Bismaleimides, Bisnadimides, and Polyaspartimides Containing Ether and Ester Linkages and Pyridine

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ABSTRACT: A series of bismaleimides (BMI) and bisnadimides (BNI) containing pyridine ring and flexible linkages were prepared and the structural characterization of the resins was carried out by elemental analysis, FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Their curing behavior were characterized by differential scanning calorimetry and thermal stability of the cured resins were investigated by thermogravimetric analysis. In addition, a series of polyaspartimides were prepared by the polyaddition of the bismalemide with various dimaines. The polymers were characterized by FT-IR, inherent viscosity, and molecular weight measurements. All the polyimides were soluble in many organic solvents, the glass transition temperature of the polyaspartimides are in the range of 194–231°C, 10% weight loss (T_{10}) takes place in the temperature range of 379–482°C in N_2 and char yield in the range of 44.31–53.31%. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1905–1914, 2008

Key words: heteroatom-containing polymers; gel permeation chromatography; differential scanning calorimetry; crosslinking

INTRODUCTION

A variety of matrix resins for composite materials have been developed, in particular of epoxy and polyimide type. Bismaleimides (BMI) and bisnadimides (BNI) are one of the several precursors for the preparation of processable and void-free heat resistant polyimides having potential applications as matrix resins. The thermoplastic polyimides exhibit processing limitations whereas the thermosetting polyimides are more processable but exhibit a more brittle mechanical response compared with the thermoplastic polyimides. Addition type polyimides have the advantages of better process flexibility because it can be used as a liquid-based resin or a prepreg material. Several maleimide and nadimide capped prepolymers have been commercially developed for high temperature resistant laminates. However, a serious disadvantage of these resins is their inherent brittleness because of high crosslinking.[1,2] Therefore, several efforts to develop matrix resins with improved flexibility, several chain-extended BMI, and BNI by incorporating flexible linkages have been reported.[3,4] However, it has been difficult to improve defects by modifying the BMI and BNI without losing their excellent thermal properties. The present work is also aimed to produce modified BMI and BNI by introducing flexible linkages and heteroaromatic rings in between the reactive sites to reduce the crosslink density and enhance the processing window without much loss in thermal stability. Michael addition of primary diamine to BMIs was also usually used to affect chain extension prior to thermal curing,[5,6] to reduce the crosslinking density and brittleness of the polymers. The poor solubility and high softening temperature, (the defects of condensation type polyimides) were also countered with high molecular-weight polyaspartimides. In this respect, it is known that the incorporation of bulky pendant groups have provided improvement in solubility of high molecular weight polyaspartimides. Introducing heteroaromic ring into the main chain of a polymer along with the aforesaid modifications would impart certain properties expected. The rigidity based on symmetry and aromaticity of pyridine ring would have contributions for the thermal stability, chemical stability, and also polarizability resulting from nitrogen atom in pyridine ring could be suitable to improve their solubility in organic solvents.[5]

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EXPERIMENTAL

Materials

Pyridine-3-aldehyde (Spectrochem, India), 2,6-dimethylphenol (Lancaster, India), *p*-nitrobenzoylchloride (Lancaster), *p*-chloronitrobenzene (Lancaster), HCl (E. Merck, India), acetic anhydride (Fischer, India), triethylamine (E. Merck, India), stannous chloride dihydrate (E. Merck, India), maleic anhydride

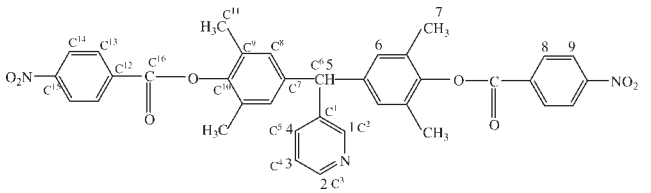
(Lancaster), nadic anhydride (Lancaster), hydrazine monohydrate, 4,4′-diaminodipheyl methane (DDM, E-Merck, India), *p*-phenylene diamine (PPD, E-Merck, India) and *m*-phenylene diamine (MPD, E-Merck, India) were used as received. All the reaction solvents such as dimethyl formamide (DMF), *N*,*N*-dimethyl acetamide (DMAc), *N*-methyl pyrollidone (NMP), dimethyl sulfoxide (DMSO), toluene, acetone, chloroform, dichloromethane, tetrahydrofuran (THF) were purified by appropriate method, distilled under atmospheric pressure/reduced pressure, and stored over 4-Å molecular sieves.

Synthesis of bis(4-amino-3,5-dimethyl phenyl)-3′-pyridyl methane (BAPM) bis(4-hydroxy-3,5-dimethyl phenyl)-3′-pyridyl methane (BHPM) and bis(4- aminophenoxy-3,5-dimethylphenyl)-3′-pyridyl methane (BAPPM)

BAPM, BHPM, and BAPPM were synthesized using the reaction methods reported by the authors.[6]

Synthesis of bis(4-nitrobenzoyloxy-3,5-dimethylphenyl)-3′-pyridylmethane (BNBPM)

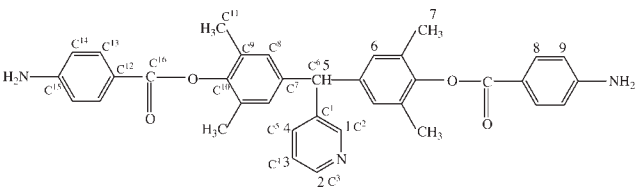
About 6.66 g of bis(4-hydroxy-3,5-dimethyl phenyl)-3′-pyridyl methane (BHPM) (0.02 mol) in 20 mL of dried DMAc was taken in a 150-mL three necked round bottomed flask equipped with nitrogen inlet, an additional funnel, and a reflux condenser. About 5.8 mL (0.042 mol) of triethylamine was added to the solution. A solution of *p*-nitrobenzoylchloride (7.78 g, 0.042 mol) in 10 mL of DMAc was then added dropwise over a period of 1 h. After complete addition the reaction mixture was stirred at 80°C for 8 h. The reaction mixture was cooled and then poured into ice-cold water. The precipitate was collected by filtration, washed thoroughly with water and methanol, and dried. The crude product was then recrystallized in ethanol, finally dried in vacuum at 70°C for 12 h. Yield = 92%.



FTIR (KBr, cm^{-1}); 2967 and 2919 cm^{-1} (C—H stretching vibration of CH_3 group), 1527 and 1346 cm^{-1} (asymmetric and symmetric stretching vibration of —NO_2 group), 1265 cm^{-1} (C—O—C stretching vibration), 1736 cm^{-1} (carbonyl stretching vibration of ester group). ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ = 8.49 (s, 1H, 1), 8.56 (d, *J* = 7.88 Hz, 1H, 2), 7.37 (t, *J* = 8.67 Hz, 1H, 3), 7.57 (d, *J* = 7.96 Hz,1H, 4), 5.41 (s, 1H, 5), 6.87 (s, 4H, 6), 2.14 (s, 12H, 7), 8.37 (dd, *J* = 10.34 Hz, 8H, 8 and 9). ^{13}C NMR (400 MHz, $CDCl_3$, ppm); δ = C^1-134.5, C^2-150.6, C^3-149.0, C^4-123.9, C^5-140.7, C^6-53.3, C^7-138.6, C^8-131.3, C^9-129.6, C^{10}-151.0, C^{11}-16.6, C^{12}-139.6, C^{13}-132.5, C^{14}-123.7, C^{15}-153.5, C^{16}-162.6.

Synthesis of bis(4-aminobenzoyloxy-3,5-dimethyl phenyl)-3′-pyridyl methane (BABPM)

In a three-necked round bottomed flask, equipped with a nitrogen inlet and water condenser, 6.31 g of (0.01 mol) BNBPM in 30 mL of ethanol was taken. About 22.56 g (0.1 mol) of stannous chloride dihydrate was added to the solution. The reaction mixture was refluxed for 4 h under N_2 atmosphere. Then, the mixture was cooled down to room temperature and poured into ice-cold water. The pH was made slightly basic by addition of 5% sodium bicarbonate and the mixture was stirred for a few hours to allow the tin salts to hydrolyze completely. The aqueous mixture was extracted with excess ethyl acetate and the organic phase was thoroughly washed with brine solution and dried over sodium sulfate. Evaporation of the excess solvent leaves (Yield = 78%) pure bis(4-aminobenzoyloxy-3,5-dimethyl-phenyl)-3′-pyridyl methane.



FTIR (KBr, cm^{-1}); 3463 and 3349 cm^{-1} (asymmetric and symmetric stretching vibration of —NH_2 group), 1629 cm^{-1} (N—H bending vibration), 2969 and 2918cm^{-1} (C—H stretching vibration of CH_3 group), 1270 cm^{-1} (C—O—C stretching vibration), 1705 cm^{-1} (carbonyl stretching vibration of ester group). ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ = 8.47 (s, 1H, 1), 8.53 (d, *J* = 7.85 Hz, 1H, 2), 7.31 (t, *J* = 8.69 Hz, 1H, 3), 7.58 (d, *J* = 7.94 Hz, 1H, 4), 5.58 (s, 1H, 5), 6.86 (s, 4H, 6), 2.05 (s, 12H, 7), 7.78 (d, *J* = 8.74 Hz, 4H, 8), 6.61 (d, *J* = 8.79 Hz, 4H, 9), 3.83 (s, 4H, 10). ^{13}C NMR (400 MHz, $CDCl_3$, ppm); δ = C^1-132.4, C^2-151.6, C^3-147.7, C^4-123.1, C^5-139.2, C^6-53.2, C^7-131.0, C^8-129.4, C^9-125.0, C^{10}-152.1, C^{11}-16.6, C^{12}-121.4, C^{13}-130.1, C^{14}-113.4, C^{15}-154.8, C^{16}-164.4.

Preparation of bis(4-maleimido-3,5-dimethylphenyl)-3′-pyridyl methane (BMI-1)

A three-necked round bottomed flask equipped with an addition funnel and a nitrogen inlet was charged

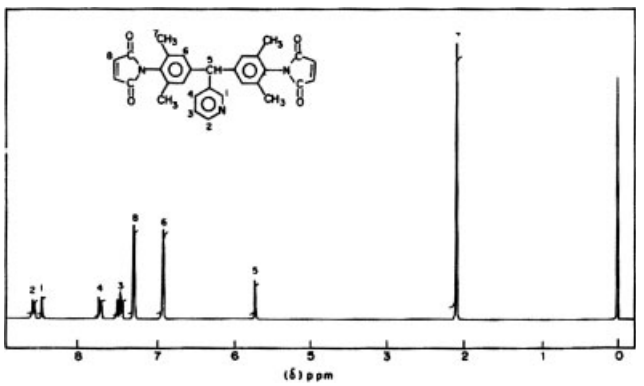
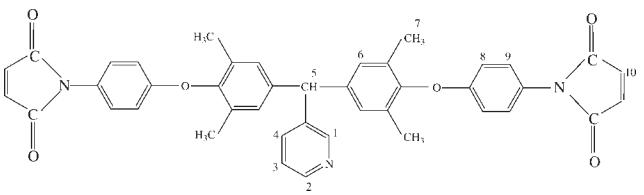
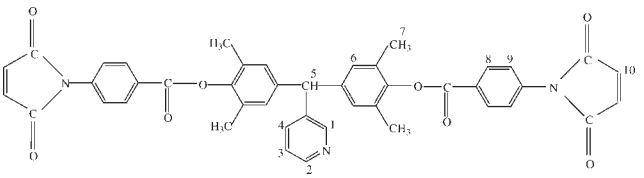


Figure 1 ^{1}H NMR spectrum of BMI-1.

with a solution of bis(4-amino-3,5-dimethyl phenyl)-3′-pyridyl methane (3.31 g, 0.01 mol) in 8 mL acetone. The flask was purged with nitrogen and then a solution of maleic anhydride (1.96 g, 0.02 mol) dissolved in acetone (10 mL) was added dropwise to the above mixture. The reaction is exothermic, so the addition was carried out in an ice water bath. The mixture was stirred for 4 h at room temperature and at 60°C for an additional 1 h. The solution was heated to 60–65°C with stirring. About 0.1 g of sodium acetate, 10 mL of acetic anhydride and 2 mL of triethyl amine were added to the preheated solution. The reaction mixture was stirred at that temperature for 6 h. The solution was cooled to room temperature and then poured into ice water with stirring. The precipitate formed was filtered, washed with a dilute solution of Na_2CO_3, water, and finally with methanol. A pale yellow solid was obtained. All other BMI were prepared by adopting the same procedure as mentioned above. Figure 1 shows the ^{1}H NMR spectrum of BMI-1. The characteristic peak for the maleimide group at 7.25 was observed. The ^{1}H NMR spectral data for other BMI and BNI are given below



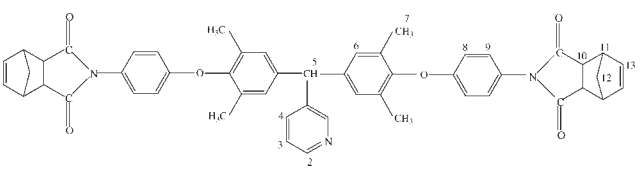
BMI-2: ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ = 8.21 (s, 1H, 1), 8.31 (d, J = 7.82 Hz, 1H, 2), 7.69 (t, J = 8.68 Hz, 1H, 3), 7.78 (d, J = 7.97 Hz, 1H, 4), 5.69 (s, 1H, 5), 6.96 (s, 4H, 6), 2.07 (s, 12H, 7), 7.04 (d, J = 8.78 Hz, 4H, 8), 7.52 (d, J = 8.76 Hz, 4H, 9), 7.24 (s, 4H, 10).



BMI-3: ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ = 8.36 (s, 1H, 1), 8.42 (d, J = 7.86 Hz, 1H, 2), 7.47 (t, J = 8.67 Hz, 1H, 3), 7.69 (d, J = 7.92 Hz,1H, 4), 5.72 (s, 1H, 5), 6.99 (s, 4H, 6), 2.12 (s, 12H, 7), 8.21 (d, J = 8.74 Hz, 4H, 8), 7.78 (d, J = 8.78 Hz, 4H, 9), 7.28 (s, 4H, 10).

Preparation of bis(4-nadimido-3,5-dimethylphenyl)-3′-pyridyl methane (BNI-1)

In a 100-mL round bottomed flask, 3.28 g (0.02 mol) of nadic anhydride in 10 mL of acetic acid was taken. The solution was heated to 120°C with stirring. To this solution 3.31 g (0.01 mol) of bis(4-amino-3,5-dimethyl phenyl)-3′-pyridyl methane was added in portions. The temperature of the reaction mixture was raised to 120°C and stirred at that temperature for 8 h. The solution was cooled to room temperature and then poured into ice water with stirring. The precipitate formed was filtered, washed with a dilute solution of sodium bicarbonate, water, and finally with methanol. Yield = 88%. All other BNI were prepared by adopting the same procedure as mentioned above. Figure 2 shows the ^{1}H NMR spectrum of BNI-1.



BNI-2: ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ = 8.25(s, 1H, 1), 8.31 (d, J = 7.83 Hz, 1H, 2), 7.31 (t, J = 8.66 Hz,1H, 3), 7.48 (d, J = 7.94 Hz, 1H, 4), 5.56 (s,

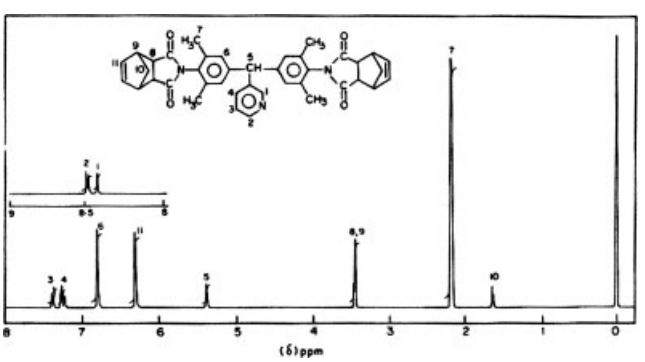
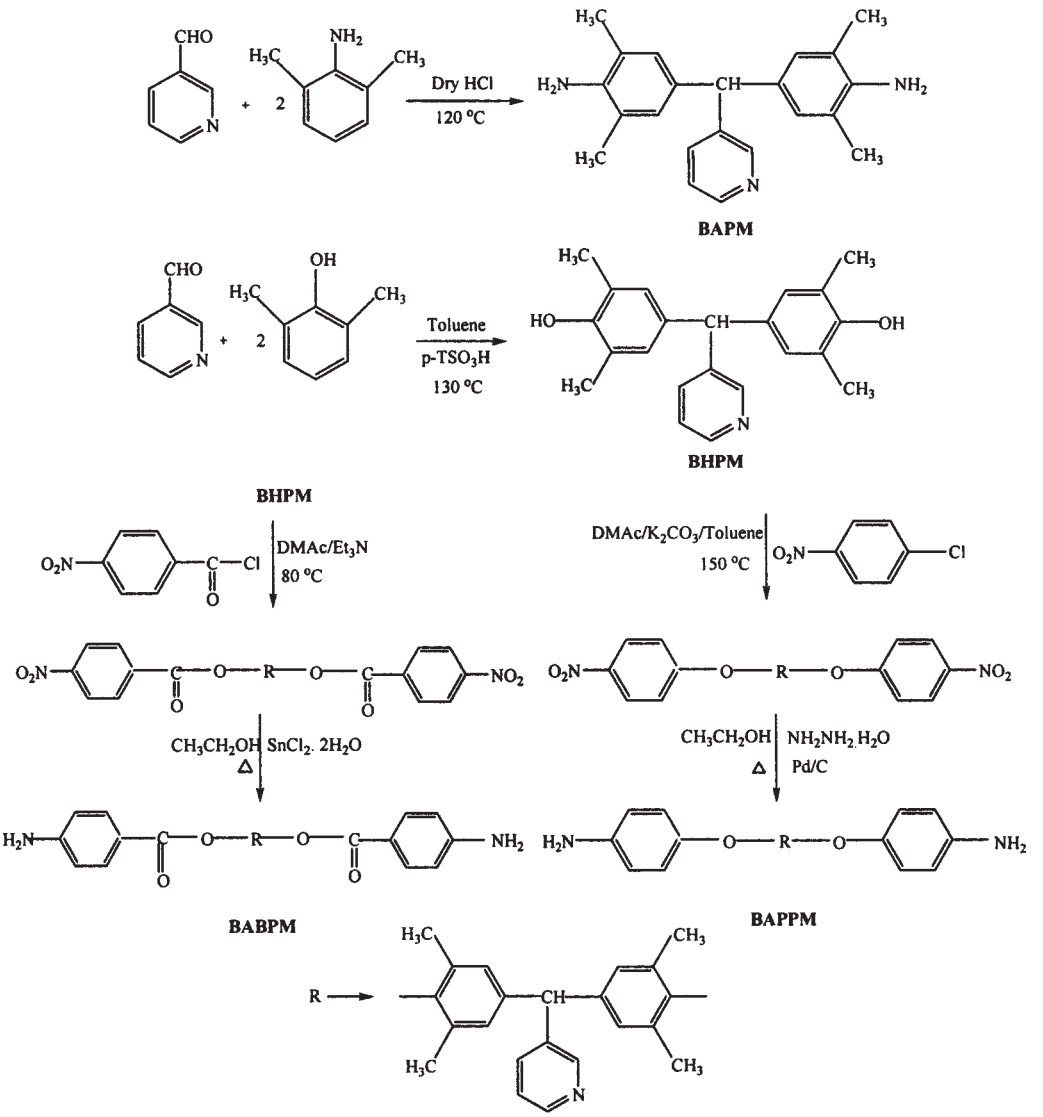
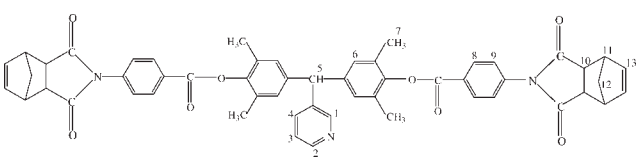


Figure 2 ^{1}H NMR spectrum of BNI-1.



Scheme 1 Synthesis of BAPM, BAPPM, and BABPM.

1H, 5), 6.90 (s, 4H, 6), 2.12 (s, 12H, 7), 7.07 (d, J = 8.77 Hz, 4H, 8), 7.68 (d, J = 8.71 Hz , 4H, 9), 3.37–3.46 (8H, 10 and 11), 1.66 (4H, 12), 6.28 (s, 4H, 13).



BNI-3: ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ = 8.39 (s, 1H, 1), 8.44 (d, J = 7.83 Hz, 1H, 2), 7.45 (t, J = 8.68 Hz, 1H, 3), 7.51 (d, J = 7.95 Hz, 1H, 4), 5.43 (s, 1H, 5), 6.79 (s, 4H, 6), 2.18 (s, 12H, 7), 8.28 (d, J = 8.79 Hz, 4H, 8), 7.89 (d, J = 8.81 Hz, 4H, 9), 3.47 (s, 4H, 10), 3.47–3.52 (8H, 10, and 11), 1.63 (4H, 12), 6.27 (s, 4H, 13).

Preparation of polyaspartimides

The general procedure for poly addition is as follows. To a 150-mL three necked round bottomed flask fitted a with magnetic stirrer and N_2 inlet, was added, 4.91 g of bismaleimide BMI-1 (0.01 mol), 1.08 g of *m*-phenylene diamine (0.01 mol), 0.2 mL of glacial acetic acid, and 40 mL of *m*-cresol. The reaction mixture was maintained at 100–105°C for 4 days with constant stirring. During this time an increase in the solution viscosity and darkening of color were noticed. The reaction mixture was trickled into excess methanol with vigorous stirring. The precipitated polymer was collected by filtration, washed thoroughly with hot ethanol, and then dried in vacuum at 110°C for 24 h. All other polyaspartimides were prepared by adopting the same procedure as mentioned above.

TABLE I
Physicochemical Characteristics of Precursors, Monomers, and Prepolymers

Code	Molecular formula	M. Pt. (°C)	Yield (%)	Elemental analysis (wt %)					
				C		H		N	
				Cal.	Found	Cal.	Found	Cal.	Found
BAPM	$C_{22}H_{25}N_3$	149	94	79.72	79.14	7.60	7.96	12.68	12.94
BHPM	$C_{22}H_{23}NO_2$	119	91	79.26	78.69	6.95	7.12	4.20	4.77
BNPPM	$C_{34}H_{29}N_3O_6$	138	89	70.95	70.38	5.07	5.61	7.30	7.84
BAPPM	$C_{34}H_{33}N_3O_2$	121	79	79.20	78.99	6.45	6.91	8.15	8.63
BNBPM	$C_{36}H_{29}N_3O_8$	161	92	68.47	68.20	4.62	4.99	6.65	6.96
BABPM	$C_{36}H_{33}N_3O_4$	142	78	75.64	74.99	5.81	6.09	7.35	7.77
BMI-1	$C_{30}H_{25}N_3O_4$	282	89	73.30	72.74	5.13	5.29	8.55	8.91
BMI-2	$C_{42}H_{33}N_3O_6$	225	85	74.65	74.08	4.92	5.13	6.22	6.62
BMI-3	$C_{44}H_{33}N_3O_8$	161	86	72.22	71.67	4.55	5.09	5.74	6.17
BNI-1	$C_{40}H_{37}N_3O_4$	258	95	77.03	76.55	5.98	6.43	6.74	7.28
BNI-2	$C_{52}H_{45}N_3O_2$	239	92	83.96	83.39	6.10	6.72	5.65	5.91
BNI-3	$C_{54}H_{45}N_3O_8$	206	94	75.08	74.51	5.25	5.83	4.86	5.39

Curing of bismaleimide and bisnadimide resins

Since the curing exotherm obtained from the DSC scan was found to be 250–350°C, initially isothermal curing of the nadimides and maleimides was done at 250°C for 1 h in air atmosphere and further cured at 300°C for 1 h followed by 1 h at 350°C.

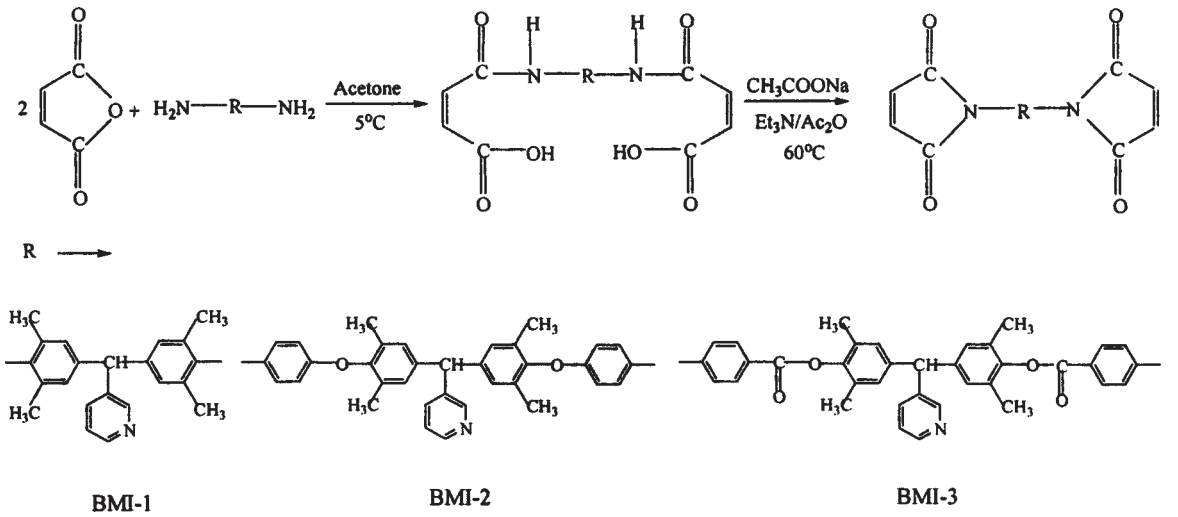
Measurements

Elemental analysis was performed on a Carlo Erba EA 1108 micro analyzer, Fourier Transform Infra Red (FTIR) spectra were recorded on a Perkin–Elmer RX1 spectrometer with KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Jeol Ex-400 spectrometer with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as reference, DSC and TGA were performed with a Q10 and Q100 series of TA instruments, respectively, at a heating rate of 10°C/min in N_2. Solubility of the polymers was tested in various solvents by dissolving 2–3 mg of the polymer with 8 mL of solvent and kept aside for 24 h with occasional shaking. If the mixture was insoluble under cold conditions, then it was heated and cooled. Wide angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a X-pert PAN analytical X-ray diffractometer using Ni-filtered Cu Kα radiation. The scanning rate was 20°/min over a range of $2\theta = 5°$–40°. Inherent viscosity measurements were conducted at 25°C in DMAc solvent using Cannon Ubbelohde viscometer. Gel permeation chromatograms were obtained from Polymer Laboratories PL-GPC-50 integrated GPC systems interfaced with a WellChrom K-2301 refractive index detector. About 5 μm PLgel mixed-C column in DMF (0.01 mol/LiBr) was used as an eluent for the polymers. The polymer solutions were filtered through 0.2 μ Teflon membranes before analysis. Number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity index (M_w/M_n) of the polyaspartimides were determined.

RESULTS AND DISCUSSION

Monomer synthesis

Three different monomers containing pyridine ring as a pendant group[6] along with flexible linkages such as ether[6] and ester were prepared.[7,8] Scheme 1 shows the synthetic routes to diamines BAPM, BAPPM, and BABPM. The diamine monomer containing pyridine as pendant group was prepared by condensation of 2,6-dimethylaniline with pyridine-3-aldehyde in the presence of an acid catalyst. The structure of the bisphenol, dinitro, and diamine compounds was confirmed by elemental analysis, FTIR, ^{1}H NMR, and ^{13}C NMR. The elemental analysis values are in good agreement with the calculated ones (Table I). In FTIR spectrum of the dinitro compound BNBPM reveals absorption bands appearing around 1527 and 1346 cm^{-1} due to asymmetric and symmetric stretching vibration of —NO_2 group. After reduction, the characteristic absorption bands of nitro group disappeared and the characteristic bands of the amino groups at 3463 and 3349 cm^{-1} (asymmetric and symmetric stretching vibration of —NH_2 group) and 1629 cm^{-1} (N—H bending vibration) appeared. The dinitro precursor compound and the monomer show characteristic absorption bands around 1705–1746 cm^{-1} due to the ester carbonyl group. The signal around 3.83 ppm in the ^{1}H NMR



Scheme 2 Synthesis of bismaleimide.

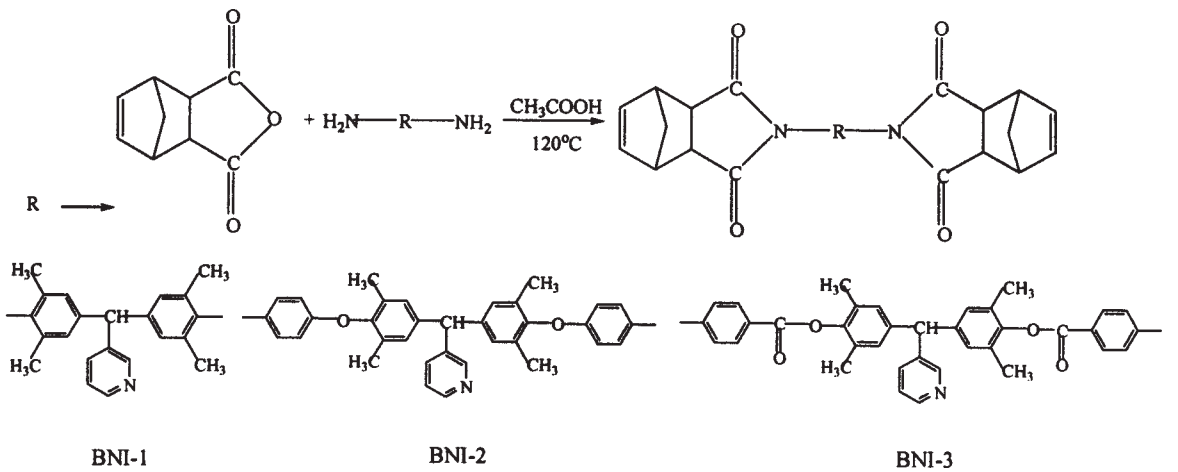
spectrum was assigned to the protons of amino groups. The signals in the range of 6.61–8.53 ppm are ascribed to the protons of the aromatic rings, and the area integration for the protons agreed with expectation. In the ^{13}C NMR spectra, the central methine carbon (C^6) of monomers and precursors resonate between 53 and 54.6 ppm confirming the formation of the proposed structure.[9] The ester carbonyl carbon (C^{16}) in the precursors and monomers resonate in the region between 162.6 and 164.4 ppm.

Synthesis of BMI and BNI

The new BMI and BNI were prepared according to the chemical reactions[10–12] outlined in Scheme 2 and 3. The BMI were prepared via a two-step method, in which the bismaleamic acid was obtained by treating the diamine with maleic anhydride, followed by cyclization with acetic anhydride and sodium acetate. The structure of BMI and BNI was identified by elemental analysis, FTIR, and ^1H NMR spectroscopy. The elemental analysis results are in good agreement with the proposed structure (Table I). In the FTIR spectra all the BMI and BNI show a strong absorption around 1709–1722 cm^{-1} and a weak absorption around 1771–1778 cm^{-1} due to symmetric and asymmetric C=O stretching vibration of imide ring. The bands around 1342–1382 cm^{-1} are due to C—N—C stretching vibration of imide ring and the band around 690 cm^{-1} is due to C=C of maleimide ring. BMI-2, BMI-3 BNI-2, and BNI-3 show a strong absorption band around 1240–1266 cm^{-1} for the C—O—C bond stretching vibration. Figures 1 and 2 show the ^1H NMR spectrum of BMI-1and BNI-1, respectively.

Properties of BMI and BNI

The solubility of BMI and BNI was tested in various organic solvents and the results are summarized in



Scheme 3 Synthesis of bisnadimide.

TABLE II
Solubility of BMI and BNI

Code	NMP	DMF	DMSO	DMAc	THF	$CHCl_3$	CH_2Cl_3
BMI-1	++	++	++	++	±	±	+
BMI-2	++	++	++	++	±	++	++
BMI-3	++	++	++	++	+	++	++
BNI-1	++	++	++	++	++	++	±
BNI-2	++	++	++	++	++	++	++
BNI-3	++	++	++	++	++	++	++

++, soluble at room temperature; +, soluble on heating; ±, partial soluble on heating; −, insoluble.

Table II. Most of the BMI and BNI are readily soluble not only in polar aprotic solvents, such as NMP, DMSO, and DMF, but also in less polar solvents such as chloroform and dichloromethane, indicating their good solution processability.

Thermal behavior of BMI and BNI such as the melting points, the polymerization temperatures (the thermally induced polymerization of the obtained BMI and BNI compounds could be observed from the exothermic peaks in the DSC thermograms) and the processing windows of the obtained compounds were measured by DSC. The thermal characteristics data are tabulated in Table III. The representative DSC curves of BMI and BNI are shown in Figure 3. From the DSC curves the onset temperature of the endothermic peak was taken as the melting point of the BMI and BNI. In general, the melting points tend to become higher with increasing molecular weight because of the increase in cohesive energy between molecules.[13] However, the BMIs and BNIs with flexible linkages contradict this general rule. Flexible groups (such as ether and ester linkages) between phenyl units of the long-chain monomer, interfere with close packing of the molecules leading to a decrease in melting point,[14] but the variation in the melting point is not very much as reported by others due to the presence of rigid pyridine moiety. The relative reactivity of monomers may be judged on the basis of T_{exo} values. It is seen that BMIs and BNIs containing the shortest bridging between the two polymerizable groups show the lowest curing temperature. Thus, the polymerization of monomers was shifted to higher temperatures when the concentration of olefinic bonds was reduced.[15] The polymerization occurs through their olefinic bonds and is believed to proceed via a free radical mechanism.[16] Upon heating of BNIs, cyclopentadiene arising from a retrograde Diels-Alder reaction is evolved but most of the evolved compound is captured by copolymerization or homopolymerization.[17,18] The first exotherm is believed to be due to thermally-induced polymerization reaction. The large exotherm which follows is due to pyrolysis of the cured bisimide. The exothermic peak of the bismaleimide and bisnadimide was broadened by the introduction of a phenoxy or benzoyloxy linkages. All the prepared BMIs and BNIs required higher curing temperature than the reported prepolymers.[14] This may be attributed to the steric hinderance of pendant pyridyl structure which reduces the reactivity and mobility of the reactive site and also make the processing window widened. T_gs of the crosslinked resins could not be detected by DSC, this could be attributed to the fact that the resin was

TABLE III
Thermal Behavior of BMI and BNI

Code	T_m (°C)	T_{exo} (°C)	T_{10} (°C)	Char yield (%)
BMI-1	282	324	462	51.06
BM1-2	225	340	441	49.81
BM1-3	161	335	397	42.06
BNI-1	258	313	447	50.86
BNI-2	239	339	432	49.65
BNI-3	206	284	394	41.12

T_{10}, temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in nitrogen; char yield, residual weight % at 800°C in nitrogen; T_m, endotherm melting temperature from DSC; T_{exo}, exotherm peak temperature from DSC.

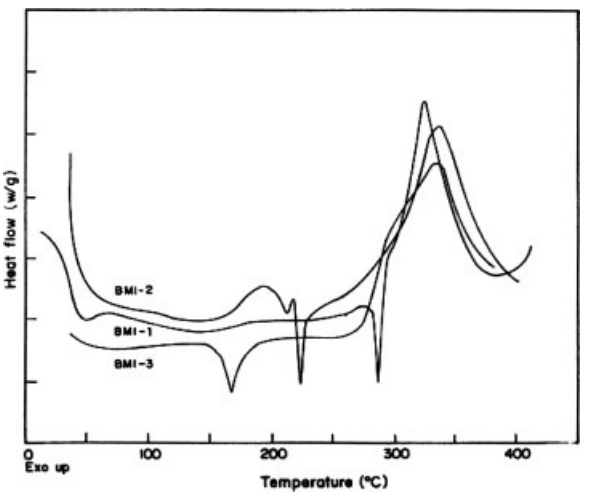
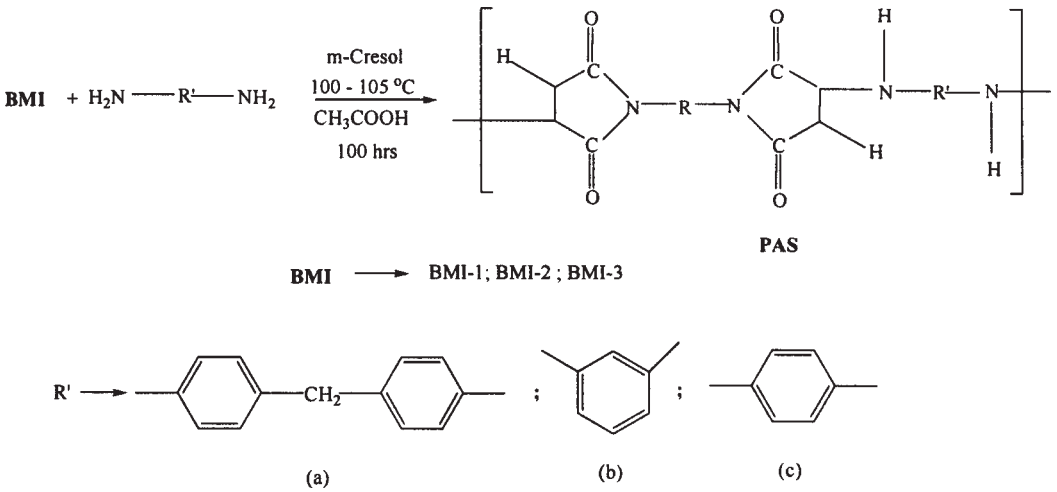


Figure 3 DSC traces of bismaleimides.



Scheme 4 Synthesis of polyaspartimides.

highly crosslinked and the change in C_p was very small.

The thermal stability of the cured resins was ascertained by thermo gravimetric analysis. The thermal stability of these resins was compared by the temperature of 10% decomposition (T_{10}) and percentage char yield at 800°C; these are presented in Table III. The thermal stability of the BMI and BNI, which are having flexible linkages, are expected to be less, but due to the presence of rigid pyridine moiety, the thermal stability of all the BMI and BNI are comparatively high. The structure of the above polymer precursors was selected in such a manner that their cured resins combined improved flexibility with a relatively high thermal stability. The presence of the flexible bridging groups such as ether and ester in the polymer backbone should reduce the brittleness of the cured resins. Hence, the cured resins obtained from these polymer precursors are expected to be less brittle than those of the ordinary BMI and BNI because larger polymer segments would be available for internal motion.

Preparation of polyaspartimides

A series of new linear polyaspartimides (PAS-1a - PAS-3d) was obtained via a Michael addition reaction[19] (Scheme 4). The effect of the reaction time on the polymer yield and molecular weight was already investigated[20] and there was no significant molecular chain growth and increase of polymer yield when reaction time was prolonged after 100 h. Therefore the polymerization time of 100 h was adopted in this study.

The structure of the polymers was confirmed by means of FTIR spectroscopy. The FTIR spectrum of representative polyaspartimide (PAS-2a) is shown in Figure 4. The band around 3339–3365 cm^{-1} is due to the N—H stretching vibration. The disappearance of band around 691 cm^{-1} due to maleimide C=C bond confirms the completion of addition reaction of the imide ring. The bands around 1773–1780 cm^{-1} and 1709–1721 cm^{-1} are due to asymmetric and symmetric stretching vibration of carbonyl group of the imide ring. The bands around 1372–1382 cm^{-1} are due to C—N—C stretching vibration of imide ring. The methyl group shows the band around 2917–2926 cm^{-1} due to C—H stretching vibration. The spectroscopic data are well in agreement with the expected structure ensuring the formation of the polyaspartimide.

Properties of polyaspartimides

The solubility of polyaspartimides was tested in various organic solvents and the results are summarized in Table IV. It is noteworthy that at room temperature most of the polymers are soluble in

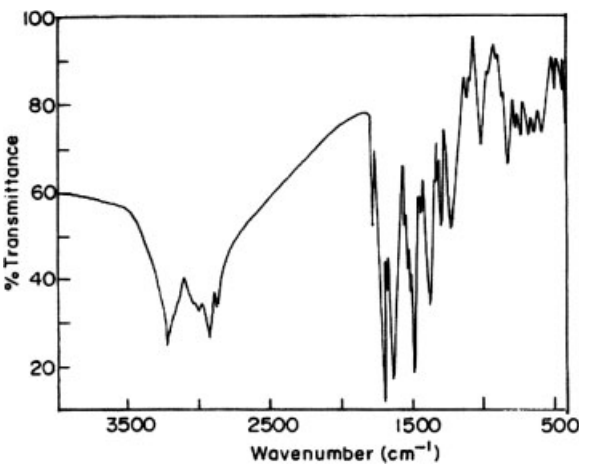


Figure 4 FTIR spectrum of PAS-2a.

TABLE IV
Solubility Behavior of Polyaspartimides

Polyaspartimide code	NMP	DMF	DMSO	DMAc	THF	$CHCl_3$
PAS-1a	++	++	++	++	±	±
PAS-1b	++	++	++	++	±	±
PAS-1c	++	++	++	++	−	−
PAS-2a	++	++	++	++	++	++
PAS-2b	++	++	++	++	++	±
PAS-2c	++	++	++	++	−	−
PAS-3a	++	++	++	++	++	++
PAS-3b	++	++	++	++	++	−
PAS-3c	++	++	++	++	±	−

++, soluble at room temperature; +, soluble on heating; ±, partial soluble on heating; −, insoluble.

highly polar solvents such as NMP, DMF, DMAc, and DMSO. Moreover, while BMI and BNI with flexible linkages were utilized (BMI-2 and BMI-3) the resulting polymers are soluble in $CHCl_3$, CH_2Cl_2, and THF. From the results shown in Table IV, the enhancement of the solubility of polyaspartimides by the incorporation of bulky pendant groups and flexible linkages is obvious, since in the literature the polyaspartimides composed of diamino diphenylmethane and commercial BMI (4,4′,-bismaleimidodiphenylmethane) show poor solubility in the test solvents.[21]

The crystallinity of the polymers was estimated by wide-angle X-ray measurements and the studies were performed with powder specimens. For most polymers, the reflection patterns are featureless, showing only broad amorphous halos. The results indicate that all the polymers are almost amorphous. This could be attributed to the introduction of the packing disruptive pyridyl pendant group, which results in increased chain distances and decreased chain-to-chain interactions thereby leading to decrease in crystallinity.[22]

The inherent viscosity of polyaspartimides was determined using Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc and the values are summarized in Table V. Compared with the other polymers the lower viscosity values of polyaspartimides obtained from *m*-phenylene diamine can be attributed to the lower reactivity of the diamine monomer containing a metaoriented amino group.[23]

The number average molecular weight, weight average molecular weight, and polydispersity index of the obtained polymers were estimated by GPC in DMF as eluent at 70°C and the values are tabulated in Table V. Number average molecular weight, M_n and weight average molecular weight, M_w are in the range of 10,000–14,600 and 22,400–37,400 respectively, with polydispersity indexes of about 2.23–2.81. These results indicate that all the polymers synthesized have high molecular weight and they are sufficient to cast tough and flexible films.

TABLE V
Inherent Viscosity, Molecular Weight, and Thermal Properties of Polyaspartimides

Polyaspartimide code	η (dL/g)	M_n	M_w	PI	T_{10} (°C)	Char yield (%)	T_g (°C)
PAS-1a	0.28	12,100	32,000	2.64	469	50.01	219
PAS-1b	0.21	10,600	29,700	2.80	475	51.68	224
PAS-1c	0.32	12,900	33,000	2.56	482	53.31	231
PAS-2a	0.28	11,800	29,000	2.46	412	46.31	201
PAS-2b	0.19	10,000	22,400	2.24	468	47.43	217
PAS-2c	0.31	12,500	33,400	2.68	476	49.34	229
PAS-3a	0.38	10,600	28,800	2.72	379	44.31	186
PAS-3b	0.31	12,000	33,400	2.78	386	47.34	194
PAS-3c	0.42	14,600	37,400	2.56	445	48.83	212

T_{10}, temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in nitrogen; char yield, residual weight % at 800°C in nitrogen; T_g, midpoint temperature base line shift on the second DSC trace heating trace of the sample after quenching from 400°C; M_n and M_w, number average and weight average molecular weight determined from GPC with DMF as eluent at 70°C; PI, polydispersity index (M_w/M_n).

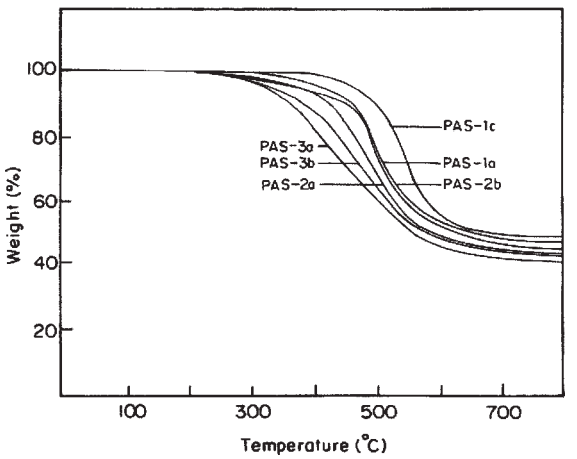


Figure 5 Thermograms of polyaspartimides in N_2 atmosphere.

Thermal properties of all the polyaspartimides were evaluated by thermogravimetry and differential scanning calorimetry. The thermal behavior data of all the polyaspartimides are summarized in Table V. The representative TGA curves of polyaspartimides obtained in nitrogen atmosphere are shown in Figure 5. All polyaspartimides show a similar pattern of decomposition and did not show significant weight loss below 380°C in nitrogen. The methyl substituent and N—H unit in the polymer chain tend to decompose along with the main chain at lower temperature as is evident from the thermogram showing a broad single stage weight loss. The initial weight loss may be due to decomposition of N—H bond and methyl groups followed by the degradation of the polymer chain at higher temperature, all showing a single broad thermogram. The T_{10} values of these polyaspartimides are in the range of 379–482°C. The char yield of the polyaspartimides is in the range of 44.31–53.31% when heated to 800°C in nitrogen, confirming that these polymers have good thermal stability and self extinguishing property. DSC measurements were carried out at a heating rate of 10°C/min in nitrogen. The T_g values of the polymers are in the range 194–231°C, depending upon the stiffness of the polymer chain. In the case of polyaspartimide containing ether linkages, lower T_g was observed because of the increased rotational movement caused by the flexible ether linkage. But the incorporation of methyl substituent ortho to the flexible linkages tends to restrict the segmental rigidity of the polymer, thereby, enhancing the T_g. The presence of bulky pendant phenyl unit also tends to enhance T_g by restricting the segmental motion of the polymer chain. Polyaspartimides containing *p*-phenylene moiety have higher T_g than those containing MPD and DDM due to increased rigidity of the polymer chain in the former due to its symmetric structure. The T_g values vary slightly and the variation is due to size effect, which directly influences the packing density, polymer aggregation and interaction of polymer chains and hence the T_g.[24]

CONCLUSIONS

A novel bismaleimide and bisnadimide containing pyridine pendant group and flexible linkages has provided excellent balance of properties in processability, solubility, and thermal stability. The new polyaspartimides resulting from the Michael addition reaction of BMI and various diamines were successfully prepared. Solubility and thermal properties of the polyaspartimides were influenced by the rigidity and symmetry of the polymer main chain. The polymers have T_g values in the range of 194–229°C and the T_{10} values in the range of 379–482°C. However, it is expected that a increase in thermal stability can be observed by the incorporation of heteroaromatic ring in the polymer main chain itself and the work is underway and the results will be reported soon.

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