

## Synthesis and Characterization of Thiophene Containing Bismaleimide and Polyaspartimides

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New class of aromatic bismaleimide containing thiophene ring were synthesized from *bis*-[(4-aminophenoxy)-6-naphthalene]-3-methyl-2-thiophenyl methane (BANTM) and maleic anhydride *via* bismaleamic acid as the intermediate followed by cyclodehydration. The structure of the monomers was confirmed by FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. Further, a series of polyaspartimides were synthesized by addition reaction of bismaleimide with various diamines. The polymers were characterized by FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The polymers exhibit good solubility in organic solvents such as NMP, DMF and DMSO. The  $T_g$  and  $T_{10\%}$  of the polyaspartimides are in the range of 199-212  $^\circ\text{C}$  and 379-487  $^\circ\text{C}$  respectively.

**Key Words:** Thiophene containing bismaleimides-polyaspartimides, FT-IR, Thermal properties.

### INTRODUCTION

Bismaleimides are thermosetting polymers which have wide applications in microelectronic and aerospace industries for making advanced composites<sup>1</sup>. They show excellent thermal and mechanical properties which make them the suitable material for use in structural applications. They also exhibit good fatigue resistance. Their usage in composites is more advantageous in comparison to condensation type polyimides even though the later exhibit better thermal and electrical properties. 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 polymerized to give highly cross linked polymer or they can be polymerized further by addition of nucleophilic difunctional reagents to give linear polymer<sup>2</sup>. 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<sup>3</sup>. 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<sup>4</sup>.

Hence, in present study a new thiophene containing diamine monomer (BANTM) was synthesized. Using the same amine, bismaleimide and polyaspartimides were also synthesized. These monomers and polymers were characterized using by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectral techniques. The solubility, thermal and inherent viscosity properties were studied.

### EXPERIMENTAL

Acetone, 3-methyl-thiophene-2-carboxaldehyde, *p*-phenylene diamine,  $\beta$ -naphthol were purchased from Sisco Research Laboratories Pvt. Ltd. Maleic anhydride (E-Merck, India), N-methyl-2-pyrrolidone (Aldrich, USA), acetic anhydride (Fischer scientific chemicals, India) sodium acetate (Spectrochem, India), were used as received. 4,4'-Diamino diphenyl methane (DDM), 4,4',3,3'-benzophenonetetracarboxylic acid dianhydride and pyromellitic dianhydride were purchased from Qualigen fine chemicals, India. N,N-dimethyl formamide (Fluka, USA) was purified by refluxing with calcium hydroxide, distilled under reduced pressure and stored over molecular sieves (4 Å).

Nicolet Impact 400 Fourier transform infrared (FT-IR) spectrometer was used to examine the structure of the precursors, monomers, prepolymers and polymers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral analysis were undertaken with acetone- $d_6$ , deuterated dimethyl sulphoxide (DMSO- $d_6$ ) as solvents and

tetramethylsilane (TMS) as reference and recorded on Bruker NMR 400 spectrometer. TGA was performed to assess the thermal stability of the polymers.

Thermograms were obtained using a TA instruments Q100 series thermo gravimetric analyzer. Differential scanning calorimetric analysis was performed on a TA instruments Q10 series. Inherent viscosity was determined to get an idea about the molecular weight of the polyimides. The measurements were conducted at 30 °C in DMAc/NMP solvent using Cannon Ubbelohde viscometer. Wide angle X-ray diffraction measurements were performed at room temperature (about 25 °C) on a X-pert PAN analytical X-ray diffractometer using CuK $\alpha$  radiation. The scanning rate was 20 °C/min over a range of 2 $\theta$  = 5–40°. The UV studies were carried out in Shimadzu UV-1601 spectrophotometer.

#### Synthesis of precursor-I (diol)

**bis-[(6-Hydroxynaphthalene)-3-methyl-2-thiophenyl]-methane (BHMN):** 1.4 g (0.0792 m) of  $\beta$ -naphthol was charged in to a three-necked round bottomed flask equipped with a reflux condenser, Dean-Stark apparatus and nitrogen inlet. To this 4.27 mL (0.0396 m) of 3-methyl-thiophene-2-carboxaldehyde, 1.56 g (0.0792 m) of *p*-toluene sulphonic acid monohydrate and 60 mL of toluene were added. The reaction mixture was refluxed at 130 °C for 18 h under nitrogen atmosphere. Water produced by the reaction was removed as azeotrope with toluene. The reaction mixture was cooled and 20 mL of 10 % aqueous solution of NaOH was added and the resulting solution was stirred. The product obtained was filtered, washed with methanol and dried. The resulting solid was recrystallized from ethanol. Yield 94 %; m.p. 170 °C. FT-IR (KBR, cm<sup>-1</sup>): 3543, 3440 (asymmetric and symmetric stretching vibration of OH group); 2943, 2983 (asymmetric and symmetric stretching vibration of C-H bond of CH<sub>3</sub> group). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  5.35 (s, 2H, a),  $\delta$  7.15 (d, 2H, b),  $\delta$  7.92 (d, 2H, c),  $\delta$  7.41 (s, 2H, d),  $\delta$  7.80 (d, 2H, e),  $\delta$  7.16 (d, 2H, f),  $\delta$  5.34 (s, 1H, g),  $\delta$  2.21 (s, 3H, h),  $\delta$  6.50 (d, 1H, i),  $\delta$  6.77 (d, 1H, j),  $\delta$  7.47 (s, 2H, k). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  C<sup>1</sup>-154.7, C<sup>2</sup>-117.4, C<sup>3</sup>-129.3, C<sup>4</sup>-109, C<sup>5</sup>-132.7, C<sup>6</sup>-129.0, C<sup>7</sup>-125.6, C<sup>8</sup>-128.5, C<sup>9</sup>-132.8, C<sup>10</sup>-40.1, C<sup>11</sup>-135.1, C<sup>12</sup>-12.2, C<sup>13</sup>-133.9, C<sup>14</sup>-124.7, C<sup>15</sup>-124.1.

#### Synthesis of precursor-II (dinitro compound)

**bis-[(4-Nitrophenoxy)-6-naphthalene]-3-methyl-2-thiophenyl-methane (BNNM):** To a 250 mL three-necked round bottomed flask equipped with a nitrogen inlet, Dean-Stark trap and a condenser, were added (3.9 g, 0.0252 m) *bis*-[(6-hydroxynaphthalene)-3-methyl-2-thiophenyl]methane (BHMN), *p*-chloronitrobenzene (5 g, 0.0126 m), anhydrous potassium carbonate (1.7 g, 0.0126 m) and DMAc (20 mL). After the mixture was stirred for 1 h, 35 mL of dry toluene was added, the reaction temperature was raised slowly and the generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 155 °C and kept at this temperature for 20 h. The resultant reaction mixture was cooled and poured into ice-cold water. The precipitate was filtered and dried in vacuum oven at 60 °C. The crude product was purified by recrystallization from ethanol to produce pale yellow crystals. Yield 85 %; m.p. 120 °C. FT-IR (KBR, cm<sup>-1</sup>): 1517, 1347 (asymmetric and symmetric stretching vibration of NO<sub>2</sub> group); 2958, 2988 (asymmetric

and symmetric stretching vibration of CH<sub>3</sub> group). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  8.15 (d, 4H, a),  $\delta$  7.18 (d, 4H, b),  $\delta$  6.96 (d, 2H, c),  $\delta$  7.59 (d, 2H, d),  $\delta$  6.99 (s, 2H, e),  $\delta$  7.47 (d, 2H, f),  $\delta$  7.16 (d, 2H, g),  $\delta$  5.34 (s, 2H, h),  $\delta$  2.21 (s, 3H, i),  $\delta$  6.50 (d, 1H, j),  $\delta$  6.57 (d, 1H, k). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  C<sup>1</sup>-141.5, C<sup>2</sup>-120.8, C<sup>3</sup>-118.4, C<sup>4</sup>-163.1, C<sup>5</sup>-152.1, C<sup>6</sup>-117.4, C<sup>7</sup>-129.3, C<sup>8</sup>-109, C<sup>9</sup>-132.7, C<sup>10</sup>-129.1, C<sup>11</sup>-125.6, C<sup>12</sup>-128.5, C<sup>13</sup>-132.8, C<sup>14</sup>-40.1, C<sup>15</sup>-135.1, C<sup>16</sup>-128.5, C<sup>17</sup>-133.9, C<sup>18</sup>-124.7, C<sup>19</sup>-124.1.

#### Synthesis of diamine

**bis-[(4-Aminophenoxy)-6-naphthalene]-3-methyl-2-thiophenyl-methane (BANTM):** In a 250 mL three-necked round bottomed flask equipped with a condenser, dropping funnel and nitrogen inlet, *bis*-[(4-nitrophenoxy)-6-naphthalene]-3-methyl-2-thiophenyl-methane (3 g, 0.00470 m) and reductive iron (0.15 g, 0.0047 m) were taken. To this mixture, 0.2 mL of conc. HCl and 10 mL of 50 % aqueous ethanol were added slowly. The mixture was refluxed with stirring for 3 h and 1 mL of ammonium hydroxide solution (10 wt %) was added slowly during 10 min. The mixture was filtered hot to remove the solvent<sup>5</sup>. The light brown solid obtained was the diamine monomer, which was further purified by recrystallization from ethanol. Yield 75 % (m.p. 152–155 °C). FT-IR (KBR, cm<sup>-1</sup>): 3448, 3336 (asymmetric and symmetric stretching vibration of NH<sub>2</sub> group); 2913, 2989 (asymmetric and symmetric stretching vibration of CH<sub>3</sub> group); 1614 (N-H bending vibration); 1233, 1156 (asymmetric and symmetric stretching vibration of C-O-C group). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  4.0 (s, 4H, a),  $\delta$  6.42 (d, 4H, b),  $\delta$  6.67 (d, 4H, c),  $\delta$  6.96 (d, 2H, d),  $\delta$  7.59 (d, 1H, e),  $\delta$  6.99 (s, 1H, f),  $\delta$  7.47 (s, 2H, g),  $\delta$  7.16 (d, 1H, h),  $\delta$  5.34 (s, 1H, i),  $\delta$  2.21 (s, 3H, j),  $\delta$  6.50 (d, 1H, k),  $\delta$  6.77 (d, 1H, l). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  C<sup>1</sup>-141.5, C<sup>2</sup>-116, C<sup>3</sup>-118, C<sup>4</sup>-147, C<sup>5</sup>-152, C<sup>6</sup>-117, C<sup>7</sup>-109, C<sup>8</sup>-129.3, C<sup>9</sup>-132.7, C<sup>11</sup>-129, C<sup>12</sup>-126.7, C<sup>13</sup>-132.8, C<sup>14</sup>-40.1, C<sup>15</sup>-132.8, C<sup>16</sup>-12.2, C<sup>17</sup>-124.7, C<sup>18</sup>-124.1.

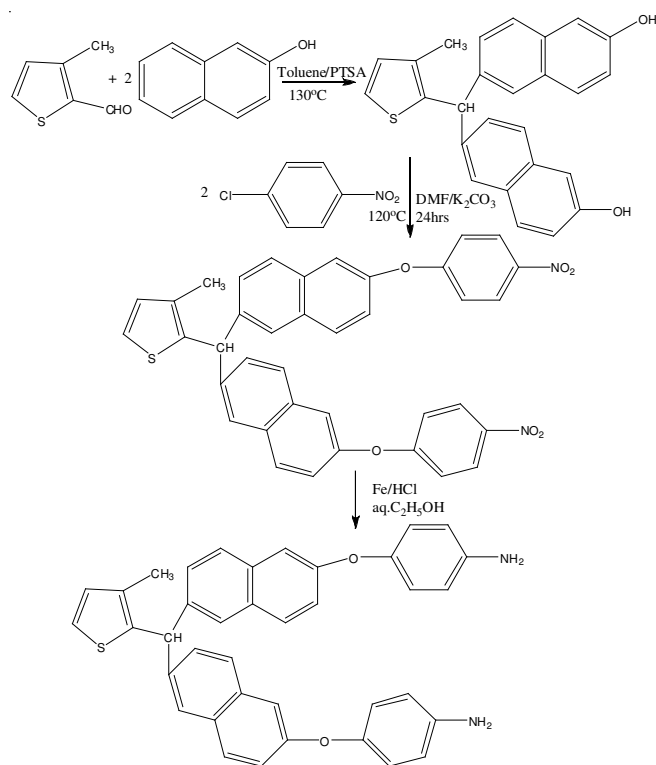
**Synthesis of bismaleimide:** Bismaleimides were prepared by reacting the diamines BANTM with maleic anhydride. BANTM (1 g, 0.00322 mol) was dissolved in 2.5 mL of DMF in a 250 mL three necked round bottomed flask equipped with a nitrogen inlet and an addition funnel. Maleic anhydride (0.61 g, 0.00644 mol) dissolved in DMF (2.5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 2 h. Viscous solution of bismaleimamic acid was formed. To this solution acetic anhydride (5 mL) and sodium acetate (0.5 g) were added. The temperature was maintained at 52–55 °C with stirring for 6 h. The slurry formed was poured into ice-cold water to yield BMI. The formed BMI was filtered and thoroughly washed with ethanol<sup>6</sup>. Yield 76 %; m.p. 196 °C. FT-IR (KBR, cm<sup>-1</sup>): 1782, 1712 (asymmetric and symmetric stretching vibration of C=O group); 2966, 2917 (asymmetric and symmetric stretching vibration of CH<sub>3</sub> group); 1358 (C-N-C stretching vibration); 692 (due to maleimide ring (C=C)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  6.94 (d, 4H, a),  $\delta$  7.60 (d, 4H, b),  $\delta$  6.90 (d, 4H, c),  $\delta$  6.96 (d, 2H, d),  $\delta$  7.59 (d, 2H, e),  $\delta$  6.99 (s, 2H, f),  $\delta$  7.47 (d, 2H, g),  $\delta$  7.16 (d, 2H, h),  $\delta$  5.34 (s, 1H, i),  $\delta$  2.21 (s, 3H, j),  $\delta$  6.50 (d, 2H, k),  $\delta$  6.77 (d, 1H, l),  $\delta$  7.42 (s, 2H, m). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm);  $\delta$  C<sup>1</sup>-135.9, C<sup>2</sup>-161.8, C<sup>3</sup>-125.9, C<sup>4</sup>-121.3, C<sup>5</sup>-117.7, C<sup>6</sup>-152.6, C<sup>7</sup>-152.1, C<sup>8</sup>-117.4, C<sup>9</sup>-109.0, C<sup>10</sup>-129.3, C<sup>11</sup>-132.7, C<sup>12</sup>-129.0, C<sup>13</sup>-125.6,

$C^{14}$ -126.7,  $C^{15}$ -128.5,  $C^{16}$ -132.3,  $C^{17}$ -40.1,  $C^{18}$ -133.9,  $C^{19}$ -19.2,  $C^{20}$ -133.9,  $C^{21}$ -124.7,  $C^{22}$ -124.1.

**Synthesis of polyaspartimides:** Polyaspartimides were synthesized by Michael addition reaction of bismaleimides with aromatic heterocyclic diamine (BANTM). The bismaleimide (1 g, 0.002321 mol) was dissolved in *m*-cresol (3.5 mL) in a three necked round bottomed flask fitted with a nitrogen inlet and condenser. The mixture was stirred at room temperature for 0.5 h. When bismaleimide was completely dissolved, the diamine (0.716 g) was added to the reaction mixture and then 0.1 mL of glacial acetic acid was added. The mixture was stirred at 100-110 °C for 96 h. Then, the mixture was poured into excess ethanol with vigorous stirring. The precipitate was filtered and washed thrice with ethanol. All other polyaspartimides were synthesized by adopting a similar procedure<sup>7</sup>. FT-IR (KBR  $\text{cm}^{-1}$ ): 3400, 3331 (asymmetric and symmetric stretching vibration of N-H group); 1777, 1710 (asymmetric and symmetric stretching vibration of C=O group); 2989, 2917 (asymmetric and symmetric stretching vibration of  $\text{CH}_3$  group); 1358 (C-N-C stretching vibration).

## RESULTS AND DISCUSSION

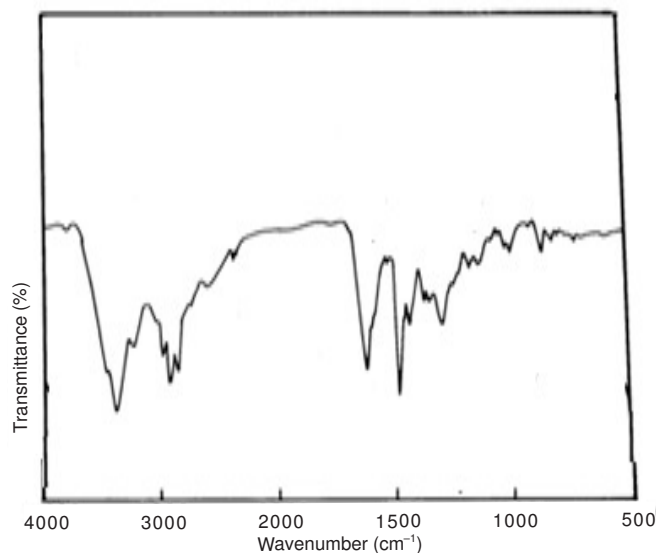
**Synthesis of precursors and monomers:** The precursor (BHNM) were synthesized from 3-methyl thiophene-2-carboxaldehyde and  $\beta$ -naphthol in the presence of toluene/*p*-toluene sulphonic acid. The structure of the precursor was confirmed by FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The precursors-2 (BNNM) was synthesized by the reaction of the BHNM with 1-chloro-4-nitro benzene in the presence of potassium carbonate. Finally, the dinitro compound was reduced by hydrochloric acid and iron to form the diamine monomers BANTM as shown in **Scheme-I**.



**Scheme-I:** Synthesis of BANTM

The diamine monomer show absorption bands around 3348 and 3412  $\text{cm}^{-1}$  due to N-H symmetric and asymmetric stretching vibrations and the absorption band around 1612-1629  $\text{cm}^{-1}$  is due to the N-H bending vibration.

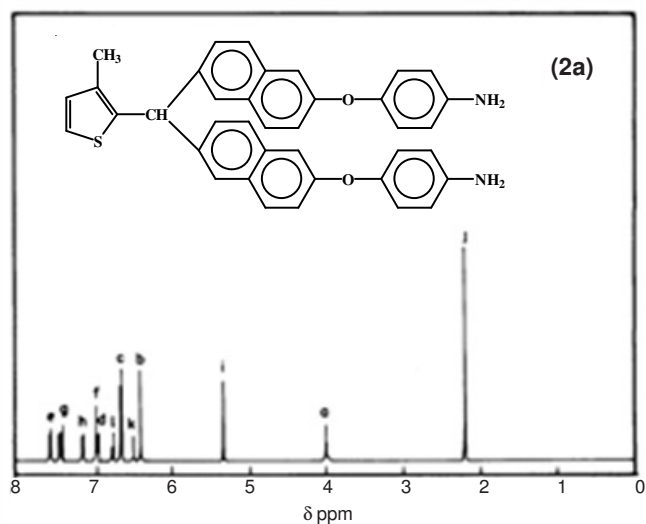
The absorptions around 2989 and 2912  $\text{cm}^{-1}$  due to the C-H stretching vibration of  $\text{CH}_3$  group as shown in Fig. 1.



**Fig. 1.** FT-IR Spectrum of MMNB

$^1\text{H}$  NMR spectrum also confirm the structure of the diamine (BANTM) monomer. The signal at 4 ppm corresponds to amino proton and that at 2.16 ppm correspond to the three methyl protons. All aromatic protons give signals between 6-8 ppm, as shown in Fig. 2a.  $^{13}\text{C}$  NMR spectrum are shown in Fig. 2b, the methyl carbon of the monomer resonate at 12.3 ppm. The methine carbon of the diamine resonate at 40 ppm. All aromatic carbons resonate around 120-162 ppm.

**Synthesis of bismaleimide:** The synthesized diamine (BANTM) was reacted with required amount of maleic anhydride to give bismaleimamic acid. The bismaleimamic acid was then cyclodehydrated using dehydrating agent acetic anhydride and sodium acetate to get a bismaleimide (BMI-1) as shown in **Scheme-II**.



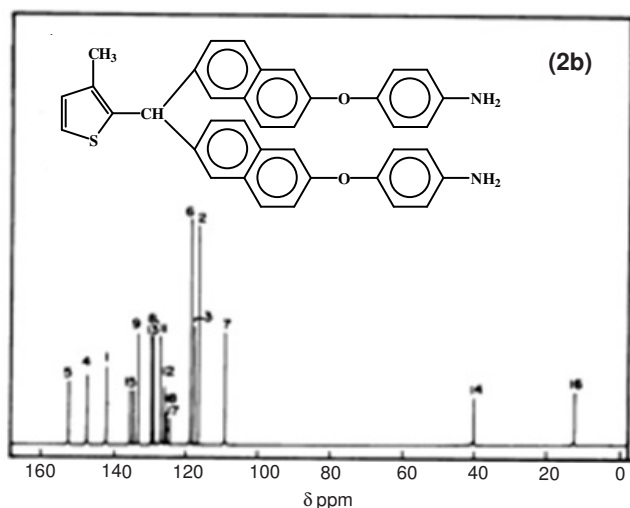
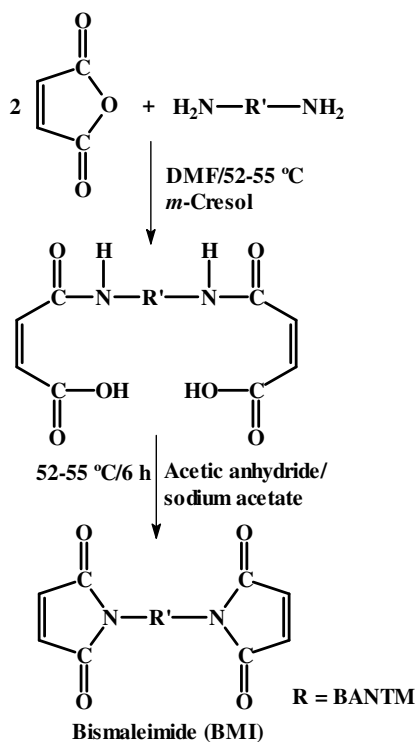


Fig. 2. (a)  $^1\text{H}$  NMR spectrum of BANTM and (b)  $^{13}\text{C}$  NMR spectrum of BANTM



Scheme-II: Synthesis of bismaleimide

The structure of the bismaleimide confirmed by FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The representative infrared spectrum (Fig. 3) of bismaleimide shows a strong absorption at  $1715\text{ cm}^{-1}$  and a weak absorption at  $1776\text{ cm}^{-1}$  due to symmetric and asymmetric  $\text{C}=\text{O}$  stretching vibrations of the imide ring, respectively.

The absence of band in the region  $3500\text{--}3300\text{ cm}^{-1}$  show that the bismaleamic acid was completely converted into bismaleimide and the absence of band at  $1545\text{ cm}^{-1}$  due to the  $\text{N-H}$  group of amide linkage also confirm the complete ring formation. The band at  $692\text{ cm}^{-1}$  is due to the  $\text{C}=\text{C}$  bond of the maleimide ring. The band at  $1386\text{ cm}^{-1}$  is due to the  $\text{C-N-C}$  stretching and the band around  $3100\text{ cm}^{-1}$  is due to the  $=\text{C-H}$  group of the bismaleimide ring.

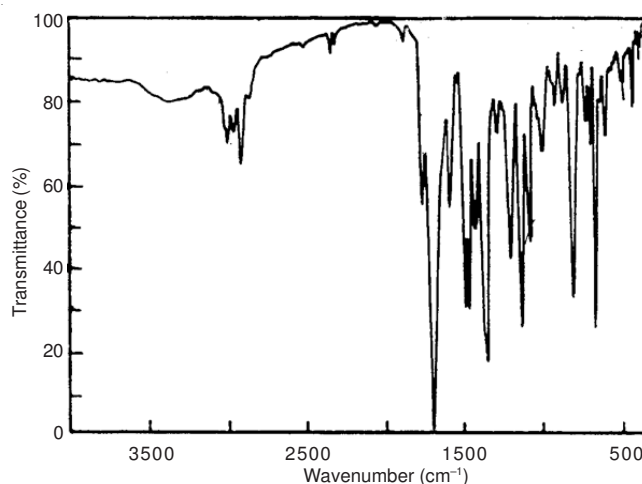


Fig. 3. FT-IR spectra of bismaleimide

The  $^1\text{H}$  NMR spectrum (Fig. 4a) of bismaleimide show the distinct signal around  $7.26\text{ ppm}$  due to four olefinic protons. The absence of signal at  $10.5\text{ ppm}$  due to the carboxylic acid protons shows complete imidization. The signal at  $2.18\text{ ppm}$  is due to the three protons of the methyl groups. All aromatic protons are accountable by the signals between  $6.9$  and  $7.08\text{ ppm}$ . The  $^{13}\text{C}$  NMR spectrum (Fig. 4b) show distinct signals for the methyl and methine carbons at  $11.8\text{ ppm}$  and  $40\text{ ppm}$ , respectively. All aromatic carbons appear between  $160.8\text{--}170.2\text{ ppm}$ .

**Preparation of polyaspartimides:** The nucleophilic addition of diamine to bismaleimide (based on aromatic amines having hetero cyclic ring), the Michael type addition, is a well-known route to synthesize linear polyaspartimides.

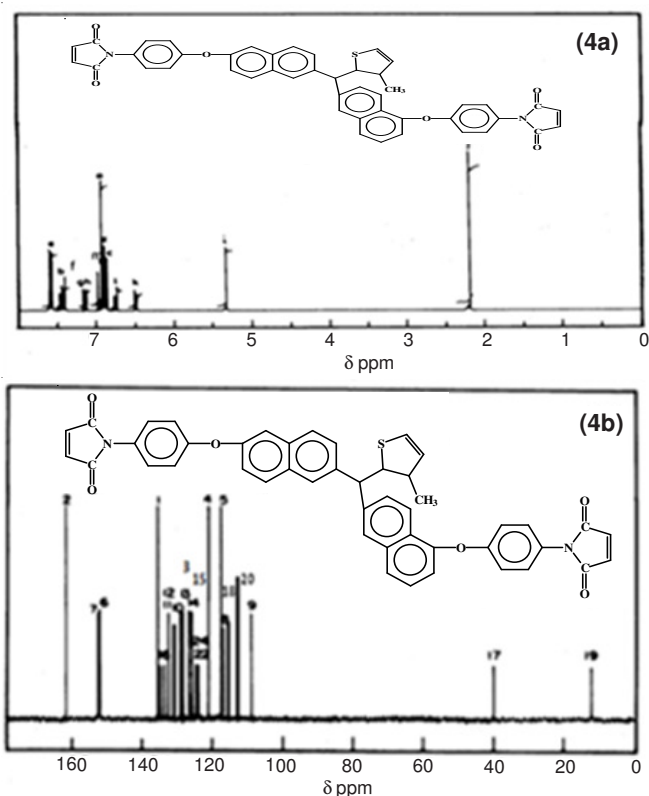


Fig. 4. (a)  $^1\text{H}$  NMR spectrum of BMI-1(MMNPP) (b)  $^{13}\text{C}$  NMR of BMI-1



The synthesized thiophene 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-III**. The structure of the polymer was confirmed by FT-IR (Fig. 5).

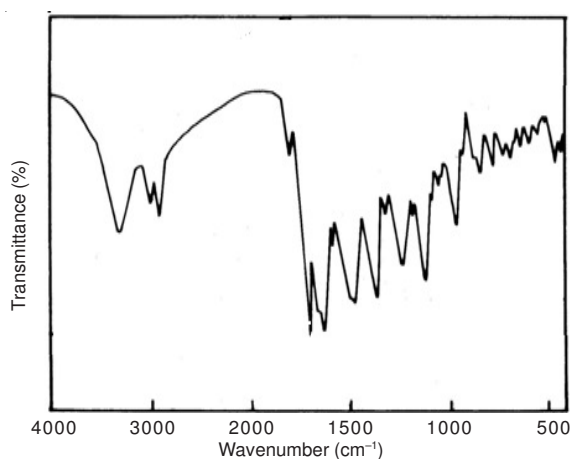
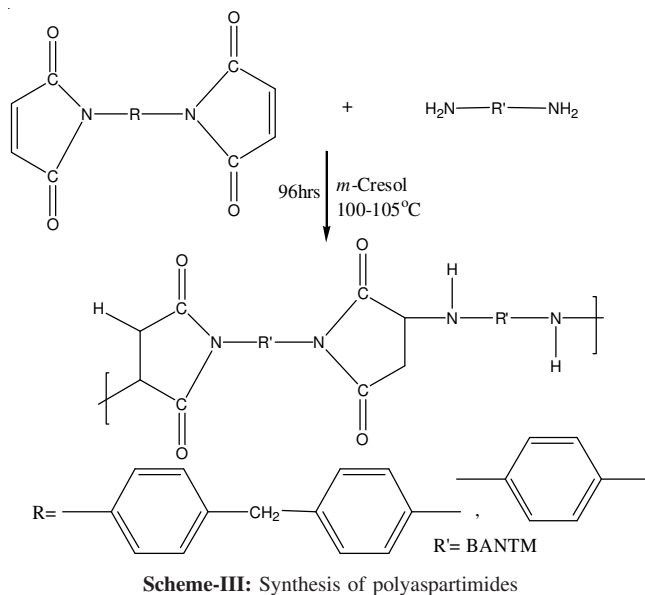


Fig. 5. FT-IR Spectra of polyaspartimides

The bands in 3365-3339  $\text{cm}^{-1}$  range are due to N-H stretching vibration. The disappearance of band at 691  $\text{cm}^{-1}$  due to maleimide C=C bond confirms completion of the addition reaction of these double bonds. The bands around 1780-1773  $\text{cm}^{-1}$  and 1720-1709  $\text{cm}^{-1}$  are due to asymmetric and symmetric stretching vibrations of the C=O group of the imide ring respectively. The bands around 1382-1360  $\text{cm}^{-1}$  are due to C-N-C stretching vibrations of the imide ring. The methyl group shows the band around 2926-2917  $\text{cm}^{-1}$  due to the C-H stretching vibrations. The spectroscopic data are well in agreement with the expected structure, ensuring the formation of polyaspartimides.

#### Properties of polyaspartimides

**Inherent viscosity:** The inherent viscosity of polyaspartimides was determined using Ubbelohde viscometer at a concentration of 0.5 dl/g in NMP and the results are presented

in Table-1. The inherent viscosity values of polyaspartimides are in the range of 0.40-0.89 dl/g<sup>8</sup>.

TABLE-1  
THERMAL PROPERTIES ( $\text{N}_2$  atms)/ $\text{O}_2$  ATMS AND  
INHERENT VISCOSITY OF POLYASPARTIMIDES

| Polymer code | In $\text{N}_2$ |                                   |                | In air                            |                | $\eta$ (dl/g) |
|--------------|-----------------|-----------------------------------|----------------|-----------------------------------|----------------|---------------|
|              | $T_g$           | $T_{10\%}$ ( $^{\circ}\text{C}$ ) | Char yield (%) | $T_{10\%}$ ( $^{\circ}\text{C}$ ) | Char yield (%) |               |
| PAS 3a       | 212             | 487                               | 52             | 490                               | 35             | 0.40          |
| PAS3b        | 242             | 469                               | 51             | 420                               | 36             | 0.56          |
| PAS 3c       | 218             | 468                               | 49             | -                                 | -              | -             |
| PAS 3d       | 207             | 445                               | 47             | 380                               | 37             | 0.89          |
| PAS 4a       | 186             | 396                               | 46             | 362                               | 35             | 0.58          |
| PAS 4b       | 199             | 379                               | 44             | 390                               | 39             | 0.78          |

**Thermal properties:** The thermal properties of the polymers were evaluated by DSC and thermogravimetric analysis (TGA) at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere and are summarized in Table-1, the DSC thermograms of the polyaspartimides (PAS-3a-4b) are shown in Fig. 6a.

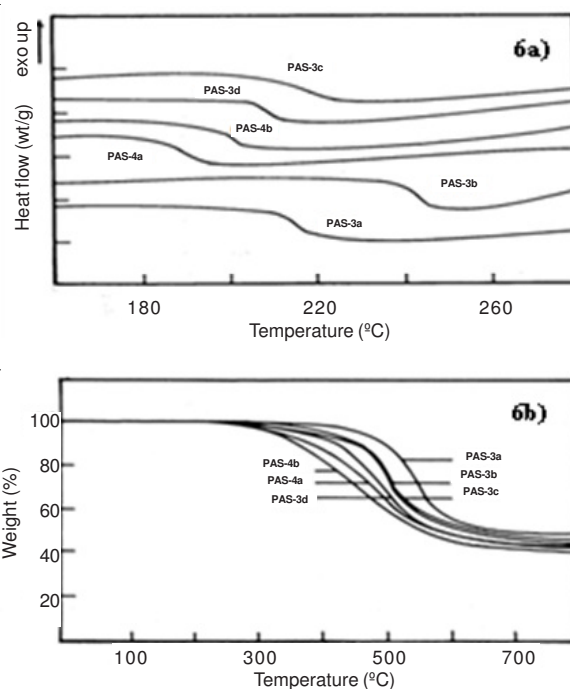


Fig. 6. (a) DSC and (b) TGA curve of polyaspartimides

The  $T_g$  values of the polymer are in the range of 199-212  $^{\circ}\text{C}$  as shown in Table-1, depending on the stiffness of the polymer chain. The thermograms of the polyaspartimide are shown in Fig. 6b. All polyaspartimides show a similar pattern of decomposition and do not show significant weight loss below 350  $^{\circ}\text{C}$  in nitrogen atmosphere. The 10 % weight loss temperatures ( $T_{10}$ ) of PAS (PAS-3a to PAS-4b) are in the range of 379-487  $^{\circ}\text{C}$  and the char yield at 800  $^{\circ}\text{C}$  in nitrogen atmosphere was found to be in the range of 44-52 %. All the polyaspartimides are stable upto the temperature of ca. 360  $^{\circ}\text{C}$  indicating the high thermal stability of the polyaspartimides<sup>9,10</sup>.

#### Conclusion

A new class of thiophene containing BMI were synthesized using the prepared diamine and maleic anhydride. These

monomers were characterized by using FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. Polyaspartimides were successfully prepared by the Michael addition reaction of the synthesized bismaleimide with the various diamines. The polymers were characterized by using FT-IR. The  $T_g$  values of the polyaspartimides are in the range of 199–212 °C. The 10 % weight loss temperatures ( $T_{10}$ ) of PAS are in the range of 379–487 °C and the char yield is in the range of 44–52 % in nitrogen atmosphere. The inherent viscosity values of polyaspartimides were found to be in the range of 0.40–0.89 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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#### REFERENCES

1. M. Kato, T. Shirga, T. Kimura, T. Fukuda, H. Matsuda and H. Nakanishi, *Polym. Adv. Technol.*, **13**, 120 (2002).
2. C.S. Wu, Y.L. Liu and Y.S. Chiu, *Polymer*, **43**, 4277 (2002).
3. Y.L. Liu and S.H. Tsai, *Polymer*, **43**, 5757 (2002).
4. C.S. Wu, Y.L. Liu and Y.S. Chiu, *Polymer*, **43**, 1773 (2002).
5. D.J. Liaw and B.Y. Liaw and J.J. Chen, *Polym. J.*, **42**, 867 (2001).
6. F. Shiliang, F.Y.C. Boey and J.M. Abadie, *Eur. Polym. J.*, **44**, 2123 (2008).
7. T.Y. Takeichi, T. Sayto, H. Agag and T. Kawauchi, *Polymer*, **49**, 1173 (2008).
8. M. Grigoras, M. Sava, G. Colotin and C.I. Simionescu, *J. Appl. Polym. Sci.*, **107**, 846 (2008).
9. R. Hariharan and M. Sarojadevi, *J. Appl. Polym. Sci.*, **108**, 1126 (2008).
10. M. Sava, *J. Appl. Polym. Sci.*, **91**, 3806 (2004).