

# Synthesis and Thermal Behaviour of Some Bismaleimides with Hexafluoroisopropylidene Groups

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*Bismaleimide monomers were used to prepare polymers in an attempt to achieve good properties. Bismaleimide BMI (1-3) were synthesized by reaction of maleic anhydride with diamines having hexafluoroisopropylidene units. Bismaleimides BMI (4-5) with ester units were synthesized by reaction between 3(4)-maleimidobenzoylchloride with diphenols. The monomers were characterized by infrared (IR), proton nuclear resonance ( $^1\text{H-NMR}$ ) spectroscopy and elemental analysis. Thermal characterization of monomers was accomplished by differential scanning calorimetry (DSC), dynamic thermogravimetric analysis (ATG) and isothermal gravimetric analysis (IGA). In this paper, the synthesis and characterization of monomers with fluoro atoms in their structure is discussed.*

*Keywords: bismaleimide, hexafluoroisopropylidene groups, synthesis, thermal properties*

Bismaleimide polymers are an important high performance polymer class, due to their attractive combination of physical, chemical and mechanical properties. They can also be used as resin matrices for advanced composites. These resins have high thermostability, tensile strength and modulus, good flame resistance, excellent chemical and corrosive resistance, as well as low water sensitivity. These compounds have good retention of thermomechanical properties even after long ageing intervals at 250°C [1-7].

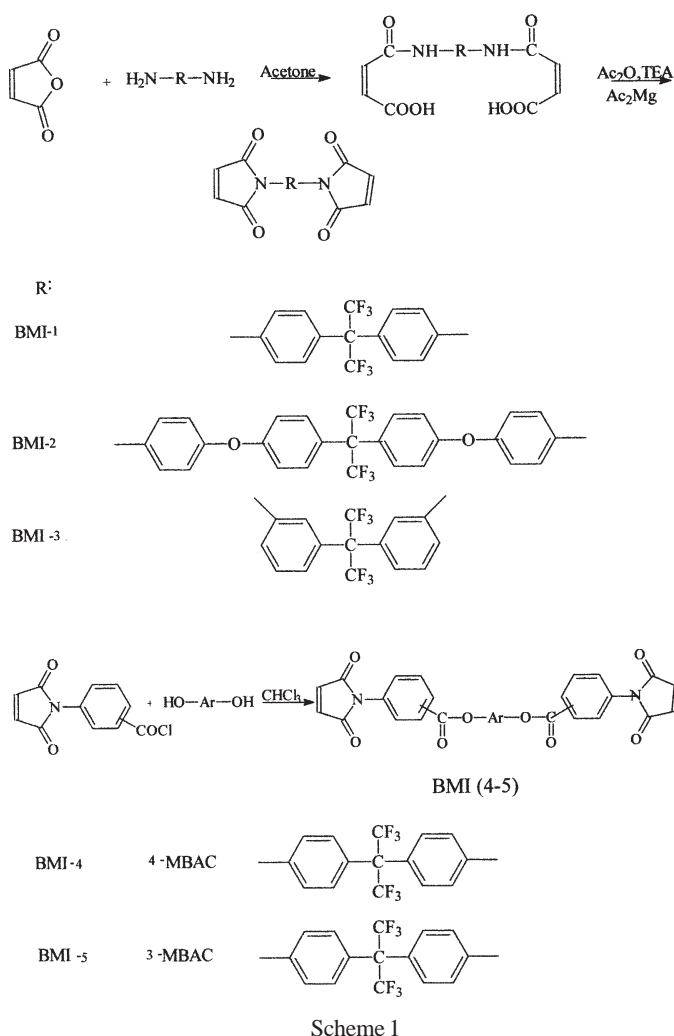
A large variety of polybismaleimides (PBMI) bearing end-capped reactive maleimide has been developed in the last year, in order to improve their processability and their properties. Still, most BMIs have also a number of disadvantages, such as: high melting and curing temperatures, poor solubility in ordinary solvents, brittleness of the final polymers due to the high crosslink density in the polymeric network [8-12]. Further attempts have been made to improve the processability and properties of these polymers by using monomers with different structures. Based on this concept, our main concern was to prepare bismaleimidic monomers having:

- hexafluoroisopropylidene groups;
- substituents in para or meta position;
- with or without ether or ester units.

## Experimental part

A scheme of the synthetic route to prepare bismaleimides is illustrated in scheme 1. Bismaleimide BMI (1-3) were synthesized [13-14].

The diamine (0.02mol) in 125 mL acetone was reacted with maleic anhydride (0.042mol) in 35 mL acetone, to give the corresponding bismaleimamic acid. In addition, the mixture was stirred for 30 min at 25°C, then the temperature was raised to 35°C. Over a period of 15 min, triethylamine (TEA) (0.02mol), acetic anhydride (0.15 mol) and magnesium acetate (0.04g) were added. The mixture was refluxed for 1.0 h under nitrogen atmosphere. The hot solution was filtered, cooled and poured into cold water. The product was washed with a solution of sodium carbonate (10%) until it becomes free from acetic acid. Finally, it was washed with water and dried in vacuum.



Bismaleimide BMI (4-5) were synthesized [18-20].  
3-Maleimido Benzoic Acid (3-MBA)  
4-Maleimido Benzoic Acid (4-MBA)

The products were prepared as described [15,16], (mp. 3-MBA; 236-240°C toluene; mp. 4-MBA; 225-230°C toluene; [15], 239-241°C and 225-228°C, respectively).

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3-Maleimido Benzoic Acid Chloride (3-MBAC)

4-Maleimido Benzoic Acid Chloride (4-MBAC)

The products were obtained as described [16]. (mp, 3-MBAC; 125-128°C dichloroethane; mp, 4-MBAC 168-171°C; [17] mp 4-MBAC, 170°.

Bismaleimides BMI (4-5) were synthesized [18].

3-MBAC or 4-MBAC (0.04 mol) in 50 mL  $\text{CHCl}_3$  was cooled in an ice bath. To this, TEA (0.025 mol) as acid acceptor and a solution of diphenol (0.02 mol) in 40 mL  $\text{CHCl}_3$  were added. After stirring for 1.0 h, the mixture was filtered and precipitated in petroleum ether. The product was filtered and treated with sodium bicarbonate solution and then thoroughly washed with water. The filtered precipitate was dried in a vacuum oven at 80°C.

#### Bismaleimide BMI-1

The product was recrystallized from acetone. Yield 71 %, mp 239-243 °C. IR (KBr)  $\text{cm}^{-1}$ : 1775 and 1715 (C=O imide), 1250-1180 (hexafluoroisopropylidene group).

Anal calcd. for  $\text{C}_{23}\text{H}_{12}\text{F}_6\text{N}_2\text{O}_4$  (%): C, 55.88; H, 2.44; F, 23.05; N, 5.66. Found: C, 56.23; H, 2.29; F, 23.37; N, 5.35.

#### Bismaleimide BMI-2

The monomer was recrystallized from DCE/ethanol. Yield 69 %, mp 146 °C, IR (KBr)  $\text{cm}^{-1}$ : 1780 and 1720 (C=O imide), 1250-1175 (hexafluoroisopropylidene group).

Anal calcd. for  $\text{C}_{35}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_6$  (%): C, 61.80; H, 2.97; F, 16.79; N, 4.12. Found: C, 62.17; H, 2.75; F, 16.97; N, 3.89.

#### Bismaleimide BMI-3

The product was recrystallized from DCE/ethanol. Yield 73 %, mp 176-178 °C. IR (KBr)  $\text{cm}^{-1}$ : 1775 and 1720 (C=O imide), 1245-1175 (-C(CF<sub>3</sub>)<sub>2</sub>).

Anal calcd. for  $\text{C}_{23}\text{H}_{12}\text{F}_6\text{N}_2\text{O}_4$  (%): C, 55.88; H, 2.44; F, 23.05; N, 5.66. Found: C, 55.49; H, 2.61; F, 22.83; N, 5.41.

#### Bismaleimide BMI-4

The monomer was recrystallized from DCE/ethanol. Yield 68%, mp 210-214 °C. IR (KBr)  $\text{cm}^{-1}$ : 1780 and 1730 (C=O imide), 1750 (C=O ester), 1215 - 1180 (-C(CF<sub>3</sub>)<sub>2</sub>).

Anal calcd. for  $\text{C}_{37}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_8$  (%): C, 60.49; H, 2.74; F, 15.51; N, 3.81. Found: C, 60.21; H, 2.53; F, 15.73; N, 3.69.

#### Bismaleimide BMI-5

The product was recrystallized from DCE/ethanol. Yield 69%, mp 121°C. IR (KBr)  $\text{cm}^{-1}$ : 1785 and 1720 (C=O imide), 1745 (C=O ester), 1225-1175 (-C(CF<sub>3</sub>)<sub>2</sub>).

Anal calcd. for  $\text{C}_{37}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_8$  (%): C, 60.49; H, 2.74; F, 15.51; N, 3.81. Found: C, 60.31; H, 2.89; F, 15.35; N, 3.72.

#### Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer, using the KBr pellet technique. <sup>1</sup>H-NMR spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 MHz, using DMSO-d<sub>6</sub> as solvent and tetramethylsilane as a internal standard. Differential scanning calorimetry (DSC) measurements were done by using a Mettler, instrument DSC 12E, with a heating rate of 10 °C/min in air. Melting points were determined with Gallenkamp hot-block melting point apparatus, by thermo-optic analysis (TOA) and DSC. TGA was carried out in air with an F. Paulik Derivatograph, at a heating rate of 12 °C/min. The volume resistivity was measured using a TETRALIN III Straton electrometer and dielectric constant was measured using a digital RLC meteo EO 711 at 1 MHz.

#### Results and discussions

The IR spectra of monomers BMI (1-5) showed characteristic carbonyl doublet in the range 1785-1775 and 1730-1715  $\text{cm}^{-1}$ . Bismaleimides BMI (4-5) exhibited an absorption band at 1750-1745  $\text{cm}^{-1}$  due to ester groups. The absorption peaks around 1250-1175  $\text{cm}^{-1}$  of monomers BMI (1-5) correspond to the hexafluoroisopropylidene groups. Figure 1 presents the infrared (IR) spectra of BMI-1.

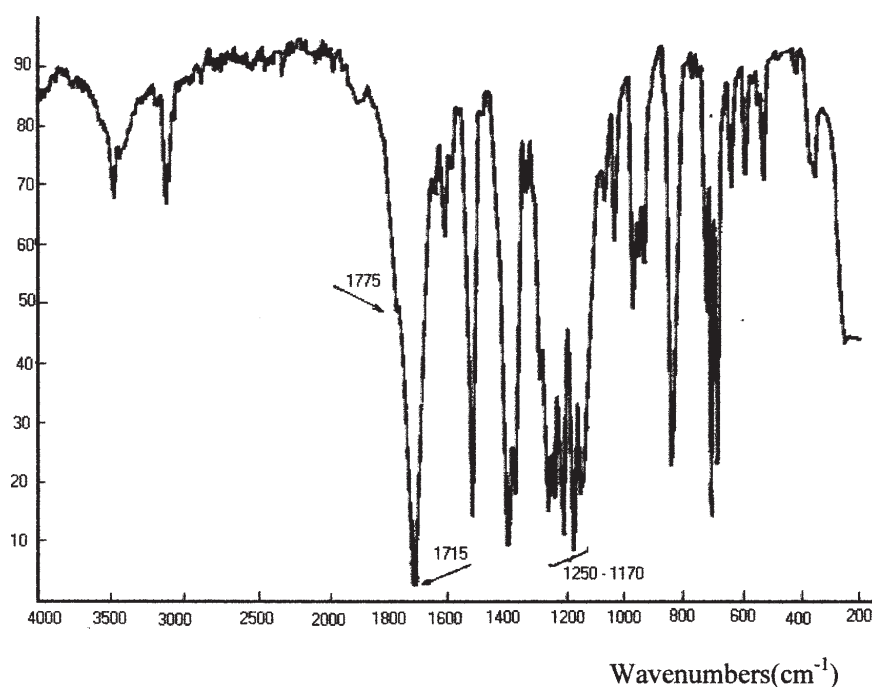


Fig. 1. The IR spectra of BMI-1

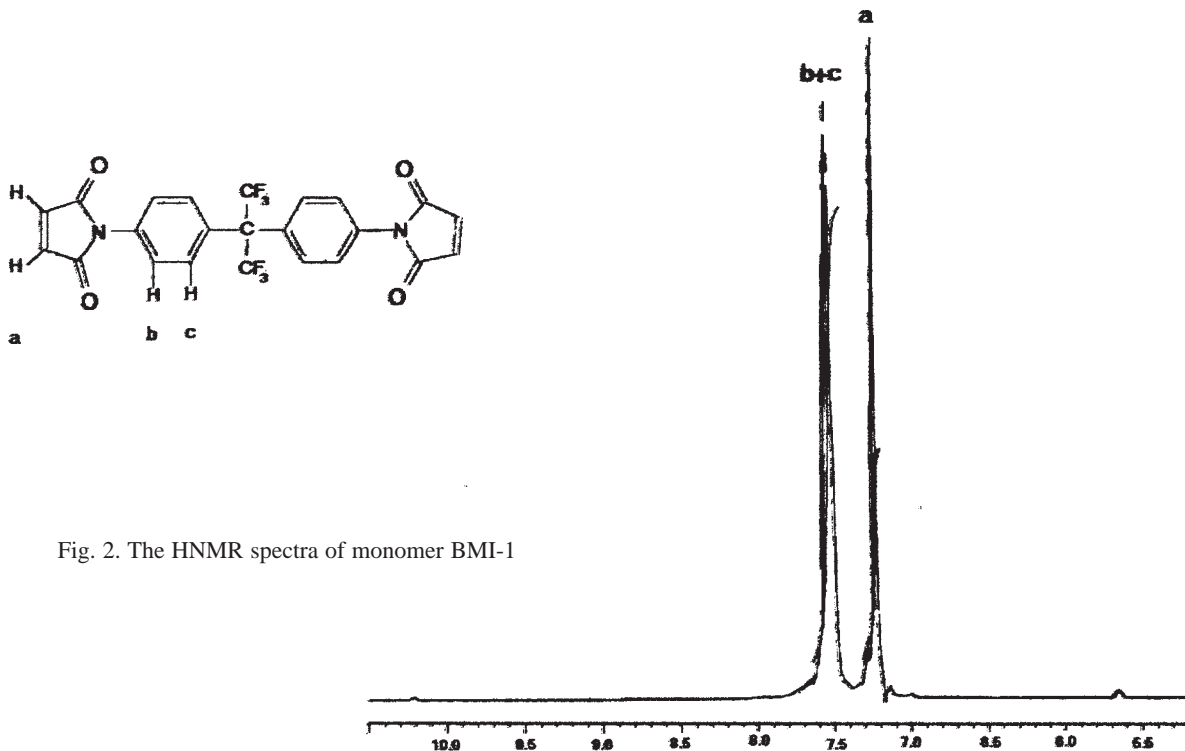


Fig. 2. The  $^1\text{H-NMR}$  spectra of monomer BMI-1

The  $^1\text{H-NMR}$  spectra of monomer BMI-1 and BMI-4 confirmed their chemical structures. Figure 2 presents the  $^1\text{H-NMR}$  spectra of bismaleimide BMI-1. The aromatic protons of monomer, appear as a doublet in the range 7.534-7.516 ppm (Ar-H, ortho to maleimide and Ar-H, ortho to  $-\text{C}(\text{CF}_3)_2$ ). Bismaleimide BMI-1 exhibited a singlet in the region 7.231 ppm associated to olefinic protons.

From figure 3 it can be seen that the aromatic protons of bismaleimide BMI-4 appear as three separated doublets in the range 8.266-8.245 ppm (Ar-H, ortho to  $-\text{COO}$ ), 7.646-7.625 ppm (Ar-H, ortho to maleimide) and 7.489-7.455 ppm (Ar-H ortho to OCO and Ar-H ortho to  $-\text{C}(\text{CF}_3)_2$ ).

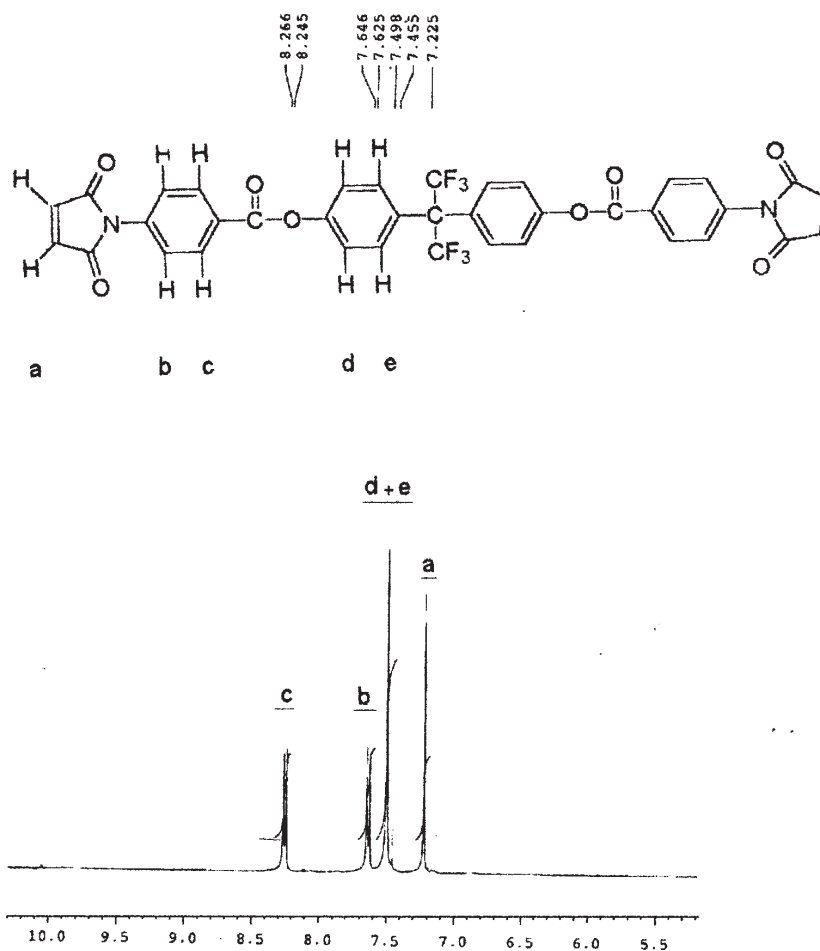


Fig. 3. The  $^1\text{H-NMR}$  spectra of monomer BMI-4

**Table 1**  
SOLUBILITY OF BISMALIMIDE MONOMERS <sup>a</sup>

Monomer	Solvent					
	NMP	DMF	CHCl <sub>3</sub>	DMSO	Toluene	Acetone
BMI-1	++	++	++	±	+	++
BMI-2	++	++	++	±	++	++
BMI-3	++	++	++	±	±	++
BMI-4	++	++	++	++	±	+
BMI-5	++	++	++	++	++	++

a. Solubility : (++) soluble at room temperature; (+) soluble on heating; (±) Partially soluble on heating

**Table 2**  
PHYSICAL AND THERMAL PROPERTIES OF THE PREPARED BISMALIMIDES

Monomer	General appearance	Yield (%)	MP (°C)	FC <sup>a</sup> (%)	DSC				TG		
					T <sub>end</sub> (°C)	T <sub>exo</sub> (°C)	T <sub>p</sub> (°C)	ΔH (kJ/mol)	IDT (°C)	PDT <sub>max</sub> (°C)	Y <sub>c</sub> (%)
BMI-1	Cream	71	224 <sup>b</sup>	23.05	240	277	-	65	393	456	39
BMI-2	Light-yellow	69	146-	16.79	154	295	261	70	360	337, 515 <sup>d</sup>	41
BMI-3	Yellow	73	176-178	23.05	186	348	291	84	375	398	36
BMI-4	Light-yellow	68	210-214	15.51	220	297	245	82	443	459, 545 <sup>d</sup>	49
BMI-5	Light-yellow	69	121 <sup>c</sup>	15.51	214	300	266	117	422	446	45

- a. Fluorine content.  
b. Melting point as measured by DSC.  
c. Melting point by TOA.  
d. Two-stage decomposition.

Also, the monomer BMI-4 showed a singlet in the region 7.225 ppm due to the olefinic protons.

The solubility of the monomers in various solvents was evaluated and is presented in table 1. All bismaleimide monomers exhibited good solubilities in NMP, DMF and CHCl<sub>3</sub>. It can be seen that the solubility in DMSO of bismaleimides BMI (4-5) was found to be higher than that of BMI (1-3) (due to the influence of ester groups). Except for the first three solvents (NMP, DMF and CHCl<sub>3</sub>) in which all BMIs are soluble, differences appear for the other three solvents (DMSO, toluene and acetone). As for DMSO, a better solubility was observed in the case of BMI (4-5), compounds bearing ester groups.

Considering the solubility in toluene, a hierarchy can be made from BMI-2 and BMI-5, which have a good solubility, to BMI-1 and finally BMI-3 and BMI-4. Taking into account the acetone, it was noticed that BMI (1-3) and BMI-5 showed a good solubility, while for BMI-4 heating is required for solubilization.

The monomers were analyzed by differential scanning calorimetry (DSC) (fig. 4). DSC curves for all bismaleimides were characterized by a sharp melting endotherm (T<sub>end</sub>) in the range 154-240°C, due to

their melting (table 2). The reactivities of these bismaleimides are in the temperature range of 245-291°C (except for BMI-1, for which the onset temperature for curing reaction was overshadowed by the melting endotherm). The monomers BMI (1-5) exhibited an exothermic transition (T<sub>exo</sub>) associated to thermal curing at 277-348°C. The onset temperatures for curing reaction (T<sub>p</sub>) are in the range 245-291°C (except for BMI-1). It is to notice that for BMI-2 and BMI-5 their onset temperature has close values, while for BMI-3 and BMI-4 the temperatures differ significantly.

Thermal stabilities of bismaleimides were evaluated by TGA. The data of the onset of initial decomposition temperature (IDT), temperature of maximum decomposition (PDT<sub>max</sub>) and percent char yield at 600°C (Y<sub>c</sub>%) are listed in table 2. The initial decomposition temperature of the compounds is in the range 375 - 443°C. Monomer BMI-4 showed the highest thermostability, whereas BMI-3 has the lowest thermostability. Ester units and substituents position have a great influence. The bismaleimide BMI-2 and BMI-4 showed two-stage decomposition. The multistage decomposition observed for BMI-2 and BMI-4 is due to the combination of different chemical segments in the polymer chain.

Electrical insulating properties of the cured bismaleimides BMI (1-5) were evaluated on the basis

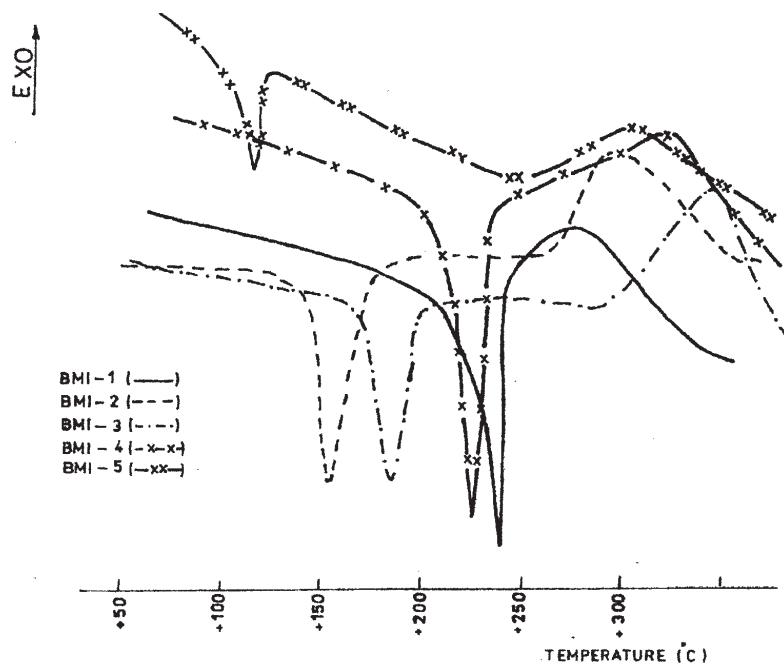


Fig. 4. DSC curves of monomers

Monomer	$\rho$ ( $\Omega \cdot \text{cm}$ ) <sup>a</sup>	$\epsilon_r^b$
BMI-1	$1.56 \times 10^{17}$	4.0
BMI-2	$3.42 \times 10^{17}$	3.4
BMI-3	$2.11 \times 10^{16}$	4.1
BMI-4	$2.86 \times 10^{16}$	3.8
BMI-5	$3.72 \times 10^{16}$	4.2

Table 3  
ELECTRICAL PROPERTIES OF  
THE CURED MONOMERS

- a. Volume resistivity  
b. Dielectric constant

of the value of their dielectric constant and electrical volume resistivity. The samples for measurements were prepared in the form of a pellet. These properties are presented in table 3. The dielectric constant of the products is in the range of 3.4-4.2 and the electrical volume resistivity ranges between  $2.11 \cdot 10^{16}$  and  $3.42 \cdot 10^{17} \Omega \cdot \text{cm}$ .

### Conclusions

A series of bismaleimides with hexafluoroisopropylidene groups having different structures ( ester or ether units, with para or meta linkages in the monomer chain) were synthesized and characterized by IR and <sup>1</sup>H-NMR spectra and elemental analysis.

Thermal characterization of these monomers was accomplished by DSC and TGA.

In addition, these compounds were characterized by electrical measurements, such as dielectric constant and volume resistivity. All properties of these monomers depend on the structure of the bridging units.

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