

# Microwave Assisted Polycondensation of Polyimides by [4,4'-(Hexafluoroisopropylidene)diphthalic anhydride, pyromellitic dianhydride] and [2,4,6-Trimethyl-*m*-phenylenediamine]. Power, Time, and Solvent Effect

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**ABSTRACT:** The microwave assisted polycondensation of two polyimides were studied using pyromellitic dianhydride (PMDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) as dianhydride monomers and 2,4,6-trimethyl-*m*-phenylenediamine (TrmPD), as diamine monomer, under microwave irradiation in DMF and DMSO solvents. The structure and performance of polymers were characterized by Fourier Transform Infrared Spectroscopy (FTIR), viscosity, density, and Thermogravimetric Analysis (TGA). The results show that the polyimides can be obtained in a short reaction time with high intrinsic viscosity and high yield. The effect of the presence of a bridging

group,  $-\text{C}(\text{CF}_3)_2-$ , in the monomer structure is apparent in the permeability parameters of the macromolecules as polymer (6FDA-TrmPD) always presents better results than polymer (PMDA-TrmPD). Properties as density and  $T_g$  increases with the time exposition to the microwave irradiation. Polyimides obtained present good thermal properties because they began to lose weight in a range of 8–16% at high temperature as 450°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2816–2824, 2010

**Key words:** microwave irradiation; polyimides; polycondensation

## INTRODUCTION

Nowadays, the use of microwave dielectric heating in organic synthesis<sup>1–12</sup> is well-known and frequently applied. In the course of years, this technique has improved, passing from the use of conventional ovens to modern instruments. Thus, modern microwave ovens have been designed with the purpose of reducing to a minimum the inherent risks of usage. In particular, since the late 1990s, the number of publications related to microwave synthesis has increased dramatically to a point where it might be assumed that, in a few years, most chemists will probably use microwave energy to heat chemical reactions on a laboratory scale. Microwave heating has been shown to dramatically reduce reaction times, increase product yields and enhance product purities by reducing unwanted side reac-

tions compared with conventional synthetic methods.<sup>13</sup> Microwave absorption by polar components of a reaction makes them more reactive under microwave irradiation in comparison to thermal heating.<sup>14</sup> Thus an increase in reaction rates decreases the apparent activation energy.<sup>15,16</sup> It was found that microwave irradiation reduces the reaction temperature and time.<sup>17</sup> Concomitant with shorter reaction times, side reactions are reduced to a minimum and consequently the purity and the polymer properties improve.<sup>18</sup> Thus, the use of microwaves has been enlarged for the synthesis of polymers<sup>19</sup> on fields as: polymeric semiconducting materials,<sup>20</sup> esterification reactions,<sup>21</sup> biodegradable polymers (polylactic acid),<sup>22</sup> degradation of polymers (degradation of polystyrene),<sup>23</sup> free radical copolymerizations,<sup>24</sup> and ring opening polymerization.<sup>25,26</sup>

There has been growing interest on the synthesis and application of optically active polymers,<sup>27,28</sup> for example, the synthesis of aromatic optically active poly(amide-imide)s<sup>29</sup> with inherent viscosity ranging from 0.23 to 0.41 dl/g and high yield (78–96%), the resulting PAIs were thermally stable and were readily soluble in common organic solvents as DMAc,

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DMF, NMP, THF, *o*-cresol, *m*-cresol, and acetone. Similar poly(ester-imide)s were synthesized from diols,<sup>30</sup> phenylalanine,<sup>31</sup> fluorinated<sup>32–36</sup> and sulfonated,<sup>37,38</sup> polyimides, which are biologically important because of their chiral structure.

Polyimides are some of the best engineering plastics because of their high thermal and oxidative stability, their good mechanical properties and excellent chemical resistance to dilute acids and organic solvents.

The use of microwave energy for the obtention of polyimides<sup>39</sup> has had great acceptance, for the synthesis of poly(piromellitimides) by means of monomers of nylon-salt-type.<sup>40,41</sup> Polyimides of aromatics dianhydrides and diisocyanates were prepared,<sup>42</sup> reducing the polymerization reaction times,<sup>41</sup> with regard to the same polymers obtained by means of conductive heating. Li et al.<sup>43</sup> synthesized poly(amic acid) (PAA), then PAA was used to make polyimide (PI) by imidization reaction at a low temperature. The PAA yield (93.56%) obtained under microwave-assisted polycondensation was higher than the PAA yield (77.50%) obtained under conventional solution polycondensation in a period of 2 h. The inherent viscosity (0.468 dL/g) of the PAA prepared by conventional heating was lower than that (up to 0.615 dL/g) of the PAA prepared by microwave irradiation. Microwave energy has been enlarged for the cure of polymers, for example, Liu et al.<sup>44</sup> investigated the cure of a nadic-end-capped polyimide resin, glass, and graphite composites containing this resin. He made glass and glass-graphite hybrid composites with flexural strengths of 372–588 MPa and moduli of 28.7–31.4 Gpa. Those materials have equivalent properties (50–80%) to composites fabricated by conventional thermal processes.

On the other hand, polyimides have also found applications in membrane technologies for gas separation in petrochemical industry; the most important characteristic for selecting a specific polyimide to be used as a membrane material in a given commercial application is permeability. The most typical way to significantly enhance the gas permeability of polyimides is to change the chemical structure and consequently the free volume. It is well recognized that increasing the free volume usually strongly increases diffusion coefficients, thereby improved permeability is obtained. In fact polyimide 6FDA-TrmPD, has one of the highest permeability values reported, 431 barrer for CO<sub>2</sub> gas,<sup>45</sup> in this use. However, those materials are usually obtained under conventional solution polycondensation in a large period of time.

As a part of a project directed to synthesis of polyimides used as membranes on gas separation, we report the synthesis and characterization of two aromatic polyimides obtained from PMDA and 6FDA

monomers under microwave irradiation. Our goal is to study: microwave power, reaction time, and solvent effects on the kinetics of the reaction and the changes produced on properties of polyimides, such as glass transition temperature  $T_g$ , density  $\rho$ , and intrinsic viscosity  $[\eta]$ , caused by the introduction of a bridging group,  $-\text{C}(\text{CF}_3)_2-$ , in the dianhydride monomer structure. The presence of  $-\text{C}(\text{CF}_3)_2-$  group, enhances free volume and facilitate their use as material for gas separation. Our experimental strategy was to combine a selected diamine TrmPD with two dianhydrides, PMDA, 6FDA. First, we studied the synthesis of the polyimide of 2,4,6-trimethyl-*m*-phenylenediamine (TrmPD) with the PMDA, system (A), then we proceeded to synthesize the polyimide 6FDA-TrmPD, system (B).

## EXPERIMENTAL

### Materials

Pyromellitic dianhydride (PMDA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and 2,4,6-trimethyl-*m*-phenylenediamine (TrmPD), dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich. DMF and DMSO were dried with zeolites A4 for 12 h before use.

### Characterization

Fourier transform infrared spectra (FTIR) were recorded in a FTIR-1605 Perkin-Elmer instrument using potassium bromide pellets. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed in a DSC821e and TGA/SDTA851e Mettler-Toledo, with a heating rate of 10°C/min under N<sub>2</sub> atmosphere. The intrinsic viscosity<sup>46–50</sup> of polymers was determined for solutions of 0.1 g/dL concentration in DMF at 25°C using an Ubbelohde viscometer.

The densities of polymer were determined by density gradient column, according with the procedure described in ASTM D 1505–85. Toluene and carbon tetrachloride with densities of 0.87–1.59 g/cm<sup>3</sup> respectively, were used.

The solubility of polyimide samples was studied dissolving approximately 10 mg polymer sample in three drops of each solvent, studied at 23°C.

### Polymerization reaction

Polymerization reactions were carried out in a monomodal microwave oven SEV Model Mic I with 600 watts of maximum power and temperature control. In a 50-mL glass reactor tube an equimolar mixture of the dianhydride, diamine and the

TABLE I  
Effect of Reaction Time, on Yield and Intrinsic Viscosities of Polyimides, 100 W of Irradiation Power and DMF Solvent

Sample code	Time <sup>a</sup> (s)	System A			System B		
		T <sup>b</sup> (°C)	Yield (%)	[η] <sup>c</sup> (dL/g)	T <sup>b</sup> (°C)	Yield (%)	[η] <sup>c</sup> (dL/g)
AF1/BF1	10/15	40	49.17	0.1682	48	89.81	0.4844
AF2/BF2	20/30	58	58.74	0.1801	71	93.95	0.4894
AF3/BF3	30/45	80	78.24	0.1885	95	96.48	0.4993
AF4/BF4	60/60	134	85.80	0.1986	134	99.21	0.5142
AF5/BF5	90/120	134	92.05	0.2273	134	99.53	0.6074
AF6/BF6	120/180	134	93.56	0.3702	134	90.70	0.2693
AF7/BF7	240/240	134	83.02	0.2967	134	83.15	0.2189
CC <sup>d</sup> .	25 <sup>e</sup>				50	72	0.46 <sup>f</sup>

<sup>a</sup> Irradiation time.

<sup>b</sup> Temperature reached at the time reaction.

<sup>c</sup> Measured at a concentration of 0.1 gDL<sup>-1</sup> in DMF at 23°C.

<sup>d</sup> Conventional heating.

<sup>e</sup> Reaction time in hours.

<sup>f</sup> Measured at a concentration of 0.5 wt % in DMAc at 35°C.

appropriate amount of solvent was poured. The homogeneous mixture was irradiated. Reaction times are listed in Table I, at a certain heating power. Temperatures were recorded automatically with an infrared probe; the thermometer is part of the microwave oven and shows the actual temperature of the reaction mixture. All operations were done under air atmosphere. The resulting polymer solution was dried at 80°C for 6 h in a vacuum oven to remove DMF or DMSO solvent. The solid polymer produced was then washed with methanol, to remove any low-molecular weight substance, as water and residual solvents and dried at 40°C for 4 h more in the oven.

### Permeability

With the aim of knowing the permeability properties, we performed a theoretical approximation of the volume occupied by the polymeric chains. These values were evaluated using eq. (1)–(4) according to Park–Paul's method.<sup>51</sup>

$$V = \sum_{k=1}^k \beta_k (V_w)_k \quad (1)$$

$$(V_0)_n = \sum_{k=1}^k \gamma_{nk} (V_w)_k \quad (2)$$

$$(FFV)_n = [V - (V_0)_n] / V \quad (3)$$

$$P = A \exp(-B/FFV) \quad (4)$$

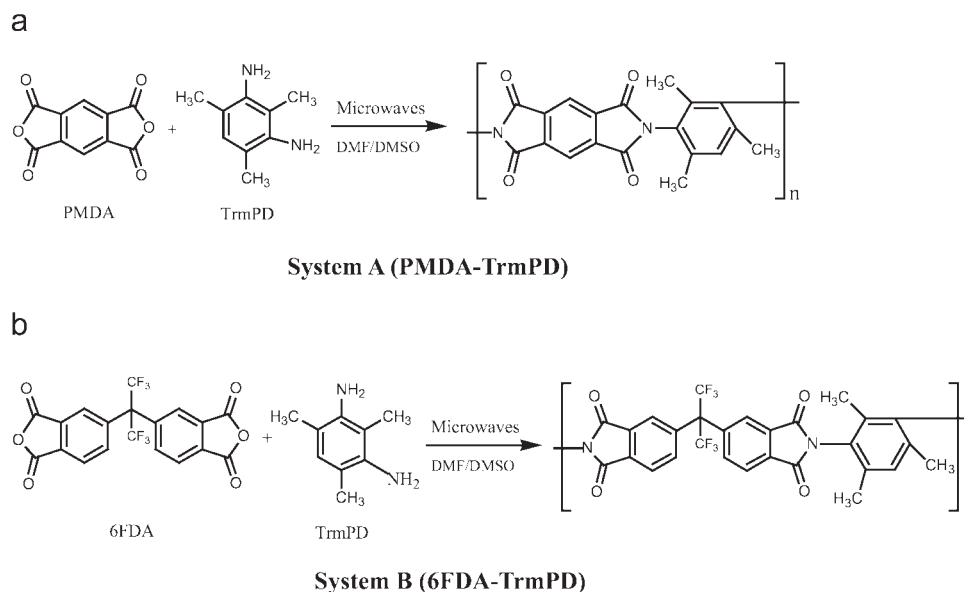
where  $V$  is the volume [cm<sup>3</sup>/mol];  $V_0$  is the volume occupied by the polymer chains;  $V_w$  is the Van Der Waals volume [cm<sup>3</sup>/mol];  $P$  is gas permeability (barrier); FFV is the fractional free volume;  $\gamma$ ,  $\beta$ ,  $A$ ,  $B$  are

empirical factors that depend on gas  $n$  and group  $k$  and were taken from reference<sup>51</sup>;  $k$  is the total number of groups into which the repeat unit structure of the polymer is divided.

### RESULTS AND DISCUSSION

The polyimidization reaction involves an A-A, B-B polycondensation synthesis to generate aromatic polyimides of the type depicted in Figure 1 (A and B). As an example (0.2181 g) 1 mmol of PMDA and (0.1502 g) 1 mmol of TrmPD, 10 mL of DMF solvent were microwave activated at 134°C, reflux solvent temperature for 2 min. It has been well recognized the fact that a solvent with high dielectric constant and dipolar moment is considered a good media for reactions activated by microwaves.<sup>41</sup> We selected two solvents, dimethylformamide DMF, boiling temperature  $T_b = 153^\circ\text{C}$ , dielectric constant  $\epsilon = 36.71$ , dipolar moment  $D = 3.86$  D, and dimethylsulfoxide DMSO,  $T_b = 189^\circ\text{C}$ ,  $\epsilon = 46.6$ ,  $D = 3.9$  D,<sup>52</sup> as the polar organic media to induce the effective homogeneous heating of our monomers.

Two polymers obtained, samples AF6, BF5, were characterized by FTIR. Figure 2 illustrates the FTIR spectra of the prepared polymers AF6 and BF5, according with this figure, the formation of the imide structure under our experimental conditions was confirmed by the presence of several infrared (IR) absorption bands located at: 1778 cm<sup>-1</sup> imide (C=O asymmetric stretching), 1728 cm<sup>-1</sup> imide (C=O symmetric stretching), 1373 cm<sup>-1</sup> imide (C–N stretching) and 730 cm<sup>-1</sup> imide (deformation of imide ring) for system A. The FTIR spectrum also shows very weak bands in the range of 3500–2500 and 1620 cm<sup>-1</sup>, which indicates the existence of –COOH

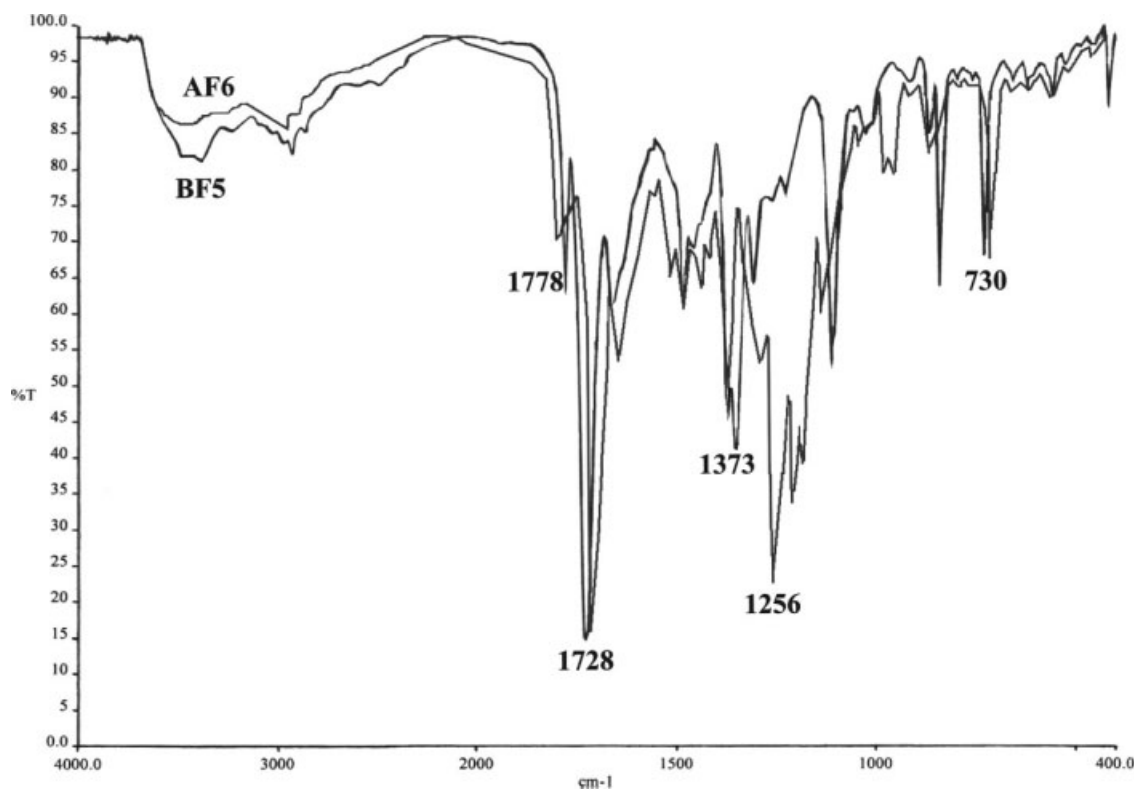


**Figure 1** Reaction schemes a and b.

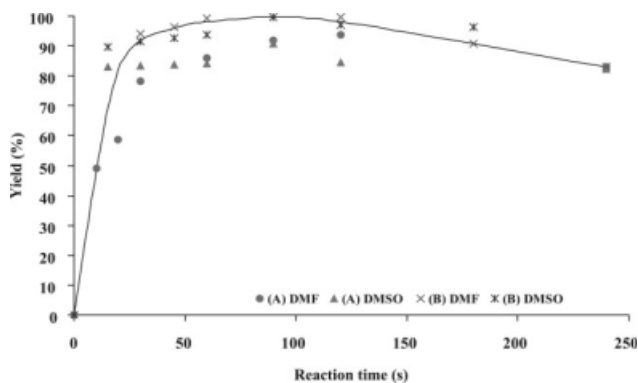
group. These absorption bands at 3500 and 1600 are characteristic of residual polyamic acid. On the other hand, system B presents absorption bands located at: 1785  $\text{cm}^{-1}$  imide (C=O asymmetric stretching), 1725  $\text{cm}^{-1}$  imide (C=O symmetric stretching), 1370  $\text{cm}^{-1}$  imide (C—N stretching), 725  $\text{cm}^{-1}$  imide (deformation of imide ring). FTIR spectra were quite similar

for both polyimides, however, a very strong absorption peak was observed at 1256  $\text{cm}^{-1}$ , which is attributable to the symmetric stretching vibration of  $-\text{CF}_3$  group present in macromolecule (B).

After confirming the imide formation in our polymers, microwave assisted polycondensation reactions at several irradiation times were performed



**Figure 2** FTIR spectra of the prepared polymers AF6 and BF5. Notice the weak presence of polyamic acid bands at 3500 and 2500  $\text{cm}^{-1}$ .



**Figure 3** Dependence of yield (%) on the reaction time, 1 mmol of PMDA-TrmPD and 6FDA-TrmPD, 10 mL of solvent at 100 W of irradiation power.

for systems A and B. Data concerning the reaction times, the polymerization reaction temperatures, yields, and the intrinsic viscosities of the obtained polyimides were collected in Table I, in this case DMF solvent was used in our experiments. Yield and the other properties were measured in each case after a second thermal posttreatment at 40°C for 4 h in a vacuum oven. First and second posttreatments at 80°C and 40°C respectively, are important to almost fully complete the imidization reaction and eliminate residual monomers and solvent.

Polymer samples were identified with two letters and one digit according to the next description, first letter corresponds to the system (A or B), second letter corresponds to the solvent used in each case, dimethylformamide (F), dimethylsulfoxide (S), the number corresponds to the microwave irradiation time, in seconds. For example, sample AF1 stands for system A, in dimethylformamide F, and 10 s of microwaves irradiation time.

Table I shows the kinetics data of 14 reactions, for microwave assisted polycondensation of A and B systems. In all cases the polymerization proceeded very fast, and for the first 50 s reaction time, temperature increases from room temperature to a maximum temperature of 90°C. After 60 s reaction time, the liquid mixtures had enough time to reach the reflux temperature for DMF, 134°C, and it remains constant for the rest of the reaction time at 586 mmHg.

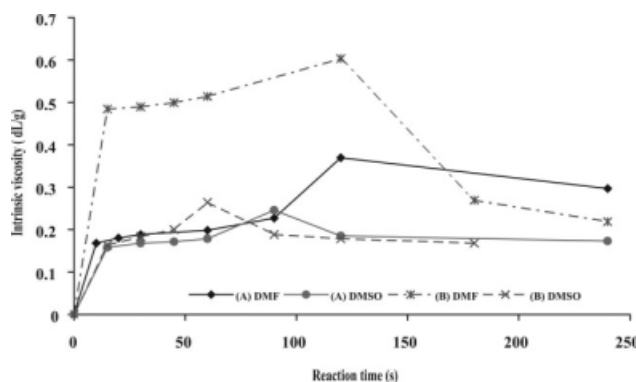
The yields under constant reaction conditions of temperature and pressure, and after 1 minute reaction time, reach more than 80 percent monomer conversion in both systems A and B. However, system B always presents a higher yield than system A. In general, the use of a solvent having both a high dielectric constant and a high boiling point, like DMF lead to quick formation of polyimides with a high intrinsic viscosity. Thus system B, at 120 s reaction time reaches 99.5% monomer conversion, this shows that the presence of one bridging group like

$-\text{C}(\text{CF}_3)_2-$  in the monomer chemical structure, produces good yields. The same effect was also observed with relation to the intrinsic viscosity of our materials. In Table I the yield and viscosity data columns present a clear evidence of high yields and high intrinsic viscosities moving in the same direction. The highest intrinsic viscosity value was recorded for system B and is equal to 0.607 dL/g, for sample BF5 this intrinsic viscosity is quite high, compared with other values reported in the literature, for example, 0.26–0.39 dL/g<sup>42</sup> for aromatic polyimides of similar chemical structures.

In Table I it is included a reference CC sample.<sup>53</sup> This polyimide was obtained by a system B and was activated by conventional heating for 25 h at 50°C. The polymerization reaction reaches a 72% yield with an intrinsic viscosity 0.46 g dL<sup>-1</sup>. A similar intrinsic viscosity 0.49 g dL<sup>-1</sup> was obtained in only 45 s microwave reaction time, sample BF3.

In Figure 3, values of yield versus time for systems A and B in two solvents, DMF and DMSO are compared. The DMF solvent produced the best polymeric materials in a record time of 1 min. Around 60 s reaction time, the monomer conversion continues increasing and for longer microwave activation, a decrement in the production of polymer was observed, this fact can be explained as produced by the reversibility of the polymerization reaction.

In Figure 4, the effect of the reaction time on the intrinsic viscosity of our polymeric materials is shown. In DMF at 23°C, system B presents intrinsic viscosity values higher than those observed in DMSO. For example, if we choose 120 s reaction time, the intrinsic viscosity value recorded, for this system B, was 0.607 dL/g in DMF and 0.178 dL/g in DMSO. When the reaction time is equal or less than 100 s, the intrinsic viscosities of polyimide A in both solvents are quite similar. For a longer reaction time the intrinsic viscosity in DMF sensibly increases.



**Figure 4** Dependence of intrinsic viscosity on the reaction time, 1 mmol of PMDA-TrmPD and 6FDA-TrmPD, 10 mL of solvent at 100 W of irradiation power.

**TABLE II**  
**Density, Total Weight Lost (%), and Glass Transition Temperature Values  $T_g$ , for the Microwave Assisted Polycondensation, in 10 mL DMF Solvent, at 100 watts, System A and B**

Sample code	System A			System B		
	$\rho^a$ (g/cm <sup>3</sup> )	$W^b$ (%)	$T_g^c$ (°C)	$\rho^a$ (g/cm <sup>3</sup> )	$W^b$ (%)	$T_g^c$ (°C)
AF1/BF1	1.2914	14.7	396.0	1.3628	12.30	290
AF2/BF2	1.2914	–	–	1.3672	–	–
AF3/BF3	1.2930	16.6	397.0	1.3672	16.68	293
AF4/BF4	1.2981	14.9	399.5	1.3717	10.92	303
AF5/BF5	1.3032	–	–	1.3886	8.2	358
AF6/BF6	1.3036	9.1	400.0	1.3717	14.20	287
AF7/BF7	1.3032	13.1	398.0	1.3673	–	–
CC <sup>d</sup>				1.3520	12	377

<sup>a</sup> Density gradient, at 23°C.

<sup>b</sup> Total weight lost at 500°C.

<sup>c</sup> From DSC. Temperature of weight lost was recorded by TGA at heating rate of 10°C/min in N<sub>2</sub>.

<sup>d</sup> Conventional heating.

The results of the density ( $\rho$ ) at 23°C, total weight lost (w%) at 500°C and the glass transition temperature ( $T_g$ ) for both system A and B, in DMF, are presented in the Table II.  $T_g$  values were recorded by Differential Scanning Calorimetry (DSC) at heating rate of 10°C/min in N<sub>2</sub>.

The effect of the presence of a bridging group in the monomer structure is apparent in the density of the macromolecules. Density of polymer system B is always higher than density of polymer system A, this results can be explained since flexible polymeric molecules like those in system B, can move closer and accommodate to form macromolecular blocks of high density, this can be confirm by the polyimides density values of 1.3036 g/cm<sup>3</sup> for system A and 1.3886 g/cm<sup>3</sup> for system B. This is an indication of the presence of regions of well packed molecules. In this case the presence of the  $-\text{C}(\text{CF}_3)_2-$  group is important, as these materials are mainly amorphous and are applied for membranes preparation.

From data collected in Table II, it is clear that weight lost at 500°C is lower for polymeric system B samples, like it was mentioned before; this system presents higher intrinsic viscosities meaning higher viscosity average molecular weights.

Table II also shows the properties: density ( $\rho$ ), total weight lost (w%), and glass transition temperature ( $T_g$ ) for the reference system B polyimide obtained by conventional heating, sample CC. The density of this sample is lower than those presented by system B polyimides obtained by microwave activation.

In reference to the total weight lost at 500°C, the CC sample shows a 12% value this value is close to the other w% values in the same table.

The glass transition temperature of CC sample is 377°C. This is the highest  $T_g$  data recorded for our polyimides. In addition, the use of microwave acti-

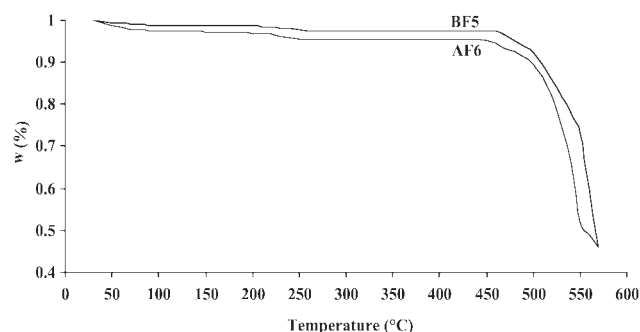
vation produced polyimides with properties quite similar to those obtained by conventional heating.

On the other hand, the total weight lost at 500°C and the  $T_g$  values for our polyimides are maintained in the same range as those recorded for the CC sample obtained by conventional heating.

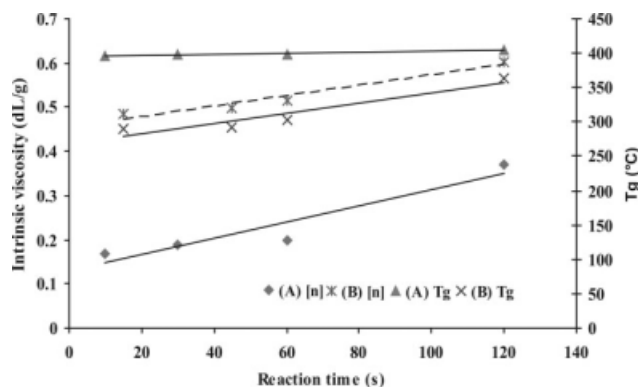
Figure 5 presents the TGA curves of polyimides AF6 and BF5 at a heating rate of 10°C/min from 30 to 600°C under nitrogen flow.

The results of TGA analysis show no significant weight loss below 450°C under nitrogen atmosphere. Curve AF6 presents significant weight loss before reaching 250°C that can be attributed to cycloimidization of the remaining polyamic acid to polyimide. After 250°C no more cycloimidization occurs and this sample does not undergo additional weight loss. The decomposition of this sample starts after 450°C and 9% of the original sample was lost at 500°C, then a clear degradation was observed.

Curve BF5 shows that this polyimide has a 2.6% weight loss under N<sub>2</sub> atmosphere at 260°C and is thermally stable after this temperature in a range from 260°C to 460°C. For this sample, the



**Figure 5** TGA curves of polyimides AF6 and BF5 at a heating rate of 10°C/min from 30 to 600°C under nitrogen flow.



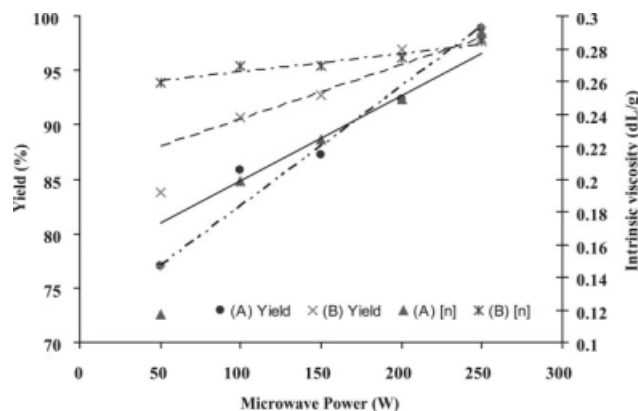
**Figure 6** Reaction time effect on intrinsic viscosity and  $T_g$  for samples of microwave assisted polycondensation, in 10 mL DMF solvent, at 100 watts, of system A and B.

decomposition starts at 460°C. The residual weight at 500°C is above 92% of the original sample under  $N_2$ .

The presence of a bridging  $-C(CF_3)_2-$  group in our system B polymer causes an important modification in the glass transition temperature; this effect can be explained by the good polymer chain flexibility producing a decrement of 40°C in the  $T_g$ . See Table II, samples AF6,  $T_g = 400^\circ C$  and BF5,  $T_g = 358^\circ C$  respectively.

Figure 6 exhibits the reaction time influence on glass transition temperature ( $T_g$ ) and intrinsic viscosity [ $\eta$ ] in both systems A and B polymers. The intrinsic viscosity can be used as a measure of the viscosity average molecular weight  $\overline{M}_{vis}$ , as they are proportional. Thus, according to our kinetic data, increasing the microwave irradiation time, polymers with high intrinsic viscosity [ $\eta$ ] and viscosity average molecular weight are obtained.  $T_g$  values presents the same trend for corresponding polyimides.

The effect of power variation on yield and intrinsic viscosity for systems A and B is summarize in Table III. Powers of 50, 100, 150, 200, and 250 watts were studied in DMF, under constant temperature of 134°C. From this table it is clear that an increment in the magnetron power increases the yield from



**Figure 7** Dependence of yield (%) and polyimide intrinsic viscosity on microwave power, in 10 mL DMF solvent, at constant irradiation time of 60 s.

76.9% to 98.8 for system A and 83.7 to 97.9% for system B. These results are also reported in Figure 7, they show a linear behavior. System B is less sensitive to microwave variation power than system A. In fact, this system B, has the highest yield, intrinsic viscosity, and density.

According to Park-Paul's method, the results of the calculation of volume [ $V$ ], the volume occupied by the polymer chains [ $V_0$ ], the fractional free volume [FFV], gas permeability [ $P$ ], and theoretical gas permeability ratio ( $P_A/P_B$ ) for both systems A and B, are presented in the Table IV.

The effect of the presence of a bridging group  $-C(CF_3)_2-$  in the polymer structure B is evident, in all parameters related to the permeability of the macromolecules. As an example, the volume value [ $V$ ], for system A, was calculated 254.7  $cm^3/mol$  while for system B was calculated 501.5  $cm^3/mol$ . The volume occupied by the polymer chains [ $V_0$ ] is moving in the same direction, it goes from 225.61 to 423.05 for  $CO_2$  gas, in both systems. As aforementioned, the introduction of a bulky bridging group  $-C(CF_3)_2-$  in polymer chains, augment the free volume since it generates a high number of microcavities among polymer chains, which is apparent in

**TABLE III**  
Power Effect on Microwave Assisted Polycondensation of System A and B, in 10 mL DMF Solvent, at Constant Irradiation Time of 60 Seconds

Sample code	Power (W)	System A			System B		
		Yield (%)	$[\eta]^a$ dL/g	$\rho^b$ (g/cm <sup>3</sup> )	Yield (%)	$[\eta]^a$ dL/g	$\rho^b$ (g/cm <sup>3</sup> )
AF8/BF8	50	76.97	0.1174	1.2981	83.79	0.2529	1.3540
AF4/BF6	100	85.80	0.1986	1.2982	90.70	0.2693	1.3717
AF9/BF9	150	87.22	0.2239	1.3032	92.78	0.2693	1.3628
AF10/BF10	200	92.38	0.2492	1.3083	96.90	0.2744	1.3628
AF11/BF11	250	98.81	0.2895	1.3083	97.91	0.2844	1.3628

<sup>a</sup> Measured at a concentration of 0.1 g dL<sup>-1</sup> in dimethylformamide at 23°C.

<sup>b</sup> Density gradient, at 23°C.

**TABLE IV**  
**Volume [V], Volume Occupied by the Polymer Chains [ $V_0$ ], Fractional Free Volume [FFV], Permeability [P], and Gas Permeability Ratio ( $P_A/P_B$ ) for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and O<sub>2</sub> gasses, Calculated According to Park-Paul's Method, for System A and B**

System	V (cm <sup>3</sup> /mol)	V <sub>0</sub> (cm <sup>3</sup> /mol)	FFV	P <sup>a</sup>	P <sup>b</sup>	(P <sub>A</sub> /P <sub>B</sub> ) <sup>c</sup>
A(CO <sub>2</sub> )	254.709	225.618	0.114	325.955	–	0.743 (CO <sub>2</sub> )
A(CH <sub>4</sub> )	254.709	233.043	0.086	9.863	–	0.439 (CH <sub>4</sub> )
A(N <sub>2</sub> )	254.709	225.972	0.113	36.939	–	0.801 (N <sub>2</sub> )
A(O <sub>2</sub> )	254.709	226.484	0.111	77.080	–	0.911 (O <sub>2</sub> )
B(CO <sub>2</sub> )	501.051	423.052	0.156	438.814	431	–
B(CH <sub>4</sub> )	501.051	437.177	0.127	22.451	26	–
B(N <sub>2</sub> )	501.051	424.975	0.152	46.085	31.6	–
B(O <sub>2</sub> )	501.051	422.651	0.156	84.620	109	–

<sup>a</sup> Theoretical permeability values in Barrer.

<sup>b</sup> Experimental permeability values in Barrer.<sup>53</sup>

<sup>c</sup> P<sub>A</sub> = permeability in system A and P<sub>B</sub> = permeability in system B, for the same gas to permeate. CO<sub>2</sub>, CH<sub>4</sub> at 35°C, and 10 atm. O<sub>2</sub>, N<sub>2</sub> at 35°C, and 2 atm.

the fractional free volume (FFV) values. From Table IV the permeability parameters, V<sub>0</sub> and FFV are not only sensitive to the bridging group in the chemical structure they are also affected by the type of gas to permeate. The decrease in kinetic diameter of the permeate gas, d<sub>k</sub> (Å), CH<sub>4</sub> (3.87) > N<sub>2</sub> (3.64) > O<sub>2</sub> (3.46) > CO<sub>2</sub> (3.3) as expected, generates an increment in permeability in the reverse order CO<sub>2</sub> (325.95 barrer) > O<sub>2</sub> (77.08 barrer) > N<sub>2</sub> (36.93 barrer) > CH<sub>4</sub> (9.86 barrer). System B presents the same trend for the corresponding CO<sub>2</sub> gas.

The theoretical ratio of permeability between both systems depends on the gas to separate, thus O<sub>2</sub> gas has the best of four permeability ratios with a value of 0.9108, while CH<sub>4</sub> gas has a low (P<sub>A</sub>/P<sub>B</sub>) ratio with a value of 0.4393.

For comparison purposes Table IV contained experimental permeability values in barrer for B system considering CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub> gasses. If we compare the literature permeability data with the theoretical permeability values calculate in this article, it is clear that they are very close to each other and other, giving a good approximation to the description of this phenomenon.

The solubility of our polymers in DMF, DMSO, THF, acetone, methanol, cyclohexane, toluene, benzene, carbon tetrachloride, and aniline was investigated at 23°C following a standard procedure. THF, DMF, DMSO, and acetone solvents gave positive results from both systems A and B. In DMF and DMSO, right after the polymer sample entered in contact with the liquid, was dissolved completely. In THF partial solubility was observed, for systems A and B after a period of 24 h, with the solution color changing from transparent to a dark violet. In acetone polymer samples dissolved partially, after 15 min for system B. In the rest of the solvents tested the polyimides did not show any change after 24 h of close contact.

## CONCLUSIONS

Microwave assisted polymerization of two aromatic dianhydrides (PMDA, 6FDA) with a diamine (TrmPD) is an efficient technique that can be used for polyimide synthesis. The macromolecules obtained have high intrinsic viscosities and good thermal properties.

The polar solvents, DMF and DMSO, used in our experiments facilitated the synthesis of polyimides, as the monomers were easily dissolved in a short time. These solvents present similar performance for the same system, but DMF solvent generates the best results for system B.

Monomer conversion increases with the exposition time to microwave irradiation in both systems A and B. Polycondensation reactions were very fast; since 92% monomer conversion was obtained in a record time of 90 seconds, sample AF5.

On the other hand, it is clear, according to our results, that increasing the microwave irradiation power generates a correspondent increment on yield and intrinsic viscosity. As an example, system A presents a change in yield from 76.9% to 98.8% at 50 and 250 watts respectively. System B presents similar behavior.

The presence of the bridging group,  $-\text{C}(\text{CF}_3)_2-$ , in the monomer structure gives flexible polymeric molecules, which enhance density, intrinsic viscosity and free volume. For this reason fractional free volume in system B (0.1556), is 36% higher than fractional free volume in system A (0.1142), see Table IV. This effect is also apparent in the permeability of the macromolecules obtained.

Since the thermal properties are influenced by the mobility of polymer chains, the presence of the bridging group,  $-\text{C}(\text{CF}_3)_2-$ , also affected thermal properties producing a decrement of 42°C in the T<sub>g</sub> value for the best polyimides obtained, samples AF6 and BF5.



Our thermal analysis reveals that the polymers synthesized were very stable since they began degradation at high temperatures (450 °C).

## References

1. Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S. J.; Mingos, D. M. P. *Chem Soc Rev* 1998, 27, 213.
2. Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. *Tetrahedron Lett* 1986, 27, 279.
3. Larhed, M.; Hallberg, A. *Drug Discov Today* 2001, 6, 406.
4. Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* 2001, 57, 9225.
5. Caddick, S. *Tetrahedron* 1995, 51, 10403.
6. Strauss, C. R.; Trainor, R. W. *Aust J Chem* 1995, 48, 1665.
7. Berlan, J.; Giboreau, P.; Lefeuvre, S.; Marchand, C. *Tetrahedron Lett* 1991, 32, 2363.
8. Stuerge, D.; Gonon, K.; Lallemand, M. *Tetrahedron* 1993, 49, 6229.
9. Cotterill, I. C.; Usyatinsky, A. Y.; Arnold, J. M.; Clark, D. S.; Dordick, J. S.; Michels, P. C.; Khmel'nitsky, Y. L. *Tetrahedron Lett* 1998, 39, 1117.
10. Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J. L.; Petit, A. *Tetrahedron* 1999, 55, 10851.
11. Strauss, C. R. *Aust J Chem* 1999, 52, 83.
12. Cablewski, T.; Faux, A. F.; Strauss, C. R. *J Org Chem* 1994, 59, 3408.
13. Glasnov, T. N.; Kappe, C. O. *Macromol Rapid Commun* 2007, 28, 395.
14. Hoogenboom, R.; Schubert, U. *Macromol Rapid Commun* 2007, 28, 368.
15. Mallon, F. K.; Ray, W. H. *J Appl Polym Sci* 1998, 69, 1203.
16. Fang, X.; Hutcheon, R.; Scola, D. A. *J Polym Science: Part A: Polym Chem* 2000, 38, 2526.
17. Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A. *Adv Polym Sci* 2003, 163, 193.
18. Wiesbrock, F.; Hoogenboom, R.; Schubert, U. *Macromol Rapid Commun* 2004, 25, 1739.
19. Bardts, M.; Gonsior, N.; Ritter, H. *Macromol Chem Phys* 2008, 209, 25.
20. Galbrecht, F.; Bunnagel, T. W.; Scherf, U.; Farrell, T. *Macromol Rapid Commun* 2007, 28, 387.
21. Amore, K. M.; Leadbeater, N. E. *Macromol Rapid Commun* 2007, 28, 473.
22. Nagahata, R.; Sano, D.; Suzuki, H.; Takeuchi, K. *Macromol Rapid Commun* 2007, 28, 437.
23. Sivalingam, G.; Agarwal, N.; Madras, G. *AIChE J* 2003, 49, 1821.
24. Stange, H.; Greiner, A. *Macromol Rapid Commun* 2007, 28, 504.
25. Yu, Z.; Liu, L. *J Appl Polym Sci* 2007, 104, 3973.
26. Li, H.; Liao, L.; Liu, L. *Macromol Rapid Commun* 2007, 28, 411.
27. Hajipour, A. R.; Zahmatkesh, S.; Ruoho, A. E. *Polym Adv Technol* 2008; DOI: 10.1002/pat.
28. Lu, J. M.; Ji, S. J.; Chen, N. Y.; Zhang, Z. B.; Sun, Z. R.; Zhu, X. L.; Shi, W. P. *J Appl Polym Sci* 2003, 87, 1739.
29. Mallakpour, S.; Kowsari, E. *Polym Adv Technol* 2005, 16, 466.
30. Imai, Y. *React Funct Polym* 1995, 30, 3.
31. Mallakpour, S.; Hajipour, A. R.; Khoei, S. *J Appl Polym Sci* 2000, 77, 3003.
32. Faghihi, K.; Zamani, K.; Mirsamie, A.; Mallakpour, S. *J Appl Polym Sci* 2004, 91, 516.
33. Wang, L.; Zhao, Z.; Li, J.; Chen, C. *Eur Polym J* 2006, 42, 1266.
34. Jang, W.; Lee, H. S.; Lee, S.; Choi, S.; Shin, D.; Han, H. *Mat Chem Phys* 2007, 207, 342.
35. Zhu, Y.; Zhao, P.; Cai, X.; Meng, W. D.; Qing, F. L. *Polymer* 2007, 48, 3116.
36. Mallakpour, S.; Kowsari, E. *Polym Bull* 2006, 57, 169.
37. Hu, Z.; Yin, Y.; Kita, H.; Okamoto, K.; Suto, Y.; Wang, H.; Kawasato, H. *Polymer* 2007, 48, 1962.
38. Shang, Y.; Xie, X.; Jin, H.; Guo, J.; Wang, Y.; Feng, S.; Wang, S.; Xu, J. *Eur Polym J* 2006, 42, 2987.
39. Dao, B. N.; Groth, A. M.; Hodgkin, J. H. *Macromol Rapid Commun* 2007, 28, 604.
40. Imai, Y.; Nemoto, H.; Kakimoto, M. *J Polym Sci Part A: Polym Chem* 1998, 34, 701.
41. Imai, Y.; Nemoto, H.; Watanabe, S.; Kakimoto, M. *Polym J* 1996, 28, 256.
42. Yeganeh, H.; Tamami, B.; Ghazi, I. *Eur Polym J* 2004, 40, 2059.
43. Li, Q.; Xu, Z.; Yi, C. *J Appl Polym Sci* 2008, 107, 797.
44. Liu, Y.; Xiao, Y.; Sun, X.; Scola, D. A. *J Appl Polym Sci* 1999, 73, 2391.
45. Martha, L. C.-G.; Joaquín Palacios-Alquisira, J. M. D. *J Membr Sci* 2007, 293, 53.
46. Solomon, O. F.; Ciută, I. Z. *J Appl Polym Sci* 1963, 6, 683.
47. Shroff, R. N. *J Appl Polym Sci* 1965, 9, 1547.
48. Abdel-Aziz, A.; Atta, A. M.; Farahat, M. S.; Boutros, W. Y. *Polymer* 1998, 39, 6827.
49. Vega, M. P.; Lima, E. L.; Pinto, J. C. *Polymer* 2001, 42, 3909.
50. Xu, Y.; Chen, C.; Zhang, P.; Sun, B.; Li, J. *J Appl Polym Sci* 2007, 103, 998.
51. Park, J. Y.; Paul, D. R. *J Membr Sci* 1997, 125, 23.
52. Dean, J. A. *Lange's Handbook of Chemistry*, 11th Ed.; McGraw-Hill: New York, 1989; pp 4-110.
53. Tanaka, K.; Okano, M.; Toshino, H.; Kita, H.; Okamoto, K.-I. *J Polym Science Part B: Polym Phys* 1992, 30, 907.