# THERMAL, MECHANICAL AND DIELECTRIC PROPERTIES OF SOME POLYASPARTIMIDES

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Bismaleimide monomers with various structures and polymers thereof were synthesized and their structures were confirmed by Fourier transformed infrared (FTIR) and proton nuclear resonance (^{1}H-NMR) spectroscopy. The resulted compounds were characterized by thermal analysis – differential scanning calorimetry (DSC) and thermogravimetry (TGA). Some of these polymers exhibited film-forming ability. Mechanical and dielectric properties of these materials were investigated.
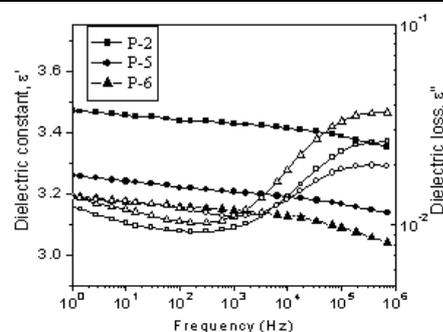
INTRODUCTION

Bismaleimide resins are among the most important compounds because of high thermal and thermooxidative stabilities, good retention of the mechanical properties even after long ageing times at 250 °C, excellent chemical, corrosion and radiation resistance, good water and fire resistance, and relatively low cost. These resins are of great interest because of their easy processability by resin transfer molding, without formation of volatile by-products.[1-8] Due to the high temperature resistance, these resins are widely used as high performance composite matrices for multilayer printed circuit boards for large scale computers, advanced composites for aerospace/aircraft industries, electrics/electronics and structural adhesives.[9-11] Also these compounds have potential applications in second order, non-linear optical (NLO) materials, due to their glass transition temperature, which maintain the critical orientation of the NLO chromophore.

These compounds are addition-type polyimides produced from bismaleimides that have unsaturated end groups. The reactivity of bismaleimide monomers is determined by the ability of their double bond to add monomers bearing an active hydrogen atom to act as a dienophyle in Diels-Alder reactions and to enter into reactions of radical and anionic homopolymerization and copolymerization with other monomers containing unsaturated bonds or with cyclic compounds (cyclobutane derivatives or heterocycles).

Unfortunately, these resins show some disadvantages, such as brittleness (due to their high crosslinking density), and high melting and curing temperature which considerable restrict their applications.[12-13]

A series of properties can be adjusted by varying the nature of aromatic ring systems and the number of flexible linkages within the polymer chain. Much effort has been dedicated to improve the processability of polyaspartimides, e.g. to find new solution systems and to modify their structures by

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introduction of bulky substituents and flexible linkages into backbone, or by polymerization.

The goal of the current research paper was to prepare new bismaleimide monomers and polymers with various structures which confer to polymer especially improved properties and easy processability.

RESULTS AND DISSCUSION

The chemical structure of all synthesized bismaleimides was confirmed by means of elemental analysis, FTIR and ^{1}H-NMR spectroscopy. The FTIR spectra of monomers showed two doublets characteristic peaks in the range 1715-1713 cm^{-1} attributed to C=O from imide group. Monomers BMI-1 and BMI-3

showed an absorption band in the range 2977-2924 cm^{-1} due to aliphatic group. All monomers exhibited bands in 1254-1240 cm^{-1} range attributed to the ether group.

The monomers were characterized also by H-NMR spectroscopy that confirmed chemical structure. Fig. 1 shows the ^{1}H-NMR spectrum of compound BMI-2. The aromatic protons appear as a doublet in the 8.034-8.011 ppm range (attributed to the protons H_e), while a doublet appears in the 7.479-7.473 ppm range (due to the aromatic protons H_f). The aromatic protons in the 7.382-7.360 ppm range are due to the protons *ortho* to maleimide. The signal in the 7.290-7.262 ppm range corresponds to the aromatic protons H_d. A triplet in the 7.199-7.177 ppm range is attributed to the aromatic protons H_c and olefinic protons.
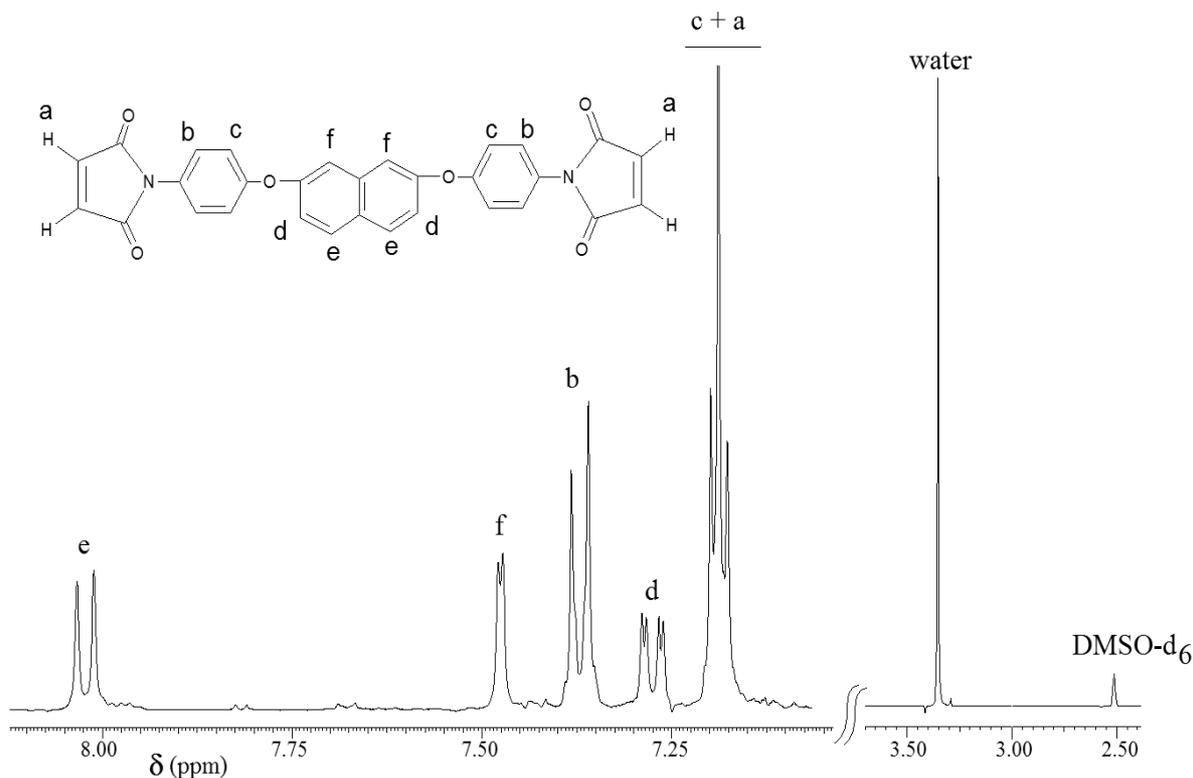

Fig. 1 – ^{1}H-NMR spectrum of monomer BMI-2.

Table 1

Physical and thermal properties of monomers BMI(1-4)

Monomer	M.P. (°C)	DSC				TGA		
		T_{end} (°C)	T_{exo} (°C)	T_p (°C)	ΔH (Kj/mol)	IDT (°C)	PDT_{max} (°C)	Y_c^{700} (%)
BMI-1	107-111	110	306	227	49	451	487	52
BMI-2	92-96	91	279	225	-	427	448, 553	50
BMI-3	173-176	178	-	234	-	394	427	36
BMI-4	196-173	177	283	215	59	455	480	53

The thermal behavior for bismaleimides BMI (1-4) was investigated by DSC and TGA and some data are presented in Table 1. The onset temperatures for curing reaction of these bismaleimides were in the 215-234 °C range. The reactivity of the C=C double bond from maleimide ring is influenced by chemical nature (electron-withdrawing or electron-donating capacity) of the residue between maleimide groups.

The thermal stability of these monomers was investigated by TGA in nitrogen. The initial decomposition temperatures (IDT) of monomers are in the region 394-455 °C. It is observed that IDT is higher for monomers BMI (1-2) and BMI-4, while BMI-3 shows smaller value of IDT. The percentage char yield at 700 °C varied between 36 and 53 %. The highest char yield (50-53 %) was observed for BMI (1-2) and BMI -4, while BMI-3

shows the least value (a higher percent for the aliphatic structure).

Polymer synthesis

A series of linear polyaspartimides was obtained by a Michael addition reaction and the results are summarized in Table 2. The polymers were synthesized by addition of the diamine, such as 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane (APEE), 4,4-diaminodiphenylether (DDE), 4-[4-[-[1-[4-(4-aminophenoxy)phenyl]-1-phenyl-ethyl]phenoxy]aniline (BAPDP) and 2,4-diamino-4'-methylazobenzene(DMAB) to bismaleimide monomers in NMP at 90-95 °C. The polymers were isolated by pouring the reaction mixture into methanol. All polymers were redissolved in fresh solvent, precipitated in a nonsolvent medium, and dried for 25 h in a vacuum oven at 75-80 °C.

Table 2

Reaction between bismaleimides and diamines

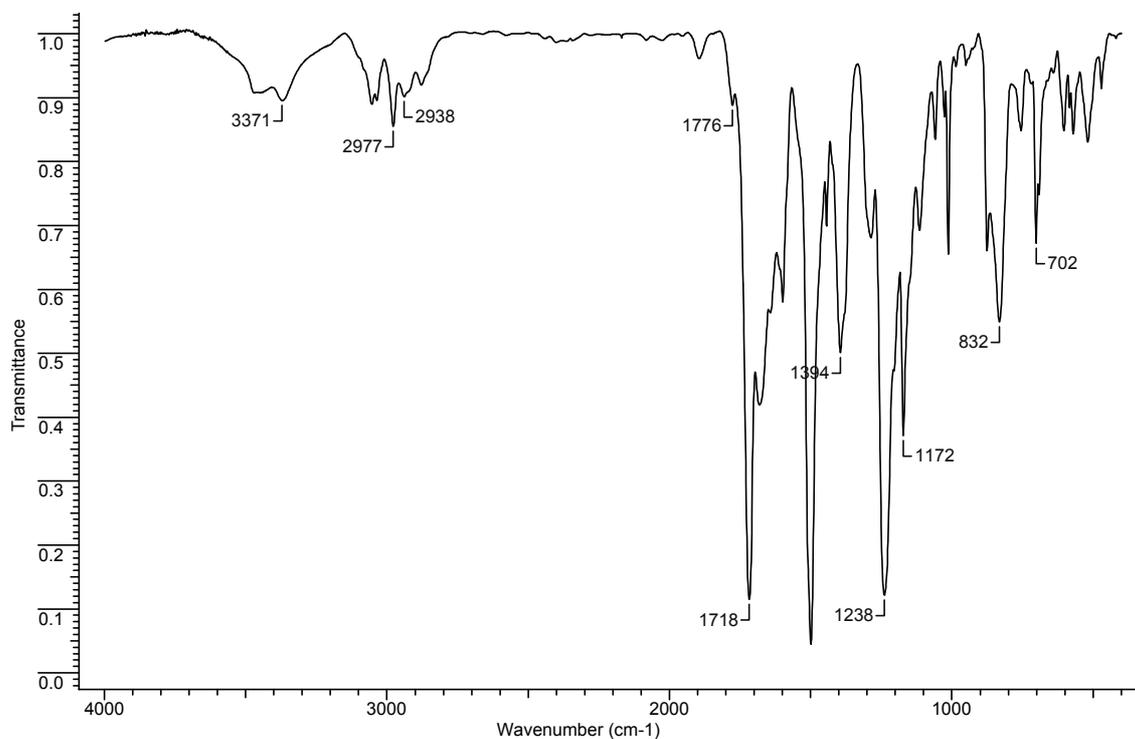| Polymer	BMI	Diamine	Reaction temp. (°C)	Reaction time (h)	Conc. (%)	Solvent	Films prop.
P-1	BMI-1	DDE	95	30	7	*m*-cresol	Flexible
P-2	BMI-2	APEE	95	20	10	NMP	Flexible
P-3	BMI-2	DDE	90	35	10	NMP	Brittle
P-4	BMI-3	DMAB	95	35	10	NMP	Flexible
P-5	BMI-4	APEE	90	20	10	*m*-cresol	Flexible
P-6	BMI-1	BAPDP	90	30	10	NMP	Brittle

Fig. 2 – FTIR spectrum of polymer P-6.

The structure of linear polyaspartimides was confirmed by means of FTIR spectroscopy. Fig. 2 presents the spectrum of polymer P-6. Two characteristic carbonyl bands around 1776 and 1718 cm^{-1} are due to asymmetric and symmetric stretching vibration. Other bands were observed in the range 2977-2938 cm^{-1} and are ascribed to aliphatic group (-CH$_3$). At the same time, the band at 1145 cm^{-1}, due to maleimide ring, disappeared, and a band at 1172 cm^{-1}, due to succinic ring, appeared, which indicated that maleimide C=C bond reacted.

The thermal properties of polymers P(1-6) were evaluated by DSC and TGA. The representative TGA curves of the polymers P(1-2) and P(4-6) obtained in nitrogen atmosphere are shown in Fig. 3 and thermal behavior data are summarized in Table 3. The T_g values of these compounds were in the range 198–225 °C, depending on the structure of the polymer chain. Polymers P-1 and P-4 did not show any glass transition temperature when heated up to 350 °C.
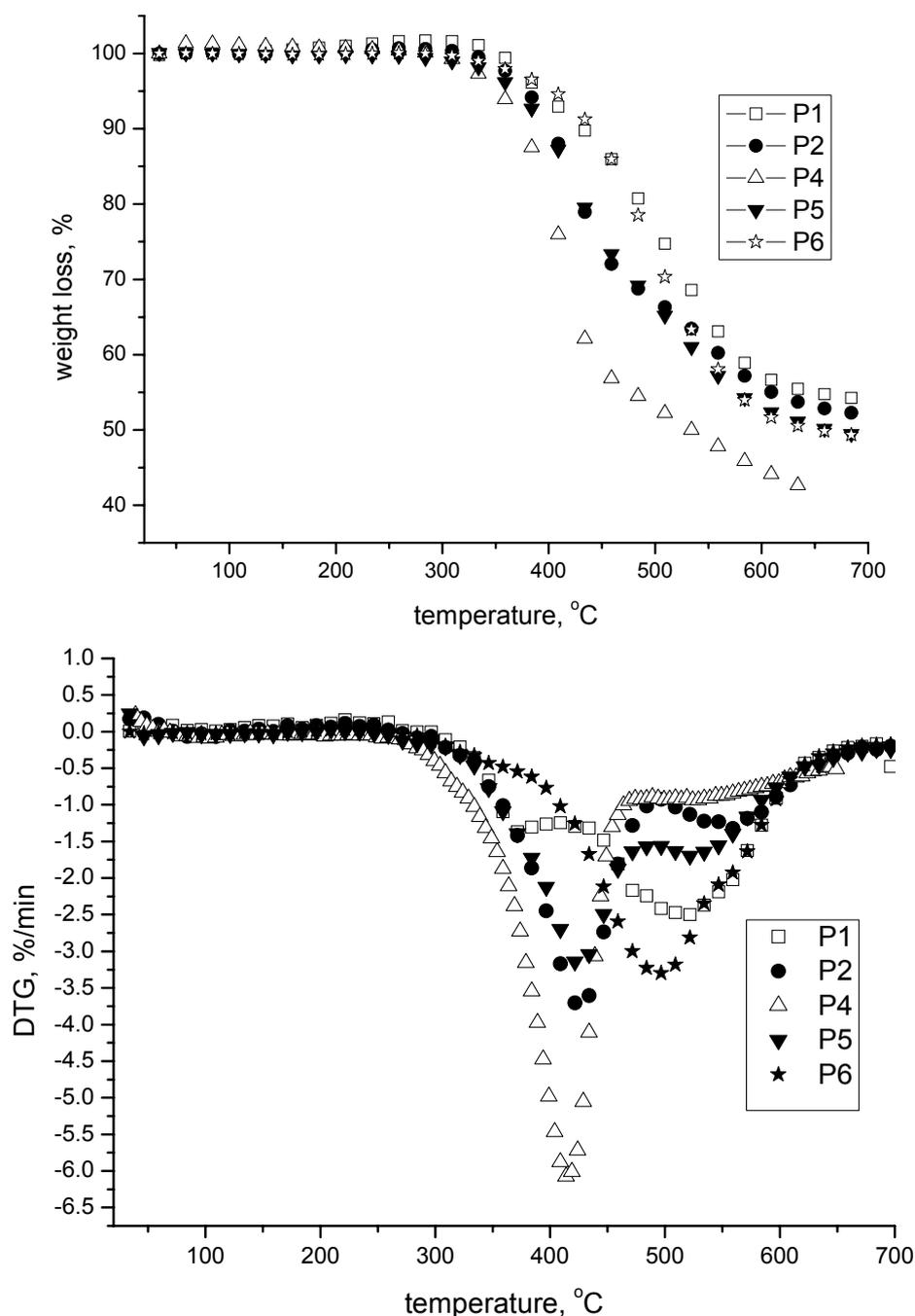

Fig. 3 – TG and DTG curves of polymers P(1-2) and P(4-6).

These polymers containing ether bridges presented a lower T_g because of the increased rotation movement caused by these flexible linkages. Also, the Tg's of these polymers were influenced by the asymmetry and irregularity which disturbed the chain interaction and induced the decrease of T_g. All polymers were stable up to 324-363 °C and the weight loss (1-3%) observed in this interval was associated with evaporation of humidity and solvent traces. The highest value of initial decomposition temperature (IDT) was obtained for polymer P-4 (based on bismaleimide BMI-3 and DMAB amine component). The polymer P-5 and P-6 showed lower IDT. The polymers P-4 and P-6 showed one maxima of decomposition (PDTmax) while the polymers P(1-3) and P-5 showed two maxima decomposition. The first PDT_{max} is in the range of 377-490 °C and is probably due to the destruction of those groups which are more sensitive to degradation. The second maximum PDT_{max} of decomposition is in the range of 508-560 °C and is due to the degradation of the polymer chain itself. The char yield (Y%) of these polymers is in the range of 40-52° C when heated to 700 °C in nitrogen (except P-3 which heated to 620 °C), confirming that these polymers have good thermal stability.

The dielectric constant and dielectric loss of the polymer 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 10^6 Hz. In Fig. 4 are represented the values of dielectric constant and dielectric loss at 25 °C of polymers P-2 and P (5-6). For signal propagating a material with low dielectric constant and loss is good for enhancing the speed and reducing the loss, so low dielectric constant and loss are necessary and characterized feature of the materials for producing high-performance dielectrics.[14] It is known that structure with low polar linkages and bulky groups show dielectric constant and low dielectric loss. From Table 4, it can be observed that polymers are characterized by slow decrease of the dielectric constant with increasing frequency because of the dipolar relaxation mechanism and values are low, of the order 10^{-2}.

All the polymers are characterized by slow decrease of the dielectric constant with increasing frequency because of the dipolar relaxation mechanism, which are better observed as peak on dielectric loss representations. Some data of dielectric constant versus frequency and temperature of polymers P(2-3) and P(5-6) are shown in Table 4.

The mechanical behavior of some polymers was investigated by stress-strain measurements on films at room temperature. The stress-strain curves of polymers P(2-4) are shown in Fig. 5 and results of measurements in Table 5. The polymer composition influences the tensile strength values, which are between 27-176 MPa. The elongation at break values all kept at the similar low level (P-2 and P(4-5), and the maximum values was 6.25 for sample P-3. The high level of rigidity of these polymers is reflected by the resin modulus. We find that all polymers have exceptionally high Young' modulus, in gigapascal (GPa) range. The value of the modulus is mainly due to the high crystallinity of the polymers. It is possible that molecular orientation contributes to the observed effects.

It is clearly observed the difference between the values of the tensile strength of P-2 and those of the other polymers. This is due to both the polymer chemical structures and the parameters used to their preparation.

Table 3

Thermal properties of polymers

Polymer	$T_g(°C)^a$	IDT(°C)	$PDT_{max}(°C)$	$T^{25}(°C)^b$	$Y_c(\%)$
P-1	-	340	377, 517	506	54
P-2	198	358	436, 560	444	52
P-3	225	338	377, 508	467	40^c
P-4	-	363	415	408	42
P-5	206	325	426, 520	445	49
P-6	211	324	490	495	49

[a] glass transition temperature; [b] the temperature at which a 25% weight loss was recorded; [c] residual weight at 620 °C.
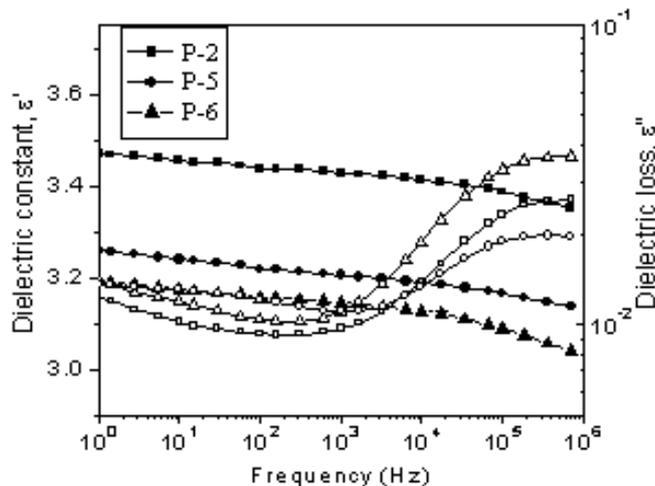
Fig. 4 – Dielectric constant ε' (filled symbols) and dielectric constant (empty symbols)
vs. frequency at 25 °C for polymers P-2 and P(5-6).

Table 4

Dielectric constant versus frequency at temperature of 100 and 150 °C of polymer P(2-3) and P(5-6)

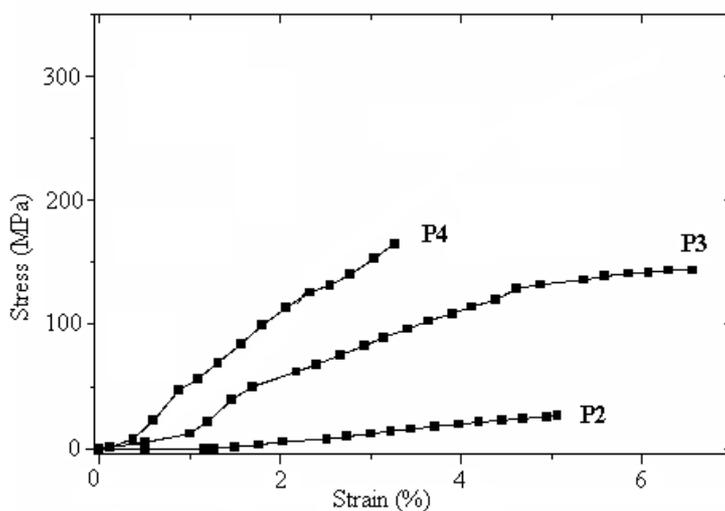| Polymer	Temp (°C)	Frequency (Hz)						
		1	10	10^2	10^3	10^4	10^5	10^6
P-2	100	3.50	3.48	3.46	3.44	3.43	3.41	3.38
P-2	150	3.80	3.65	3.63	3.61	3.57	3.54	3.51
P-3	100	3.85	3.75	3.67	3.61	3.58	3.55	3.52
P-3	150	10.67	7.00	6.08	5.53	5.08	4.70	4.42
P-5	100	3.37	3.35	3.33	3.31	3.29	3.27	3.23
P-5	150	3.48	3.45	3.44	3.42	3.39	3.36	3.32
P-6	100	3.08	3.05	3.02	3.00	2.97	2.96	2.93
P-6	150	6.21	4.29	3.88	3.69	3.57	3.48	3.41

Fig. 5 – The stress-strain curves of polymer P(2-4).

Table 5

Mechanical properties of P(2-5)

Sample	Tensile strength (MPa)	Young's Modulus (GPa)	Elongation (%)
P-2	27	0.87	3.74
P-3	145	3.88	6.25
P-4	176	6.68	3.07
P-5	111	1.92	4.40

EXPERIMENTAL

Materials

Maleic anhydride (Fluka, Germany), acetic anhydride (Merck, Darmstadt, Germany), triethyl amine (Fluka, Germany) are commercially available products and were used as received. 1,2-Bis[2-(4-aminophenoxy)ethoxy]ethane(APEE), 4-[4-[-[1-[4-(4-aminophenoxy)phenyl]-1-phenyl-ethyl]phenoxy]aniline (BAPDP) were prepared according to the method Feld *et al.*[15] 2,4-diamino-4'-methylazobenzene(DMAB) were prepared according to the method given in the literature.[16] 4,4'-Diaminodiphenyl ether (DDE) (Fluka) has been provided by commercial source and purified by recrystallization. Commercial solvents as acetone (Fluka, Germany) were used as received. *N*-methyl-pyrrolidone (NMP) (Fluka) was dried and purified by a standard method.

General procedure for the preparation of bismaleimide and polyaspartimide

Bismaleimides BMI(1-4) were synthesized following the literature, *via* the reaction of maleic anhydride with various diamines according to Scheme 1.

The monomers BMI(1-4) were synthesized according to literature[17], by the reaction of maleic anhydride with various diamines (Scheme 1). The diamine (0.02 mol) dissolved/suspended in 50 mL acetone was reacted with maleic anhydride (0.04 mol) in 40 mL acetone to give the corresponding bismaleamic acid. The mixture was stirred for 30 min at 20-25 ºC, and then the temperature was raised to 40 ºC. During a period of 10 min, triethylamine (0.02 mol), acetic anhydride (0.15 mol) and magnesium acetate (0.04 g) 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 free from acetic acid. Finally, it was washed with water and dried in vacuum.

Synthesis of polymers

The polyaspartimides with various structures were synthesized by Michael addition of diamines to bismaleimides.[18]

Into a 50-mL three-necked flask fitted with a mechanical stirrer, a thermometer, and a nitrogen inlet, bismaleimide (0.01 mol), diamine (0.01 mol) in NMP or *m*-cresol as solvent (up to 10 % of monomer concentration) and a small amount of acetic acid were charged. The reaction mixture was kept in a water bath at 90-95 °C, for different time intervals. The polymer was isolated by pouring the reaction mixture into methanol. All polymers were redissolved in fresh solvent, precipitated in a nonsolvent medium, and dried for 20 h in a vacuum oven at 80 °C. The synthesis pathway to prepare these polymers is illustrated in Scheme 2.

Bismaleimide BMI-1
The monomer was recrystallized from DMF/water; yield 68%; m p 107-111 °C; FTIR (KBr), ν (cm^{-1}) 2977-2924 (-CH$_3$), 1773 and 1715 (C=O imide), 1240 (-O-). Anal. Calcd for C$_{40}$H$_{28}$N$_2$O$_6$ (%): C, 75.93, H, 4.46, N, 4.42; found: C, 75.58, H, 4.23, N, 4.59.
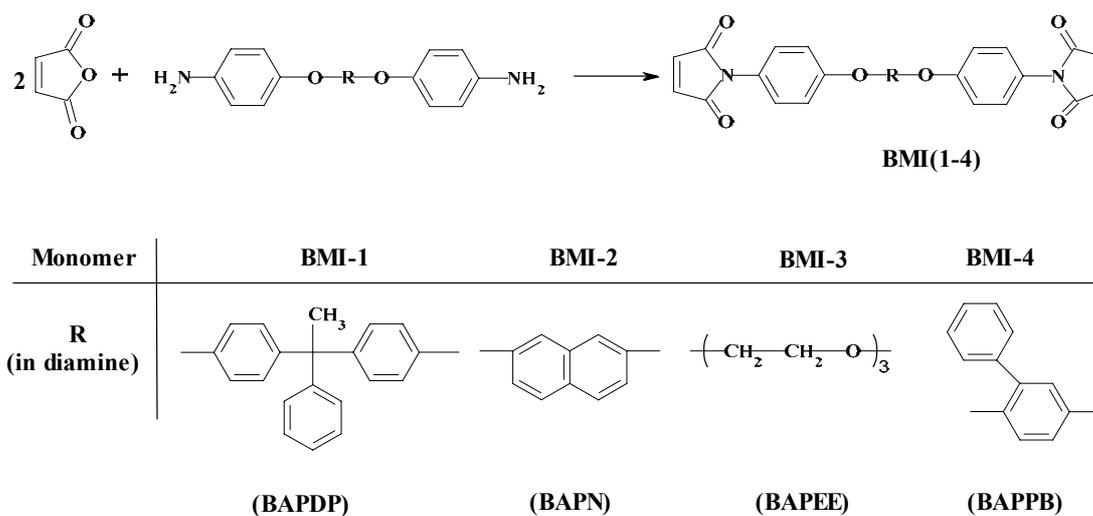
Bismaleimide BMI-2
The product was recrystallized from DCE/ethanol; yield 69%; m p 92-96 °C; FTIR (KBr), ν (cm^{-1}) 1773 and 1713 (C=O imide), 1247 (-O-); Anal Calcd for C$_{30}$H$_{18}$N$_2$O$_6$ (%) C, 71.71, H, 3.61, N, 5.57; found: C, 71.39, H, 3.43, N, 5.36.
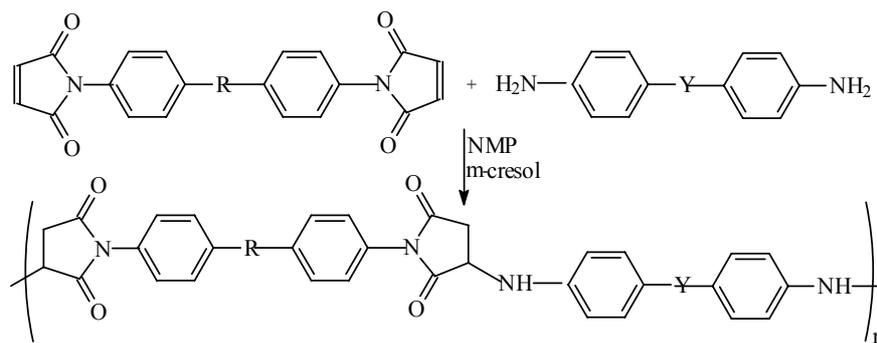
Bismaleimide BMI-3
The monomer was recrystallized from CHCl$_3$/methanol; yield 71; mp 168-173 °C; FTIR (KBr), ν (cm^{-1}) 2969-2873 (-CH$_2$), 1715 and 1770 (C=O imide), 1254 (-O-); Anal Calcd for C$_{26}$H$_{24}$N$_2$O$_8$ (%) C, 59.45, H, 5.44, N, 6.30; found: C, 60.07, H, 5.23, N, 6.05.

Bismaleimide BMI-4
The product was recrystallized from DCE/ethanol; yield 72%; m p 169-173 °C; FTIR (KBr), ν (cm^{-1}) 1773 and 1713 (C=O imide), 1241 (-O-); Anal Calcd for C$_{32}$H$_{20}$N$_2$O$_6$ (%) C, 72.72, H, 3.81, N, 5.30; found; C, 73.11, H, 3.43, N, 5.16.

BMI(1-4)

Monomer	BMI-1	BMI-2	BMI-3	BMI-4
R (in diamine)				
	(BAPDP)	(BAPN)	(BAPEE)	(BAPPB)

Scheme 1

Scheme 2

Polymer	P-1	P-2	P-3	P-4	P-5	P-6
Bismaleimide	BMI-1	BMI-2	BMI-2	BMI-3	BMI-4	BMI-1
Diamine	DDE	APEE	DDE	DMAB	APEE	BAPDP

MEASUREMENTS

The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer and the ^{1}H-NMR spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 MHz, using DMSO-d_6 as solvent and tetramethylsilane as an internal standard. DSC measurements were performed with a Pyris Diamond DSC, Perkin Elmer USA system, under nitrogen atmosphere (nitrogen flow 120 mLmin^{-1}, sample mass 3–4 mg, heating rate 10 ºCmin^{-1}). Melting points of diamines were determined with a Gallenkamp hot-blok melting point apparatus. TGA was carried out using a Mettler Toledo TGA/SDTA851e-thermogravimetric analyzer, under nitrogen flow (20 mLmin^{-1}) at a heating rate of 10 ºCmin^{-1} for polyaspartimides and in air for bismaleimides from room temperature to 700 ºC, and 3-5 mg of sample mass. Measurements of the dielectric properties were done using Novocontrol Dielectric Spectrometer Concept 40 equipped with Alpha Frequency Response Analyzer and Novocontrol Quatro Cryosystem which allowed temperature control in dry nitrogen atmosphere with a stability better than 0.1º C. The mechanical behavior of these polymers was investigated by stress-strain measurements of films at room temperature on TIRA TEST2161 apparatus, Machinenbau GmbH Ravenstain, Germany. Measurements were run at an extension rate of 1 mm/min, at room temperature.

CONCLUSIONS

Bismaleimide monomers and polyaspartimides with various structures containing flexible linkages were synthesized and characterized. The cured bismaleimide resins were stable up to 324-363 °C.

Thermal properties of monomers and polymers were influenced by the rigidity, symmetry and conditions of reaction. Some of these polymers possess films forming ability. The dielectric properties of these films were evaluated from -100 to 200 °C and frequency range used for measurements was from 1 to 10^6 Hz.

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