



STUDIES ON THE PREPARATION AND CHARACTERIZATION OF POLYIMIDES CONTAINING ANTHROQUINONE

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ABSTRACT

Processable heat resistant polymers are a recent development in the search for thermo stable polymers in which a compromise is required between process ability without much loss of thermal stability. By reacting 1, 4-dihydroxy anthraquinone with p-Chloronitrobenzene to give the dinitrocompound. Reduction of this dinitrocompound by using Fe/HCl gives the diamine. Polyimides were synthesized from this diamine reacted with PMDA. The polyimides obtained by this technique were characterized by FTIR ¹H-NMR ¹³C-NMR Spectroscopy. The solubility of these polyimides were tested in several solvents and found that they have good solubility in polar aprotic solvents such as NMP, DMF, DMAC, etc. The viscosity of the polyimides were determined and found to be in the range of **0.53 to 1.76 dl/g**. All the Polyimides showed amorphous pattern according to wide angle X-ray diffraction measurements. Optical properties of the polyimides were studied using UV-visible spectrophotometer (λ_0 **302-351°C**). The thermal stability of the polymer was tested by using DSC and the Tg are in the range (**239-249°C**) showing the high thermal stability of the prepared polymers.

1. INTRODUCTION

In the last twenty years there has been a flurry of activity in the synthesis of new polymer systems. This interest has developed largely as a result of the increased need for advanced materials. It is evident that material advances have been the key to significant technology break through throughout history. In less than twenty years, advanced composites have become established as efficient high- performance structural materials and their use is expanding rapidly[1,2]. In the recent years high value specialty polymers, such as those used in some engineering and aerospace engineering are being used in more demanding applications, require even higher specifications. High performance polymers such as polyimides have become an increasingly important class of materials in the field of aerospace and microelectronic industry[3].

Polymeric materials have a vast potential for exciting new applications in the foreseeable future. Polymer uses are being developed in such diverse areas as: conduction and storage of electricity, heat and light, molecular based information storage and processing, molecular composites, unique separation membranes, revolutionary new forms of food processing and packaging, health, housing and transportation. Indeed, polymers will play an increasingly important role in all aspects of life.

2. EXPERIMENTAL SECTION

2.1 Materials and methods

Ammonium acetate, stannous chloride, 1,4-dihydroxy anthraquinone and anhydrous potassium carbonate, palladised carbon(Pd/C), were purchased from Sisco Research Laboratories Pv, 2,6-dimethyl aniline(Alrich, india), Hydrochloric acid(HCl, spectrochem, india), Acetone (SRL,india), Maleic anhydride(E-Merck, India), triethylamine(Spectrochem, india), β -naphthol,N-methyl 2-pyrroindone(Alrich, wiscons,USA), N,N-dimethyl formamide (Fluka,st,lowis,MO,USA) purified by refluxing with calcium hydroxide distilled under reduced pressure and stored over molecular sieves 4A^o), diethyl amine(Spectrochem, mumbai, india), P-toluene-sulphonoc acid monohydrate(Ferak, USA), Acetic anhydride(Fischer, india), sodium acetate(Nacalai, extra pure reagent), 2,6-dimethyl phenol, p-phenylene diamine (SRL,India), 1-chloro4-nitrobenzene and anhydrous calcium chloride were purchased from (Qualigen chemicals, India). 4,4'-diamino diphenyl methane (DDM), 4,4',3,3'-benzophenonetetracarboxylic acid dianhydride and pyromellitic dianhydride were purchased from (Lancaster, USA)



2.1 MONOMER SYNTHESIS

2.1.1 SYNTHESIS OF DIAMINE

Synthesis of 1,4-bis (p-nitro phenoxy) anthraquinone

1, 4-dihydroxy anthraquinone (4g, 0.01667mol) and 1-chloro-4-nitrobenzene (5.24g, 0.033mol) were dissolved in 100ml of DMF in a 250 ml RB flask. Then, K_2CO_3 (2.3g, 0.0167mol) was added and the solution was heated at $120^\circ C$ for 24hr [4,5].The mixture was allowed to cool and then poured into 800ml of water to give a precipitate which was collected, washed dried repeatedly with water and dried. The crude product was recrystallized from ethanol. (83%)

REDUCTION OF 1, 4 BIS (P-NITRO PHENOXY) ANTHRAQUINONE:

A mixture of 1.5ml of conc. Hydrochloric acid and 10ml of 50%aqueous ethanol was added slowly to a mixture of 3g of 1,4-bis(p-nitro phenoxy) anthraquinone(0.0083mol).reductive iron (0.1g) and 10ml of aqueous ethanol in a 250 ml three necked RB flask equipped with a mechanical stirrer and thermometer [6]. The mixture was stirred with refluxing for 3hr, and 1ml of ammonium hydroxide solution (10 wt %) was added slowly to the mixture during 10 min. The mixture was hot filtered to remove solvent, a solid was got; it should be 1, 4-bis (p-Amino phenoxy) anthraquinone. (92%)

2.2 PREPARATION OF DIANHYDRIDE:

2.2.1. SYNTHESIS OF 4- NITROPHthalONITRILE

STEP 1:

Synthesis of 4-Nitrophthalimide

Phthalimide (3g, 0.0204mol) was added to a 32 mL mixture of concentrated H_2SO_4 and 70% HNO_3 (6:1v/v) at $0-10^\circ C$. The solution was added to slowly warm to room temperature and held for 4hr. The solution was added to ice water and stirred. The 4-Nitrophthalonitrile crystallized and precipitated out of the ice water. The product was collected by vacuum filtration, washed with ice cold water, and air dried overnight; yield: 31.5 g (80%) [7].

Step 2:

Synthesis of 4-Nitrophthalamide

4-Nitrophthalamide (5.79g, 0.0300 mol) was added to NH_4OH (33%)(20ml) with stirring to form a yellow suspension. The suspension was allowed to react for 24 hrs at room temperature. A yellow precipitate, 4-Nitrophthalamide, was collected using vacuum filtration, washed with ice cold water, air dried overnight; yield 60.1 g(95%).

Step 3: Synthesis of 4- Nitrophthalonitrile:

$SOCl_2$ (8.35 mL, 0.1144 mol) was added drop wise under nitrogen purge to dry DMF (20 mL), which had been cooled to $0-5^\circ C$. The solution was allowed to stir for 15 min at $0-5^\circ C$.The 4-Nitrophthalamide(60.1g,0.286 mol) was then added and the solution was allowed to slowly warm to room temperature and react for 18hr under nitrogen purge[8].The solution was then slowly added to ice water to crystallize and precipitate the product. The 4-Nitrophthalonitrile was collected using vacuum filtration, washed with ice cold water, and allowed to air dry overnight; yield:45.2g (92%).

2.2.1.1 PREPARATION OF BIS (4-HYDROXY-3, 5-DIMETHYL) 4-CHLORO PHENYL METHANE:



0.08 moles of 2, 6 dimethyl phenol (9.7g) was treated with hydrochloric acid, till the solid gets dissolved. Then 0.02 moles (4 ml) of 4-chlorobenzaldehyde was added to it under a nitrogen atmosphere. The temperature was gradually raised to 134°C, and stirred for 2hrs. The reaction mixture was neutralized with Na OH, and precipitated in hexane. The precipitated bisphenol was filtered and dried over CaCl₂ (92%) [9].

2.2.1.2 PREPARATION OF BIS (4-2,3-DICYANOPHENYL-3, 5-DIMETHYL)4-CHLORO PHENYLMETHANE

2.5g (0.0077 mol) of the synthesized bisphenol was reacted with 5g of 4- Nitrophthalonitrile (0.034 moles) in the presence of 5.628g (0.0410 mol) of K₂CO₃ and NMP as solvent. The reaction was carried out for 24 hrs at room temperature in nitrogen atmosphere[10]. The bisphthalonitrile formed was precipitated in cold water, filtered, and dried over CaCl₂.

2.2.1.3 HYDROLYSIS OF BIS (4-2, 3-DICYANOPHENYL-3, 5- DIMETHYL) 4- CHLORO PHENYLMETHANE:

43g (0.0059 mol) of the synthesized bisphthalonitrile was refluxed with 6.618 g (0.118 mol) of KOH, in the presence of 20.5 mL of ethanol and 20.5 ml of distilled water for 48 hrs at 134°C. The hot solution was filtered to remove insoluble impurities[11,12,13], the P^H was reduced by adding 0.1N HCl, as HCl was added, the tetra carboxylic acid formed precipitated out. The formed tetra carboxylic acid was filtered and dried over CaCl₂.

2.2.1.4 PREPARATION OF DIANHYDRIDE

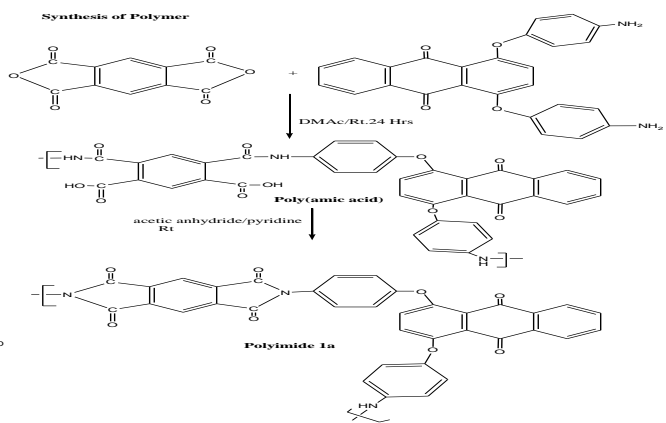
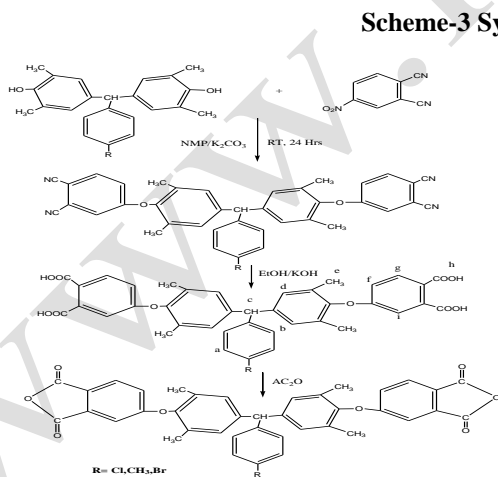
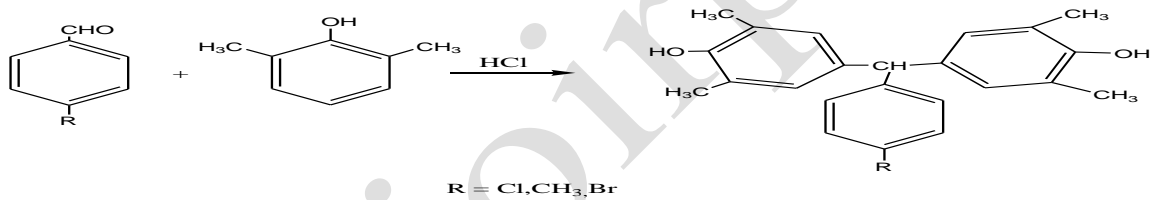
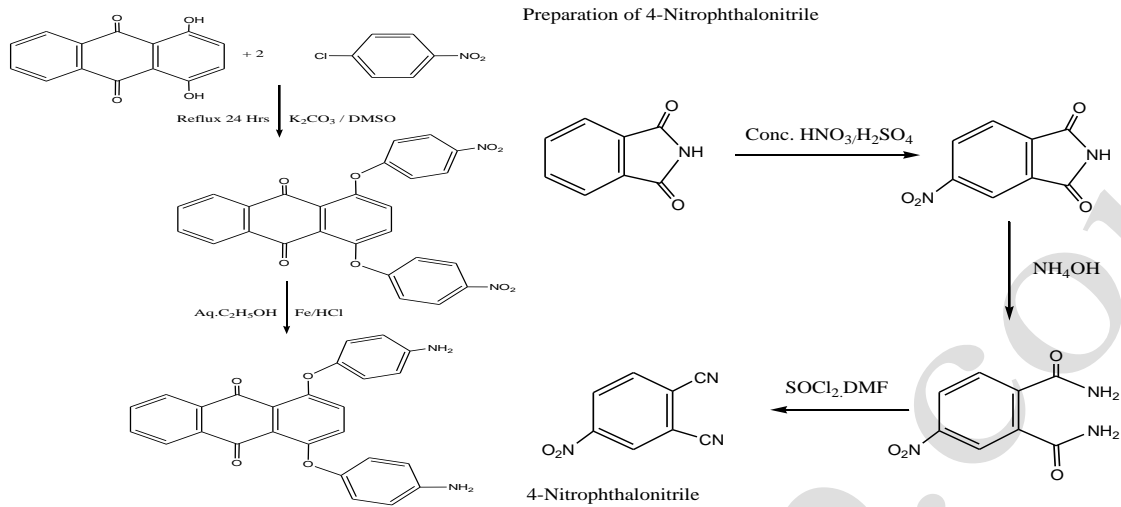
2.5g (0.0037 mol) of synthesized tetra carboxylic acid was refluxed with 15 mL of acetic acid and 15 mL of acetic anhydride for 24 hrs at 134°C. The hot filtrate was cooled and dianhydride crystals separated out, which was stored over anhydrous CaCl₂.

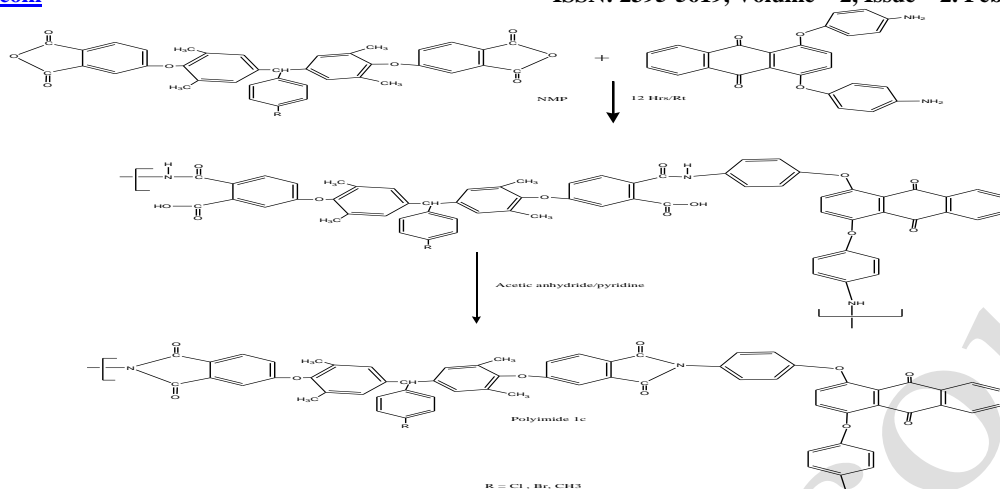
3.1 SYNTHESIS OF POLYIMIDES:

Utilizing BAAD as diamine monomer, three kinds of novel Polyimides were synthesized by polycondensation of diamine with, PMDA, BTDA and newly synthesized novel dianhydride. Diamine (4g, 0.0045 mol) was dissolved in NMP in a 100ml of three necked flask fitted with a nitrogen inlet and mechanical stirrer, then PMDA (7.738g, 0.0045 mol) was added to the solution with stirring, then the reaction was allowed to carry through 24 hr at room temperature to yield a viscous poly (amic acid) solution with 15% of solid content. The Polyimides obtained by chemical imidization method, a mixture of 6 ml acetic anhydride and 4 ml pyridine was added into the PAA solution and was remained 24 hr with stirring at room temperature. The solution containing Polyimides was poured into ethanol to produce a precipitate, the precipitate was collected by filtration and washed with ethanol thoroughly, and then it was dried at 80°C for 2hr and 120°C for 6hr under vacuum, successively[14].

Polyimides BAAD/BTDA, BAAD/ newly synthesized novel dianhydride were synthesized from the polymerization of 1-equiv. of BTDA/synthesized dianhydride, respectively, at 15% Solid content in NMP in the same method as Polyimide BAAD/PMDA.

SCHEMES:





Scheme-7 Synthesis of Polyimide 1c

4.RESULTS AND DISCUSSION

4.1 SYNTHESIS OF DIAMINE:

4.1.1 synthesis of 1, 4-bis (p-nitrophenoxy) anthraquinone:

1, 4-bis (p-nitrophenoxy) anthraquinone was synthesized from 1,4-dihydroxyanthraquinone and p-chloronitrobenzene. Figure 4.1.1 shows the FTIR spectra of 1, 4-bis (p-nitrophenoxy) anthraquinone. Characteristic bands observed at 1511 and 1344 cm^{-1} shows the asymmetric and symmetric stretching vibrations of NO_2 group. The band appear at 3091 cm^{-1} shows the aromatic CH- groups.

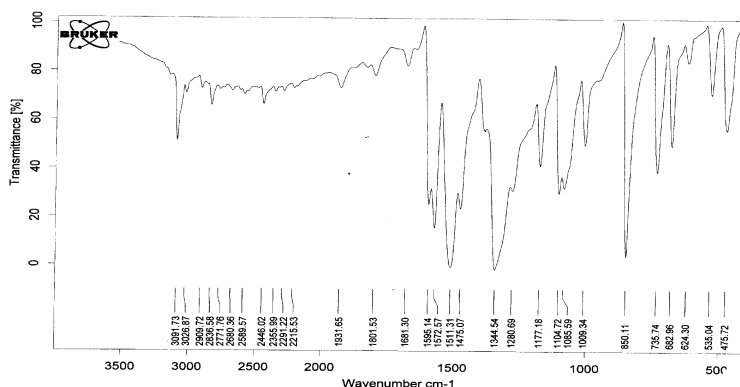


Figure 4.1.1 FT-IR spectra of dinitro compound

4.1.2 Synthesis of 1, 4-bis (p-aminophenoxy) anthraquinone:

It is synthesized by reducing the dinitro compound. Figure 4.1.2.1 shows the FT-IR spectra of diamine compound. The characteristic band observed at 3460 and 3330 cm^{-1} indicates the asymmetric and symmetric stretching vibrations of NH_2 . The band appears at 1628 cm^{-1} shows the NH - bending vibrations. The band observed at 3058 cm^{-1} indicates the aromatic CH- groups. Figure 4.1.2.2 shows the ^1H NMR spectrum of diamines compound. ^1H NMR (400MHz, CDCl_3 , ppm); δ - 4.0 ppm (s,4H,1), δ -6.42 ppm (d,4H,2), δ -6.67 ppm (d,4H,3) δ -7.17 (d,2H,4), δ -7.55 ppm (m,2H,6), δ -7.80 ppm (m,2H,6)

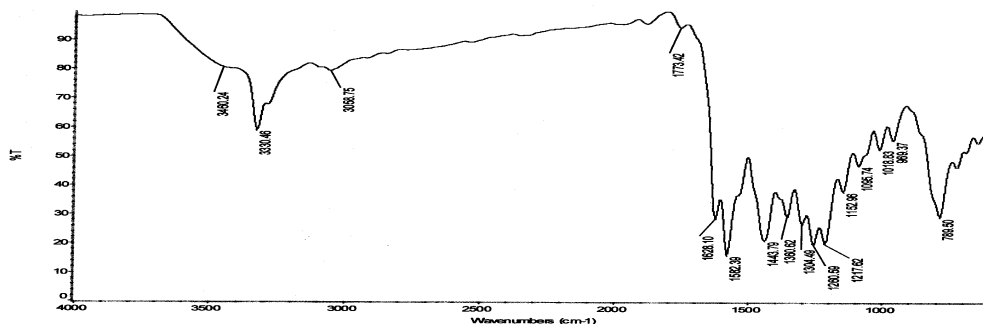


Figure 4.1.2.1 FT-IR Spectra of diamine(BAAD)

4.2 SYNTHESIS OF DIANHYDRIDE:

4.2.1 SYNTHESIS OF 4-NITROPHTHALIMIDE

Figure 4.2.1 shows the FT-IR spectra of 4-nitrophthalimide. The characteristic band appears at 1563 and 1380 cm^{-1} indicates the presence of asymmetric and symmetric stretching vibrations of NO_2 . The band appears at 1743 and 1782 cm^{-1} is due to the presence of $\text{C}=\text{O}$ in the imide ring.

4.2.2 Synthesis of 4-nitroPhthalamide

Figure 4.2.2 shows the FT-IR spectra of 4-nitroPhthalamide. The characteristic band appears at 3415 and 3201 cm^{-1} indicate the presence asymmetric and symmetric stretching vibrations of NH_2 . The band appears at 1564 and 1384 cm^{-1} due to asymmetric and symmetric stretching vibrations of NO_2 .

4.2.3 SYNTHESIS OF 4-NITROPHTHALONITRILE

4-Nitrophthalonitrile was synthesized as per the reported procedure (Michael Jameson Sumner et al 2003). The synthesis involves nitration of phthalimide, hydrolysis of 4-nitrophthalimide and finally dehydration of 4-nitrophthalimide. Figure 4.2.3.1 shows the FT-IR spectrum of 4-nitrophthalonitrile. Characteristic bands observed at 1564 cm^{-1} and 1378 cm^{-1} are due to asymmetrical and symmetrical stretching of nitro group respectively. The sharp band at 2242 cm^{-1} is due to the presence of the nitrile groups. The FTIR spectrum confirms the formation of 4-nitrophthalonitrile. $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ -8.4(s,1 H,1), δ -8.6 ppm (s,1H,2), δ -9.03 ppm(s,1H,3). Figure 4.2.3.2 shows the $^1\text{H NMR}$ spectrum of 4-nitrophthalonitrile. Three aromatic protons are present, which show signals in the range of 8-10 ppm. All the three aromatic protons are shifted considerably down field due to the presence of strong electron withdrawing groups like nitrile and nitro groups. The most deshielded proton is the proton placed between a nitro and cyano group. It shows a chemical shift of 9.03 ppm. The $^1\text{H NMR}$ spectrum confirms the structure of 4-nitrophthalonitrile. The formation of 4-nitrophthalonitrile is confirmed by elemental analysis (Table 1). The experimental values are found to be in good agreement with the theoretical values.

4.2.4 SYNTHESIS OF BISPENOLS:

The bisphenols were synthesized by a condensation reaction between 2, 6-dimethylphenol and different aromatic aldehydes in the presence of HCl. Figure 4.2.4 shows the FTIR spectrum of the bisphenol. The spectra show a broad band in the region of 3400-3600 cm^{-1} due to the presence of free OH-groups. Characteristic band at 1480 cm^{-1} is due to the ring stretching and band at 1136 is due to ring bending. Figure 4.2.4.1 shows the $^1\text{H NMR}$ spectrum of the bisphenol. The sharp intense signal at 2.2 ppm is attributed to the 12 aliphatic methyl protons; the resonance signal at 5.3 ppm is due to the benzylic protons. The signals in the range of 6.7 to 7.2 ppm are attributed to the presence of aromatic protons and the broad signal at 4.5 ppm is attributed to the phenolic protons.

^1H NMR (400 MHz, CDCl_3 , ppm): δ -2.2ppm (s,12H,1), δ -4.5 ppm (s,2H,2), δ -5.3 ppm (s,1H,3), δ -6.7 (s,4H,4), δ -7.2 ppm (d,2H,6), δ -7.1 ppm (d,2H,5). Figure 4.2.4.2 shows the ^{13}C NMR spectrum of the bisphenol. The signal at 15.90ppm is attributed to the aliphatic methyl carbon, signal at 55.4ppm is attributed to benzylic carbon and the signal at 150.4 ppm is attributed to the carbon atoms bearing -OH groups. The signals occurring between 120-140 ppm are attributed to the aromatic carbons present in the structure. The ^1H -NMR and ^{13}C -NMR Spectrum confirm the formation of bisphenol.

C^{13} NMR (400MHz, CDCl_3 , ppm); δ - ^1C -15.9, ^2C -55.4, ^3C -150.4, ^4C -130.1, ^5C -128.5, ^6C -138.5.

4.2.5 SYNTHESIS OF TETRACARBOXYLIC ACID:

The synthesized bisphthalonitrile was hydrolyzed in the presence of KOH, ethanol and distilled water to get the tetra carboxylic acid. Figure 4.2.5.1 shows the FT-IR spectra of the obtained tetra carboxylic acids. These spectra show a broad band at 3400-3600 cm^{-1} due to the -OH moiety in -COOH. The sharp band at 1758 cm^{-1} is due to the presence of the C=O group in -COOH, and the band around 1220-1230 cm^{-1} is attributed to C-O-C stretching. The disappearance of band at 2240 cm^{-1} confirms the hydrolysis of nitrile group to acid. H NMR (400 MHz, CDCl_3 , ppm): δ -2.02ppm (s,12H,5), δ -5.59 ppm (s,1H,7), δ -6.98 ppm (d,2H,2), δ -3.30 (s,4H,1), δ -7.85 ppm (d,2H,9), δ -7.0 ppm (s,4H,6), δ -7.36ppm (d,2H,8), δ -7.23 ppm (s,1H,4), δ -7.40 ppm (d,2H,3).

Figure 4.2.5.2 shows the ^1H NMR spectrum of the synthesized tetra carboxylic acid. The intense signal at 2.02 ppm indicates the presence of 12 aliphatic protons. The singlet at 5.59ppm is attributed to the presence of benzylic proton and the signals found in the range of 6.98-8 ppm are attributed to the aromatic protons. The broad signal at 3.3ppm may be attributed to the acidic proton. Figure 4.2.5.3 shows the ^{13}C NMR spectrum of the synthesized tetra carboxylic acid. It confirms the formation of the tetra carboxylic acid through two singlets obtained at 168 and 169 ppm. The signals at 16 and 55 ppm are attributed to the aliphatic methyl carbon and benzylic carbon respectively. The signals obtained in the range of 110-140 ppm are attributed to the aromatic carbons. The FT-IR, ^1H -NMR and ^{13}C NMR confirm the structure of formed tetra carboxylic acid.

4.2.6 SYNTHESIS OF DIANHYDRIDE:

The tetra carboxylic acid formed was refluxed with acetic anhydride and acetic acid at 134 $^\circ\text{C}$, for 16 hrs to yield the dianhydride. Figure 4.2.6 shows the FT-IR spectra of the dianhydride. The characteristic bands of the dianhydride are seen in the FT-IR spectrum. Sharp bands at 1852 cm^{-1} and 1734 cm^{-1} indicate the presence of O-C=O stretching, and a sharp band at 1217 and 1072 cm^{-1} are attributed to C-O-C stretching and bending respectively.

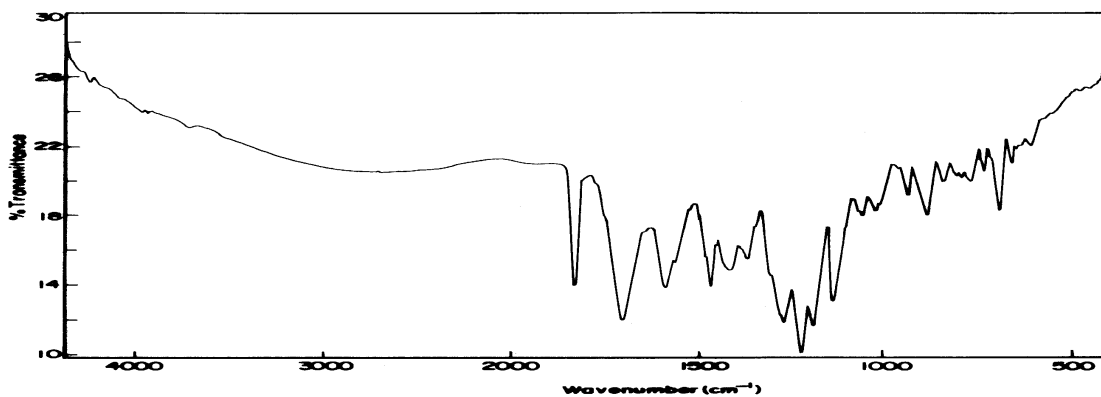


Figure4.2.6 FT-IR spectrum of dianhydride

4.3 SYNTHESIS OF POLYIMIDES

4.3.1 SYNTHESIS OF PMDA BASED POLYIMIDE

PMDA based Polyimide was synthesized from 1,4-bis(p-aminophenoxy)anthraquinone and pyromellitic dianhydride(PMDA). **Figure 4.3.1** shows the FT-IR spectra of polyimide-1a. The characteristic band appears at 1782 and 1721 cm^{-1} shows the asymmetric and symmetric stretching vibrations of C=O group in the imide ring. The band appears at 1350 cm^{-1} indicates the presence of CN-stretching vibrations. This confirms the structure of polyimide.

4.4 DSC (DIFFERENTIAL SCANNING CALORIMETRY)

Thermal properties of all the polyimides were evaluated by thermogravimetry and differential scanning calorimetry was carried out for polyimides (1a-1c) at a heating rate of 10°C. The glass transition temperature of all polyimides are in the range of 229-249°C. The representative DSC is shown in figure 4.4. The T_g values from the DSC thermo grams are shown in the table 4.4.

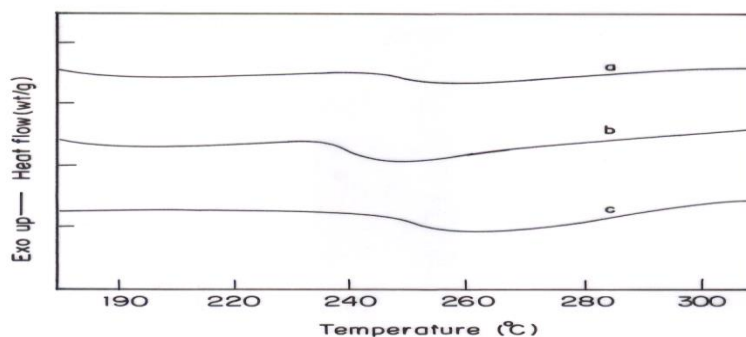


Figure 4.4 DSC curves of Polyimides

[1a=PMDA+BAAD, 1b=BTDA+BAAD, 1c= BAAD+ newly synthesized novel dianhydrides]

4.5 TGA (THERMOGRAVIMETRIC ANALYSIS)

The thermal stability of the polyimides in nitrogen atmosphere was evaluated from TG analysis and is shown in Fig.4.5. The polyimide-1a has thermal stability upto 487°C and has the residual mass value 41.51% at 800°C. The polyimide-1b has thermal stability upto 490°C and has the residual mass value 40.42% at 800°C. The polyimide-1c has thermal stability upto 429°C and has the residual mass value 44.52% at 800°C.

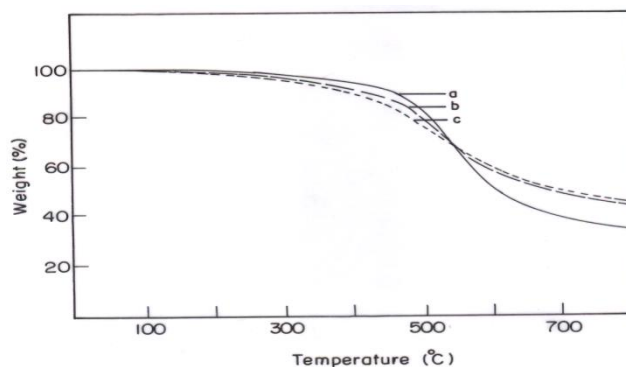


Figure4.5 Thermograms of Polyimides

Table-1 Thermal properties of polyimides

Polyimide code	polyimide	Char yield (%)	Tg (° c)
PI-1a	BAAD + PMDA	47.21	247
PI-1b	BAAD + BTDA	40.21	249
PI-1c	BAAD + Newly synthesized novel dianhydride	52.74	239

[a=PMDA+BAAD, b=BTDA+BAAD, c= BAAD+ newly synthesized novel dianhydrides]

4.6 CRYSTALLINITY

The crystallinity of the polymers was estimated by wide angle X ray measurements and the studies were performed with powder specimens. The results indicate that all the polymers are almost amorphous.

4.7 OPTICAL PROPERTIES

Electron conjugation in polymers can be investigated using UV- visible spectroscopy, strong conjugation leads to absorption at higher wavelength. In principle, the % wavelengths of the most onset transmission and the % transmission are qualitatively associated with the electron conjugation length of the polymeric chain backbones (Li et al 1999). The representative UV- visible spectra of polyimides obtained from various diamines and dianhydrides at a concentration of 5×10^{-3} mol/L in NMP solution are shown in figures 4.7.1 and the cut off wavelength and percentage transmittance at 500 nm from the spectra are tabulated in table4.7. Polyimides derived from PMDA show strong absorption with a high cut-off wavelength due to the electronic conjugation structure of PMDA.

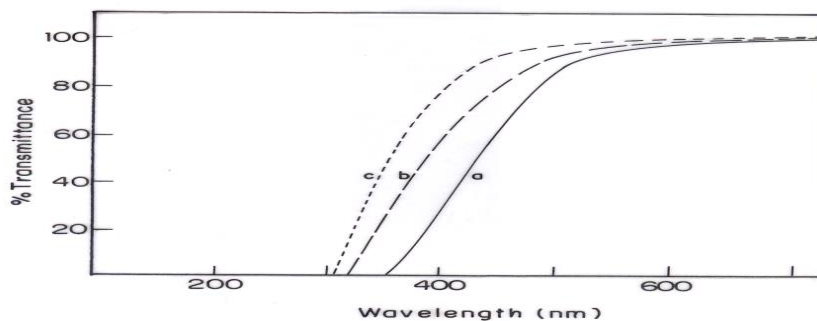


Figure 4.7.1 UV-Visible Spectra of polyimides

SOLUBILITY

The solubility of polyimides (two step method) was tested in various organic solvents and the results were summarized in table4.8. The synthesized polyimides were soluble in polar aprotic solvents such as NMP, DMF, DMAc etc.



CODE	POLYIMIDE	λ_o (nm)	% TRANSMITTANCE
PI-1a	PABA+ PMDA	351.2	98
PI-1b	PABA+BTDA	315.4	96
PI-1c	PABA+NOVEL DIANHYDRIDE	302.5	88

Table4.7

Optical properties of polyimides

SOLUBILITY STUDIES

CODE	Polyimide	NMP	DMF	DMSO	DMAC	THF
PI-1a	BAAD+PMDA	++	++	++	++	++
PI-1b	BAAD+BTDA	++	++	++	++	++
PI-1c	BAAD+Cl based PI	++	++	++	++	++
PI-1d	BAAD+Br based PI	++	++	++	++	++
PI-1e	BAAD+CH3 based PI	++	++	++	++	++

+++-Completely soluble at room temperature; ++-Completely soluble on heating

Table-3 Solubility behaviour of polyimides prepared by two step method (Chemical imidization)

Table-2
Elemental Analysis Data

Compound	Carbon %	Hydrogen %	Nitrogen %
4-nitrophthalonitrile	T= 55.59 E= 56.08	T= 1.73 E= 2.25	T= 24.2 E= 23.01

T-Theoretical, E -Experimental

5 CONCLUSIONS

Antraquinone containing diamine were synthesized from 1,4 p-hydroxy anthraquinone and p-chloronitrobenzene and then reducing them. Dianhydrides were prepared multi step synthesis involving synthesis of bisphenols, bisphthalonitriles and tetra carboxylic acid. The structures of the compounds synthesized were

