

CHAPTER III

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

3.0 PRESENT INVESTIGATION, RESULTS AND DISCUSSION

Aromatic polyimides exhibit high thermal stability and generally they are made by condensation of diamine and dianhydride; (Scheme 1) whereas polyesters are derived from diacid and diol (scheme 2). The principle drawback of these polyimides is the fact that they have an off gas, water, upon curing. This byproduct causes voids in finished products unless removed during final cure. Hence alternatively unsaturated and groups (maleimides) and soluble oligomerc which can be cured by addition type were developed. Using preformed imide structured monomers is also attractive choice and various Poly(esterimide)s were reported. We thought it will be interesting to have increased flexibility by incorporating suitable alkyl groups as substituents to main chain of poly(ester-imide)s where in processibility and thermal stability is combined together. Therefore we have investigated synthesis of imide structure containing bisphenols and used them to obtain novel and new aromatic poly(ester-imides) using 3-pentadecyl phenol as starting material.

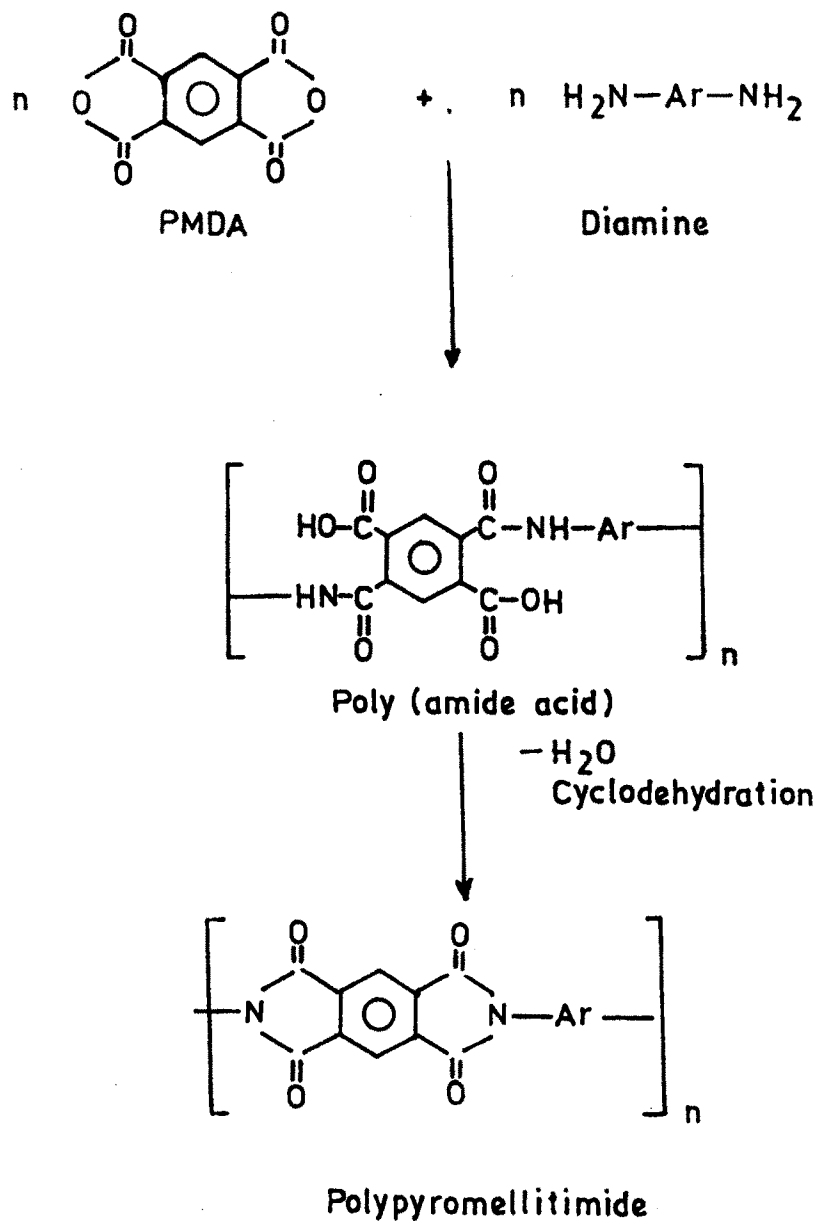
3.1 3-Pentadecenyl Phenol (Cardanol or Anacardol)

When commercial cashewnutshell liquid was distilled under reduced pressure, 3-pentadecadienyl phenol (anacardol) was obtained as a pale yellowish liquid.

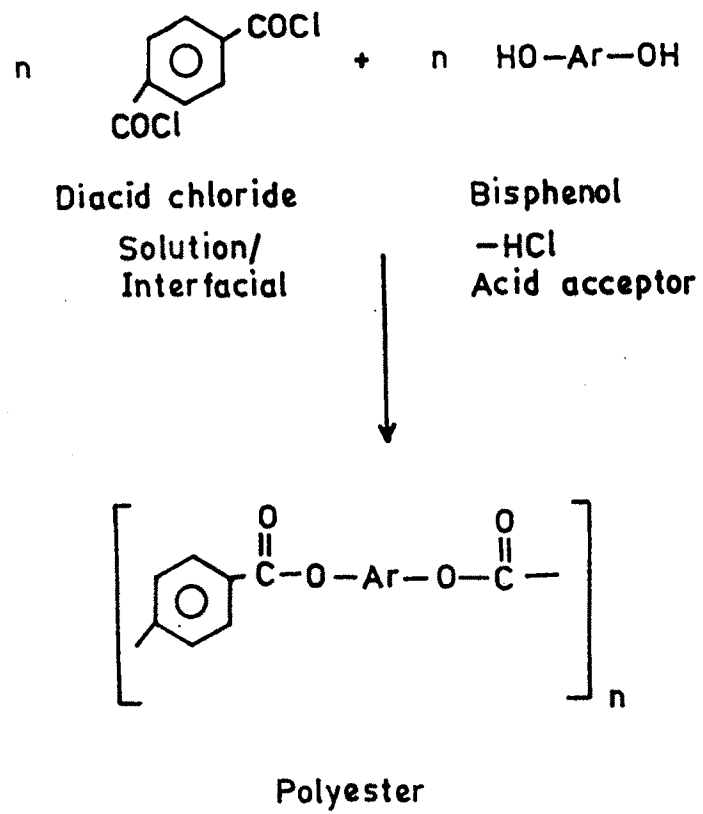
Yield : 50% , b.p. 195-200°C/2 mm.

3.2 3-Pentadecylphenol (Tetrahydroanacardol)

(1) Anacardol when catalytically reduced over Raney nickel catalyst at 600 psi. hydrogen pressure at 70°C. in a parr



SCHEME 1 : SYNTHESIS OF POLYIMIDE.



SCHEME 2 :SYNTHESIS OF POLYESTER.

autoclave gave 3-pentadecylphenol (tetrahydroanacardol). The crude product after crystallisation from pet other (40-60°) gave a white waxy product. Yield 90%, m.p. 50-51°C.

(ii) Hydrogenation of anacardol was also carried out, using Raney nickel catalyst in a Parr medium pressure reactor. At higher temperature (150°C and 150 psi. hydrogen pressure) period of hydrogenation could be reduced to 4 hours, but required precise control of temperature. At temperatures higher than 160°C. control of process to obtain 3-pentadecylphenol without the contamination by the nucleus hydrogenated product may be difficult, since the time of hydrogenation would be too short.

Distillation of crude material under reduced pressure gave white solid product. Yield 85-90% m.p. 51°C.

3.3 4-Nitro-3-pentadecyl Phenol

3-Pentadecylphenol was nitrated with fuming nitric acid (sp.gr. 1.5) below 10°C, in chloroform, when mixed mononitro isomers of 4-nitro-3-pentadecylphenol and 6-nitro-3-pentadecyl phenol were obtained. 4-Nitro isomer was separated from the 6-nitro isomer by selective solubility of the latter in petroleum ether (60-80°) at freezing temperature. Crude 4-nitro-3-pentadecyl phenol was recrystallised from pet. ether (60-80°). Yield 35%, m.p. 70-71°C.

6-Nitro-3-pentadecyl phenol can be obtained from filtrate after removing the solvent and crystallisation from ethyl alcohol. Yield 22% , m.p. 39°C.

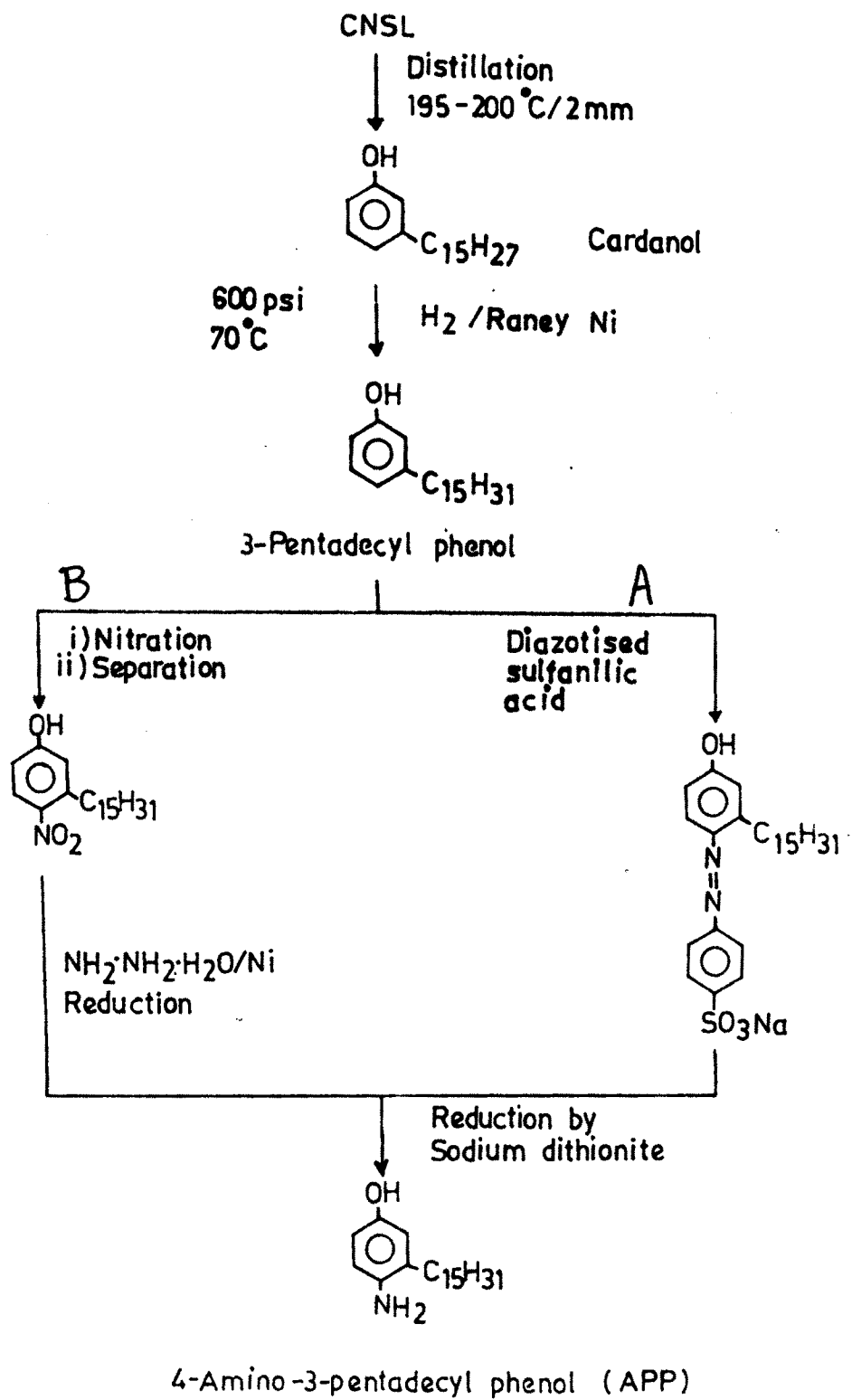
3.4 4-Amino-3-Pentadecyl phenol

1) 4-nitro-3-pentadecyl phenol was reduced to the corresponding aminophenol by using Raney nickel catalyst and hydrazinehydrate. Crude 4-amino-3-pentadecyl phenol was crystallised from pet. ether (100-120°) or ethyl alcohol. Yield 62.5%, m.p. 105-106°C.

2) 4-Amino-3-Pentadecyl phenol via diazonium salt

A suspended solution of diazotised sulphanilic acid dihydrate in ethyl alcohol was slowly added to the alcoholic solution of sodium salt of 3-pentadecyl phenol cooled at 0°C, where upon coupling of the diazotised sulphanilic acid with 3-pentadecyl phenol took place resulting in the formation of a red azo dye solution. The red-dye solution was further reduced with a saturated sodium dithionite solution at about 75°C. when the red colour was changed to pale tan colour. This solution was cooled to 0°C. when crude 4-amino-3-pentadecyl phenol was obtained, which was crystallised from ethyl alcohol. Yield 75%, m.p. 105-106°C.

4-Amino-3-pentadecylphenol can be obtained by two different routes (scheme 3). In the present study 4-amino-3-pentadecylphenol was obtained following route 'A', as it gave better yields (75% based on 3-pentadecylphenol). This route is selective to give only 4-amino-3-pentadecyl phenol on reduction of diazo intermediate which could be used directly without isolation whereas, route 'B' requires isomer separation of the 6-and- 4-nitro derivatives of 3-pentadecylphenol and gave lower yields (24%).



SCHEME. 3 : Preparation of 4-amino-3-pentadecyl phenol.

IR spectrum of 4-amino-3-pentadecyl phenol (Fig.1) showed absorption bands of primary aromatic amine at 3200 and 3300 cm^{-1} . Mass spectrum showed molecular ion peak (M^+) = 319.

3.5 Imide Containing bisphenol

The bisphenol monomer that contained preformed imide linkages; imide group containing bisphenol; N, N'-bis(4-hydroxy-2 pentadecylphenol) pyromellitimide (II) was prepared by the reaction of APP with pyromellitic acid dianhydride (PMDA) in 82% yields as detailed in experimental section. The reactions are depicted in scheme 4.

The monomer (II) has two imide rings and two reactive bisphenol moieties, with pendant pentadecyl groups, hence (II) can act as typical bisphenol. Therefore (II) has been used in the preparation of new poly (ester-imide)s by reaction with aromatic diacidchlorides.

The reaction of aminophenols with dianhydride has been reported (26-28) by simply refluxing in N.N. dimethyl formamide; and Dine Hart et al have studied some properties of substituted N.N - diphenylpyromellitimides (29). In the present investigation reaction of APP and PMDA has been performed in m-cresol for the reasons explained below.

The synthesis of (II) proceeds in two steps; the first step was the formation of the amic-acid species from the reaction between the aromatic amine group and the anhydride group; the

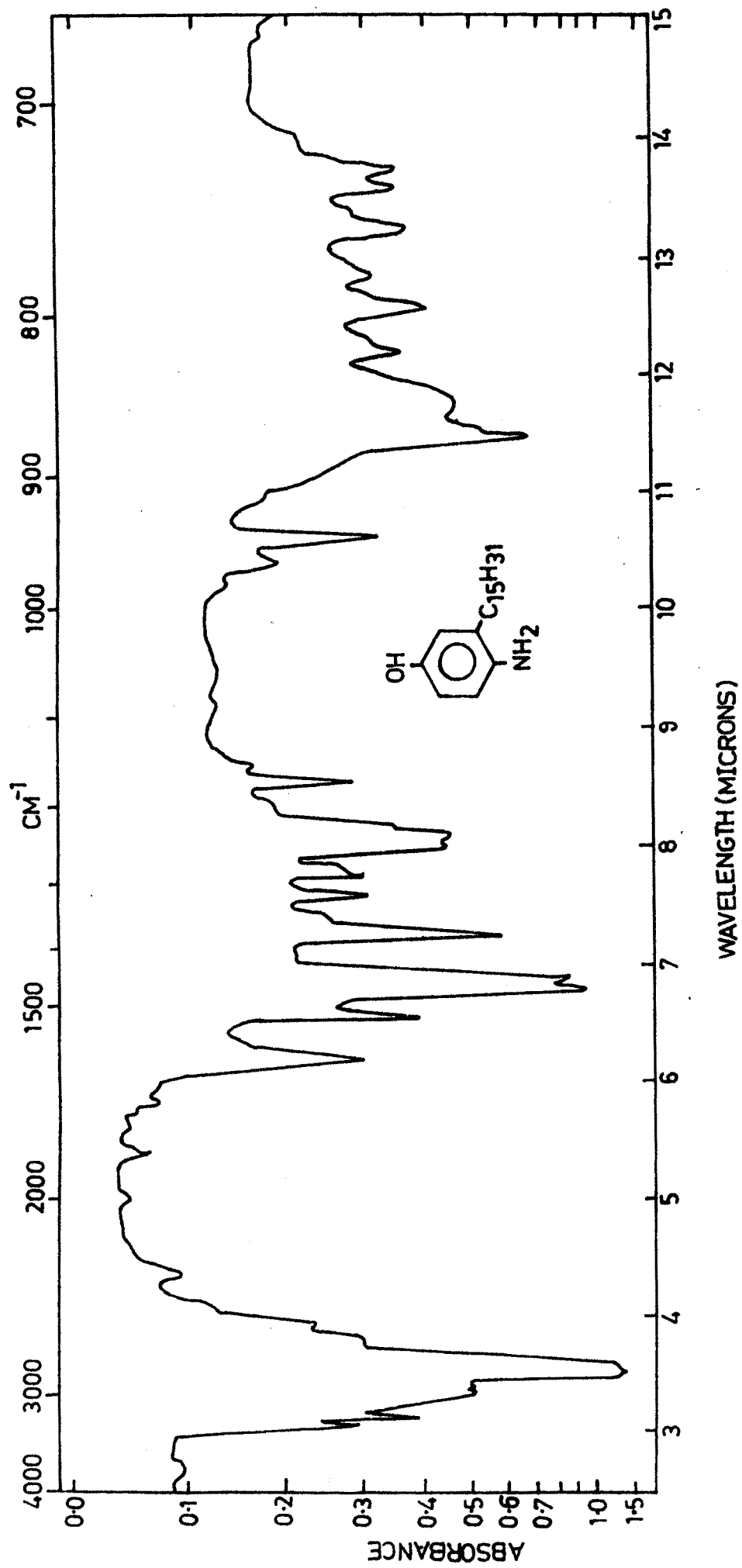
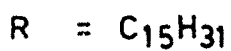
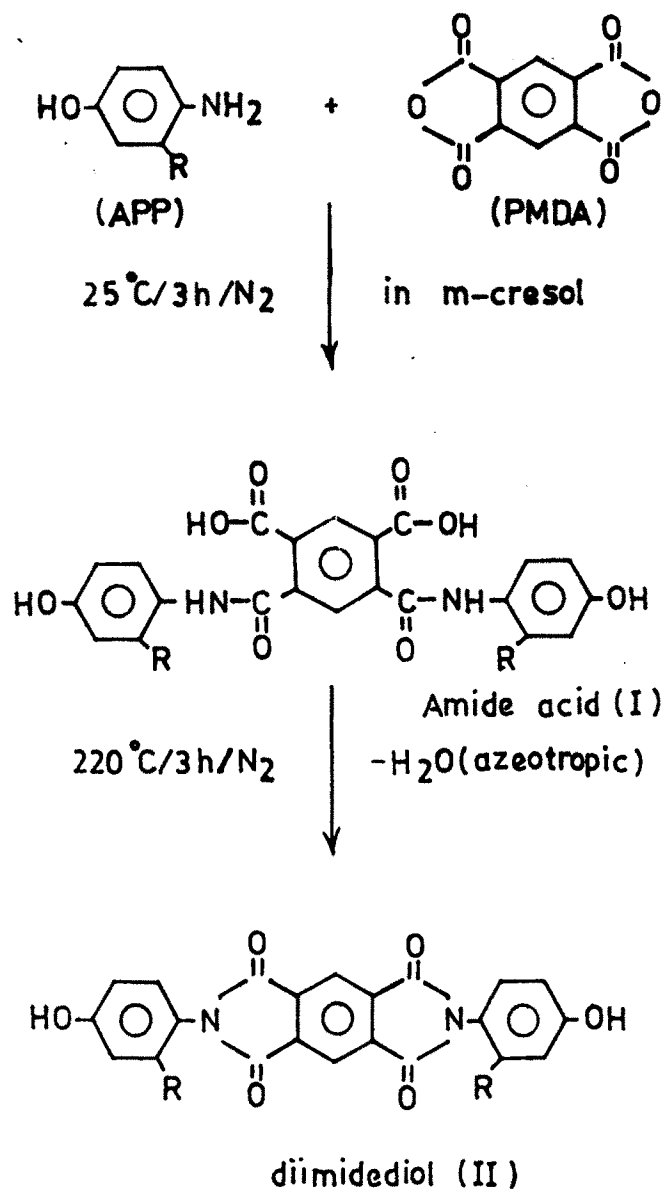


FIG. 1 : IR SPECTRUM OF 4-AMINO-3-PENTADECYL PHENOL



SCHEME 4. : Synthesis of N,N'-Bis(4-hydroxy-2-pentadecyl phenyl) pyromellitic diimide.

second step was the formation of the imide linkage by the cyclisation of the amic-acid linkage with the subsequent release of water.

The first step of the reaction proceeded in m-cresol at room temperature under a nitrogen atmosphere for 3 hours. The complete formation of the amic-acid species is carefully performed as it is very sensitive to the presence of water, which can hydrolyse the amic-acid linkage back to diacid and an amine. Water can also react with the dianhydride and hydrolyse it to the diacid species thus lowering its reactivity towards the aromatic amine at room temperature. Because of this sensitivity to water, precautions were taken to keep a dry nitrogen at all times.

Both starting materials and the amic acid form (1) are completely soluble in m-cresol. Once the amic-acid species was formed the temperature of the reaction was raised to 220°C and the nitrogen purge rate was increased. m-Cresol was solvent of choice for such reactions.

Reaction of PMDA and aminophenol was not performed in glacial acetic acid, as amic-acid precipitated out of reaction mixture and remain largely uncyclised even after several hours of heating in refluxing acetic acid. Cyclisation in dry solid state at 200°C. produced impure imide on slow conversion of amic-acid into imide. Similarly the use of DMF and DMAC for the preparation of pure imide was discontinued, because previous work had shown that direct reaction of these solvents with PMDA

was possible. Pyridine was not sufficiently good solvent for many of the compounds and DMSO was both objectional to use and unstable above 150°C. NMP have problems of high solubility of imide and the consequent difficulty of crystallisation.

The corresponding diimidebisphenol prepared from 4-aminophenol and PMDA(29) was pale yellow platelets and melted with decomposition at 495-500°C.

3.6 Characterisation of imidebisphenol (II)

The structure of (II) was identified by IR, NMR and elemental analysis. IR spectra of the (II) (fig.2) showed characteristic absorption bands at 1772, 1720 (Imide I) 1384 (Imide II), 1122 (Imide III), 719 cm^{-1} (Imide IV) of imide structure. Imide I band is attributed to the stretching vibrations of two carbonyl that are weakly coupled. Imide-II, III and IV bands have been assigned to axial, transverse and out of plane vibration of cyclic imide structure. The absence of bands at 1670-1650 (amide I), 1530-1520 (amide II), 1410, 1312 and 885 cm^{-1} in the amide spectra showed the complete transformation of (I) into (II). The bands observed at the 1616, 1582 and 1500 cm^{-1} are pronounced for aromatic moiety, where as phenolic hydroxy group appeared as broad absorption at 3560 to 3222 cm^{-1} .

The H-1-NMR spectral values of the (II) (fig.3) supported the structures proposed. Aromatic protons in the range of 6.5 to 8.2 are differentiated as those of PMDA moiety at 8.2 because of it's singlet (2H) and chemical shift. As the PMDA ring is subjected to the cumulative -I and -R influences of four

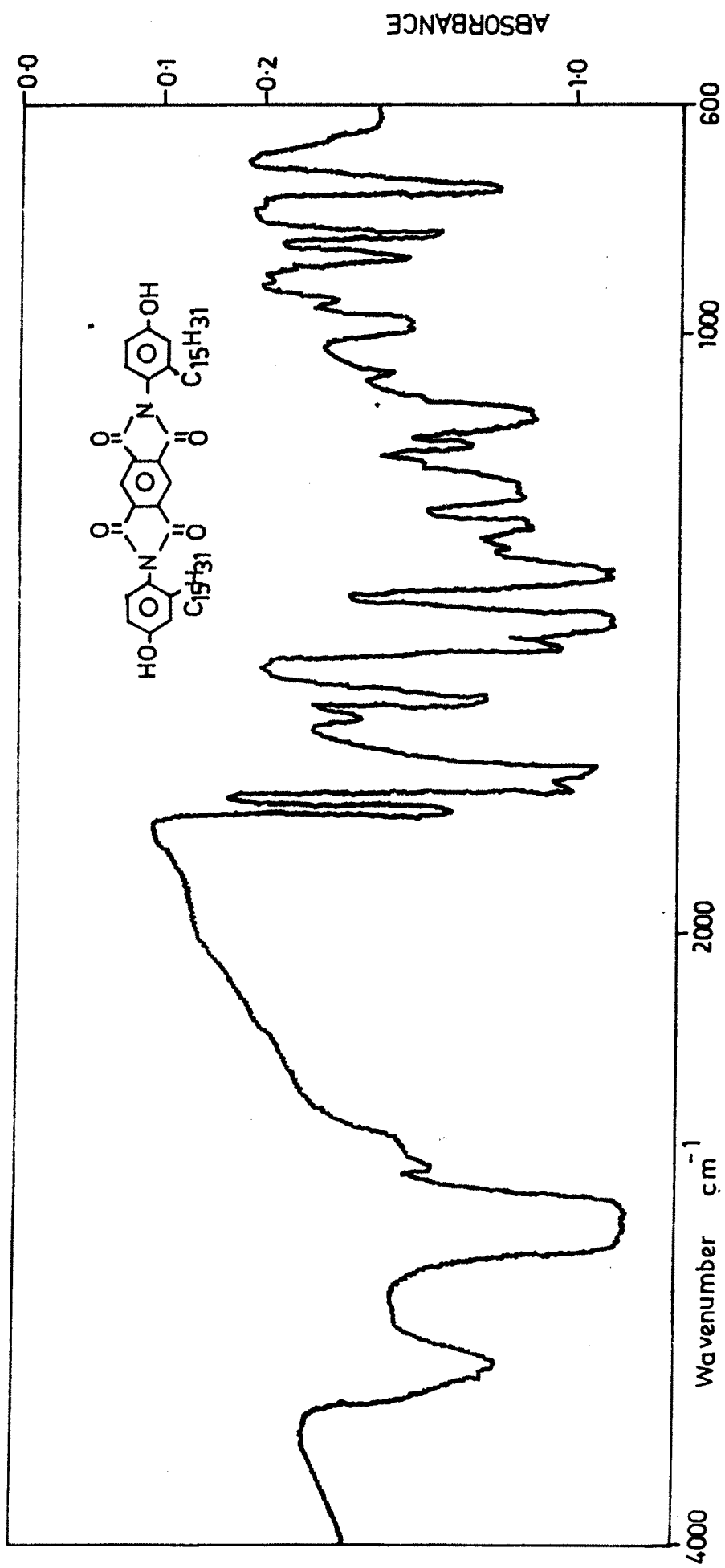


Fig. 2 :IR spectrum of (II).

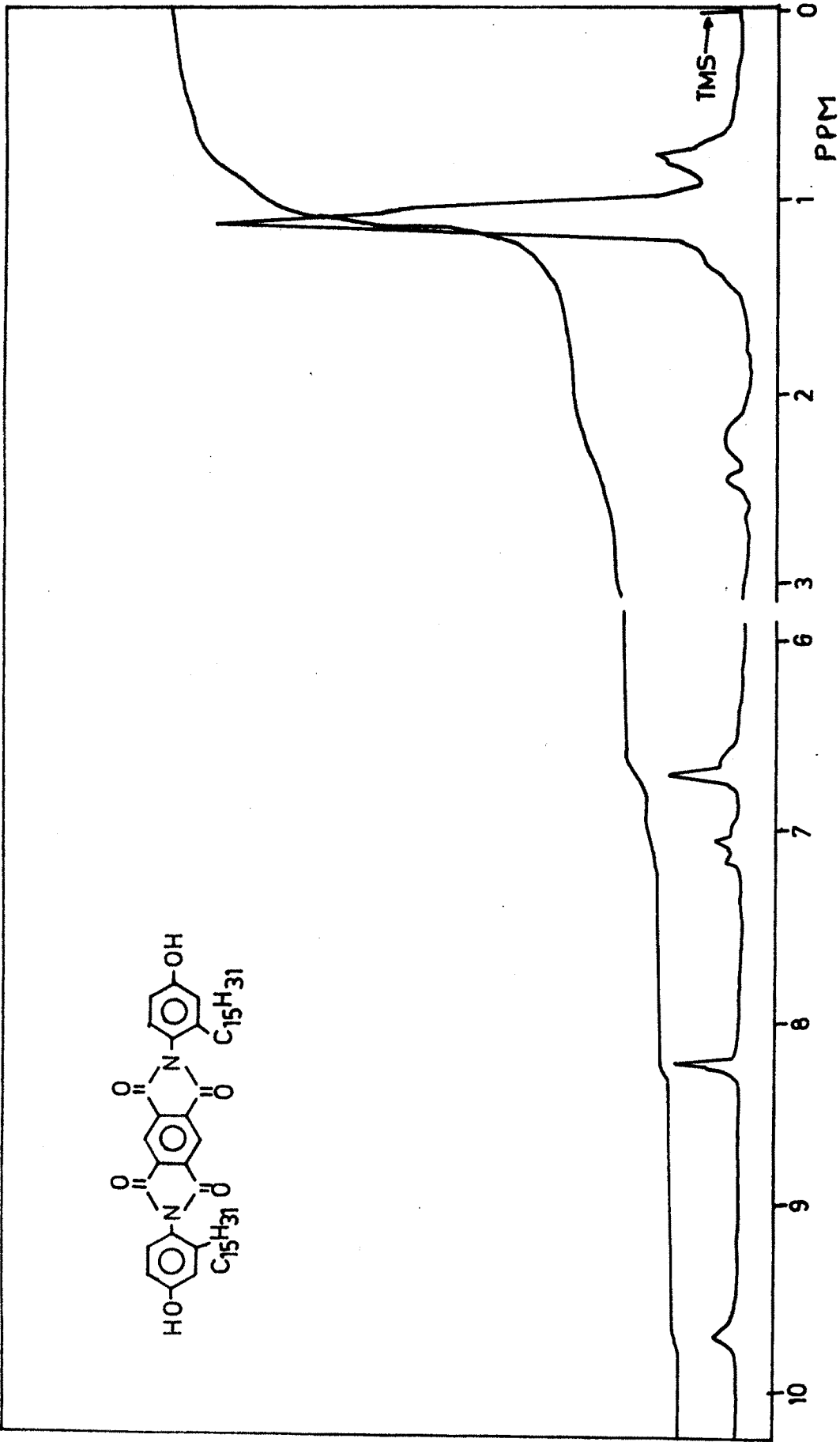
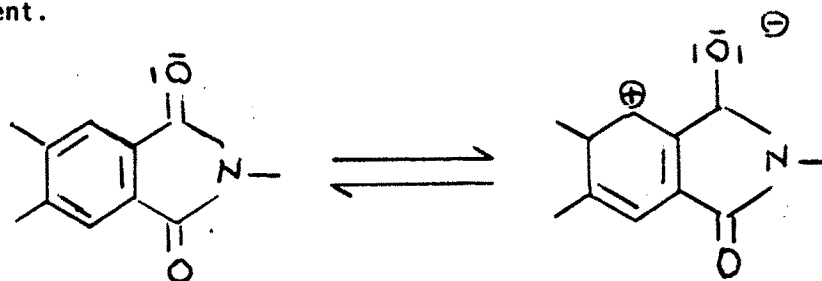


Fig. 3: ^1H NMR spectrum of (II).

carbonyl groups it is consequently considered to become electron deficient.



The signal at 6.5 to 7.2 δ are assignable to protons of penta-decyl substituted aromatic ring.

Aliphatic protons of $C_{15}H_{31}$ substituen showed signals at 0.8 to 2.2 δ of which the signal (triplet) at 0.8 δ is due to CH_3 protons and signal at 2.2 δ is due to benzylic protons. Other $(CH_2)_{13}$ protons appear as broad singlet because of overlapping. The broad hump signal at 9.7 δ is assigned to hydroxyl group para to imide structures and hence down field considerably. Integration agrees well with the estimated intensity.

The structure of (II) was also confirmed by ^{13}C NMR spectroscopic studies. Fig.4 shows ^{13}C spectrum of (II) obtained by the fourier -transform - NMR (FT-NMR) which is further improved by decoupling the protons from ^{13}C . Since C-C and C-H scalar interactions are not detected, every magnetic site is, represented by an individual signal. Thus the spectrum simplified under the conditions of complete proton decoupling showed nine signals for aromatic and carbonyl carbons in 114-167 ppm region, where as aliphatic carbons due to pentadecyl substituent appear in 14-32 ppm region. Only one ^{13}C NMR signal for C=O, indicated that all

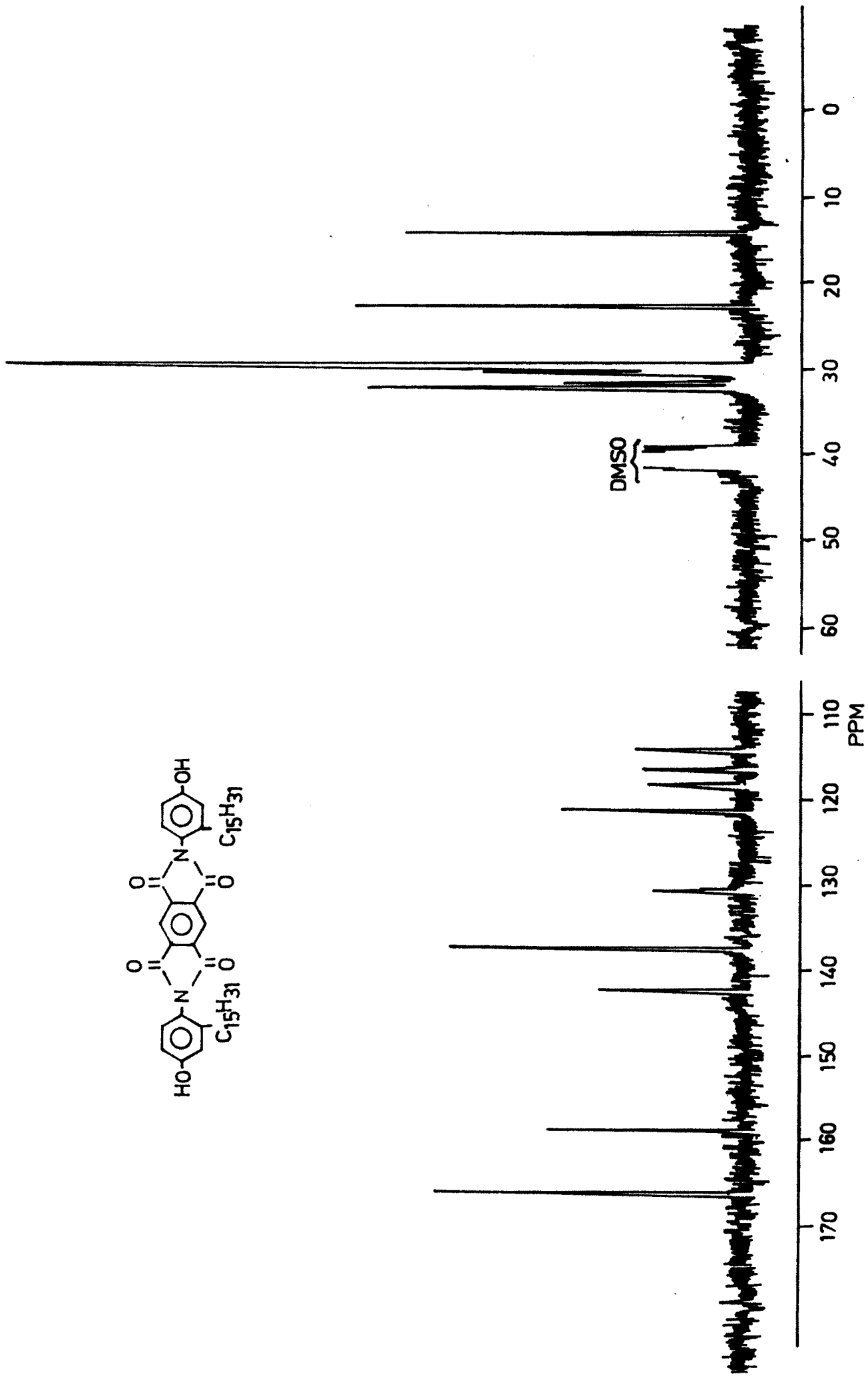
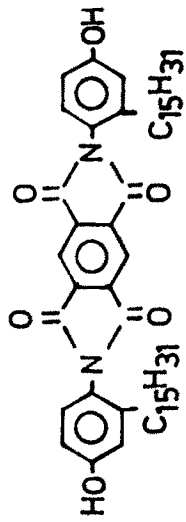
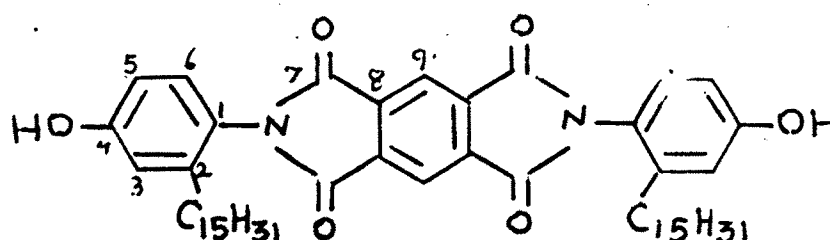


Fig. 4 : ^{13}C NMR spectrum of (II) (full spectrum 1H -decoupled).

carbonyls are equivalent and they are imide C=O only i.e. carbonyl due to -CONH and -COOH groups are absent suggesting complete imidisation of intermediate yielding pure diimide bisphenol as represented by structure (II). Relatively large chemical shift of ^{13}C -NMR (200 ppm) compared to ^1H -NMR has made ^{13}C -NMR a powerful technique in an elucidation of the structure.



Because of the lack of multiplicity in the conventional decoupled ^{13}C spectrum (fig.4), it is not an easy matter to identify which carbon signals are which, Although ^{13}C signals and ^1H signals are approximately equally affected in their chemical shifts by their surrounding, it is very useful in assigning ^{13}C spectrum to be able to say with more certainty than simply a chemical shift argument that a particular ^{13}C signal comes from the carbon atom that carries an identifiable proton. Several multi-phase experiments make this possible.

The first thing is to know whether the carbon atom in question is a quaternary, methine, methylene or methyl carbon. This can be done using off resonance decoupling where in incomplete collapse of the multiplicity occurs, and singlets, doublets, triplets and quartets are observed for above mentioned carbons

respectively. More elaborate procedures allow the separate plotting of subspectra respectively from CH_3 , CH_2 and CH carbons. These are used in preference to off-resonance decoupling. Fig.5 shows DEPT- ^{13}C NMR spectrum of (II).

In this technique (DEPT - Distortionless Enhancement by polarisation Transfer) three successive ^{13}C spectra, one containing only the methines, one only the methylenes and one only the methyls are recorded. Correlation of DEPT- ^{13}C -NMR (fig. 5) with conventional decoupled - ^{13}C full spectrum (fig. 4) enabled to identify the individual signals. In DEPT- spectrum in the region of low field (114-167) ppm, only four methine (CH) signals remain (130.74, 118.30, 116.42 and 114.10 ppm) which are assigned to C9, C5, C3 and C6. The five remaining carbon signals are (166.31, 142.26, 137.45(2) and 121.26 ppm) due to quaternary carbons assigned to C7 ($\text{C}=\text{O}$), C4, C1 and C8 and C2.

The carbon signals in high field region are obviously due to aliphatic pentadecyl substituent of which CH_3 is distinct in DEPT- spectrum (14.13 ppm), where as benzylic CH_2 appeared at 31.84 ppm. Signals at 31.34, 30.16, 29.60, 29.28, 22.59 are due to (CH_2)₁₃.

The mass spectrum of (II) showed the expected parent peak at m/e of 820 as pyromellitimide exhibit molecular ions (30). Satisfactory microanalysis were obtained for the purified (II).

When reaction of APP with PMDA was performed in P-cresol and toluene, the yields of (II) were low; whereas for syntheses,

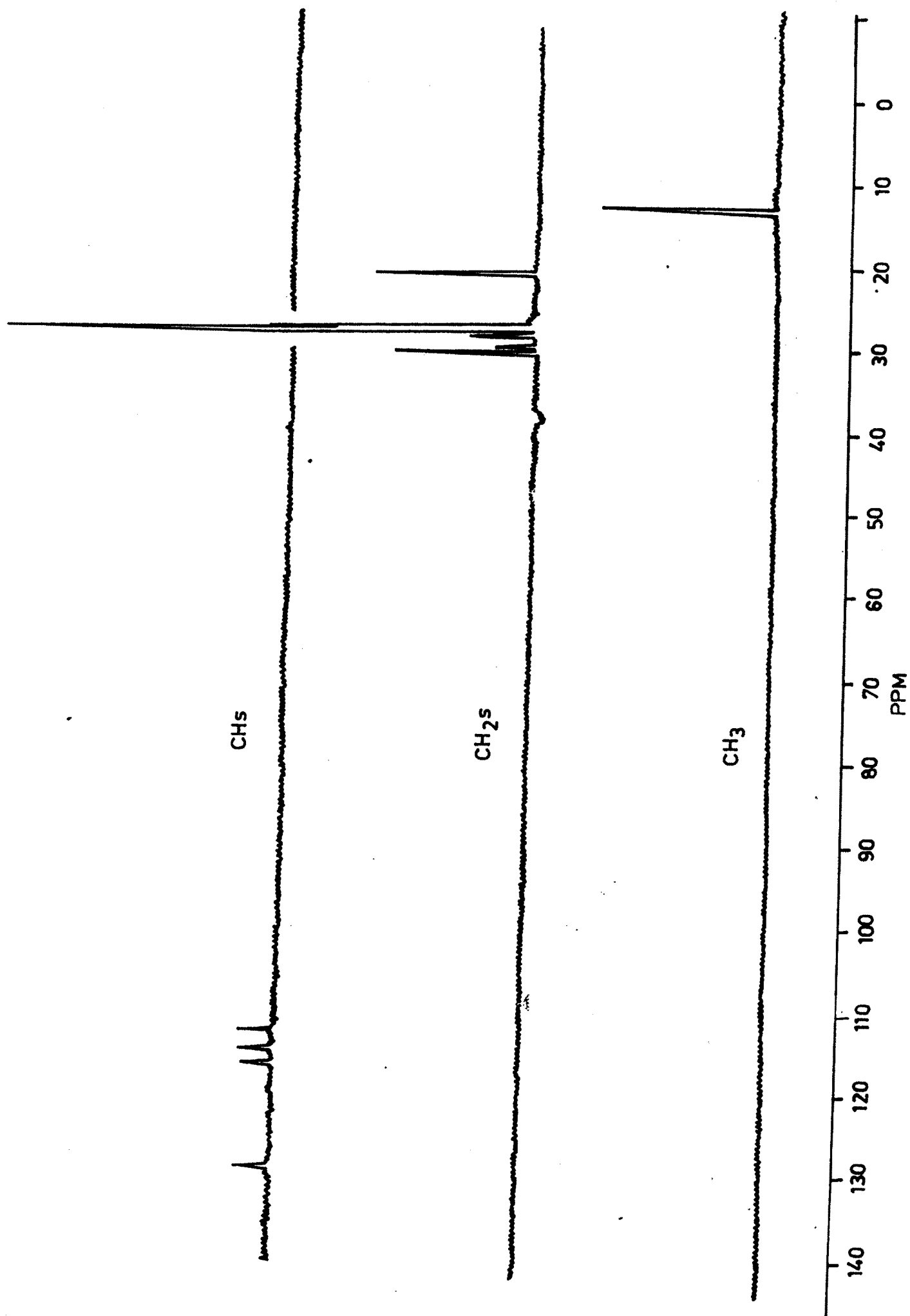


Fig. 5 : ^{13}C -NMR spectrum (DEPT) of II.

carried out in NMP and subsequent cyclisation of amide acid either by thermal or chemical treatment produced partially imidised (II). The IR spectra (Fig. 6) of amide acid intermediate (I) showed broad absorption at 3640 and 3220 cm^{-1} absorption bands indicate the amide structure. Chemical treatment of I with acetic anhydride-pyridine at room temperature for twelve hours resulted in cyclisation of (I) into (II): the IR spectrum of whose is shown in fig. 7; indicated forming imide structure (1780, 1760, 1730, 1384, 1122, 720 cm^{-1}), however there are absorption bands at 1650 and 1520 cm^{-1} also, suggesting partial imidisation. Thermal cyclisation of (I) at 120 $^{\circ}$ C/mm for 3 hours gave product whose IR spectrum (Fig. 8) showed almost complete disappearance of amide absorption band (1680, 1650 and 880 cm^{-1}) and presence of strong bands at 1780, 1730, and 1710 cm^{-1} due to imide formation. The absorptions at 3640 and 3220 cm^{-1} in IR spectrum of I (fig. 6) also shifted to 3540 and 3280 cm^{-1} .

Therefore one pot synthesis of (II) in m-cresol was preferred.

3.7 Acid Chloride Synthesis

Isophthaloyl chloride and terephthaloyl chloride were prepared from the corresponding diacids, by reacting the diacids with thionyl chloride in the presence of pyridine as a catalyst as shown below. Both these acid chlorides were purified by vacuum distillation and recrystallisation from dry n-hexane. The yield and physical constant values of IPC and TPC were good.

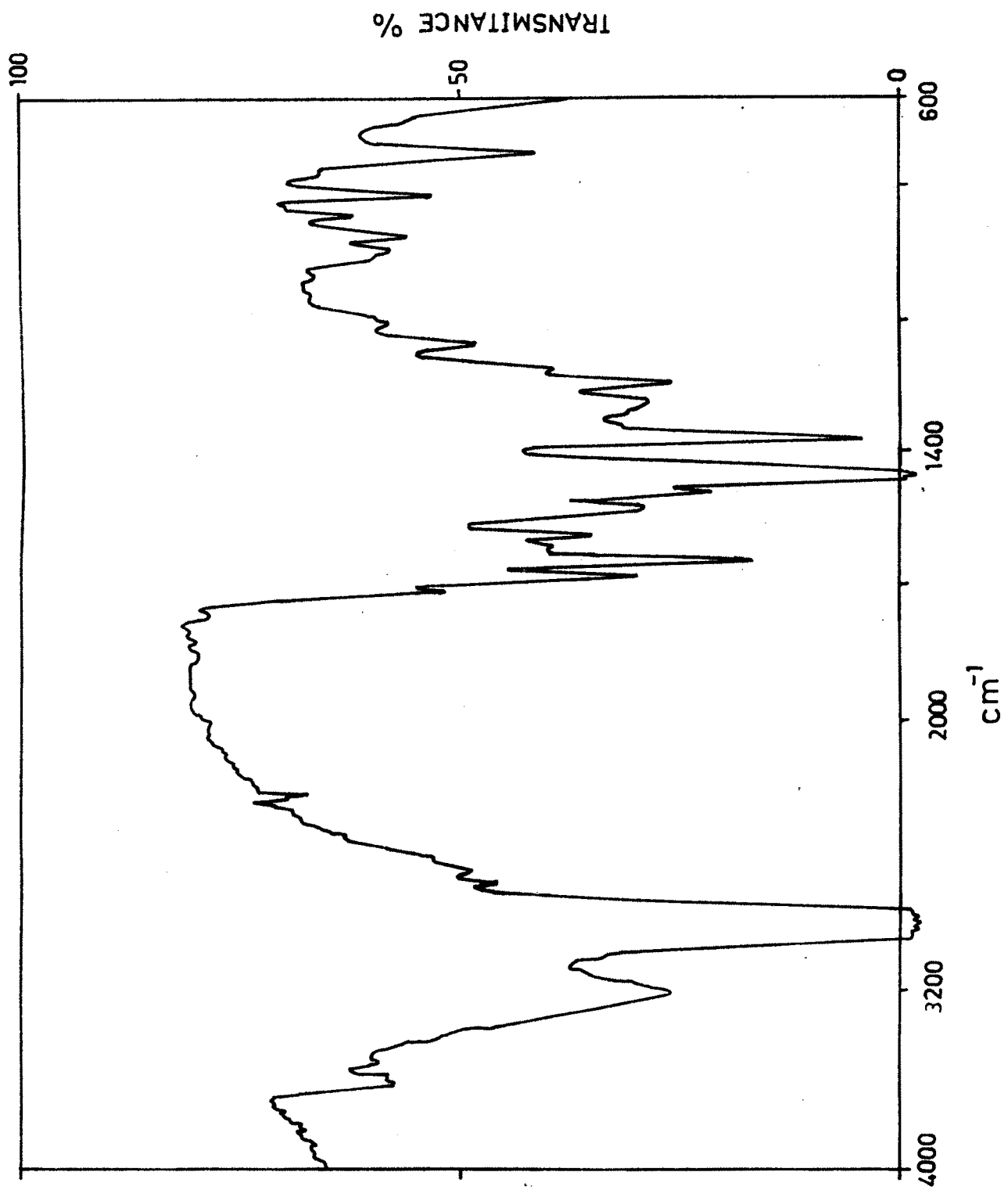


Fig. 6 :IR spectrum of poly (amide acid) I.

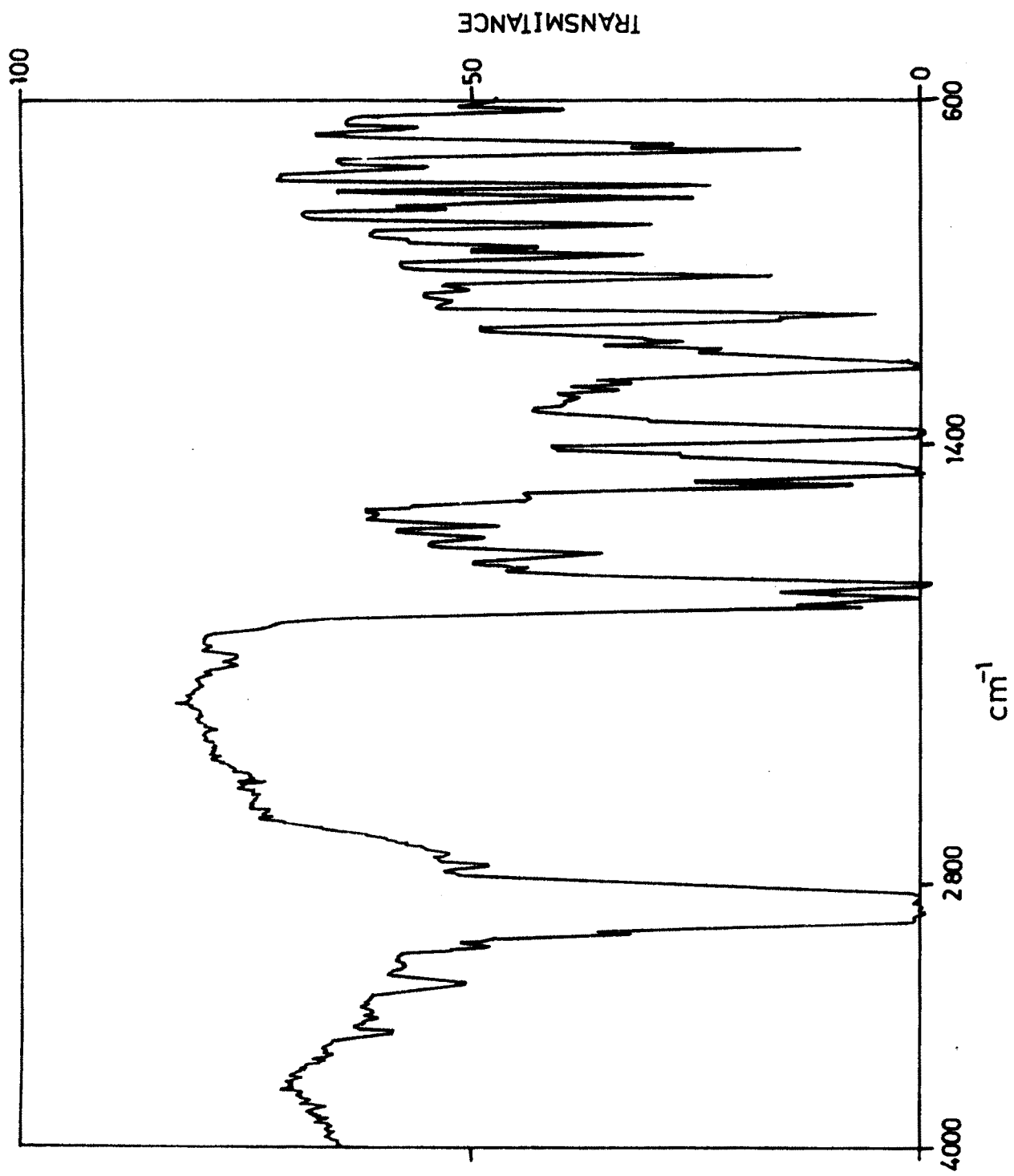


Fig 7 : IR spectrum of partially imidised amide acid (Chemical method).

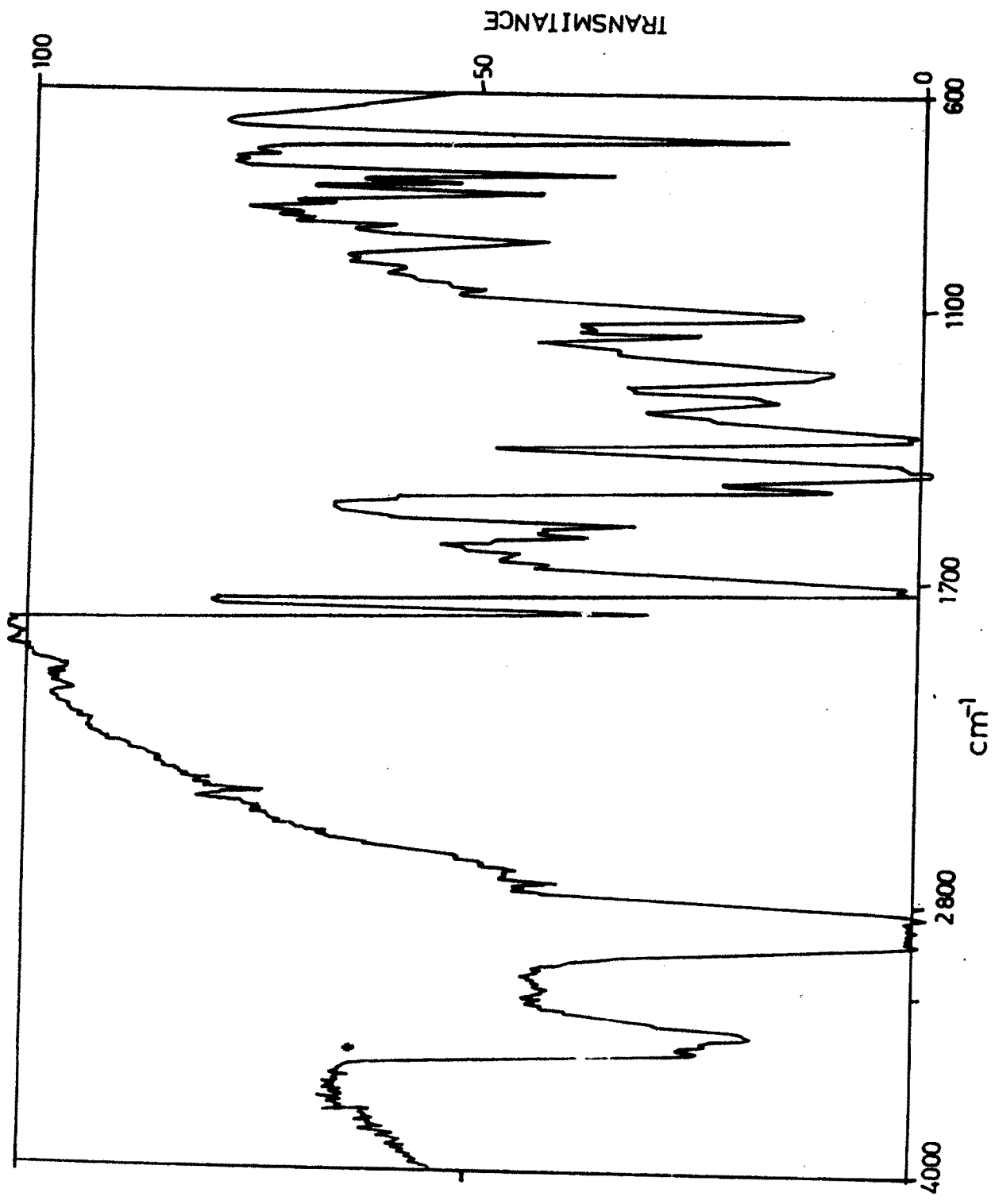
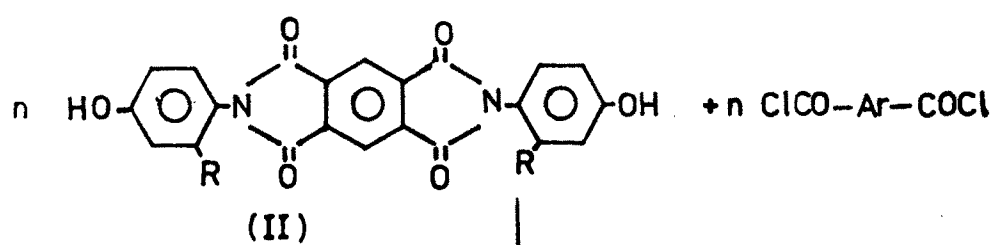
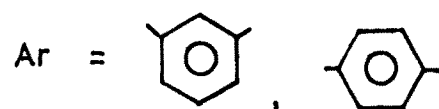
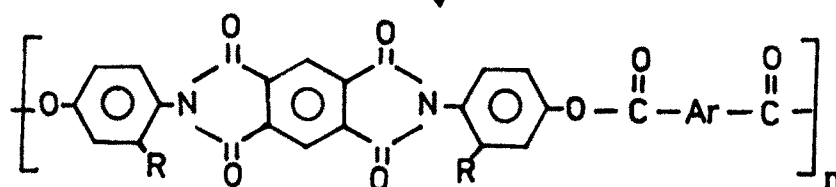


Fig 8 : IR spectrum of partially imidised amide acid (Thermal treatment).



NMP-LiCl/Pyridine
25 °C, 1hr and 90 °C, 6hr



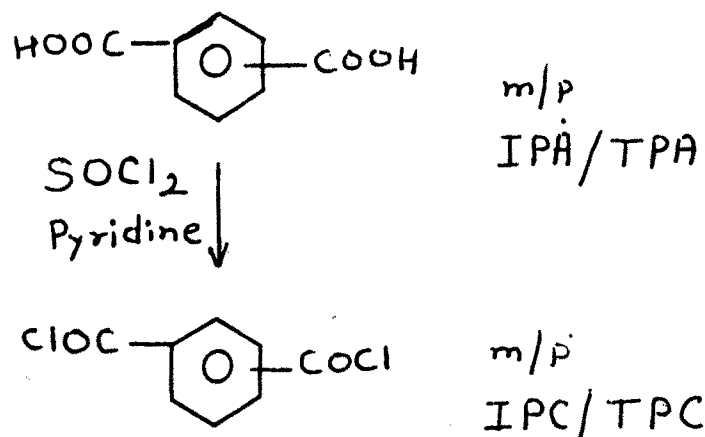
SCHEME. 5 : SYNTHESIS OF POLY (ESTER IMIDE)S.

TABLE I
 Synthesis of Poly (Ester-imide)s from (II)

Polymer	Diacid chloride (mole %)		Yield %	(η) inh. (dL/g)
	TPC	IPC		
A	100	--	84.2	0.101
B	50	50	77.9	0.132
C	-	100	80.0	0.127

a) Polymerisation was carried out with 1 m mol of each monomer in 4ml of NMP containing 6% LiCl at 25° C for 1/2 hr; and at 80° C for 6 hrs.

b) Measured at a concentration of 0.5 dL/g in NMP at 30°C



3.8 Poly(ester-imide)s : Aromatic poly(ester-imide)s were synthesised by the polycondensation of (II) with IPC and TPC (Scheme 5). It is anticipated that the long pentadecyl substituent would impart flexibility to resulting polymers due to plasticizing effect of C₁₅ alkyl chain. It is also expected that due to bulky substituent disruption of regular structure would result into amorphous nature for these poly(ester-imide)s. Polymerisation was carried by the conventional solution polymerisation in NMP-Pyridine, and a fair amounts of poly (ester-imide)s (78-84%) were obtained for IPC, TPC and (IPC + TPC) copolymers.

3.9 Characterisation of Poly(ester-imide)s

The physical property data of these poly(ester-imide)s is given in Table I. The inherent viscosity of polymers ranged from 0.10 to 0.13 dL/g in NMP. It is observed that the poly(ester-imide)s synthesised from II and IPC/TPC did not reach high molecular weight as indicated by their lower inherent viscosity

and their inability to form films. This could possibly be due to the low nucleophilicity of hydroxyl groups in (II) and steric effects of bulky pentadecyl group.

Morechal studied monomeric diamine/diacid/diimide dyes usable for polycondensation and found that when 3,4,9,10 perylene tetracarboxylic anhydride was treated with P-phenylenediamine to give diamine dye which when polycondensed with terephthaloyl chloride gave a low molecular weight product³¹ because of steric factors.

The IR spectra of the poly(ester-imide)s (fig. 9) showed characteristic bands at 1780 cm^{-1} and 1720 cm^{-1} (imide-I), 1370 cm^{-1} (imide II), 1120 cm^{-1} (imide III), 720 cm^{-1} (imide IV) and $1716\text{-}1726\text{ cm}^{-1}$ (ester-carbonyl).

Thus additional absorptions in IR spectra of poly(ester-imide)s due to ester linkage were observed. Two characteristic absorptions arising from the C=O and C-O groups; due to ester are possible. Ester carbonyl bands are intense, twice as strong as ketone carbonyl. The strong IR absorption band at 1717 cm^{-1} in the IR spectrum of poly(ester-imide)s indicate the presence of ester group in addition of imide structure. (imide C=O at 1776 cm^{-1}).

The C-O stretching mode gives rise to strong absorption in the region $1300\text{-}1000\text{ cm}^{-1}$. Particularly for benzoates (α , β - & other unsaturated ester) the strong bands in the approximate regions, $1310\text{-}1250$ and $1150\text{-}1100\text{ cm}^{-1}$ are often found, which are helpful in identifying these groups. The IR spectrum of poly(ester-imide)s showed absorption bands at 1245 and 1111 cm^{-1} .

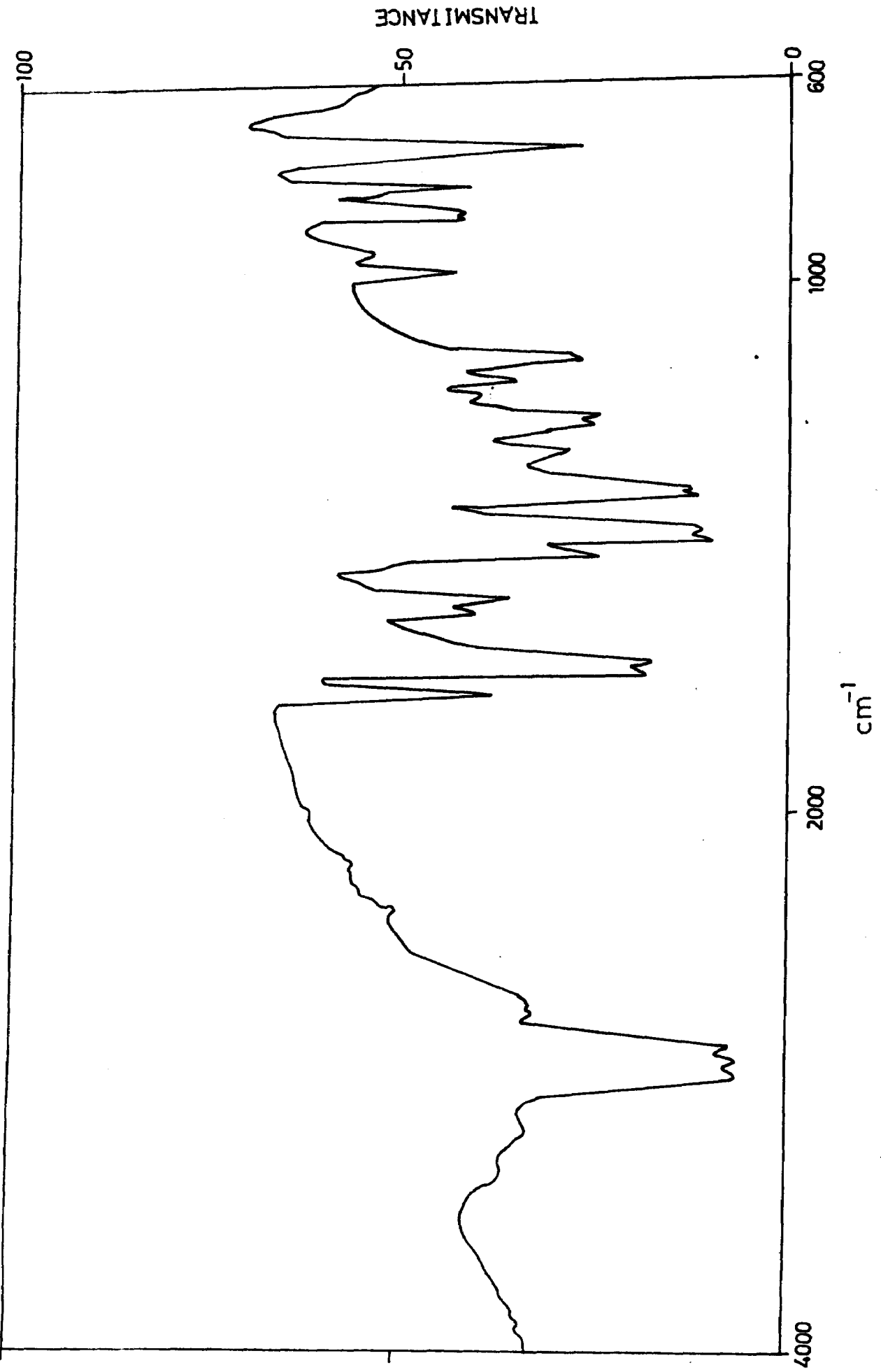


Fig. 9 : IR spectrum of poly (ester-imide) C, [II + IPC].

No detectable hydroxy absorption bands at $3500-3200\text{ cm}^{-1}$ was observed.

3.10 Solubility of Poly(ester-imide)s

Solubility of the poly(ester-imide)s was determined for powdery sample in excess solvent.

All the poly(ester-imides) were soluble in polar aprotic organic solvents such as N-methylpyrrolidone (NMP), N,N-dimethylacetamide (DMAC), N, N-dimethyl formamide (DMF) etc. Polymers were also soluble in tetrahydrofuran (THF) and in hot chlorinated solvents (viz. tetrachloro ethane, TCE; chloroform) hot acetone, m-cresol and concentrated sulfuric acid. They were insoluble in benzene, hexane, methanol and water.

The solubility data for these poly(ester-imide)s is listed in Table II. Increased solubility may be related to the presence of the long chain pentadecyl group; because unsubstituted analoges of diimide-diol(II) viz. N, N-diphenyl pyromellitimide and several of its p-substituted derivatives and their corresponding macromolecules were insoluble and infusible.

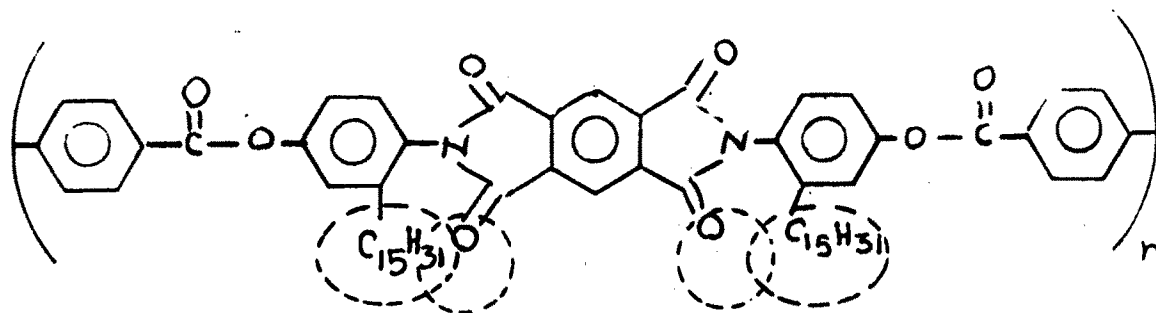
For diphenyl pyromellitimide and most of its parasubstituted derivation, it was assumed that these compounds have considerable interaction between closely packed molecules and hence infusible and insoluble in nature.

With the substituted analoges the steric effect of the substituent comes into play. The presence of larger group such as CH_3 , Cl etc makes coplanarity of A and B rings impossible.

TABLE II Solubility data of Poly(ester-imide)s

Sr.No.	SOLVENT	A	B	C
1.	NMP	++	++	++
2.	DMAC	++	++	++
3.	DMF	++	++	++
4	THF	++	++	++
5.	m-Cresol	+	+	+
6	Chloroform	+	+	+
7	TCE	+	+	+
8	Acetone	+	+	+
9	Methanol	-	-	-
10	Benzene	-	-	-
11	Hexane	-	-	-

++ = Soluble + = Soluble on heating, - = Insoluble



This interferes with the close packing of the molecules and also with the molecular interaction. Hence the low softening point. High solubility of many of these compounds was suggested due to some disruption of order. The same reasons are possibly applicable with poly (ester-imide)s derived from (II), wherein very bulky nature of pentadecyl substituents is expected to hinder the close packing more effectively, making polymers amorphous and soluble in solvents.

3.11

CONCLUSIONS

A new preformed imide containing aromatic bisphenol (II) monomer was synthesised by the reaction of PMDA with APP at 220°C. in m-cresol and was characterised by spectroscopy. The monomer(II) paved a convenient route to the insertion of imide linkages in the polyester backbone by its polycondensation with IPC/TPC. However viscosities are somewhat lower. These poly(ester-imide)s containing pendant pentadecyl substituents along main chain were soluble in many organic solvents.

Scope for further work

We have shown the feasibility of the poly(ester-imide)s synthesis by reaction by aromatic diacidchloride and diimide bisphenol(II). The polycondensation was studied by solution polymerisation whereas it can also be studied by conventional interfacial technique. This study will be of help to see if higher molecular weight poly(ester-imide)s from II could be obtained. This reaction can further be studied in detail for various other aminophenols as comonomer with II and aromatic diacidchlorides. A study of thermal properties of these poly(ester-imide)s and co-polymers will give information on maximum use temperature.

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