Chapter – 3

Results and Discussion

3.0 Results and Discussion : -

3.1 Introduction : -

Aromatic polyimides have earned a reputation as high-performance materials because of their excellent thermal stability, chemical resistance and outstanding mechanical properties.[112] However the majority of polyimides have limited applications because of their infusibility and insolubility in organic solvents [113-114]. To extend the utility of such high – performance materials, many copolyimides, such as poly(amide-ester-imides)s[115], poly(amide-imides)s[116], poly(imide-carbonates)s[117] and poly(ester-imides)s[118] were reported. The solubility of the polyimide can be improved by incorporating aliphatic linkages, but their thermostabilites are depressed. For increasing solubility without significantly decreasing thermostability the synthesis of poly(amide - imide)s seemed more promising.

In our laboratory, to enhance the solubility of high temperature resistant polymers, number of new and novel polyfunctional tetraphenylated and / or cardo moieties have been synthesised, characterised and polymerised to yield soluble high performance materials. Joshi et al[119-121] reported synthesis and characterization of silicon containing ordered poly(amide - imide)s from bis[(3-carboxyphenyl) 4-benzamide]dimethyl silane, (3-BCPBDS) and bis[(4-carboxyphenyl) 4-benzamide]dimethyl . silane, (4–BCPBDS) with various aromatic diamines, by Yamazaki's phosphorylation method. The polymers showed very high viscosity, increased solubility and good thermal stability.

Basutkar et al[111] presented series of new aromatic polyamides, polyimides and poly(amide-imide)s and their copolymers by low temperature polycondensation from novel diamine 2,5-bis(3-aminophenyl)-3,4-diphenyl

thiophene. The polymers showed solubility in aprotic organic solvents and also possessed excellent thermal stability. He also presented polyamides, polyimides and poly(amide - imide)s from two isomeric diamines, 2,5 bis[(3/4 – aminophenyl) 4-benzamide] – 3,4-diphenyl thiophene, containing preformed amide linkages. Polymers showed good solubility and thermal stability.

3.2. TMA based poly(amide - imide)s : -

Trimellitic anhydride (TMA) is widely used for the synthesis of preformed imide group containing carboxylic acids. For example, TMA can be reacted with amino-aromatic / aliphatic acids followed by chemical / thermal imidization to obtain trimellitimide group containing diacids.[122 - 124] The aromatic content of the diacid can be changed by the proper choice of the compounds used for the reaction with TMA. The ultimate properties of the polymers derived from imide-diacids depend on the nature of amino acid used for the synthesis of imide-acids.

The diimide – diacid (based on MDA / SDA) were used as starting materials for the synthesis of processable poly(amide - imide)s[125-126] and poly(ester-imide)s[127]. Earlier addition type polyimides have been developed by researchers to overcome the processing difficulties encountered with polyimides[128]. Packirisamy et al [129] reported the synthesis of diimide-diacids through the reaction of PMDA / BTDA with 3 – and 4 – aminobenzoic acids, and these diimide-diacids were used for the synthesis of addition-types poly(amide - imide)s.

Trimellitimido group containing diacids have been extensively used for the synthesis of poly(amide-imide)s [122 - 124, 130], poly(ester-imides)s [131-132],

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poly(imide-hydrazide)s[133] and poly(amide – imide – hydrazide)s.[133] Incorporation of a trimellitimido group into polymer backbone is known to improve it's tensile and mechanical properties[131-132]. Though trimellitimide group containing acids have been extensively studied for the synthesis of different types of polymers, there appears to be little information on the use of phenylated compounds with TMA.

Hence, in the present work, diimide-diacid containing highly phenylated moiety, viz. 2,5 – bis (4-trimellitimidophenyl) – 3,4 – diphenylthiophene, has been synthesized and used as a building block for preparing poly(amide - imide)s and copoly(amide - imide)s.

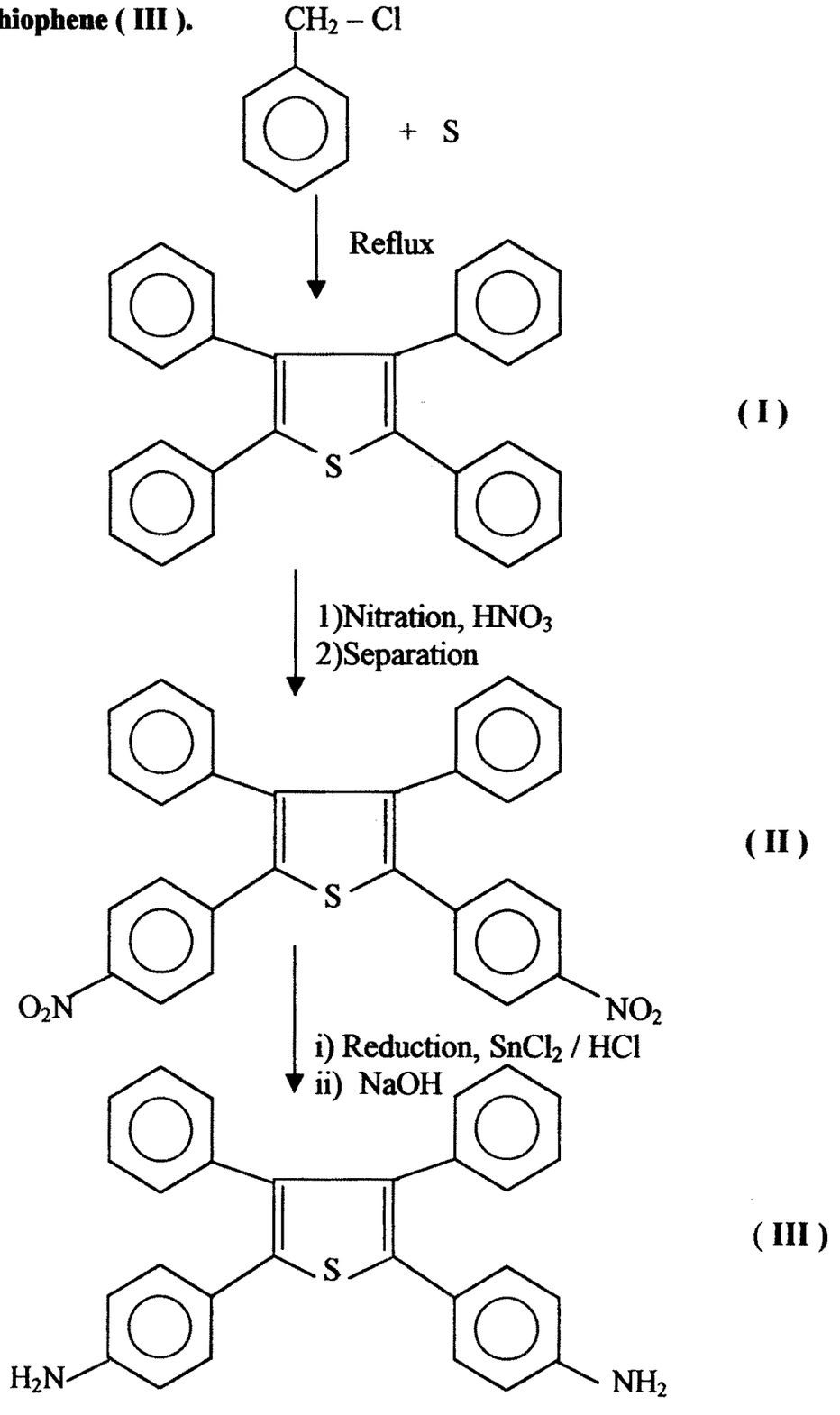
3.3. Phenylated diimide diacid :-

Among the various diimide-diacids possible, 2,5–bis(4-trielllitimidophenyl)- 3,4- diphenyl thiophene (IV) has been chosen as it has higher aromatic content, highly phenylated moiety and related structures have been earlier reported to yield soluble high – performance polymers. As the diimide – diacid (IV) is synthesized from (III) and TMA, it is anticipated that poly(amide – imide)s and copoly(amide – imide)s prepared from (IV) will have better solubility yet retaining good tensile, mechanical and thermal properties.

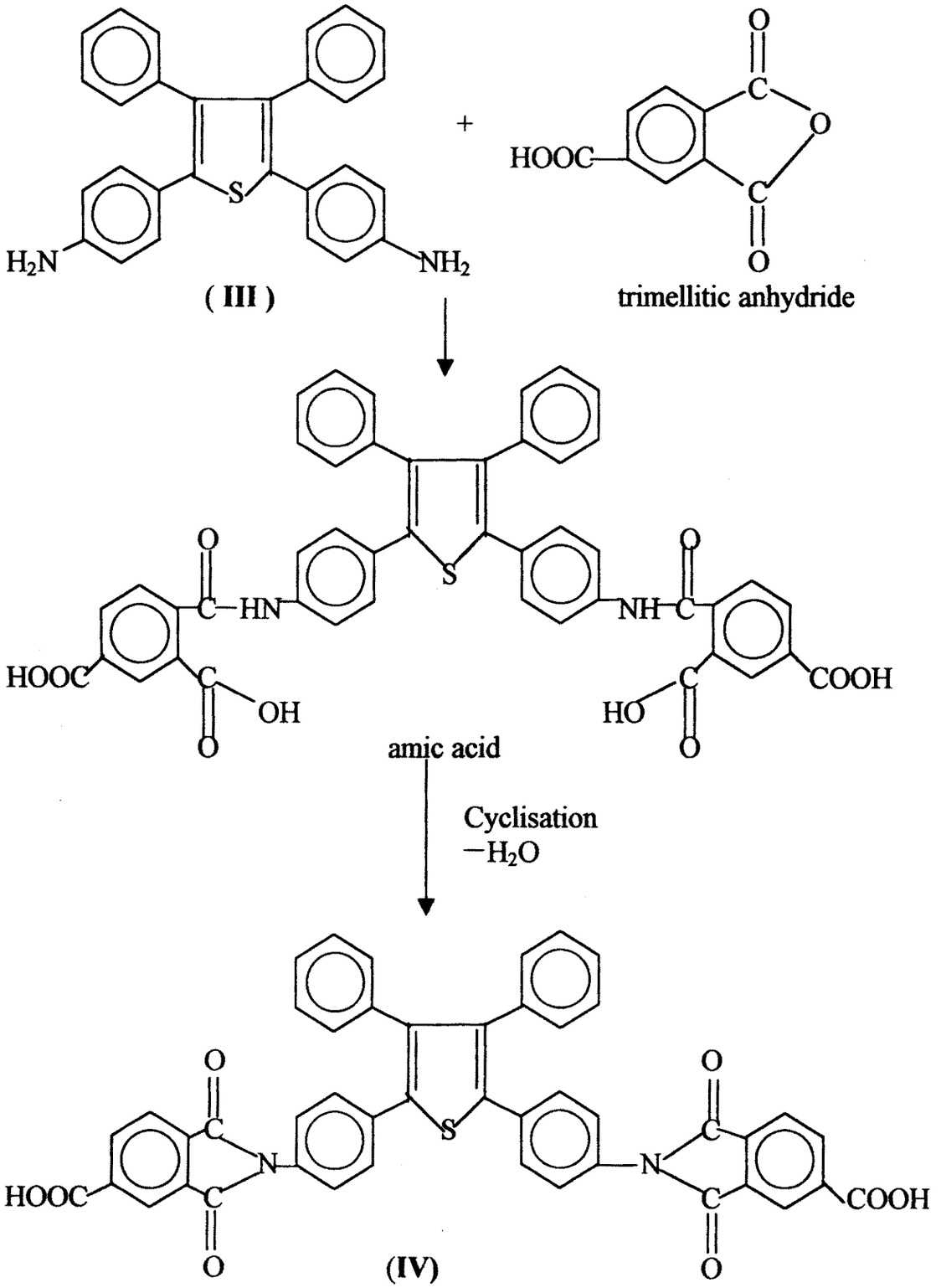
3.4. Synthesis of diimide diacid monomer (IV) : -

The novel dicarboxylic acid, 2,5-bis (4-trimellitimidophenyl) –3,4-diphenyl thiophene (IV) was synthesized in several steps. (Scheme-A and B). As per literature [111] procedure tetraphenyl thiophene (I) was prepared in good yields by refluxing benzyl chloride with sulphur. It was recrystallised from

SCHEME. A- Synthesis of 2,5 – bis (4 – aminophenyl) – 3, 4 – diphenyl thiophene (III).



SCHEME B- Synthesis of 2,5-Bis(4-trimellitimidophenyl)-3,4-diphenylthiophene. (IV)



dichloromethane – methanol system. The IR spectrum (KBr) of (I) showed absorption at 3060 (aromatic C-H), 1595 (aromatic C=C) and 1435 cm^{-1} (thiophene).

The dinitroderivative (II) of tetraphenyl thiophene was synthesized by nitration, using the reagent; concentrated nitric acid in glacial acetic acid. (II) was recrystallised from glacial acetic acid to give long yellow needles of 2,5-bis(4-nitrophenyl)-3,4-diphenyl thiophene (II). The IR spectrum (KBr) showed absorption at 1510 and 1340 cm^{-1} (- NO_2). The 2,5-bis (4-aminophenyl) –3,4-diphenyl thiophene (III) was prepared by reduction of (II) with stannous chloride and concentrated hydrochloric acid. Product was purified and recrystallised from toluene. The infrared spectrum of (III) (KBr) showed absorptions at 3420 and 3340 cm^{-1} (-NH stretching). 2,5-bis (4-trimellitimidohenyl)–3,4-diphenyl thiophene, i.e. diimide-diacid (IV) was synthesized through the reaction of (III) with trimellitic anhydride in dry dimethylacetamide under nitrogen, followed by thermal/chemical imidization with acetic anhydride and pyridine.

3.5 Characterisation of diimide-diacid (IV) :-

The diimide-diacid (IV) was characterised by elemental analysis, acid value, infrared, NMR spectra and mass spectra.

3.5.1 Elemental Analysis : -

Elemental analysis data of (IV) is given in experimental section. Percentages of carbon, hydrogen, nitrogen and sulphur found in (IV) are in good agreement with that of the calculated values.

3.5.2 Acid Value : -

Acid value calculated for (IV) is 146.5 mg KOH/g. Acid value found was 145.4 mg KOH/g. DSC scan of (IV) suggest that (IV) do not melt up to 345°C and undergo degradation / decomposition above this temperature.

3.5.3 Solubility : -

Solubility of (IV) in different solvents was checked and it dissolved in highly polar solvents such as DMF, DMAc, DMSO, NMP and partly soluble in acetone.

3.5.4 IR spectral analysis : -

The IR spectrum of (IV) is shown in Fig. 1. The characteristic imide absorption bands were observed at 1778, 1709, 1385 and 729 cm^{-1} in the IR spectrum of (IV). The broad band around 3436 cm^{-1} is due to –OH of the carboxylic acid groups. The IR spectrum of (IV) showed total absence of absorption bands of amide I and amide II (1640,1550 cm^{-1} respectively) indicating complete cyclisation to imide.

3.5.5 NMR spectral analysis : -

The ^{1}H NMR spectrum of (IV) is shown in Fig. 2. It shows multiple signals in the region 8.7 to 10.2 PPM due to aromatic protons present in the compound (IV). The signal due to –COOH group appears at 13.5 PPM. Peak corresponding to imide carbonyl in the ^{13}C-NMR spectrum of (IV) appears at 166.6 PPM where as peak, corresponding to carbonyl of carboxylic acids appear

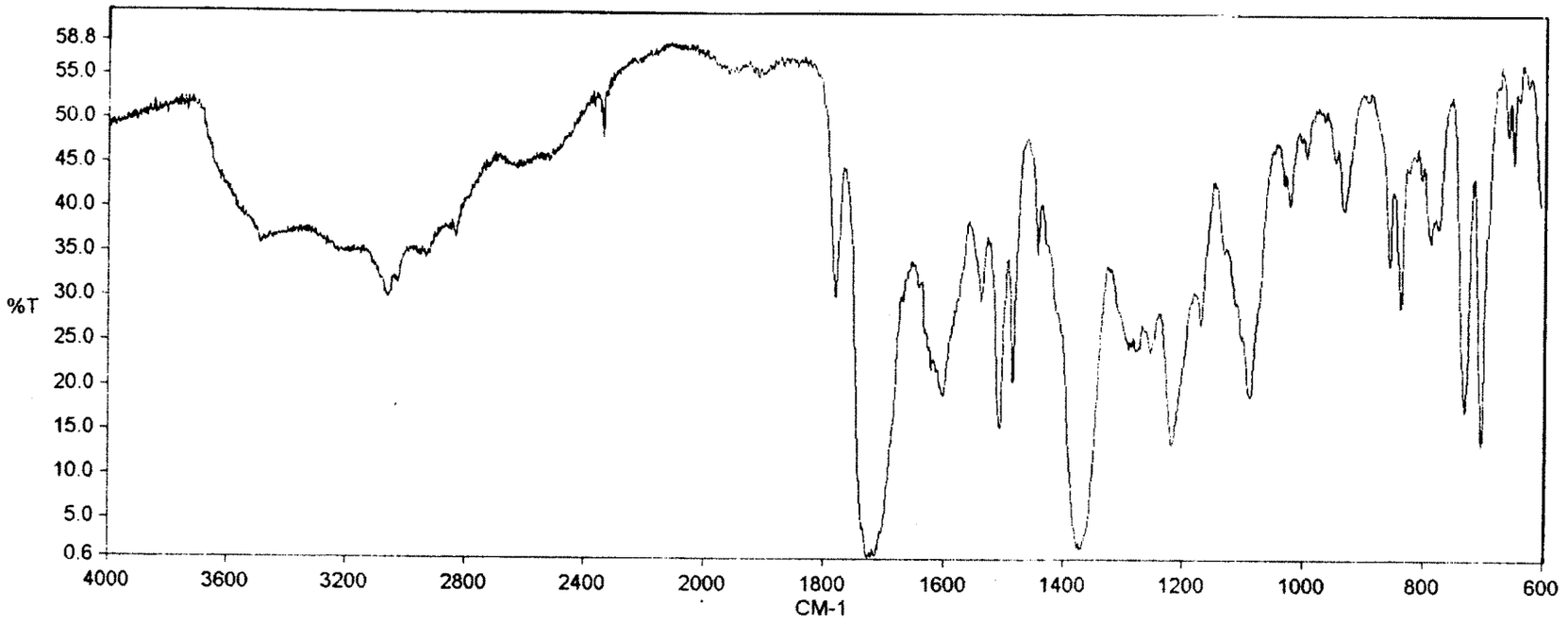


Fig. :- 1: IR of 2,5 - bis (4- trimellitimido phenyl) -3, 4 - diphenyl thiophene (IV).

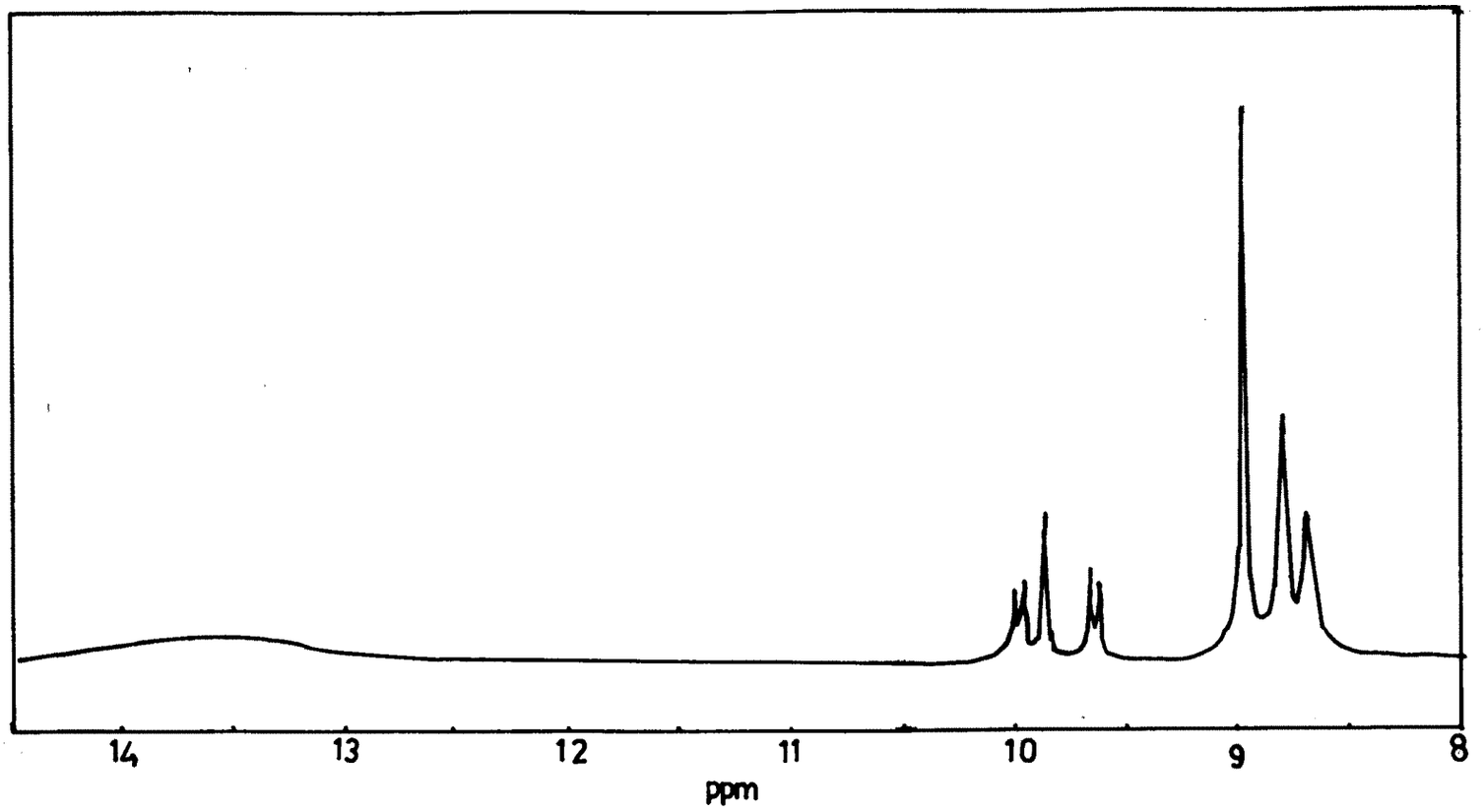


Fig. :- 2 : NMR of 2,5 - bis (4- trimellitimido phenyl) -3, 4 - diphenyl thiophene (IV).

at 165.7, PPM. Multiple peaks corresponding to aromatic carbons appear in the region 123-137 PPM in the ^{13}C NMR spectrum of (IV).

In order to confirm the assignments of the chemical shifts due to carbonyl group of carboxyl groups and carbonyl group of imides, gated decoupling techniques can be used to obtain quantitative ^{13}C NMR spectrum of (IV). The intensities of the peaks at 166.6 and 165.7 PPM in the 2:1 ratio; confirming the assignments.

3.5.6 Mass spectral analysis : -

The mass spectrum of diacid (IV) was consistent with proposed structure; the peak at (m/e) 766 corresponds to the molecular ion peak. The fragementation peaks at m/e 576 and 386 indicate loss of carboxy imidophenyl units (Fig. 3).

3.6 Polymerisation of (IV) : -

Among the methods for reacting –COOH and $-NH_2$, direct polycondensation is the most convenient approach for synthesizing high molecular weight polymers on a laboratory scale. Triphenyl phosphite – promoted polycondensation for the synthesis of polyamides was reported by Yamazaki et al [64] in 1975. Recently Russo et al [134] applied this method to the preparation of polyamides (Kevlar type) with a very high inherent viscosity of about 9.0 dL / g.

Mechanism of direct amidation was postulated by Ogata and Tanaka [135], Yamazaki et al [136] and Aharoni et al [137]. These reactions have been proposed to proceed via the N-phosphonium salts of pyridine followed by aminolysis.

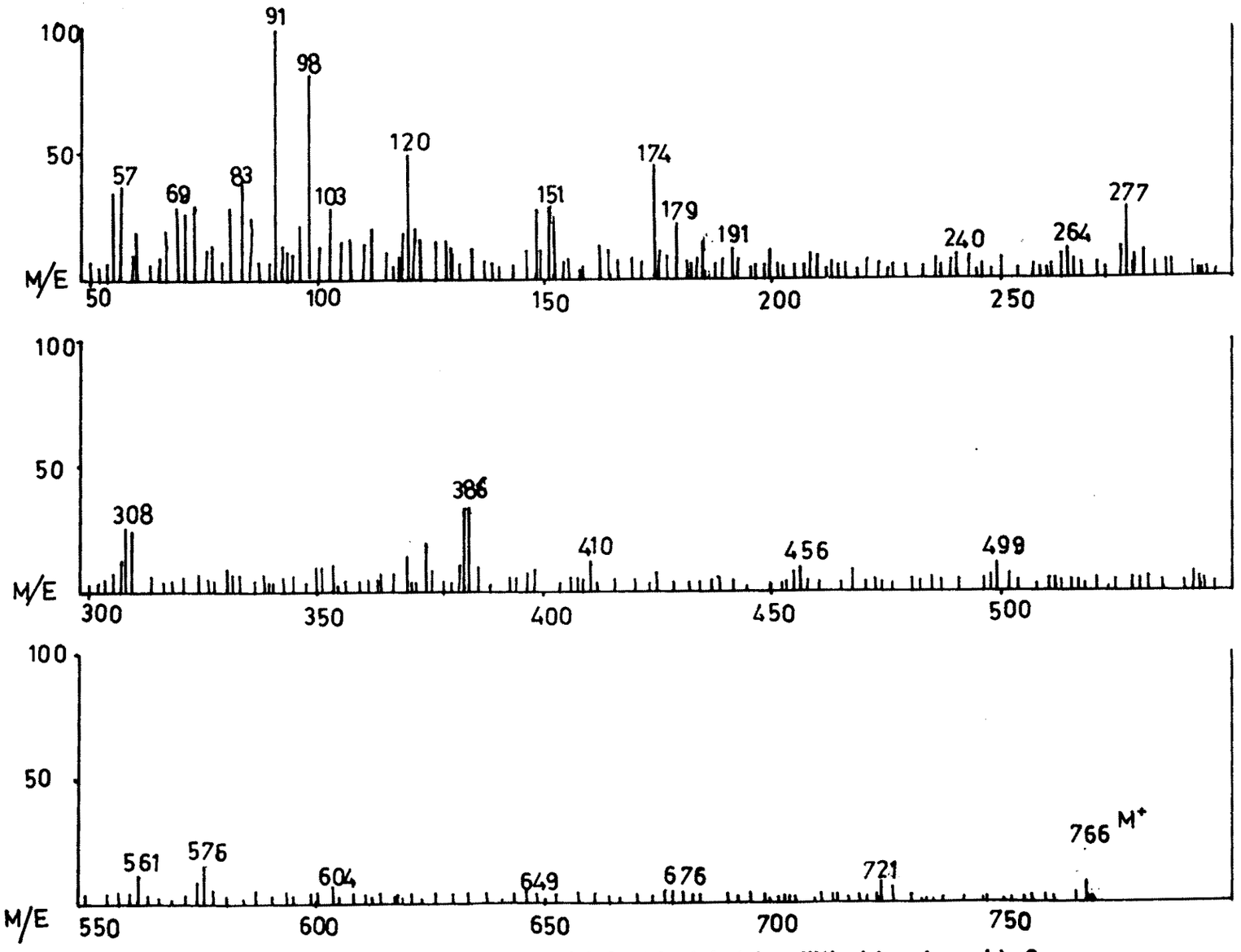
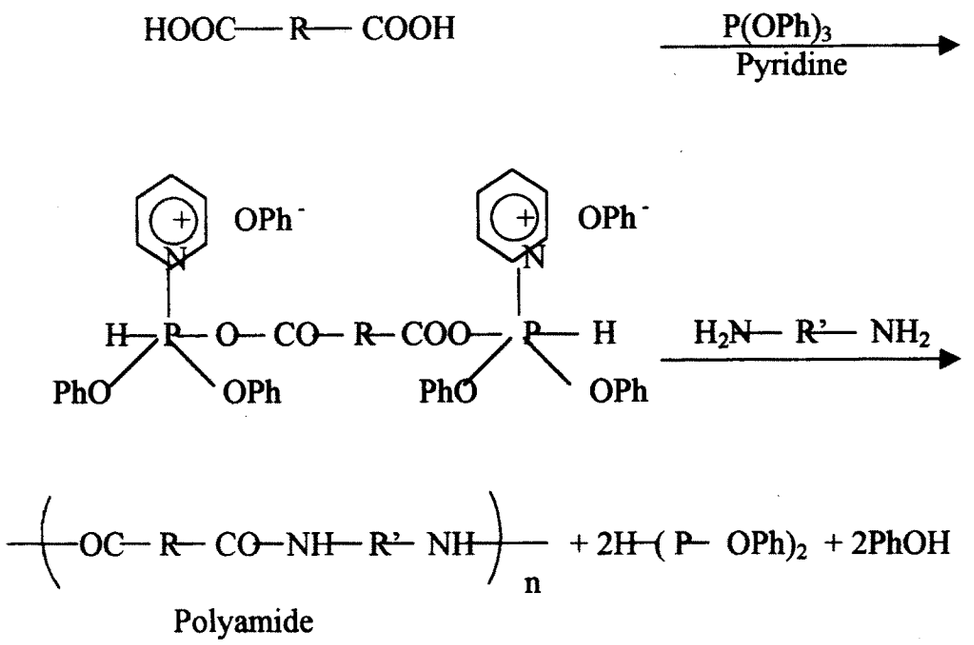


Fig. :- 3 : Mass spectra of 2,5 - bis (4- trimellitimido phenyl) -3, 4 - diphenyl thiophene (IV).



3.6.1 Philosopy of objectives : -

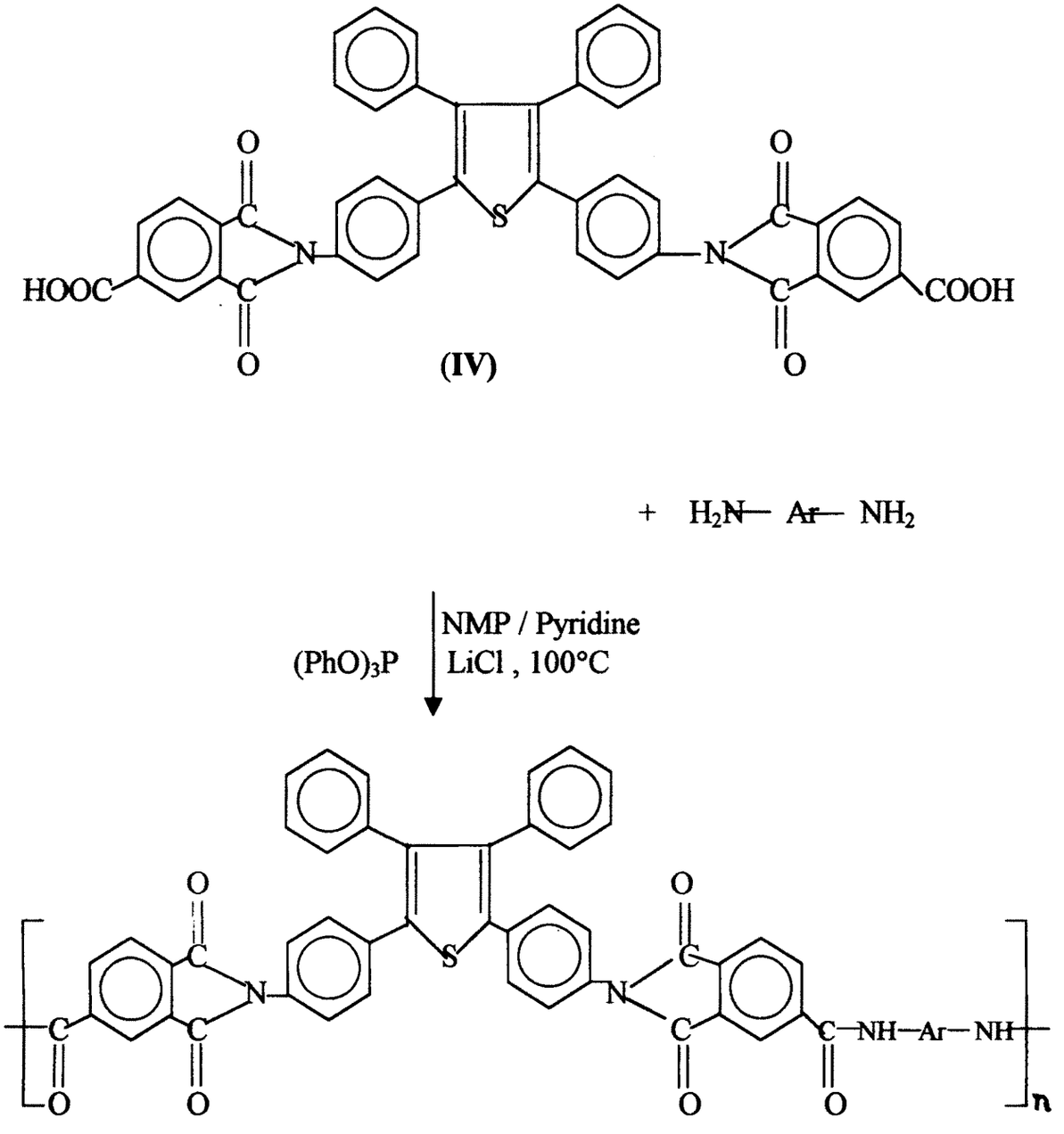
Direct polycondensation gives low results in both molecular weight and yields when applied to wholly aliphatic monomers mainly for two reasons, a) the absence of suitable solvents for highly crystalline aliphatic polyamides and b) too high basicity of the aliphatic amino group. Therefore no attempts were made to incorporate aliphatic diamines in the present studies. Further it would also bring down the thermal stability to some extent. Hence studies were restricted to the use of aromatic diamines with different structural moieties. In our laboratory Ubale et al [138] synthesized aromatic-aliphatic phenylated polyamides from the novel dicarboxylic acid, 2-5 – bis(4-carboxy methylene phenyl)-3,4- diphenyl thiophene and 2,5 – bis(4-carboxy phenyl) –3,4 – diphenyl thiophene with various aromatic diamines (by direct polycondensation method). Polyamides showed good solubility because of incorporation of pendant phenyl groups in tetraphenyl thiophene unit and the aliphatic methylene spacer. There

was no appreciable loss in thermal stability of these polyamides.Though the synthesis of (IV) was reported by Yang et. al [110] no information is available on synthesis of copoly (amide - imide)s or poly(amide - imide)s from 1,5 naphthalene diamine and (IV). Hence in present study (IV) was polycondensed with 1,5 naphthalene diamine by Yamazaki's reaction. Further there are no reports on polymerisation of (IV) using lithium chloride, though Yang reported the used of calcium chloride to obtain polymers. It is well known that the use of lithium chloride results into higher molecular weight polymers than corresponding polymers obtained by the use of calcium chloride. Again poly(amide - imide)s prepared by Yang et. al [110]. had limited solubility. Therefore in the present investigations in order to arrive at structure – property correlations of poly(amide - imide)s; a series of poly(amide - imide)s from variety of aromatic diamines and two series of copoly(amide - imide)s have been synthesised.

3.6.2 Poly(amide - imide)s : -

Series of poly(amide - imide)s were synthesized form 2,5 – bis (4 – trimellitimido phenyl) – 3,4 – diphenyl thiophene, (IV) by direct polycondensation using Yamazaki's phosphorylation method. Triphenyl phosphite was used as the condensing agent, where in the mixture of NMP and pyridine (4:1 by volume) containing 8 wt % anhydrous lithium chloride was employed as solvent (Scheme. C). The polymerizations were carried out at 100°C for 3 h. The codes and physical constant of different diamines used are given in Table – I.

SCHEME C- Synthesis of poly(amide - imide)s from (IV) and various aromatic diamines.



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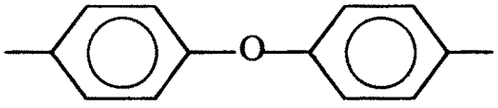

P – 1

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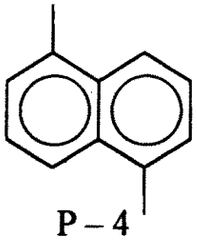

P – 4

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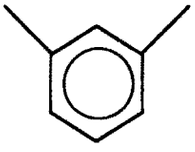

P – 2

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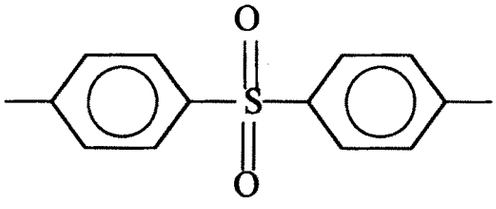
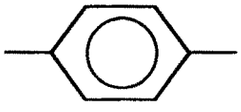


P – 5



P – 3

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Table :- I : Codes and physical constants of the aromatic diamines used.

Sr.No	Name	Code	M.P.(°C)
1)	4,4' – Diaminodiphenyl ether	ODA	190 – 192
2)	*m*- Phenylene diamine	*m*- PDA	64 – 66
3)	*p*-Phenylene diamine	*p*-PDA	143 – 145
4)	1,5 – Diamino naphthalene	NDA	185 – 187
5)	4,4'- Diamino diphenyl sulphone	SDA	175 – 177
6)	2,5-Bis (4-aminophenyl)-3,4 – diphenyl thiophene	TPTPDA	273 – 274

The polymerisation proceeds smoothly giving highly viscous solution. The precipitation of polymers during polymerisation does not take place due to the use of anhydrous lithium chloride. Yang et al reported the polymers which precipitated out during polymerisation, leading to formation of low molecular weight polymers. We overcome this drawback by the use of lithium chloride. The resulting homogenous solutions were precipitated by pouring the viscous solution into methanol. The polymers were purified by dissolving in dry dimethyl acetamide and reprecipitating by methanol.

The results of poly(amide - imide)s from 2,5-bis(4-trimellitimido phenyl) –3,4-diphenyl thiophene are given in Table II.

All the polymers were obtained in almost quantitative yield (93 to 99 %) except P-4 (NDA) 83.10%) as a pale yellow fibrous materials.

Table :– II : Comparative data on yield, viscosity and glass transition temperature of poly(amide – imide)s from(IV) and aromatic diamines[a].

Diamine	Polymer	Yield(%)		Viscosity [b] dL/g		Tg (°C)[c]	
		Present	REF	Present	REF	Present	REF
ODA	P – 1	99.03	100	2.01	1.47	320	320
m-PDA	P – 2	95.69	97	1.24	1.36	300	334
p-PDA	P – 3	98.92	95	0.92	0.49	360	333
NDA	P – 4	83.10	—	1.27	—	320	—

a) Polymerization was carried out with 1mmol each of diamines and IV.

b) Viscosity measured at concentration of 0.5 g/dL in DMAc containing LiCl at 30°C

c) Determined by DSC analysis at a heating rate of 10°C/ min under nitrogen.

REF[110] : Data from Yang C.P. and Yen Y.Y., J. Polym.Sci. A: Polym. Chem., Ed., 30,1855, (1992).

3.6.3 Copoly (amide - imide)s : -

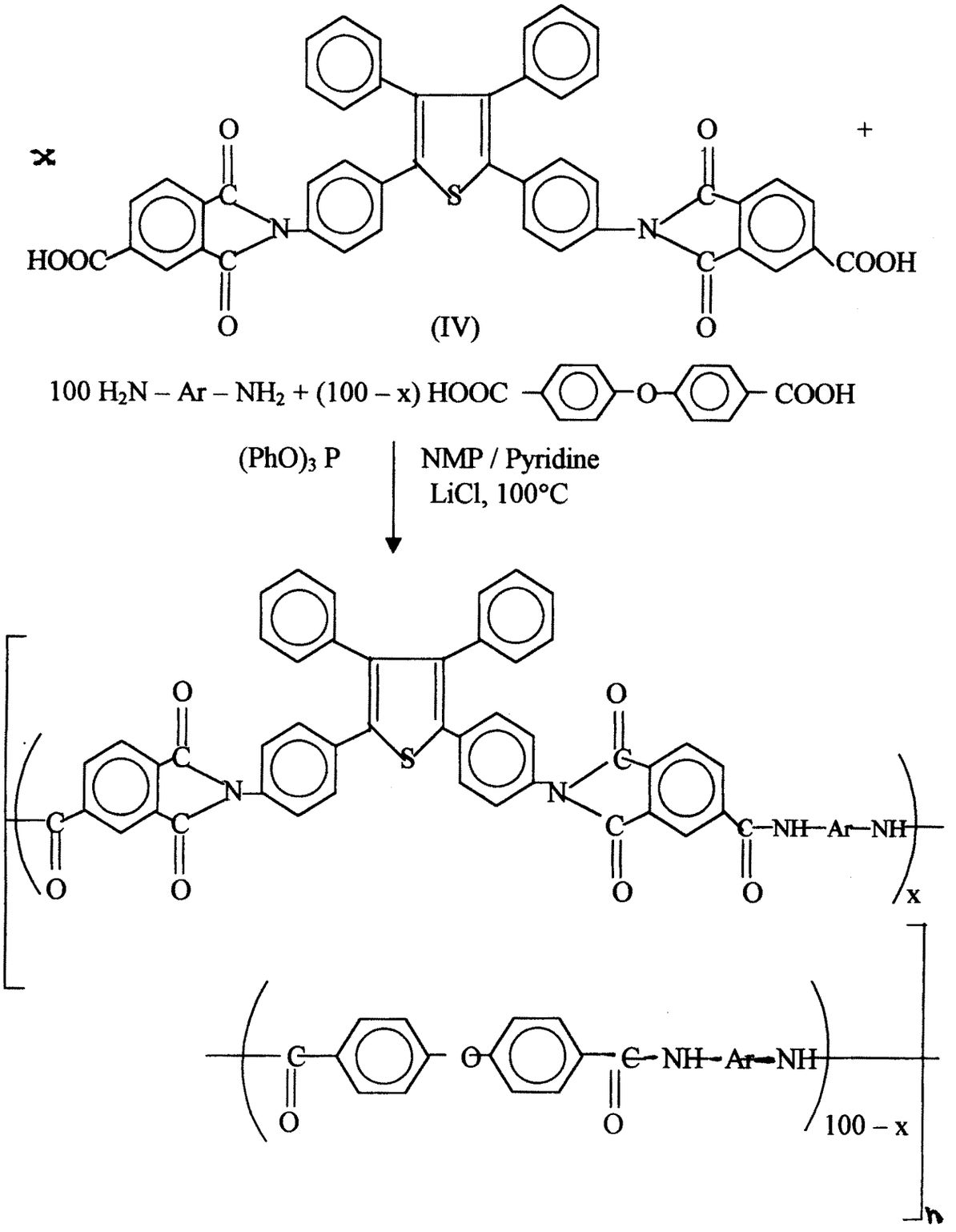
Copolymers were prepared from aromatic diamines containing flexible ether and sulphone linkage and diacid (IV), to study the effect on solubility and the thermal stability. The poly(amide - imide)s prepared by Yang et al[110] reported limited solubility. We have adopted the copolymerisation technique to enhance the solubility and processesbility by proper choice of aromatic diamines, and also by judicious choice of oxy-bis (benzoic acid) co-monomer into polymer backbone.

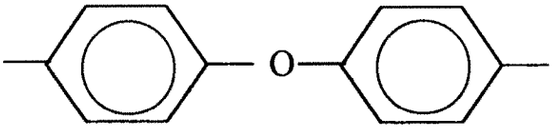
Series of copoly(amide - imide)s were synthesized from 2,5-bis(4-trimellitimido phenyl) –3,4-diphenyl thiophene (IV) with oxy-bis benzoic acid and aromatic diamines (ODA/SDA) by Yamazaki's direct polycondensation method. Triphenyl phosphite was used as the condensing agent where in the mixture of NMP and pyridine (4:1 by volume) containing 8 wt% anhydrous lithium chloride was employed as solvent. (Scheme – D). The polymerisaiton was carried out at 100 °C for 3 h. The polymerisatin proceeds smoothly giving viscous solution. The resulting copolymers were precipitatied by pouring the viscous solution in methanol. The polymers were purified by dissolving in dry DMAc and reprecipitating by methanol.

The results of copoly(amide - imide)s from 4,4' diamino diphenyl ether (ODA) i.e. CPO-1 to 4 and P-1 are given in Table – III, and those of copoly(amide - imide)s from SDA are given in Table - IV.

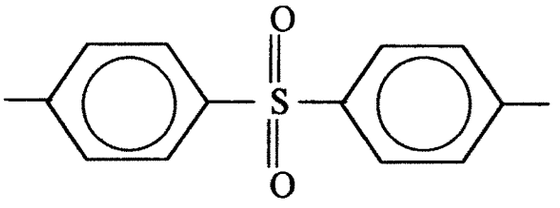
All these copolymers were obtained in almost quantitative yield (99.11 to 99.62%) as a white to pale yellow fibrous material. As quantity of diimide-diacid

SCHEME- D: Synthesis of Co - poly(amide - imide)s from aromatic diamines with (IV + o – BBA).



Ar = 

CPO	−1	−2	−3	−4	P−1
mol % x	0	25	50	75	100

Ar = 

CPS	−1	−2	−3	−4	P−5
mol % x	0	25	50	75	100

Table :– III : Synthesis of copoly(amide - imide)s from ODA and (IV + o- BBA[c]).[a]

Polymer Code	Diamine	Diacid (mol%)		Yield	Viscosity [b]
	ODA	o-BBA	IV	%	dL/g
CPO– 1	100	100	—	99.52	1.74
CPO – 2	100	75	25	99.11	2.52
CPO – 3	100	50	50	99.27	3.41
CPO – 4	100	25	75	99.62	4.48
P – 1	100	—	100	99.03	2.01

a) Polymerization was carried out with 1mmol of each diacid and diamine.

b) Viscosity measured at concentration of 0.5 g/dL in DMAc containing LiCl at 30°C.

c) *o*- BBA, 4,4' – oxy bis(benzoic acid.).

Table :– IV: Synthesis of copoly(amide - imide)s from SDA and (IV + o-BBA).

Polymer Code	Diamine	Diacid (mol%)		Yield	Viscosity [b]
	SDA	o-BBA	IV	%	dL/g
CPS – 1	100	100	—	98.93	1.22
CPS – 2	100	75	25	99.17	0.54
CPS – 3	100	50	50	98.49	0.59
CPS – 4	100	25	75	99.05	0.84
P – 5	100	—	100	93.04	0.58

a) Polymerization was carried out with 1mmol of each diacid and diamine.

b) Viscosity measured at concentration of 0.5 g/dL in DMAc containing LiCl at 30°C.

monomer (IV) increased colour of copolymers become yellowish and more fibrous in nature.

3.6.4 Characterisation of polymers : -

These polymers and copolymers were, characterised by viscosity, IR, solubility, and thermal stability, to realise that solubility can be improved by copolymerisation without scarifying the thermal stability.

3.6.4.1. Viscosity : -

The reduced viscosities of these poly(amide - imide)s were in the range of 0.92 to 2.01 dL/g. These viscosity values are better than those reported by Yang et al [110] for P-1 and P-3. This is attributed to the effect of lithium chloride. The poly(amide - imide)s give the transparent and flexible films when cast from the solution of poly(amide - imide)s in DMAc; once-again confirming the formation of high molecular weight poly(amide - imide)s.

The reduced viscosity of copoly(amide - imide)s CPO –1 to 4, and P-1 are in the range of 1.74 to 4.48 dL/g. As a mol% of dimide diacid (IV) increased the viscosity increased (Table –II, CPO-1 – 4). These copolymers gave the transparent and flexible films when cast from the solution of copolymer in DMAc, implying the formation of high molecular weight copolymers. Viscosity values for there copoly(amide - imide)s are higher than poly(amide - imide)s.

The yield and viscosities of copoly(amide - imide)s from 4,4' diamino diphenyl sulphone (SDA) i.e. CPS –1 to 4 and P –5 were summarised in Table - (IV). These copolymers were obtained in almost quantitative yield (98.49 to 99.17 %) as a white to pale yellow fibrous material, with increasing quantity

of (IV) colour of copolymers become yellowish. The reduced viscosities of these copolymers were in the range of 0.54 to 1.24 dL/g. Copolymers gave transparent films showing the formation of high molecular weight polymers.

3.6.4.2. IR spectra : -

The polymers were characterised by the infrared spectroscopy. The IR spectrum of poly(amide - imide)s (P-1 to P-5) showed the characteristic imide carbonyl absorption at 1779, 1720 and 702 cm^{-1} and amide absorption at 3320 cm^{-1} (-N-H). The disappearance of bands at 3340 cm^{-1} and 3350 cm^{-1} indicated that all the acid and amine groups have reacted to yield high molecular weight poly(amide - imide)s. Fig. 4 and Fig. 5 show the IR spectra of P-3 and P-5 respectively.

The copolymers CPO-1 to 4, P-1 and CPS-1 to 4, P-5, were also characterised by the infrared spectroscopy. The IR spectrum of copoly(amide - imide)s showed the characteristic absorption bands at 1779, 1720 and 700 cm^{-1} corresponding to imide carbonyl, 3332 (-NH strech) and 1660 cm^{-1} amide carbonyl for CPO-2 to 4, P-1 and CPS-2 to 4, P-5. In CPO-1 (Fig. 6), CPO-3 (Fig 7) and CPS-1 (Fig. 8), CPS –3 (Fig. 9). IR spectra showed bands at 3327 cm^{-1} (-NH), and 1660, 1590 cm^{-1} amide carbonyl. In CPO-1 and CPS-1 imide carbonyl bands are absent.

The absence of bands at 3440 and 3350 cm^{-1} indicated that all the acid and amine group have reacted to yield high molecular weight copoly(amide - imide)s. It is interesting to note that the intensity of absorption bands at 1780 cm^{-1} (due to imide group) increased along the copolymer series as the mol % of diimide diacid (IV) increased.

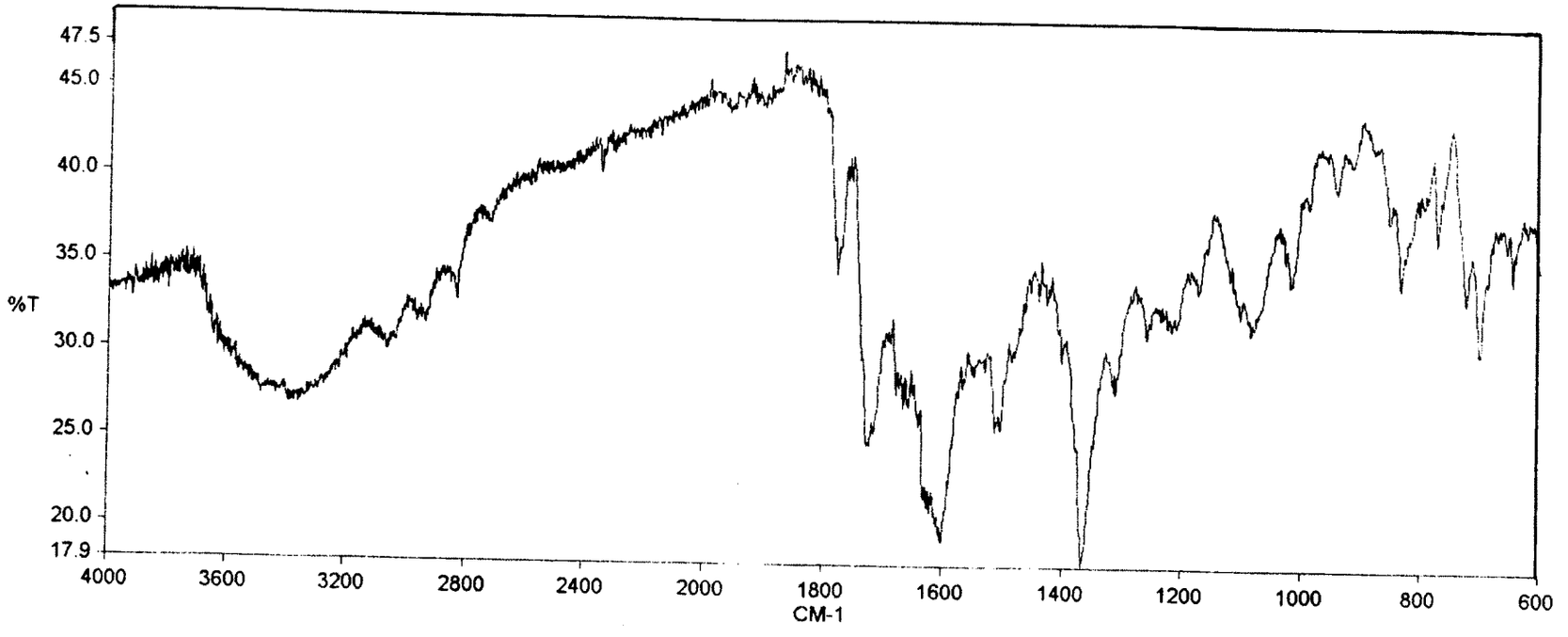


Fig. :- 4 : IR spectrum of P - 3.

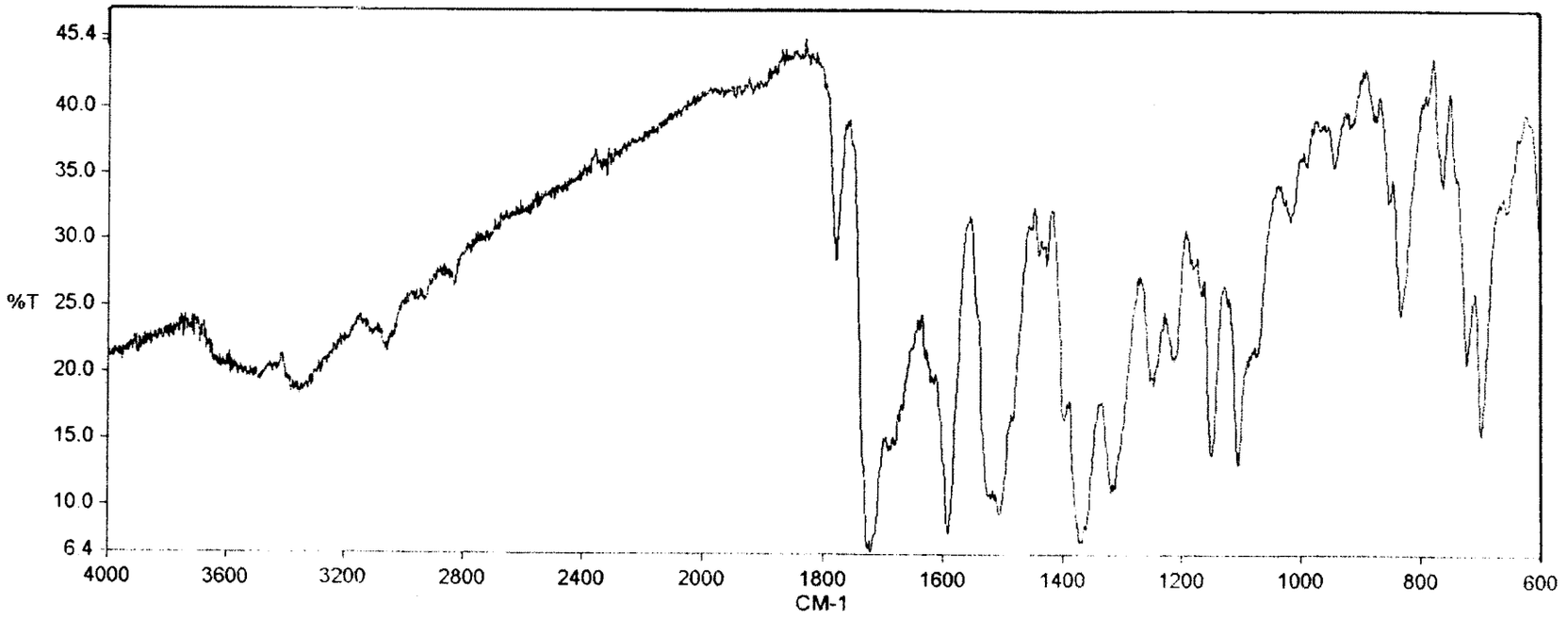


Fig. :- 5 : IR spectrum of P - 5.

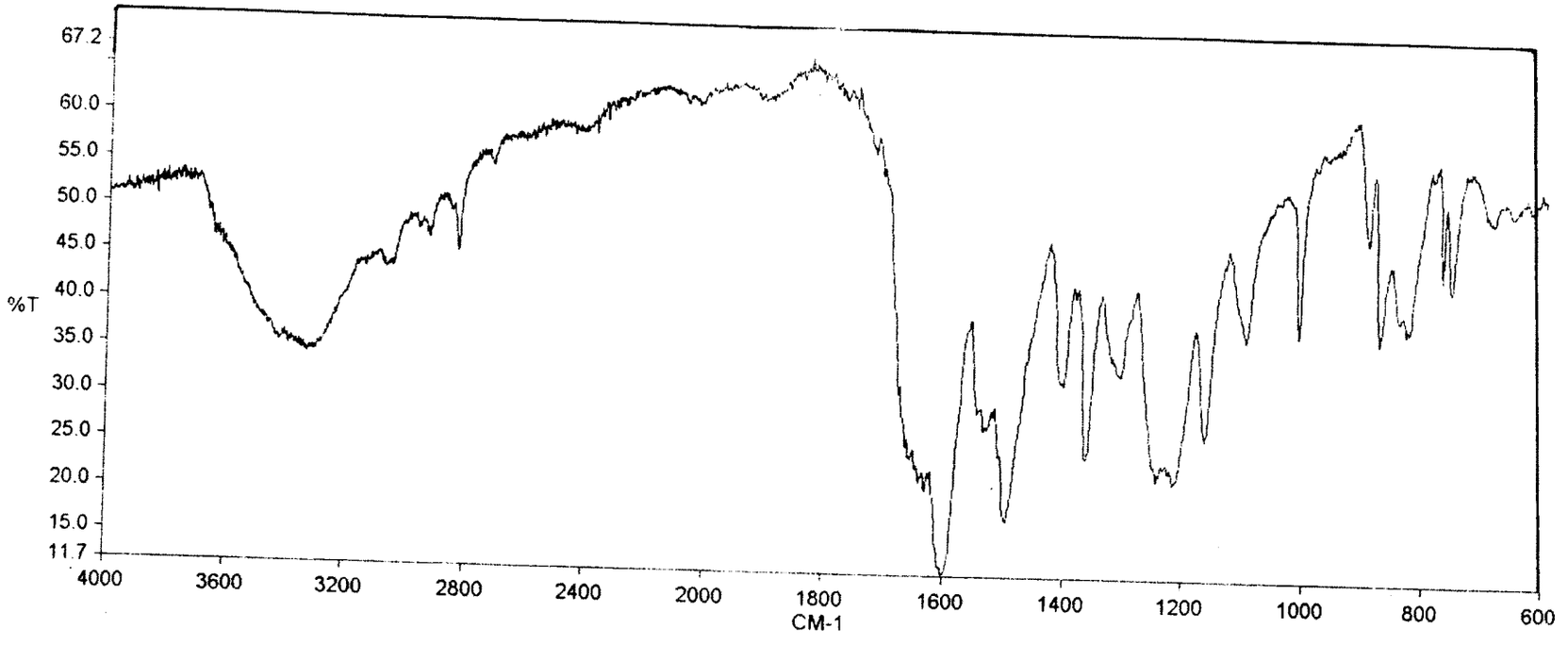


Fig. :- 6 : IR spectrum of CPO - 1.

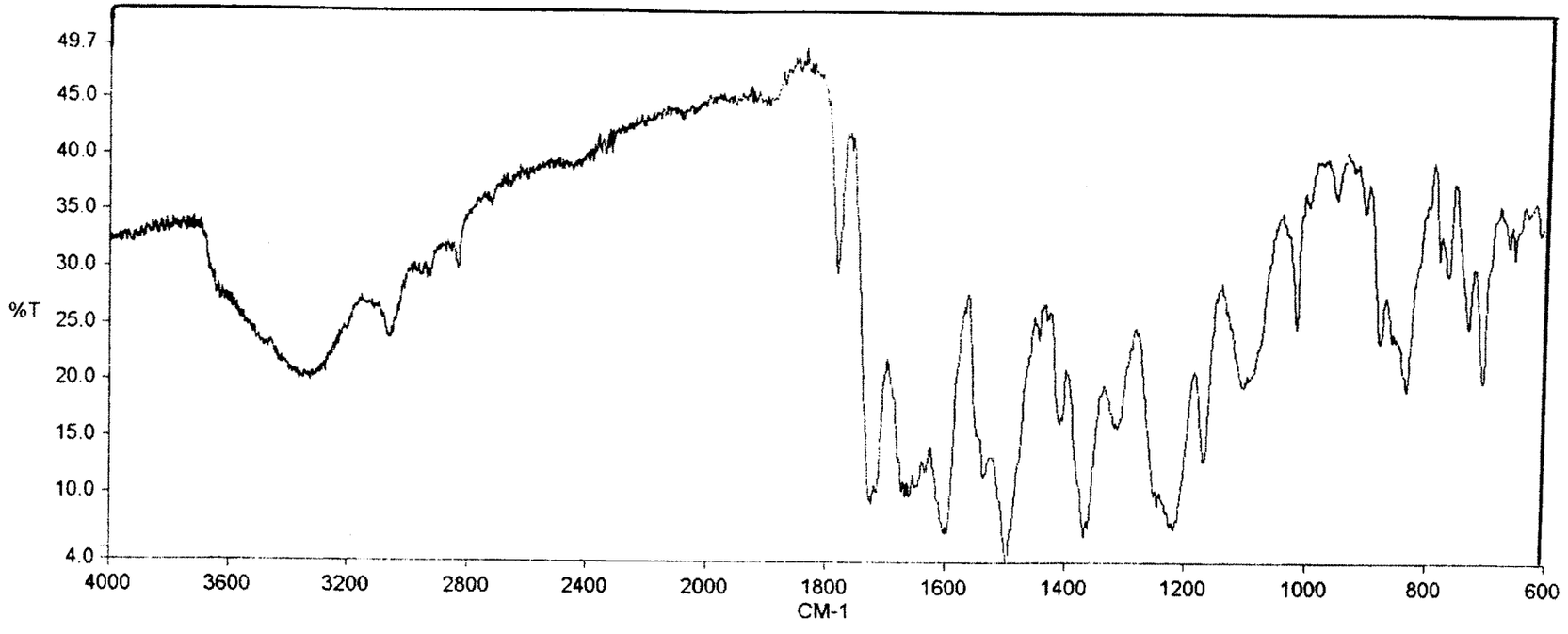


Fig. :- 7 : IR spectrum of CPO - 3.

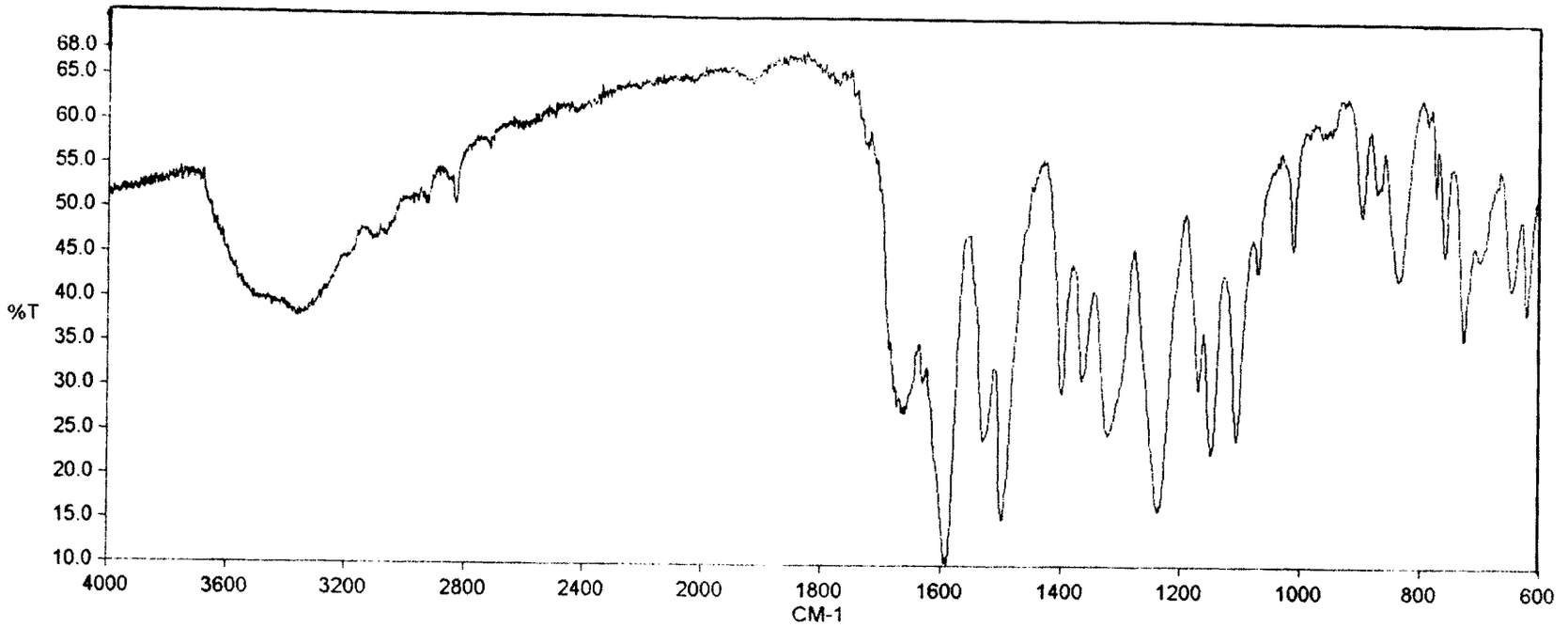


Fig. :- 8 : IR spectrum of CPS - 1.

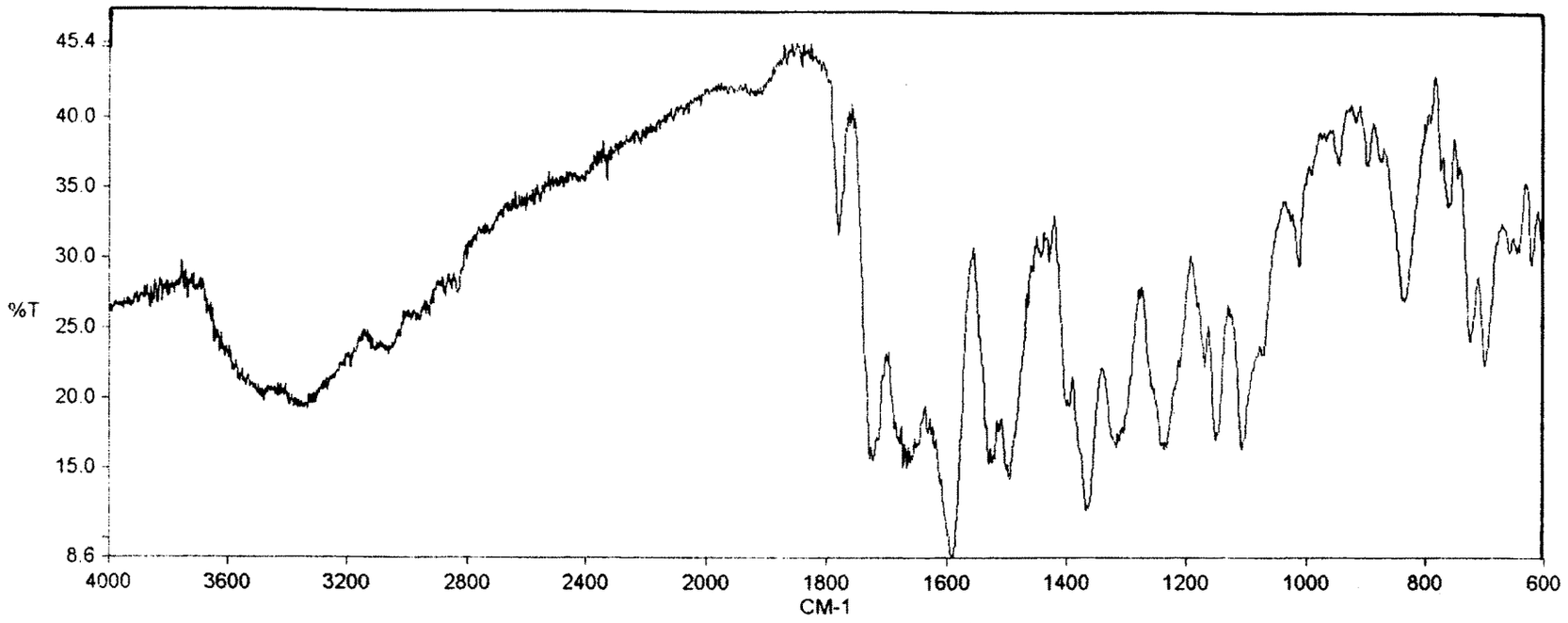


Fig. :- 9 : IR spectrum of CPS - 3.

3.6.4.3. Solubility : -

The solubility characteristics of poly(amide - imide)s are tabulated in Table-V. The solubilities of polymers were determined in different common organic solvents. A 3% solution of polymer in solvent was taken as a criterion for solubility. It was observed that poly(amide - imide)s exhibited better solubility in various aprotic solvents such as DMAc, DMSO, NMP, DMF, Pyridine, m-Cresol and Conc. H_2SO_4 but were insoluble in chlorinated solvents like $CHCl_3$, DCM, TCE etc. Solubility characteristic were better than the polymers reported by Yang et al [110]. and this may be attributed to the use of lithium chloride (inline of calcium chloride) during polymerization which aided homogenous solution polymerization and avoided precipitation of more crystalline polymer during the course of reaction.

The solubility characteristic of CPO-1 to 4, P-1 are tabulated in Table- VI and solubilities of CPS-1 to 4,P – 5, are summarised in Table-VII. The solubilites of copolymers were determined in different common organic solvents. Solubility was checked qualitatively. It was observed that copolymers exhibited very good solubility in various solvents such as DMAc, DMSO, NMP, DMF, Pyridine, *m*-cresol and Conc. H_2SO_4 but were insoluble in chlorinated solvents like $CHCl_3$, DCM, TCE etc. In case of copolymers CPO-1 to CPO-4, P-1, it was found that as a quantity of diimide diacid 2,5-bis(4-trimellitimidophenyl)-3,4-diphenyl thiophene (IV) increased the solubility of copolymers increased with increasing thermal stability.

CPS-1 to 4,P-5, copolymers showed better solubility than CPO-1 to 4,P-1 copolymer better this may be attributed to the sulphone linkage in polymer

Table :– V : Solublility of poly(amide - imide)s derived from IV and various aromatic diamines .

Solvent ↓ / polymer →	P- 1	REF	P - 2	REF	P - 3	REF	P - 4	REF
DMAc	+ +	+	+ +	+ +	+	+	+ —	N/A
DMSO	+ +	—	+ +	+ +	+	+	+ —	
NMP	+ +	+ +	+ +	+ +	+	+	+ —	
DMF	+ —	—	+ —	+ +	+ —	+ —	—	
Pyridine	+ +	—	+	+	+ —	—	+ —	
m-Cresol	+ —	—	+ +	+	+ —	+	+ —	
Conc.H_2SO_4	+ +	+ +	+ +	+ +	+ +	+ +	+ +	

REF : See Table – II.

N/A : Not applicable.

++ ; Soluble at room temperature.

+ ; Soluble on heating.

+ — ; Partly soluble.

— ; Insoluble.

Table :- VI : Solubility of copoly(amide - imide)s from ODA and (IV + o- BBA).

Solvent ↓ / Polymer →	CPO – 1	CPO - 2	CPO - 3	CPO – 4	P – 1
DMAc	—	+ +	+ +	+ +	+ +
DMSO	—	+ +	+ +	+ +	+ +
NMP	+ —	+ +	+ +	+ +	+ +
DMF	—	+	+ +	+ —	+ —
Pyridine	—	+ —	+	+	+ +
m-Cresol	—	+ —	+	+	+ —
Conc.H_2SO_4	+ —	+ +	+	+	+ +
Nitrobenzene	—	—	—	—	—
Chloroform	—	—	—	—	—
DCM	—	—	—	—	—
TCE	—	—	—	—	—
THF	—	—	—	—	—
EtOH	—	—	—	—	—

+ + ; Soluble at room temperature.

+ ; Soluble on heating.

+ — ; Partly soluble.

— ; Insoluble.

Table :– VII : Solubility of copoly(amide - imide)s from SDA and (IV + o-BBA).

Solvent ↓ / Polymer →	CPS – 1	CPS - 2	CPS - 3	CPS - 4	P – 5
DMAc	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +
NMP	+ +	+ +	+ +	+ +	+ +
DMF	+ +	+ +	+ +	+ +	+ +
Pyridine	+ +	+ +	+ +	+ +	+ +
m-Cresol	+ —	+ +	+ +	+ +	+ +
Conc.H_2SO_4	+ +	+ +	+ +	+ +	+ +
Nitrobenzene	+ —	+—	+ —	+—	+—
THF	+ —	+ —	+ —	+—	+—
Chloroform	—	—	—	—	—
DCM	—	—	—	—	—
TCE	—	—	—	—	—
EtOH	—	—	—	—	—

+ + ; Soluble at room temperature.

+ ; Soluble on heating.

+ —; Partly Soluble.

— ; Insoluble.

backbone, and comparatively lower molecular weight of SDA based copolymers. The copolymer CPS-1-4, P-5 were soluble in aprotic solvents at room temperature partly soluble in nitrobenzene, THF and insoluble in chlorinated solvents.

3.6.4.4. Thermal properties of poly(amide - imide)s : -

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry in nitrogen atmosphere. The TG curves are compared in Fig. 10-12. Fig. 13-14 represent the DSC curves of poly(amide - imide)s. Table-II incorporates the glass transition temperature (Tg), of poly(amide - imide)s and the glass transition temperatures are in the range of 300 to 360 °C.

All these poly(amide - imide)s showed a similar pattern of decomposition with no weight loss below 415 °C in nitrogen. The polymers showed T_{10} between 450 to 500 °C.

The overall thermal stability of polymers follow the trend,

$$P3 = P5 > P4 > P2 > P1$$

As per comparison of Ti values, the slightly higher thermal stability of P-3 / P-5 compared to others is due to the higher aromatic nature of p-phenylene / naphthalene and presence of the sulphone group.

Thermal behavior of all the copoly(amide - imide)s was evaluated by means of thermogravimetry and differential scanning calorimeter. The TG curves are shown in Fig. 11-12. Fig. 13 represents the DSC Curves of CPO-2 to 3. Fig 12 and 14 show TG and DSC curves of CPS-1 to 4. and P-5.

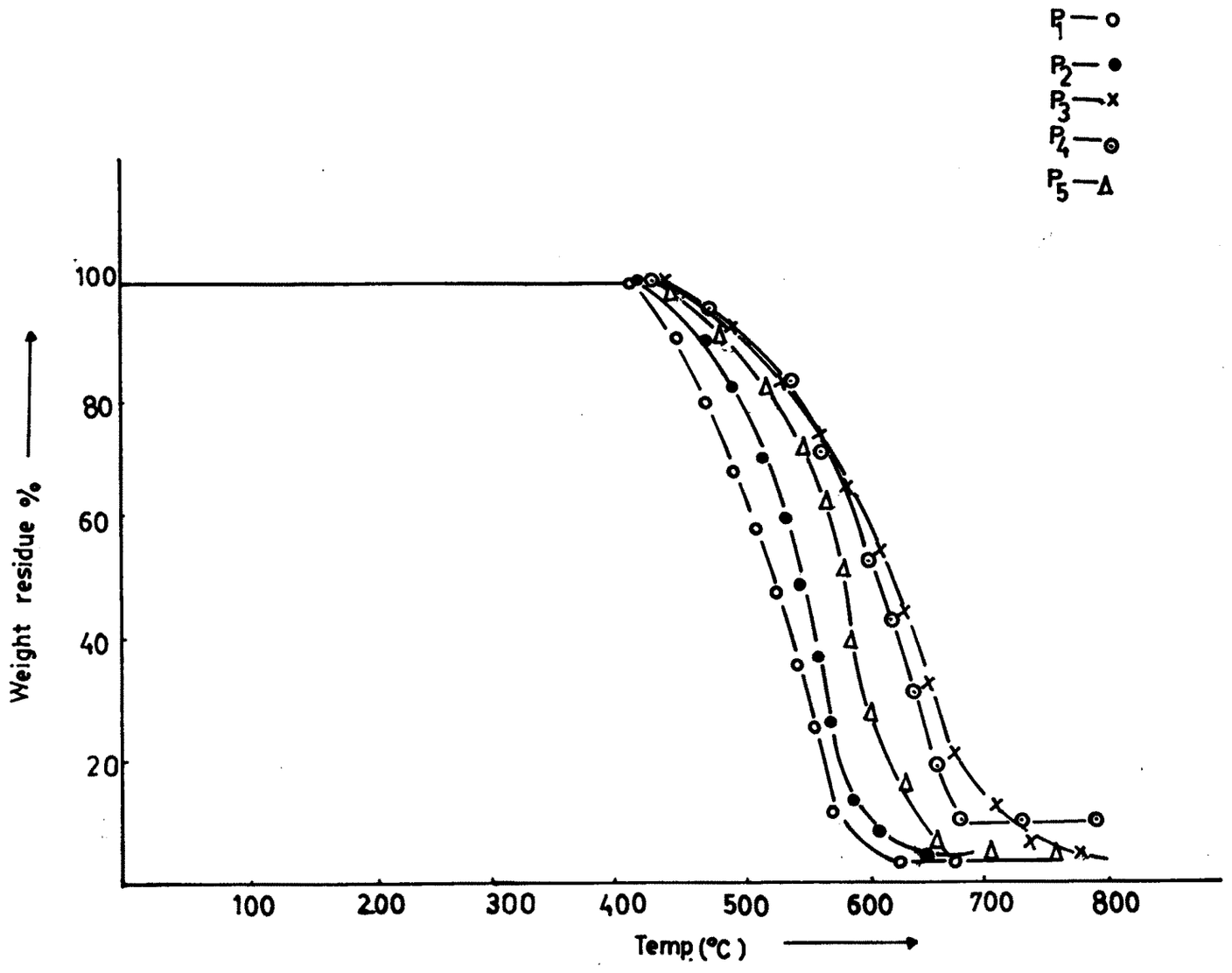


Fig. :- 10 : TG curves of polymers P- 1 to P- 5.

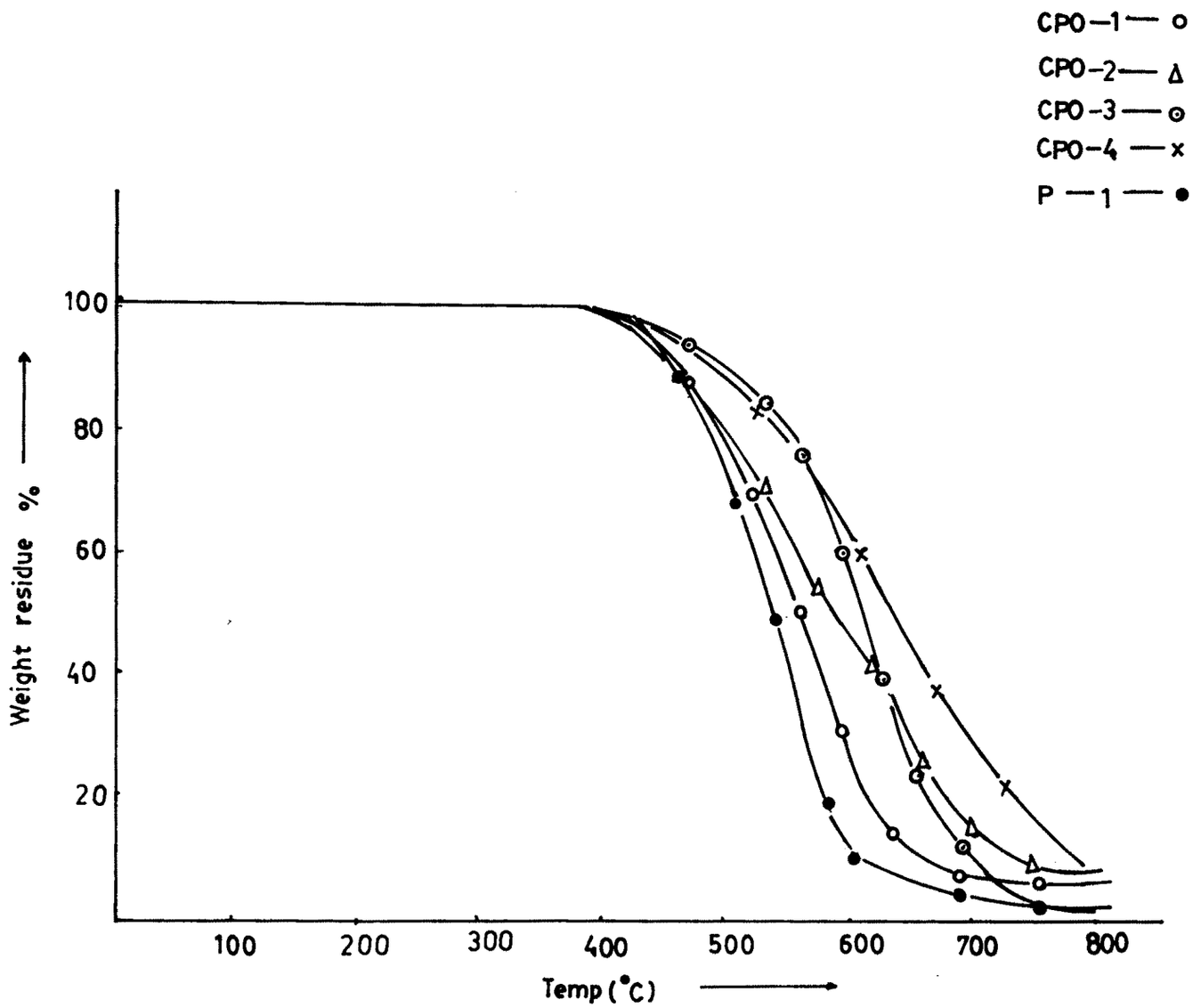


Fig. :- 11 :TG curves of CPO - 1 to CPO - 4, P- 1.

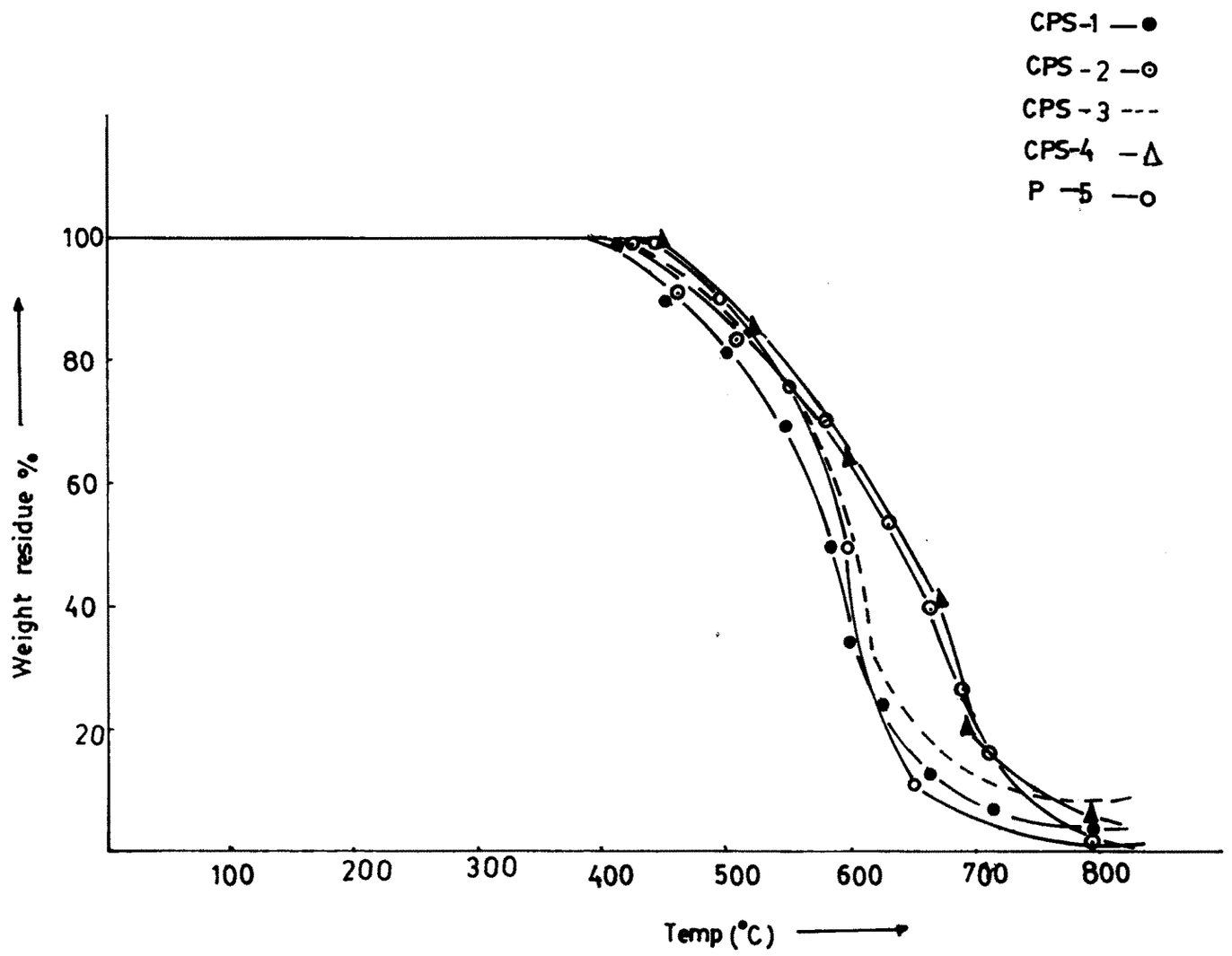


Fig. :-12 : TG curves of CPS - 1 to CPS - 4, P- 5.

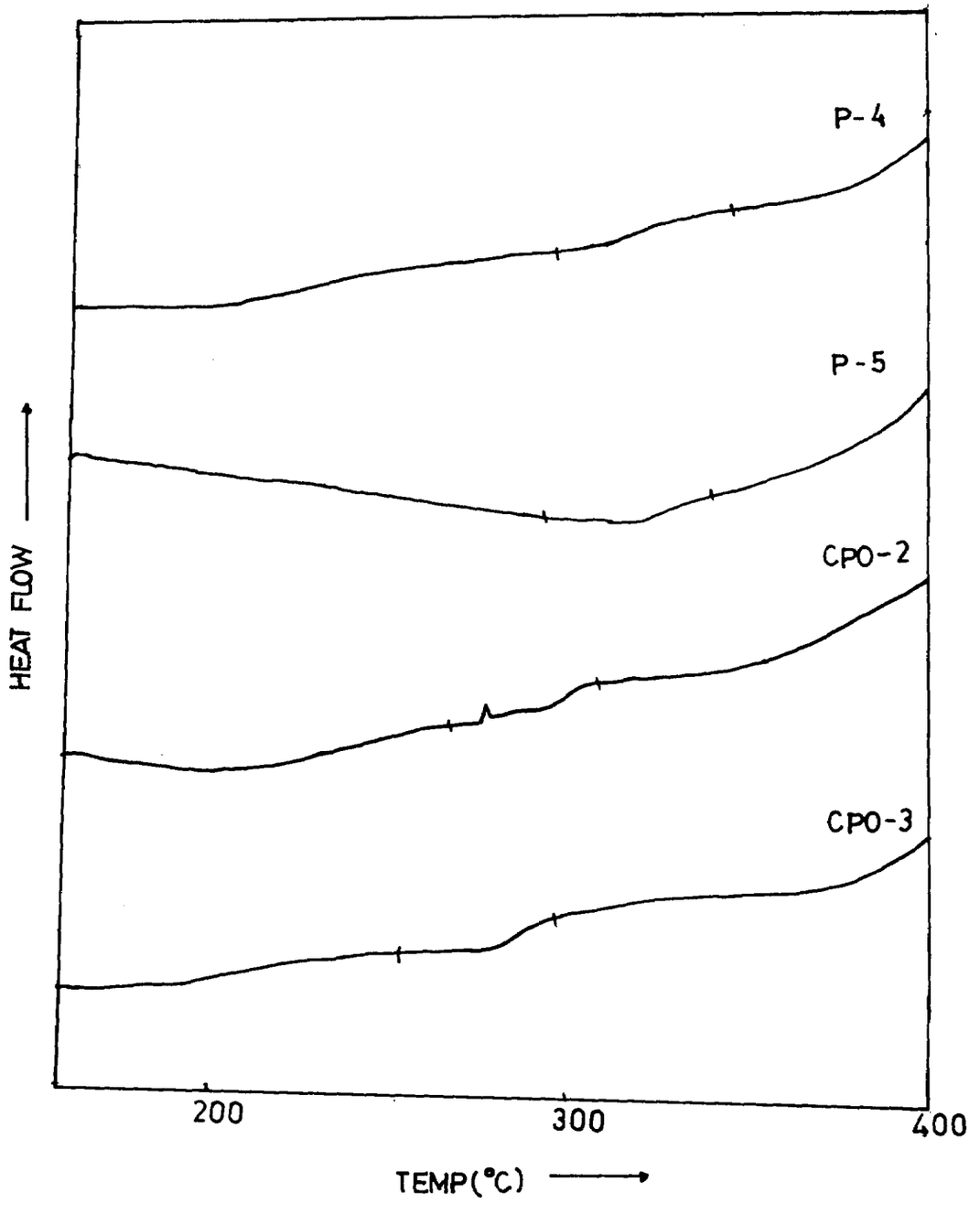


Fig. :- 13 : DSC curves of P - 4, P - 5 and CPO - 2, CPO - 3.

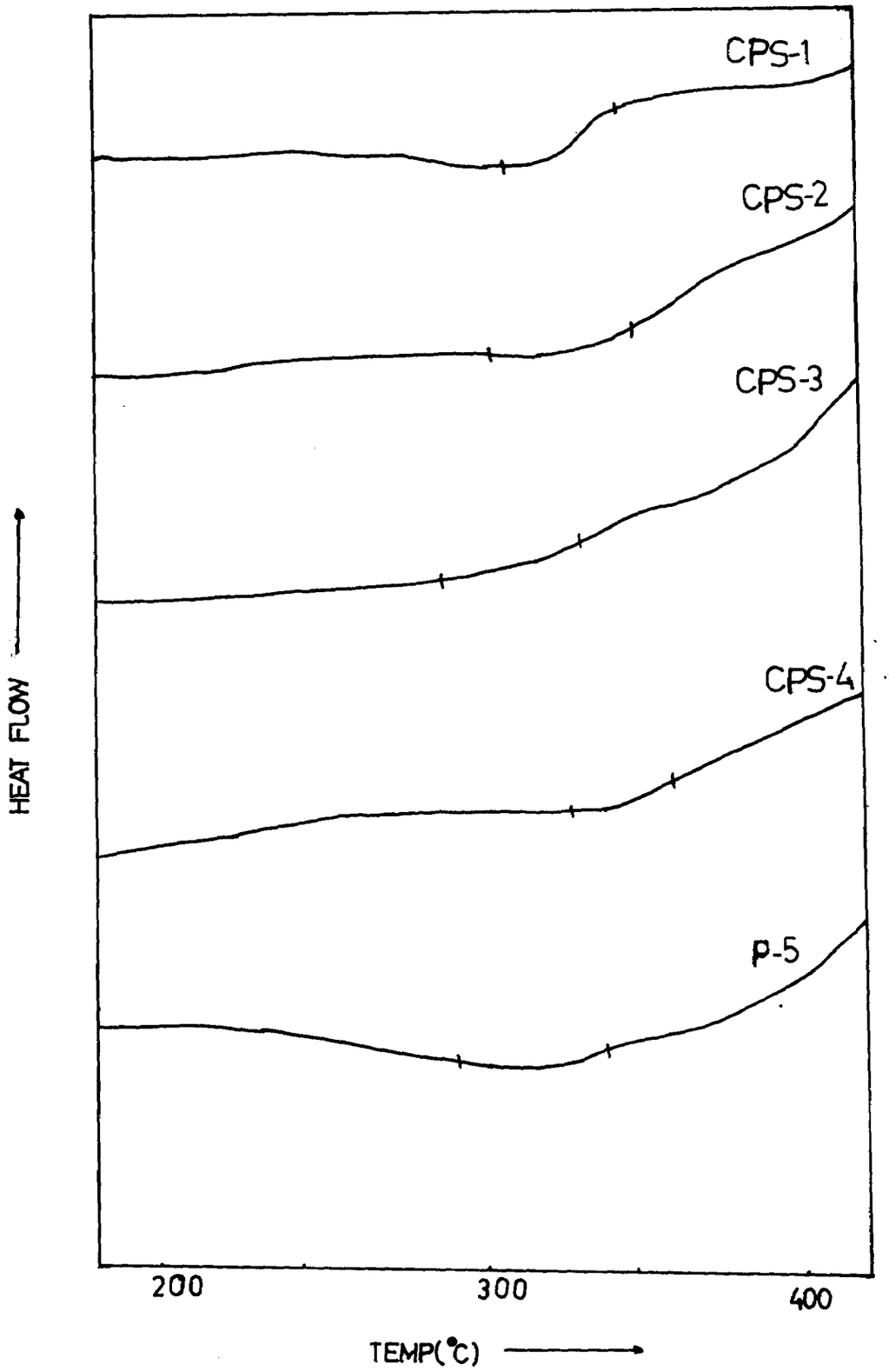


Fig. :- 14 DSC curves of CPS - 1 to CPS - 4, P - 5.

Table-VIII and IX incorporate the thermal data such as glasss transition temperature (Tg), initial decomposition temperature (Ti), temperature of 10% wt. loss (T_{10}) and 50% wt. loss temperature (T_{50}), for [CPO-1 to CPO-4 and P-1], and for [CPS-1 to CPS-4 and P-5] respectively.

Copoly(amide-imide)s i.e. CPO-1 to 4, P-1 have the glass transition temperature in the range of 252 to 325°C and copolymers from 4,4' diaminodiphenyl sulphone i.e. CPS-1 to 4, P-5 showed glass transition temperature in the range of 312 to 340°C. The glass transition temperature follow the trend.

CPO-4 > CPO-3 > CPO-2 > CPS-1 > and
CPS-3 > CPS-4 > CPS-1 > CPS-2.

Aromatic and imide group content are responsible for the considerable change in Tg with the change in the mol % of (IV). In general higher the aromatic and imide moieties, higher is the Tg, in view of the higher reigidity imparted.

All the copoly(amide - imide)s showed a similar pattern of decomposition with no weight loss below 407 °C in nitrogen. These copolymers showed T_{50} in the range of 560 to 655°C. It is interesting to note that for the copoly(amide - imide)s derived from ODA / SDA have almost similar thermal stability because the linkage of ether / sulfone have similar stability towards high temperature. However along the series of copoly(amide - imide)s as the mol % of (IV) increased, the thermal stability of copolymers increased. This may be assigned to increased imide group content as mol % of (IV) increased. Similar observation have been made earlier wherein polyimides had higher thermal stability than the corresponding polyamides.

Table :– VIII : Thermal analysis of copoly(amide - imide)s from ODA and (IV +o-BBA)[a].

Polymer code	Temp. for various % decomposition			Tg (° C)[e]
	T_i [b]	T_{10} [c]	T_{50} [d]	
CPO – 1	420	455	560	252
CPO – 2	407	460	590	275
CPO – 3	410	505	610	280
CPO – 4	425	495	655	320
P – 1	415	455	535	325

a) Thermogravimetric analysis at heating rate of 10 °C / min. under nitrogen.

b) Temperature at which initial loss of mass observed.

c) Temperature at which 10 % weight loss observed.

d) Temperature at which 50 % weight loss observed.

e) Determined by DSC.

Table :- IX :Thermal analysis of copoly(amide - imide)s from SDA and (IV + o-BBA)[a]

Polymer code	Temp. for various % decomposition			Tg (° C)[e]
	T_i [b]	T_{10} [c]	T_{50} [d]	
CPS – 1	407	450	585	315
CPS – 2	420	470	640	312
CPS – 3	420	480	600	340
CPS – 4	440	490	650	340
P – 5	440	490	590	330

a) Thermogravimetric analysis at heating rate of 10 °C / min under nitrogen.

b) Temperature at which initial loss of mass observed.

c) Temperature at which 10 % weight loss observed.

d) Temperature at which 50 % weight loss observed.

e) Determined by DSC.

3.6.4.5 X-ray diffraction studies : -

The wide-angle x-ray diffraction pattern of poly(amide - imide)s, P-4 and P-5 are given in Fig. 15. It is observed that poly(amide - imide) P-4 exhibits higher level of crystallinity, and P-5 is amorphous in nature.

The higher crystalllinity observed with polymer P-4, is attributed to the higher symmetry and more aromatic naphthalene base. Greater chain symmetry leads to close chain packing which in turn results in higher degree of crystallinity. The higher imide and aromatic content increased the brittleness of the system.

Unlike in P-4, copoly(amide - imide)s cause random placement of monomers, which reduces the orderly arrangements of polymer chains resulting in reduced crystallinity and leading to amorphous nature.

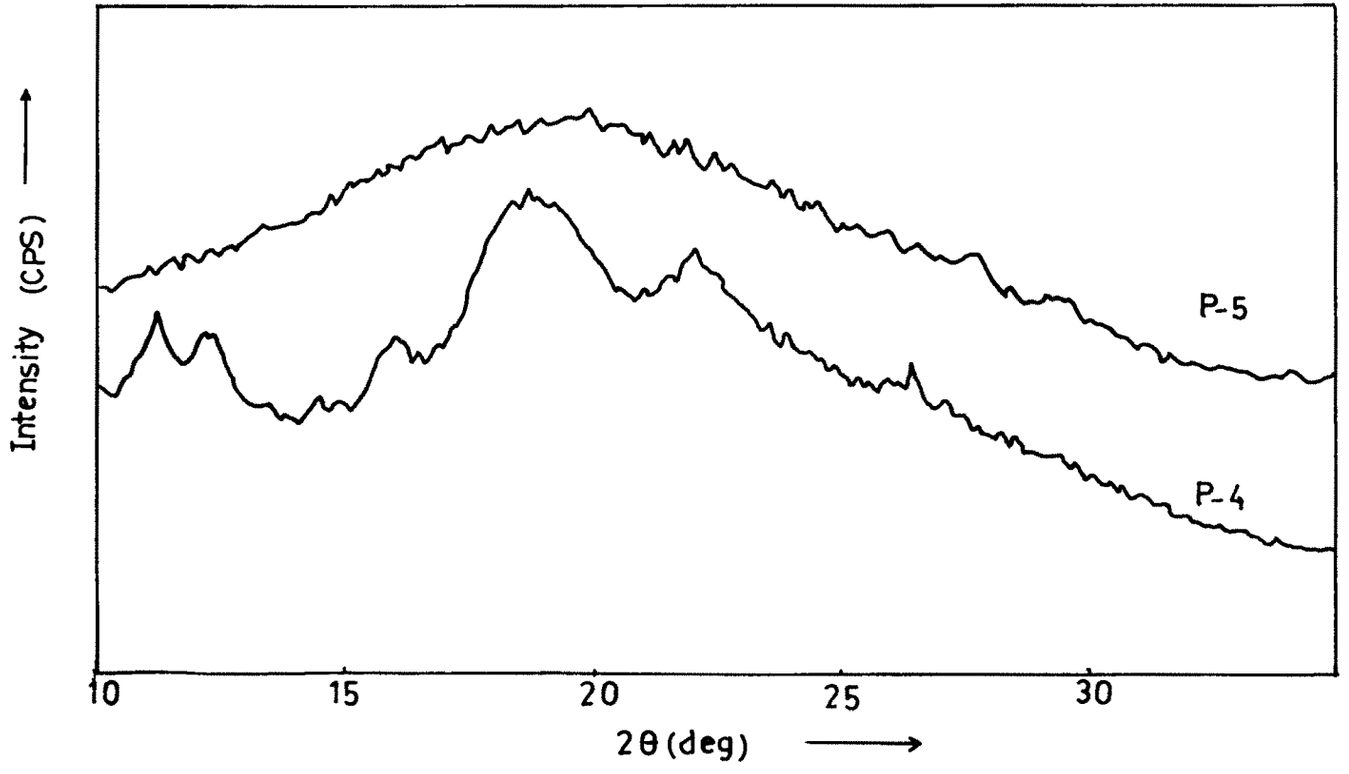


Fig. :- 15 : XRD pattern of P - 4 and P - 5.