Study of Some Aromatic Polyimides Containing Methylene Units

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Physical properties, such as thermal and dielectric characteristics, of some aromatic polyimides which contain methylene units have been investigated. The results indicated that the polymers were highly thermostable with decomposition temperature over 450°C and low dielectric constants. The thermogravimetrical values processed by differential method Freeman-Caroll showed that the activation energies and reaction orders are lower in air than in nitrogen.

Keywords: methylene units, polyimides, thermal characterization, activation energy, dielectric constants

Polyimides are an important class of high-performance polymers. Excellent mechanical and electrical properties as well as high-temperature stability make these polymers suitable for applications in the aerospace industry as high-performance composites and in the electronics industry as high-temperature coatings [1-4]. However, difficulty in processability has slowed the widespread use of these polymers by making them expensive and limiting their applicability. 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. 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]. Polyimides are the most thermally stable polymers due to their high glass transition and high decomposition temperatures and are useful in long-term service at high temperatures. Therefore, studying the physical properties of polyimides is of both scientific greatness and engineering applied importance.

This paper presents the physical properties of two series of polyimides derived from aromatic diamines containing flexible methylene bridges such as 4,4'-diamino-diphenylmethane or 3,3'-dimethyl-4,4'-diaminodiphenyl-methane, and three different aromatic dianhydride 4,4'-isopropylidene-diphenoxy)bis(phthalic anhydride), benzophenonetetracarboxylic dianhydride or hexa-fluoroisopropylidendiphthalic dianhydride.

Experimental part

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

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.
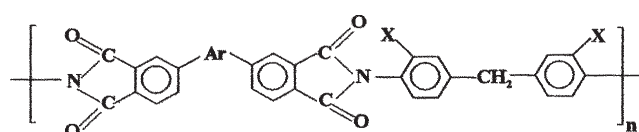
Ia: Ar = - O-C_6H_4- $C(CH_3)_2$ - C_6H_4- O -;   X = H ;
Ib: Ar = CO;   X = H ;
Ic: Ar = $C(CF_3)_2$;   X = H ;
Id: Ar = - O-C_6H_4- $C(CH_3)_2$ - C_6H_4- O -;   X = CH_3
Ie: Ar = CO;   X = CH_3
If: Ar = $C(CF_3)_2$;   X = CH_3

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

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 in air and nitrogen flow (20 cm³min⁻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, 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 midpoint 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 Column 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.

Dielectric spectroscopy measurements of the polymer films were performed using an experimental set-up from Novocontrol at room temperature and various frequencies (in the range of 10⁻² - 10⁶ Hz). The system was equipped with an Alpha high resolution dielectric analyzer, the impedance analyzer HP 4191A and temperature controller Quatro version 4.0.

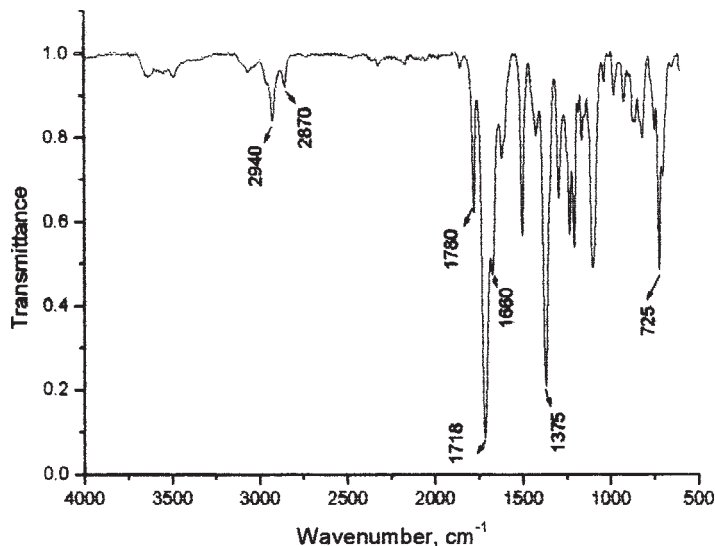** email: isava@icmpp.ro; Tel: 40-232 217 454*
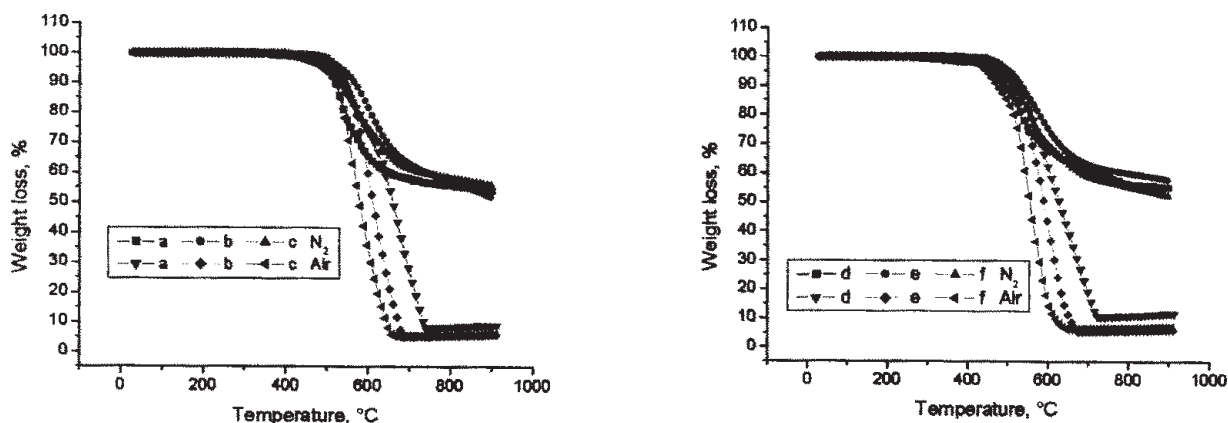
Fig. 1. FTIR Spectrum of the polymer **Ie**

Fig. 2. TGA curves of polyimide films

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 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.

All the polymers are easily soluble in dimethylacetamide (DMA), N-methylpyrrolidone (NMP), N,N'-dimethyl-formamide (DMF) and dimethylsulfoxide (DMSO). Their good solubility may be explained by the presence of methyl groups or isopropylidene or hexafluoro-isopropylidene 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 methyl groups might also lead to a distortion of the packing of 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'-diamino-diphenylmethane. Similar behaviour was observed when these diamines were used in other aromatic polymers [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 in air, at a heating rate of 10°C/min. The TGA curves are presented in figure 2.

Both series of polyimides degrade faster in air than in nitrogen. Thus, the starting decomposition temperature (5% weight loss) of the first series of polyimides is in the range of 516-530°C in nitrogen and in the range of 487-503 °C in air. The second series of polyimides decompose in the range of 495-503°C in nitrogen and in the range of 445-475°C in air. 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 macromolecular chains suffer a thermo-oxidative degradation. Thus, the surrounding water vapours 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. Consequently, 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$_2$O [20]. Therefore the residual mass is so low in air, 3-5%, in comparison with 52-58%, in nitrogen. In nitrogen

Table 1

Table 1
THERMAL PROPERTIES OF AROMATIC POLYIMIDES Ia-f

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

[a]Glass transition temperature; [b]Temperature of 5% weight loss of polymers; [c]Maximum decomposition temperature; [d]Residual weight at 900°C.
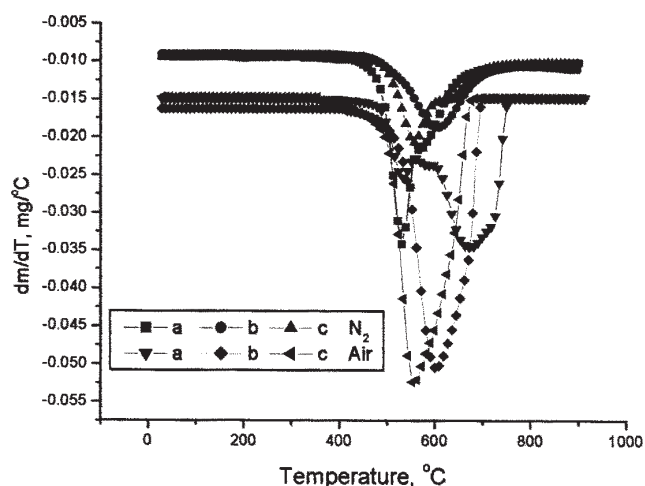

Fig. 3. DTG curves of the samples Ia, Ib and Ic in air and nitrogen

Fig. 4. DTG curves of the samples Id, Ie and If in air and 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), are presented in figures 3 and 4.

As can be seen from these curves the decomposition of polyimides is faster in air than in nitrogen. The weight loss at maximum rate of decomposition temperature is in the range of 14-15% in nitrogen and in the range of 20-30% in air, for the first series of polymers, Ia, Ib and Ic. The introduction of methyl units in the diamine component in the second series of polymers led to the increase of weight loss at maximum rate of decomposition temperature being 16-17% in nitrogen and 33-56% in air. That proves once again that the introduction of methyl substituents in the diamine monomer slightly decreases the thermal stability of the polymers.

All the polyimides 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 these substituents [19].

For the first stage the thermogravimetrical values, under supposition that activation energy does not depend of conversion degree, were processed by differential methods Freeman-Carroll [21] and the results are presented in table 2.
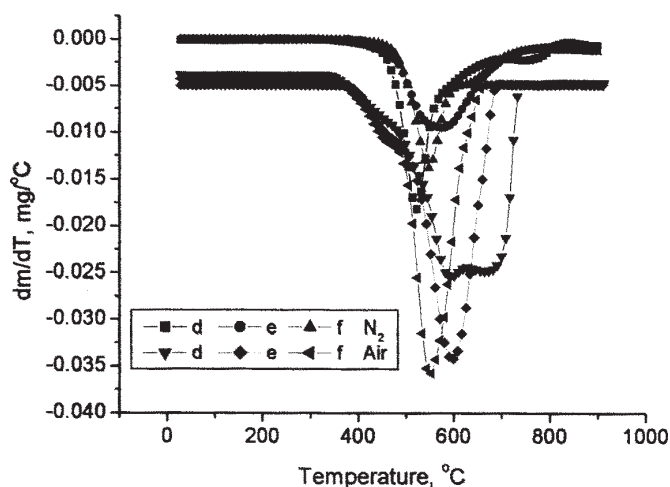
The overall rate of polymer degradation is commonly described by equation (1).

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

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

$$\alpha = \frac{m_i - m(t)}{m_i - m_f} \qquad (2)$$

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; Ea is activation energy; R is universal constant of gases; T is absolute temperature in K and $F(\alpha)$ is the reaction model.

The Freeman and Carroll [21] method assumes $F(\alpha)=(1-\alpha)^n$ and considers incremental differences in dα/dT, (1-α) and (1/T) which leads to the expression:

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

where n is reaction order.

This expression can be used to determine the value of Ea by plotting

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

Table 2
KINETIC CHARACTERISTICS CORRESPONDING TO THE FIRST DEGRADATION STEP

Polymer	In air			In nitrogen		
	n	Ea (kJ/moll)	ln A	n	Ea (kJ/mol)	ln A
Ia	0.60±0.001	204.79±2.22	25.41±0.42	0.63±0.001	307.13±1.64	41.19±0.26
Ib	1.51±0.002	171.58±2.96	17.86±0.24	1.04±0.001	143.21±1.15	13.93±0.17
Ic	1.17±0.001	102.25±1.58	8.72±0.98	1.01±0.001	253.28±1.88	31.78±0.28
Id	0.24±0.001	88.70±1.16	6.28±0.18	1.13±0.009	264.95±1.30	35.28±0.21
Ie	1.03±0.001	136.75±1.06	13.20±0.15	1.18±0.003	131.41±2.46	13.20±0.38
If	0.66±0.002	99.12±2.34	11.68±0.40	0.90±0.001	216.40±1.84	26.59±0.28

n = reaction order; Ea = activation energy; A = pre-exponential factor

Table 3
MECHANICAL AND DIELECTRIC PROPERTIES OF THE POLYMERS

Polymer	Strain, %	Stress, MPa	Dielectric constant at frequency,					
			1Hz	10Hz	100Hz	1kHz	10kHz	100kHz
Ia	8.8	79.5	3.25	3.22	3.20	3.17	3.16	3.14
Ib	4.2	87.4	3.48	3.45	3.42	3.40	3.38	3.34
Ic	-	-	2.91	2.89	2.87	2.86	2.85	2.84
Id	4.4	62.4	3.08	3.05	3.02	3.003	2.99	2.96
Ie	4.4	81.5	3.32	3.29	3.26	3.24	3.22	3.18
If	2.3	19.7	2.88	2.85	2.83	2.82	2.80	2.78

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

The determined activation energy for these polyimides in air is lower than in nitrogen, which shows that polymers are easier to decompose in air than in nitrogen except for polymers obtained from benzophenontetracarboxylic dianhydride which showed close values. The same trends are found in the pre-exponential factors. 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.

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.

The electrical insulating properties of polymer films were evaluated on the basis of their dielectric constant. The values of the dielectric constant at 10 kHz were in the range of 2.80-3.38. As it can be seen from table 2 these polymers exhibited lower dielectric constant values compared to H-Film, a polyimide which is prepared from pyromellitic dianhydride and 4,4'-diaminodiphenylether and which is one of the most common polyimides used as dielectric in microelectronics applications, having a dielectric constant of 3.5 [5]. The dielectric constant of polymers decreased gradually with increasing frequency because the response of the electronic, atomic and dipolar polarizable units vary with frequency. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units to orient fast enough to keep up with the oscillation of the alternative electric field [22-24]. The polymer Ic and If exhibited lower dielectric constant values due to the presence of 6F groups because of the less efficient chain packing and increased free volume that decreased the concentration of polar groups. In addition, the strong electronegativity of fluorine atoms results in very low polarizability of C-F bonds, thus decreasing the dielectric constant [25,26]. On the other hand the incorporation of two methyl groups on the diamine component leads to an increase in the free volume and a resultant decrease of the molecular packing [18,19]. As a consequence, the polyimides which contain methyl substituents (Id, Ie and If) showed slightly lower dielectric constant in comparison with the other polyimides (Ia, Ib and Ic).

Conclusions

The polyimides investigated in this study, based on aromatic diamines containing methylene bridges, show high thermal stability with decomposition temperature being above 445°C in air and 495°C under nitrogen atmosphere 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 Tg are slightly lower. 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. The activation energy of the decomposition in air is lower than in nitrogen. The free standing films having the thickness of tens of micrometers exhibit good mechanical properties.

The presence of two methyl groups on the diamine component leads to a slightly lower dielectric constant values.

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