# Synthesis and Properties of Novel Organosoluble Bismaleimides and Polyaspartimides Containing Bis(4-maleimido-3, 5-dimethyl phenyl) Halo Phenyl Methane

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**ABSTRACT:** A series of bismaleimides was synthesized from bis(4-amino-3, 5-dimethylphenyl) (X) phenyl methane (X = 3′chloro, 3′-bromo, 3′-benzyloxy, 4′-chloro, 4′-fluoro) and maleic anhydride. The bismaleimides were subsequently polymerized with various diamines by Michael addition to yield novel polyaspartimides. All the polymers exhibited good solubility in organic solvents and the inherent viscosity of the polymers were in the range of 0.40–0.56 dL/g, which is good enough to fabricate composites and films. The tempera-ture at which 10% weight loss occurred was in the range of 390–441°C. The polymers had high glass transition tempera-ture in the range of 205–275°C and left about 31.95–84.20% char yield at 800°C indicating that they have good self-extin-guishing property. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1126–1135, 2008

**Key words:** polyimides; halogenated; thermal properties; X-ray; viscosity

## INTRODUCTION

Polyimides are high performance polymers, which have remarkable temperature resistance, mechanical and electrical properties.[1] However, polyimides, which are thermoplastic in nature, have some drawbacks such as insolubility, infusibility, and evolution of vola-tiles during the ring formation, leading to poor proces-sibility. Extensive research are undergoing all over the world to develop a potential material to overcome these drawbacks. One approach involves synthesizing thermosetting bismaleimides. They are the leading class of polyimides with excellent thermal and me-chanical properties, which made them popular to be used in electronic industry and also in advanced com-posites.[2–4] They also exhibit excellent hot wet strength retention and fatigue resistance.[5]

Bismaleimides are defined as low molecular weight difunctional monomers, which contain imide moieties in their back bone structure and have terminal reactive groups (C=C), which undergo homo and/or copoly-merization by thermal treatment or in the presence of catalyst. The double bonds present in bismaleimides are highly electron-deficient, which can be self poly-merized thermally to give a highly crosslinked net-work, exhibiting good thermal, chemical, and me-chanical properties superior to the epoxy resin.[6,7] They have wide applications in electronic industries such as multilayered printed circuit boards for com-puters[8–10] and in aerospace industries.[11] Bismale-imides bridge the temperature performance gap between epoxy- and condensation type polyimides. They have become one of the important high performance ther-mosetting engineering plastics. They have easy pro-cessing similar to epoxies unlike the condensation type polyimides. Further, they can be fabricated into composite sheets by casting techniques and also using fiber as reinforcement. One of the major drawbacks is their brittleness (due to their high crosslink density), which restricts their utility. To overcome these draw-backs, any dinucleophilic reagent can be added to the bismaleimide (thereby reducing the crosslink density).

Polyaspartimides can be prepared by reacting a di-amine with a bismaleimide. The main aim of bismale-imide/diamine concept was to increase the molecular weight between crosslinks, to improve the ductility of the bismaleimides.

In the present study, a new type of organosoluble thermosetting bismaleimides and thermoplastic poly-aspartimides were synthesized from the diamines bis (4-amino-3,5-dimethyl phenyl)(X) phenyl methane (where X = 3′-chloro,3′-bromo,3′-benyloxy,4′-chloro,4′-fluoro).[12] The presence of Cl, Br, F, —OCH$_2$C$_6$H$_5$ group would increase solubility by enhancing the free volume and polar interactions with solvents.[13–15] The prepared

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polyaspartimides are expected to have good viscosity and thermal properties.

## EXPERIMENTAL

### Materials

*m*-Bromobenzaldehyde, *p*-chlorobenzaldehyde, *p*-fluorobenzaldehyde, *m*-benzyloxybenzaldehyde, and *m*-chlorobenzaldehyde were purchased from E-Merck (Germany) and used without any further purification, 2,6-dimethylaniline (Aldrich), hydrochloric acid (HCl, Spectrochem), *N*-methyl-2-pyrrolidone (NMP, E-Merck), *p*-phenylene diamine (PPD,E-Merck), 4,4′-diamino diphenyl ether (ODA, SRL), 2,6-diaminopyridine (DAP, Aldrich) maleic anhydride (Spectrochem), tetrahydrofuran (THF, Fischer, India), and *N,N*-dimethyl acetamide (DMAc, E-merck, India) were used as received in the present study. *N,N*-dimethyl formamide (DMF, E-Merck) was purified by refluxing with CaO, distilled under reduced pressure and stored over 4 Å molecular sieves.

### Monomer synthesis

Synthesis of bis(4-amino-3, 5-dimethyl phenyl) (X) phenyl methane

The syntheses of various substituted diamines were carried out according to procedures reported by elsewhere.[12] A three-necked flask equipped with reflux condenser, a $N_2$ inlet, and a bent inlet for dry HCl was charged with 2,6-dimethyl aniline (0.04 mol, 4.84 g). Dry HCl (0.045 mol, 5 mL) was passed into the reaction vessel for 30 min. The solid obtained was melted by heating around 100°C. To this solution, various substituted benzaldehyde (0.018 mol) was added dropwise. After complete addition, the reaction mixture was stirred at room temperature for 1 h. Then, the temperature was slowly raised and maintained at 120°C for 6 h. The reaction mixture was cooled and the pH was brought to 7, the solid product obtained was filtered, washed repeatedly with methanol, and dried in vacuum oven at 60°C for 12 h.

Synthesis of bis(4-maleimido-3, 5 dimethyl phenyl) (X) phenyl methane

Various bis(4-maleimido-3, 5-dimethyl phenyl) substituted (X) phenyl methane (X = 3′-chloro, 3′-bromo, 4′-fluoro, 4′-chloro, 3′-benzyloxy) were prepared from the corresponding substituted diamines and maleic anhydride. A Three-necked flask equipped with an addition funnel and nitrogen inlet was charged with a solution of synthesized diamine (0.05 mol) in THF. Maleic anhydride (9.81 g, 0.1 mol) dissolved in THF was added dropwise to the above mixture. The solution was stirred for 4 h at room temperature and at 70°C for additional 6 h. The precipitate of bismaleamic acid was collected, washed with fresh THF to remove excess reactant, and then it was dried in vacuum at 60°C for 12 h.
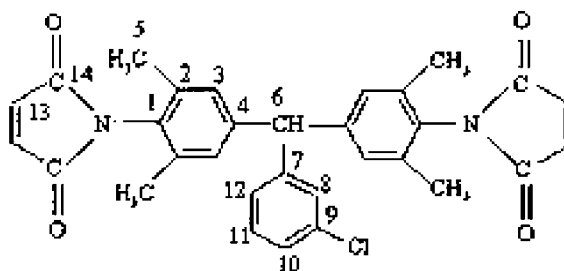
IR (KBr, cm$^{-1}$), 3320 (*N*—H), 1720 (C=O stretching), 1612 (*N*—H bending). $^1$H-NMR-(CDCl$_3$), $\delta$ = 10.44–10.50(s, 2H, COOH).

0.05 mol of bismaleamic acid in 20 mL of DMF was charged in to a 250-mL round-bottomed flask. The solution was maintained at 75°C for 3 h with stirring. Acetic anhydride (25 mL) and 0.25 g of sodium acetate were added to the preheated solution. The temperature of the reaction mixture was raised to 90°C and then stirred for 6 h. The reaction mixture was poured into cold water to yield bismaleimide. All other bismaleimides were synthesized by adopting the similar procedure.

*BMCM.* Yield 91%, IR (KBr) $\tilde{v}_{max}$ (cm$^{-1}$) : 1715,1776 (C=O symm and asymm stretch), 1379 (C—N—C stretch), 2924 (CH$_3$ stretch), 1088 (C—Cl stretch), 691 (—C=C— stretch), 3104 (=C—H stretch); $^1$H-NMR(500 MHz, CDCl$_3$) : $\delta$ 6.86(4H,s, Ha), 5.34(1H,s, Hb), 2.16(12H,s, Hc), 7.20(1H,s, Hd), 7.18–7.20(1H,d, He), 7.06–7.08(1H,d, Hf), 6.96–6.99(1H,t, Hg), 7.22(4H,s, Hh); $^{13}$C-NMR(125 MHz, CDCl$_3$) : C$^1$-127.1, C$^2$-136.9, C$^3$-129.4, C$^4$-142.8, C$^5$-17.80, C$^6$-55.50, C$^7$-141.1, C$^8$-130.6, C$^9$-134.6, C$^{10}$-127.8, C$^{11}$-130.1, C$^{12}$-128.0, C$^{13}$-134.2, C$^{14}$-169.8; Anal. Calcd for C$_{31}$H$_{25}$N$_2$O$_4$Cl: C, 70.92%, H, 4.79%, *N*, 5.33%; found: C, 69.99%, H, 4.98%, *N*, 5.42%.
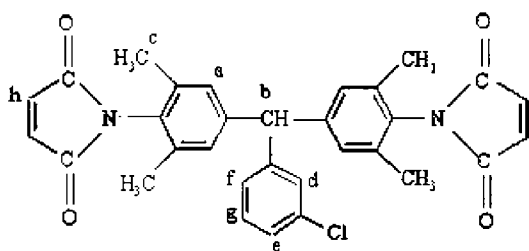


*BMBM.* Yield 89%, IR (KBr) $\tilde{v}_{max}$ (cm$^{-1}$): 1715,1774 (C=O symm and asymm stretch), 1373 (C—N—C stretch), 2922 (CH$_3$ stretch), 1072 (C—Br stretch), 690 (—C=C— stretch), 3104 (=C—H stretch); $^1$H-NMR(500 MHz, CDCl$_3$): 6.87(4H,s, Ha), 5.35(1H,s, Hb), 2.16(12H,s, Hc), 7.22(1H,s, Hd), 7.16–7.18(1H,d, He),

7.04–7.06(1H,d,Hf), 6.90–6.93(1H,t,Hg), 7.25(4H,s, Hh); $^{13}$C-NMR(125 MHz, CDCl$_3$): $C^1$-127.4, $C^2$-134.8, $C^3$-129.1, $C^4$-141.0, $C^5$-18.20, $C^6$-54.80, $C^7$-142.2, $C^8$-133.2, $C^9$-122.8, $C^{10}$-129.8, $C^{11}$-131.1, $C^{12}$- 129.0, $C^{13}$-134.3, $C^{14}$-163.2; Anal. Calcd for $C_{31}H_{25}N_2O_4Br$: C, 65.38%, H, 4.42%, $N$, 4.92%; found: C, 65.10%, H, 4.52%, $N$, 4.99%.
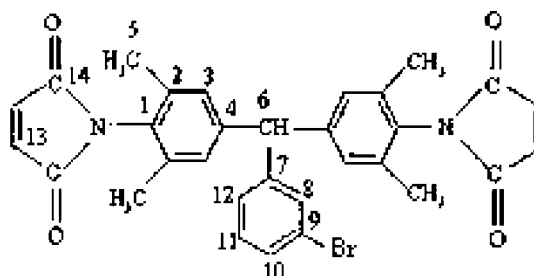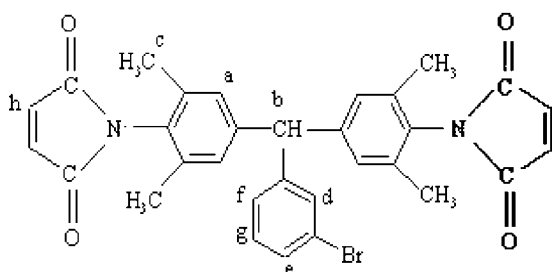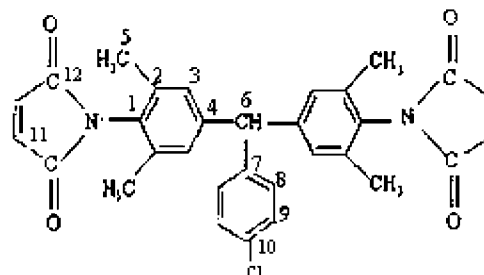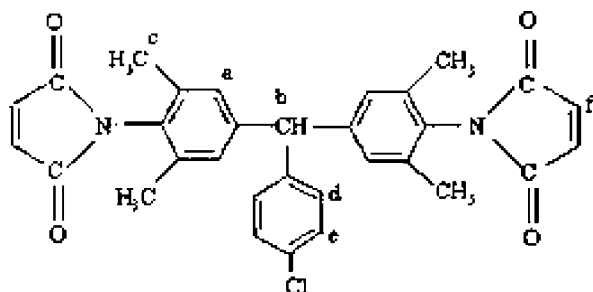




*BMPFM.* Yield 89%, IR (KBr) $\tilde{v}_{max}$ (cm$^{-1}$): 1716,1780 (C=O symm and asymm stretch), 1376 (C—N—C stretch), 2924 (CH$_3$ stretch), 1156 (C—F stretch), 691 (—C=C- stretch), 3103 (=C—H stretch); $^1$H-NMR(500 MHz, CDCl$_3$): 6.84(4H,s, Ha), 5.39(1H,s, Hb), 2.16(12H,s, Hc), 6.97–6.99(2H,d, Hd), 7.08–7.10(2H,d, He), 7.25(4H,s, Hf); $^{13}$C-NMR(125MHz, CDCl$_3$): $C^1$-127.6, $C^2$-137.0, $C^3$-129.5, $C^4$-144.4, $C^5$-18.10, $C^6$-55.40, $C^7$-137.0, $C^8$-133.8, $C^9$-115.2, $C^{10}$-133.1, $C^{11}$-134.4, $C^{12}$-169.6; Anal. Calcd. for $C_{31}H_{25}N_2O_4F$: C, 73.21%, H, 4.95%, $N$, 5.50%; found: C, 72.62%, H, 5.14%, $N$, 5.78%.
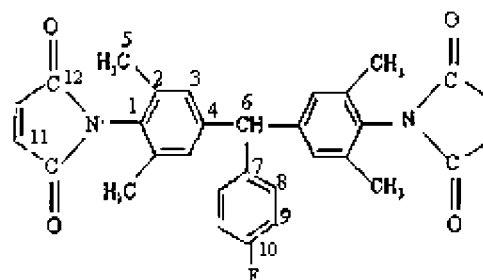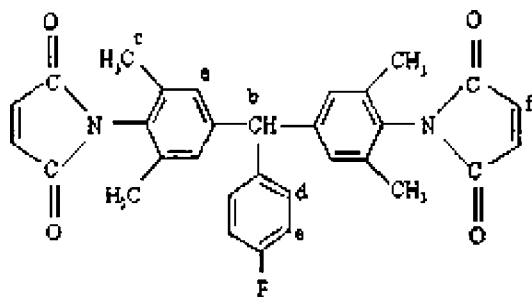




*BMPCM.* Yield 90%, IR (KBr) $\tilde{v}_{max}$ (cm$^{-1}$): 1715,1776 (C=O symm and asymm stretch), 1375 (C—N—C stretch), 2922 (CH$_3$ stretch), 1088 (C—Cl stretch), 689 (—C=C— stretch), 3099 (=C—H stretch); $^1$H-NMR(500 MHz, CDCl$_3$): 6.90(4H,s, Ha), 5.30(1H,s, Hb), 2.18(12H,s, Hc), 7.05–7.07(2H,d, Hd), 7.08– 7.10(2H,d, He), 7.26(4H,s, Hf); $^{13}$C-NMR(125 MHz, CDCl$_3$): $C^1$-127.7, $C^2$-137.1, $C^3$-129.5, $C^5$-18.40, $C^6$-55.50, $C^7$-137.1, $C^8$-130.2, $C^9$-123.6, $C^{10}$-131.0, $C^{11}$-134.3, $C^{12}$-169.6; Anal. Calcd. for $C_{31}H_{25}N_2O_4Cl$: C, 70.92%, H, 4.79%, $N$, 5.33%; found: C, 69.78%, H, 4.83%, $N$, 5.47%.

*BMBOM.* Yield 91%, IR (KBr): 1710,1780 (C=O symm and asymm stretch), 1376 (C—N—C stretch), 2923 (CH$_3$ stretch), 1243 (C—O—C stretch), 691 (—C=C—stretch), 3098 (=C—H stretch); $^1$H-NMR(500 MHz, CDCl$_3$): 6.96(4H,s, Ha), 5.44(1H, s, Hb), 2.10(12H,s, Hc), 5.03(1H,s, Hd),7.29–7.46(1H,m,He,Hf,Hg,Hh,Hi,Hj,Hk)

7.25(4H,s,Hl); $^{13}$C-NMR(125 MHz, CDCl$_3$):C$^1$-127.7, C$^2$-137.0, C$^3$-129.6, C$^4$-144.7, C$^5$-18.18, C$^6$-52.0, C$^7$-136.9, C$^8$-115.1, C$^9$-166.2, C$^{10}$-111.2, C$^{11}$-129.4, C$^{12}$-121.4, C$^{13}$-62.60, C$^{14}$-159.8, C$^{15}$-114.1, C$^{16}$-129.5, C$^{17}$-122.0; Anal. Calcd. for C$_{38}$H$_{32}$N$_2$O$_5$: C, 76.49%, H, 5.40%, *N*, 4.69%; found: C, 76.19%, H, 5.49%, *N*, 4.81%.
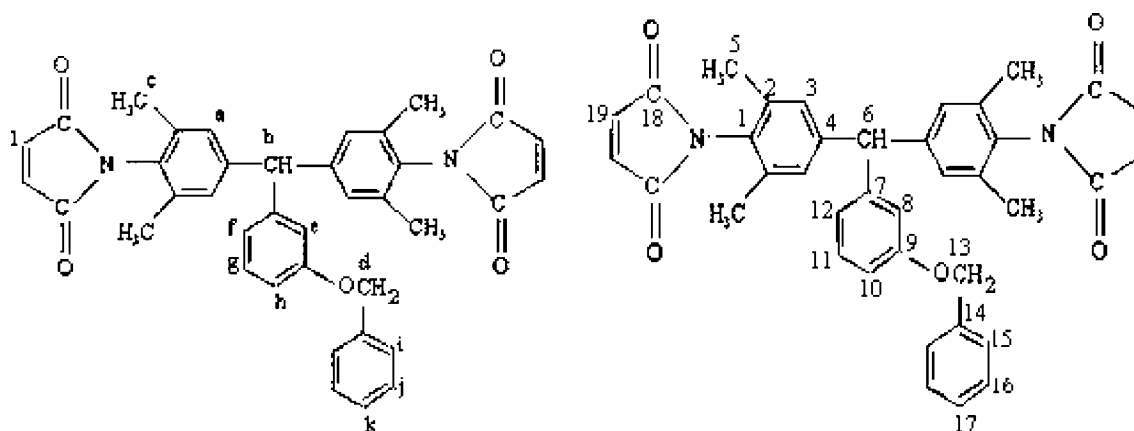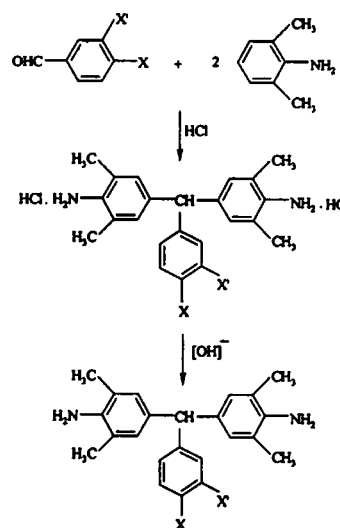


## Polymer synthesis

A 150-mL three-necked flask fitted with a N$_2$ inlet, reflux condenser, and a thermometer was charged with (0.01 mol) of BMI in 15 mL of *m*-cresol. The solution was stirred at room temperature, while the BMI completely dissolved, 1.08 g (0.01 mol) of diamine (*p*-phenylene diamine or 2.6-diaminopyridine or oxydianiline) and 0.5 mL of glacial acetic acid were added into the flask. The reaction mixture was stirred at 100°C for 96 h. The resulting viscous solution was poured into excess ethanol with vigorous stirring and the polymer, thus precipitated out from the nonsolvent was filtered, washed thrice with hot ethanol, and dried under vacuum at 60°C overnight. All other polymers were prepared by following the same procedure mentioned above.

## Measurements

Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet spectrometer with KBr pellet. $^1$H-NMR and $^{13}$C-NMR spectra were recorded using Jeol Ex-400 spectrometer with CDCl$_3$ as the solvent. The $^1$H chemical shifts were calibrated by using tetra methyl silane (TMS). Elemental analysis was performed on a Carlo Erba EA 1108 micro analyzer; DSC and TGA were performed with a Perkin–Elmer 7 series thermal analyzer system at a heating rate of 10°C/min. The inherent viscosity was measured with an Ubbelohde viscometer using a 0.5 g/dL solution in NMP at

30°C. The solubility was determined by mixing 0.025 g of the sample in 10 mL of the solvent at room temperature. Solubility was determined visually. X-ray diffraction measurements were performed on a Philips PW 1730-10 X-ray diffractometer using Cu Kα radiations.



| X' | Cl | Br | H | H | OCH$_2$C$_6$H$_5$ |
|---|---|---|---|---|---|
| X | H | H | F | Cl | H |
| MONOMER | BACM | BABM | BAPFM | BAPCM | BABOM |

**Scheme 1** Synthesis of diamine.

## RESULTS AND DISCUSSION

### Monomer synthesis

Various bis(4-amino-3, 5-dimethyl phenyl) substituted (X) phenyl methane (X = 3′-chloro, 3′-bromo, 4′-fluoro, 4′-chloro, 3′-benzyloxy) were prepared from the corresponding substituted benzaldehyde and 2,6-dimethyl aniline as shown in Scheme 1. The structure of the diamines was confirmed by elemental analysis, FTIR and $^1$H-NMR.[12] The various substituted diamines were then reacted with required amount of maleic anhydride to give bismaleamic acid (I). The bismaleamic acid was then cyclodehydrated using cyclodehydrating agents (acetic anhydride and sodium acetate) as shown in Scheme 2. The structure was confirmed by elemental analysis, FTIR, $^1$H, and $^{13}$C-NMR. The elemental analysis data were found to be in good agreement with the proposed structure. The representative infra red spectrum of bismaleimide (BMCM, Fig. 1) shows strong absorption at 1715 cm$^{-1}$ and a weak
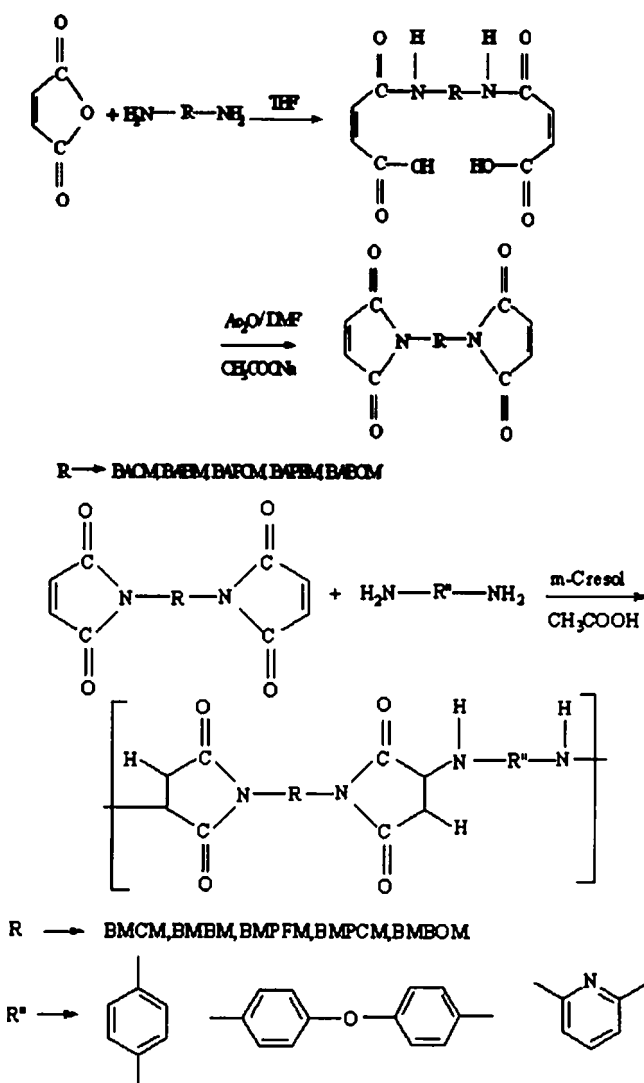


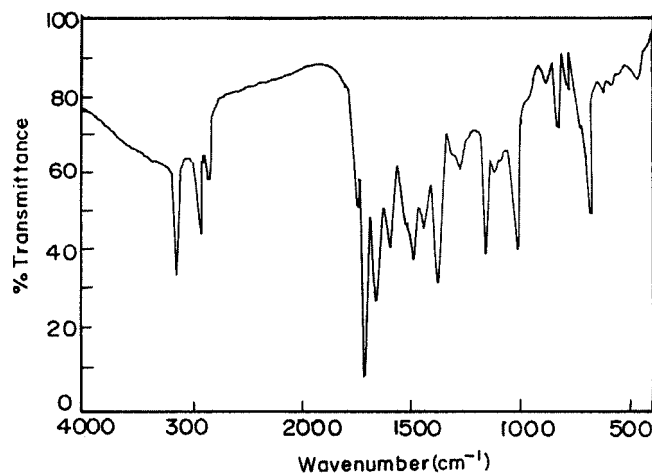**Figure 1**  FTIR spectrum of bismaleimide (BMCM).

absorption at 1776 cm$^{-1}$ due to asymmetric and symmetric C=O stretching vibration of the imide ring respectively. The absence of band at 3300–3500 cm$^{-1}$ shows that bismaleamic acid was completely converted into bismaleimide and the absence of band at 1545 cm$^{-1}$ due to N—H group of amide linkage also confirms the complete ring formation. The band at 692 cm$^{-1}$ is due to C=C of maleimide ring. The band at 1386 cm$^{-1}$ is due to C—N—C stretch and the band around 3100 is due to =C—H group of bismaleimide ring. The $^1$H-NMR spectrum (Fig. 2) of bismaleimide (BMCM) shows the distinct signal at 7.26 ppm due to four olefinic protons and the absence of signal at 10.5 ppm due to —COOH protons shows the complete imidization and the signal at 2.18 ppm is due to 12 protons of methyl group. All other aromatic protons are accountable in the region of 6.9–7.08 ppm and the $^{13}$C-NMR spectra show distinct signals for all the carbon atoms in the region 17.8–169.8 ppm. The representative $^{13}$C-NMR spectrum of bismaleimide (BMCM) is shown in Figure 3. All other bismaleimides show signals in the same region, ensuring the formation of bismaleimide.

### Polymer synthesis

The nucleophilic addition of diamines to aromatic bismaleimide, the Michael type addition, is a well-known route to linear polyaspartimides. The synthesized bismaleimides and an equivalent amount of aromatic diamines were stirred together in *m*-cresol containing a catalytic amount of glacial acetic acid to promote the polymerization as shown in Scheme 2. The structure of the polymer was confirmed by elemental analysis and FTIR. The elemental analysis data of polyaspartimides are given in Table I. The calculated and found values of all the polymers are in good agreement with the proposed structure suggesting the formation of polyaspartimide. The yield obtained was also good. The
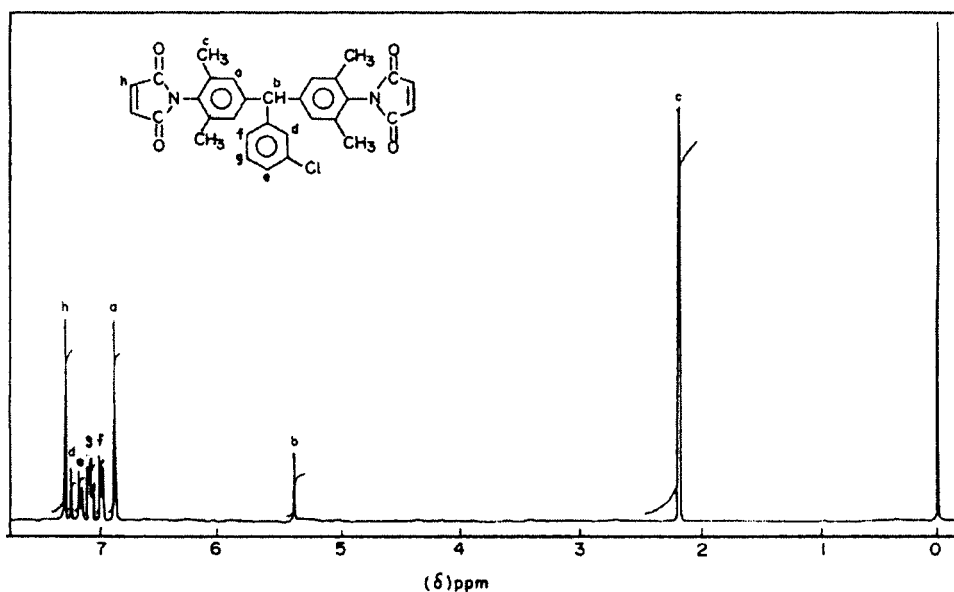


**Scheme 2**  Synthesis of bismaleimide.

**Figure 2** ^{1}H-NMR spectrum of bismaleimide (BMCM).

structure of polymers was confirmed by means of IR spectroscopy. The characteristic bands in the IR spectra are tabulated in Table II. The representative IR spectrum of polyaspartimide (PAS$_{1a}$) is shown in Figure 4. 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 vibration of carbonyl group. The bands around 1360–1382 cm$^{-1}$ are due to C—N—C stretch of imide ring. The methyl group shows the band around 2917–2926 cm$^{-1}$ due to C—H stretching vibration. The Cl, Br, and F substituents show characteristic bands around 1089, 1072, and 1157 cm$^{-1}$ respectively. The spectroscopic data are well in agreement with the expected structure ensuring the formation of the polyaspartimide.

## Properties of polyaspartimides

### Inherent viscosity

The inherent viscosity of polyaspartimides was determined using Ubbelohde viscometer at a concentration of 0.5 g/dL in NMP and the results are tabulated in Table III. All the polyaspartimides show the viscosity values, which are enough for the fabrication of composites and films. The viscosity values of polyaspartimides are in the range 0.40–0.56 dL/g. The viscosity value of polyaspartimides containing oxy linkage are low because of the presence of flexible linkage present in the polymer backbone, which decreases the stiffness of the polymer, hence the viscosity.[16] Polyaspartimides containing p-phenylene moiety exhibit higher

viscosity in comparison to polyaspartimides containing pyridine because of the presence of rigid phenylene moiety present in it.

### Solubility

The solubility of polyaspartimides was tested in various organic solvents and the results are summarized in Table IV. The polyaspartimides containing p-phenylene diamine moiety exhibit limited solubility. They are soluble in polar aprotic solvents such as DMF, DMAc, and NMP. Though introduction of bulky group on the polymer chain should impart solubility, they exhibit limited solubility due to symmetric and
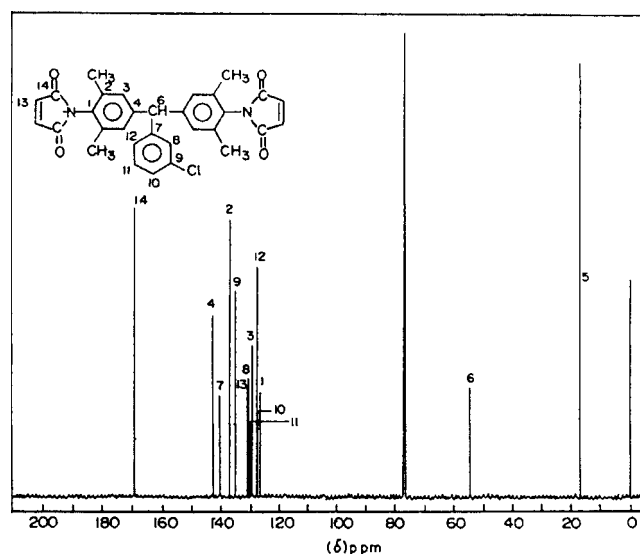


**Figure 3** ^{13}C-NMR spectrum of bismaleimide (BMCM).

**TABLE I**
**Elemental Analysis Data of Polyaspartimides**

| Code | Molecular formula | Yield (%) | Carbon | | Hydrogen | | Nitrogen | |
|---|---|---|---|---|---|---|---|---|
| | | | Calcd. | Found | Found | Calcd. | Found | Calcd. |
| $PAS_{1a}$ | $C_{37}H_{33}N_4O_4Cl$ | 92 | 70.18 | 69.57 | 5.67 | 5.25 | 9.14 | 8.84 |
| $PAS_{1b}$ | $C_{36}H_{32}N_5O_4Cl$ | 89 | 68.18 | 67.40 | 5.50 | 5.08 | 11.35 | 11.04 |
| $PAS_{1c}$ | $C_{43}H_{37}N_4O_5Cl$ | 88 | 71.21 | 70.81 | 5.73 | 5.14 | 7.53 | 7.72 |
| $PAS_{2a}$ | $C_{37}H_{33}N_4O_4Br$ | 87 | 65.58 | 64.82 | 5.24 | 4.90 | 8.57 | 8.26 |
| $PAS_{2b}$ | $C_{36}H_{32}N_5O_4Br$ | 91 | 63.72 | 63.24 | 4.94 | 4.75 | 10.62 | 10.32 |
| $PAS_{2c}$ | $C_{43}H_{37}N_4O_5Br$ | 89 | 67.10 | 66.85 | 5.43 | 4.84 | 6.93 | 7.27 |
| $PAS_{3a}$ | $C_{37}H_{33}N_4O_4F$ | 87 | 72.06 | 71.5 | 5.71 | 5.39 | 9.32 | 9.08 |
| $PAS_{3b}$ | $C_{36}H_{32}N_5O_4F$ | 84 | 70.00 | 69.68 | 5.42 | 5.22 | 11.44 | 11.33 |
| $PAS_{3c}$ | $C_{43}H_{37}N_4O_5F$ | 89 | 72.86 | 72.06 | 6.45 | 5.26 | 7.51 | 7.90 |
| $PAS_{4a}$ | $C_{37}H_{33}N_4O_4Cl$ | 81 | 70.19 | 69.49 | 5.66 | 5.25 | 9.14 | 8.84 |
| $PAS_{4b}$ | $C_{36}H_{31}N_5O_4Cl$ | 84 | 68.18 | 67.39 | 5.52 | 5.08 | 11.29 | 11.04 |
| $PAS_{4c}$ | $C_{43}H_{37}N_4O_5Cl$ | 89 | 71.21 | 70.79 | 5.70 | 5.14 | 7.51 | 7.72 |
| $PAS_{5a}$ | $C_{44}H_{40}N_4O_5$ | 90 | 74.97 | 74.26 | 6.14 | 5.72 | 8.24 | 7.94 |
| $PAS_{5b}$ | $C_{43}H_{39}N_5O_5$ | 87 | 73.17 | 72.39 | 6.03 | 5.56 | 10.23 | 9.92 |
| $PAS_{5c}$ | $C_{50}H_{44}N_4O_6$ | 85 | 75.35 | 74.95 | 6.15 | 5.56 | 6.84 | 7.03 |

rigid structures.[17] Polyaspartimides containing oxy linkages exhibit excellent solubility even in common solvents such as $CHCl_3$ and THF. It could be attributed to the incorporation of bulky pendant groups and presence of flexible linkage in the polymer due to which there would be a considerable decrease in the rigidity and a lowering of energy of internal rotation for the polymer chain, thus reducing the crystallinity and improving the solubility.[18] Polyaspartimides containing pyridine moiety exhibit better solubility in comparison with p-phenylene moiety, though the presence of pyridine group should enhance the polymer rigidity. The incorporation of bulky pendant group in the polymer chain decreases the intermolecular forces between the polymer chains, because of looser packing of polymer chains. The effect of halo substitution on

the solubility was also studied. Polyaspartimides containing chloro and bromo substituent exhibit limited solubility in comparison with fluoro substituent. The incorporation of fluorine atom enhances solubility, due to the electron polarizability of C—F bonds and the polar interaction of fluorine atom with solvents is much more in comparison with Cl and Br. Polyaspartimides containing benzyloxy unit exhibit better solubility due to the presence of bulky phenyl group which enhances free volume, thereby increasing solubility.

The crystallinity of the polymers was evaluated by wide-angle X-ray diffraction measurements with $2\theta$ measurements from $10°$ to $40°$. Polyaspartimides containing p-phenylene moiety ($I_a,II_a,III_a,IV_a$) show crystalline pattern. This may be due to the presence of highly symmetric p-phenylene moiety in the polymer backbone. All other polymers exhibit amorphous pattern. This may be attributed to the presence of bulky

**TABLE II**
**FTIR Spectral Data of Polyaspartimides**

| Code | Wave number (cm$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | C=O | | N—H | C—N | $CH_3$ | C—X |
| | Asymm. | Symm. | | | | |
| $PAS_{1a}$ | 1776 | 1713 | 3363 | 1382 | 2924 | 1090 |
| $PAS_{1b}$ | 1778 | 1716 | 3350 | 1372 | 2925 | 1089 |
| $PAS_{1c}$ | 1779 | 1720 | 3348 | 1360 | 2921 | 1089 |
| $PAS_{2a}$ | 1776 | 1712 | 3358 | 1378 | 2922 | 1071 |
| $PAS_{2b}$ | 1777 | 1713 | 3351 | 1375 | 2923 | 1072 |
| $PAS_{2c}$ | 1778 | 1711 | 3362 | 1379 | 2924 | 1074 |
| $PAS_{3a}$ | 1776 | 1714 | 3344 | 1379 | 2924 | 1157 |
| $PAS_{3b}$ | 1780 | 1720 | 3351 | 1375 | 2922 | 1152 |
| $PAS_{3c}$ | 1779 | 1716 | 3349 | 1378 | 2923 | 1158 |
| $PAS_{4a}$ | 1776 | 1711 | 3351 | 1378 | 2917 | 1088 |
| $PAS_{4b}$ | 1778 | 1716 | 3353 | 1372 | 2925 | 1090 |
| $PAS_{4c}$ | 1775 | 1716 | 3341 | 1378 | 2926 | 1089 |
| $PAS_{5a}$ | 1776 | 1713 | 3339 | 1373 | 2919 | – |
| $PAS_{5b}$ | 1775 | 1714 | 3365 | 1376 | 2924 | – |
| $PAS_{5c}$ | 1773 | 1709 | 3347 | 1380 | 2921 | – |
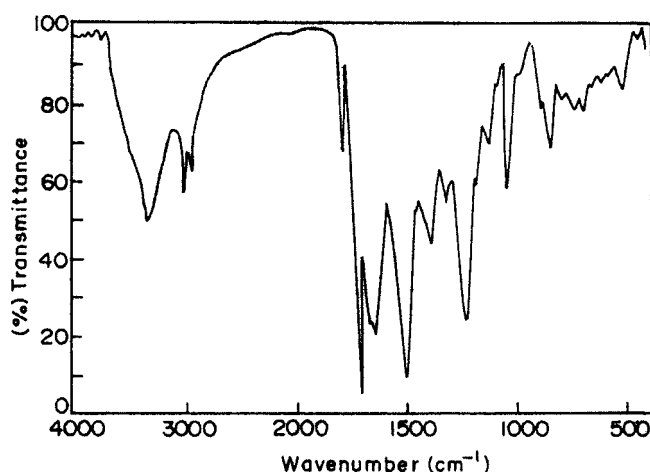


**Figure 4** FTIR spectrum of polyaspartimide $PAS_{1a}$.

**TABLE III**
**Inherent Viscosity of Polyaspartimides**

| Code | Polyaspartimide | $\eta$ (dL/g) |
|------|-----------------|---------------|
| PAS$_{1a}$ | BMCM + PPD | 0.51 |
| PAS$_{1b}$ | BMCM + DAP | 0.46 |
| PAS$_{1c}$ | BMCM + ODA | 0.40 |
| PAS$_{2a}$ | BMBM + PPD | 0.54 |
| PAS$_{2b}$ | BMBM + DAP | 0.50 |
| PAS$_{2c}$ | BMBM + ODA | 0.45 |
| PAS$_{3a}$ | BMPFM + PPD | 0.49 |
| PAS$_{3b}$ | BMPFM + DAP | 0.46 |
| PAS$_{3c}$ | BMPFM + ODA | 0.41 |
| PAS$_{4a}$ | BMPCM + PPD | 0.50 |
| PAS$_{4b}$ | BMPCM + DAP | 0.45 |
| PAS$_{4c}$ | BMPCM + ODA | 0.42 |
| PAS$_{5a}$ | BMBOM + PPD | 0.56 |
| PAS$_{5b}$ | BMBOM + DAP | 0.50 |
| PAS$_{5c}$ | BMBOM + ODA | 0.40 |



**Figure 5** Curing behavior of BMCM/$p$-phenylene diamine.

pendant groups, which enhance the looser chain packing, and the presence of flexible ether linkages, which lower the energy of internal rotation of the polymer chain thus reducing the crystallinity and increasing the solubility.

Cure behavior of bismaleimide

The curing characteristics of BMCM/$p$-phenylene diamine blend were studied using DSC and the result is shown in Figure 5. In the case of pure BMI, a sharp endothermic peak at 250°C was due to the melting, and an exothermic peak observed at 348°C was due to the polymerization reaction between the two double bonds. In the case of BMPCM/diamine adduct, DSC was first scanned up to 120°C; then the sample was quenched and rescanned again. The DSC curves show only one broad endothermic peak at 185°C, probably

this may be due to chain extension reaction between bismaleimides and melted diamine and the endothermic peak was shifted to lower temperature. Similar results were obtained by Wang et al.[19] The above results show that chain extension occurs at lower temperature and homopolymerization at higher temperature.

Thermal properties

Thermal properties of all the polyaspartimides were evaluated by thermogravimetry (TG) and differential scanning calorimetry. The thermal behavior data of all the polymers are summarized in Table V. The representative thermogram of polyaspartimides PAS$_{3a}$ and PAS$_{5a}$ are shown in Figure 6. All polyaspartimides show a similar pattern of decomposition and did not show significant weight loss below 350°C in nitrogen. The ODA-based polyaspartimides show a single stage decomposition with 10% weight loss occurring in the range 390–410°C. The methyl substituent and N—H unit in the polymer chain tend to decompose along

**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$_{3c}$ | ++ | ++ | ++ | ++ | ++ | ++ |
| PAS$_{4a}$ | ± | ± | ± | ± | − | − |
| PAS$_{4b}$ | ++ | ++ | ± | ++ | − | − |
| PAS$_{4c}$ | ++ | ++ | ++ | ++ | ++ | ++ |
| PAS$_{5a}$ | ++ | ++ | ++ | ++ | ++ | ++ |
| PAS$_{5b}$ | ++ | ++ | ++ | ++ | ++ | ++ |
| PAS$_{5c}$ | ++ | ++ | ++ | ++ | ++ | ++ |

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

**TABLE V**
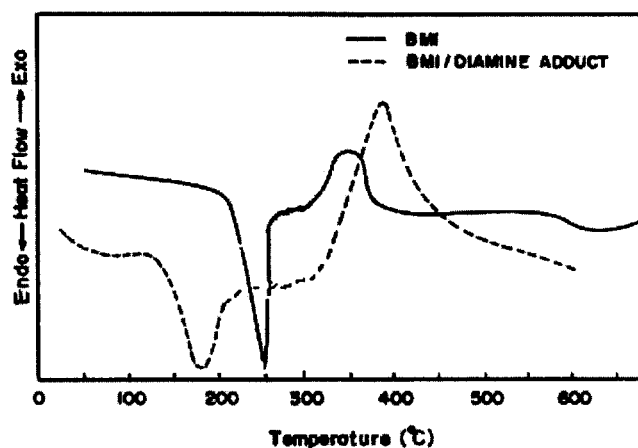**Thermal Properties of Polyaspartimides**

| Code | Polyaspartimide | $T_g$ | $T_{10}$ | Char yield (%) |
|------|-----------------|-------|----------|----------------|
| PAS$_{1a}$ | BMCM + PPD | 258 | 437 | 43.46 |
| PAS$_{1b}$ | BMCM + DAP | 245 | 416 | 49.27 |
| PAS$_{1c}$ | BMCM + ODA | 215 | 408 | 84.20 |
| PAS$_{2a}$ | BMBM + PPD | 264 | 424 | 44.20 |
| PAS$_{2b}$ | BMBM + DAP | 252 | 420 | 46.23 |
| PAS$_{2c}$ | BMBM + ODA | 220 | 410 | 40.60 |
| PAS$_{3a}$ | BMPFM + PPD | 260 | 422 | 47.96 |
| PAS$_{3b}$ | BMPFM + DAP | 235 | 405 | 47.08 |
| PAS$_{3c}$ | BMPFM + ODA | 210 | 390 | 46.65 |
| PAS$_{4a}$ | BMPCM + PPD | 275 | 440 | 42.27 |
| PAS$_{4b}$ | BMPCM + DAP | 262 | 425 | 48.77 |
| PAS$_{4c}$ | BMPCM + ODA | 225 | 410 | 31.95 |
| PAS$_{5a}$ | BMBOM + PPD | 252 | 441 | 48.12 |
| PAS$_{5b}$ | BMBOM + DAP | 238 | 421 | 44.71 |
| PAS$_{5c}$ | BMBOM + ODA | 205 | 403 | 43.14 |

with the main chain at lower temperature as is evident from the thermogram showing a broad single stage weight loss. All other polymers show two-stage decomposition. The initial weight loss occurs due to N—H and methyl group and the second weight loss occurs due to the degradation of the polymer chain at higher temperature. The $T_{10}$ values of these polyaspartimides are in the range of 390–441°C. Thermal stability of the polymers is determined by the strength of the weakest bond present in it. The strength of this bond varies depending on the extent of conjugation in the polymer. In general, electron-withdrawing substituent decreases the electronic conjugation and hence the thermal stability, which is evident from the $T_{10}$ value.

The char yield of the polyaspartimides are in the range of 31.95–49.27% when heated to 800°C in nitrogen confirming that these polymers have better thermal stability and good self extinguishing property. DSC measurements were carried out at a heating rate of 20°C/min in nitrogen. The $T_g$ values of the polymers are in the range 205–275°C (Table V), depending upon the stiffness of the polymer chain. The representative DSC thermogram of polyaspartimide PAS$_{3a/3b,\ and\ 3c}$ are shown in Figure 7. Incorporation of methyl substituent in the bismaleimide 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.[20] Polyaspartimides containing $p$-phenylene moiety and pyridine moiety have high $T_g$ due to increased rigidity of the polymer chain. However, in the case of polyaspartimides containing ether linkages, lower $T_g$ was observed because of the increased rotational movement caused by the flexible ether linkage between two phthalimide units.[21] The introduction of the pendant phenyl group with halo substituent resulted in smaller changes in the $T_g$ values obtained
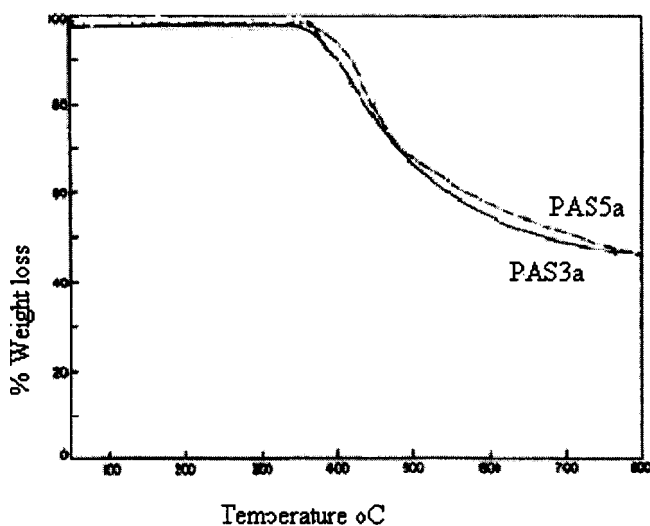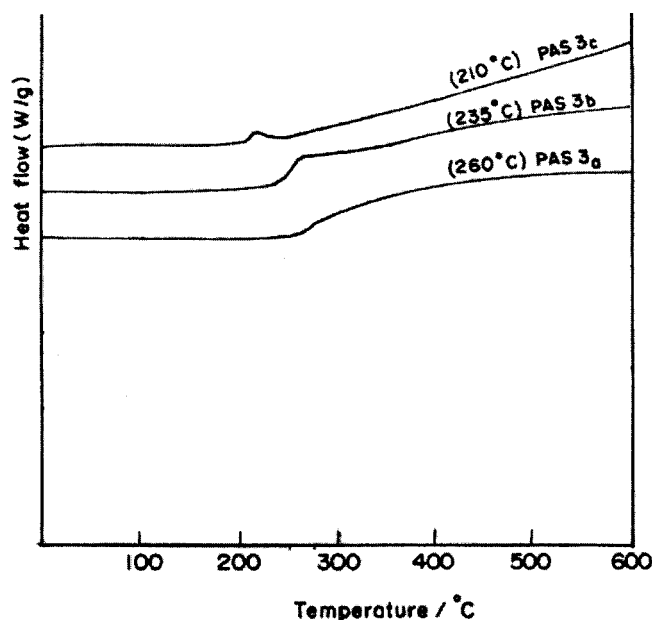


**Figure 7** DSC thermogram of polyaspartimide PAS$_{3a}$, PAS$_{3b}$, and PAS$_{3c}$.

from DSC analysis. The effect of Cl, Br, and F substituents on the $T_g$ was studied. 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 $T_g$.[22] However, the effect of meta and para substitution on the $T_g$ shows that $p$-Cl imparts more aggregation compared to meta substituents (due to much increase in free volume) as is evident from the $T_g$ values. Polyaspartimides containing $p$-phenylene moiety show higher $T_g$ in comparison with the polyaspartimides containing pyridine moiety, which may be due to the rigidity and better packing of the polymer chain.

## CONCLUSIONS

A new class of bismaleimides containing chloro, bromo, fluoro, and benzyloxy moieties was synthesized and characterized using FTIR, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis. Polyaspartimides were successfully prepared by Michael addition reaction of the synthesized bismaleimides with various diamines and characterized using FTIR and elemental analysis. The polymers are amorphous and their solubility in different organic solvents was significantly enhanced by the incorporation of pendant groups and they have a wide gap between glass transition temperature and decomposition temperature. The inherent viscosity values were found to be in the range of 0.41–0.56 dL/g, which indicates that these materials are considered good processable polymeric materials. Thus, this series of polyaspartimides may find use as membranes for



**Figure 6** TGA curves of polyaspartimides PAS$_{3a}$ and PAS$_{5a}$.

gas separation, in the microelectronics and composite industry.

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