CHAPTER-III

PRESENT INVESTIGATION

RESULTS AND DISCUSSION

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

Polyarylates are an important class of high performance engineering plastics which find use in a number of diverse applications (8). Although these days poly (ethylene terephthalate), PET, is one of the important commerical polyesters, completely aromatic polyesters i.e. polyarylates derived from BP-A, bisphenols, phenolphthalein and terephthaloyl chloride are well known for their chain stiffness and thermal stability (21). It was of considerable interest to investigate the thermal stability and other physical properties of these aromatic polyesters from aromatic diacid chlorides by incorporating some new monomer units (comonomer) in the polymer backbone. Data on the synthesis and properties of various types of polyarylates including cardo, self-coloured, self-protecting, carbonate containing, stereoregular and block arylates have been examined (10). For increasing the solubility of polymers flexible groups or linkages, i.e. -O-, -CO-, -S-, $-SO_2$,siloxane, kinked structures etc. have been incorporated. Several other functional monomers containing cardo and/or pendant phenyl groups have been utilised for the processible polymer characteristics (22). Aromatic polyamides and polyimides based on N-phenyl- 3,3-bis [4-(p-aminophenoxy)phenyl] phthalimidines were amorphous and readily soluble in various polar solvents (23). The use of silylated bisphenols (24, 25) in the synthesis of polymers resulted in high molecular weight products.

3.1 Cardo polyesters

Phenolphthalein is an important building block for the condensation polymers and polyesters derived from it have been reported to exhibit valuable set of properties. Just like phenolphthalein, phenolphthalein derivatives such as phenolphthaleinimidine, phenolphthalein-anilide etc. are also useful for the synthesis of high molecular weight polymers. These polymers have improved solubility, high heat resistance and high thermal stability. They have ability to retain effective mechanical parameters at elevated temperatures (20). The aromatic cardo linkages are of special interest owing to its effect on the the thermal and solubility characteristics(Table-I) An incorporation of phthalide/phthalimidine cardo moiety in aromatic polyesters provides greater stability towards thermal degradation compared to the BP-A derived ones (26) without any deteriotion in solubility properties. Some phenolphthalein and silicon containing polyesters are found to be good candidate as the gas separation memberanes (27).

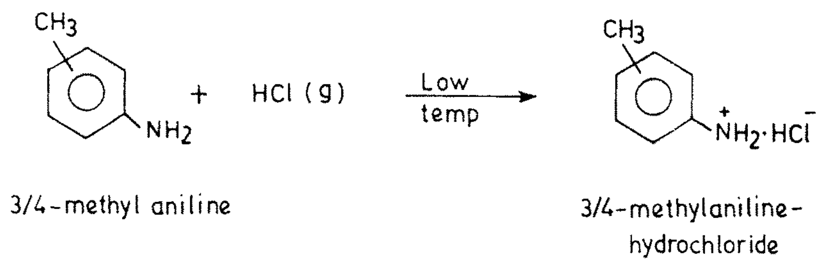
We have been investigating synthetic routes to high performance polymers, such as polyimides, polyamides containing modified monomers to enhance the processing of typical rigid rod materials by improving the solubility of polymers without much loss in thermal stability. Silicon containing polymers with improved solubility from tetraphenylthiophenediamine(28) pentadecyl substituted sulfone ether diamine(29), and phenolphthaleinanilide (30) with increased solubility of polymers have been reported. Phenolphthaleinimidine and phenolphthaleinanilide based high performance polymers viz. polyesters, polyetherketones, have been reported by McGrath et al. (31, 32).

However, no investigation has been made on the effect of systematic modification of polyesters by the incorporation of the phenolphthalein-N-3-methyl anilide or -N-4-methyl anilide (i.e. phenolphthalein N-m/p-toluile) groups in the aromatic polyester backbone. Hence this investigation on the synthesis and characterisation by IR, NMR, Mass and elemental analysis of two new cardo bisphenols viz. phenolphthalein-N-m-toluile and phenolphthalein-N-p-toluile was undertaken. It was postulated that the combination of terephthaloyl moiety and these new aminated derivatives of phenolphthalein would lead to new heat resistant and highly soluble polyesters. Therefore characterisation and properties of two series of new cardo aromatic polyesters derived from 3-PMA and/or 4-PMA (by solubility, viscosity, IR, NMR) were studied. The thermal stability and solubility of these aromatic polyesters are possibly associated with the effect of cardo-phenolphthalein-N-m/p-toluile group on the polymer backbone and the influence of chemical structure of such groups on the properties of polyarylates have to be discussed as in following sections.

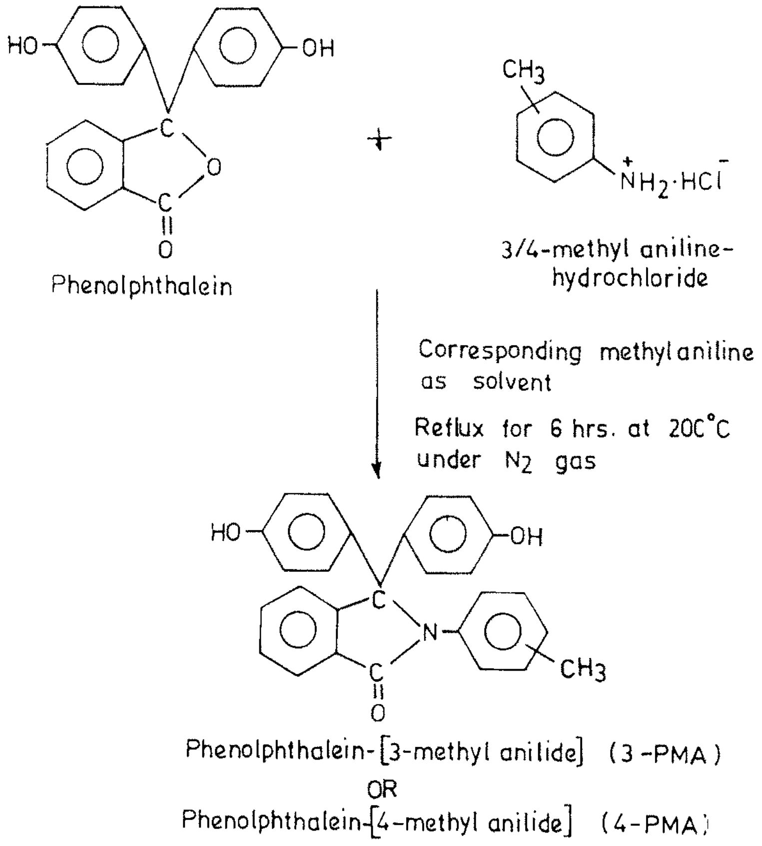
3.2 Synthesis Of Monomers

Two new cardo phthalide containing bisphenols phenolphthalein-N-(3-methyl anilide), 3-PMA and phenolphthalein-N-(4-methyl anilide), 4-PMA were synthesised in two steps starting from m/p-toluidine according to (scheme-I). Cardo bisphenol of isomeric structures were tailored from two isomeric aromatic amines and the specific aromatic methyl substituted aromatic amine was incorporated in the phenolphthalein's phthalide segment to obtain desired-N-(methyl anilide). Thus phenolphthalein 3-methyl anilide (3-PMA) was obtained in 63% yield by refluxing a mixture of phenolphthalein and m-toluidine-hydrochloride in the presence of m-toluidine as a solvent. Similarly,

Scheme I : Synthesis of 3/4 - methyl aniline hydrochloride



Synthesis of phenolphthalein-[3/4-methyl anilide]



phenolphthalein-4-methyl anilide (4-PMA) was obtained from phenolphthalein, p-toluidine-hydrochloride and p-toluidine as a solvent. The yield of 4-PMA was 62% (scheme-I). These monomers were recrystallised from methanol to obtain extra pure grade bisphenols as purity of reactants is very important criterion to achieve high molecular weight polymers.

The formation of bisphenol monomers was confirmed by IR, NMR, Mass spectra and elemental analysis. Purity and structure of monomers was chekced by the elemental analysis of 3/4-PMA which showed a good agreement for C, H and N percentage of samples with those of calculated values. The IR spectrum of phenolphthalein (fig. 1) exhibited characteristic strong absorption band for -OH group at 3375 cm^{-1} and for $\underset{\underset{O}{\|}}{-c-}$ group of phthalide ring at 1733 cm^{-1} and for -c-o- at 1271 - 1259 cm^{-1} . The IR spectrum of monomer bisphenols i.e. 3-PMA and 4-PMA (fig 2 and fig 3 respectively) exhibited characteristic absorption band for -OH group at 3469 cm^{-1} whereas strong absorption band at 1664 cm^{-1} was due to ring amide i.e. N-tolyl lactum carbonyl ($\underset{-C=O}{\overset{}{-N-}}$ PhMe). Absorption bands at 2963 cm^{-1} and 2828cm^{-1} indicate asymmetric and symmetric C-H strechng of CH_3 group attached to aromatic ring. Absence of absorption peak at 1733 cm^{-1} indicate that oxygen in the phthalide ring was replaced by N-tolyl group. If the lactone ring of the phenolphthalein moiety were in the open acid form, two strong peaks would appear at 1575 cm^{-1} and 1700 cm^{-1} representing the hydrogen bonded and non-hydrogen bonded acid

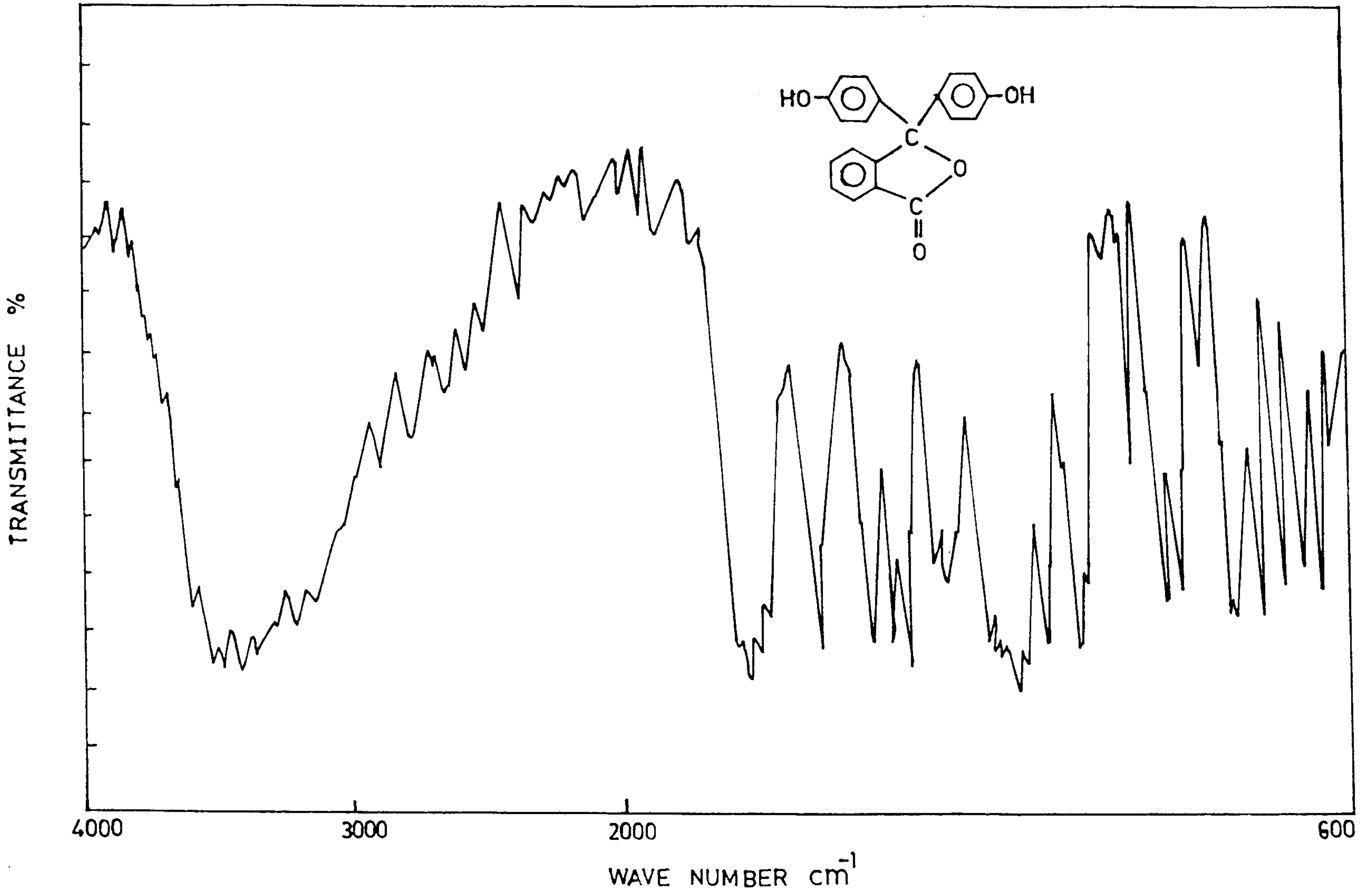


FIG. 1 :IR SPECTRUM OF PHENOLPHTHALEIN

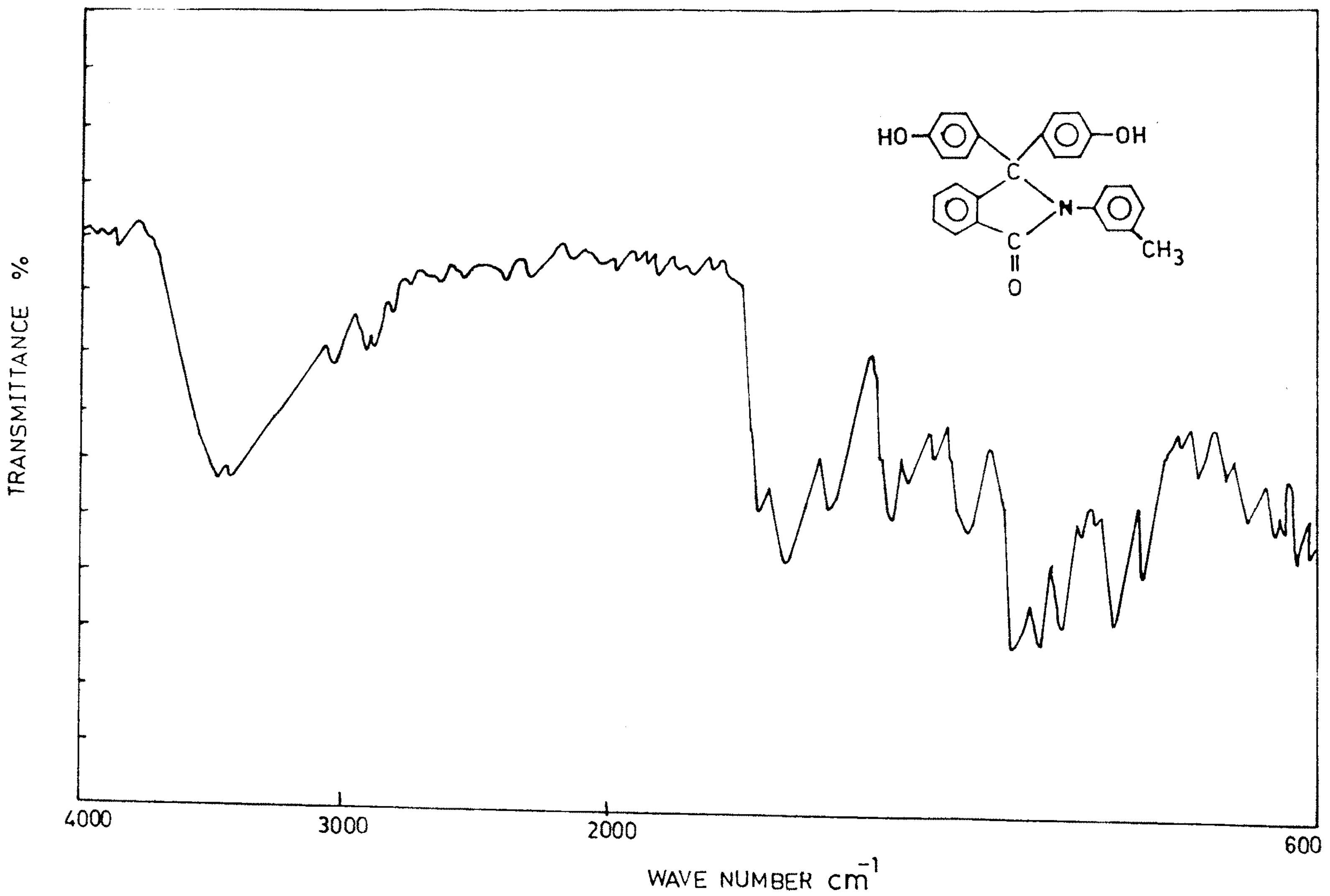


FIG. 2 : IR SPECTRUM OF 3-PMA.

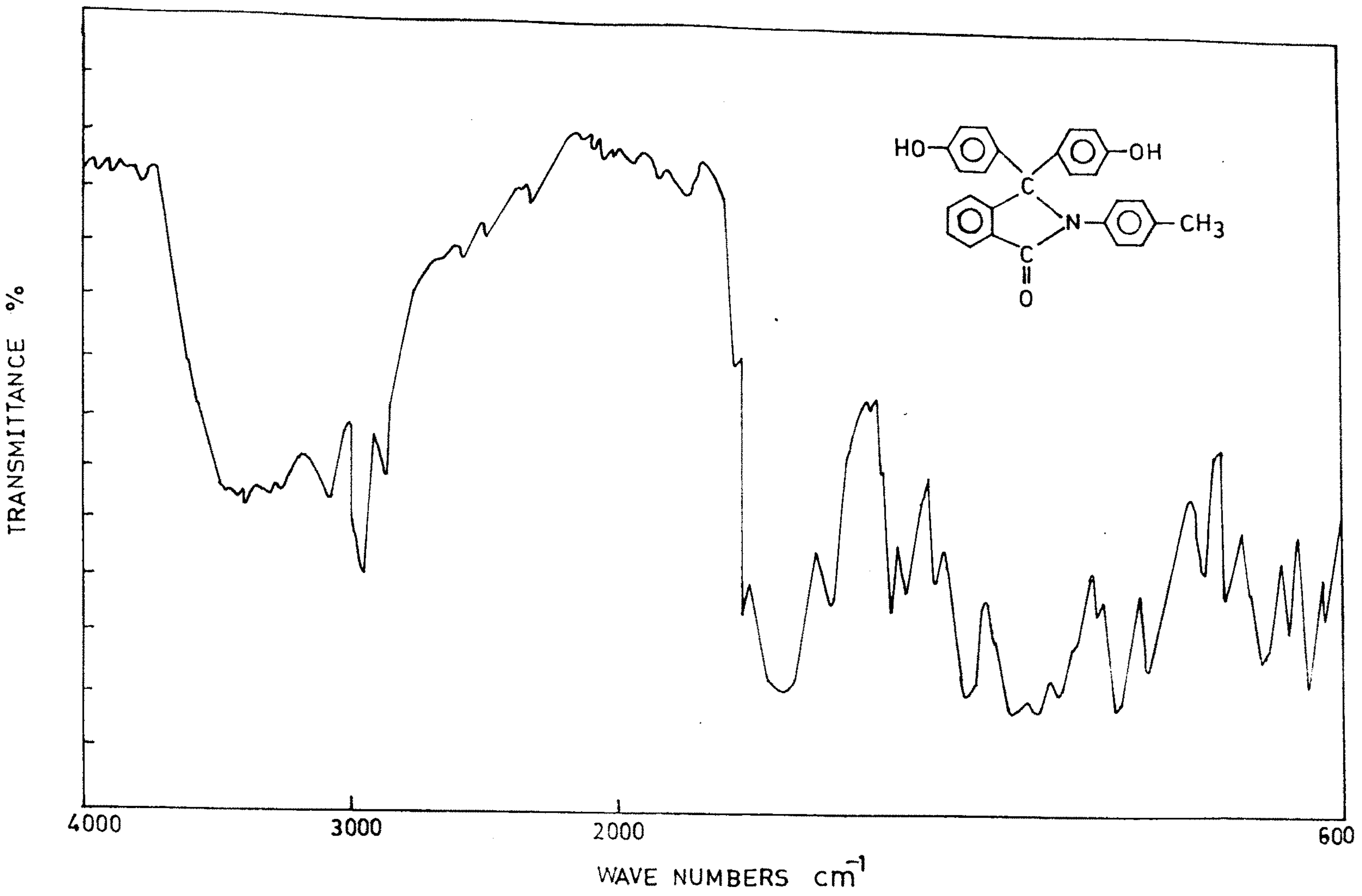


FIG. 3 :IR SPECTRUM OF 4-PMA.

carbonyls (33). Instead only a strong lactone carbonyl peak at 1733 cm^{-1} in phenolphthalein and strong lactam carbonyl peak at 1664 cm^{-1} in 3-PMA and 4-PMA indicate that the lactone ring in phenolphthalein and lactam ring in 3-PMA and 4-PMA remained intact.

Proton-NMR spectra of bisphenol monomers 3-PMA and 4-PMA were consistent with the structures assigned to them. H-1 NMR spectrum of 3-PMA is presented in fig.4. Broad NMR peak (singlet) at 9.55 δ (2H) is assignable to hydroxy functionals. Multiplets in the region of 6.5 to 8 δ (16H) represent all aromatic protons of which the ring proton ortho to phthalide carbonyl appeared at 7.8 δ (1 H) as doublet.Other aromatic protons of this ring appeared at 7.25δ(1H) doublet, 7.5 δ (2H), (dd). Whereas the aromatic protons of bisphenol ring and 3-methyl anilide ring overlap in the region 6.55 to 7.2 δ (12H). Singlet at 2.15 δ (3H) indicate methyl protons of N-tolyl group. H-1 NMR spectrum of 4-PMA is presented in fig.5.Singlet at 9.25 δ (2H) indicate OH group protons. Multiplets in the region of 7.8 to 6.5 δ (16H) represent aromatic protons. Among these aromatic protons of bisphenol rings and 4-methyl anilide ring protons appear as doublet of doublet (two sets) due to p-disubstituted pattern in the region 6.55 - 6.95 δ (12H). The signal at 7.75 δ (doublet, 2H) is assigned to aromatic proton ortho to carbonyl group of phthalide ring, whereas the remaining protons of the same ring appeared at 7.45 δ (2H, multiplet) and 7.15 δ (1H, doublet). The assignment is based on chemical shift, integration and splitting pattern of NMR

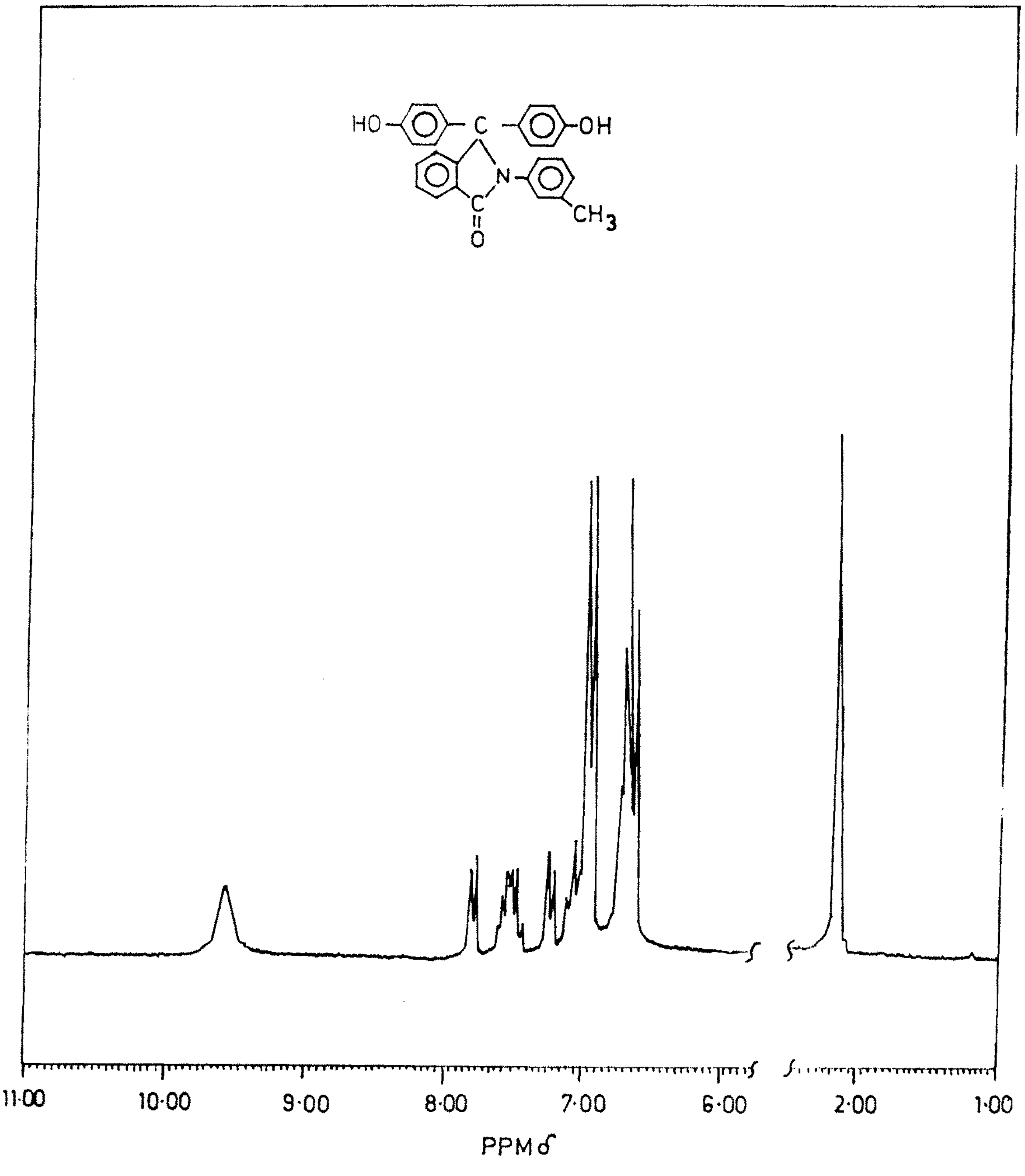


Fig. 4 : H-1 NMR spectrum of 3-PMA.

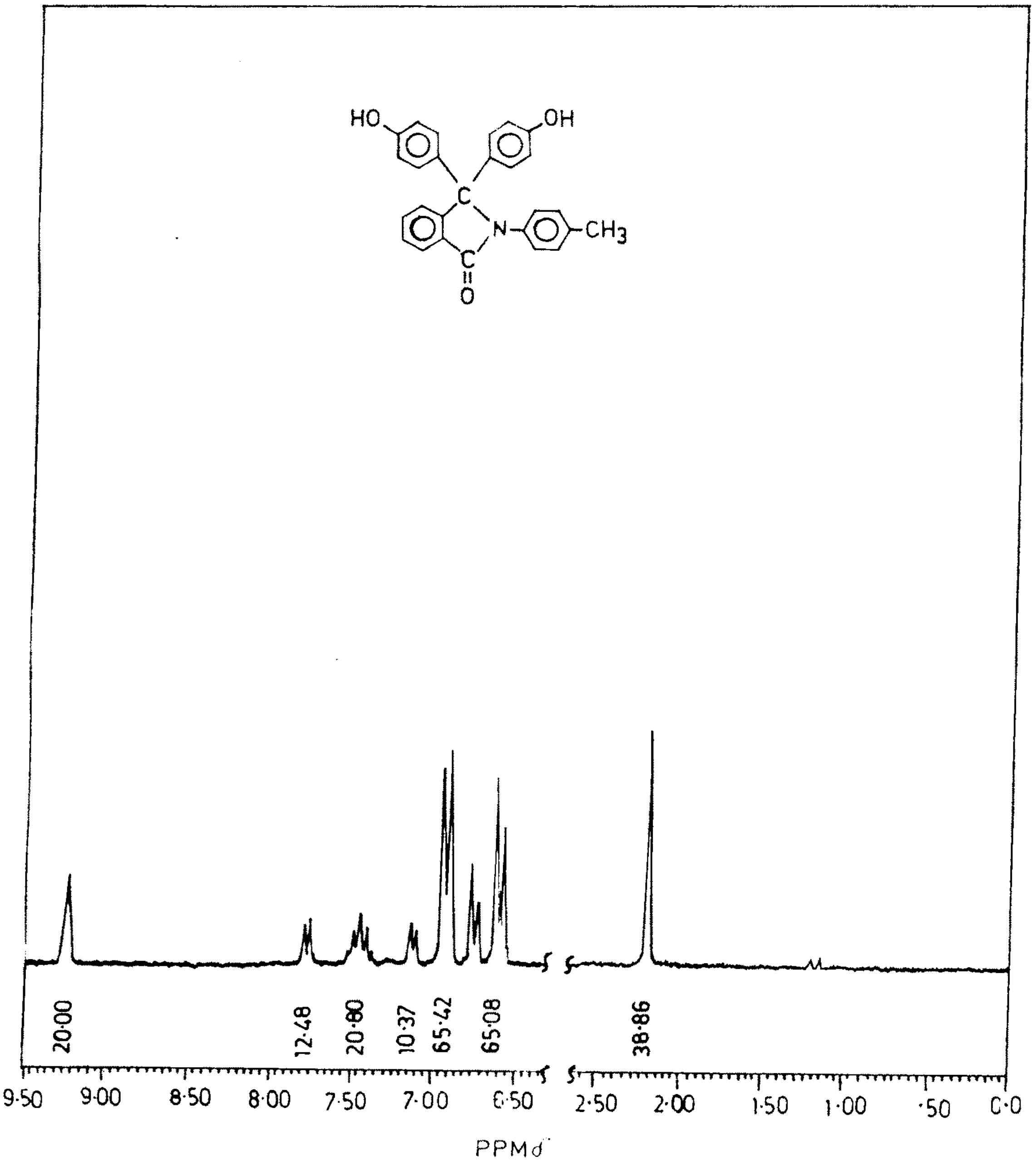


Fig 5 :H-1 NMR spectrum of 4-PMA.

peaks and is comparable to literature values for similar class protons. Singlet at 2.2 δ (3H) indicate methyl protons.

Mass spectrum of 3-PMA is presented in fig. 6. Molecular ion (M^+)peak appeared at m/e 407 indicating molecular formula weight of 3-PMA which is consistent with the molecular structure as proposed. Peak at m/e 314 and 224 corresponds to molecular fragment (M-93), (M-93-90) formed on loss of units such as $-C_6H_5OH$ and/or $C_6H_4.CH_3$ etc. The strong peak at m/e 91 corresponds to tropilium ion. The peak at m/e 314 is the base peak. Terephthalic acid chloride (TPC) was synthesised by refluxing mixture of terephthalic acid, dry pyridine and thionyl chloride for 12 hours. The residue, after removal of excess of thionyl chloride was vacuum distilled and the distillate recrystallised from dry hexane to offer extra pure TPC in very good yields.

3.3 Synthesis Of Polymers

Aromatic polyesters are usually prepared by the solution or interfacial reaction between aromatic dicarboxylic-acid chlroides, bisphenols and ester exchange reaction under severe conditions (34). Few processes operating under mild conditions and direct reaction of free acids with bisphenols have been developed and their mechanistic features were studied in model reactions and applied with limited success to the preparation of polyesters (35). In the present investigation most widely performed technique was adopted. A series of polyesters was synthesised by polycondensation of phenolphthalein and 3/4-PMA with terephthaloyl chloride by interfacial polymerisation

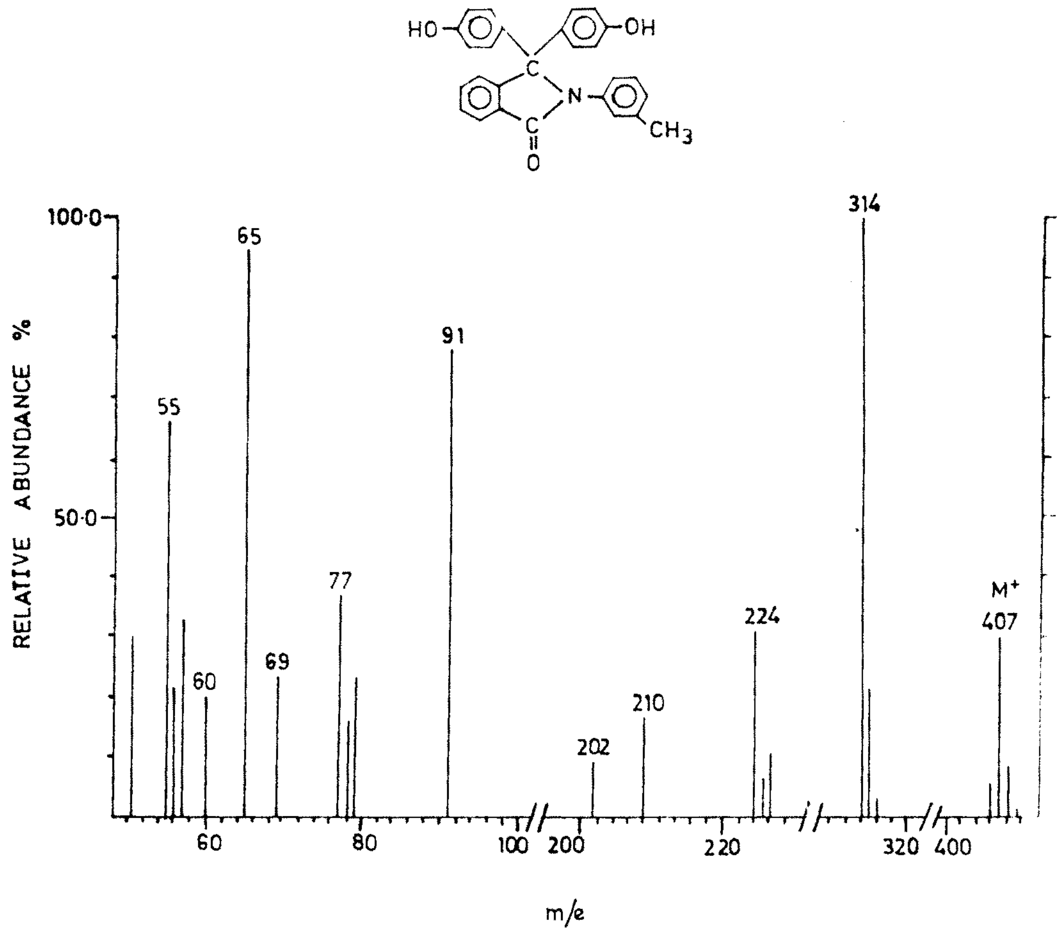


FIG. 6 :MASS SPECTRUM OF 3-PMA.

method (36) wherein alkali was utilised to remove away the hydrogen chloride evolved during the reaction from the reaction site. The resultant polymers are white solids whose yield and reduced viscosity values are tabulated in Table-II. Similarly the series of polyesters was syntehesised by polycondensation of phenolphthalein and 3/4-PMA with terephthaloyl chloride by low-temperature solution polymerisation technique. (Scheme II and III). The polycondensation was carried out in dichloromethane (DCM) using triethylamine as acid acceptor. The yield and reduced viscosity values are also presented in Table-II. A comparative study on the properties of these two isomeric polyesters synthesised by two different techniques was made.

The results of interfacial method and low-temperature solution polymerisation method revealed that for the polymers prepared in the present studies the formation of high molecular weight polyesters in high yields can be conveniently obtained by low-temperature solution polymerisation method, wherein polycondensation reactions proceeded in a homogenous state throughout the reaction and polymer precipitate formed when trickling the obtained polymer solutions into the stirring hexane . If an early precipitation occurs during the polycondensation itself due to poor solubility of the polymer chains then less than satisfactory results of molecular weight are expected. In all cases of present polymerisation studies, clear and viscous solutions were obtained because of phenolphthalein-N-3/4-methyl anilide 'cardo' structures.

Table-II Percentage Yield and reduced viscosity values of polyesters$^{(a)}$

Sr No.	Method of Synthesis / Polymer(b)	Interfacial Method		Low-temp. Solution Polymerisation	
		% yield	Viscosity ⓒ η_{red} dL/g	% yield	Viscosity ⓒ η_{red} dL/g
1.	PTPC	61.9	0.67	95.1	0.69
2.	NMTC	53	0.39	96.8	0.83
3.	NPTC	54	0.31	98.7	0.74

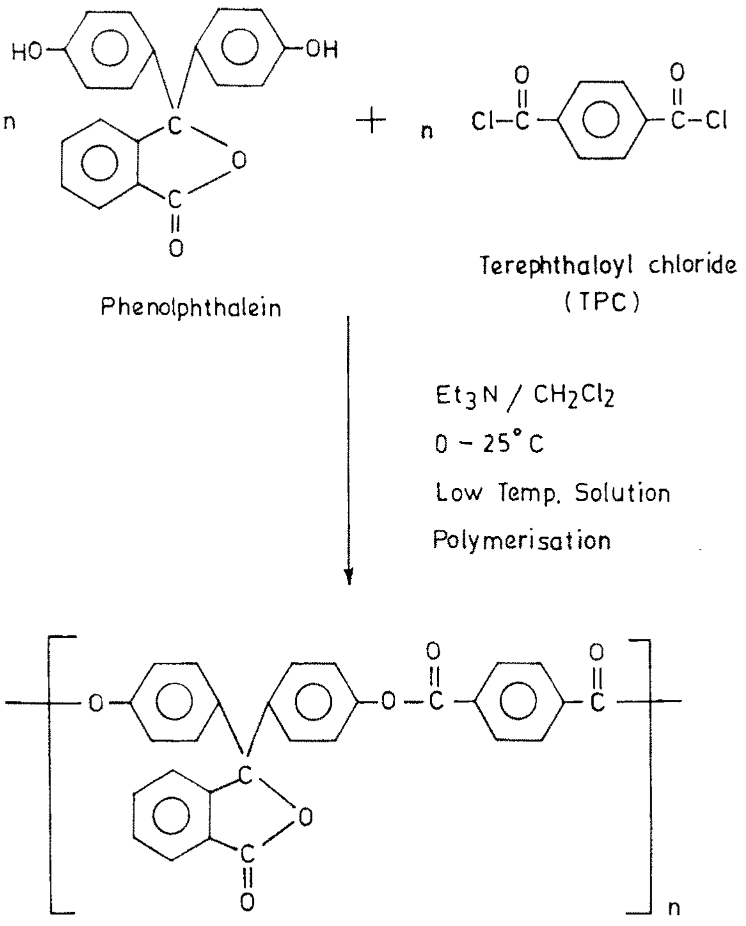
a) Polymerisation was carried out with 1 m mole bisphenol and 1 m mole of terephthaloyl chloride

b) PTPC : Phenolphthalein + TPC

NMTC : Phenolphthalein - N-3-methylanilide (3-PMA) + TPC
NPTC : Phenolphthalein - N-4-methylanilide (4-PMA) + TPC

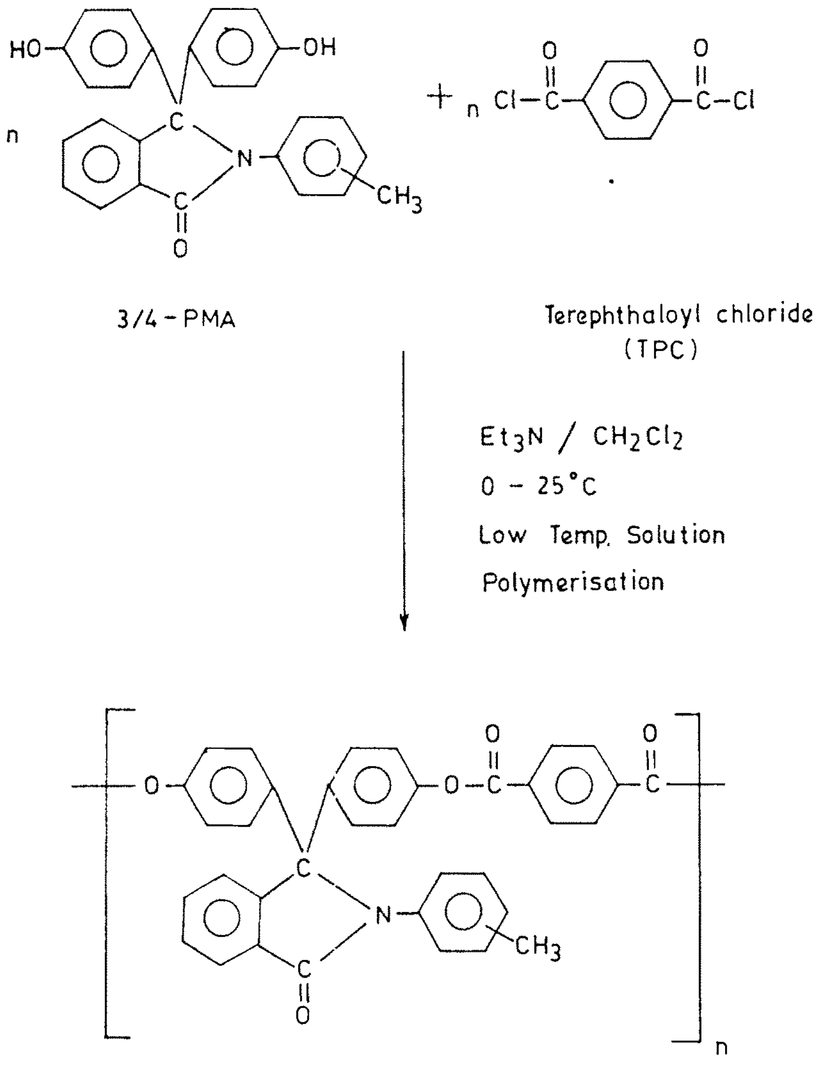
c) Measured with 0.5% (w/v) solution of polyester in sym-tetrachloroethane-phenol, (40/60 w/w) at 25°C.

Scheme II : Synthesis of poly (Phenolphthalein Terephthalate)



Poly (Phenolphthalein Terephthalate)

Scheme III : Synthesis of polyesters from 3/4-PMA



3/4-PMA

Terephthaloyl chloride (TPC)

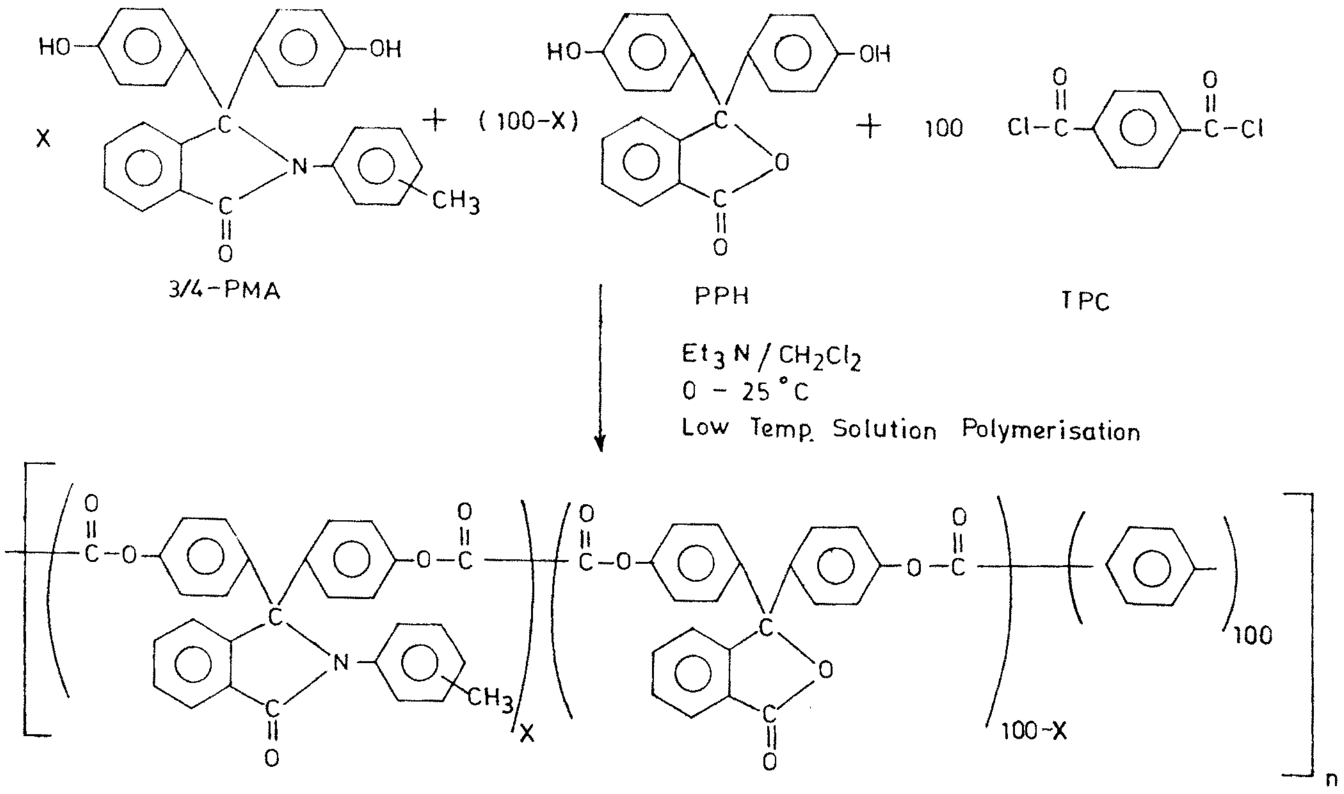
Et_3N / CH_2Cl_2
0 - 25°C
Low Temp. Solution Polymerisation

Polyester

To investigate the effect of partial replacement of phenolphthalein (PPH) with 3/4-PMA, copolyesters (IA-IIIA) and (IB-IIIB) containing 25-75 mole % 3/4-PMA and 75-25 mole % of PPH were synthesised by low-temperature solution polymerisation method (Scheme-IV). The results of synthesis of polyesters are given in Table-III for the polyesters IA-IIIA and Table-IV for the polyesters IB-IIIB. All these polyesters were obtained in good yields as a colourless, powdery or fibrous materials. These polyesters are characterised by IR, NMR spectra and elemental analysis.

The results of elemental analysis for carbon, hydrogen and nitrogen for the polyesters were in good agreement with the calculated values, confirming the repeat unit structures. IR spectrum of Poly (Phenolphthalein Terephthalate) i.e. PTPC showed two strong absorptions attributed to the carbonyl group at 1779 cm^{-1} and 1739 cm^{-1}. Absorption bands in the region of 3400-3100 cm^{-1} due to -OH group were absent indicating high molecular weight polyester. IR spectrum of polyester of 3-PMA i.e. NMTC is presented in fig. 7, wherein absorption band at 1735 cm^{-1} indicate carbonyl group and -c-o- at 1241 cm^{-1} and at 1069 cm^{-1}. This indicate the presence of an ester group of polyester main chain. Additionally it also showed a strong absorption peak at 1698 cm^{-1} assignable to ring amide i.e. N-tolyl lactam carbonyl ($-\underset{\diagup C=O}{\underset{|}{N}}-PhMe$). Absence of absorption peak at 3469 cm^{-1} in IR spectrum of polyester indicate that -OH group have completely involved in the polymerisation, to yield high

Scheme IV : Synthesis of Copolyesters



X -	0	25	50	75	100
Polyester -	PTPC	I-A/B	II-A/B	III-A/B	NMTC/NPTC

Table-III : Synthesis of Copolyesters of 3-PMA(a)

Sr No.	Polymer (b)	Composition of Diols mole %		Yield %	Viscosity(c) η red dL/g
		PPH	3-PMA		
1.	PTPC	100	-	95.1	0.685
2.	I-A	75	25	95.3	0.368
3.	II-A	50	50	99.2	0.557
4.	III-A	25	75	96.9	0.580
5.	NMTC	--	100	96.8	0.834

(a), (b), (c) as in Table II

PPH - Phenolphthalein

Table-IV : Synthesis of Copolyesters of 4-PMA[(a)]

Sr No.	Polymer (b)	Composition of Diols mole %		Yield %	Viscosity[(c)] η red dL/g
		PPH	4-PMA		
1.	PTPC	100	--	95.1	0.685
2.	I-B	75	25	98.7	0.556
3.	II-B	50	50	98.2	0.473
4	III-B	25	75	96.8	0.412
5	NPTC	--	100	98.4	0.739

(a), (b), (c) in Table II

PPH - Phenolphthalein

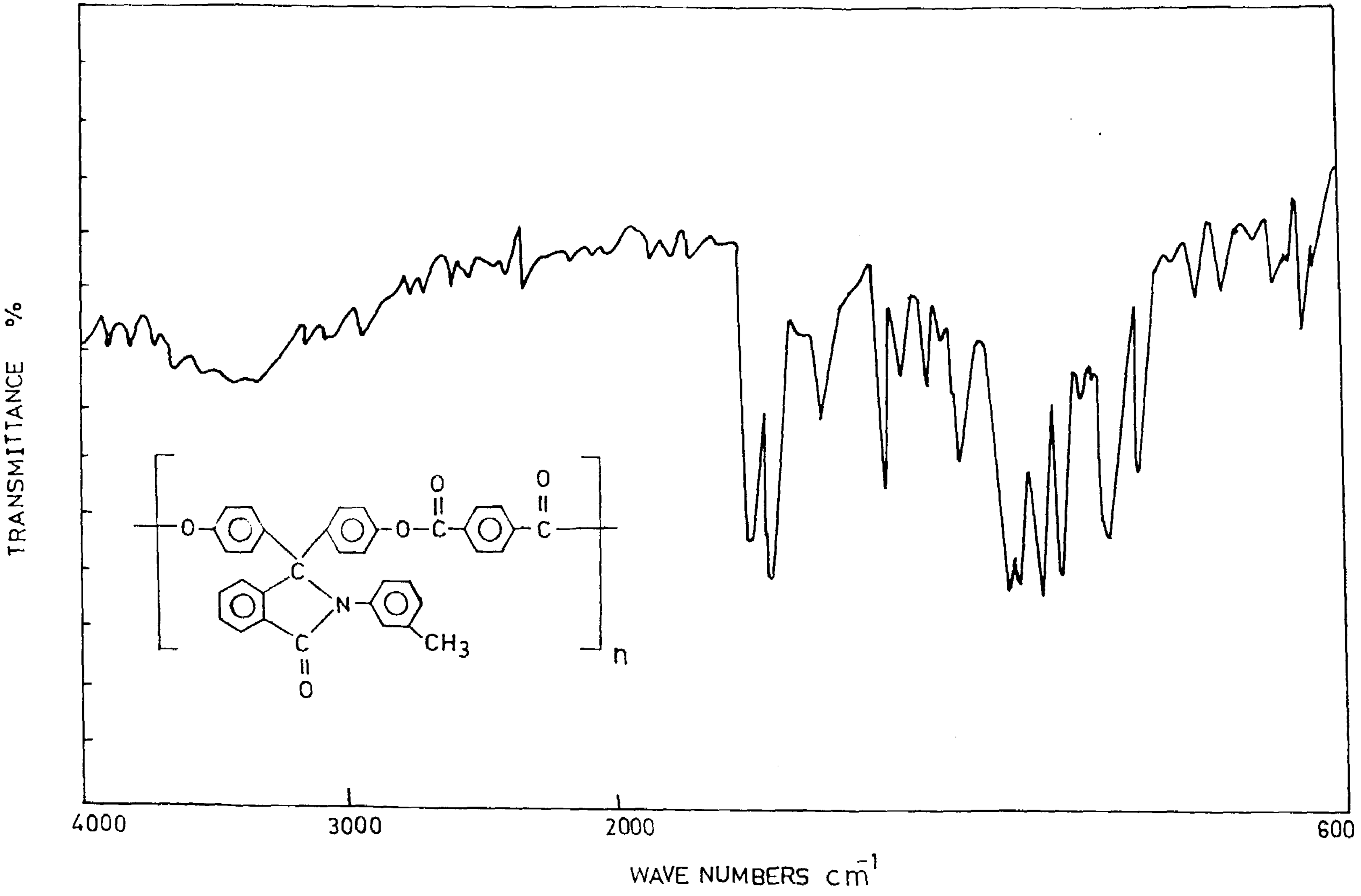


FIG. 7 :IR SPECTRUM OF POLYESTER OF 3-PMA.

molecular weight polyester. IR spectrum of polyester of 4-PMA i.e. NPTC is shown in fig. 8. It is analogus to the IR spectrum of NMTC (fig.7) except the fingerprint region.

Copolyesters IIA and IIB contain 50:50 mole percent of PPH and 3/4-PMA. IR spectra of copolyesters of IIA and IIB are presented in fig. 9 and fig.10 respectively. These spectra indicate absorption peak at 1733 cm^{-1} and 1697 cm^{-1} showing the presence of carbonyl group of the phthalide of the phenolphthalein and N-tolyl lactam carbonyl group of 3/4-PMA respectively. This confirms the incorporation of both phenolphthalein and 3-PMA or 4-PMA moieties in the polyester main chain.

H-1 NMR spectrum of poly (phenolphthalein terephthalate) i.e. PTPC is presented in fig. 11. Singlet at 8.3 δ (4H) is due to protons of aromatic ring of terephthaloyl moiety. Doublet at 8 δ (1H) is due to proton adjacent to the lactone carbonyl group (i.e.phthalide group). Aromatic protons 7.2 to 7.6 δ (8H), doublet of doublet, of bisphenol-phenylene units are easily characterised due to specific splitting pattern. Similarly we can assign the different protons of phthalide pendant group based on chemical shift, splitting nature and integration of signals.

H-1 NMR spectra of polyesters of 3-PMA and 4-PMA i.e. NMTC and NPTC are consistent with structures assigned to them. H-1 NMR spectrum of polyester NMTC is presented in fig.12. whereas fig.13 represents H-1-NMR spectrum of polyester NPTC.

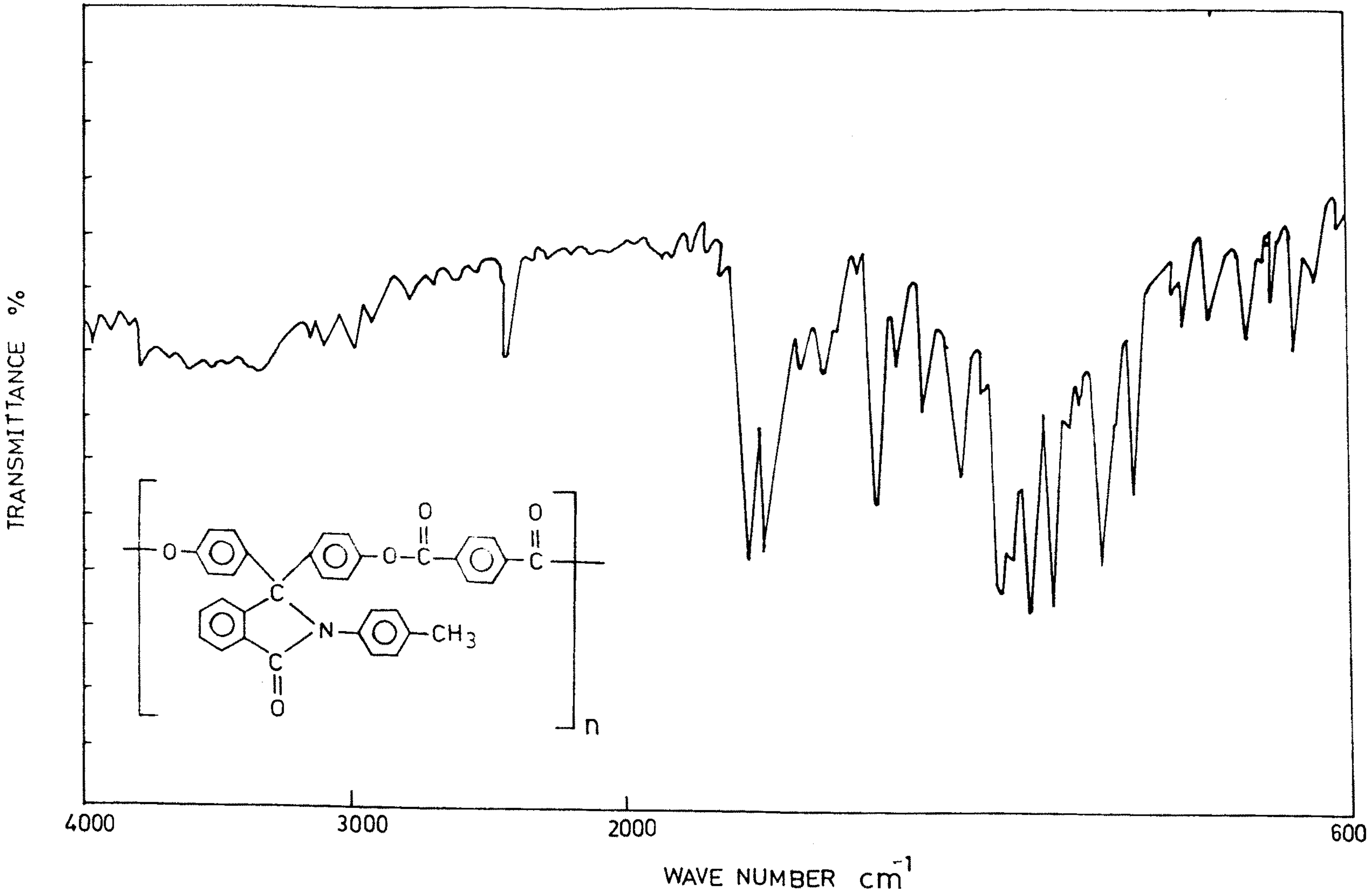


FIG. 8 :IR SPECTRUM OF POLYESTER OF 4-PMA.

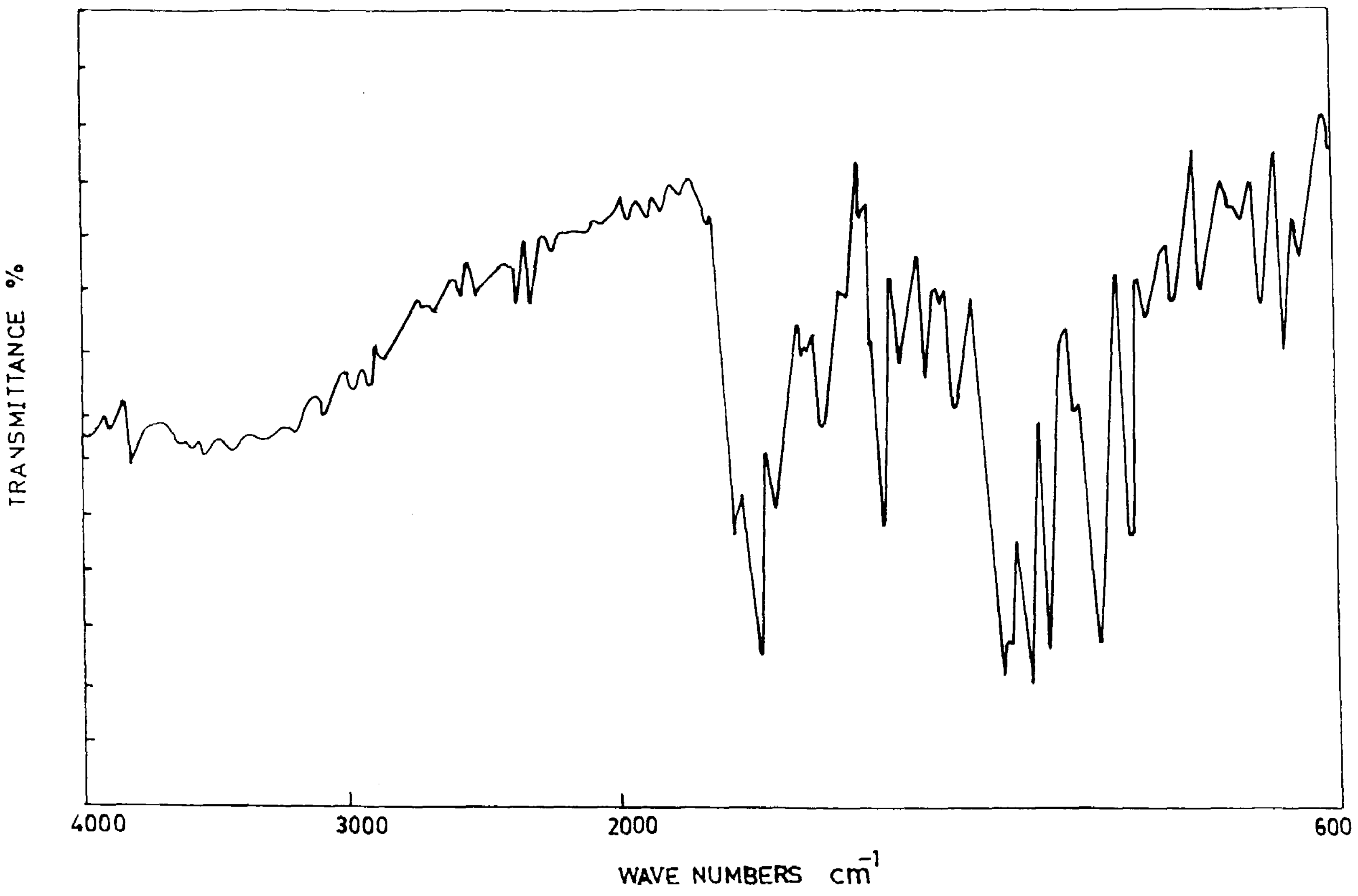


FIG. 9 :IR SPECTRUM OF COPOLYESTER - II A.

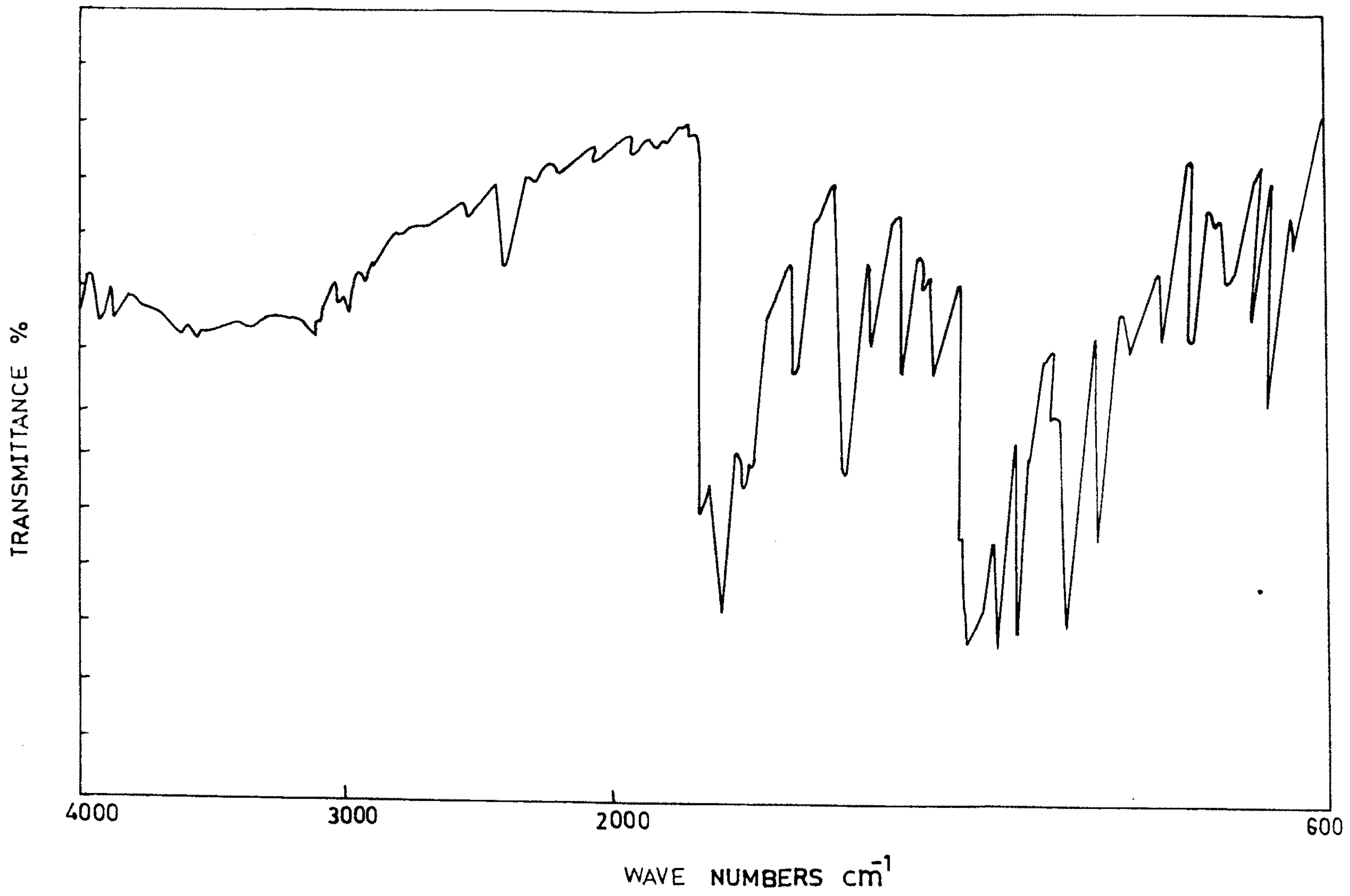


FIG. 10 :IR SPECTRUM OF COPOLYESTER - II B.

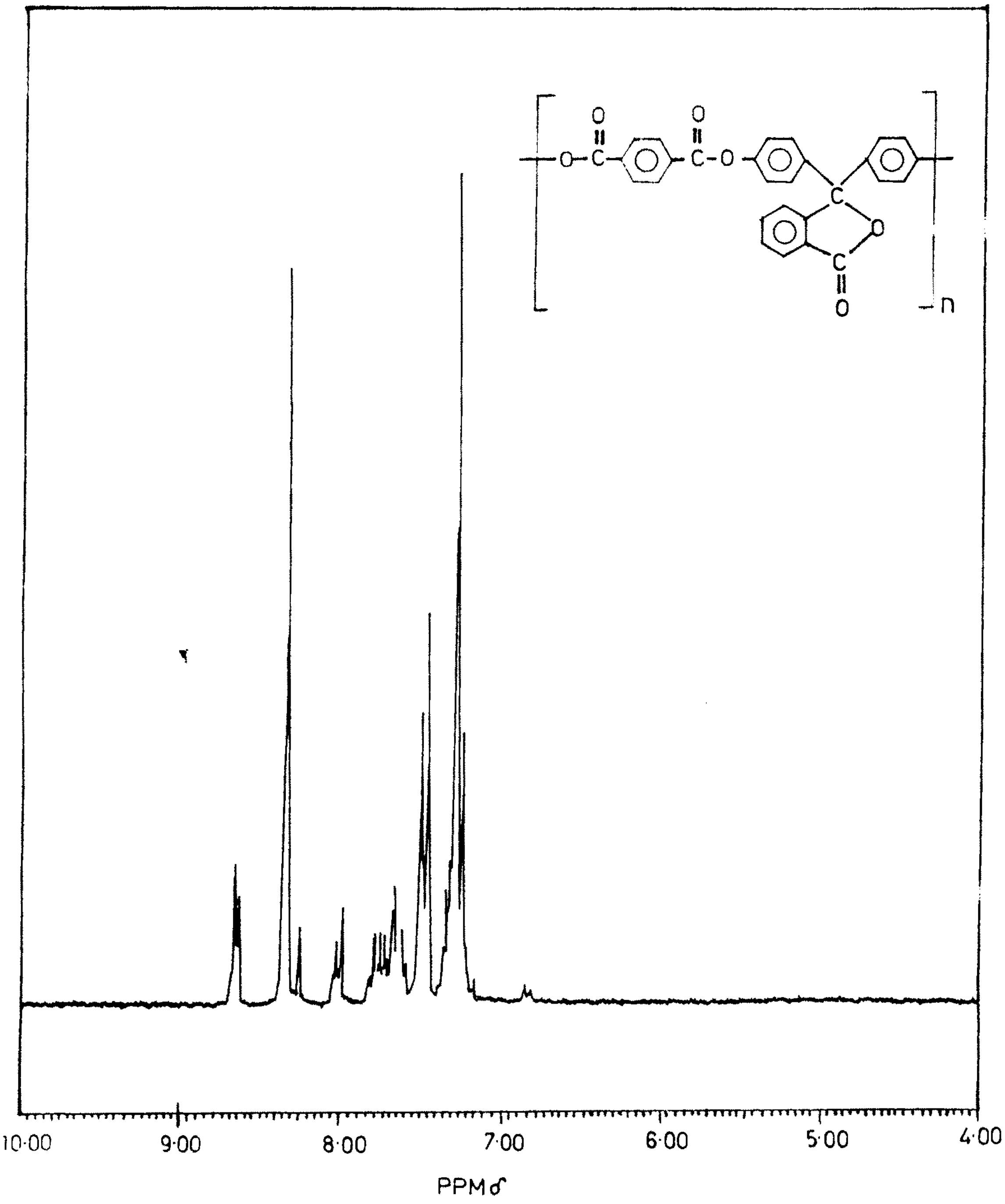


FIG. 11 :H-1 NMR spectrum of polyester PTPC.

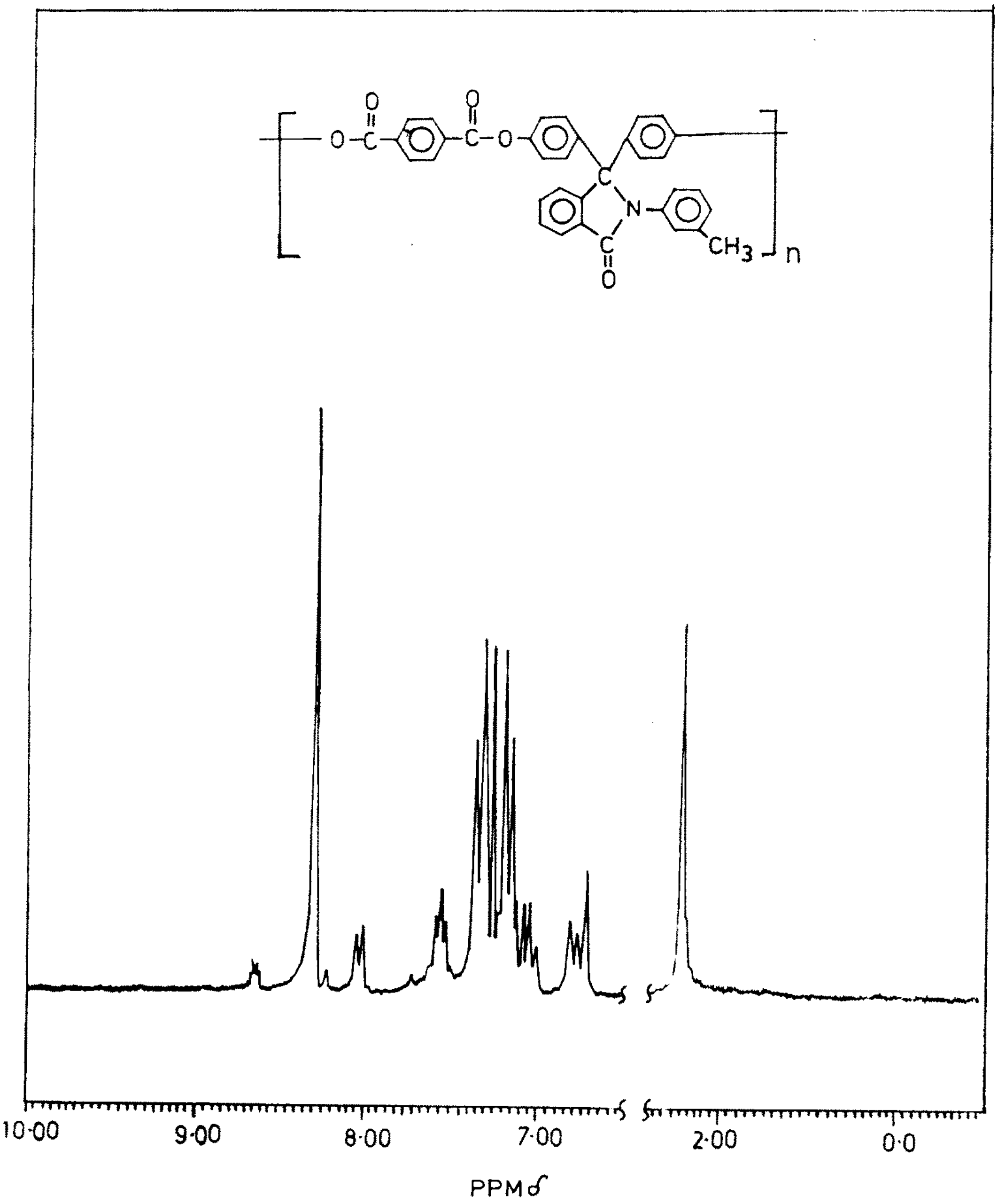


Fig. 12 :H-1 NMR spectrum of polyester NMTC.

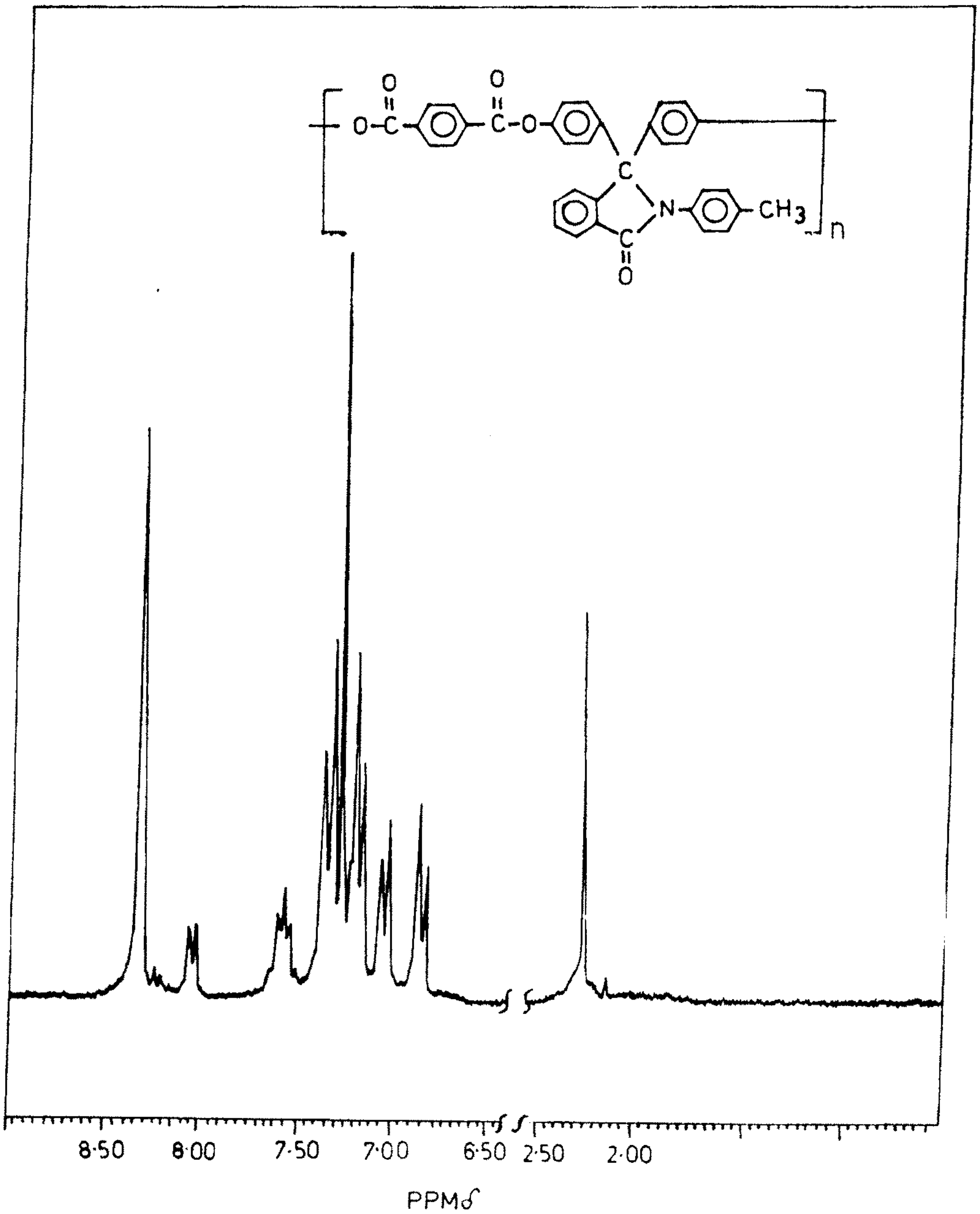


Fig. 13 :H-1 NMR spectrum of polyester NPTC.

Interpretation of signals in figure 13 is as below.

NMR signals due to aromatic protons at 7.1 to 7.4 δ (8H) are differentiated and are attributed to 1,4 disubstituted bisphenol phenylene protons due to doublet of doublet splitting. Singlet at 8.4 δ (4H) can be assigned to aromatic protons of terephthaloyl moiety, as they appear most downfield. Aromatic proton ortho to phthalide carbonyl appeared at 8.1 δ (1H, doublet), whereas aromatic protons of 4-methyl-anilide ring appeared at 6.6 to 7.1 δ as doublet of doublet (4H). Remaining peak at 7.65 δ is due to aromatic protons of phthalide ring. The values are consistent with the literature reports. Singlet at 2.3 δ (3H) indicate methyl protons of the 4-methyl substituent in anilide ring confirming that oxygen of the phthalide ring has been replaced by N-tolyl group and 4-PMA moiety is part of polyester. H-1 NMR spectrum of polyester of 3-PMA i.e. NMTC shown in fig.12 is analogus to the spectrum of NPTC. Singlet (3H) due to methyl group at 2.2 δ confirms the structure of polyester derived from 3-PMA, whereas assignments of aromatic protons is based on above discussion. Absence of -OH group signal in the NMR spectra of these polyesters indicate building of high molecular weight molecule whereby hydroxy groups of bisphenols are completely utilised and concentration of end-group is very very low. Thus polyesters gave NMR spectra consistent with expected and assigned structures.

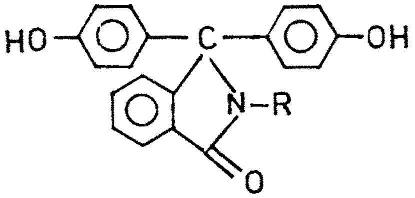
3.4 Viscosity

As shown in the Table-III and Table-IV polyesters and copolyesters exhibited reduced viscosities in the range of 0.37 to 0.83 dL/g. A tough, transparent and flexible films could be cast from dichloromethane or chloroform solutions of polyesters (NMTC and NPTC) indicating the formation of reasonably high molecular weight polymers. These values are comparable to those in Table V. On comparing the reduced viscosities of copolyesters IA, IIA and IIIA, it was found that reduced viscosity increases through IA-IIIA as the mole percent of 3-PMA increases, whereas it decreases through IB-IIIB as the mole percent of 4-PMA increases. The reason for getting higher reduced viscosity for polyesters based on 3-PMA may be the position of electron releasing methyl group which influences the nucleophilic properties of the 3-PMA and 4-PMA, making 4-PMA less nucleophilic and resulting in comparatively lower reduced viscosity. This has been reported for few other diols wherein a electron releasing group increase the nucleophilic properties of the phenolate anion to favour higher inherent viscosities (37, 38).

3.5 Solubility

The solubility of polyesters and copolyesters was tested in various solvents at room temperature and the results are summarised in Table VI and Table VII. All the polymers were completely soluble in polar aprotic solvents viz. N,N-dimethyl

Table-V Cardo Polyarylates with phthalimidine groups and terephthaloyl chloride[a]



Sr. No.	Bisphenol (R =)	η_{red} in tricresol (dL/g)	Softening temperature °c (from thermomechanical curves)
1	H	0.60	315
2	C_2H_5	0.77	300
3	C_2H_4Cl	0.60	360
4	C_2H_4OH	0.80	270
5.	CH_2-CH=CH_2	0.66	crosslinked on heating
6	C_6H_5	0.64	310
7	C_6H_5	0.50	302 (Tg) [b]

a) from V.V.Korshak, S.V.Vinogradova, S.N.Salazkin and L.I.Komarova, Eur. Polym, J. 10, 967 (1974)

b) M.S.Lin and E.M. Pearce, J. Polym.Sci, Polym. Chem. Ed. 19, 2659, (1981) Table-VI : Solubility of Polyesters of 3-PMA in Different Solvents [a]

Sr. No.	Polymer / Solvent	PTPC	NMTC	I-A	II-A	III-A
1	DMAc	++	++	++	++	++
2	DMF	++	++	++	++	++
3	NMP	++	++	++	++	++
4	m-Cresol	++	++	++	++	++
5	Conc.H_2SO_4	++	++	++	++	++
6	DCM	++	++	++	++	++
7	TCE	++	++	++	++	++
8	Phenol + TCE (60:40 mixt)	++	++	++	++	++
9	DMSO	++	±	±	±	±
10	Formic Acid	-	-	-	-	-
11	Acetone	-	-	-	-	-
12	Methanol	-	-	-	-	-

++ soluble at room temperature

± partly soluble

- insoluble

Table-VII : Solubility of Polyesters of 4-PMA in Different Solvents[a]

Sr No	Polymer / Solvent	PTPC	NPTC	I-B	II-B	III-B
1	DMAc	++	++	++	++	++
2	DMF	++	++	++	++	++
3	NMP	++	++	++	++	++
4	m-Cresol	++	++	++	++	++
5	Conc.H_2SO_4	++	++	++	++	++
6	DCM	++	++	++	++	++
7	TCE	++	++	++	++	++
8	Phenol + TCE (60:40 mixt)	++	++	++	++	++
9	DMSO	++	±	±	±	±
10	Formic Acid	-	-	-	-	-
11	Acetone	-	-	-	-	-
12	Methanol	-	-	-	-	-

++ soluble at room temperature,

± partly soluble

- insoluble

acetamide (DMAc), N, N-dimethyl formamide (DMF), N-methyl-2-pyrolidone (NMP) and chlorinated solvents such as sym. tetrachloroethane, dichloromethane (DCM) etc.

The higher solubility of polymers with the phthalide and phthanilide group can probably be explained (25) by the large size, polarity and asymmetry of these groups. The high solubility of polymers in various solvents is attributed to the introduction of cardo group with N-tolyl group along the polymer chains. Good solubility is inherent in polyarylates with phthalimidine group as well as those with phthalide group i.e. the influence of phthalide and phthalimidine groups on solubility (and higher softening temperature) is approximately the same. The phtalimidine groups are responsible for excellent solubility of polyarylates in various organic solvents, from such solutions tough films can be cast.

Improved solubility of polyesters IA-IIIA and IB-IIIB may also be caused by random sequence of monomers in the polymer backbone due to copolymerisation effect, which provided an increased entropy of the system. All polyesters and copolyesters were partly soluble in dimethyl sulfoxide (DMSO). They did not dissolve in formic acid, methanol, acetone.

3.6 Crystallinity

The ability of the cardo polyarylates to be crystallised depends not only on the nature of the cardo group but also on its placement with respect to other groups of the polymer chain. The cardo polyarylates of phenolphthalein are crystalline to some extent only in the case when a diacid with the cardo group in the molecule is used as the acid component. Due to this in spite of the asymmetry of the phthalide group, the macromolecule as a whole became more symmetrical. The degree of crystallinity of polymers is mostly dependent upon the symmetry of monomers employed for their preparaion. The crystallinity of present polyesters was studied by wide angle XRD obtained in powder and the diffractograms of polyesters are presented in fig. 14 and fig. 15, in terms of intensity Vs 2θ where θ is the angle of diffraction (Bragg angle). All these polymers had very similar diffraction patterns. The polyesters investigated in the present studies showed partly crystalline structure as evidenced from intense sharp and narrow diffraction peaks in the range of 25 to 35° 2θ values, in addition to broad and diffused humps in the region of 0 to 20° 2θ values for most of the polyesters derived from 3/4-PMA and TPC.

In general most of the cardo polyarylates are amorphous primarily because of the bulky pendant structure, however TPC component has rigid para-orientation and symmetry renedering polyesters with a small degree of crystallinity i.e. semicrystalline. These polyesters from 3-PMA and 4-PMA with TPC are having more degree of crystallinity than earlier reported silicon containing polyesters derived from phenolphthalein - anilide or copolyesters from various moles of phenolphthalein - anilide and phenolphthalein (30).

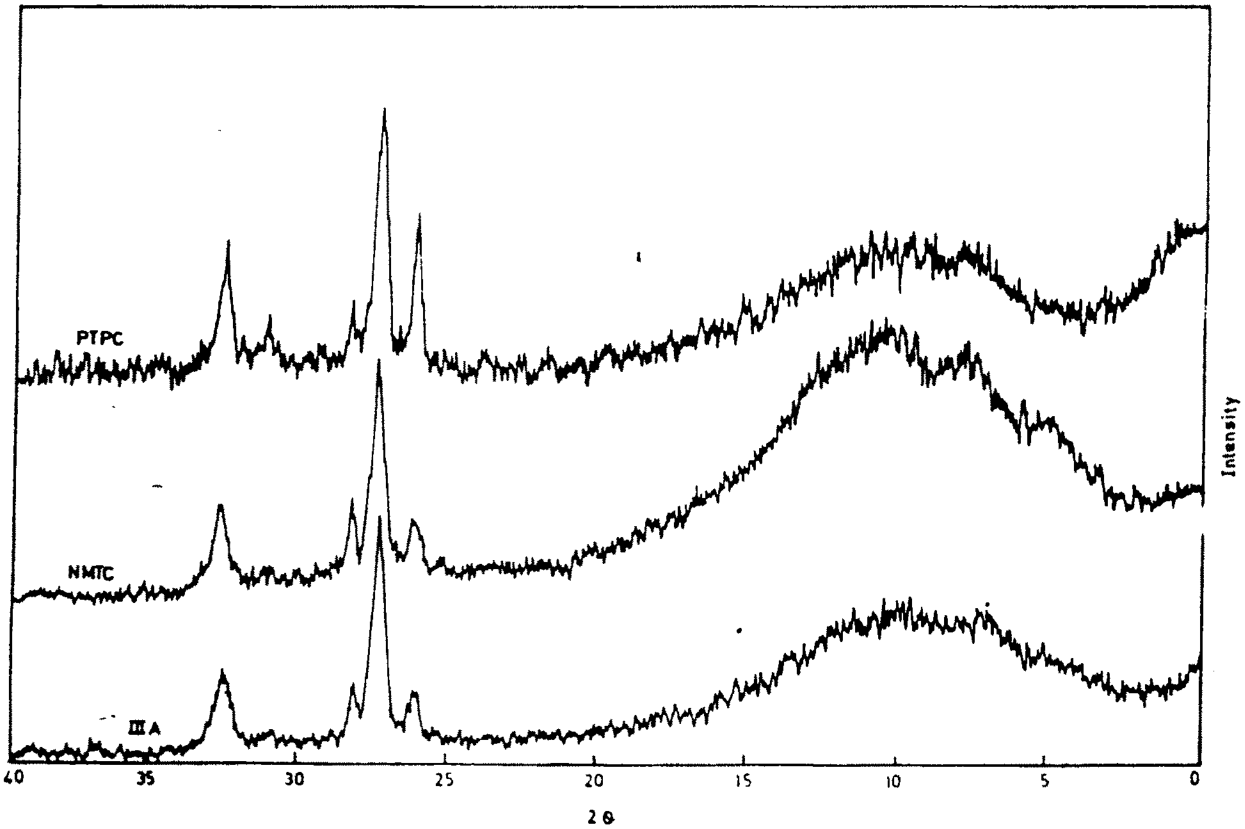


Fig. 14 : X-ray diffractograms of polyesters PTPC, NMTC and III A.

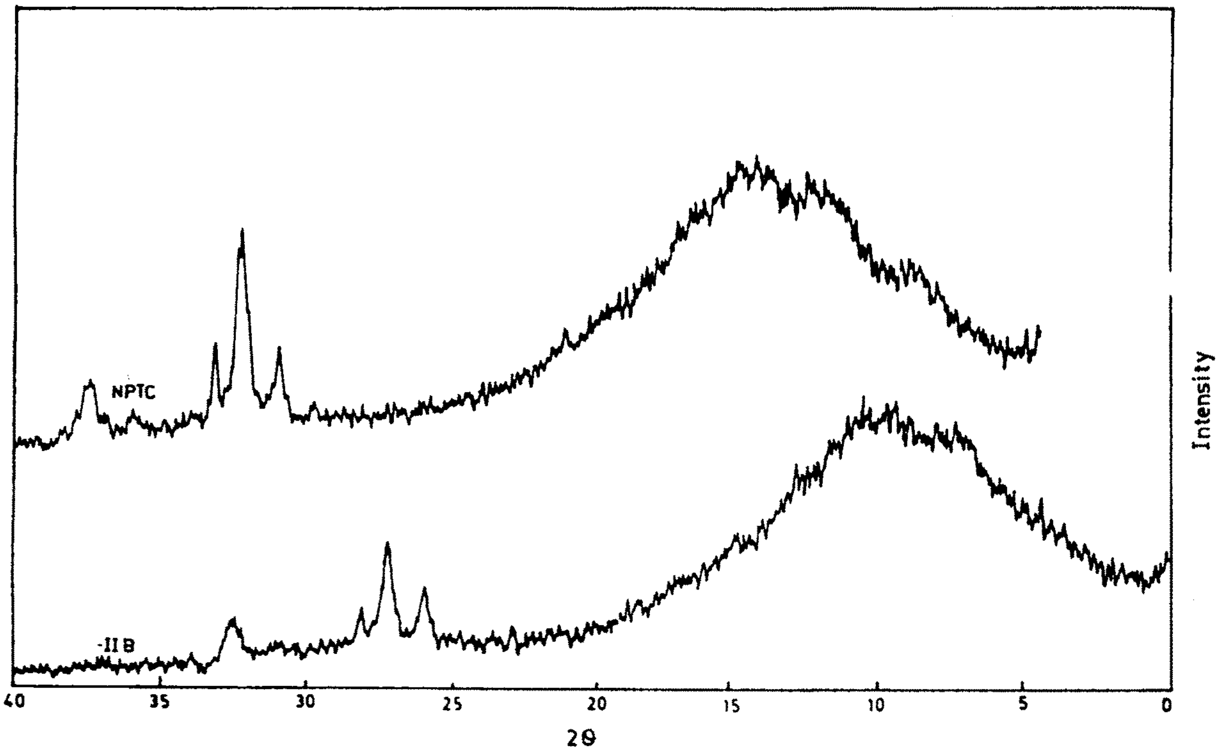
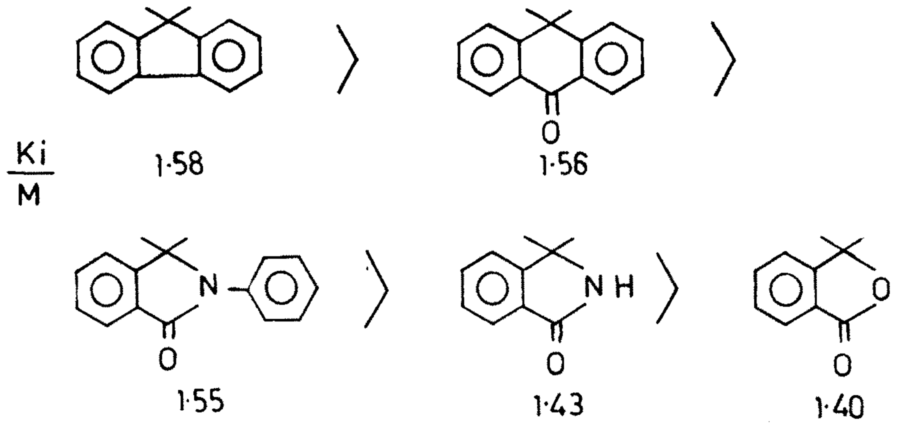


Fig 15 :X ray diffractograms of polyesters NPTC and II B.

3.7 Thermal Properties

The studies on thermal properties were planned with dynamic thermal analysis including differntial scanning calorimeter (DSC) and thermogravimetric analysis (TGA). However, due to breakdown of the TG-DSC unit (Rigaku) in the department the data is not available. Analysis is to be performed at RSIC. The Table-V represents the glass transition temperature, softening temperature values for some cardo polyesters (20). The values range from 270 to 360°C, and for ethylanilide (R = C_2H_5) softening temperature is 300°C. We expect similar value for R = Me, i.e. 3-PMA/4-PMA derived polyester. When the thermal stability of the polymers derived from terephthalic acid was characterised by thermogravimetric analysis conducted at a heating rate of 20°C/min, in nitrogen atmosphere, the on set of decomposition temperature was about 360 to 400°C, depending on dihydricphenol (10). Similar trend values are expected for the polyesters with phenolphthalein-N-3/4-methylanilide cardo groups as illustrated by following series indicating the effect of nature of cardo groups on thermal stability.



Thus the thermal stability of polyesters NMTC/NPTC containing 3-PMA/4-PMA cardo bisphenols will be nearly equal or little lower than that of the corresponding polyesters based on phenolphthalein-anilide i.e. thermal stability of polyesters synthesised in present studies will be more than that of corresponding polyesters derived from phenolphthaleinimidine and phenolphthalein.

Overall better thermal stability and improved solubility of polyesters NMTC/NPTC and the copolyesters IA-IIIA, IB-IIIB may offer these materials as one of the potential candidates for high performance applications; where a high heat resistance, processibility and mechanical parameters are needed.

CONCLUSIONS

Two series of new aromatic cardopolyesters and copolyesters were synthesised from novel bisphenols derived from phenolphthalein viz. phenolphthalein-N-3-methylanilide and phenolphthalein-N-4-methylanilide with terephthaloyl chloride by a low-temperature solution polymerisation procedures in excellent yields. These new bisphenols and resulting polyarylates were characterised by spectroscopy, viscosity, XRD, solubility tests. Polyesters were partly crystalline with reduced viscosities in the range of 0.36 to 0.83 dL/g in sym-tetra- chloroethane-phenol, (40/60 w/w). Polymers readily dissolved in many common organic solvents and tough, strong, flexible films could be cast. Solubility, viscosity and thermal properties of these new cardo polyarylates are comparable to those of corresponding phenolphthalein / phenolphthaleinanilide based polyesters and correlated to structure of cardo-bisphenols.

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