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Preparation and characterization of new structures of bismaleimides

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New bismaleimide compounds containing various structures (ester, ether, amide units) were synthesized by the reaction of bisphenols or diamines with 3 or 4-maleimidobenzoyl chloride. The monomers were characterized by Fourier transformed infrared (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. Thermal characterization of monomers was accomplished by differential scanning calorimetry (DSC) and dynamic thermogravimetric analysis (TGA).

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1. Introduction

Bismaleimide resins are a class of polyimides obtained by polyaddition reactions of bismaleimide compounds having unsaturated end groups. These resins contain unsaturated double bonds which can be thermally polymerized without the formation of volatile by-products (that can cause voids) and can be processed in a manner similar to the epoxies.

These resins are among the most important compounds used in the electronics/electrics, nuclear and aerospace/aircraft industry because of their high thermal and thermooxidative stability, excellent chemical, radiation and corrosion resistance, good water resistance, fire resistance and good retention of thermomechanical properties even after long ageing times at 250ºC. Owing to their high performance–to cost ratio, excellent processability, balance of thermal, electrical and mechanical properties, bismaleimide resins have become one of the most important high performance thermosetting engineering plastics with various applications [1-7].

All these make them attractive for various applications such as high-performance composite matrices for multi-layer printed circuit boards for large-scale computers, advanced composites for optoelectronics, aerospace industries, structural adhesives and for fabrication of high-performance electrooptical devices [8-16]. Major applications of these resins are printed circuit boards carbon-fiber composites for aero-engines and military aircraft.

Polybismaleimides have potential applications in second order, non-linear optical (NLO) materials, due to their high glass transition temperatures which maintain the critical orientation of the NLO chromophores [17-18].

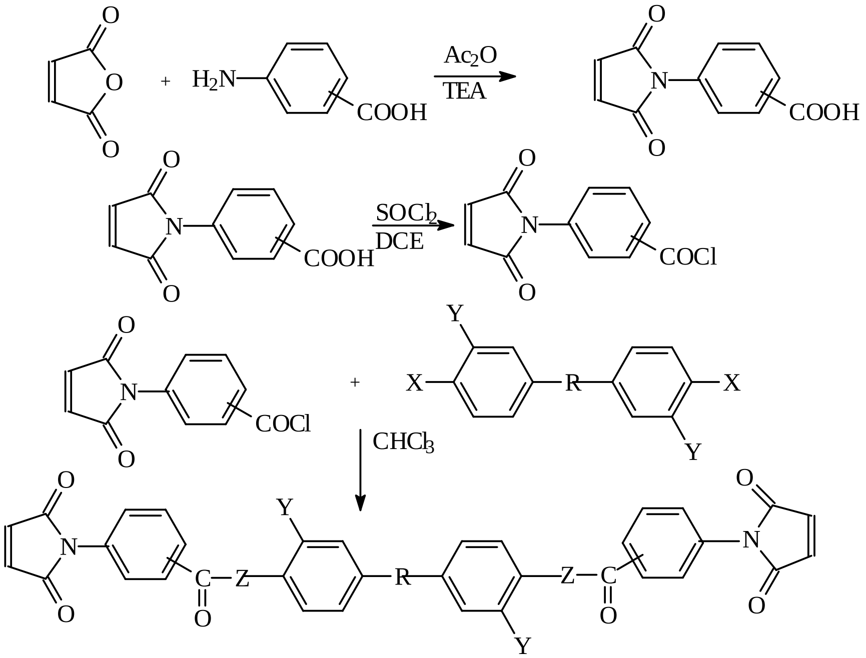
Bismaleimides are interesting candidates for high temperature applications but suffer from relative brittleness because of their highly crosslinked structures. Also, these compounds have high melting and curing temperatures, solvent retention, which limit their processability [19-22].

The insertion of atoms or groups of atoms in the backbone of monomers which improves the processability and solubility can be used to reduce the brittleness of these compounds. It is still considered desirable to synthesize new bismaleimide monomers in order to improve the processing properties of resins which they constitute and to improve the physical and mechanical properties of the cured polymers. This article presents a study of the influence of the monomer structures on the polymer properties.

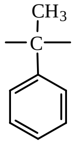
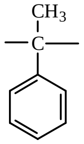
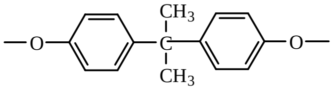
2. Experimental

2.1. Materials

The materials used in this research were: maleic anhydride (Fluka, Buchs, Germany), 3(4)-aminobenzoic acid (Fluka, Buchs, Germany), thionyl chloride from Merch was freshly distilled, 3,3'-dimethoxybenzidine (Fluka, Buchs, Germany), 4,4'(1-phenylethylidene)bisphenol (Aldrich), 2,2-bis[(4-amino-phenoxy)phenyl]propane (Aldrich), acetic anhydride (Merck), triethylamine (Fluka). Commercial solvents such as acetone (Chimopar SA), 1,2-dichloroethane (Fluka, Buchs, Germany), chloroform (Chemical Company) were dried and purified by standard methods.



BMI(1-4)

Monomer	X	R	Y	Z	Phenyl substitude
BMI—1	—OH		—H	—O—	para
BMI—2	—OH		—H	—O—	meta
BMI—3	$—NH_2$	—	$—OCH_3$	—NH	para
BMI—4	$—NH_2$		—H	—NH	meta

Scheme 1

2.2. General procedure for the preparation of bismaleimides BMI(1-4)

Monomers BMI(1-4) were synthesized following the literature [23], via the reaction of 3 or 4-maleimidobenzoyl chloride with various biphenols or diamines, according to Scheme 1.

3-Maleimido Benzoic Acid (3-MBA)

4-Maleimido Benzoic Acid (4-MBA)

The products were prepared as described [24], mp 3-MBA: 236-240ºC toluene; mp 4-MBA: 225-230ºC toluene. Reference [25], 239-241ºC and 225-228ºC, respectively.

3-Maleimido Benzoic Acid Chloride (3-MBAC)

4-Maleimido Benzoic Acid Chloride (4-MBAC)

The products were prepared as described in literature [26]; 3-MBAC: 125-128ºC; 4-MBAC: 169-171ºC. Reference [27], mp 4-MBAC 170ºC.

Bismaleimide monomers were synthesized following the literature:

3-MBAC or 4-MBAC (0.1mol) in 100 mL $CHCl_3$ was cooled in an ice bath. Triethylamine (0.05 mol) as acid acceptor and a solution of diphenol or diamine (0.05 mol) in 75 mL $CHCl_3$ was added. After stirring for 1.0-1.5 h, the mixture was filtered and precipitated in petroleum ether. The product was filtered and treated with sodium bicarbonate solution, and then thoroughly washed (3 times) with water. The filtered precipitated product was recrystallized.

Bismaleimide BMI-1

The monomer was recrystallized from acetone/water. Yield 71%, mp 230-234ºC, FTIR cm^{-1}: 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, 73.71; H, 3.83; N, 4.36.

Bismaleimide BMI-2

The product was recrystallized from acetone. Yield 68%, mp 136°C, FTIR cm^{-1}: 1773 and 1720 (C=O imide), 1745 (C=O ester).

Anal calcd. for $C_{42}H_{28}N_2O_8$ (%): C,73.23; H, 4.09; N, 4.07. Found: C, 74,13; H, 3.87; N, 4.23.

Bismaleimide BMI-3

The monomer was recrystallized from DMF. Yield 73%, mp 298-302ºC, FTIR cm^{-1}: 1774 and 1719 (C=O imide), 3435 (NH-amide), 1256 (-O- ether).

Anal calcd: for $C_{36}H_{26}N_4O_8$(%): C,67.28; H, 4.07; N, 8.71. Found: C, 67.75; H, 3.83; N, 8.97.

Bismaleimide BMI-4

The product was recrystallized from acetone. Yield 70%, mp 125ºC, FTIR cm^{-1}: 1775 and 1719 (C=O imide), 3365 (NH-amide), 1229 (-O- ether).

Anal. Calcd. for $C_{49}H_{36}N_4O_8$(%): C, 72.76; H, 4.48; N, 6.92. Found: C, 73.07; H, 4.69; N, 7.13.

2.3 Measurements

The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 M7, using DMSO-d_6 as solvent and tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) measurements were performed using a Du Pont Instruments 912 DSC apparatus with a heating rate of 10ºC/min in N_2. Polarized light microscopy (PLM) investigations were performed with an OlympusBH-2 polarized light microscope fitted with a THMS600/HSF9I hot stage magnification 200x. Melting points were determined with a Gallenkap hot-block melting point apparatus. TGA was carried out in air, with a F. Paulik Derivatograph at a heating rate of 12ºC/min.

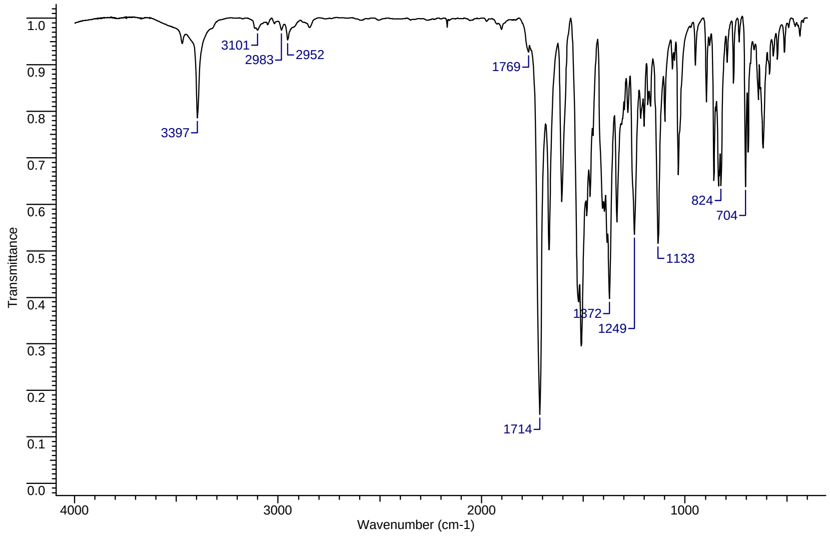


Fig. 1. The FTIR spectrum of BMI-3

3. Results and discussion

3.1. FTIR analysis

The chemical structure of monomers BMI(1-4) was confirmed using spectroscopic FTIR and ^{1}H-NMR and elemental analysis. The FTIR spectra of bismaleimide monomers bearing ester or amide groups showed the carbonyl doublet characteristic peak in the range of 1780-1770 and 1725-1710 cm^{-1} due to C=O from imide group. All compounds showed an absorption band at 2993-2928 cm^{--1} attributed to $–CH_3$ groups, whereas BMI-3 and BMI-4 exhibited a band at 1256 and 1229 cm^{-1} respectively, due to ether units. Also, an absorption band at 1734 and 1745 cm^{-1} appeared for the monomers BMI-1 and BMI-2 due to ester groups. The monomers BMI-3 and BMI-4 showed absorption bands at 3435 and 3365 cm^{-1} attributed to amide groups. Figure 1 presents the FTIR spectrum of BMI-3.

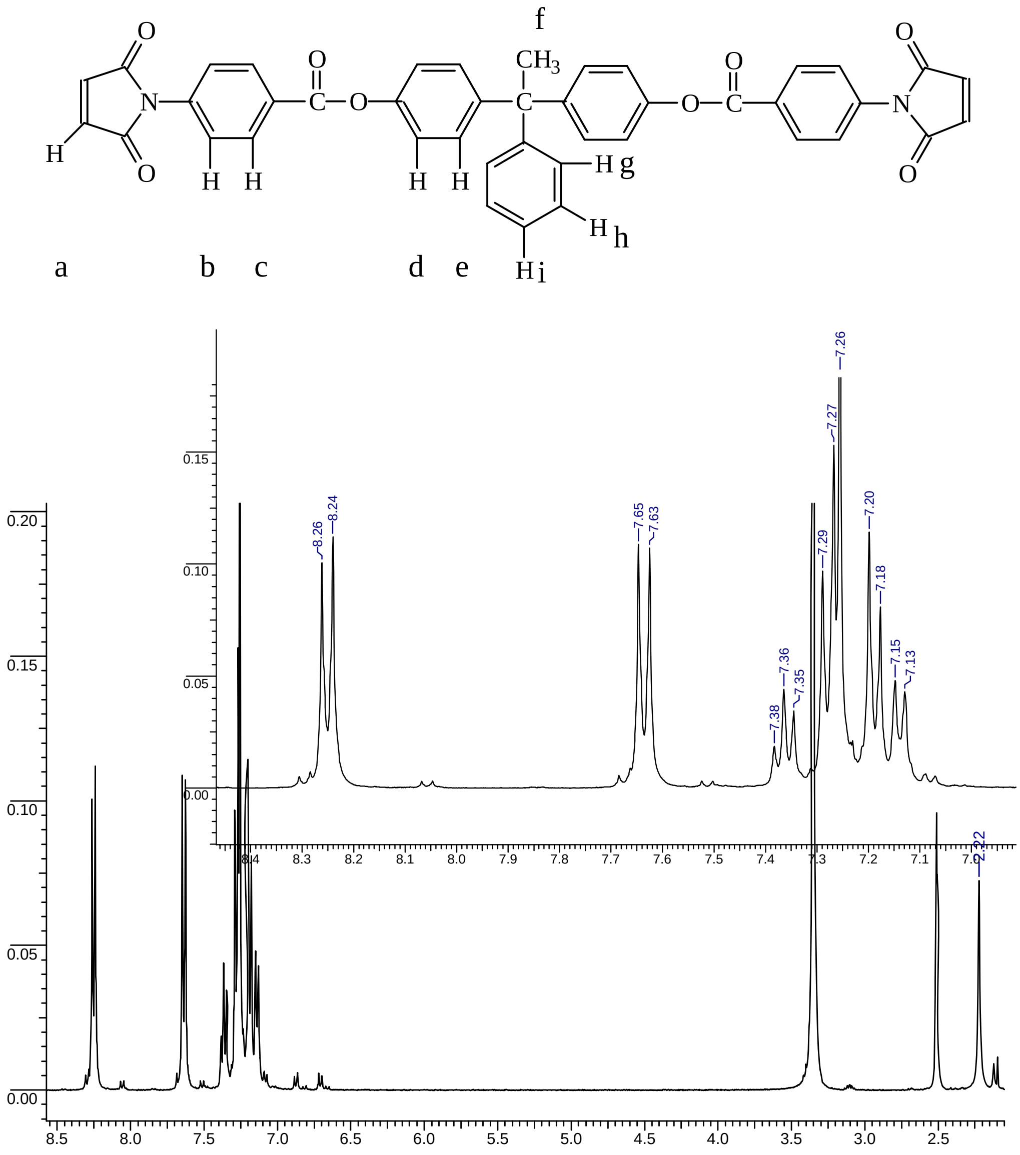


Fig. 2. The ^{1}H-NMR spectrum of BMI-1.

3.2. ^{1}H-NMR analysis

The ^{1}H-NMR spectrum of BMI-1 (Figure 2) confirmed its chemical structure as follows: aromatic protons of bismaleimide BMI-1 appear as two doublets in the range 8.262-8.240 ppm (attributed to aromatic protons ortho to –C=O ester group) and another doublet in the range 7.647-7.625 ppm (due to aromatic protons ortho to maleimide). Aromatic protons in the range 7.290-7.268 ppm and 7.199-7.177 ppm are due to protons from neighborhood of –O– and $–C(CH_3)_2$ units respectively on the main chain. Other aromatic protons appear in the range 7.383-7.346 ppm for H_h, 7.221-7.210 ppm for H_i and 7.140-7.125 ppm for H_g respectively (protons on the pendant phenyl group). Also, the ^{1}H-NMR spectrum showed a singlet at 2.224 ppm attributed to protons of methyl group, and a singlet at 7.245 ppm due to olefinic protons.

Elemental analysis data showed a good concordance between the calculated and experimental values of percentage weight for C, H and N.

3.3. Thermal characterization

Thermal characterization of monomers was accomplished by differential scanning calorimetry (DSC), polarizing light microscopy (PLM) and dynamic thermogravimetric analysis (TGA).

The DSC curves for the monomers BMI(1-2) and BMI-4 were characterized by a sharp melting endotherm

(T_{end}) in the temperature range 135-231°C and it is due to the melting of these monomers. These compounds exhibited an exothermic transition associated with thermal curing at 156-203°C. The onset temperature for curing reaction (T_p) in the case of bismaleimide BMI(1-2) was in the range 172-249°C. The onset temperature for curing reaction in the case of monomer BMI-4 was overshadowed by melting endotherm. The higher onset of cure of BMI-1 may be due to the high electron-withdrawing capacity of the atom groups on the main chain.

Melting point of BMI-3 could not be recorded by DSC when heated from room temperature to 340°C, although it was observed to darken at about 290°C. However, if the capillary apparatus was preheated to 285°C prior to inserting the sample, the sample melted, flowed and polymerized. Crosslinking occurred almost instantly after melting.

Table I. Physical and Thermal Properties of the Bismaleimides.

Monomer	**General appearance**	**MP (°C)**	**T_{end} (°C)**	**T_p (°C)**	**IDT (°C)**	**PDT_{max} (°C)**	**Y_c (%)**
BMI-1	White	230-234	231	249	426 (449) [a]	450, 500 (460)	29 (47)
BMI-2	Light-yellow	136[b]	151	172	340	385, 590	33
BMI-3	Yellow	298-302	-	-	415	620	49
BMI-4	Light-yellow	125[b]	135	-	367	510, 660	20

[a] Numbers in parentheses indicate the values in nitrogen atmosphere (BMI-1)

[b] Melting point as measured by DSC

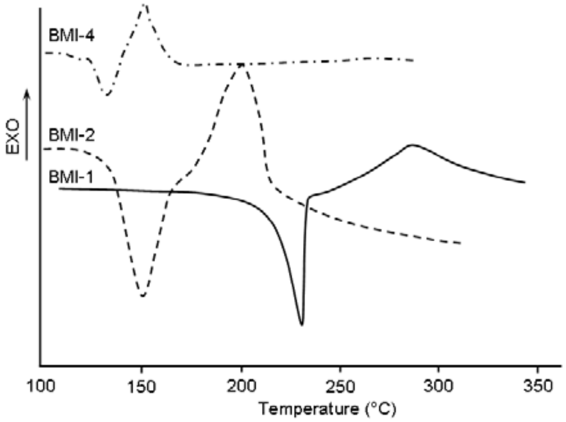
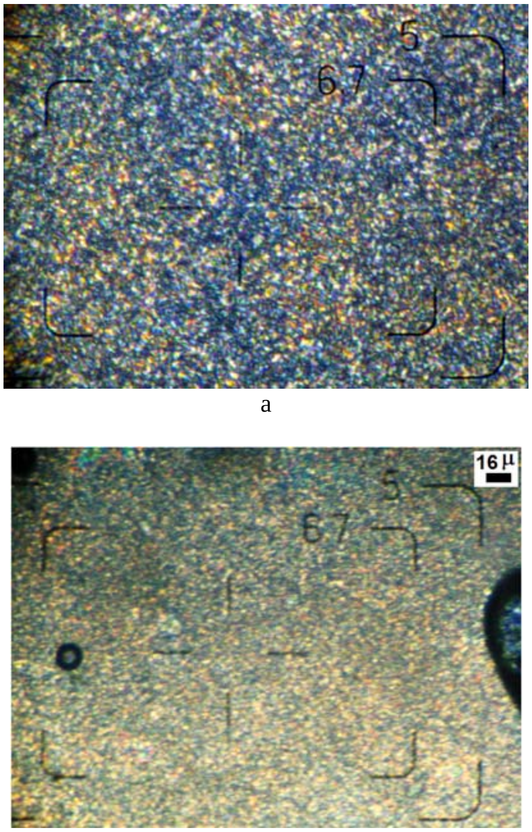


Fig. 3. DSC scans of bismaleimide monomers BMI (1-2) and BMI-4 in nitrogen atmosphere at heating rate of 10 ºC/min

Liquid crystalline phases were not observed for BMI-3. It appears that the melting behavior is only evident when the heating rate is sufficiently fast to preclude extensive crosslinking of the sample during the heating process.

Also, the bismaleimides BMI(1-4) have been investigated by using polarizing light microscopy (PLM). Under PLM it was observed that samples BMI-1 and BMI-2 presented a strong birefringence with a granular texture (Figure 4) which is difficult to assign to a known liquid crystalline phase [28].

Liquid crystalline phases were not observed for BMI-3 and BMI-4.



a

b

Fig. 4. Optical polarized light microscopy images of: a) BMI-1, 239°C, magnification 400x; b) BMI-2, 117°C, magnification 200x.

The thermal stabilities of cured resins were evaluated by TGA (Figure 5 and Table I). The decomposition of these compounds with various structures starts between 340 and 426°C and the rapid weight loss (PDT_{max}) occurs in the region 385-660°C under air. From Table I it can be seen that the initial decomposition temperature (IDT) in air was lower than that in N_2 (for monomer BMI-1). In the air atmosphere the starting temperature of weight loss varied from 340°C for monomer BMI-2 to 426°C for bismaleimide BMI-1. The bismaleimides BMI(1-2) and BMI-4 showed two-stage decomposition. The multi-stage decomposition observed for these monomers is due to the combination of chemically different segments in the polymer chain. The bismaleimide BMI-1 and BMI-3 possessed better thermooxidative stability than BMI-2 and BMI-4.When the functional group was originally in 3 (i.e., meta) position, thermal stability was lower than the functional group was in 4 (i.e., para) position. Considering IDT as a thermostability criterion, the following order can be established: BMI-1> BMI-3 > BMI-4 > BMI-2. The compound BMI-3 showed the highest value of char yield at 700°C (Y_c), compared to monomers BMI(1-2), and BMI-4.

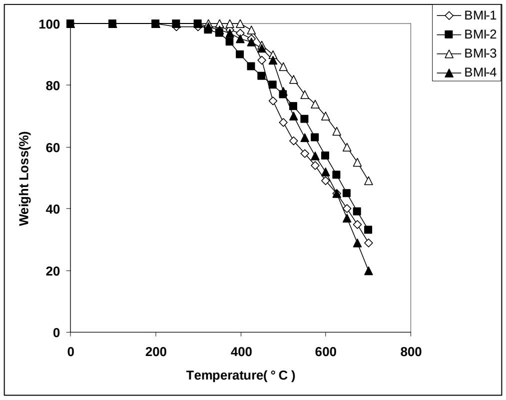


Fig. 5. TGA curves of bismaleimides BMI(1-4)

4. Conclusion

Bismaleimide monomers with various structures (ether, ester, amide units, with para or meta linkages in the monomer chain and other groups between benzene rings) were synthesized. The structure of monomers was confirmed by spectroscopy (FTIR and ^{1}H-NMR) and elemental analysis. Thermal behavior of these monomers was accomplished by differential scanning calorimetry and using hot stage PLM. The thermal stability of the samples was investigated by TGA in air. The reactivity and thermal stability of the monomers BMI(1-4) depend on the structure of the bridging units as well as the substituent position. These bismaleimide monomers may be potential candidates for thermoset material in composite manufacture.

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