

Synthesis and Characterization of processable heat resistant poly (amide-imides) for high temperature applications

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Summary

A series of new polyamide-imides with high thermal stability were synthesized by direct polycondensation of imide containing diamines with various aromatic diacids using polar aprotic solvents. In this technique triphenylphosphite (TPP) and pyridine were used as condensing agents to form polyamide-imide through N-phosphonium salts of pyridine. The various imide containing diamines were prepared by reacting dianhydride (PMDA, BPTDA) with aromatic diamines such as phenylene diamine, 3,3'-dichloro 4,4'-diaminodiphenylmethane and 2,6-diaminopyridine in 1:2 ratio. The diacids containing flexible ether units were prepared by treating diol with aromatic acid (2,4-dichlorobenzoic acid). The polyamide-imides obtained by this technique were characterized by elemental analysis, FTIR and ¹H-NMR. The solubility of these polyamide-imides was found to be good in polar aprotic solvents such as NMP, DMF, and DMAc etc. The viscosity of the polyamide-imides were determined and found to be in the range of 1.21 to 1.76 dl/g indicating the formation of high molecular weight polymers. The thermal stability of the polymers was tested using DSC and the T_g values are in the range of 207-234°C showing the high thermal stability of the prepared polymers.

Introduction

Wholly aromatic polymers such as polyimides and polyamides have already been noted for their high temperature resistance and excellent physico mechanical properties. They are difficult to process due to their insolubility in organic solvents and infusibility [1-6]. Considerable effort has been made to improve their processing properties by structural modifications. One such method is the synthesis of copolymers. Aromatic poly (amide-imide) s are high performance materials with good compromise between thermal stability and processability when compared with polyamides or polyimides of analogous structure [7-12]. Hence in this study poly (amide-imides) having heat resistant characters, less color and improved solubility were synthesized. Generally dianhydrides with polyalicyclic structures improve the color of the polymers but heat resistance is sacrificed [13]. Although fluorinated monomers are effective in decreasing coloration the monomers are too costly to be

utilized [14]. Therefore, in the present study, commercially available and cheap monomer BPTDA was condensed with three different diamines to prepare new diamines with preformed imide rings which were then reacted with flexible aromatic diacids to synthesis poly (amide-imides). Since this monomer has flexible ether linkages it is expected to decrease the coloration and improve the solubility of polymers. Further, for clear understanding of the effect of incorporation of flexible diacid, the properties of these polymers has been compared with the polymers prepared using pyridine 2, 5 dicarboxylic acids.

Experimental

Materials

2, 4-Dichloro benzoic acid (SRL), p-phenylene diamine (SRL) 2, 6-Pyridine diamine, 4,4'-diamino 3,3'-dichloro diphenyl methane (E-Merck) were used as received. BPTDA (3, 3', 4, 4' benzophenone tetra carboxylic acid anhydride, E-Merck) was recrystallised from acetic anhydride before use. 4, 4'-Dihydroxy benzophenone (Lancaster) and Bisphenol-A (Spectrochem) were used as received. N-methyl 2 pyrrolidone (NMP, Spectrochem) and Pyridine (Spectrochem) were purified by distillation under reduced pressure and stored over 4Å molecular sieves. Triphenyl phosphite (TPP, E-Merck) was used as received. Anhydrous calcium chloride was dried under reduced pressure at 150°C for six hours prior to use.

Monomer synthesis

Synthesis of diimide-diamines

BPTDA (1.61g, 0.005 moles) was dissolved in 10ml of m-Cresol in a 150ml flask, equipped with N₂ inlet and 1.09g (0.01 moles) of 2, 6- diamino pyridine was added to it in one portion. To this mixture 1ml of isoquinoline and 45ml of toluene were then added, and refluxed for about 5 hours. The water thus formed was distilled off azeotropically in a Dean stark trap. Heating was continued to distill off the residual toluene. After cooling, the solution was poured into excess methanol with vigorous stirring and the precipitated product was isolated by filtration and dried in vaccum at 90°C for 24 hours. A number of imide containing diamines were prepared using similar procedure.

Diimide-diamine-IA

(IR, **Figure-1**, KBr, cm⁻¹) 3387 (N-H stretching vibration), 1778 (imide carbonyl asymmetric stretching vibration), 1717 (imide carbonyl symmetric stretching vibration), 1620 (N-H bending vibration), 1369 (C-N-C stretching vibration), 728 (imide ring deformation).

Diimide-diamine-IB

(IR, KBr, cm⁻¹) 3452 (N-H stretching vibration), 1786 (imide carbonyl asymmetric stretching vibration), 1721 (imide carbonyl symmetric stretching vibration), 1632 (N-H bending vibration), 1375 (C-N-C stretching vibration), 721 (imide ring deformation).

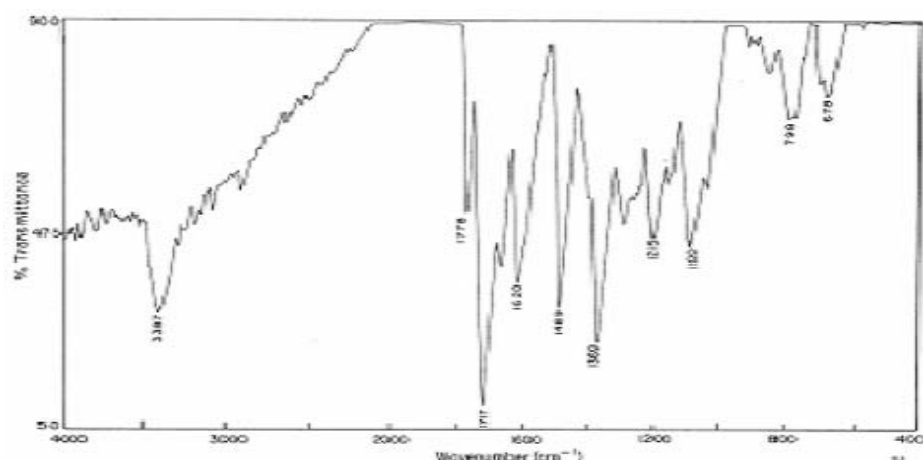


Figure. 1 FTIR Spectrum of Diimide-Diamine

Diimide-diamine-IC

(IR, KBr, cm^{-1}) 3400 (N-H stretching vibration), 1782 (imide carbonyl asymmetric stretching vibration), 1726 (imide carbonyl symmetric stretching vibration), 1626 (N-H bending vibration), 1367 (C-N-C stretching vibration), 678 (imide ring deformation), 798 (C-Cl stretching vibration) 2928 (C-H stretching of $-\text{CH}_2$).

Synthesis of diacids

A 150ml round bottomed flask equipped with a reflux condenser and N_2 inlet was charged with a solution of 3.81g (0.02mole) of 2,4 dichlorobenzoic acid in 10ml of dried DMF. To this about 2.149g (0.01mole) of dihydroxy benzophenone was added in one portion with constant stirring. After complete dissolution of dihydroxy benzophenone 2.76g (0.02mole) of potassium carbonate was added to the solution and allowed to reflux for 12 hours. The solution thus obtained was cooled and poured into water. The precipitated product was filtered, washed with hot water and dried in vacuum oven at 70°C for 24 hours. Similar procedure was followed to prepare the diacid with bisphenol moiety.

Diacid IIb

(IR, **Figure 2**, KBr, cm^{-1}) 3422 (-OH stretching vibration of acid hydroxyl group), 1700 (carbonyl stretching vibration), 1601 (-OH bending vibration of acid hydroxyl group), 1220 (C-O-C stretching vibration).

Diacid IIc

(IR, **Figure 3**, KBr, cm^{-1}) 3420 (-OH stretching vibration of acid hydroxyl group), 1720 (carbonyl stretching vibration), 1610 (-OH bending vibration of acid hydroxyl group), 1210 (C-O-C stretching vibration), 2980 (-CH stretching vibration of $-\text{CH}_3$ group).

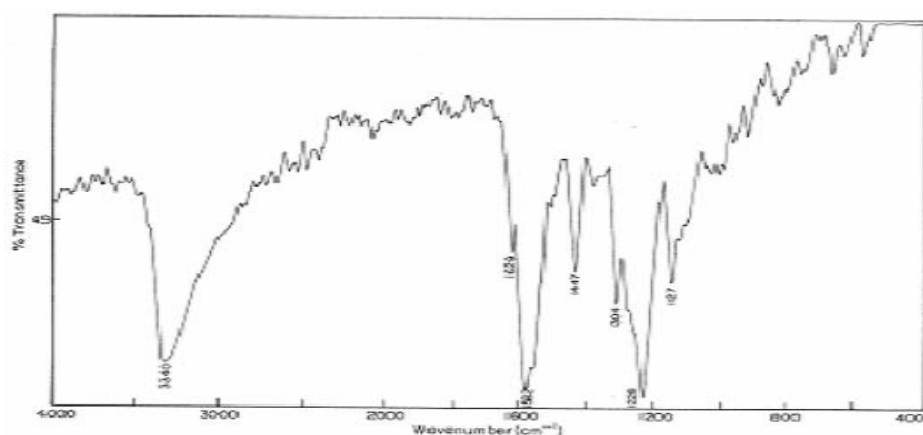


Figure. 2 FTIR Spectrum of Diacid II b

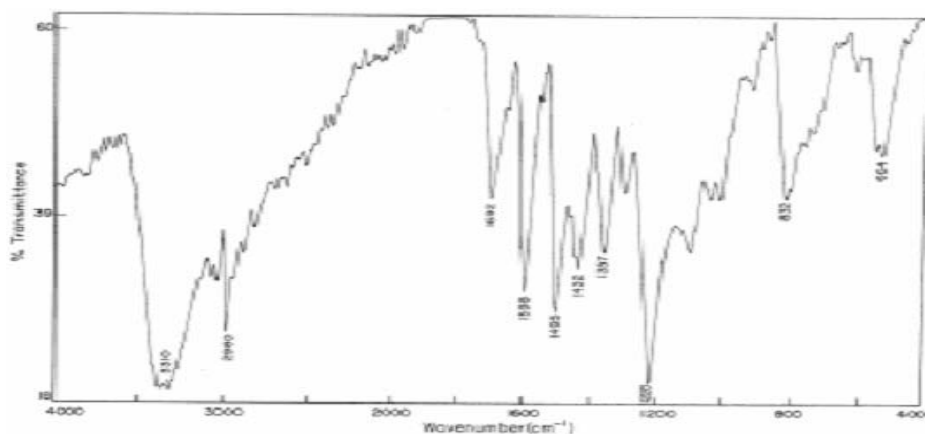


Figure. 3 FTIR Spectrum of Diacid II c

Polymer synthesis

Synthesis of Poly (amide-imide) s

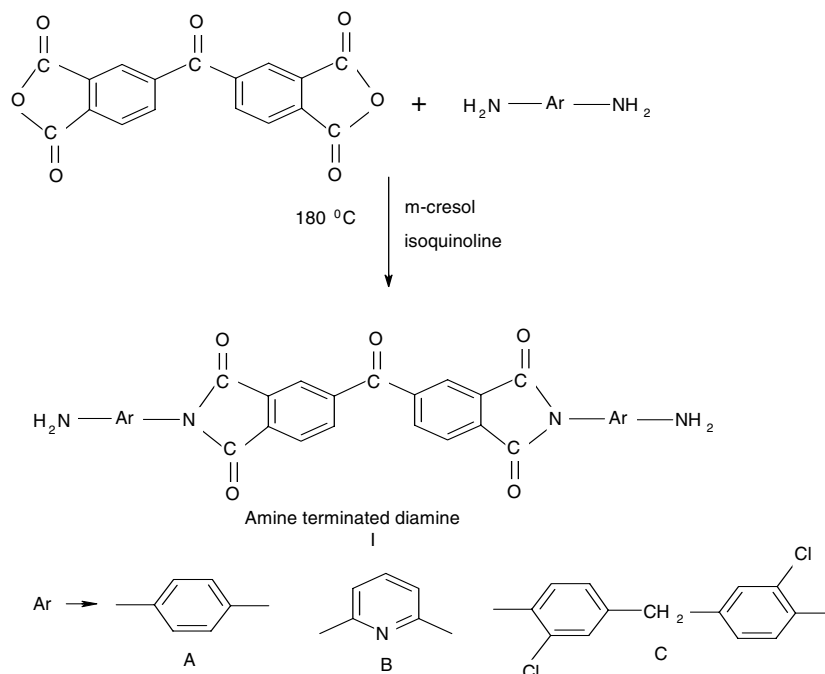
A mixture of 0.522g (1mmole) of diacid, 0.502g (1mmole) of diimide-diamine with phenylene moiety, 0.30g of CaCl_2 , 0.6ml of TPP and 1ml of pyridine in 5ml of NMP was heated with stirring at 100°C for 3 hours. The viscosity of the reaction solution increased after 1 hour and an additional volume of NMP was added to carryout the reaction in homogeneous medium. At the end of the reaction, the polymer solution was slowly trickled into stirred methanol, to precipitate the product. The polymer was washed with hot water and methanol, filtered and dried in vacuum. All the other poly (amide-imide) s were synthesized in similar procedure. A typical set of IR spectra is shown in Figure-4.

Measurements

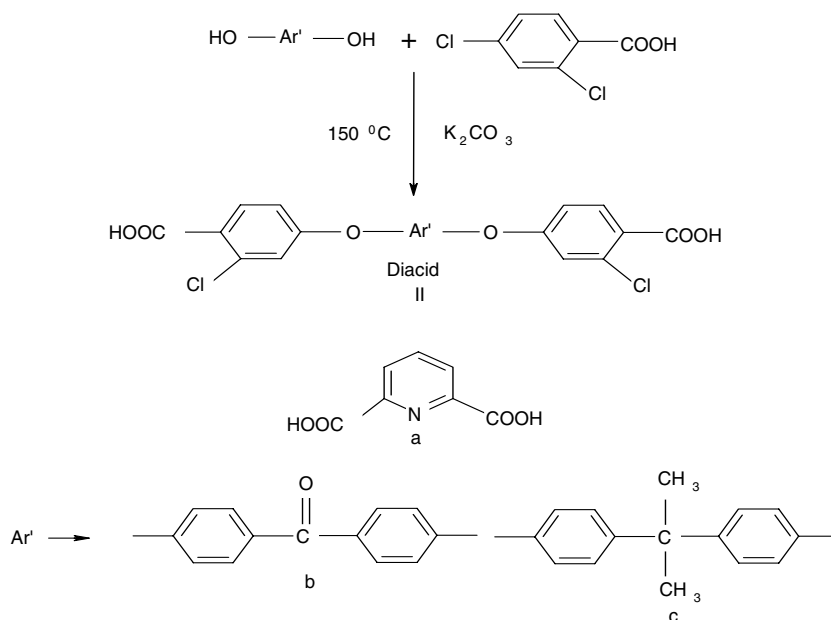
Infrared spectra were recorded on a Nicolet Fourier transform infrared spectrometer. ¹H-NMR spectra were obtained on a Jeol Ex-400 spectrometer. Elemental analysis was carried out with a Perkin Elmer model 2400. The inherent viscosities of all polymers were measured at 0.5 g dL⁻¹ in NMP using Ubbelohde viscometer at 300°C. Thermogravimetric data were obtained on a Dupont 2100 model in flowing Nitrogen at a heating rate of 200°C/min. Differential scanning calorimetry (DSC) analysis was performed on a Dupont 2100 Differential scanning calorimeter with a heating rate of 200°C/min in nitrogen atmosphere.

Results and Discussion

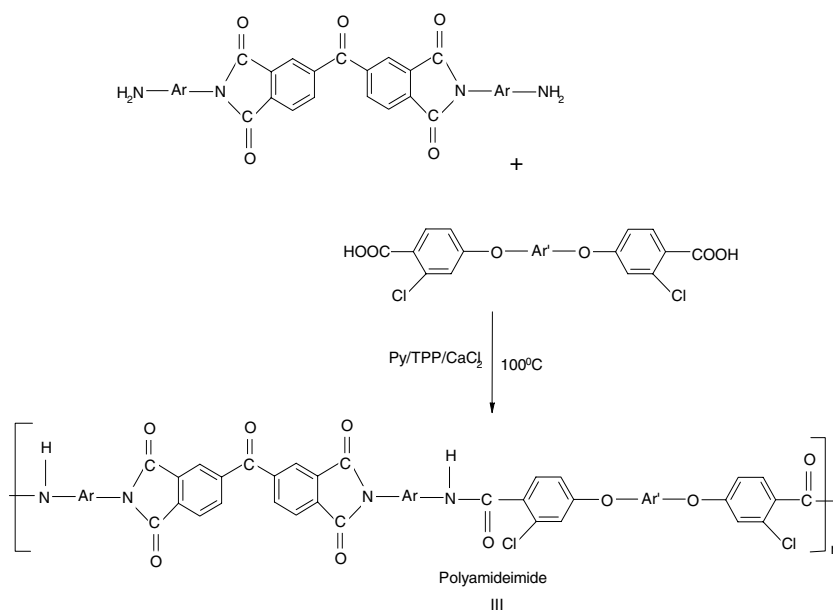
Poly amide-imides were synthesized in three steps starting from diamines and BPTDA to prepare three different diimide-diamines (scheme 1) followed by the preparation of diacids using 2,4-dichlorobenzoic acid and diols (Scheme 2), which was then reacted with the above prepared diimide-diamines by direct polycondensation (Scheme 3) to prepare poly (amide-imides). The amidation reaction proceeds through two steps, in the first step diphenoxy aminophosphine is formed, which is then attacked by the available carboxylic acid with the formation of two final products, an amide group and a diphosphite. The conversion of TPP to DPP is exothermic by 32–65 kcal/mol; thus it provides the driving force for the reaction. In NMP at 100 °C interaction between TPP and pyridine appears to be nonexistent or negligible [15].



SCHEME 1



SCHEME 2



SCHEME 3

All the polymers prepared are characterized by elemental analysis and FTIR spectroscopy (**Figure 4**).

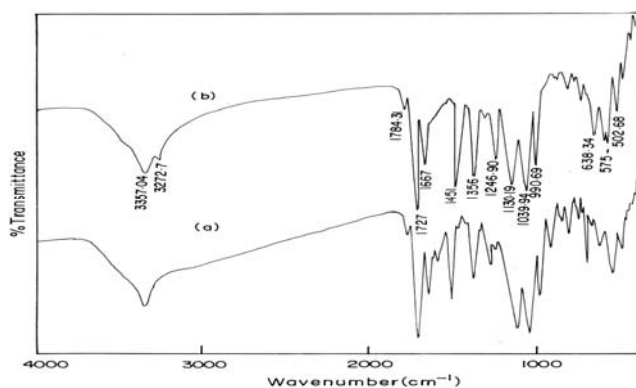
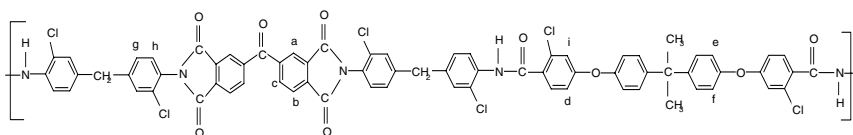


Figure. 4 FTIR spectra of poly (amide-imide) s

The found values of the elemental analysis data correlate well with the calculated values (**Table 1**). The typical IR spectrum of polymer displays characteristic absorption bands for the imide ring at 1783cm^{-1} and 1720cm^{-1} due to asymmetrical and symmetrical C=O stretching vibration and 1110 and 763cm^{-1} due to imide ring deformation. The absorptions of the amide groups appear around 3379cm^{-1} and 1650cm^{-1} . The C-N-C imide ring vibration was observed around 1388cm^{-1} . The structure of poly (amide-imide) was also confirmed by $^1\text{H-NMR}$ spectroscopy. Representative $^1\text{H-NMR}$ spectrum of poly(amide-imide)s is given in **Figure-5**.



The protons H_a , H_b and H_c adjacent to the carbonyl group of the imide ring (ortho oriented protons) resonate at the farthest downfield region ($8.1-8.3\delta$) owing to the inductive effect and resonance. The protons H_e , H_d , H_f ortho oriented to aromatic ether are shifted to the slightly up field region ($7.62-7.65\delta$) due to shielding effect [16]. A singlet around 7.3δ corresponds to H_i proton. The protons H_g and H_h appear at lower delta value than the other protons because it was less affected by other protons. The $-\text{CH}_2$ proton appears at about 2.9δ . The $-\text{NH}$ protons are observed at 4.1δ , and the intense signal at 1.7δ may correspond to methyl protons.

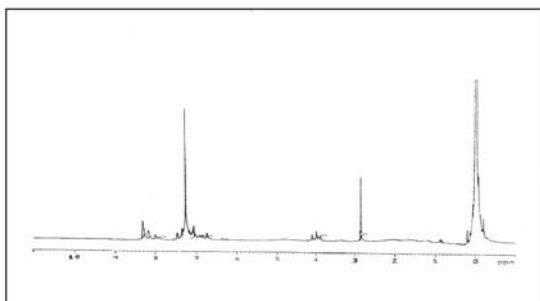


Figure. 5 $^1\text{H-NMR}$ Spectrum of poly (amide-imide)

Table 1 Elemental analysis of poly (amide-imide-imide) s

S.No	Polymer	Molecular Formula & Weight	Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	III _{Aa}	(C ₃₄ H ₁₇ N ₇ O ₇) _n	C=64.25 F=62.92	C = 2.70 F = 2.75	C=15.43 F=15.09
2	III _{Ba}	(C ₃₆ H ₁₉ N ₇ O ₅) _n	C=68.25 F=67.19	C = 3.02 F = 3.14	C=11.05 F=10.99
3	III _{Ca}	(C ₅₀ H ₂₇ N ₅ O ₇ Cl ₄) _n	C=63.11 F=61.77	C = 2.86 F = 2.92	C = 7.36 F = 7.17
4	III _{Ab}	(C ₅₆ H ₃₄ N ₆ O ₉ Cl ₂) _n	C=66.87 F=66.52	C = 3.41 F = 3.78	C = 8.36 F = 8.19
5	III _{Bb}	(C ₅₈ H ₃₆ N ₄ O ₉ Cl ₂) _n	C=69.44 F=69.00	C = 3.62 F = 3.91	C = 5.59 F = 5.07
6	III _{Cb}	(C ₇₂ H ₄₄ N ₄ O ₉ Cl ₆) _n	C=65.42 F=65.12	C = 3.36 F = 3.48	C = 4.24 F = 4.10
7	III _{Ac}	(C ₅₄ H ₂₈ N ₆ O ₁₀ Cl ₂) _n	C=65.40 F=65.02	C = 2.85 F = 3.00	C = 8.47 F = 7.98
8	III _{Bc}	(C ₅₆ H ₃₀ N ₄ O ₁₀ Cl ₂) _n	C=67.95 F=67.03	C = 3.06 F = 3.28	C = 5.66 F = 5.17
9	III _{Cc}	(C ₇₀ H ₃₈ N ₄ O ₁₀ Cl ₆) _n	C=64.29 F=63.97	C = 2.93 F = 3.08	C = 4.28 F = 4.00

Polymer properties

Solubility

Solubility of poly (amide-imide) s was tested qualitatively in various solvents. The solubility data are given in **Table 2**. Polyamide-Imides (III_{Ab}-III_{Cc}) are easily soluble at room temperature in polar aprotic solvents such as DMF, DMAc, NMP and DMSO. Some of the polyamide-imides are also soluble in less polar solvents such as m-cresol and THF. The improved solubility of these polyamide-Imides can be explained by the presence of flexible units like bisphenol-A and benzophenone as well as the amide linkages in the polymer backbone. Due to these units, the packing of macromolecular chains in tight structures through hydrogen bonding between amide groups is probably disturbed and consequently the increase in free volume enables the solvent molecule to penetrate easily in the polymer chains and solubilize them. Polyamide-Imides III_{Aa} to III_{Ca} are comparatively less soluble because of the presence of rigid pyridine moiety in the polymer backbone. Polyamide-Imide III_{Ca} shows higher solubility than the other relative Polyamide-Imides (III_{Aa} and III_{Ca}), which may be due to the presence of dichloro diamino diphenyl methane unit along with BPTDA. The higher solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

Table 2 Solubility of the prepared polyamide – imides

Polymers	DMF	DMAc	NMP	CHCl ₃	DMSO	THF
III _{Aa}	++	++	++	+	++	-
III _{Ba}	++	++	++	+	++	+
III _{Ca}	+++	+++	+++	+	+++	+
III _{Ab}	+++	+++	+++	+	+++	-
III _{Bb}	+++	+++	+++	++	+++	+
III _{Cb}	+++	+++	+++	++	+++	+
III _{Ac}	+++	+++	+++	+	+++	+++
III _{Bc}	++	++	++	++	++	-
III _{Cc}	+++	+++	+++	+	++	+

+++ - Highly soluble , ++ - Soluble on standing,
 + - Sparingly Soluble , - - Insoluble

Inherent Viscosity and Moisture absorption

The inherent viscosity of all the polymers was measured at a concentration of 0.5g/dL in DMAc using Ubbelohde viscometer at 30°C and the values are tabulated in **Table 3**.

Table 3 Viscosity and Moisture absorption of the polymers

S.No	Polymer	Viscosity dL/g	Moisture absorption %
1	III _{Aa}	1.72	1.80
2	III _{Ba}	1.69	1.37
3	III _{Ca}	1.70	2.14
4	III _{Ab}	1.38	2.43
5	III _{Bb}	1.33	2.00
6	III _{Cb}	1.21	2.60
7	III _{Ac}	1.52	2.40
8	III _{Bc}	1.55	2.18
9	III _{Cc}	1.42	2.82

The inherent viscosity values of the prepared polymers are in the range of 1.30-1.72dL/g, indicating high molecular weight of the polymer. The viscosity values of pyridine series are high compared to the benzophenone and bisphenol containing polymers, which is due to the presence of highly rigid pyridine moiety in the polymer backbone. Moisture absorption of the polymers are in the range 1.37 to 2.82%. The polymers with pyridine moiety show lower moisture absorption, which is due to the rigid close packing structure.

Optical properties

In general the colored nature of aromatic polymers is due to the presence of electronic conjugation, intermolecular and intramolecular CTC interactions (or) both [17]. From a previous report, we also know that the colorlessness of the polymers was affected by the diamine segments between two amide groups.

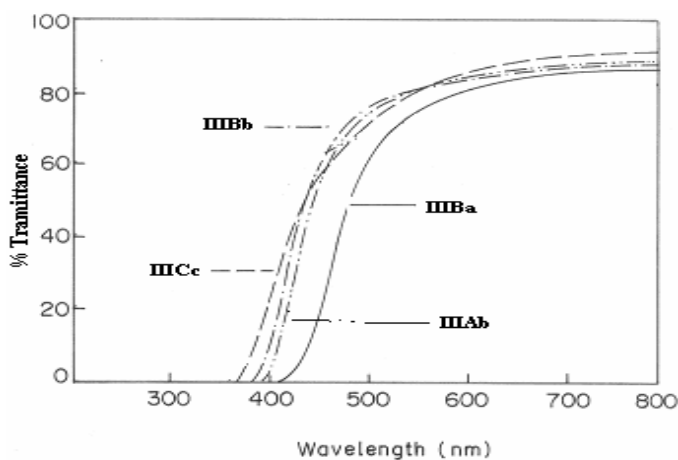


Figure. 6 UV-Visible spectrum of poly (amide-imide) s

In the present study, the above two facts are proved to be true by subjecting the polymer samples to UV spectroscopy (**Figure 6**) in which the benzophenone series polymers showed a shorter cutoff wavelength than the pyridine series polymers. This can be explained as follows. The presence of flexible ether linkages and benzophenone moiety has decreased the close chain packing there by restricted the CTC formation. The bisphenol series polymers showed lower cutoff wavelength than the benzophenone series, which may be due to the presence of methyl groups, which disrupts the extended electronic conjugation, resulting in decreased color.

Thermal properties

The thermal properties of the prepared Poly (amide-imides) were investigated by means of DSC as well as TGA. The results are shown in **Table-4**. The glass transition temperature (T_g) determined in the second heating runs of DSC measurements of the investigated PAIs is in the range 211-234°C. The DSC curves are shown in **Figure 7**.

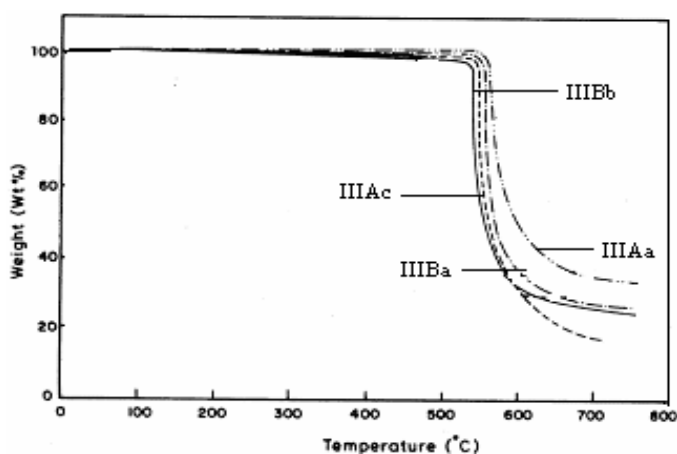


Figure. 7 Thermograms of poly (amide-imide) s

The T_g values of the poly (amide-imides) exhibit a linear decrease with the increase in the length of the long flexible chains, which increases the flexibility of the polymer backbone and thus the chain mobility. The polymers III_{Ca}, III_{Cb} and III_{Cc} have the lowest thermal stability than the other polymers containing rigid pyridine and phenylene moieties. This behavior can be explained by the presence of methylene units which are more vulnerable to thermo-oxidative processes [18-20].

Table 4 Thermal properties of polymers

S.No	Polymer	T _g °C	T ₁₀ °C	Char yield %
1	III _{Aa}	228	594	62
2	III _{Ba}	234	587	66
3	III _{Ca}	224	578	51
4	III _{Ab}	214	566	59
5	III _{Bb}	218	561	58
6	III _{Cb}	207	542	52
7	III _{Ac}	220	576	53
8	III _{Bc}	221	574	59
9	III _{Cc}	212	571	48

The thermal stability of the poly (amide-imides) was studied using TGA analysis conducted at a heating rate of 20°C/min under N₂ atmosphere. The TG curves of the polymers are shown in **Figure 8**.

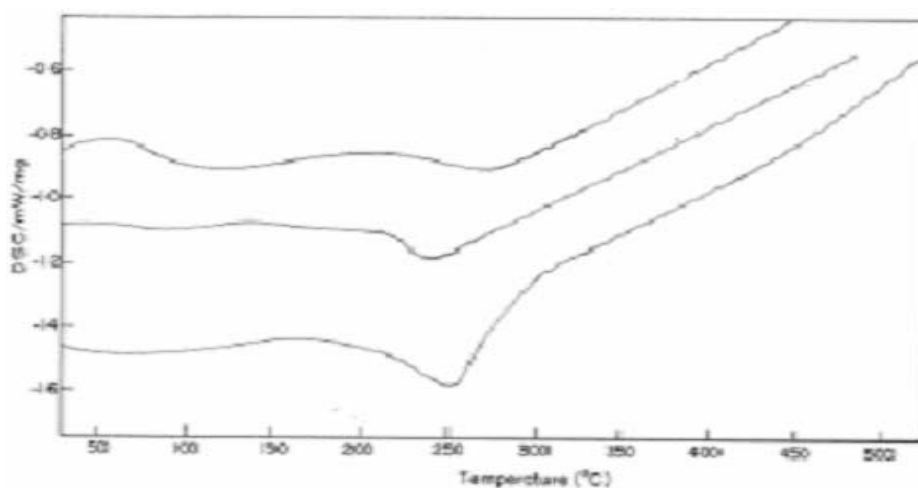


Figure. 8 DSC Curves of poly (amide-imide)s

The temperature at which 10% weight loss occurs was recorded to be in the range 571-594°C. Increasing char formation could limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and decrease the thermal conductivity of the polymer consequently to limit the polymer's flammability. The

anaerobic char yield is more than 55% (for all the polymers) and the absence of significant weight loss upto approximately 500°C shows that the polymers have high intrinsic fire resistance i.e. thermal stability.

Conclusions

A set of flexible dicarboxylic acid monomers containing benzophenone and bisphenol moieties and different diamines with preformed imide rings were successfully prepared and used to synthesis a series of poly (amide-imide) s. These PAIs exhibited excellent solubility in various organic solvents. The prepared polymers possess good thermal stability, flame retardency and light colour. Thus, these PAIs could be considered as new processable high-performance polymeric materials.

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References

1. Cassidy PE. (1980) Thermally stable polymers. New York: Marcel Dekker.
2. Ahmad Banihashemi, Hassan Firoozifar, (2003) European Polymer Journal 39, 281.
3. Preston J, Dobinson F. (1964) J Polym Sci B; 2:1171.
4. Bier G. (1969) Adv Chem Ser ; 91:612.
5. Preston J. In: Mark HF, Bikales NM, Overberger CG, Menges G, editors (1988) Encyclopedia of polymer science and technology, vol.111. New York: Wiley Interscience; p.81.
6. Lin J, Sherrington DC. (1994) Adv Polym Sci; 111:177.
7. Yun-Hi Kim, Seong-Kuk Ahn, and Seon-Ki Kwon, (2001) Bull. Korean Chem Soc, vol-22, 5, 451-452.
8. Beltramo M. (1993) Eng Plast; 6:40.
9. Shahram Mehdipour-Ataei, Ahmad Amirshaghghi, (2004) European Polymer Journal, 40,503–507.
10. Beltramo, M. (1993) Eng Plastics, 6, 40.
11. Billerbeck, C. J.; Henke, S. J. (1985) Engineering Thermoplastics; Dekker: New York.
12. Yang CP, Hsiao SH. (1989) Macromol Chem; 190:2119.
13. Chin-Ping Yang, Rwei-Shin Chen, Kuei-Shi Hung, (2001) Polymer, Vol-42, 4569-4577.
14. Der-Jang Liaw, Been-Yang Liaw, (1999) Polymer, vol-40, 3183- 3189.
15. Michaela Simionescu, Mihai Marcu, Maria Cazacu, (2002) European Polymer Journal.
16. Ching-Ping-Yang, Rwei-Shin, Chi-Shu Wei, (2002) Polymer Engineering and Science, 42,1220-1230.
17. Bhuvana.S, Hariharan.R, Sarojadevi.M, (2005) J Macromol Sci, part A, Pure and applied chem., 42, 1-12.
18. Wilson D, Stenzenberger.H.D, Hergenrother P.M, editors, (1990) Polyimides, Glasgow, Black&Sons.
19. Sheng-Huei Hsiao and Li-Min Chang, (2000) High Perform. Polym. 12, 285–298.
20. Hariharan R, Anuradha. G, Bhuvana.S, Sarojadevi.M, (2004) J Polym Resear., 11,239-245.