

2 Present Investigation Results and Discussion

It is well known that wholly aromatic polyamides (aramids) such as poly (m-phenylene isophthalamide) and poly (p-phenylene terephthalamide) exhibit high thermal stability and excellent mechanical properties.[25,26]. Fabrication of most aramids, however, was extremely difficult because of their high softening temperatures and insoluble nature in most organic solvents. Recently, new processible engineering plastics possessing moderately high softening temperatures and solubility in some organic solvents have been required in practical use. Attempts for increasing the solubility of polyamides have been made through the introduction of flexible bonding in the polymer backbone and bulky pendant groups such as methoxy, phenoxy or phenylthio to the main chain.[27,28] We have reported that introduction of pendant phenyl groups [29], main chain silicon [30], with pendant phenyl groups and silicon and bulky alkyl group [31] into aromatic polyamides improved solubility of polyamides in organic solvents.

In the present study, methyl and pentadecyl groups were chosen as pendant groups. Thus, a series of aramids was prepared by the polycondensation of 2-methyl-1,4-benzenediamine and 2-pentadecyl-1,4-benzenediamine, (obtained by using an indigenously available raw material cashewnut shell liquid) with aromatic diacid chlorides.

Properties of these polyamides having pendant groups were compared with those of the polyamides having no pendant group derived from 1,4-benzenediamine/4,4'-diaminodiphenyl-ether and aromatic diacid chlorides.

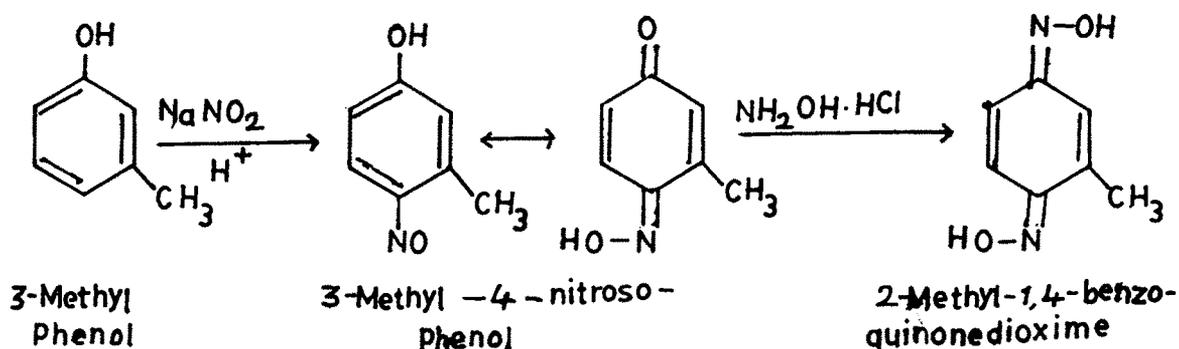
Thus the purpose of the present study was to modify the basic diamine structure of 1,4-benzenediamine with methyl or pentadecyl group substituents and to utilise these novel diamines in the preparation of aromatic polyamides. The effect of the ring substitution on polymer properties has been assessed to correlate the structure-property relation.

2-Methyl-1,4-benzenediamine (MBDA), although reported earlier has been prepared by using a different reduction conditions. Polyamides based on 2-pentadecyl-1,4-benzenediamine (PBDA) are being reported for the first time, though PBDA has been used to obtain polyimides. [32]

2.1 2-Alkyl substituted benzenediamines

Methyl or pentadecyl substituted aromatic diamines were prepared following the reported methods.[33] Both the diamines were obtained by reduction of the corresponding quinonedioxime by hydrazinehydrate- Ni catalyst system for the first time. The general reaction schemes for the preparation of the quinonedioxime and diamines are shown in Figure 2 and Figure 3. The physical constants, elemental analysis and yields of all compounds synthesised are given in experimental section.

2-Methyl-quinonedioxime (2-methyl-2,5 - cyclohexadiene 1,4 - dionedioxime) was prepared as described in literature. [34,35]



In the present study dioximes have been reduced with hydrazine in the presence of hydrogenation catalyst such as Raney Nickel, which is used to promote the decomposition of hydrazine to nitrogen (or ammonia) and hydrogen. Thus this reduction procedure is equivalent to catalytic hydrogenation in which the decomposing hydrazine serves as a source of hydrogen. Thus by employing this procedure high pressure hydrogenation in Parr reactor is not absolutely necessary and reduction can be performed in general chemistry laboratory. This procedure gives 2,5-toluene-diamine (MBDA) as pure compound without any contamination of any other possible isomeric toluenediamines. Commercially adopted process of nitration of toluene yields only traces of 2-5-dinitro-toluene as illustrated in Figure 1.

The diamines were purified by distillation under vacuum and recrystallisation from petroleum ether. They were shown to be pure, single compounds on the basis of thin layer chromatography and the data on elemental analysis, and m.p. IR, NMR and mass spectra are presented in Figures 3 to 5 for 2-methyl-1,4-benzenediamine (MBDA) and in Figures 6 to 8 for 2-pentadecyl-1,4-benzenediamine (PBDA).

2.1.1 Characterisation of MBDA and PBDA

The IR spectra of MBDA and PBDA showed absorptions in the range of 3250-3190 cm^{-1} due to primary amine. Mass spectrum of MBDA (Figure 6) shows molecular ion (M^+) as base peak at 122. The main fragmentation of MBDA involved loss of HCN from (M^+) or ($m-1$) $^+$ ions.



Mass spectrum of PBDA (Figure 9) gave molecular ion peak (M^+) = 318 as base peak and fragmentation of $C_{15}H_{31}$ alkyl group. Loss of $-CH_2$ in succession (14 mass units) was observed upto 121. Thereafter decomposition pattern was almost similar to that of MBDA.

The NMR spectrum of MBDA (Figure 5) showed δ values for aromatic protons at $\delta = 6.40$ (3H) and aliphatic protons at $\delta = 2.13$ (3H, singlet, CH_3 group). The presence of amine groups was also observed in NMR spectrum at $\delta = 3.30$ (4H, singlet) and it was exchangeable with D_2O .

The NMR spectrum of PBDA (Figure 8) showed multiplet at $\delta = 6.6$ (3H, aromatic) and signals at $\delta = 2.05$ (2H, benzylic- CH_2), $\delta = 1.25$ [26 H, $(\text{CH}_2)_3$] and $\delta = 0.90$ (3H, CH_3) for pentadecyl group. Amino group signal appeared at $\delta = 4.05$ (4H, singlet) and was exchangeable when treated with D_2O .

2.2 Polyamides

A series of novel aromatic polyamides have been prepared from the reaction of isophthaloyl chloride (IPC) terephthaloyl chloride (TPC) and diamines. Low temperature solution polymerisation technique or interfacial polymerisation technique was used to prepare the aromatic polyamides. The general structure is shown in Figure 10. Polyamides prepared from ODA and BDA have excellent thermal stability and were prepared in the present studies again for comparison purpose under identical reaction conditions. In a similar fashion, all polyamides presented in Table II, and III were prepared using IPC / TPC and diamines such as BDA / MBDA / PBDA / ODA following low temperature solution polymerisation and interfacial polymerisation procedures, as described by Morgon. [36]

Presence of moisture causes adverse effect on building up of molecular weight of aromatic polyamides in low-temperature solution polycondensation process. Therefore due care was taken to conduct the reactions under nitrogen atmosphere and perfectly dry conditions.

2.2.1 Characterisation of Polymers

Polyamides were characterised by inherent viscosity and IR spectra.

IR :

The infrared spectra of the representative polyamides are given in Figures 11 to 14.

Infrared spectra of all the polyamides showed characteristic absorptions, such as bands associated with the amide linkage, especially the 3350-3300 cm^{-1} (N-H stretching) vibration of secondary amides, 1670-1650 cm^{-1} (amide I band $\text{>C}=\text{O}$ stretching vibration), 1530-1520 cm^{-1} (amide II band due to a N-H deformation vibration). The absorptions at 2960 and 1450 cm^{-1} were ascribed to C-H aliphatic stretch in case of polyamides obtained from MBDA / PBDA. The polymers derived from ODA showed a band at 1225 cm^{-1} assignable to (C-O-C) asymmetric stretch.

Viscosity :

These aramids had inherent viscosities in the range of 0.18 to 0.68 dL/g. Data on the inherent viscosity (η_{inh}) of the polymer samples presented in Table II and Table III reveals that the trend in the values of η_{inh} of polymer samples prepared from IPC and various benzenediamine is MBDA > PBDA. This can also be the trend in the average molecular weights of the polymer samples. In case of BDA based polymer with TPC the premature precipitation of polymer may

Table II : Low Temperature Solution Polymerisation^a

Sr.No.	Monomers ^b	Yield %	η_{inh}^c (dL/g)	Remarks
1.	ODA + TPC	80.0	-	polymer insoluble
2.	ODA + IPC	98.6	0.52	-
3.	BDA + TPC	84.2	very low	polymer precipi- -tated during reaction.
4.	BDA + IPC	95.1	0.58	-
5.	MBDA + IPC	91.0	0.18	-

a. Polymerisation performed with 1 mMol each of diamine and diacid chloride in 8 ml DMAC at 10°C / 2 hour and 25°C / 20 hour.

b. ODA = 4,4'-Diaminodiphenylether
 BDA = 1,4-Benzenediamine
 MBDA = 2-Methyl-1,4-benzenediamine
 PBDA = 2-Pentadecyl-1,4-benzenediamine
 IPC = Isophthaloyl chloride
 TPC = Terephthaloyl chloride

c. In concentrated sulfuric acid with 0.5 % solution at 30°C.

Table III : Interfacial Polymerisation^a

Sr.No.	Monomers ^b	polymer code	Yield %	η_{inh} (dL/g)	Remarks
1.	ODA + TPC	A	81	0.3	
2.	ODA + IPC	B	77	0.27	
3.	BDA + TPC	C	97.9	0.34	
4.	MBDA + TPC	D	60	0.68	
5.	PBDA + TPC	E	71.2	0.54	PBDA-aq. Na ₂ CO ₃ not homogenous hence 2 ml chloroform was added.
6.	BDA + IPC	F	88.6	0.36	
7.	MBDA + IPC	G	53	0.55	
8.	PBDA + IPC	H	62.3	0.33	

a Polymerisation performed with 1 mMol each of acid chloride, diamine and 2 mMol sodium carbonate in 5 ml water and 1.6 ml chloroform at 5-10^oC temperature.

b & c as in Table I .

be the reason for lower molecular weight (low viscosity). Taking into account steric hindrance of the pendant bulky pentadecyl group in the PBDA it is quite reasonable that molecular weight of the polyamides prepared from PBDA are lower^{than} those for polymers based on MBDA. The literature contains many examples of polyamides with bulky substituents such as methyl or chloro on at least one of the carbon atoms of the phenyl ring ortho to the amido group, but in every case the degree of polymerisation, as indicated by viscosity, is adversely affected [37,40]. Similar results are found for present polyamides based on PBDA.

However, it may be noted that higher molecular weight polyamides from PBDA could be synthesised using recently reported activated reagent procedure [41-43].

Solubility

Table IV shows solubility behaviour of the alkyl (methyl or pentadecyl) pendant polyamides. All the polymers were soluble in many of the amide solvents with or without lithium chloride added, and all polymers were insoluble in other solvents such as chloroform, benzene, acetone and methanol. Polyamides G and H, having IPC (m-phenylene linkage) and methyl / pentadecyl substituent in diamine component (MBDA / PBDA) were more soluble than the others.

Table IV : Solubility of Aromatic Polyamides^a

Sr.No.	Polymer	Solvent				
		DMAC	DMSO	DMF	NMP	Conc. H ₂ SO ₄
1.	A	+ ^b	-	-	-	++
2.	B	++	++	+ ^b	++	++
3.	C	±	±	±	±	++
4.	D	±	-	-	±	++
5.	E	+ ^b	±	±	±	+ ^c
6.	F	±	++ ^b	++ ^b	++ ^b	++
7.	G	++	++	++ ^b	++	++
8.	H	++	+ ^b	+ ^b	++	++

a. ++ soluble at room temperature, + soluble on heating, ± partially soluble, - insoluble. Tested at concentration of 0.1g of polymer / 3-5 ml of solvent.

b. LiCl added.

c. almost soluble.

DMAC = N,N-Dimethylacetamide

DMSO = Dimethylsulfoxide

DMF = Dimethylformamide

NMP = N-Methyl-2-pyrrolidone

On the basis of the molecular structure of PBDA it can be anticipated that nonplanar and amorphous polymers would exhibit higher rates of dissolution compared to other aromatic polyamides, and this was observed for the polymers presented in this study. Specifically, polymer from PBDA and IPC dissolved quickly in DMAC, NMP at ambient temperatures and with stirring and at not more than 100°C in LiCl-containing DMSO / DMF. The polymers dissolved freely in concentrated sulfuric acid. The solution of each polyamide sample in concentrated sulfuric acid on dilution with water furnished the precipitated polymer, which was found to be identical with the original sample.

However, the TPC based polyamides were insoluble in most organic solvents, except hot DMAC containing LiCl.

Elemental Analysis

Elemental analysis of diamines and intermediate compounds are given in experimental section and agrees well with the calculated values. Elemental analysis, for C,H and N of the polymer samples was not carried out because it is expected that large amount of residue would remain behind in the combustion boat due to high thermal stability of the polymers. Therefore the estimated values of C,H and N would be much lower than expected, even the total time given for combustion in furnace be doubled and the furnace temperature

raised by about 100°C above the normal temperature. This is also the experience of other workers who have worked with thermally stable polymers.[44-45]

Thermal Stability

Primary thermogram curves for the polyamides are shown in Figure 15 and Figure 16. The experiments were conducted in air, i.e. under the conditions in which polyamides are normally used, at a heating rate of 10°C / min. Temperature characteristics such as initial decomposition temperature (T_0) and temperature for 10 % weight loss (T_{10}) were calculated and are given in Table V.

All the polymers are characterised by the same shape of TGA curves, except that TGA curves for PBDA based polymers (polyamides E and H) begin to breakdown at much lower temperatures than other polyamides and this was assignable to rapid loss of $C_{15}H_{31}$ unit of side chain. Further analysis indicated that the thermal stability of polyamides (D and E) based on TPC was higher than that of corresponding polyamides (G and H) obtained from IPC. It is reasonable to have para-linked polyamides (derived from TPC) thermally more stable than meta-linked (IPC based) polyamides. Again it was observed that although T_0 values for polymers D and G, decrease by introduction of methyl group substituent in

Table V : Thermal Properties of Aromatic Polyamides^a

Sr.No.	Polymer	T ₀ ^{o C} ^b	T ₁₀ ^{o C} ^b
1.	A	306	433
2.	B	386	444
3.	D	334	474
4.	E	284	317
5.	F	379	474
6.	G	305	458
7.	H	246	315

a. by TGA at heating rate of 10^o C/min in air.

b. T₀ = Initial decomposition temperature.

T₁₀ = 10 % weight loss temperature.

MBDA as compared to unsubstituted polyamides, the T_{10} values for polyamides are more or less the same indicating that once initial loss of methyl-group has taken place the main backbone is as much stable as BDA/ODA based polyamides. Adduci [46] also has shown that methyl substitution in sulfone ether diamine generally increased initial weight loss of polysulfone etheramides. Polyamides studied in the present investigation began to decompose around 250-380°C in air, with 10 % weight loss being recorded at 315-440°C on the TG curves. At this temperature the aromatic diamine component of the polymer backbone is mostly unaffected, but thermal decomposition and the chain scission of methyl / alkylene linkage in the aliphatic substituent may be occurring. Similar results were obtained by Imai and coworkers for aromatic-aliphatic polyamides prepared from ODA and aliphatic dibasic acids. [47]

The thermal stability of investigated polyamides, except polymers E and H based on PBDA is typical of the aromatic polyamide class, namely the onset of decomposition in air was in the 350°C range. The lower values of T_0 and T_{10} for polyamides E and H indicate that the thermal stability of aromatic polyamide decreased due to pentadecyl groups in the diamine component.



Further these polyamides obtained from PBDA were less thermostable than the polyimides from PBDA and dianhydride reported earlier.[32]

DSC :

Differential scanning calorimetry on powder polymer sample showed weak but reproducible endotherms around 99°C and 177°C for polyamide E derived from PBDA and TPC (Figure 16).

From the data presented following generalised conclusions can be reached regarding the relative stability of various linking groups as well as the effect of such structural modifications as pendant groups.

1. For polymers containing phenylene groups, the following correlation between orientation and stability appears to prevail : $p > m$.
2. The introduction of heteroelements or groups such as O,S,-CONH-into the backbone or aromatic or heterocyclic polymers has a slight adverse effect as short term stability as measured by TGA.
3. The introduction of alkylene groups into the backbone or side chain decreases both thermal and oxidative stability. As the length of the alkylene chain increases, stability generally decreases.,and

4. CNSL, an indigenously available agricultural byproduct, can be utilised to synthesise thermally stable aromatic polyamides having good solubility in some organic solvents.