



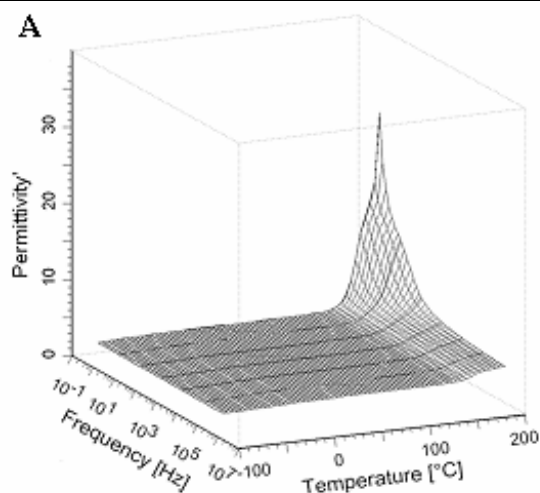
## NEW BISMALIMIDE-BASED POLYASPARTIMIDES: THERMAL, DIELECTRIC AND MORPHOLOGICAL PROPERTIES

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Some bismaleimide monomers, BMI(1-4), were synthesized from diamines with various structures and maleic anhydride and by the reaction of maleimidobenzoic chloride with 4,4'-(1-phenylethylidene)bisphenol, BMI-5. Chain extension of these bismaleimides was accomplished by incorporating ether or ester groups. Thermogravimetric analyses indicated that the cured bismaleimide resins are stable from 294 to 455 °C. Polyaspartimides P(1-8) based on BMI(1-5) were prepared by the Michael addition of diamines to bismaleimides. Some of these polymers exhibited film-forming ability. The quality of these films was studied by atomic force microscopy (AFM). Dielectric constants of the polymers films varied between 3.00 and 3.45 at a frequency of 1 kHz and from 2.96 to 3.43 at a frequency of 100 kHz. The obtained bismaleimide-based polymers had the combined advantages of low dielectric constant and dielectric loss, good-temperature resistance and good processability. These new polymers will contribute to extend the field of their applications as high performance polymers.



### INTRODUCTION

Thermosetting polyimides, a leading class of high performance polymers, are prepared from bismaleimides (BMI<sub>s</sub>), low molecular weight building blocks having reactive groups which undergo polymerization by thermal or catalytic means. Polyaspartimides are well known for their excellent processability<sup>1,2</sup> and high thermal and thermooxidative stability,<sup>3,4</sup> good retention of the mechanical properties even after long ageing times at 205°C,<sup>5</sup> excellent chemical, radiation and corrosion resistance,<sup>6</sup> good water resistance, fire resistance<sup>7</sup> and relatively low cost. BMI<sub>s</sub>-based

polymers offer temperature performance and price in comparison with polyimides and epoxies, and, because they cured by an addition reaction rather than a condensation one, they mitigate problems with emitted volatiles. Also, these polymers have a low dielectric constant and dielectric loss.<sup>8</sup> Due to the high temperature resistance, these products are widely used as high performance composite matrices for multilayer printed circuit boards for large scale computers,<sup>9</sup> advanced composites for aerospace industry<sup>10</sup> and structural adhesives.<sup>11</sup> Also, these characteristics of composite materials make them suitable for structural applications such as automobiles and marine vehicles, electronic and

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nuclear industries where a high degree of performance is required.<sup>12,13</sup>

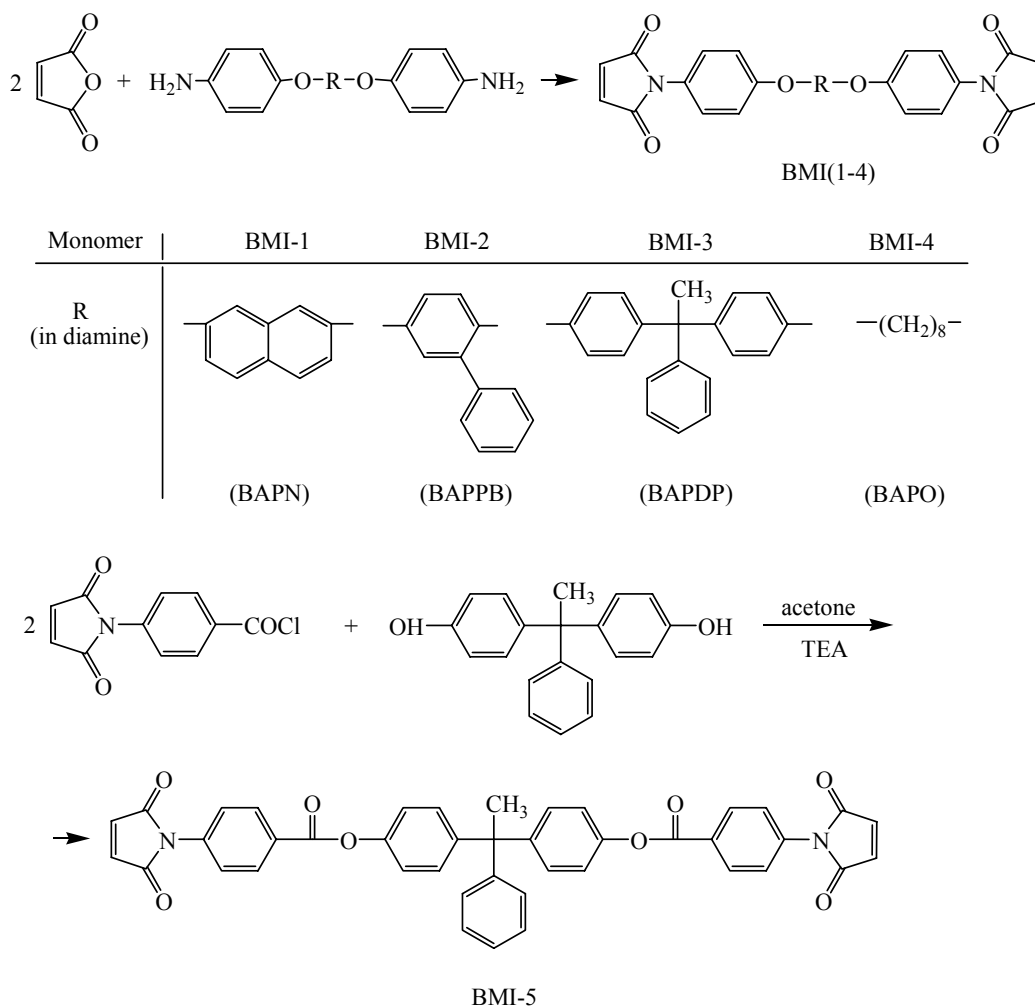
Some recent studies show that polymers based on bismaleimide monomers have potential applications in second order non-linear optical (NLO) materials due to their orientation of the NLO chromophore, or in fabrication process of photo-alignment layers.<sup>14,15</sup>

Unfortunately, these polymers show some disadvantages, such as brittleness (due to their high crosslink density), poor solubility in ordinary solvents, and high melting and curing temperatures, which considerably restrict their applications.<sup>16,17</sup> Attempts to reduce brittleness by way of lowering cross-link density through structural modification toughening etc. adversely affect the high temperature performance. Also, bismaleimide monomers and diamines were varied systematically with the target of identifying a system with a dielectric constant as lowest possible but without compromising the thermal properties.

This paper presents a series of polyaspartimides bearing ether flexible linkages in their main chain aiming at the influence of the chemical structure on their film-forming capability, thermal and dielectric properties, and surface morphology.

## RESULTS AND DISCUSSION

The bismaleimide monomers BMI(1-4) were prepared from the corresponding diamines and maleic anhydride by a modification of the method reported by White *et al.*<sup>18</sup> (Scheme 1). The chemical structure of all synthesized compounds was confirmed by means of elemental analysis, FTIR and <sup>1</sup>H-NMR spectroscopy. The FTIR spectra of bismaleimide monomers showed two characteristic peaks in the range 1776-1773 and 1717-1713 cm<sup>-1</sup> attributed to C=O from imide group. Monomer BMI-5 showed an absorption band at 1732 cm<sup>-1</sup> due to the ester group, while BMI(1-4) exhibited bands at 1249-1240 cm<sup>-1</sup> attributed to the ether group.



Scheme 1 – Synthesis of bismaleimides BMI(1-5).

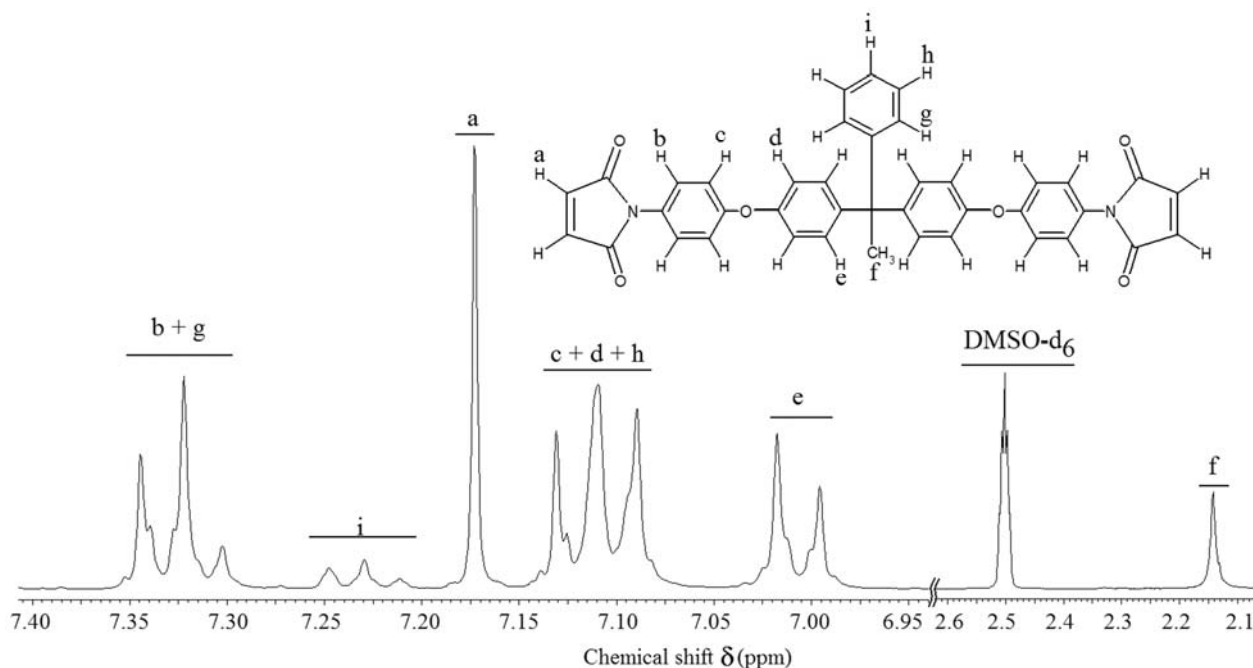
Fig. 1 –  $^1\text{H-NMR}$  spectrum of bismaleimide BMI-3 .

Table 1

Basic thermal data for the synthesized monomers

Monomer	mp (°C)	$T_{\text{end}}^{\text{a}}$ (°C)	$T_{\text{p}}^{\text{b}}$ (°C)	IDT <sup>c</sup> (°C)	PDT <sub>max</sub> <sup>d</sup> (°C)	$Y_{\text{c}}^{\text{e}}$ (%)
BMI-1	92-96	91	225	427	448,553	50
BMI-2	196-173	177	215	455	480	53
BMI-3	107-111	110	227	451	487	52
BMI-4	106 <sup>f</sup>	112	231	294	362,555	18
BMI-5	212-216	230	243	449	460	46

<sup>a</sup> endothermic peak temperatures were evidenced by DSC. <sup>b</sup> onset temperature for curing reaction. <sup>c</sup> initial decomposition temperature. <sup>d</sup> maximum decomposition temperature. <sup>e</sup> residual weight percent at 700 °C. <sup>f</sup> melting point was determined by DSC.

The  $^1\text{H-NMR}$  spectra of bismaleimides BMI(1-5) confirmed their chemical structure. Fig. 1 shows the  $^1\text{H-NMR}$  spectrum of compound BMI-3. The aromatic protons appeared as multiplets in the ranges 7.34-7.30, 7.13-7.09, and 7.02-6.99 ppm, and a triplet in the range 7.25-7.21 ppm. A singlet at 7.17 ppm was attributed to the olefinic protons, while a singlet at 2.14 ppm was ascribed to the protons of the methyl group.

The thermal behavior of monomers was investigated by DSC, and thermal stability of cured BMI<sub>s</sub> was evaluated by TGA in nitrogen (Table 1). DSC measurements indicated that the onset temperatures for curing reaction were in the range 215-243 °C. The reactivity of the C=C double bond from maleimide ring is influenced by the chemical nature of the residue between maleimide groups. A higher electron-withdrawing capacity of the maleimide substituents induces a higher cure temperature and a slower cure rate. Therefore, the

higher onset of BMI-5 curing might be due to the high electron-withdrawing nature of the ester units between the maleimide groups. The initial decomposition temperatures (IDT) of monomers ranged between 294 and 455 °C and a rapid weight loss occurred in the region 362-555 °C. The percentage char yield at 700 °C varied between 18 and 53%.

A series of linear polyaspartimides was obtained by a Michael addition reaction (Scheme 2). The inherent viscosity, measured at a concentration of 0.5 g/dL in NMP at 25 °C, of the resulted polyaspartimides was between 0.29 and 0.48 dL/g. The highest value was recorded for polymer P-3. The structure of the polymers was confirmed by means of FTIR spectroscopy. Figure 2 presents the spectrum of polymer P-1. Two characteristic carbonyl bands around 1776 and 1717  $\text{cm}^{-1}$  are due to asymmetric and symmetric stretching vibration. Other bands were observed in the range 2974-2876  $\text{cm}^{-1}$  and ascribed to

aliphatic groups ( $\text{CH}_2$ ). The absorption peak at  $1240\text{ cm}^{-1}$  corresponded to the ether groups. At the same time, the band at  $1150\text{ cm}^{-1}$ , due to maleimide ring, disappeared and a band at  $1172\text{ cm}^{-1}$ , due to succinic ring, appeared, which indicated that maleimide  $\text{C}=\text{C}$  bond reacted.

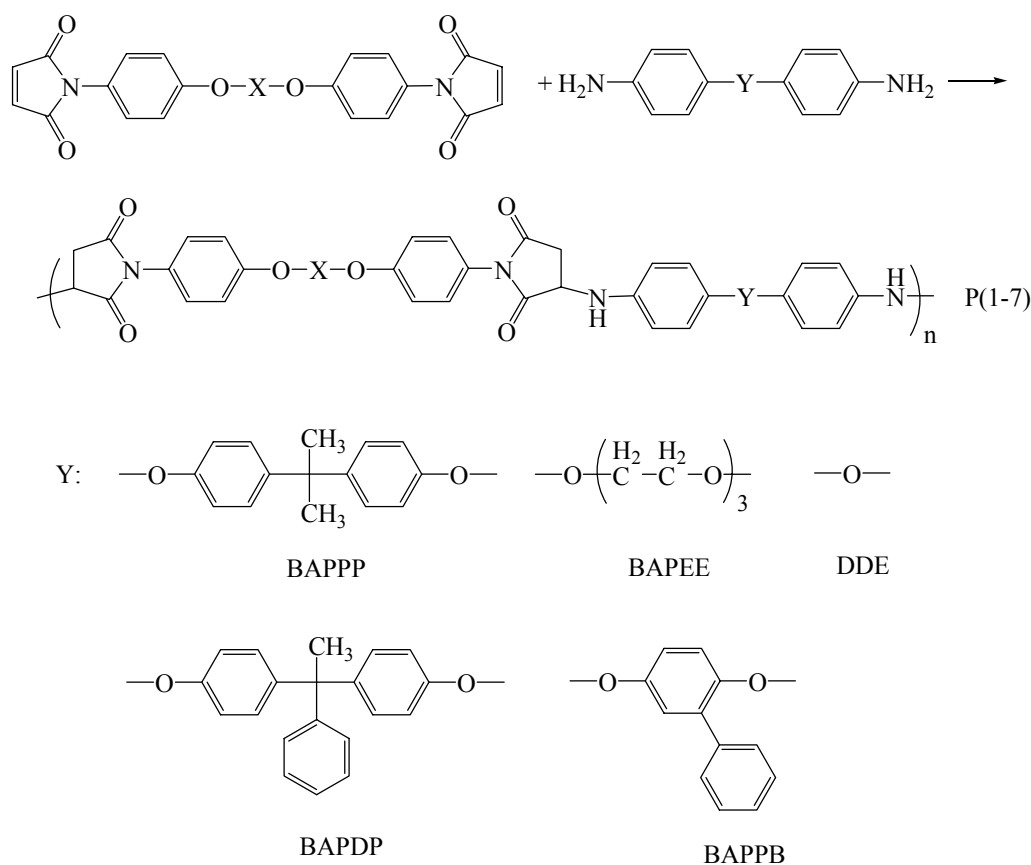
To study the surface morphology and texture parameters such as average height and root mean square roughness of the polymer film surfaces (Table 2), AFM height imaging was performed in air, at room temperature, in tapping mode. The two dimensional (2D) height images, within the same scan areas of  $1 \times 1\ \mu\text{m}^2$  are shown in Fig. 3.

As can be easily seen, the surface topography could be influenced by many factors, including the chemical composition. P-1, P-2 and P-3 surfaces were covered with individual small, spherically shaped formations, P-1 surface showing slight tendency of agglomeration, whereas the P-5 sample presented a more uniform and smoother

surface. The lower value of  $H_a$  parameters of P-5, compared with those found for P-1, P-2 and P-3, was reflected also by a lower root mean square roughness, in which roughness parameters ranged in the following order:  $Sq_{P-1} > Sq_{P-3} > Sq_{P-2} > Sq_{P-5}$ . Moreover, the evaluation of texture parameters indicated that the bulky polymer chain in sample P-1 could induce the higher value of roughness.

The 3D AFM images provided further qualitative and quantitative information and showed the variable heights of the globular formations (see Fig. 3, Ac, Bc and Cc) for P-1, P-2 and P-3 samples. Thus, it could be seen that P-1 sample showed spherical formations larger than those obtained for the other samples.

The thermal properties of polyaspartimides P(1-8) were evaluated by DSC and TGA in nitrogen atmosphere. The thermal behavior data of these compounds are summarized in Table 3.



polymer	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
bismaleimide	BMI-3	BMI-1	BMI-2	BMI-3	BMI-4	BMI-1	BMI-5	BMI-3
diamine	BAPEE	BAPEE	BAPEE	BAPDP	BAPPB	DDE	BAPPP	DDE

Scheme 2 – Synthesis and structure of polyaspartimides P(1-8).

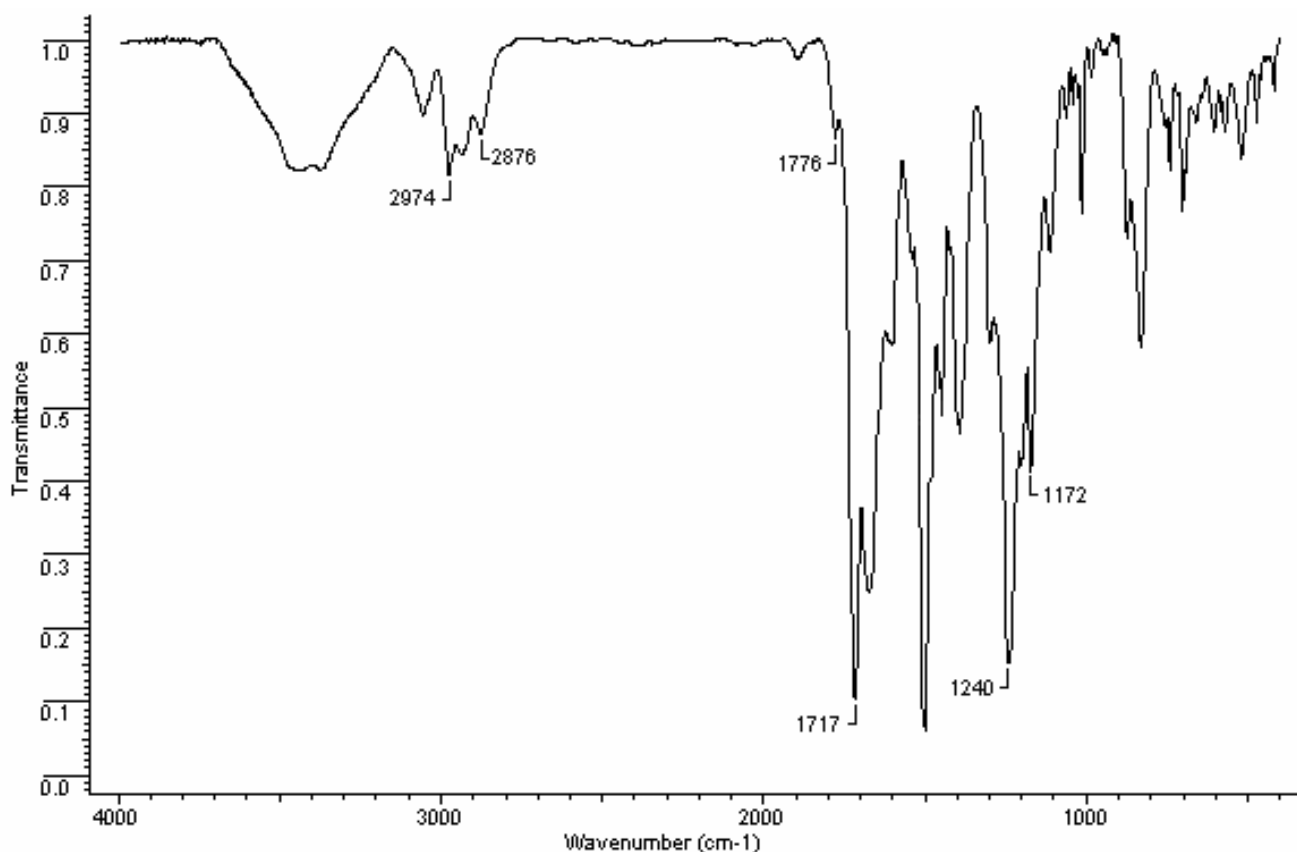


Fig. 2 – FTIR spectrum of polymer P-1.

Table 2

Roughness parameters calculated from 1 x 1  $\mu\text{m}^2$  AFM images obtained on polymer films

Samples	Roughness parameters		Grain characteristics	
	Ha (nm)	Sq (nm)	Number of grains collected	Average diameter (nm)
P-1	15.9	4.3	115	36±5
P-2	4.1	1.1	60	18±2
P-3	3.6	1.0	80	24±3
P-5	3.5	0.8	-	-

The  $T_g$  values of the compounds were in the range 198-225 °C, depending on the stiffness of the polymer chain. The polymers containing ether bridges presented a lower  $T_g$  because of the increased rotation movement caused by these flexible linkages.<sup>19</sup>  $T_g$ 's were also influenced by the asymmetry and irregularity, which disturbed the chain interaction and induced the decrease of  $T_g$ . At the same time, the attachment of bulky substituents on the aromatic units resulted in an increase of rigidity of polymer backbone and the consequent hindrance brought about the increase of  $T_g$ .

All polymers were stable between 324 and 360 °C and the weight loss (1-3 %) observed in this interval was associated with evaporation of humidity and solvent traces. The highest value of IDT was obtained for polymer P-7 based on bismaleimide BMI-5, having ester groups, and BAPPP amine component. The polymers P-3 and P-4 showed lower IDT. The char yield of the polyaspartimides was in the range 42-54 % when heated to 700 °C in nitrogen (except P-6 which heated to 620 °C), confirming that these polymers had good thermal stability (Fig. 4).

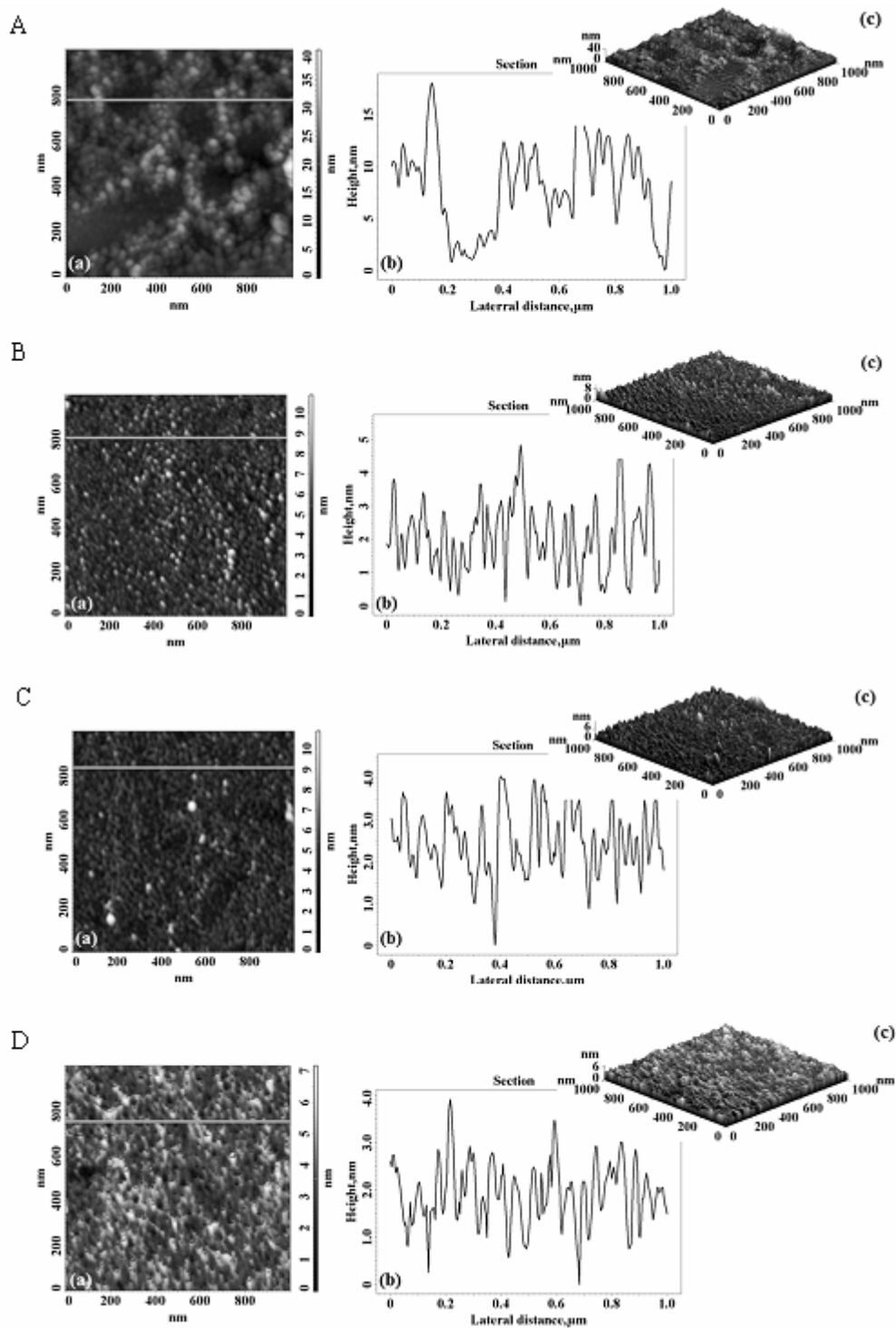


Fig. 3 – 2D (a) and 3D AFM images (c) and cross-section profile taken along the solid line from 2D image (b) of the structured surface corresponding to polymers P-1 (A), P-2 (B), P-3(C) and P-5 (D).

Table 3

Thermal properties of polymers P(1-8)

Polymer	$T_g^a$ (°C)	IDT <sup>b</sup> (°C)	PDT <sub>max</sub> <sup>c</sup> (°C)	$T_{10}^d$ (°C)	$Y_c^e$ (%)
P-1	206	355	492, 502	410	47
P-2	198	358	436, 560	390	52
P-3	206	325	426, 520	397	49
P-4	211	324	490	440	49
P-5	201	347	444	404	42

Table 3 (continued)

P-6	225	338	377, 508	356	40 <sup>f</sup>
P-7	-	366	334, 416, 542	349	47
P-8	206	355	492, 502	410	47

<sup>a</sup> glass transition temperature; <sup>b</sup> initial decomposition temperature; <sup>c</sup> maximum decomposition temperature; <sup>d</sup> the temperature at which 10% weight loss was recorded; <sup>e</sup> residual weight percent at 700 °C; <sup>f</sup> residual weight percent at 620°C.

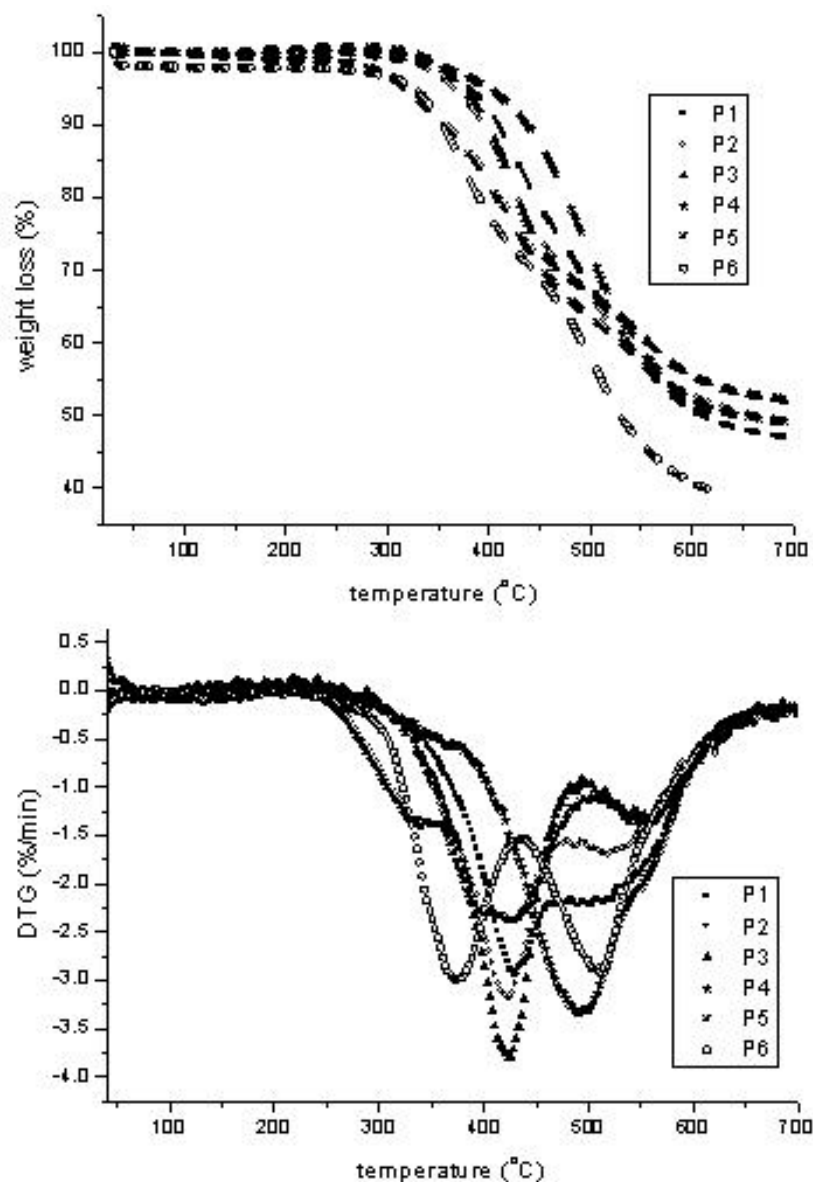


Fig. 4 – TG and DTG curves of polymers P(1-6).

The dielectric properties (dielectric constant and loss) of the polyaspartimide films were evaluated from -100 to 200°C at a heating rate of 2 °C/min. The frequency range used for measurements was from 1 to 10<sup>6</sup> Hz. For signal propagating, a material with low values of dielectric constant and dielectric loss is good for enhancing the speed and reducing the loss, so low dielectric constant and dielectric loss are

characteristic features of the materials used for producing high-performance dielectrics.<sup>20</sup>

It is known that structures with low polar linkages and bulky groups are characterized by low values of dielectric constant and dielectric loss, on one hand due to the low polarity of the groups and, on the other hand, due to the less efficient chain packing that leads to an increase in the free volume of the polymer.

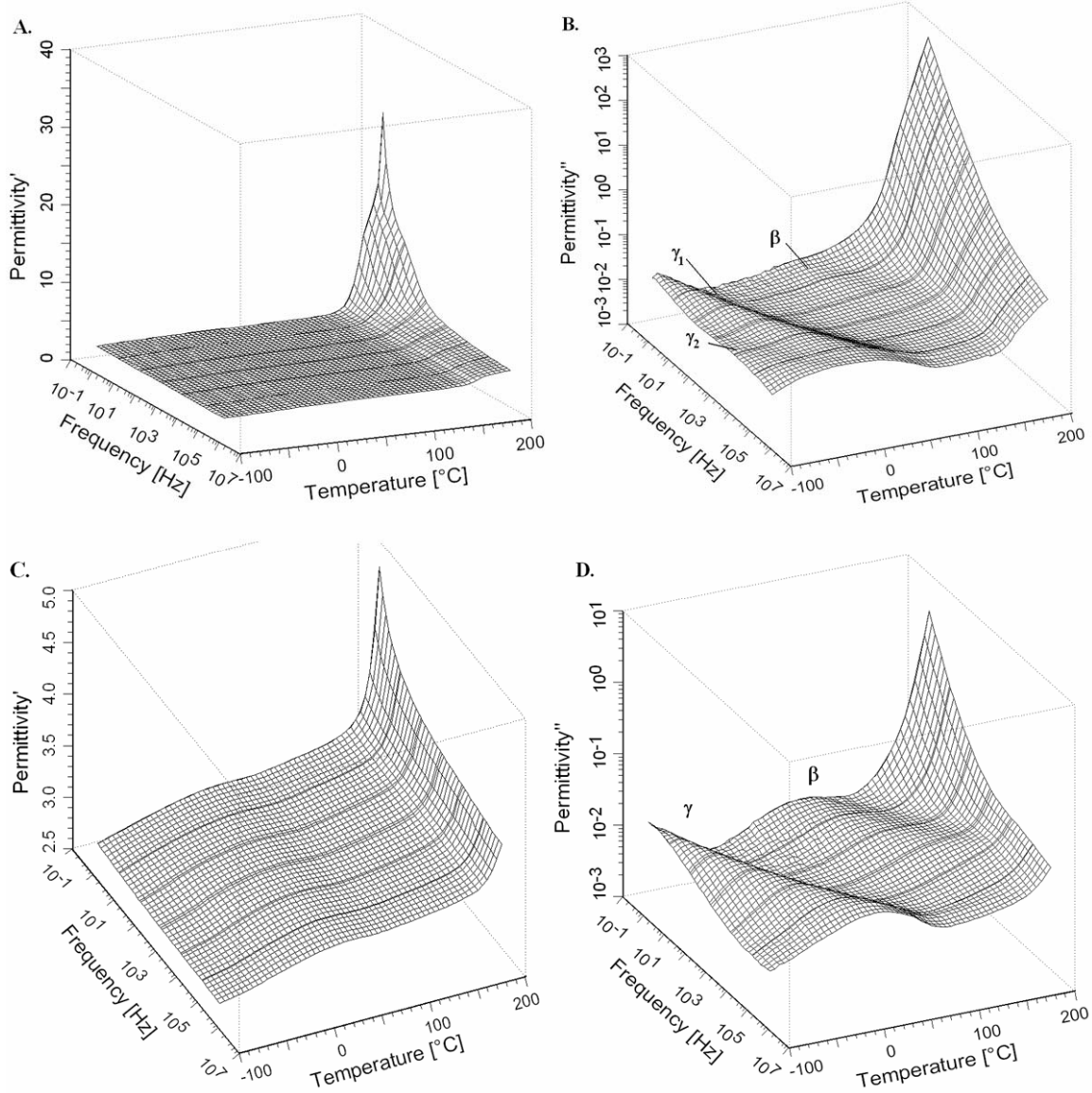


Fig. 5 – Temperature and frequency dependencies of dielectric constant (A, C) and dielectric loss (B, D) for P-1 and P-4.

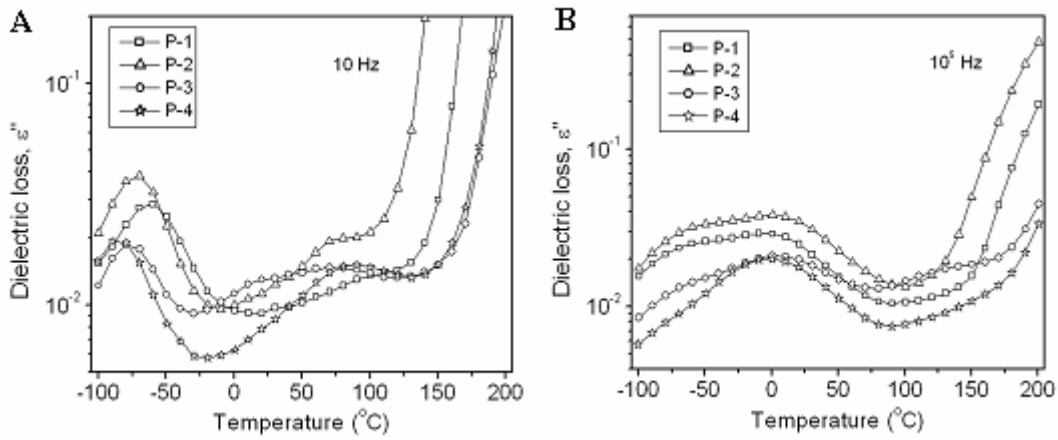


Fig. 6 – Variation of dielectric loss with temperature at (A) 10 Hz and (B) 10<sup>5</sup> Hz.

The dependence of the dielectric constant and dielectric loss on the temperature and frequency is

a very important factor to consider for dielectric materials applications. The typical 3D plots of the



dielectric properties are portrayed in Fig. 5 for P-1 and P-4. The dielectric constants of these polymers showed a small and gradual increase with temperature up to 175 °C. This exhibited a much faster increasing trend with further increasing temperature above 175 °C and at lower frequencies especially for polymer P-2. This increase was attributed to the increased mobility of charge carriers which might accumulate at interfaces like the polymer-electrode one, leading to interfacial polarization phenomena that could be orders of magnitude larger than the dielectric response due to molecular fluctuations.<sup>21</sup> In the same temperature range the dielectric loss increased abruptly due to the increased conductivity losses. This effect was more pronounced for P-4 which had the lowest  $T_g$  value (198 °C), because the segmental mobility correlated with the glass transition permits an easier transport of electric charges. Below the  $T_g$ , in -100 to +200 °C temperature range, all the polymers exhibited secondary relaxations observed as loss peaks or shoulders, Fig. 5 (B and D):  $\gamma$  and  $\beta$  for P-4 and  $\gamma_1$ ,  $\gamma_2$  and  $\beta$  for P-1. Similar relaxation behavior was reported for polyimides with different structures.<sup>22-24</sup>

Although studied quite extensively, the exact molecular mechanisms underlying  $\gamma$  and  $\beta$  relaxations for polyimides are not elucidated.<sup>24</sup> For  $\gamma$  relaxation it was evidenced that this encompassed both the coupled water molecules and limited motions such as phenyl ring oscillations,<sup>25,26</sup> while  $\beta$  relaxation was generally correlated with motions in the dianhydride moieties. Also, for polyimides it was evidenced the existence of two  $\gamma$  relaxations for the ones that had both *p*-phenyl and *m*-phenyl groups in the amine units compared to those having only *p*-phenyl in structure which presented a single  $\gamma$  relaxation. A somehow similar behavior was observed in the present case because the polyaspartimides with ethylene oxyethylene units in the amine component presented  $\gamma_1$  and  $\gamma_2$  relaxations, while P-4 with more rigid aromatic groups in the amine part presented only one  $\gamma$  relaxation process in negative temperature domain, as illustrated in Fig. 5 (B and D) and 6. For the lower frequencies,  $\gamma_2$  relaxations were situated at lower temperatures than the measured ones and  $\beta$  relaxation could be distinguished with a peak around +100°C. At higher frequency, the two  $\gamma$  relaxations were in the measured range, but  $\beta$  relaxation shifted to higher temperature was overlapped by conductivity losses (Fig. 6B).

## EXPERIMENTAL

**Materials.** The materials used in this research were: maleic anhydride, triethylamine (TEA), 4,4'-oxydianiline (DDE), 2,7-dihydroxynaphthalene, (Fluka, Germany), acetic anhydride (Merck, Germany), *p*-chloronitrobenzene, 2-phenylhydroquinone, 4-[1-(4-hydroxyphenyl)-1-phenylethyl]phenol, 1,8-octanediol, 4,4'-(1-phenyleneethylidene)bisphenol triethylene glycol (Aldrich, USA), and sodium carbonate (Chimopar SA, Romania). Commercial solvents such as acetone, 1,2-dichloroethane (DCE) (Chimopar SA, Romania), ethanol, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) (Fluka, Germany) were dried and purified by standard methods. Magnesium acetate (Fluka, Germany) and potassium carbonate (Chimopar SA, Romania) were dried at 120 °C in vacuum before use. The diamines used in this study, except DDE, were prepared according to the method of Feld *et al.*<sup>27</sup> with some modifications, and are as follows: 1,4-bis(4-aminophenoxy)-2-phenylbenzene (BAPPB), 4-[4-[1-(4-aminophenoxy)phenyl]-1-phenyl-ethyl]phenoxy]aniline (BAPDP), 1,8-bis(4-aminophenoxy)octane (BAPO), 2,7-bis(4-aminophenoxy)naphthalene (BAPN), 2,2-bis[(4-aminophenoxy)phenyl]propane (BAPPP) and 1,2-bis-[2-(4-aminophenoxy)ethoxy]ethane (BAPEE).

### General procedure for the preparation of bismaleimides

**BMI (1-4).** Monomers BMI(1-4) were synthesized following the literature, *via* the reaction of maleic anhydride with various diamines according to Scheme 1.<sup>28</sup> Monomer BMI-5 was synthesized following the literature.<sup>29</sup> 4-Maleimidobenzoylchloride (4-MBC) (0.04 mol) in 50 ml acetone was cooled in an ice bath. To this solution, TEA (0.025 mol) as acid acceptor and a solution of 4,4'-(1-phenylethylidene)bisphenol (0.02 mol) in 40 mL acetone were added. After stirring for one hour, the mixture was filtered and precipitated in *n*-hexane. The product was filtered and treated with a sodium bicarbonate solution and thoroughly washed with water. The filtered precipitate was dried in vacuum oven at 90 °C. The monomer was recrystallized from acetone/ethanol.

Bismaleimide BMI-1 was recrystallized from DCE/ethanol; yield 69 %; m.p. 92-96 °C; FTIR (KBr),  $\nu$  (cm<sup>-1</sup>): 1773 and 1713 (C=O imide), 1247 (-O-); Anal. calcd. for C<sub>30</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub> (%): C 71.71, H 3.61, N 5.57; found: C 71.39, H 3.94, N 5.36.

Bismaleimide BMI-2 was recrystallized from DCE/ethanol; yield 72 %; m.p. 169-173 °C; FTIR (KBr),  $\nu$  (cm<sup>-1</sup>): 1773 and 1713 (C=O imide), 1241 (-O-). Anal. calcd. for C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub> (%): C 72.72, H 3.81, N 5.30; found: C 73.11, H 3.43, N 5.16.

Bismaleimide BMI-3 was recrystallized from DMF/water; yield 68 %; m.p. 107-111 °C; FTIR (KBr),  $\nu$  (cm<sup>-1</sup>): 2977-2924(-CH<sub>3</sub>), 1773 and 1715 (C=O imide), 1240 (-O-). Anal. calcd. for C<sub>40</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub> (%): C 75.93, H 4.46, N 4.42; found: C 75.58, H 4.23, N 4.59.

Bismaleimide BMI-4 was recrystallized from DCE/ethanol; yield 71 %; m.p. 106 °C; FTIR (KBr),  $\nu$  (cm<sup>-1</sup>): 2935-2851 (-CH<sub>2</sub>), 1765 and 1709 (C=O imide), 1249 (-O-). Anal. calcd. for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub> (%): C 68.83, H 5.77, N 5.73; found: C 68.61, H 5.46, N 5.47.

Bismaleimide BMI-5 was recrystallized from acetone/ethanol; yield 69 %; m.p. 225-230 °C. FTIR (KBr),  $\nu$  (cm<sup>-1</sup>): 1776 and 1717 (C=O imide), 1732 (C=O ester). Anal.

calcd. for  $C_{42}H_{28}N_2O_8$  (%): C 73.23, H 4.09, N 4.07; Found C 72.68, H 3.96, N 4.31.

**Synthesis of polyaspartimides P(1-8).** The polyaspartimides were synthesized by the Michael addition of diamines to bismaleimides in NMP at 95.<sup>30</sup>

**Measurements.** The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer (Germany) and the <sup>1</sup>H-NMR spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 MHz (Germany), using DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane as an internal standard. DSC measurements were performed with a Pyris Diamond DSC, Perkin Elmer system (USA), under nitrogen atmosphere (nitrogen flow 120 mL/min, sample mass 3–4 mg, heating rate 10 °C/min). Melting points of diamines were determined with a Gallenkamp hot-blok melting point apparatus. The inherent viscosities of polymer solutions in NMP (measured at a concentration of 0.5 g/dL) were determined at 25 °C using an Ubbelohde suspended level viscometer (Germany). Elemental analysis was done with a Perkin-Elmer 2400 Series II CHNS/O Elemental Analyzer (Perkin-Elmer, UK). AFM images were collected in semicontact mode using a scanning probe microscope Solver PRO-M with commercially available NSG10 cantilever (NT-MDT, Moscow, Russia). TGA was carried out using a TGA/SDTA851e-thermogravimetric analyzer (METTLER TOLEDO, Columbus, OH, USA), under nitrogen flow (20 mL/min) at a heating rate of 10 °C/min for polyaspartimides and in air for bismaleimides from room temperature to 700 °C, and 3-5 mg of sample mass. Measurements of the dielectric properties were done using Novocontrol Dielectric Spectrometer Concept 40 (Germany) equipped with Alpha Frequency Response Analyzer and Novocontrol Quatro Cryosystem which allowed temperature control in dry nitrogen atmosphere with stability better than 0.1 °C.

## CONCLUSIONS

Bismaleimide monomers and polyaspartimides containing flexible linkages were successfully prepared by Michael addition reaction of bismaleimides and diamines. The polymers were characterized by thermal, dielectric, and spectroscopic methods. Thermal properties of monomers and polymers were influenced by the rigidity, symmetry and conditions of reaction. The polymers had *T<sub>g</sub>* values in the range 198-225 °C and IDT values in the range 324-366 °C. The dielectric constant values of the polymer films P(1-4) at -100 °C were in the range 2.58–3.05 and at 150 °C varied between 3.08 and 3.57 at a frequency of 10<sup>4</sup> Hz. It is expected that these polymers, which combine advantages of good dielectric constant, high-temperature resistance and easy processing, would contribute to extend the field of their applications as high performance polymers.

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