

DOI:**ABSTRACT**

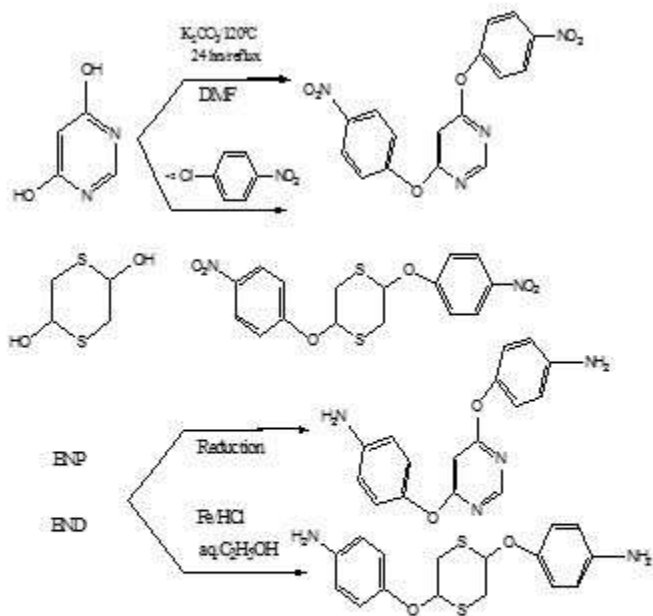
Bismaleimides containing pyrimidine and dithiane group were synthesized from the diamines **APPB and APDB** and maleic anhydride via bismaleimic acid as the intermediate followed by cyclodehydration. The structure of the monomers was confirmed by FT-IR, ¹H-NMR and ¹³C-NMR spectral techniques. Further, a series of polyaspartimides were synthesized by addition reaction of bismaleimides with the prepared diamines. The polymers were characterized by using FT-IR, ¹H-NMR and ¹³C-NMR. All the polymers are soluble in aprotic solvents such as NMP, DMF, DMAc and DMSO. The activation energies (E_a) of the thermal curing were calculated using Ozawa and Kissinger method from DSC (E_a 103 KJ/mol and 106 KJ/mol). The T_g and $T_{10\%}$ of the polyaspartimides are in the range of 199-280°C and 360-480°C respectively.

KEYWORDS: pyrimidine and dithiane containing bismaleimide-polyaspartimides, thermal properties.

INTRODUCTION

Bismaleimides are thermosetting polymers which have wide applications in microelectronic and aerospace industries for making advanced composites. They show excellent thermal and mechanical properties which make them the right material for use in structural applications. They also exhibit good fatigue resistance [1]. Their usage in composites is more advantageous in comparison to condensation type polyimides even though the latter exhibit better thermal and electrical properties[2]. This is because condensation type polyimides evolve volatile by products during ring formation which decreases their stability and hence utility. Bismaleimides can be further polymerized through the double bond present in maleimide ring, which are electron deficient due to the presence of electron withdrawing carbonyl group on both sides. These double bonds can be self polymerized to give highly cross linked polymer [3, 4] or they can be polymerized further by addition of nucleophilic difunctional reagents to give linear polymer. Polyaspartimides are a class of polyimides which are linear and possess more facile properties. Polyaspartimides also have good thermal stability. The chemical modifications such as incorporation of flexible ether linkage on the main chain and/or introduction of bulky pendent group on the diamine help in producing a wide class of bismaleimides and polyaspartimides with improved utility. Presence of flexible ether linkage would decrease the rigidity and also lower the energy of internal rotation of the polymer chain, decrease the crystallinity and improve the solubility [5,]. Incorporation of a bulky pendent group is expected to decrease the close packing of polymer chains which decreases the intermolecular forces of attraction thereby improving the processability of the polymer[6]. Hence, in the present study a set of thermosetting bismaleimides and thermoplastic polyaspartimides were synthesized from the prepared diamines (**APPB, APDB**). The monomer and polymers were characterized by FT-IR, ¹H-NMR and ¹³C-NMR spectral techniques. The solubility, thermal and flame retardancy properties were studied.

Schemes:



Scheme 1 Synthesis of APPB and APDB

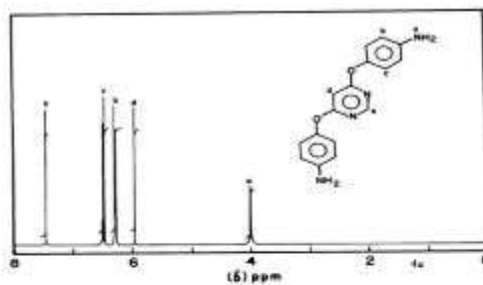


Figure 1 ^1H-NMR spectrum of BNP

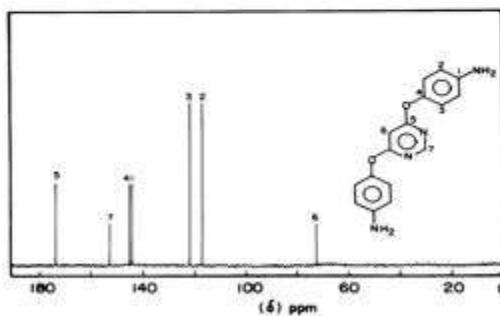
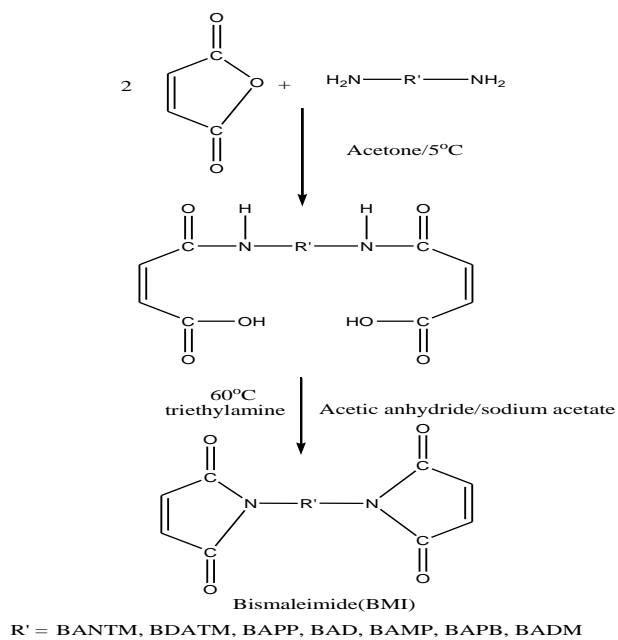
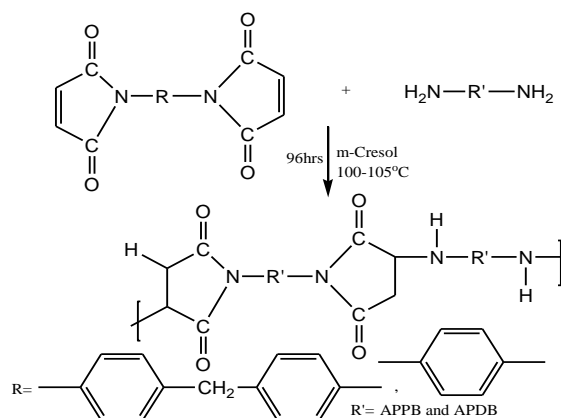


Figure 2 ^1H-NMR spectrum of BNP



Scheme 2 Synthesis of Bismaleimides



Scheme 3 Synthesis of Polyaspartimide

Synthesis of bismaleimides

The synthesized diamines (**APPB**, **APDB**) were reacted with required amount of maleic anhydride to give bismaleimamic acid (I). The bismaleimamic acid was then cyclodehydrated using dehydrating agent acetic anhydride and sodium acetate to get a series of bismaleimides (BMI-1, BMI-2,) as shown in **scheme 2**

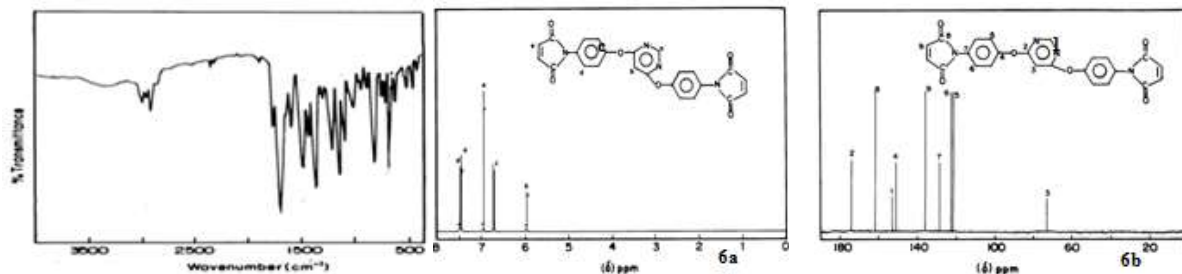


Figure 3 FT-IR spectrum of BNP Figure 4a ¹H-NMR spectrum of BNP and 4b) ¹³C-NMR-of BNP

Table 1 FT-IR spectral data of BMIs and DSC datas

Code	Wave number(cm-1)					DSC datas		
	>C=O		C-N-C		C-O-C	-C=C-	Melt(°c)	Curing(°C)
	Symm	Asy	Bend	Str				
BMI1	1716	1777	1197	1386	1241	691	148-150	220
BMI-2	1721	1786	1185	1368	1221	688	156	250

The ¹H-NMR spectrum (figure 4a) of bismaleimides show the distinct signal around 7.00 ppm due to four olefinic protons. The absence of signal at 10.5 ppm due to the carboxylic acid protons shows complete imidization. All aromatic protons are accountable by the signals between 6.0 and 7.5 ppm. The ¹³C-NMR spectrum (figure 4b) show all aromatic carbons appear between 121 -178 and the pyrimidine ring C-H carbon resonate at 75 ppm.

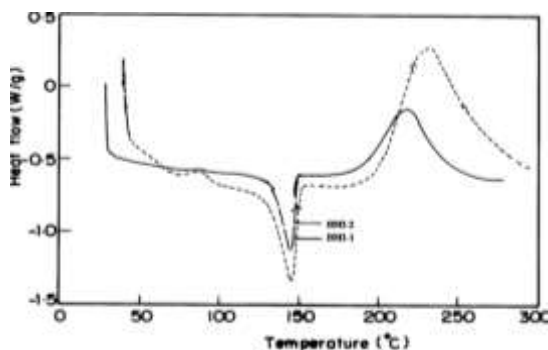


Figure 5 DSC traces of bismaleimides and TGA curve of Polyaspartimides in N₂ atmosphere

BMI	Kissinger method		Ozawa method	
	Ea(KJ/mol)	R	Ea(KJ/mol)	R
BMI-1	103	0.9881	106	0.9893
BMI-2	87.8	0.9966	94	0.9984

Preparation of polyaspartimides

The nucleophilic addition of diamines to bismaleimides (based on aromatic amines having hetero cyclic ring), the Michael type addition, is a well-known route to synthesize linear polyaspartimides [7]. The synthesized pyrimidine and dithaine containing bismaleimide and an equivalent amount of aromatic diamine were stirred together in m-cresol containing a catalytic amount of glacial acetic acid to promote the polymerization as shown in scheme 3.

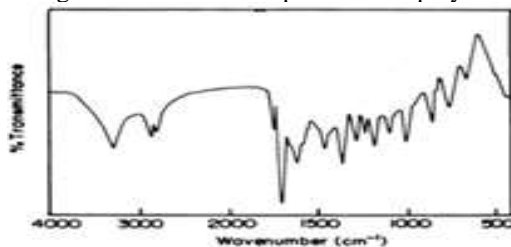


Figure 6 FT-IR spectrum of PAI

The structure of the polymer was confirmed by FT-IR (Figure 6). The bands around 3339-3365 cm⁻¹ are due to N-H stretching vibration. The disappearance of band at 691 cm⁻¹ due to maleimide C=C bond confirms completion of the addition reaction of these double bonds. The bands around 1773-1780 cm⁻¹ and 1709-1720 cm⁻¹ are due to asymmetric and symmetric stretching vibrations of the C=O group of the imide ring respectively. The bands around 1360-1382 cm⁻¹ are due to C-N-C stretching vibrations of the imide ring. The spectroscopic data are well in agreement with the expected structure, ensuring the formation of polyaspartimides.

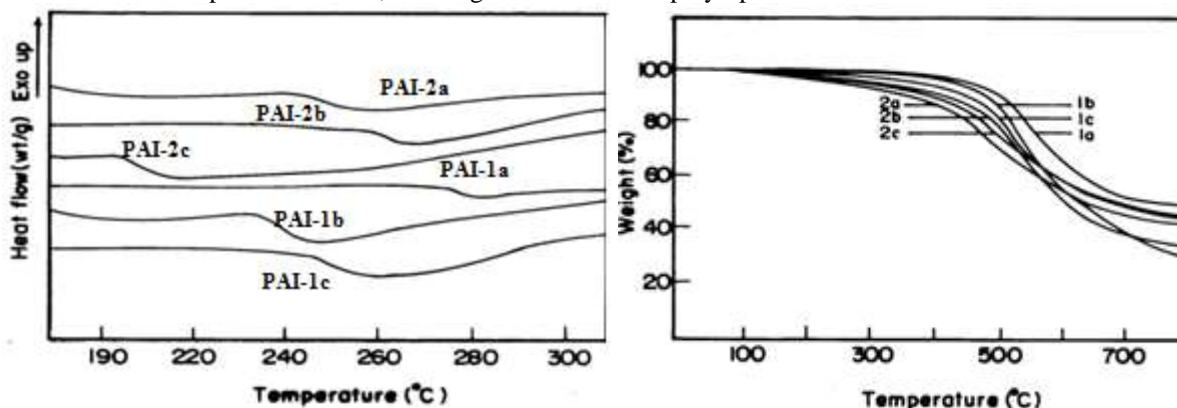


Figure 7a DSC traces of Polyaspartimides and b) TGA curve of PAIs

Table 1 Thermal properties (N_2 atms)/ O_2 atms and inherent viscosity of polyaspartimides

PAIs	In N_2			In air		η dl/g
	T_g	T_{10} (°C)	Char yield (%)	T_{10} (°C)	Char yield (%)	
PAIs-1a	280	480	52	490	40	0.45
PAIs-1b	240	420	38	469	38	0.57
PAIs-1c	245	380	49	444	35	-
PAIs-2a	252	360	47	388	37	0.88
PAIs-2b	260	362	46	380	40	0.59
PAIs-2c	199	350	46	420	38	0.79

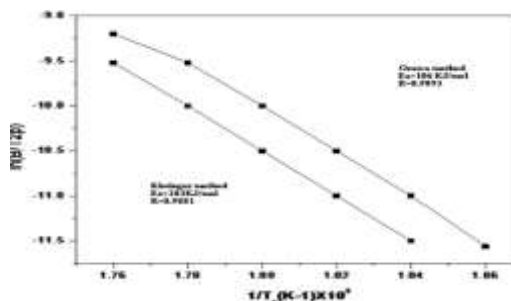
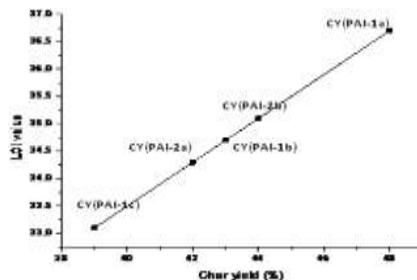


Figure 8 Kinetic plots of BMI

Flame resistance

The flame retardancy of the polyaspartimide was confirmed by their LOI (Limiting oxygen index) value. The LOI value of the polymer system should be above the threshold value 26 (The polymers which have a threshold value greater than 26 have high flame retardancy), to render them self-extinguishing and for their qualification for many applications requiring good flame resistance. The LOI value was calculated by using Krevelen's equation,



$$LOI = 17.5 + 0.4(\sigma) \quad (1)$$

Figure 9 LOI value of Polyaspartimides

where σ is the percentage of char yield. The obtained values were plotted against the corresponding char yield. The curve thus obtained (Figure 9) was linear showing that the LOI increases with increasing char yield. The polyaspartimides prepared in the present study have LOI value in the range of 32.7-46.7. Thus, the developed polyaspartimides can be considered as good flame retardant materials [8,9].

CONCLUSIONS

A set of pyrimidine and dithiane containing BMI's were synthesized using the prepared diamines Polyaspartimides were successfully prepared by the Michael addition reaction of the synthesized bismaleimides with the diamines namely **APPB** and **APDB**. The monomers and polymers were characterized by using FT-IR, 1H -NMR and ^{13}C -NMR. The T_g value of the polyaspartimides are in the range of 199-280°C. The 10% weight loss temperatures (T_{10}) of PAS are in the range of 360°C-480°C and the char yield is in the range of 38-52% in nitrogen atmosphere. The inherent viscosity values of polyaspartimides were found to be in the range of 0.45 – 0.88 dl/g, which indicates that these materials can be considered as easily processable polymeric materials. Thus, this series of polyaspartimides may find use as membranes for gas separation, as well as in the micro electronics and composite industries.

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