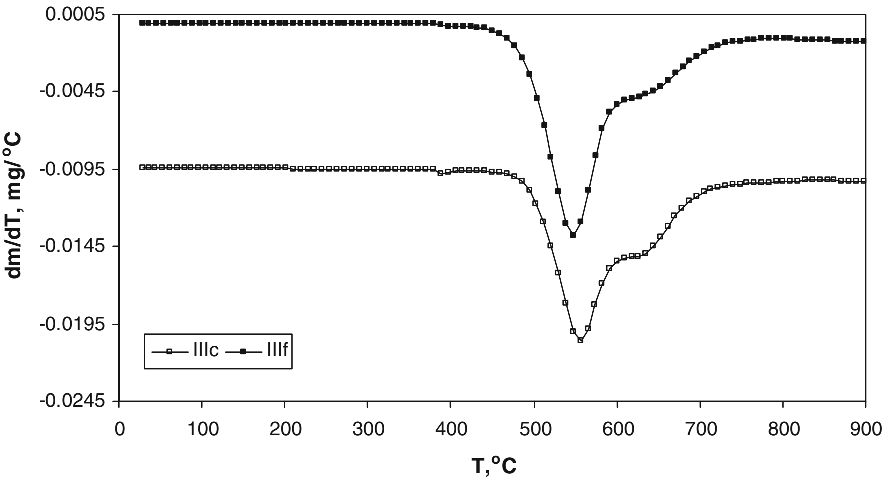


Fig. 6 DTG curves of the samples **IIIc** and **IIIf**

Table 3 Kinetic characteristics corresponding to the first degradation step

Sample	n	E_a (kJ/mol)	ln A
IIIa	0.63 ± 0.001	307.13 ± 1.64	41.19 ± 0.26
IIIb	1.04 ± 0.001	143.21 ± 1.15	13.93 ± 0.17
IIIc	1.01 ± 0.001	253.28 ± 1.88	31.78 ± 0.28
IIId	1.13 ± 0.009	264.95 ± 1.30	35.28 ± 0.21
IIIe	1.18 ± 0.003	131.41 ± 2.46	13.20 ± 0.38
IIIf	0.90 ± 0.001	216.40 ± 1.84	26.59 ± 0.28

n reaction order degree, E_a activation energy, A pre-exponential factor

$$\Delta \ln\left(\frac{d\alpha}{dT}\right) = n\Delta \ln(1-\alpha) - \left(\frac{E_a}{RT}\right)\Delta\left(\frac{1}{T}\right) \tag{3}$$

where n is reaction order.This expression can be used to determine the value of E_a by plotting

$$\left[\frac{\Delta \ln(d\alpha/dT)}{\Delta \ln(1-\alpha)}\right] \text{against} \left[\frac{\Delta(1/T)}{\Delta \ln(1-\alpha)}\right] \tag{4}$$

The intercept gives the reaction order, n. E_a can be calculated from the slope.

The kinetic characteristics suggest the complexity of the thermal degradation through successive reactions, accompanied by exothermal processes and confirm the high thermal stability of the polymers without methyl substituents.

Glass transition temperature of the polymers was in the range of 200–287 °C with higher values for polyimides containing hexafluoroisopropylidene units (Table 1). The presence of isopropylidene groups together with ether linkages introduces much more flexibility to the macromolecular chain and decreases the

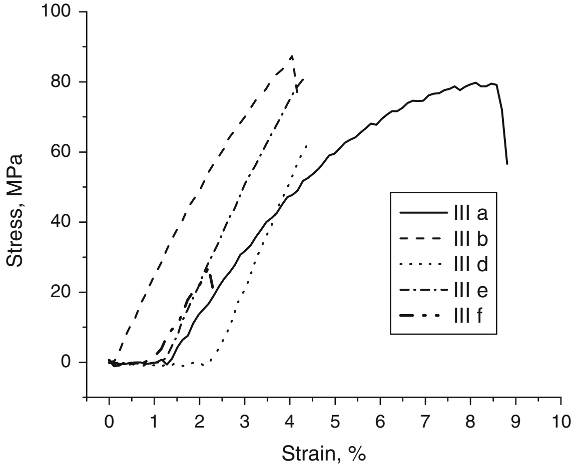


Fig. 7 Stress–strain curves of the polymers

glass transition of the polymers **IIIa** and **IIId**. On the other hand, as can be seen from Table 1, the introduction of methyl substituents into the diamine segment increased the glass transition of the corresponding polyimides **IIId**, **IIIe**, and **IIIf**, due to the steric effect of the these substituents [20].

Flexible free-standing films were prepared by casting the DMA solutions of polymers. These films were subjected to tensile tests and the results are shown in Fig. 7. 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. These values, as well as those regarding the thermal stability, are similar to those reported for related polyimides based on the same dianhydrides which reacted with other diamines [24, 25].

Conclusions

Two series of aromatic polyimides were prepared by polycondensation of various aromatic dianhydrides with two aromatic diamines containing methylene bridge; one diamine contains also a methyl substituent on each benzene ring. These polymers are soluble in polar aprotic solvents and can be cast into thin and very thin films from such solutions. The polyimides show high thermal stability with decomposition temperature being above 480 °C under nitrogen and 430 °C in air, and glass transition in the range of 200–287 °C. 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 T_g are slightly lower. The free-standing films having the thickness of tens of micrometers exhibit good mechanical properties. All these films have a strong adhesion to glass substrates. These characteristics make the present polymers potential candidates for applications as high performance materials.

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