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Synthesis and Characterization of Polyaspartimides Containing Anthracene Moiety

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ABSTRACT

A new type of aromatic *bis*-maleimides (BMI) containing anthracene group were synthesized from *bis*(4-amino-3,5-dimethyl phenyl) anthramethane (BMAM) and maleic anhydride via *bis*-maleamic acid as an intermediate followed by cyclodehydration to BMI. The structure was confirmed by Fourier transform infrared (FTIR), ^{1}H-NMR, and elemental analysis. In addition, a series of polyaspartimides were synthesized by the addition reaction of BMI with various diamines. The polymers were characterized by IR and elemental analysis, and they exhibit good solubility in organic solvents such as NMP, DMF, and DMSO. The polymers also exhibit good thermal stability. T_g of polyaspartimides are in the range of 212–270°C and $T_{10\%}$ wt loss are above 406–486°C.

Key Words: Anthracene moiety; *bis*-Maleimides; Characterization; Polyaspartimide.

INTRODUCTION

Thermosetting polyimides have several key physical properties which have led to their success in specialized applications. *bis*-Maleimides (BMI) are a leading class of thermosetting polyimides, and their excellent processability and balance of thermal and

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mechanical properties have made them extremely popular in advanced composites and electronics.[1–4] One important approach to thermosetting polyimides is the non-stoichiometric Michael-addition reaction between BMI and aromatic diamine with BMI in excess. Since the double bond of N-substituted maleimide is electron deficient due to the two neighboring carbonyl groups, nucleophillic species are easily added via a Michael-type addition reaction.[5–9] On the other hand, this electron deficient double bond can also be self polymerized thermally to get a highly crosslinked network without the formation of volatile by-products, which offers considerable advantage in processing over the conventional condensation type polyimides. Thus, these thermosetting polyimides have attracted considerable attention as an important matrix resin for high performance composites used in military aircraft and engines.[10–12]

Although many studies have been devoted to BMI and their polymers, till now there is no report on BMI containing an anthracene unit, thus the present study was carried out on the synthesis and characterization of a new BMI containing anthracene unit as the pendant group in its backbone. The Michael addition of this BMI with several other diamines was carried out in *m*-cresol to produce linear polyaspartimides. The main aim of incorporating the anthracene pendant in the polymer is to increase the molecular weight between the crosslinks in order to improve the ductility of the host poly(*bis*-maleimide). It was expected that amine addition reaction would cause extension of a network chain, which reduces the crosslink density and increases the flexibility of the cured network.

EXPERIMENTAL

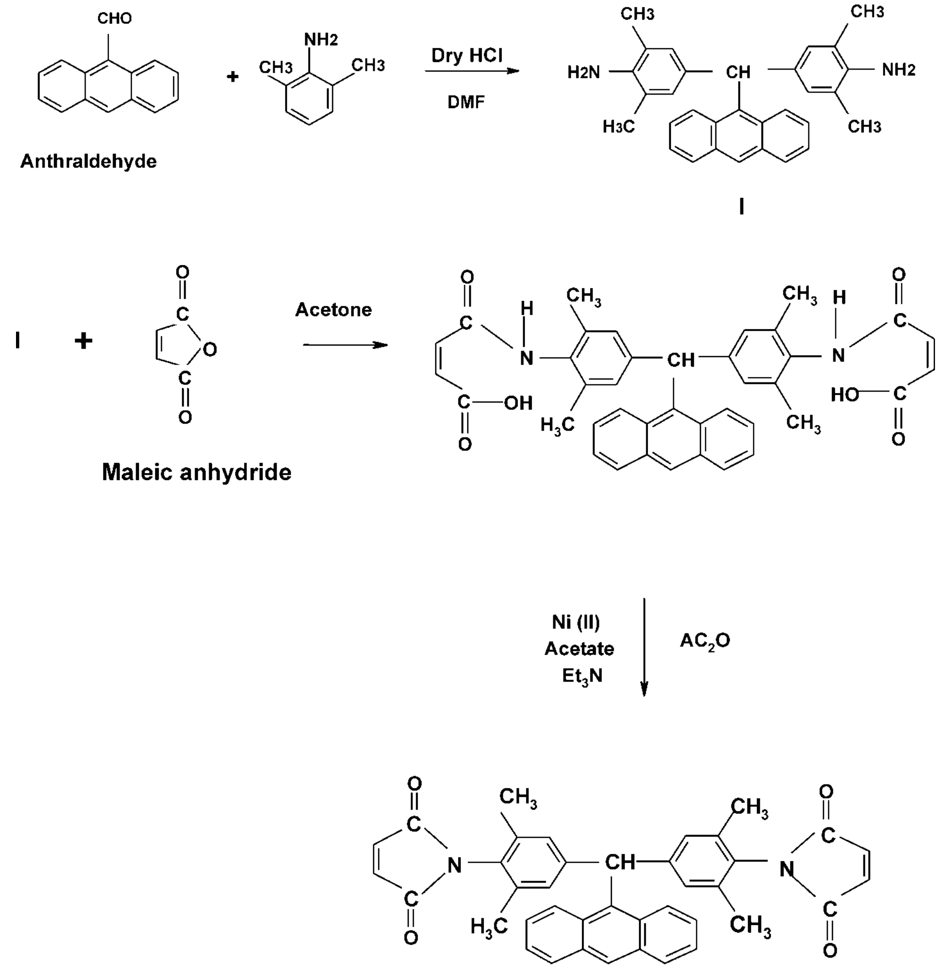
Materials

9-Anthraldehyde (E. Merck, Mumbai, India), 2,6-dimethylaniline (Aldrich, Wisconsin, WI, USA), hydrochloric acid (HCl, Spectrochem), acetone (SRL), maleic anhydride (E. Merck, Mumbai, India), diethyl amine (Spectrochem, Mumbai, India) and nickel(II) acetate (SRL) were used as received. *p*-Phenylene diamine was sublimed at about 100°C under vacuum. 4,4′-Diamino diphenyl methane and 4,4′-diamino diphenyl sulphone were recrystallized from a benzene and ethanol mixture. *N*-Methyl 2-pyrrolidone (Aldrich, Wisconsin, WI, USA) was used as received. *N*,*N*-Dimethyl formamide (Fluka, St. Louis, MO, USA) was purified by refluxing with calcium hydride, distilled under reduced pressure and stored over molecular sieves 4A) These were used in the present study.

Monomer Synthesis

Synthesis of *bis*(4-Amino-3,5-dimethyl Phenyl) Anthra Methane

The diamine was prepared by using the procedure which was already reported by us[13] as shown in Sch. 1. A three-necked flask equipped with a reflux condenser, nitrogen inlet, and a bent inlet for dry HCl was charged with 2,6-dimethylaniline (24.2 g, 0.2 mol). Dry HCl gas (22.7 mL, 0.25 mol) was passed into the reaction vessel for 90 min. The solid obtained was dissolved in the required quantity of DMF. To this solution, anthraldehyde solution (20.6 g, 0.1 mol) in DMF was added dropwise. After complete addition, the



II

BMAM

Scheme 1. Preparation of *bis*(4-maleimido-3,5-dimethyl phenyl) anthra methane (BMAM).

reaction mixture was stirred at room temperature for 4 hr. Then, the temperature was slowly raised and maintained at 110°C for another 5 hr. The reaction mixture was cooled and the pH was brought to 7 using sodium carbonate. The solid product obtained was filtered, washed repeatedly with methanol and dried in a vacuum oven for 24 hr at 65°C. Yield 83%, IR (KBr) cm^{-1}; 3451 and 3380 asymmetric and symmetric stretch of NH; 1613 N–H bending vibrations; 2960, 2914 C–H stretch of CH_3 group; the absence of a peak at 1664 cm^{-1} due to C=O stretch of anthraldehyde shows the completion of the reaction. ^1H NMR ($CDCl_3$), 2.16 δ (S, 12H) CH_3, 4.8 δ (S, 4H) NH_2, 6.9 δ (S, 4H) phenyl protons, 7.2–8.4 δ (m, 9H), elemental analysis is calculated for $(C_{31}H_{30}N_2)_n$: C 86.5%, H 6.98%, N 6.51%. Found: C 86.4%, H 6.96%, N 6.50%, MP 182°C.

Synthesis of *bis*(4-Maleimido-3,5-dimethyl Phenyl) Anthra Methane

The BMAM was synthesized as shown in Sch. 1. A three-necked flask equipped with an addition funnel and a nitrogen inlet was charged with the solution of BAAM (0.01 mol, 5.08 g) in acetone. Maleic anhydride (0.02 mol, 1.96 g) dissolved in acetone was added dropwise to the above mixture. An exothermic reaction was observed, rapid formation of a precipitate of *bis*-maleiamic acid occurred on mixing the reactants together and the mixture was stirred for 4 hr at room temperature. Then 0.01 g nickel(II) acetate and 15 mL triethyl amine were added to the reaction vessel, and the entire mixture was refluxed. Acetic anhydride of 56.8 mL was added to the reaction mixture and heating was continued for an additional 8 hr at 60°C. The mixture was diluted with water and chilled to crystallize BMI which was dried in vacuum at 70°C.

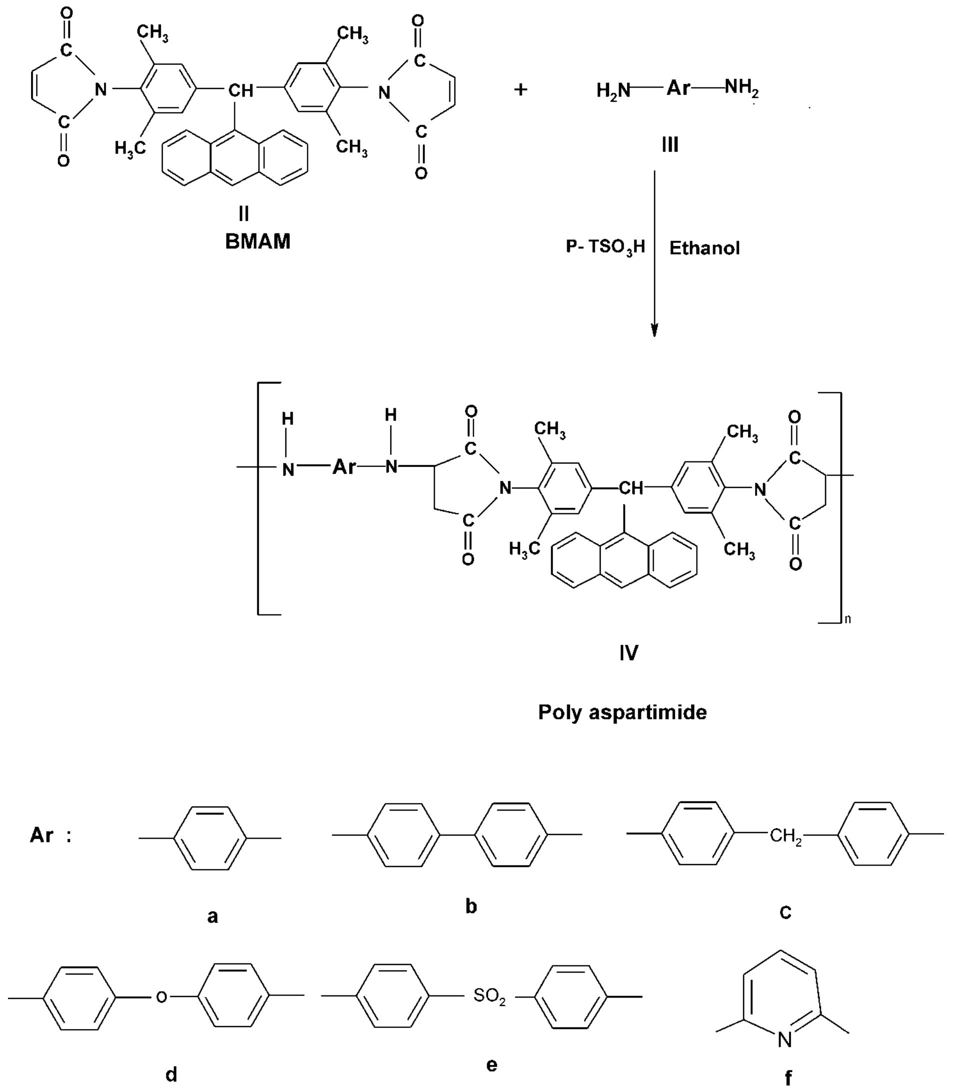
MP 245°C, yield 92%, IR (KBr, cm^{-1}) 1710, 1774 cm^{-1} (symmetric and asymmetric C═O stretching of the imide ring), 691 cm^{-1} (C═C), 1372 and 1150 cm^{-1} (C–N–C stretching), 2929 cm^{-1} (C–H of CH_3). ^{1}H-NMR ($CDCl_3$, δ) 7.15 (s, 4H, olefinic), 7.3–8.00 (m, 14H, aromatic), 2.16 δ (s, 12H) CH_3. Elemental analysis calculated for $(C_{39}H_{30}N_2O_4)_n$, C 79.31%, H 5.12%, N 4.74%. Found C 77.12%, H 5.01%, N 5.04%.

Polymer Synthesis

The polyaspartimide was synthesized as shown in Sch. 2. A 150 mL three-necked flask fitted with a thermometer and nitrogen inlet was charged with (5.90 g, 0.01 mol) of BMAM in DMF. The mixture was stirred while BMAM completely dissolved. Then 1.08 g (0.01 mol) of *p*-phenylene diamine (IV_a) and 0.1 g of *p*-toluene sulphonic acid were added into the flask. The reaction mixture was stirred at 100°C for 96 hr and poured into excess ethanol with vigorous stirring. The precipitate was filtered and washed three times with hot ethanol, and dried under vacuum at 70°C for 24 hr. Yield- 86%, IR (KBr, cm^{-1}) 3380, 3436 (asymmetric and symmetric stretch of –NH), 1640 (–NH bending vibration), 1720, 1776 (symmetric and asymmetric stretching of imide ring). All other polymers (IV_{b-f}) were prepared by adopting a similar procedure.

Measurements

Fourier transform infrared spectra were recorded on a Nicolet spectrometer with KBr pellet. ^{1}H NMR spectra were recorded using a Joel Ex-200 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 viscosities were 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.



Scheme 2. Preparation of polyaspartimide.

RESULTS AND DISCUSSION

A new type of BMI was synthesized in two steps starting from anthraldehyde and 2,6-dimethylaniline as shown in Sch. 1. The diamine was prepared by adopting a new procedure. The structure of the diamine monomer was confirmed by FTIR, ^{1}H-NMR, and elemental analysis which are in good agreement with the proposed structure. The BMI containing anthracene moiety was prepared via a two-step method, having the formation of *bis*-maleiamic acid as the intermediate step. It was then cyclodehydrated with acetic anhydride, nickel(II) acetate and triethylamine to give BMI. The IR spectra of BMI (Fig. 1)

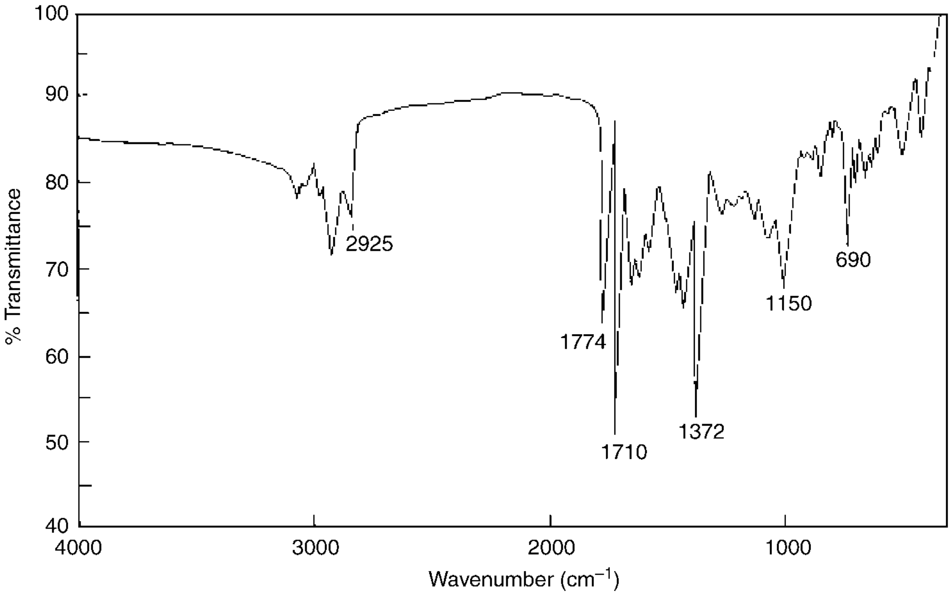


Figure 1. The FTIR spectrum of BMI.

show absorption at 1714 and 1775 cm^{-1} due to symmetric and asymmetric C=O stretching vibrations of the imide ring. The band at 1383 cm^{-1} is due to C–N–C stretching vibrations and the band at 690 cm^{-1} is due to a C=C stretch of maleimide ring. ^{1}H-NMR spectrum (Fig. 2) also confirms the formation of BMI. The signal at 7.15 ppm is due to four olefinic protons. The signal at 7.00–8.1 ppm is due to aromatic protons and the signal at 2.16 ppm is due to 12 protons of the CH_3 groups. Absence of a signal at 10.38 ppm due to carboxylate protons of *bis*-maleamic acid confirms that BMI ring closure has taken place completely from *bis*-maleamic acid. Elemental analysis of BMI (Table 1) is in agreement with the proposed structure.

The synthesis of polyaspartimide takes place by the nucleophillic addition of diamine to BMI.[14–16] In our study, BMAM was synthesized, followed by further polymerization with diamines to get a new class of polyaspartimides as shown in Sch. 2. The structure of the obtained polymer was confirmed by elemental analysis and FTIR. Elemental analysis data for all the polyaspartimides (Table 1) agree with the calculated values. The FTIR spectrum of polyaspartimide (BMAM-*p*-phenylene diamine) is given in Fig. 3. The absorptions at 3380, 3436 cm^{-1} are due to N–H stretching vibration. The band at 1640 cm^{-1} is due to N–H bending vibration, and the bands at 1720 and 1774 cm^{-1} are due to C=O stretch of the imide ring. Absence of band at 691 cm^{-1} due to C=C, confirms the complete addition of diamine to BMI. All other polymers (IV_{b-f}) show same characteristic peaks confirming the formation of polyaspartimide.

The solubilities of polyaspartimides in various solvents are tabulated in Table 2. Almost all polymers are readily soluble in aprotic solvents such as NMP, DMAc, and DMF. All polymers exhibit good solubility except IV_a and IV_f, while other polymers IV_{b-e} exhibit good solubility even in common solvents such as $CHCl_3$, dichloromethane, and acetone. The lower solubility of IV_a and IV_f may be due to the rigid and symmetric

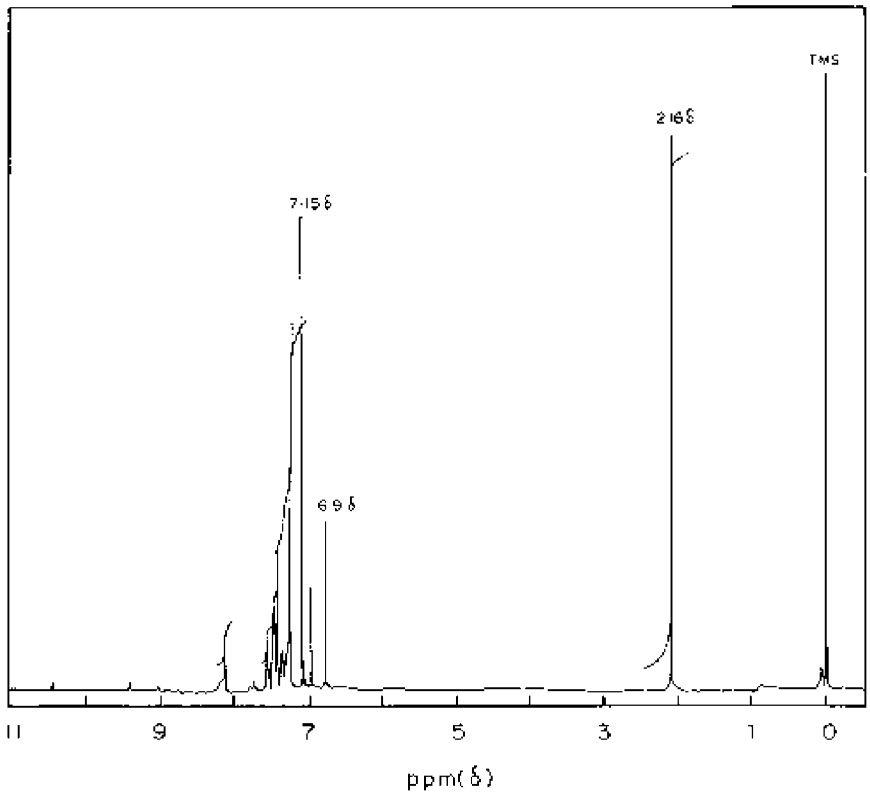


Figure 2. The ^{1}H-NMR spectrum of BMI.

Table 1. Elemental analysis of BMAM and polyaspartimides.

S. no	BMAM/ polymer	Molecular formula & weight	Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	BMAM	$(C_{39}H_{30}N_2O_4)_n$ $(590.57)_n$	C = 79.31 F = 77.12	C = 5.12 F = 5.01	C = 4.74 F = 5.04
2	IV_a	$(C_{45}H_{38}N_4O_4)_n$ $(698.71)_n$	C = 77.35 F = 77.1	C = 5.48 F = 5.95	C = 8.02 F = 8.33
3	IV_b	$(C_{51}H_{42}N_4O_4)_n$ $(774.79)_n$	C = 79.05 F = 78.66	C = 5.46 F = 6.24	C = 7.23 F = 6.99
4	IV_c	$(C_{52}H_{44}N_4O_4)_n$ $(788.82)_n$	C = 79.17 F = 76.59	C = 5.62 F = 6.20	C = 7.10 F = 6.38
5	IV_d	$(C_{51}H_{42}N_4O_5)_n$ $(790.78)_n$	C =77.46 F = 77.72	C = 5.35 F = 4.90	C = 7.09 F = 6.64
6	IV_e	$(C_{51}H_{42}N_4O_6S)_n$ $(838.83)_n$	C = 73.02 F = 73.0	C = 5.04 F = 5.14	C = 6.68 F = 6.58
7	IV_f	$(C_{44}H_{37}N_5O_4)_n$ $(699.69)_n$	C = 75.52 F = 74.12	C = 5.33 F = 5.92	C = 10.01 F = 9.02

Notes: C–calculated value; F–found value.

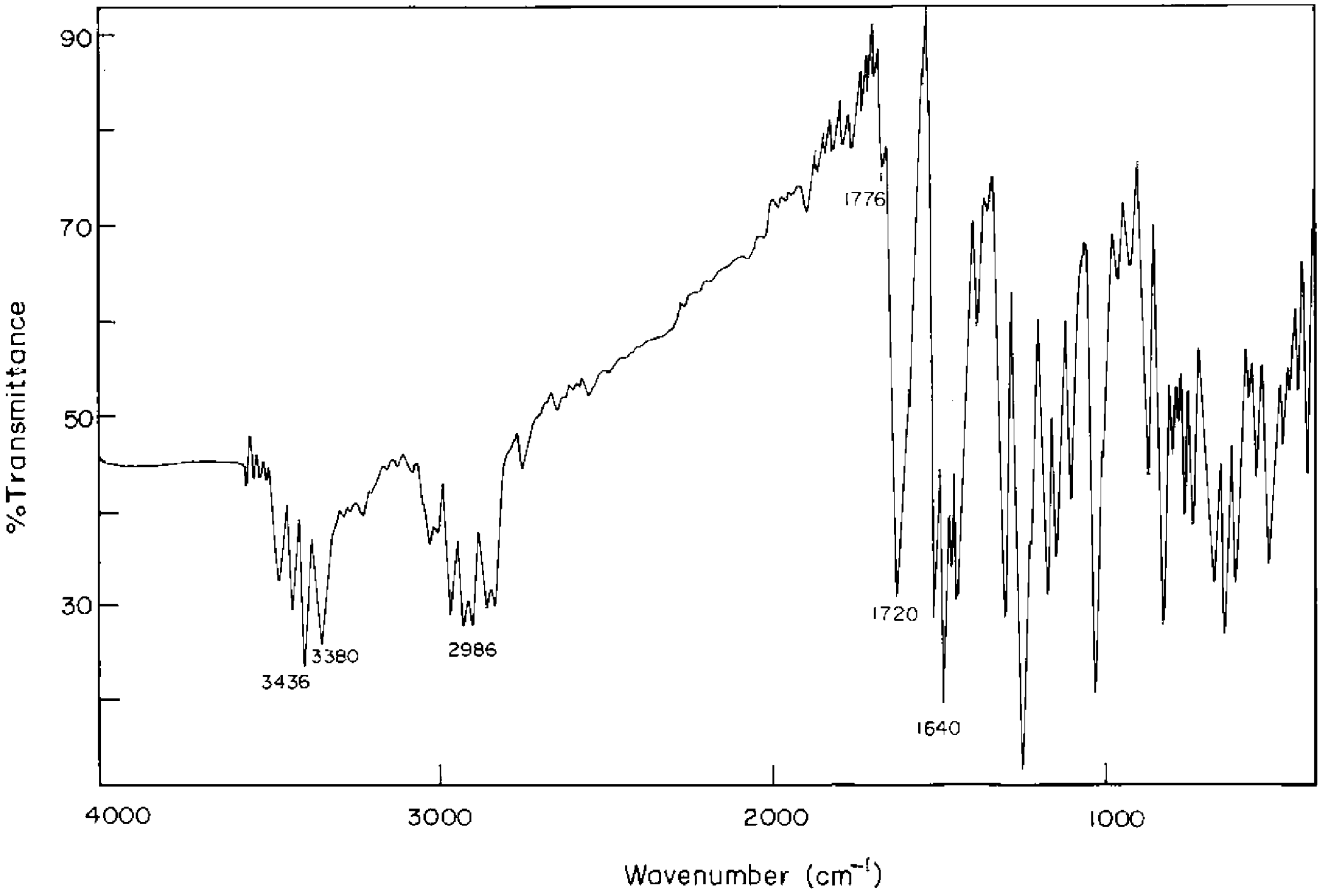


Figure 3. The FTIR spectrum of aspartimide (IVa).

Table 2. Solubility of polyaspartimides.

S. no	Polymer	NMP	DMAc	DMF	DMSO	$CHCl_3$	Acetone	Pyridine	Dichloro methane
1	IV_a	+ h	+ h	+ h	+ h	–	–	±	–
2	IV_b	+ h	+ +	+ +	+ +	±	–	+ +	±
3	IV_c	+ +	+ +	+ +	+ +	±	±	+ +	±
4	IV_d	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
5	IV_e	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
6	IV_f	+ h	+ h	+ h	+ h	–	–	±	–

Notes: + + completely soluble; ± sparingly soluble; – insoluble; + h soluble under hot condition.

structure of diamine cross linkers used (*p*-phenylene diamine and 2,6-diamino pyridine), whereas IV_{b-e} the solubilities were much higher because of the presence of flexible linkages in the diamine crosslinkers which reduce the energy of internal rotation of the polymer chain thus, reducing the crystallinity. A similar trend is observed by other authors.[17] Thus, the introduction of a bulky pendant group in the polymer back bone of polyaspartimide has increased the solubility due to a decrease in the intermolecular forces between the polymer chains as a result of looser packing of polymer chains compared with the unsubstituted polymers. Therefore, the crystallization tendency is markedly reduced and the solubilities are significantly enhanced.[18] The inherent viscosities ($\acute{\eta}$) of the polymers are summarized in Table 3. All polymers exhibit relatively low viscosity values in the range of 0.31–0.53 dL/g except the polymer IV_f due to the presence of a rigid and symmetric pyridine diamine unit in the structure. Polymer IV_e has the lowest viscosity among all the polyaspartimides, which may be due to lower basicity of the diamine due to a electron withdrawing group (sulphone) present.[7] The viscosity range of these polymers are good enough for application in fabricating fiber reinforced composites. The thermal behavior of the polymers was evaluated by means of TGA and DSC. The thermal analysis data of the polymers are given in Table 4. The DSC curves of all the polyaspartimides are given in Fig. 4. All the polymers exhibit good glass transition temperatures in the range of 212–270°C, which depends upon the structure of diamine, polymer IV_f exhibits high T_g since incorporation of pyridine has increased the rigidity of the polymer main chain and hence, the T_g. Polyaspartimides with naphthalene unit incorporated in the BMI backbone

Table 3. Inherent viscosity of the polyaspartimides.

S. no	Polymer	Inherent viscosity η (dL /g)
1	IV_a	0.53
2	IV_b	0.44
3	IV_c	0.50
4	IV_d	0.48
5	IV_e	0.31
6	IV_f	0.86

Table 4. Thermal properties of polyaspartimides.

S. no	Polymer	(Tg in °C)[a]	(T10 °C)[b]	Char yield (%)[c]
1	$\mathrm{IV_a}$	238	464	64.2
2	$\mathrm{IV_b}$	223	470	46.8
3	$\mathrm{IV_c}$	212	451	50.2
4	$\mathrm{IV_d}$	220	443	56
5	$\mathrm{IV_e}$	203	406	54.8
6	$\mathrm{IV_f}$	270	486	51.3

[a] Mid point temperature base line shift on the second DSC heating trace (scan rate = 10°C/min) of the sample after quenching from 400°C.

[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min.

[c] Residual weight % at 800°C in nitrogen.

has T_g in the range of 192–231°C depending on the nature of the diamine.[7] In a similar way, polyaspartimides prepared in the present study having anthracene as the pendant unit have T_g values from 203–238°C except for the one with pyridine diamine as the crosslinker (270°C). It is evident that the incorporation of a bulky anthracene unit has decreased the T_g of polyaspartimides compared to that with *p*-phenylene diamine based BMI.[18]

Thermo gravimetric analysis data reveal that these polymers are stable up to 400°C. The TGA curves of the prepared polyaspartimides are given in Fig. 5. The temperature at which 10% weight loss takes place are in the range of 406–486°C. Polymer $\mathrm{IV_e}$ has the lowest thermal stability in comparison to other polymers since it has weak bridging bond in the diamine which breaks at higher temperature and the char yield percentage range confirms that these polymers ($\mathrm{IV_{a-f}}$) exhibit high thermal stability.

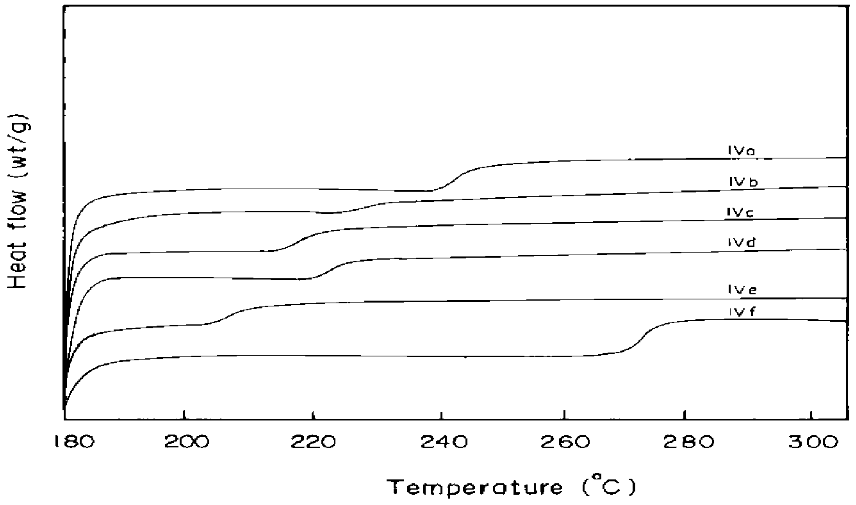


Figure 4. The DSC curves of polyaspartimides (in N_2 at heating rate of 10°C/min).

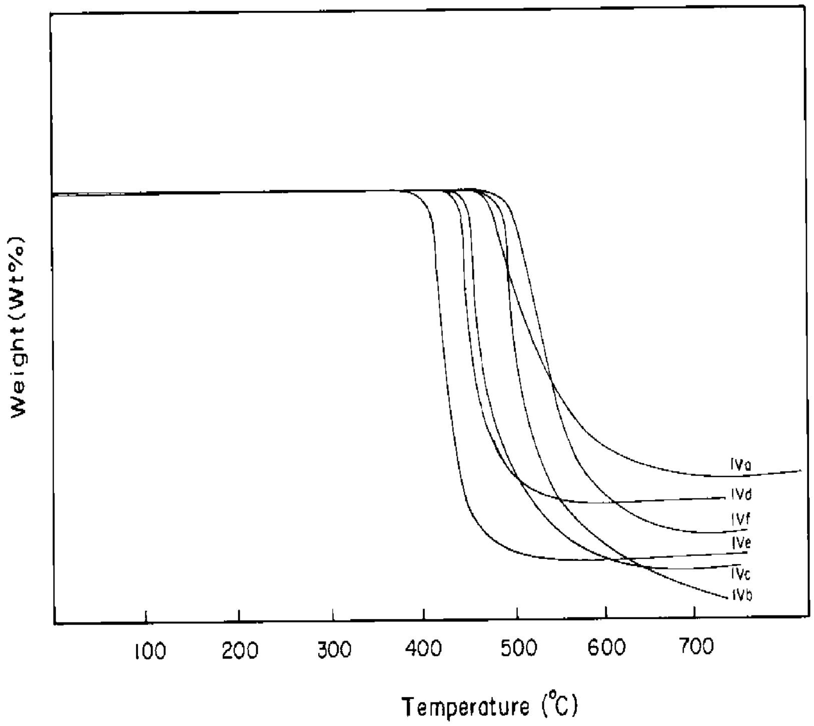


Figure 5. The TGA of polyaspartimide.

CONCLUSION

A new type of BMI containing anthracene moiety was synthesized and characterized using FTIR, ^{1}H-NMR, and elemental analysis. It was further polymerized to polyaspartimides with various diamines, the structures of which were confirmed using FTIR and elemental analysis. These polymers exhibit excellent solubility and thermal stability. The polymers have T_g in the range of 203–270°C. The inherent viscosities were found to be in the range of 0.31–0.86 dL/g. The viscosity values indicate that these materials are considered to be good processable polymeric materials.

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