AIMS AND OBJECTIVES

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Number of thermotropic liquid crystalline polymers are now known. Many of the results are often contradicting and clear picture regarding the effect of chemical constitution on liquid crystalline properties do not evolve as polymeric systems are more complex compared to low molecular weight liquid crystals. Homopolymers of p-hydroxybenzoic acid commercially exploited, however the role of liquid crystalline order was not known. Couple of patents on copolymers of hydroxy aromatic acids indicate the interest in the field and its industrial importance.

It was proposed in the present work to synthesize polymeric systems with varying structure and correlate the effect of chemical constitution on liquid crystalline properties of polymers.

It was proposed to homopolymerize and copolymerize hydroxy aromatic acids to study the role of different parameters on the liquid crystalline properties of homopolymers and copolymers.

Some of the polymers were to be post-polymerized in liquid crystalline phase to study the effect of ordered phase on the post-polymerized samples.

1. PREPARATION OF HOMOPOLYMERS AND COPOLYMERS FROM HYDROXY AROMATIC ACIDS:

1.1 PREPARATION OF HOMOPOLYMERS:

1.1.1 Preparation of Monomer; 3-Methoxy-4-hydroxybenzoic acid (Vanillic acid) (VA):

3-methoxy-4-hydroxybenzoic acid (VA) was prepared by the method reported in the literature (364).

4.3 mol. 97 % KOH, 2.7 mol 85 % NaOH and 50 ml. water were taken in a 2 lit.beaker. The beaker was kept on an electric hot plate equipped with an efficient mechanical stirrer. The mixture was stirred and heated upto 160°C, then the heating was stopped and 25 gm.of vanillin was added. After a short time, temperature increased upto 180°C-185°C indicating a vigorous exothermic reaction. An additional 127 gm.(total of 1 mol.) of vanillin was gradually added to the reaction mixture during the period of 12 to 15 minutes at a rate sufficient to maintain the reaction temperature with constant stirring. Stirring was continued for further 5 minutes. The hot plate was removed and the mixture was allowed to cool to about 150°C-160°C. Water was then added to dissolve the fused mass and sulfur dioxide gas was passed through it for a minute. When reaction mixture cooled to room temperature, it was acidified with

6N HCl keeping the mixture cool. Solid material was washed with water, filtered and dried. The product was recrystallized from water using 12 lit. per 100 gm. of vanillic acid; M.P. 209°C (literature:209°C) (364). The yield was about 89 %.

1.1.2 Homopolymerization (Polycondensation):

Polycondensation reaction was adopted to prepare the homopolymers from different hydroxy aromatic acids.

The hydroxy aromatic acids were purchased from HPC Co, except vanillic acid. Vanillic acid was prepared in the laboratory. Hydroxy aromatic acids were recrystallised from water and were used for the polycondensation reaction.

Solvents used in the polycondensation reaction were of high purity. All solvents were distilled and dried using anhydrous calcium chloride.

Following hydroxy aromatic acids were used to prepare homopolymers:

1) 4-hydroxybenzoic acid (PHB).
2) 3-methoxy-4-hydroxybenzoic acid (Vanillic acid)(VA).
3) 2-hydroxybenzoic acid (OHB),
4) 3-hydroxybenzoic acid (MHB).

The hydroxy aromatic acids were homopolymerized by two different methods; para substituted acids were polymerized by using thionyl chloride as condensing agent (Method-1), ortho- and meta- substituted acids were first converted to their acid chlorides, the acid chlorides were then polymerised in nitrobenzene solvent (Method-2).

Method-1: Homopolymerization of para-substituted acids by using thionyl chloride as condensing agent:

4-hydroxybenzoic acid (2.0 gm) was taken in 50 ml. round bottom quickfit flask containing 3 ml. dry benzene. 3 ml. of thionyl chloride was added as condensing agent to the flask. The care was taken against moisture absorption by providing calcium chloride guard tube on the condensor. The whole mass was heated on the water-bath by keeping the temperature between 80°C-90°C for the specific time period. After the reflux period of the desired time interval was over, the whole mass was cooled and the ice-cold water was added to the flask and shaken well. The solid material was then filtered and washed with ice-cold water, followed by ethanol washings to remove unreacted 4-hydroxybenzoic acid. The solid polymer was dried in vacuum and the melting point and transition temperatures were determined. The data is summarised in Table-11.

Table-11

Polyesters of 4-Hydroxybenzoic acid (PHB) in air using Thionyl chloride as condensing agent :

:Poly(4-oxybenzoates):

Sr. No.	Polymer	Solvent	Heating hours on water-bath/oil-bath	Transition Temperatures (°C)		
				Smectic	Nematic	Isotropic
1	HP_1	Xylene	1	306	-	324 P
2	HP_2	Xylene	3	301	-	318 P
3	HP_3	Xylene	6	327	-	340 P
4	HP_4	Toluene	1	274	-	315 P
5	HP_5	Toluene	3	297	316	323 P
6	HP_6	Toluene	6	-	-	>350
7	HP_7	Benzene	1	271	-	313 P
8	HP_8	Benzene	3	269	-	303 P
9	HP_9	Benzene	6	-	279	315 P
10	HP_{10}	Nitrobenzene	15 minutes	255	-	350 P
11	HP_{11}	Nitrobenzene	3	-	-	>350
12	HP_{12}	Nitrobenzene	3(210°C; oil-bath)	-	-	>350
13	HP_{13}	Xylene	3(140°C; oil-bath)	-	-	>350
14	HP_{14}	Toluene	3(110°C; oil-bath)	-	-	>350

P : Sample post-polymerizes and becomes solid.

To study the effect of temperature, time and solvent on the homopolymerization of 4-hydroxybenzoic acid, number of variations were tried. Table-11 summarizes all such variations carried out in the present investigation and the transition temperatures of the resultant polymers. The elemental analysis of the polymeric samples was carried out and the results are satisfactory. The analytical data is summarized in Table-16.

All the polymeric samples obtained from 4-hydroxybenzoic acid are insoluble in common organic solvents like ethanol, ether, acetone, tetrahydrofuran (THF), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), phenols, N-methyl pyrrolidone (NMP) etc. The polymers are soluble in 98 % H_2SO_4.

Similarly, homopolymers from vanillic acid, 2-hydroxybenzoic acid and 3-hydroxybenzoic acid were prepared and processed.

Different relevant data are summarized in Tables-12 and 13.

Some of the polymeric samples obtained from vanillic acid are soluble in common organic solvents.

Table-12

Polyesters of Vanillic acid in air using Thionyl chloride as condensing agent;

: Poly(4-oxy-3-methoxybenzoates):

Sr. No.	Polymer	Solvent	Heating hours on water-bath/ oil-bath	Transition Temperatures (°C)		
				Smectic	Nematic	Isotropic
1	V_1	Xylene	3	-	123	224 P
2	V_2	Xylene	6	-	179	237 P
3	V_3	Xylene	3(140°C; oil-bath)	-	-	>350
4	V_4	Benzene	3	-	215	295 P
5	V_5	Benzene	2	-	155	265 P
6	V_6	Benzene	6	-	-	>350
7	V_7	Toluene	3	-	125	238 P
8	V_8	Toluene	6	-	-	>350
9	V_9	Toluene	3(110°C; (oil-bath)	125	190	301 P
10	V_{10}	Toluene	1(110°C; oil-bath)	-	155	265 P
11	V_{11}	Nitrobenzene	3	-	-	>350
12	V_{12}	Nitrobenzene	1(210°C; oil-bath)	-	-	>350
13	V_{13}	Nitrobenzene	1	-	164	241 P

P : Sample post-polymerizes and becomes solid.

Table-13

Homopolyesters of o- and m-hydroxybenzoic acid in air using Thionyl chloride as condensing agent:

:Poly(2 -oxybenzoates) and Poly(3-oxybenzoates):

Sr. No.	Polymer	Solvent	Heating hours on water-bath/oil-bath	Transition Temp. (°C)*		
				Smectic	Nematic	Isotropic
1	OHB_1	Toluene	24(110°C;oil-bath)	-	-	155
2	OHB_2	Toluene	14(110°C;oil-bath)	-	-	060
3	OHB_3	Benzene	8	-	-	142
4	OHB_4	Xylene	10(140°C;oil-bath)	-	-	163
5	OHB_5	Nitrobenzene	3(210°C;oil-bath)	-	-	125
6	OHB_6	Xylene	18(140°C;oil-bath)	-	-	169
7	MHB_1	Toluene	4	-	-	085
8	MHB_2	Toluene	4(110°C;oil-bath)	-	-	140
9	MHB_3	Benzene	4	-	-	130
10	MHB_4	Benzene	2½	-	-	045
11	MHB_5	Nitrobenzene	½(210°C;oil-bath)	-	-	210
12	MHB_6^a	Nitrobenzene	2(210°C;oil-bath)	-	-	>350
13	OHB_7^b	Nitrobenzene	2(210°C;oil-bath)	-	-	149

* All polymers in isotropic phase are in the form of viscous liquid

a: Polymerization was carried out after preparing acid chloride of m-hydroxybenzoic acid.

b: Polymerization was carried out after preparing acid chloride of o-hydroxybenzoic acid.

The solubility behaviour of the polymers is summarized in Table - 14.

The solubility behaviour of the polymeric samples obtained from 2-hydroxybenzoic acid and 3-hydroxybenzoic acid is summarized in Table-15.

Method-2 : Homopolymerization of ortho- and meta-substituted benzoic acids (365):

Hydroxybenzoyl chloride was prepared by heating respective hydroxybenzoic acid (2.0 gm.) with thionyl chloride (3 ml.) and dry benzene (3 ml.) at 80°C followed by the removal of excess of thionyl chloride and benzene by distillation at 80°C under reduced pressure. They were suspended in freshly distilled nitrobenzene (4 ml.) and heated on an oil-bath (210°C) for two hours in air. The mixture was cooled, and diluted with alcohol, the solid seperates which was filtered, washed with ethanol and dried in vacuum. The melting points were determined. The data is summarized in Table-13.

The elemental analysis of the polymeric samples was carried out and the results were satisfactory. The analytical data is summarized in Table-16.

Table-14

Solubility Behaviour of Different Polyesters of Vanillic acid:

Sr. No.	Polymer	Solubility Behaviour					
		Ethanol	DMF	DMSO	Phenol	NMP	H_2SO_4(98%)
1	V_1	(-)	(+)	(+)	(+)	(+)	(+)
2	V_2	(-)	(+)	(+)	(+)	(+)	(+)
3	V_3	(-)	(-)	(-)	(±)	(±)	(+)
4	V_4	(-)	(+)	(+)	(+)	(+)	(+)
5	V_5	(-)	(-)	(-)	(±)	(±)	(+)
6	V_6	(-)	(-)	(-)	(±)	(±)	(+)
7	V_7	(-)	(+)	(+)	(+)	(+)	(+)
8	V_8	(-)	(-)	(-)	(±)	(±)	(+)
9	V_9	(-)	(-)	(-)	(±)	(±)	(+)
10	V_{10}	(-)	(-)	(-)	(±)	(±)	(+)
11	V_{11}	(-)	(-)	(-)	(±)	(±)	(+)
12	V_{12}	(-)	(-)	(-)	(±)	(±)	(+)
13	V_{13}	(-)	(-)	(-)	(±)	(±)	(+)

(+) : Soluble.

(±) : Partly soluble.

(-) : Insoluble.

Phenol : m-cresol, o-cresol, p-chlorophenol.

Table-15

Solubility Behaviour of Homopolyesters of o- and m-hydroxybenzoic acid :

Sr. No.	Polymer	Solubility Behaviour			
		DMF	DMSO	NMP	Phenol
1	OHB_1	(+)	(+)	(+)	(+)
2	OHB_2	(+)	(+)	(+)	(+)
3	OHB_3	(+)	(+)	(+)	(+)
4	OHB_4	(+)	(+)	(+)	(+)
5	OHB_5	(+)	(+)	(+)	(+)
6	OHB_6	(+)	(+)	(+)	(+)
7	OHB_7	(-)	(-)	(-)	(-)
8	MHB_1	(+)	(+)	(+)	(+)
9	MHB_2	(+)	(+)	(+)	(+)
10	MHB_3	(+)	(+)	(+)	(+)
11	MHB_4	(+)	(+)	(+)	(+)
12	MHB_5	(+)	(+)	(+)	(+)
13	MHB_6	(-)	(±)	(±)	(-)

(+) : Soluble.

(±): Partly soluble.

(-) : Insoluble.

Table-16

Elemental Analysis of Different Homopolyesters:

Sr. No.	Polymer	Found	
		C %	H %
	Poly(4-oxybenzoate)		
1	HP_2	65.88	3.44
2	HP_6	68.63	3.92
3	HP_9	67.85	3.71
4	HP_{10}	65.74	4.28
5	HP_{11}	68.81	3.74
6	HP_{16}	68.78	3.15
	Poly(4-oxy-3-methoxybenzoate)		
7	V_2	62.58	4.74
8	V_5	63.24	4.82
9	V_7	63.14	3.76
10	V_8	61.59	3.67
11	V_9	61.88	5.28
12	V_{12}	62.78	4.92
13	V_{14}	62.31	4.38
14	V_{16}	63.01	5.12
	Poly(2-oxybenzoate)		
15	OHB_1	65.89	3.34
16	OHB_3	68.53	3.23
17	OHB_5	66.75	3.74
18	OHB_7	68.53	3.47

Table-16 (contd)

Sr.No.	Polymer	Found	
		C %	H %
	Poly (3-oxybenzoate)		
19	MHB_1	67.58	3.16
20	MHB_3	65.76	3.45
21	MHB_5	68.54	3.24
22	MHB_6	68.69	3.38

i) Molecular formula of the repeating unit for homopolyesters prepared from PHB, OHB and MHB: $C_7H_4O_2$;
Required : C = 70 %; H = 3.30 %.

ii) Molecular formula of the repeating unit for homopolyesters prepared from VA : $C_8H_6O_3$.
Required C = 64.00 % ; H = 4.00 %.

Solubility behaviour of polymeric samples in different solvents is summarized in Table-15.

1.2 PREPARATION OF COPOLYMERS:

1.2.1 Copolycondensation of 2-hydroxybenzoic acid with 3-hydroxybenzoic acid by using thionyl chloride as condensing agent:

A mixture of 2-hydroxybenzoic acid (2 gm.) and 3-hydroxybenzoic acid (2 gm.) as monomers was taken in 50 ml. round bottom quickfit flask containing 5 ml. dry nitrobenzene as a solvent. 4 ml. of thionyl chloride was added as condensing agent. The care was taken against moisture absorption by providing calcium chloride guard tube on the dry condensor. The whole mass was heated on an oil-bath for specific time period. After the reflux period was over, the whole mass was cooled and poured in ice-cold water and shaken well. The material was then filtered and washed with ice-water, followed by cold alcohol washings to remove unreacted monomers and the solvent. The solid polymers was dried in vacuum. One more copolymer with different molar ratio was prepared under same experimental conditions (Table-17).

The melting points were determined (Table-17).

Table - 17

Copolyesters of o-and m-hydroxybenzoic acid in air using Thionyl chloride as condensing agent : Poly (2-Co-3-oxybenzoates) :

Sr. No.	Polymer	Heating hours on oil-bath	Transition Temperatures (°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	O-Co-M_1^a	2½ (210°C)	-	-	228	(-)	(±)	(±)	(±)
2	O-Co-M_2^b	2½ (210°C)	-	-	180	(-)	(±)	(±)	(±)

a : OHB=0.25 mole and MHB = 1.00 mole.

b : OHB=1.00 mole and MHB= 1.00 mole.

(±): Partly soluble.

(-): Insoluble.

Elemental analysis of the polymeric samples was carried out. The results were satisfactory. The data is summarized in Table-22. The solubility behaviour in different solvents is summarized in Table-17.

1.2.2 Copolymerization of 4-hydroxybenzoic acid with 3-hydroxybenzoic acid and 3-methoxy-4-hydroxybenzoic acid using Thionyl chloride as condensing Agent:

Different molar porportions of hydroxy aromic acid monomers were taken and the copolymerization was carried out as follows:

A mixture of 4-hydroxybenzoic acid (2 gm.) and 3-hydroxybenzoic acid (0.1 gm.) as monomers was taken in 50 ml. round bottom quickfit flask containing 3.0 ml. dry benzene as solvent, 3.0 ml. of thionyl chloride was added as condensing agent. The whole mass was heated on the water-bath by keeping temperature between 80°C-90°C for four hours. After the reflux period was over, the whole mass was cooled and poured in ice-cold water and shaken well. The material was then filtered and washed with ice-cold water, followed by cold ethanol washings to remove unreacted monomers. The solid polymer was dried in vacuum.

To study the effect of molar ratios on the mesomorphic nature of polymers, different copolymers were prepared by varying the ratio of PHB : MHB. The transition temperatures, elemental analysis and the ratios of PHB : MHB are summarised in Tables-18, 22.

Some of the polymeric samples are insoluble in common organic solvents but they are soluble in 98 % H_2SO_4. Solubility behaviour of the copolymers is summarized in Table-19.

By varying the molar ratios of PHB and VA, copolymers were prepared by following above method. Different relevant data are summarized in Tables-20 to 22.

1.3 POST-POLYCONDENSATION OF POLYMERS:

1.3.1 Post-polycondensation of Homopolymers:

The homopolymers of PHB (HP_3) (Table-11) and VA (V_7) (Table-12) exhibiting mesophases were post-polymerized by heating them in different conditions (Tables-23 and 24) in liquid crystalline state. The thermal and mesogenic behaviour of the post-polymerized samples are summarized in Tables-25 and 26.

All the post-polymerized samples are insoluble in common organic solvents, but are soluble in 98 % H_2SO_4.

Table - 18

Co-polyesters of 4-hydroxybenzoic acid and 3-hydroxybenzoic acid in air using Thionyl chloride as condensing agent : Poly(4-Co-3-oxybenzoates):

Sr. No.	Polymer	Molar proportion of PHB	Molar proportion of OHB	Transition Temperatures (°C)		
				Smectic	Nematic	Isotropic
1	P-Co-M_1	1.00	0.05	-	150	302 P
2	P-Co-M_2	1.00	0.10	-	150	302 P
3	P-Co-M_3	1.00	0.15	160	225	302 P
4	P-Co-M_4	1.00	0.25	145	231	289 P
5	P-Co-M_5	1.00	0.50	-	190	301 P
6	P-Co-M_6	1.00	0.80	-	085	205
7	P-Co-M_7	1.00	1.00	056	-	130
8	P-Co-M_8	0.25	1.00	-	064	106
9	P-Co-M_9	0.50	1.00	-	062	106
10	P-Co-M_{10}	0.80	1.00	-	060	135

P : Sample post-polymerizes and becomes solid.

Table - 19

Solubility Behaviour of Different Co-polyesters of 4-hydroxy benzoic acid and 3-hydroxybenzoic acid:

Sr. No.	Polymer	Solubility Behaviour DMF	DMSO	NMP	Phenol
1	P-Co-M_1	(-)	(-)	(-)	(-)
2	P-Co-M_2	(-)	(-)	(-)	(-)
3	P-Co-M_3	(-)	(-)	(-)	(-)
4	P-Co-M_4	(-)	(-)	(-)	(-)
5	P-Co-M_5	(-)	(+)	(+)	(+)
6	P-Co-M_6	(-)	(+)	(+)	(+)
7	P-Co-M_7	(-)	(+)	(+)	(+)
8	P-Co-M_8	(+)	(+)	(+)	(+)
9	P-Co-M_9	(+)	(+)	(+)	(+)
10	P-Co-M_{10}	(+)	(+)	(+)	(+)

(+) : Soluble.

(-) : Insoluble.

Phenol : p-cresol, o-cresol, p-chlorophenol.

Table - 20

Co-polyesters of 4-hydroxybenzoic acid and 3-methoxy-4-hydroxybenzoic acid in air using Thionyl chloride as condensing agent : Poly(4-oxybenzoates-Co-4'-oxy-(3'-methoxy)benzoates:

Sr. No.	Polymer	Molar proportion of PHB	Molar proportion of VA	Transition Temperatures (°C)		
				Smectic	Nematic	Isotropic
1	VB_1	1.00	0.005	205	281	303 P
2	VB_2	1.00	0.010	-	190	285 P
3	VB_3	1.00	0.10	-	145	308 P
4	VB_4	1.00	0.20	-	127	306 P
5	VB_5	1.00	0.40	-	105	311 P
6	VB_6	1.00	0.80	-	079	>325
7	VB_7	1.00	1.00	-	099	>325
8	VB_8	0.10	1.00	-	100	159*
9	VB_9	0.20	1.00	-	100	159*
10	VB_{10}	0.40	1.00	-	100	290 P
11	VB_{11}	0.80	1.00	-	100	321 P

P : Sample post-polymerizes and becomes solid.

* : Nematic phase in second turn.

Table - 21

Solubility Behaviour of Different Co-polyesters of 4-hydroxybenzoic acid and 3-methoxy-4-hydroxybenzoic acid:

Sr. No.	Polymer	Solubility Behaviour			
		DMF	DMSO	NMP	Phenol
1	VB_1	(-)	(-)	(±)	(±)
2	VB_2	(-)	(-)	(±)	(±)
3	VB_3	(-)	(+)	(+)	(+)
4	VB_4	(-)	(+)	(+)	(+)
5	VB_5	(-)	(+)	(+)	(+)
6	VB_6	(±)	(+)	(+)	(+)
7	VB_7	(±)	(+)	(+)	(+)
8	VB_8	(±)	(+)	(+)	(+)
9	VB_9	(±)	(+)	(+)	(+)
10	VB_{10}	(-)	(+)	(+)	(+)
11	VB_{11}	(-)	(+)	(+)	(+)

(+) : Soluble.

(±) : Party soluble.

(-) : Insoluble.

Phenol : p-cresol, o-cresol, p-chlorophenol.

Table-22

Elemental Analysis of Different Copolyesters Prepared from Hydroxyaromatic acids:

Sr.No.	Polymer	Found C %	Found H %
	Poly(2-Co-3-oxybenzoate)		
1	O-Co-M_1	68.91	3.52
2	O-Co-M_2	68.63	3.92
	Poly(3-Co-4-oxybenzoate)		
3	P-Co-M_1	67.35	3.30
4	P-Co-M_2	68.52	3.81
5	P-Co-M_3	68.27	3.58
6	P-Co-M_4	69.92	3.41
7	P-Co-M_5	68.72	3.22
8	P-Co-M_6	67.18	3.18
9	P-Co-M_7	66.84	3.45
10	P-Co-M_8	68.50	3.29
	Poly(4-oxybenzoate-Co-4'-(3'-methoxy)-oxybenzoate)		
11	VB_1	64.43	3.61
12	VB_3	64.03	3.50
13	VB_5	65.86	3.71
14	VB_6	64.30	3.65
15	VB_8	64.74	3.44
16	VB_9	65.48	3.16
17	VB_{11}	64.51	3.08

i) Molecular formula for the repeating unit for the copolymers prepared from OHB and MHB, PHB and MHB: $C_{14}H_8O_4$
Required : C =70.00%; H=3.30%

ii) Molecular formula for the repeating unit for the copolymers prepared from PHB and VA: $C_{15}H_{10}O_5$
Required : C = 66.66%; H =3.70%

Table - 23

Post-polycondensation of HP_3 polymer in Different Environment:

Sr. No.	Polymer	Variation in parameters	Code No. of post-polymerized sample
1	HP_3	Heating between 310°C-330°C for 20 minutes in nitrogen atmosphere.	HP_{15}
2	HP_3	Heating between 310°C-330°C for 1 hr. and 20 minutes in nitrogen atmosphere.	HP_{16}
3	HP_3	Heating between 310°C-330°C for 20 minutes in nitrogen atmosphere and under reduced pressure (77 mm. of Hg).	HP_{17}
4	HP_3	Heating between 310°C-330°C for 6 hrs in nitrogen atmosphere and under reduced pressure (77 mm. of Hg).	HP_{18}
5	HP_3	Heating between 310°C-330°C for 30 minutes in nitrogen atmosphere and under reduced pressure (0.5 mm. of Hg).	HP_{19}
6	HP_3	Heating between 310°C-330°C for 20 minutes in air.	HP_{20}

Table - 24

Post-polycondensation of V_7 polymers in Different Environment:

Sr. No.	Polymer	Variation in parameters	Code No. of post-polymerized sample
1	V_7	Heating between 225°C-235°C for 20 minutes in air under atmospheric pressure.	V_{14}
2	V_7	Heating between 225°C-235°C for 20 minutes in nitrogen atmosphere under atmospheric pressure.	V_{15}
3	V_7	Heating between 225°C-235°C for 20 minutes in nitrogen atmosphere under reduced pressure (77 mm.of Hg).	V_{16}
4	V_7	Heating between 225°C-235°C for 30 minutes in nitrogen atmosphere under reduced pressure (0.5 mm. of Hg).	V_{17}

Table -25

Comparision of Transition Temperatures of Post-polymerized Homopolyesters with original polymer (HP_3):

Sr.No.	Polymer	Transition Temperatures(°C)		
		Smectic	Nematic	Isotropic
1	HP_3	327	-	340 P
2	HP_{15}	-	-	>350
3	HP_{16}	-	-	>350
4	HP_{17}	-	-	>350
5	HP_{18}	-	-	>350
6	HP_{19}	-	-	>350
7	HP_{20}	-	-	>350

P : Sample post-polymerizes and becomes solid.

Table - 26

Comparision of Transition Temperatures and Solubility Behaviour of Post-polymerized Homopolyesters with Original Polymer (V_7):

Sr. No.	Polymer	Transition Temperatures (°C)			Solubility Behaviour				
		Smectic	Nematic	Isotropic	Ethanol	DMF	DMSO	Phenol	NMP
1	V_7	-	125	238 P	(-)	(+)	(+)	(+)	(+)
2	V_{14}	-	-	>350	(-)	(-)	(-)	(±)	(±)
3	V_{15}	-	-	>350	(-)	(-)	(-)	(±)	(±)
4	V_{16}	-	-	>350	(-)	(-)	(-)	(±)	(±)
5	V_{17}	-	-	>350	(-)	(-)	(-)	(±)	(±)

P: Sample post-polymerizes and becomes solid.

(+) : Soluble.

(+) : partly soluble.

(-) : Insoluble.

Phenol : m-cresol, o-cresol, p-chlorophenol.

1.3.2 Post-polycondensation of co-polymers:

The mesogenic copolyesters of PHB and MHB (P-Co-M_5) and (P-Co-M6) (Table-18) were post-polymerized by heating them at 260°C to 270°C in nitrogen atmosphere under reduced pressure (0.5 mm of Hg) for 30 minutes in liquid crystalline state (Table-27). The melting points, transition temperatures and solubility behaviour of the post-polymerized samples are summarized in Table-28.

The mesogenic copolyesters of PHB and VA (BV_4 and BV_7) (Table-20) were post-polymerized by heating them at 250C to 260°C in nitrogen atmosphere under reduced pressure (0.5 mm. of Hg) for 30 minutes in liquid crystalline state (Table-29).

The melting points, transition temperatures and solubility behaviour of post-polymerized samples are summarized in Table-30.

1.4 MIXTURE STUDY OF HOMOPOLYESTERS:

Three polymeric samples HP_7 (smectogen), HP_9 (nematogen) (Table-11) and V_2 (nematogen) (Table-12) were doped with optically active natural d-camphor. A homogeneous mixture of polymers and d-camphor in desired proportion was prepared by heating the mixture in a sealed glass tube in an

Table-27

Post-polycondensation of Co-polyesters under reduced pressure:

Sr.No.	Polymer	Parameters	Code No. of post-polymerized sample
1	P-Co-M_5	Heating between 260°C-270°C for 30 minutes in nitrogen atmosphere under reduced pressure (0.50 mm of Hg).	P-Co-M_{11}
2	P-Co-M_6	Heating between 260°C-270°C for 30 minutes in nitrogen atmosphere under reduced pressure (0.50 mm of Hg).	P-Co-M_{12}

Table-28

Comparision of Transition Temperatures and Solubility Behaviour of Post-polymerized Co-polyesters with original polymers:

Sr.No.	Polymer	Transition Temperatures °C			Solubility Behaviour			
		Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	P-Co-M_5	-	190	310 P	(+)	(+)	(+)	(+)
2	P-Co-M_{11}	-	210	265 P	(-)	(-)	(-)	(-)
3	P-Co-M_6	-	085	205	(+)	(+)	(+)	(+)
4	P-Co-M_{12}	-	115	305 P	(-)	(-)	(-)	(-)

P : Sample post-polymerizes and becomes solid.

(+) : Soluble.

(-) : Insoluble.

Phenol: P-cresol, o-cresol, p-chlorophenol.

Table-29

Post-polycondensation of Co-polyesters under reduced pressure :

Sr. No.	Polymer	Parameters	Code No. of post-polymerized sample
1	VB_4	Heating between 250°C-260°C in nitrogen atmosphere under reduced pressure (0.5 mm. of Hg) for 30 minutes.	VB_{12}
2	VB_7	Heating between 250°C-260°C in nitrogen atmosphere under reduced pressure for 30 minutes. (pressure 0 5 mm of Hg)	VB_{13}

Table-30

Comparision of Transition Temperatures and Solubility Behaviour of Post-polymerized Co-polymers with original polymers:

Sr. No.	Polymer	Transition Temperatures (°C)			Solubility Behaviour			
		Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	VB_4	-	127	306P	(+)	(+)	(+)	(+)
2	VB_{12}	-	190	308P	(-)	(-)	(-)	(-)
3	VB_7	-	099	>325	(+)	(+)	(+)	(+)
4	VB_{13}	-	-	>325	(-)	(-)	(-)	(-)

P: Sample post-polymerizes and becomes solid.

(+) : Soluble.

(-) : Insoluble.

Phenol : p-cresol, o-cresol, p-chlorophenol.

oil-bath till they melt and then liquid was quenched. The solid homogeneous mixture was crushed into powder and transition temperatures were determined. ~~Tables~~-31 to 33 summarize the percentage weight of d-camphor in polymer and transition temperatures of the mixtures.

2. PREPARATION OF POLYESTERS:

2.1 Preparation of Polyesters from 1,2-bis(4'-carboxy-phenoxy) ethane:

2.1.1 Preparation of Monomer; 1,2-bis(4'-carboxy-phenoxy)-ethane:

1,2-bis(4'-carboxy-phenoxy)ethane was prepared by the method reported in literature (367,368).

27.6 g p-hydroxy benzoic acid (0.2 mol.) was dissolved in 100 ml. 22.4 % KOH solution (0.4 mol.) in 250 ml. round bottom quickfit flask. 20.68 gm 1,2-dibromoethane (0.11 mol.) was added to the flask and the whole mass was refluxed for 3 to 4 hours. Then the reaction mixture was transferred in a beaker and was diluted with water till the sodium salt of the acid dissolved completely. The solution was then acidified with concentrated HCl. Solid mass was filtered, washed with alcohol to remove unreacted p-hydroxy-benzoic acid. Solid mass was redissolved in DMF and reprecipitated out by adding excess of alcohol. The process

Table-31

Mixture study

Polymer + optically active compound:

(d-camphor; M.P. 179.75°C) (366).

Polymer (HP_7) $\xrightarrow{271^\circ C}$ S $\xrightarrow{313^\circ C}$ P (Table-11).

Sr. No.	Weight % of d-camphor in polymer	Transition Temperatures (°C)		
		Smectic	Nematic	Isotropic
1	20 %	200	252	313 P
2	40 %	191	210	330 P
3	60 %	-	207	325 P
4	80 %	-	210	321 P

P : Sample post-polymerizes and becomes solid.

Table- 32

Mixture study

Polymer + Optically active compound:

(d-camphor; M.P. 179.75°C) (366)

Polymer (HP_9) $\xrightarrow{279°C}$ N $\xrightarrow{315°C}$ P. (Table-11)

Sr. No.	Weight % of d-camphor in polymer	Transition Temperatures (°C)	
		Cholesteric	Isotropic
1	20 %	245	323 P
2	40 %	230	320 P
3	60 %	225	335 P
4	80 %	205	331 P

P: Sample post-polymerizes and becomes solid.

Table-33

Mixture study

Polymer + Optically active compound:

(d-camphor, M.P. 179.75°C) (366)

Polymer (V_2) $\xrightarrow{179^\circ C}$ N $\xrightarrow{237^\circ C}$ P. (Table-12).

Sr. No.	Weight % of d-amphor in polymer	Transition Temperatures (°C)	
		Cholesteric	Isotropic
1	20 %	175	290 P
2	40 %	115	290 P
3	60 %	105	270 P
4	80 %	105	285 P

P : Sample post-polymerizes and becomes solid.

was repeated twice to get pure white product; M.P. 352°C (reported 352°C) (367,368). The yield was 80 %.

2.1.2 Preparation of Diacid chloride of 1,2-bis[(4'-carboxy-phenoxy) ethane: (369)

Diacid chloride of 1,2-bis[(4'-carboxy-phenoxy)-ethane was prepared by reacting 1,2-bis[(4'-carboxy-phenoxy)-ethane(1.0 mol.) with thionyl chloride (2.5 mol.) in a round bottom flask and heating them on a water-bath till the evolution of hydrochloric acid ceased. One to two drops of dry pyridine was used in the reaction as catalyst. Excess of thionyl chloride was distilled off under reduced pressure using a water pump and the acid chloride left behind as a residue was used in the reaction without further purification.

2.1.3 Preparation of polyesters (Solution polycondensation):

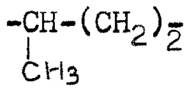
Diacid chloride of 1,2-bis(4'-carboxy-phenoxy)]ethane (BCPE) was condensed with different dihydroxy monomers.

$$\underset{\text{(BCPE)}}{Cl{-}CO{-}C_6H_4{-}O{-}CH_2{-}CH_2{-}O{-}C_6H_4{-}CO{-}Cl} \; + \; \underset{\text{Dihydroxy monomer}}{HO{-}R{-}OH} \longrightarrow$$

$$\underset{\text{BE}}{\left[OC{-}C_6H_4{-}O{-}CH_2{-}CH_2{-}O{-}C_6H_4{-}COO{-}R{-}O \right]_n}$$

R = $-(CH_2)_2-$,

BE$_1$

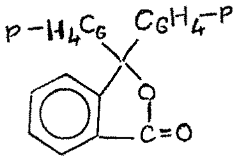


$-\underset{|}{CH}-(CH_2)_2-$ with CH_3 on the CH: $-CH(CH_3)-(CH_2)_2-$,

BE$_2$

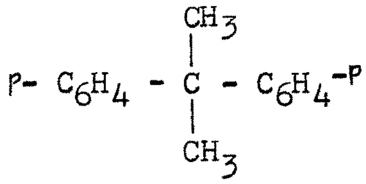
p- C_6H_4-p,

BE$_3$



,

BE$_4$



$$\text{p-}\ C_6H_4 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} - C_6H_4\text{-p}$$

BE$_5$

Ethylene glycol (0.01 mol.) was dissolved in dry pyridine (5 ml.) and was added slowly in a quickfit 50 ml round bottom flask containing magnetic needle and a solution of diacid chloride of 1,2-bis(4'-carboxy-phenoxy)ethane (0.01 mol.) in dry pyridine (10 ml.) with stirring keeping the flask in ice-bath. The reaction mixture was stirred continuously with guard tube on the flask and temperature was allowed to rise to room temperature (23°C) with constant stirring and stirred further for six hours. At the end of six hours, the whole mass was acidified with cold 1:1 hydrochloric acid. The solid product was filtered, washed with dilute hydrochloric acid followed by washing of water for complete removal of mineral acid. The polymer was further purified by solvent non-solvent method. The process was repeated twice. DMSO was used as solvent and alcohol was used as non-solvent in the process. The solid polymer was dried and melting points and transition temperatures were determined.

Similarly, other polyesters from diacid chloride of 1,2-bis(4'-carboxy-phenoxy)ethane were prepared by condensing it with different aliphatic and aromatic dihydroxy compounds by the process as described above. All the polyesters were also purified as described above.

Transition temperatures and solubility behaviour of the polyesters are summarized in Table-34.

Elemental analysis of the polyesters was carried out and the results were satisfactory. The analytical data is summarized in Table-37.

2.1.4 Preparation of Model Compound: 4(4'-methylphenyl) 1,2-bis-oxy-ethane-benzoate:

4 (4'-methylphenyl)-1,2-bis-oxy-ethane-benzoate was prepared by condensing diacid chloride of 1,2-bis(4'-carboxy-phenoxy)ethane with p-cresol as described below:

p-cresol (0.02 mol.) was dissolved in dry pyridine (10 ml.) and was added slowly with stirring to the cold solution of diacid chloride of 1,2-bis(4'-carboxyphenoxy)-ethane (0.01 mol) in 10 ml dry pyridine. The mixture was

Table - 34

Solution Polycondensation of diacid chloride of 1,2-bis (4'-carboxy-phenoxy)ethane with different dihydroxy monomers:

Sr. No.	Polymer	Dihydroxy monomers	Transition Temperatures(°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	Phenol	NMP
1	BE_1	Ethylene glycol	101	-	174	(+)	(+)	(+)	(+)
2	BE_2	1-Methyl propylene glycol	-	031	203	(+)	(+)	(+)	(+)
3	BE_3	Hydroquinone	215	261	>325	(-)	(-)	(±)	(±)
4	BE_4	Phenolphthalein	-	147	194	(+)	(+)	(+)	(+)
5	BE_5	Bisphenol-A	-	136	188	(+)	(+)	(+)	(+)

(+) : Soluble.

(-) : Insoluble.

(±) : Partly soluble.

Phenol : O-cresol, p-cresol, m-cresol, p-chlorophenol.

heated on a water-bath for an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid. The precipitate was washed with cold dilute sodium hydroxide solution followed by cold water. The ester was recrystallized several times from alcohol until constant melting points and transition temperatures were obtained. The yield was about 60 %. The analytical data is as under:

	C %	H %
Required :	71.70 ;	5.39
Found :	71.80 ;	5.43

Transition Temperature : Crystal 212°C I (185°C)N.

2.2 Preparation of Polyesters of p-azoxybenzoic acid:

2.2.1 Preparation of Monomer; p-azoxybenzoic acid:

p-azoxybenzoic acid was prepared by the method reported in the literature (370, 371).

A mixture of 25.00 gm. p-nitrobenzoic acid, 30 gm. arsenious acid (anhydride) and 42.5 gm. NaOH in 250 ml. water was warmed at 70°C for an hour. A solid mass separated out (as the sodium salt of p-azoxybenzoic acid is sparingly soluble in water). Sufficient quantity of water was added to dissolve the sodium salt of the acid.

The solution was acidified with dilute hydrochloric acid to precipitate p-azoxybenzoic acid. The acid in the form of yellowish powder was purified by washing of hot water several times followed by washing of ethanol and was dried. p-azoxybenzoic acid does not melt but becomes darker in colour when heated to high temperature (240°C). The yield was 80 %.

p-azoxybenzoic acid was further confirmed by preparing its diethyl ester.

2.2.1a Preparation of Ethyl p-azoxybenzoate (372):

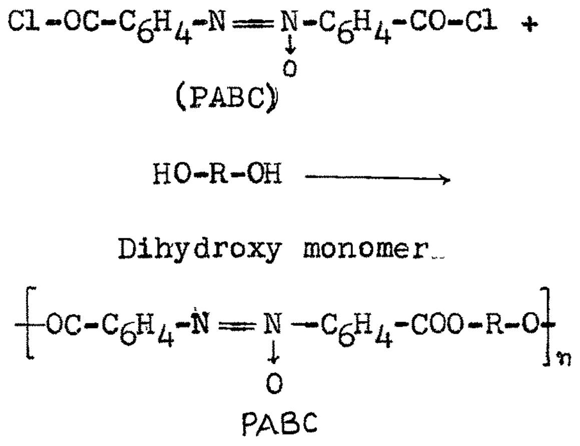
p-azoxybenzoic acid was dissolved in liquor ammonia, from this solution, the silver salt of the acid was precipitated out by treatment with silver nitrate solution. Silver salt was then dried (3.0 gm.) and reacted with ethyl iodide (3.0 gm.) in 30.0 ml. benzene on water-bath under reflux condenser for two hours. The benzene solution was filtered out from solid silver iodide which was washed thoroughly with benzene. The washing and the filtrate were mixed and solvent was evaporated. The red mass so obtained was recrystallized several times from ethanol into fine light orange plates. The yield was 75 %; (crystal 140°C smectic 222.5°C isotropic)
(reported ; crystal 140°C smectic 222.5°C isotropic) (372).

2.2.2 Preparation of p-azoxybenzoyl chloride (369):

p-azoxybenzoyl chloride was prepared as described in experimental part (2.1.2) and was used in the next reaction without further purification.

2.2.3 Preparation of Polyesters:

p-azoxybenzoyl chloride (PABC) was condensed with different dihydroxy monomers.

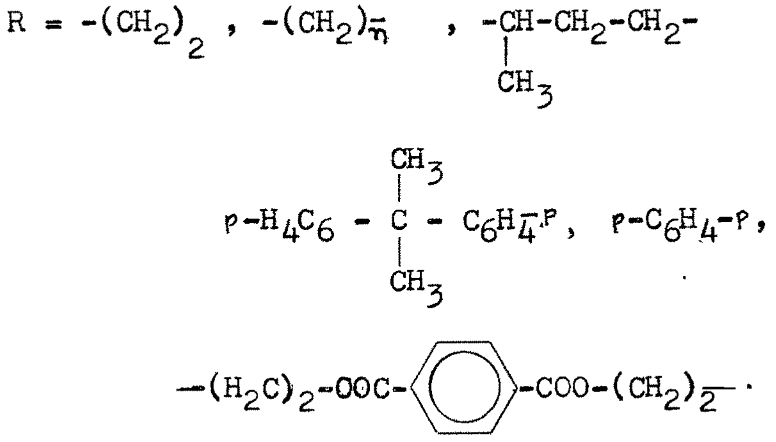


$$Cl\text{-}OC\text{-}C_6H_4\text{-}N{=}\underset{\downarrow O}{N}\text{-}C_6H_4\text{-}CO\text{-}Cl \; + \; HO\text{-}R\text{-}OH \longrightarrow \left[OC\text{-}C_6H_4\text{-}N{=}\underset{\downarrow O}{N}\text{-}C_6H_4\text{-}COO\text{-}R\text{-}O\right]_n$$

(PABC)

Dihydroxy monomer

PABC



$$R = -(CH_2)_2 \, , \; -(CH_2)_n \, , \; -\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_2\text{-}$$

$$p\text{-}H_4C_6 - \overset{CH_3}{\underset{CH_3}{C}} - C_6H_4\text{-}p \, , \;\; p\text{-}C_6H_4\text{-}p \, ,$$

$$-(H_2C)_2\text{-}OOC\text{-}C_6H_4\text{-}COO\text{-}(CH_2)_2- \, .$$

2.2.3a Solution Polycondensation:

Different polyesters were prepared by condensing p-azoxybenzoyl chloride (0.01 mol.) with different aliphatic and aromatic dihydroxy compounds (each 0.01 mol.) as described in experimental part (2.1.3).

Polyesters were purified by solvent non-solvent method. p-chlorophenol was used as solvent for the polymers which are soluble in this solvent and alcohol was used as non-solvent for the process. The solid polymers were dried and melting points and transition temperatures were determined.

Transition temperatures and solubility behaviour of the polymers are summarized in Table-35.

Elemental analysis of the polymers was carried out and the results are satisfactory. The analytical data is summarized in Table-37.

2.2.3b Interfacial Polycondensation:

In a beaker (in ice-bath) containing a solution of ethylene glycol (0.01 mol.) dissolved in NaOH solution (0.07 mol NaOH in 50 ml. water), a solution of p-azoxybenzoyl chloride (0.01 mol.), dissolved in 50 ml of distilled

Table - 35

Solution Polycondensation of p-azoxybenzoyl chloride with different dihydroxy monomers:

Sr. No.	Polymer	Dihydroxy compounds	Solvent used in reaction	Reaction condition		Transition Temperatures (°C)			Solubility Behaviour			
				period (hr)	Temp. (°C)	Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	$PABC_1$	Ethylene glycol	Pyridine	1	85	-	-	220*	(-)	(-)	(-)	(+)
2	$PABC_2$	Ethylene glycol	Pyridine	2	23	-	-	>350	(-)	(-)	(-)	(+)
3	$PABC_3$	Ethylene glycol	NMP	4	23	-	-	>350	(-)	(-)	(-)	(+
4	$PABC_4$	Ethylene glycol	Pyridine	4	23	-	-	>350	(-)	(-)	(-)	(+)
5	$PABC_5$	Ethylene glycol	TCE[(a)]	-	23	-	-	>350	(-)	(-)	(-)	(-)
6	$PABC_6$	Polyethylene glycol	NMP	1	23	-	-	>350	(-)	(-)	(-)	(-)
7	$PABC_7$	Polyethylene glycol	TCE[(a)]	-	23	-	-	>350	(-)	(-)	(-)	(-)
8	$PABC_8$	1,3-butylene glycol	NMP	4	23	-	-	>350	(-)	(-)	(-)	(+)
9	$PABC_9$	1,3-butylene glycol	TCE[(a)]	-	23	-	-	>350	(-)	(-)	(-)	(-)
10	$PABC_{10}$	Bisphenol-A	Pyridine	1	85	-	-	>350	(-)	(-)	(-)	(-)
11	$PABC_{11}$	Hydroquinone	Pyridine	1	85	-	-	245*	(-)	(-)	(-)	(-)
12	$PABC_{12}$	Bishydroxy ethylene-terephalate	Pyridine	1	85	-	-	275*	(-)	(-)	(-)	(-)

(a) : Interfacial polymerization, TCE : Trichloroethane, * : Highly viscous liquid.
Phenol : o-, m-, p-cresol.

tetrachloro ethylene (TCE) was added slowly with agitation. The agitation was slow in the beginning and then speeded up towards the end of the addition period. After five minutes, i.e. after complete addition of ethylene glycol solution, the solid mass was filtered, washed with water till free from alkali and dried. The polymer was purified by solvent non-solvent method. The method was repeated twice to get pure polymer. The melting points and transition temperatures were determined.

Similarly, polyethylene glycol and 1,3-butylene glycol was condensed with p-azoxybenzoyl chloride as described above.

Transition temperatures and solubility behaviour of the polymers are summarized in Table-35.

Elemental analysis of the polymers was carried out and the results are satisfactory. The analytical data is recorded in Table-37.

2.2.4 Preparation of Model Compound: (4'-methyl phenyl)-p-azoxybenzoate:

(4'-methyl phenyl)-p-azoxybenzoate was prepared by condensing p-azoxybenzoyl chloride (0.01 mol. in 10 ml. dry pyridine) with p-cresol (0.02 mol. in 5 ml. dry pyridine) as described in experimental part (2.1.4). The ester was recrystallized from acetic acid several times until constant melting point and transition temperatures were obtained. The yield was about 60 %. The analytical data is as under:

	C %	H %	N %
Required	72.01 ;	4.72 ;	6.01
Found	71.14 ;	4.92 ;	5.87

Transition Temperature : crystal 153°C N >300°C d.

2.3 Preparation of Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy benzalazine:

2.3.1 Preparation of Monomer; 3,3'-dimethoxy-4,4'dihydroxy-benzalazine:

3,3'-dimethoxy-4,4'-dihydroxy benzalazine was prepared by the method reported in the literature (373).

A mixture of powdered hydrazine sulphate (13.0 gm; 0.1 mol.), 280 ml. water and 15.6 ml. concentrated aqueous ammonia (d.0.88) were taken in 500 ml. conical flask. 30.4 gm. (0.2 mol.) of vanillin (recrystallized) in alcohol was added to the flask. in portions over a period of 30 to 60 minutes. Stirring was continued during the addition of vanillin. Mixture was further stirred for an hour. Yellow solid mass was separated out, filtered, washed with water and recrystallized from alcohol; M.P. 173-174°C. The yield was about 85%.

The analytical data is as under:

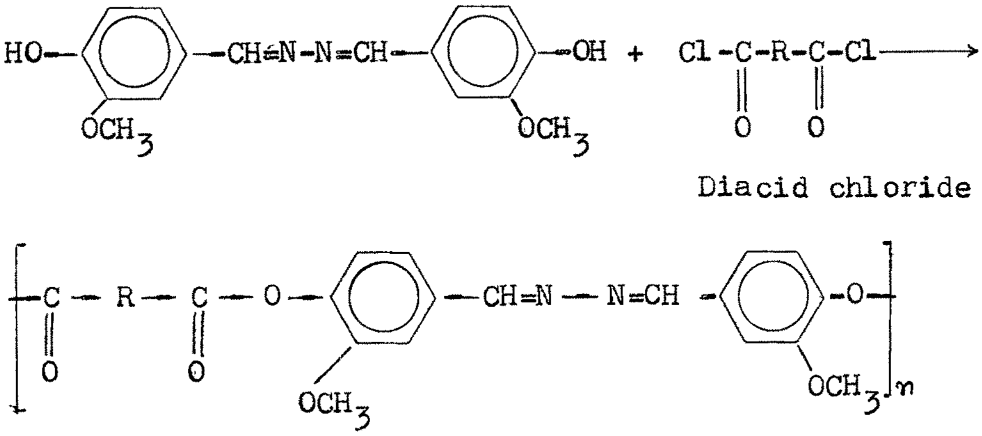
		C%	H%	N%
Required	:	64.00;	5.33;	9.33
Found	:	64.12;	5.41;	9.21

2.3.2 Preparation of Diacid chlorides of different aliphatic and aromatic diacids:

Diacid chlorides of terephathalic acid, Isophthalic acid, adipic acid, p-azoxybenzoic acid, 1,2-bis(4'-carboxy-phenoxy) ethane, 2,2-bis(4'-carboxy-ethoxy phenyl) propane were prepared ad described in experimental part (2.1.2) and were used in the next reaction without further purification.

2.3.3 Preparation of Polyesters (Solution Polycondensation):

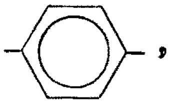
3-3'-dimethoxy-4-4'-dihydroxy-benzalazine was condensed with different diacid chlorides.



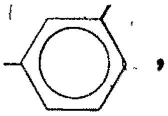
AZ

R = $-(CH_2)_4-$,

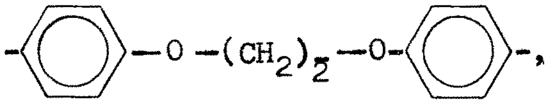
AZ_1



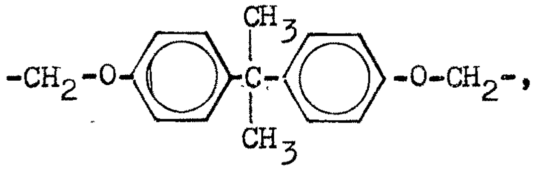
AZ_2



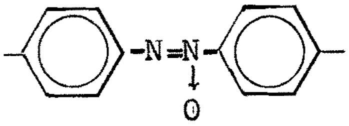
AZ_3



AZ_4



AZ_5



AZ_6

Different polyesters were prepared by condensing 3,3'-dimethoxy-4,4'dihydroxy benzalazine (0.01 mol.) with different diacid chlorides (each 0.01 mol.) as described in experimental part (2.1.3).

In case of adipoyl chloride, N-methyl pyrrolidone was used as solvent instead of pyridine as it gave better product.

Polyesters were purified by solvent non-solvent method. DMSO was used as solvent and alcohol was used as non-solvent for the process. The solid polymers were dried and melting points and transition temperatures were determined.

Transition temperatures and solubility behaviour of the polymers are summarized in Table-36.

Table - 36

Solution polycondensation of 3,3'-dimethoxy-4,4'-dihydroxybenzalazine with different diacid chlorides:

Sr. No.	Polymer	Diacid chlorides	Transition Temperatures (°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	AZ_1	Adipoyl chloride	-	-	155	(+)	(+)	(+)	(+)
2	AZ_2	Terephthaloyl chloride	-	-	>350	(-)	(-)	(-)	(-)
3	AZ_3	Isophthaloyl chloride	-	180	230	(+)	(+)	(+)	(+)
4	AZ_4	Diacid chloride of 1,2-bis(4'-carboxyphenoxy) ethane	-	127	296 P	(+)	(+)	(+)	(+)
5	AZ_5	Diacid chloride of 2,2-bis(4'-carboxyethoxyphenyl)propane	-	-	130	(+)	(+)	(+)	(+)
6	AZ_6	p-Azoxybenzoyl chloride	240	-	290	(-)	(-)	(-)	(-)

P : Sample post-polymerizes and becomes solid.

(+) : Soluble.

(-) : Insoluble.

Phenol : o-, p-, m-cresol, p-chlorophenol.

Elemental analysis of the polymers was carried out and the results are satisfactory. The analytical data is recorded in Table-37.

2.3.4 Preparation of Model Compound; 3,3'-dimethoxy-4,4'-di(4"-methoxy-benzoyloxy)benzalazine:

3,3'-dimethoxy-4,4'-di(4"-methoxy benzoyloxy) benzalazine was prepared by condensing 3,3'-dimethoxy-4,4'-dihydroxy-benzalazine (0.01 mol. in 10 ml. pyridine) with anisoyl chloride (0.02 mol. in 5 ml. pyridine) as described in experimental part (2.1.4). Anisoyl chloride was prepared from anisic acid as described in experimental part (2.1.2) The ester was recrystallized from DMF several times until constant melting point and transition temperatures were obtained. The yield was about 60 %. The analytical data is as under:

	C %	H %	N %
Required	67.61 ;	4.93 ;	4.93
Found	66.90 ;	4.82 ;	4.91

Transition Temperature : Crystal 258°C N 280°C I.

3. PREPARATION OF POLYAMIDES:

3.1 Preparation of Polyamides from 1,2-bis(4'-carboxy-phenoxy)ethane:

3.1.1 Preparation of Monomer; 1,2-bis(4'-carboxy-phenoxy)-ethane and its diacid chloride:

Table - 37

Elemental Analysis of Different Polyesters:

Sr. No.	Polymer	Elemental Analysis Found (%)			Required (%)			Molecular formula
		C	H	N	C	H	N	
1	BE_1	64.93	6.10	-	65.87	4.88	-	$C_{18}H_{16}O_6$
2	BE_2	64.85	3.87	-	67.43	5.62	-	$C_{20}H_{20}O_6$
3	BE_3	67.97	4.42	-	70.21	4.23	-	$C_{22}H_{16}O_6$
4	BE_4	72.80	4.12	-	75.30	5.26	-	$C_{36}H_{24}O_8$
5	BE_5	70.29	3.20	-	73.97	4.11	-	$C_{31}H_{26}O_6$
6	$PABC_1$	60.37	3.54	8.84	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
7	$PABC_2$	60.48	3.71	8.76	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
8	$PABC_3$	61.02	3.33	8.59	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
9	$PABC_4$	60.55	3.42	8.59	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
10	$PABC_5$	61.14	3.15	8.90	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
11	$PABC_6$	60.08	3.15	8.54	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
12	$PABC_7$	59.76	4.14	8.79	61.54	3.85	8.97	$C_{16}H_{12}O_5N_2$
13	$PABC_8$	62.25	3.91	7.63	63.53	4.71	8.02	$C_{18}H_{16}O_5N_2$
14	$PABC_9$	61.89	3.83	7.32	63.53	4.71	8.02	$C_{18}H_{16}O_5N_2$
15	$PABC_{10}$	71.69	4.80	5.37	72.81	4.60	5.86	$C_{29}H_{22}O_5N_2$
16	$PABC_{11}$	65.67	3.45	7.58	66.66	3.33	7.77	$C_{20}H_{12}O_5N_2$
17	$PABC_{12}$	60.19	3.54	4.96	61.90	3.96	5.55	$C_{26}H_{20}O_9N_2$
18	AZ_1	63.13	4.91	6.35	64.39	5.36	6.83	$C_{22}H_{22}O_6N_2$
19	AZ_2	65.15	3.34	6.03	66.97	4.19	6.51	$C_{24}H_{18}O_6N_2$
20	AZ_3	64.87	3.17	6.34	66.97	4.19	6.51	$C_{24}H_{18}O_6N_2$
21	AZ_4	68.87	4.58	4.44	67.84	4.59	4.95	$C_{32}H_{26}O_8N_2$
22	AZ_5	67.12	4.39	4.24	69.07	5.26	4.61	$C_{33}H_{33}O_8N_2$
23	AZ_6	64.68	3.54	9.65	65.45	3.99	10.18	$C_{30}H_{22}O_7N_4$

of diacid chloride (0.01 mol.) of 1,2-bis(4'-carboxy-phenoxy)]ethane in dry pyridine (10 ml.) with stirring in cold condition. The reaction mixture was stirred continuously with guard tube on the flask for one and a half hour by maintaining the temperature between 0 to 5°C. After the stirring period was over, the whole mass was acidified with cold 1:1 HCl. The solid product was filtered, washed with dilute HCl followed by washing of water for complete removal of mineral acid. The polymer was washed with DMF twice followed by alcohol to remove unreacted monomers and to get pure polymer. The solid polymer was dried and melting points and transition temperatures were determined. Polymer was purified by solvent non-solvent method. N-methyl pyrrolidone was used as solvent and alcohol was used as non-solvent.

Similarly, other polyamides from diacid chloride of 1,2-bis[(4'-carboxy-phenoxy)ethane were prepared by condensing it with different aliphatic and aromatic diamines by the process as described above.

Transition temperatures and solubility behaviour of the polyamides are summarized in Table-38.

Elemental analysis of the polyamides was carried out and the results are satisfactory. The data is

Table - 38

Solution polycondensation of diacid chloride 1,2-bis(4'-carboxy-phenoxy)ethane with different Diamines:

(a) Solvent : Pyridine (dry)
(b) Reaction period : 1½ hrs.
(c) Reaction temperature : 0 to 5°C.

Sr. No.	Polymer	Diamines	Transition Temperatures (°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	BEA_1	1,2-diamino ethane	-	160	288	(+)	(+)	(+)	(+)
2	BEA_2	1,3-diamino propane	-	138	281	(+)	(+)	(+)	(+)
3	BEA_3	1,6-diamino hexane	-	(275)*	280	(±)	(±)	(+)	(+)
4	BEA_4	4,4'-diaminodiphenyl methane	-	-	>325	(-)	(-)	(-)	(-)
5	BEA_5	p-Phenylene diamine	-	-	>325	(-)	(-)	(-)	(-)
6	BEA_6	Benzidine	-	-	>325	(-)	(-)	(-)	(-)

* : Mesophase observed during cooling.
(+) : Soluble.
(±) : Partly soluble.
(-) : Insoluble.
Phenol : o-cresol, p-cresol, m-cresol, p-chlorophenol.

summarized in Table-42.

To study the effect of temperature and time on the polymerization, two more variations were tried. Tables-39 to 40 summarize the variations and transition temperatures of resultant polymers.

3.1.4 Preparation of Model Compounds:

Following four model compounds were prepared as described in the experimental part (2.1.4). Model compounds 1 to 3 were recrystallized from DMF whereas model compound number 4 was recrystallised from acetic acid.

1) 1,2-bis(4'-amidophenyl-phenoxy)ethane:

	C %	H %	N %
Required	74.66 ;	4.89 ;	6.22
Found	74.54 ;	4.73 ;	6.12

Transition Temperature : > 300°C.

2) 1,2-bis(4'-methyl-4"-amidophenyl-phenoxy)ethane;

	C %	H %	N %
Required	75.00 ;	5.83 ;	5.83
Found	74.82 ;	5.22 ;	5.48

Transition Temperature : > 300°C.

3) 1,2-bis(4'-methoxy-4"-amidophenyl-phenoxy)ethane:

Table - 39

Solution polycondensation of diacid chloride of 1,2-bis(4'-carboxy-phenoxy)ethane with different Diames:

(a) Solvent : pyridine (dry).
(b) Reaction period : 1½ hours.
(c) Reaction Temperature : 23°C (Room temp.).

Sr. No.	Polymer	Diamines	Transition Temperatures (°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	BEA_1	1,2-diamino ethane	-	-	>325	(-)	(+)	(+)	(+)
2	BEA_2	1,3-diamino propane	155	-	230	(-)	(+)	(+)	(+)
3	BEA_3	1,6-diamino hexane	-	240	272	(-)	(+)	(+)	(+)
4	BEA_4	4,4'-diamino diphenyl methane	-	-	>325	(-)	(-)	(-)	(-)
5	BEA_5	p-Phenylene diamine	-	-	>325	(-)	(-)	(-)	(-)
6	BEA_6	Benzidine	-	-	>325	(-)	(-)	(-)	(-)

(+) : Soluble.
(-) : Insoluble.
Phenol : O-, p- & m-cresol, p-chlorophenol.

Table-40

Solution polycondensation of Diacid chloride of 1,2-bis-(4'-carboxy-phenoxy)ethane with different Diamines:

(a) Solvent : pyridine (dry).

(b) Reaction period : 12 hrs.

(c) Reaction temperature : 23°C (Room temp.).

Sr. No.	Polymer	Diamines	Transition Temperatures (°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	BEA''_1	1,2-diamino ethane	-	-	285	(-)	(-)	(+)	(+)
2	BEA''_2	1,3-diamino propane	-	-	233	(±)	(+)	(+)	(+)
3	BEA''_3	1,6-diamino hexane	215	-	270	(±)	(+)	(+)	(+)
4	BEA''_4	4,4'-diamino diphenyl methane	-	-	>325	(-)	(-)	(-)	(-)
5	BEA''_5	p-phenylene diamine	-	-	>325	(-)	(-)	(-)	(-)
6	BEA''_6	Benzidine	-	-	>325	(-)	(-)	(-)	(-)

(+) : Soluble.

(±) : partly soluble.

(-) : Insoluble.

Phenol: O-, p-, m-cresol, p-chlorophenol.

	C %	H %	N %
Required :	70.00 ;	5.46 ;	5.46
Found :	69.89 ;	5.45 ;	5.36

Transition Temperature : > 300°C.

4) 1,2-bis(2'-chloro-4'-nitro-4''-amidophenyl-phenoxy)-ethane:

	C %	H %	N %
Required :	62.23 ;	3.70 ;	10.37
Found :	61.93 ;	3.43 ;	10.06

Melting point : 143°C.

3.2 Preparation of Polyamides from 2,2-bis(4'-carboxy-ethoxy-phenyl)propane:

3.2.1 Preparation of Monomer; 2,2-bis(4'-carboxy-ethoxy-phenyl)propane:

2,2-bis(4'-carboxy-ethoxy-phenyl)propane was prepared by the method reported in literature (374, 375).

In a 500 ml. round bottom flask containing 22.8 gm. (0.1 mol.) bisphenol-A and 23.5 gm. (0.25 mol.) monochloroacetic acid, 16.4 gm. (0.41 mol.) NaOH in 100 ml. water was added slowly with constant stirring keeping the temperature below 40°C. The reaction mixture was refluxed for 4 to 5 hours. The cooled reaction mixture was diluted with water.

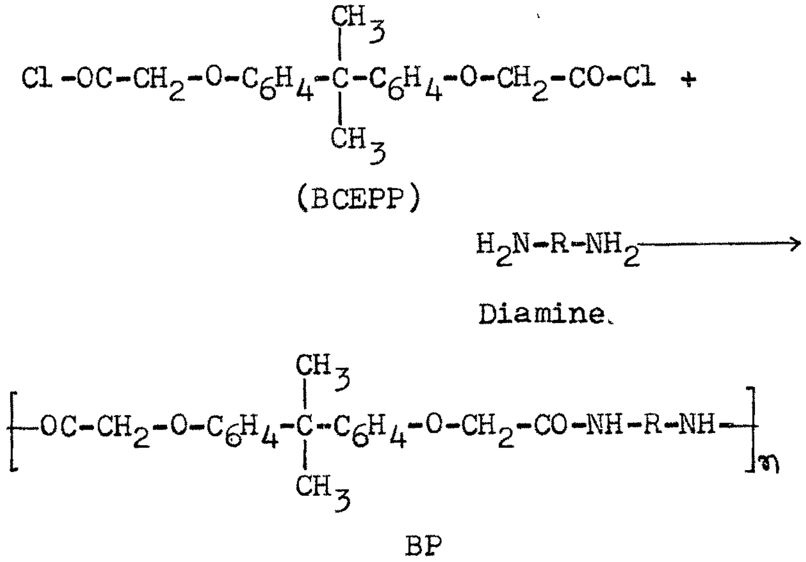
The solution was then acidified with cold dilute hydrochloric acid. Solid mass was filtered, washed with water till free from mineral acid and was recrystallized from glacial acetic acid and dried; M.P. 173-174°C (Reported 174-178°C)(374). The yield was about 60 %.

3.2.2 Preparation of Diacid chloride of 2,2-bis(4'-carboxy-ethoxy-phenyl)propane:

Diacid chloride of 2,2-bis(4'-carboxy-ethoxy-phenyl)-propane was prepared as described in experimental part (2.1.2) and was used in the next reaction without further purification.

3.2.3 Preparation of Polyamides:

Diacid chloride of 2,2-bis(4'-carboxy-ethoxy-phenyl)-propane was condensed with different diamines.



$$Cl\text{-}OC\text{-}CH_2\text{-}O\text{-}C_6H_4\text{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}C_6H_4\text{-}O\text{-}CH_2\text{-}CO\text{-}Cl \;+$$

(BCEPP)

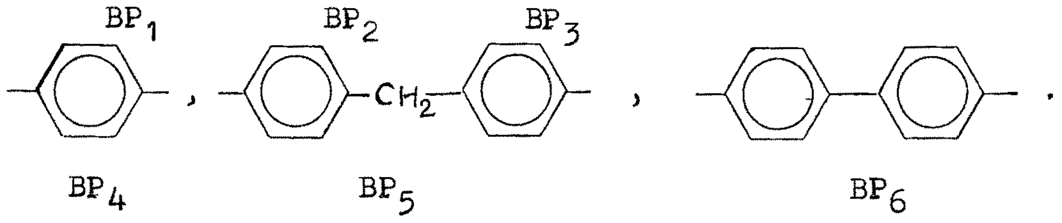
$$H_2N\text{-}R\text{-}NH_2 \longrightarrow$$

Diamine

$$\left[\text{-}OC\text{-}CH_2\text{-}O\text{-}C_6H_4\text{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}C_6H_4\text{-}O\text{-}CH_2\text{-}CO\text{-}NH\text{-}R\text{-}NH\text{-}\right]_n$$

BP

R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_6-$,



Different polyamides were prepared by condensing diacid chloride of 2,2-bis(4'-carboxy-ethoxy-phenyl)propane (0.01 mol.) with different aliphatic and aromatic diamines (each 0.01 mol.) as described in the experimental part (3.1.3). N-methyl pyrrolidone was used as a solvent instead of pyridine.

Polyamides were purified by solvent non-solvent method. DMF was used as solvent and alcohol was used as non-solvent in the process.

Transition temperatures and solubility behaviour of the polymers are summarized in Table-41.

Elemental analysis of the polymers was carried out and results are satisfactory. The analytical data is recorded in Table-42.

3.2.4 Preparation of Model Compound; 2,2-bis(4'-amidophenyl-methoxyphenyl)propane:

2,2-bis(4'-amidophenyl-methoxyphenyl) propane was prepared by condensing p-toluidine (0.02 mol) with diacid chloride

Table - 41

Solution polycondensation of Diacid chloride of 2,2-bis(4'-carboxy ethoxy-phenyl)]propane with different Diamines:

Sr. No.	Polymer	Diamines	Transition Temperatures (°C)			Solubility Behaviour			
			Smectic	Nematic	Isotropic	DMF	DMSO	NMP	Phenol
1	BP_1	1,2-diamino ethane	-	-	104	(+)	(+)	(+)	(+)
2	BP_2	1,3-diamino propane	-	-	097	(+)	(+)	(+)	(+)
3	BP_3	1,6-diamino hexane	-	-	100	(+)	(+)	(+)	(+)
4	BP_4	4,4'-diamino-diphenyl methane	-	-	149	(+)	(+)	(+)	(+)
5	BP_5	p-phenylene diamine	-	-	195	(+)	(+)	(+)	(+)
6	BP_6	Benzidine	-	145	256	(+)	(+)	(+)	(+)

(+) : Soluble.

Phenol : O-, p-, m-cresol, p-chlorophenol.

Table-42

Elemental Analysis of Different Polyamides:

Sr. No.	Polymer	Elemental Analysis						Molecular formula
		Found (%)			Required (%)			
		C	H	N	C	H	N	
1	BEA_1	64.53	3.42	6.89	67.08	5.59	8.70	$C_{18}H_{18}O_4N_2$
2	BEA_2	64.26	4.15	7.03	67.05	5.88	8.24	$C_{19}H_{20}O_4N_2$
3	BEA_3	65.28	5.01	6.55	69.10	6.81	7.34	$C_{22}H_{26}O_4N_2$
4	BEA_4	72.38	3.54	4.03	75.02	5.17	6.04	$C_{29}H_{24}O_4N_2$
5	BEA_5	73.49	3.74	4.92	74.66	4.89	6.22	$C_{22}H_{18}O_4N_2$
6	BEA_6	68.53	3.22	5.43	70.58	4.81	7.49	$C_{28}H_{22}O_4N_2$
7	BP_1	66.36	6.38	6.47	68.48	6.52	7.61	$C_{21}H_{24}O_4N_2$
8	BP_2	67.68	5.56	6.42	69.10	6.81	7.35	$C_{22}H_{26}O_4N_2$
9	BP_3	68.91	7.04	6.01	70.74	7.54	6.60	$C_{25}H_{30}O_4N_2$
10	BP_4	73.47	5.37	4.23	75.88	5.93	5.53	$C_{33}H_{30}O_4N_2$
11	BP_5	71.43	4.82	6.03	72.11	5.77	6.73	$C_{25}H_{24}O_4N_2$
12	BP_6	73.96	5.71	5.48	75.60	5.69	5.69	$C_{31}H_{28}O_4N_2$

of 2,2-bis(4'-carboxy-ethoxy-phenyl)propane (0.01 mol.) using N-methyl pyrrolidone as solvent as described in the experimental part (2.1.4). The amide was recrystallized from DMF. The yield was about 65 %.

	C %	H %	N %
Required :	75.86 ;	6.51 ;	5.36
Found :	75.54 ;	6.62 ;	5.19

Melting point : 163°C.

4. PREPARATION OF COPOLYESTERS:

4.1. Preparation of Copolyesters from Dimethylterephthalate and Ethylene glycol using Hydroxy aromatic acids as Mesogenic Moiety:

4.1.1 Preparation of Monomers:

4.1.1a Preparation of 4-hydroxycinnamic acid:

4-hydroxycinnamic acid was prepared by the method reported in the literature (376).

4-hydroxybenzaldehyde (0.02 mol.), malonic acid (0.04 mol.), dry pyridine (8 ml.) and piperidine (three drops) were mixed and heated at 100°C for three to four hours on a steam-bath in a round bottom flask. The mixture was poured on ice (25 gm.) containing concentrated hydrochloric acid

(25 ml.). The precipitates were filtered and washed with dilute hydrochloric acid, followed by water. Compound was recrystallized from ethanol. Yield of the product was 85 - 90 %. Melting point 214°C (d): (Reported 214°C d.)(377).

4.1.1b Preparation of 4-acetoxycinnamic acid:

4-acetoxycinnamic acid was prepared by the general method adopted for the preparation of aspirin from salicyclic acid (378).

p-hydroxycinnamic acid (0.05 mol.), acetic anhydride (0.05 mol.) and 0.5 gm.of fused sodium acetate were mixed and heated on sand-bath for an hour in a round bottom flask. The mixture was poured in cold water. Solid product was filtered, washed with water. Compound was recrystallized from hot water, M.P. 201°C (reported 200-5°C) (377). The yield was about 95 %.

4.1.1c Preparation of 3-methoxy-4-hydroxybenzoic acid (Vanillic acid):

3-methoxy-4-hydroxybenzoic acid was prepared as described in experimental part (1.1.1).

4.1.1d Preparation of 3-methoxy-4-acetoxybenzoic acid:

3-methoxy-4-acetoxybenzoic acid was prepared by the general method adopted for the preparation of aspirin from salicylic acid (378).

Vanillic acid (0.05 mol), acetic anhydride (0.05 mol.) and concentrated H_2SO_4 (three drops) were mixed and stirred for five minutes in a round bottom flask. The reaction mixture was poured in cold water. The solid separated was filtered and washed with water. The product was recrystallized from hot water; M.P. 110°C (Reported 110°C) (379). The yield was about 90 %.

4.1.1e Preparation of 6-hydroxy nicotinic acid:

6-hydroxy nicotinic acid was prepared by the known method as described in the literature (380).

6-hydroxy-nicotinic acid was prepared from methyl coumalate which was prepared from coumalic acid. The series of preparative stages are as under (Fig.19).

(I) Preparation of Coumalic acid:

In a 500 ml. round bottom flask, a mixture of malic acid (18.0 gm) and concentrated H_2SO_4 (18.0 ml.) was taken. Three 5.0 ml portion of fuming H_2SO_4 (SO_3 25%) were then added in the flask at an interval of 45 minutes. The mixture was heated on a water-bath for 2 hours. The mixture was poured on ice (80 gm). Solid was filtered, washed with

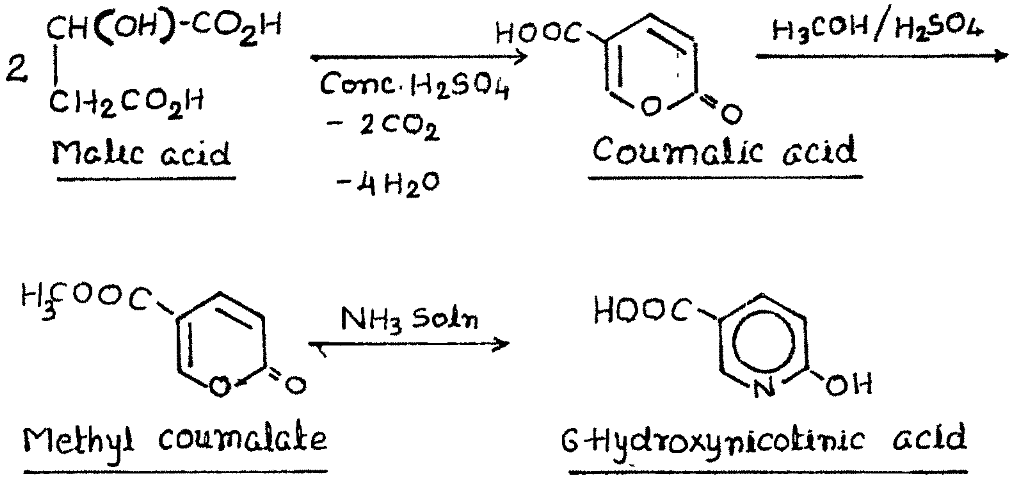


FIG.19: Route of Synthesis for 6-Hydroxynicotinic acid.

ice-water and recrystallized from methanol, M.P. : 206-208°C (Reported 206-208°C) (380). The yield was about 62 %.

(II) Preparation of Methyl Coumalate:

In 250 ml. round bottom flask containing 100 ml. concentrated H_2SO_4, 35 gm. (0.22 mol.) of finely powdered coumalic acid was added slowly keeping the internal temperature of the flask below 30°C by cooling in ice-water-bath. In this mixture, 50 ml. of methanol was added with continuous stirring in small portion so that temperature of the reaction mixture does not rise above 35°C. Then the reaction mixture was heated on boiling water bath for 1.5 hours. About 150 ml. of sodium carbonate, as slurry in water, was added in a cold reaction mixture to neutralize it. It was filtered, methyl coumalate was purified by vacuum sublimation. M.P. tellies with literature (47°C) (380). The yield was about 18.0 gm. (47 %).

(III) Preparation of 6-hydroxynicotinic acid:

In 250 ml. beaker (in ice water-bath) containing 20 ml. of NH_3 solution (d. 0.88) and 30 ml. water, 18 gm. (0.105 mol.) of methyl coumalate was added with stirring over a period of 5 minutes maintaining the temperature below 20°C. The resulting dark solution was stirred for a further 45 minutes at 20°C. It was then poured to a boiling aqueous NaOH prepared from 40 gm NaOH and 250 ml water. Reaction mixture was boiled for 5 minutes and was cooled to 10°C. Concentrated hydrochloric acid was then added with stirring to precipitate out the product maintaining the temperature at 30°C. Acidified solution was allowed to stand for 1.5 hours at 0-5°C. Yellow crystalline solid was filtered, washed with water and air-dried. M.P. tellies with literature (299-300°C decomposition) (380). The yield was about 8.5 gm.(58 %).

4.2 Condensation of Dimethyl terephthate, ethylene glycol and p-hydroxy/p-acetoxy aromatic acids (224):

A three necked 150 ml. round bottom flask provided with heating mental was charged with required quantity of monomers in different molar proportion as described in Table-43 and 0.0015 mol. calcium acetate as catalyst. One of the side necks of the flask was fitted with a distillation trap topped by a condenser to collect the low molecular weight byproducts evolved during the reaction and thermometer cap with thermometer and parafin oil were kept in another neck to measure the internal temperature of the flask. The copolymerization was carried out in nitrogen atmosphere by inserting the nitrogen inlet tube from the mouth of the flask.

Table-43

Copolymerization of Dimethylterephthalate (DMT) and Ethylene glycol (EG) with p-hydroxy/p-acetoxy aromatic acids as mesogenic moiety :

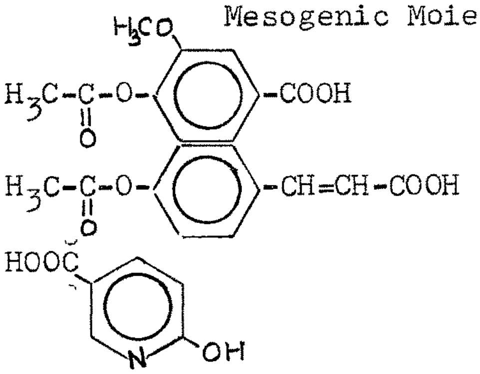
Sr. No.	Polymer	DMT (mol)	EG (mol)	Mesogenic moiety (mol)
		System-A		
1	MP_1	1.0	1.7	0.3
2	MP_2	1.0	1.5	0.5
3	MP_3	1.0	0.8	1.2
		System-B		
4	MP_4	1.0	1.7	0.3
5	MP_5	1.0	1.5	0.5
6	MP_6	1.0	0.8	1.2
		System-C		
7	MP_7	1.0	1.7	0.3
8	MP_8	1.0	1.5	0.5
9	MP_9	1.0	0.8	1.2

Mesogenic Moiety

System - A :

System - B :

System - C :



The temperature of the reaction was permitted to rise rapidly upto 150°C, at this temperature the material melted. There upom the temperature of the reaction mixture was again permitted to rise upto 190°C during the period of an hour. After that, the heating mental was adjusted in such a way that the internal temperature of the flask raised by 10°C during the period of an hour. In this condition the reaction mixture was heated upto 240°C. There upon, the reaction mixture was allowed to cool and when the temperature reached below 200°C, the reaction mixture was poured into a glass-disc. The solid material was crushed, made in powder form, washed with alcohol. After that each polymer was purified by solvent non-solvent method. The process was repeated twice to get pure polymeric product. o-chlorophenol was used as solvent and alcohol was used as non-solvent in the process. The melting point and transition temperatures were determined.

Table-44 summarises the transition temperatures and solubility behaviour of the polymers.

4.2.1 Post-polymerization:

Polymers (MP_2) and (MP_5) (Table-43) were post-polymerized as described below:

A three necked 150 ml. round bottom flask provided with heating mental was charged with polymer (MP_2) and assembly

Table-44

Copolymerization of DMT and EG with p-Ho-/p-Acetoxy aromatic acid:

Sr. No.	Polymer	Transition Temperatures (°C)		Solubility Behaviour			
		Smectic	Isotropic	DMF	DMSO	NMP	Phenol
1	MP_1	107	161	(±)	(±)	(±)	(+)
2	MP_2	110	165	(±)	(±)	(±)	(+)
3	MP_3	135	165	(±)	(±)	(±)	(+)
4	MP_4	188	241	(-)	(±)	(±)	(+)
5	MP_5	099	184	(-)	(±)	(±)	(+)
6	MP_6	155	198	(-)	(±)	(±)	(+)
7	MP_7	129	205	(±)	(±)	(±)	(+)
8	MP_8	118	165	(±)	(±)	(±)	(+)
9	MP_9	121	156	(±)	(±)	(±)	(+)
10	MP^a_{10}	-	190	(-)	(-)	(-)	(±)
11	MP^b_{11}	-	250	(-)	(-)	(-)	(-)

a : Post-polymerization of polymer sample (MP_2).

b : Post-polymerization of polymer sample (MP_5).

(+) : Soluble.

(±) : Partly soluble.

(-) : Insoluble.

Phenol : p-, m-, and o-cresol and p-chlorophenol.

was set up as in previous experiment. Then the flask was charged with nitrogen gas. The temperature of the reaction mixture was permitted to rise rapidly upto 150°C. The temperature was allowed to rise gradually upto 210°C during the period of an hour. Thereupon, the heating mental was adjusted in such a way that the temperature increased upto 250°C during the period of five hours. After reaching the temperature 250°C, vacuum (27.0 mm. of Hg) was applied and heating was continued at same temperature (250°C) for further 2½ hours. Then vacuum was released and the flask was allowed to attain atmospheric pressure gradually and mixture was allowed to cool. When temperature reached just below 200°C, it was poured into glass-disc. The product was crushed, made in powder form, washed with alcohol and finally polymer was purified by solvent non-solvent method. The process was repeated twice to get pure polymers.

Polymer sample (MP_5) was also post-polymerized by the same procedure.

The melting points of post-polymerized samples were determined. Table 44 summarizes transition temperatures and solubility behaviour of the polymers.

5. CHARACTERIZATION OF POLYMERS:

The elemental analysis of polymer samples was carried out as mentioned in the previous section.

The polymers were characterized by infrared spectroscopic method.

All the polymers were screened during heating by using a polarizing microscope to check their melting behaviour and mesogenic character.

Model compounds were prepared to characterize polymers and to understand their mesogenic behaviour.

Solution viscometry study of polymers was also carried out to characterize the polymers by obtaining their intrinsic viscosity $[\eta]$. Intrinsic viscosity $[\eta]$ of all polymers was obtained by " one point" method. Further, this method was confirmed by obtaining intrinsic viscosity $[\eta]$ of couple of polymeric samples with different concentration at same temperature.

Some of the samples were studied by using DSC/DTA apparatus to correlate the transition temperatures obtained by thermal polarizing microscopy. Thermogravimetric analysis (TGA) was carried out to determine the thermal stability of some of these polymers.

5.1 Transition Temperature Measurements:

The transition temperatures were determined by using a polarizing microscope provided with a mettler FP-2 heating stage.

Slides are prepared by three different methods (a) in the first method, the substance is taken on a slide and heated to little more than the mesophase temperature at which stage a cover slip is placed over it and then made to cool off. (b) In the second method, the compound is heated upto the isotropic liquid point, then the cover slip is put over it and allowed to cool off. (c) In the third method, the substance is first dissolved in a suitable solvent and then a few drops of the solution are placed on a slide and the solvent is allowed to evaporate. Thereafter, a cover slip is placed over it.

The microscope was standardized by taking melting points and/or transition temperatures of very pure but known substances like benzoic acid, succinic acid, p-azoxy anisole, vanillin , p-anisal-p-phenetidine, p-azoxyphenotole.

To determine the various transitions,a glass slide carrying a thin section of the material with a cover slip on it was observed under microscope. The slide was inserted into the specimen chamber of the heating stage and the temperature was raised fast (5°C/min.) to find out the approximate transition temperatures. The measurements were then repeated and near the transition to be observed, the rate of heating was regulated to about 1°C/min. The changing temperatures over the temperature ranges were carefully observed and recorded as the appearance of focal conic, plane, hemeotropic and threaded structures of smectic and nematic phases emerge under polarized light. Formation of isotropic liquid is already marked by the field of vision becoming extinct in polarized light. All observations were repeated several times, in case of any doubt, the compounds were purified again and then were subjected to the study under microscope a fresh.

However, there are some special aspects of polymers when they are studied for their mesogenic properties. The mesogenic-isotropic transition temperatures could not be determined, as during heating at higher temperatures due to further polymerization, polymer becomes solid. The characterization of smectic mesophase is also difficult as many times classical focal conic structure is not clearly visible. The care is taken in the characterization of smectic and nematic phases by often pressing cover slip and observing the homogeneous phases under the microscope. Over and above this, each mesophase was characterized by contact method. The polymer was placed on the slide and a low molecular weight liquid crystalline compound exhibiting nematic or smectic phase was placed adjacent to it and heated on the microscope heating stage. From the miscibility of the two phases the polymer is characterized as the one exhibiting smectic or nematic mesophases.

5.2 Characterization of Mesophases by contact Method (16, 313, 381, 382):

To characterize and ascertain about the smectic and nematic mesophases of the polymer samples following low molecular weight liquid crystal compounds were used. The nematogen is miscible continuously with the polymer exhibiting nematic mesophase range. When nematogen was heated along with smectogenic polymer samples, two phases were distinctly observed indicating that polymer samples exhibit smectic phase. Similarly, smectogen is miscible continuously with the polymer exhibiting smectic mesophase in the smectic range. When this smectogen was heated along with nematogenic polymer sample, two phases were distinctly observed indicating that polymer samples exhibit nematic phase.

(1) Methyl 4-(4'-n-ethoxybenzoyloxy)-benzylidene-4"-aminobenzoate (383);

$$K \xrightarrow{187^\circ C} N \xrightarrow{330.0^\circ C} \text{Decomposition.}$$

(For the polymers obtained from p-hydroxybenzoic acid (Table-11), copolymers obtained from p-hydroxybenzoic acid and vanillic acid (Table-20) and polymers obtained from 1,2-bis(4'-carboxy-phenoxy)ethane (Table-34,38,39).

2) Methyl 4-(4'-n-pentyloxybenzoyloxy)benzylidene-4"-aminobenzoate (383);

$$K \xrightarrow{155^\circ C} S \xrightarrow{205^\circ C} N \xrightarrow{280^\circ C} \text{Isotropic.}$$

(For the polymers obtained from p-hydroxybenzoic acid and m-hydroxybenzoic acid (copolymers) (Table-18)

3) Methyl 4(4'-n-hexyloxybenzoyloxy)benzilidene-4"-aminobenzoate (383);

$$K \xrightarrow{150^\circ C} S \xrightarrow{214.5^\circ C} N \xrightarrow{272^\circ C} \text{Isotropic.}$$

(For the polymers obtained from 1,2-bis-(4'-carboxyphenoxy)ethane (Table-34).

4) Methyl 4-(4'-n-heptyloxybenzoyloxy)benzilidene-4"-aminobenzoate (383);

$$K \xrightarrow{142^\circ C} S \xrightarrow{218^\circ C} N \xrightarrow{252^\circ C} \text{Isotropic.}$$

(For the polymers obtained from vanillic acid (Table-12), polymers obtained from 1,2-bis(4'-carboxy-phenoxy)ethane (Table-38,39) and copolymers of p-hydroxybenzoic acid and vanillic acid (Table-20).

5) Methyl 4-(4'-n-octadecyloxybenzoyloxy)benzilidene-4"-aminobenzoate (377);

$$K \xrightarrow{102^\circ C} S \xrightarrow{213^\circ C} \text{Isotropic.}$$

(For the polymers obtained from melt polymerization (Table-44), copolymers of p- and m-hydroxybenzoic acids (Table-18) and polymers of 1,2-bis(4'-carboxy-phenoxy)-ethane (Table-39).

6) 4(4'-n-dodecyloxybenzoyloxy)-3-methoxybenzilidene-4"-anisidine (384);

$$\mathrm{K}\xrightarrow{88^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{104^{\circ}\mathrm{C}}\text{Isotropic.}$$

(For the copolymers of p- and m-hydroxybenzoic acids (Table-18).

7) 4(4'-n-propyloxybenzoyloxy)-3-methoxy benzylidene-4"-anisidine (384);

$$\mathrm{K}\xrightarrow{135^{\circ}\mathrm{C}}\mathrm{N}\xrightarrow{191}\text{Isotropic.}$$

(For the polymers obtained from 1,2-bis(4'-carboxyphenoxy)ethane (Table-34) and polymers obtained from 2,2-bis(4'-carboxy-ethoxy-phenyl)propane (Table-41) and polymers obtained from 3,3'-dimethoxy-4,4'-dihydroxybenzalazine (Table-36).

5.3 IR Spectral Study:

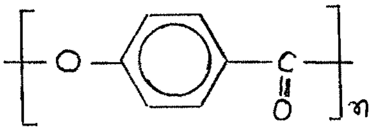
Model compounds and polymer samples were screened by using Nujol/KBr pellets in the range of infra-red frequency. The samples were analyzed on Perkin-Elmer Spectrophotometer. The data are given in Tables-45 to 53.

5.4 Viscometric Study:

5.4.1 Introduction:

Many methods for the measurement of viscosity are reported (385) but those which make use of the capillary

Table- 45



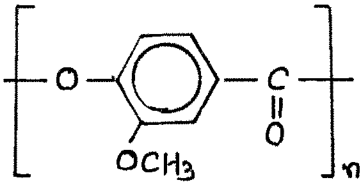
Poly(4-oxybenzoate)

IR Spectral Data

IR stretching Vibrations (Cm^{-1})

HP_2	HP_6	HP_{10}	HP_{16}
3440	3500	3445	3500
1735	1750	1725	1750
1600	1610	1625	1615
1540	1525	1525	1525
1420	1425	1425	1425
880	885	885	890

Table-46



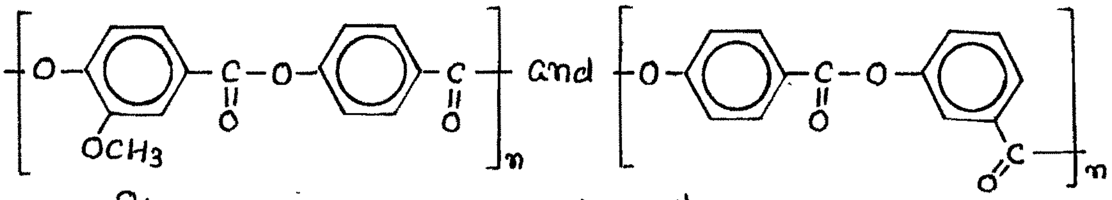
Poly(4-oxy-3-methoxybenzoates)

IR Spectral Data

IR Stretching Vibrations (cm^{-1})

Nujol	Polymer (V-2)
2920 - 2970	3340
1440	2920
1355	1720
	1685
	1580
	1495
	855
	810
	740

Table- 47



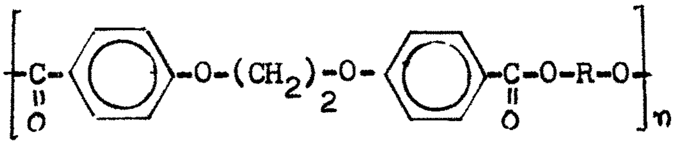
Poly[(4-oxy-3-methoxybenzoate)-Co-4'-oxybenzoate and Poly[(4-Co-3-oxybenzoate)

IR Spectral Data

IR stretching Vibrations (cm^{-1})

VB_7	$P-Co-M_5$
1740	1740
1610	1610
1510	1450
1460	855
855	810
810	755
755	

Table - 48

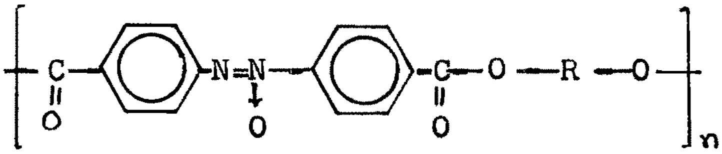


IR Spectral Data

IR stretching Vibrations (cm^{-1})

BE_1	BE_3	Model-1
2940	2900	2940
1700	1700	2340 1730
1600	1575	1610
1575	1550	1525
1500	1480	1430
1475	1420	1270
1260	1230	1250
840	840	850

Table - 49

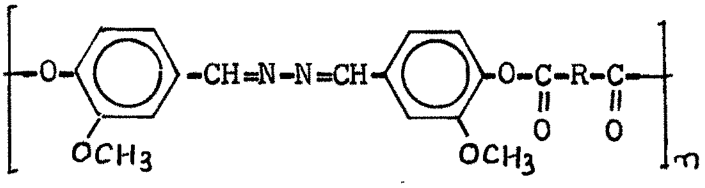


IR Spectral Data

IR stretching Vibrations (cm^{-1})

$PABC_1$	$PABC_8$	$PABC_{10}$	$PABC_{11}$	Model Compound
2940	2940	2950	1775	1740
1775	1780	1730	1720	1610 1515
1590	1590	1590	1590	1470
1450	1550	1495	1495	1420
1400	1450	1450	1450	870
1330	1330	1355	1400	
850	850	870	850	

Table - 50

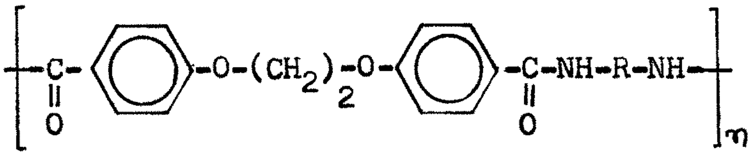


IR Spectral Data

IR stretching Vibration (cm^{-1})

AZ_1	AZ_4	Model
3410	2800	3440
2940	1440	3020
1750	1715	2950
1620	1585	2850
1500	1360	1735
860	1230	1610
	910	1515
	820	1270
		850

Table - 51

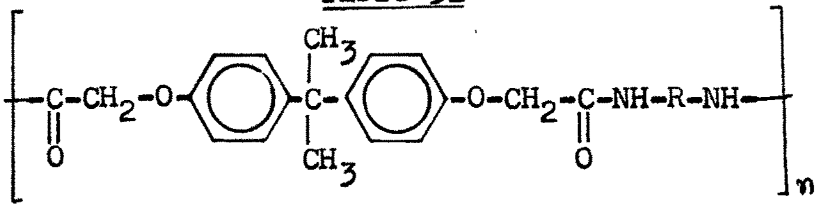


IR Spectral Data

IR stretching Vibrations (cm^{-1})

BEA_3	BEA_5	Model
3300	3310	3325
2920	2920	2900-2960
1705	1700	1650
1600	1600	1610
1570	1570	1510
1495	1505	1460
1445	1445	1315
1240	1240	1245
840	840	835

Table-52

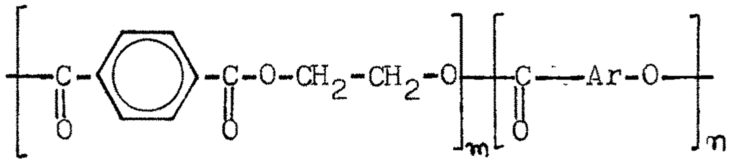


IR Spectral Data

IR stretching Vibrations (cm^{-1})

BP_4	BP_6	Model
3350	3380	3400
2920	2950	2980
1650	1675	1690
1600	1600	1610
1530	1495	1510
1500	1430	1235
1355	1360	825
820	820	

Table-53



IR Spectral Data

IR stretching Vibrations (cm^{-1})

MP_1	MP_2	MP_4	MP_5	MP_7	MP_8
3440	3450	3420	3410	3410	3410
2950	2950	2930	2940	2940	2945
1710	1715	1710	1710	1710	1710
1590	1590	1600	1600	1655	1660
1505	1500	1500	1500	1600	1600
1400	1445	1400	1430	1590	1535
865	865	865	865	1435	1495
760	830	820	820	1360	1360
720	755			860	865
				830	830

are well suited for our purpose. It is a unique property that dilute polymer solution has much higher viscosity than that of pure solvent. This is because pressure of the dissolved macromolecules on the solution increases the energy dissipation in the laminar flow over that for the pure solvent flow by the polymer segments. This large difference in viscosity, and various functions derived therefrom are usually measured to produce information about the nature of microstructure of the polymer under study. It will be proper to define viscosity functions which are being estimated for this purpose.

The ratio of the viscosity of a dilute polymer solution (η) to that of a pure solvent (η_0) of equal density and of equal hydrokinetic pressure is approximately equal to the polymer-solvent efflux-time ratio in the capillary viscometer. The latter ratio is designated as the relative viscosity (η_{rel}) or as the viscosity ratio (386) (Dimentionless ratio):

$$\eta_{rel} = \frac{\eta}{\eta_0}$$

Because η_{rel} approaches 1 and not zero as the solution becomes more dilute, the relative viscosity obviously does not denote the polymer's ability to increase the viscosity of the dispersion medium. To compensate for this discrepancy, the relative viscosity is diminished by 1; a new term results that is denominated as the specific viscosity (η_{sp}), increment due to all solute molecules. The specific viscosity relationship may be expressed by the equivalent form;

$$\eta_{sp} = (\eta - \eta_0)/\eta_0$$

where η is the viscosity of the solution
and η_0 that of the solvent.

The specific viscosity is not yet the intensive function derived because it increases with concentration. When the specific viscosity, divided by the concentration expressed in a new quantity known as the reduced viscosity (η_{red}), increment per unit solute concentration at given concentration or the viscosity number is obtained.

$$\eta_{red} = \eta_{sp}/C$$

where C is concentration in g/dl

Viscosity may also be expressed by logarithmic relation (387) termed either the inherent viscosity (η_{inh}) or the logarithmic viscosity number and be defined as $\ln \eta_{rel}/C$

$\eta_{inh} = \ln \eta_{rel}/C$ where C is concentration in gm/dl.

Usually the reduced and inherent viscosities have different values for a given concentration, the latter being lower. Neither of this term is independent of concentration, but they are usually linear functions of concentration in dilute solutions which can be extrapolated to a common intercept as the concentration approaches zero (388). The common limiting value of either of these functions in infinity dilute solution is called the intrinsic viscosity $[\eta]$, the limiting viscosity number.

$$[\eta] = \left[\frac{\eta_{sp}}{C}\right]_{C \to 0}$$

The intrinsic viscosity is the intensive property which permits the determination of molecular weight and the solution dimension of macromolecules.

The linear relationship between the reduced viscosity and the concentration is expressed by the Huggin's equation (389). It is employed to estimate intrinsic viscosity.

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 c.$$

In the relation K' is Huggin's constant and is obtained by plotting η_{sp}/C versus C. The intercept yields $[\eta]$ and k' is calculated from the value of the slope which is equal to k'$[\eta]$.

Similarly kraemer (387) relationship

$$\frac{\ln \eta_{rel}}{C} = [\eta] - K''[\eta]^2 c$$

can be applied to the experimental data and $[\eta]$ can be determined from the plot of

$$\frac{\ln \eta_{rel}}{C} \text{ vs } C.$$

The methods known as one point methods are also used to calculate intrinsic viscosity $[\eta]$ which avoids entirely the use of some constants such as k' and K". These one point methods have certain inbuilt limitations.

They assume the linear behaviour between C and η_{sp}/C and /or ln η_{rel}. Other modification are also used which involve the constants. In the present study our main interest was the comparision of viscosity data within the similar polymeric systems, hence the following equation was used which is recommended for the one point method (390).

$$[\eta] = \frac{2\left(\eta_{sp} - \ln \eta_{rel}\right)^{\frac{1}{2}}}{C}$$

where C is the concentration g/dl.

5.4.2 Experimental:

The polymer samples have been characterized by measuring their intrinsic viscosity. Standardized suspended type Ubbelohde viscometer was used for the measurement of viscosity of the polymer samples in suitable solvents. The viscometer was washed with chromic acid, rinsed several times with distilled water and finally with acetone and dried.

Solvents used for preparing the polymer solutions were purified by distillation before use. The solvents were filtered through G-3 sintered glass funnel. The solvent was carefully introduced in the clean viscometer held vertically in the thermostat and allowed to stand for ten minutes to attain the constant temperature. The average flow time was measured by taking the three independent readings.

The required amount of well powdered and dried polymer was dissolved in suitable solvent. The clear solution was filtered through G-3 sintered glass funnel. The solution thus prepared was carefully introduced in a viscometer held vertically in thermostat. It was allowed to attain the thermostat temperature. The flow time was measured atleast three times and the average flow time was noted. From the mean efflux time different viscosities were calculated and are summarized in Tables-54 to 64.

Similarly, viscosities of some of the polymers were measured by taking different concentrations of polymers at the same temperature.

η_{sp}/C against C was plotted and the straight line obtained was extrapolated to zero concentration to obtain the value of intrinsic viscosity $[\eta]$ for the system.(Fig.20).

The intrinsic viscosity $[\eta]$ of the polymer samples obtained from graphical method by taking different concentration of the polymer sample tallies with the values obtained by "one point" method as shown in Table-65.

Table-54

Viscosity data of Homopolymers of 4-hydroxybenzoic acid

Poly(4-oxybenzoates) (Table-11):

i) Solvent : Conc. H_2SO_4 (98 %).

ii) Temperature : 25°C.

iii) Concentration : 2 %, 0.5 % for sample HP_{19}.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	HP_1	1.0540	0.0553	0.0267	0.0270
2	HP_2	1.0670	0.0670	0.0325	0.0321
3	HP_3	1.0830	0.0822	0.0403	0.0402
4	HP_4	1.0660	0.0662	0.0323	0.0323
5	HP_5	1.0740	0.0738	0.0358	0.0363
6	HP_6	1.0840	0.0845	0.0402	0.0426
7	HP_7	1.0600	0.0601	0.0282	0.0294
8	HP_8	1.0960	0.0693	0.0332	0.0355
9	HP_9	1.0800	0.0800	0.0385	0.0392
10	HP_{10}	1.0750	0.0746	0.0359	0.0363
11	HP_{11}	1.1120	0.1091	0.0525	0.0534
12	HP_{12}	1.1230	0.1233	0.0582	0.0592
13	HP_{13}	1.1030	0.1028	0.0490	0.0495
14	HP_{14}	1.0990	0.0930	0.0461	0.0463
15	HP_{15}	1.0930	0.0933	0.0462	0.0474
16	HP_{16}	1.0960	0.0959	0.0458	0.0453
17	HP_{17}	1.1400	0.1393	0.0655	0.0644
18	HP_{18}	1.1430	0.1429	0.0668	0.0679
19	HP_{19}	1.0370	0.0374	0.0731	0.0736
20	HP_{20}	1.0900	0.0899	0.0436	0.0429

Table-55

Viscosity data of Homopolymers of 3-methoxy-4-hydroxybenzoic acid (Vanillic acid); Poly(4-oxy-3-methoxybenzoates) (Table-12):

i) Solvent : DMF for samples V_1, V_2, V_4 and V_7.
Conc. H_2SO_4 (98%) for remaining samples.

ii) Concentration: 1% for samples V_1, V_2, V_4 and V_7, 0.5 % for remaining samples.

iii) Temperature : 25°C.

Sr. No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	V_1	1.0600	0.0604	0.0640	0.0769
2	V_2	1.1040	0.1038	0.0998	0.0990
3	V_3	1.0380	0.0381	0.0746	0.0750
4	V_4	1.2360	0.2358	0.2114	0.2178
5	V_5	1.0390	0.0389	0.0760	0.0765
6	V_6	1.0420	0.0420	0.0820	0.0825
7	V_7	1.1320	0.1321	0.1244	0.1261
8	V_8	1.0380	0.0381	0.0746	0.0750
9	V_9	1.0430	0.0427	0.0834	0.0844
10	V_{10}	1.0334	0.0334	0.0659	0.0660
11	V_{11}	1.0460	0.0458	0.0894	0.0900
12	V_{12}	1.0290	0.0358	0.0557	0.0597
13	V_{13}	1.0140	0.0137	0.0272	0.0273
14	V_{14}	1.0230	0.0229	0.0451	0.0453
15	V_{15}	1.0330	0.0328	0.0645	0.0648
16	V_{16}	1.0360	0.0359	0.0704	0.0708
17	V_{17}	1.0370	0.0377	0.0732	0.0738

Table-56

Viscosity data of polyesters of o- and m-hydroxybenzoic acids: Poly(2-oxybenzoates)and poly(3-oxybenzoates) (Table-13):

i) Solvent : DMF.

ii) Concentration : 0.5 %.

iii) Temperature : 30°C.

Sr. No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	OHB_1	1.131	0.133	0.249	0.253
2	OHB_2	1.113	0.112	0.213	0.216
3	OHB_3	1.131	0.133	0.249	0.253
4	OHB_4	1.174	0.173	0.320	0.327
5	OHB_5	1.163	0.163	0.303	0.309
6	OHB_6	1.204	0.204	0.372	0.381
7	MHB_1	1.138	0.141	0.258	0.264
8	MHB_2	1.123	0.123	0.232	0.235
9	MHB_3	1.152	0.153	0.280	0.288
10	MHB_4	1.081	0.082	0.157	0.158
11	MHB_5	1.235	0.235	0.422	0.434
12	MHB_6	-	-	-	- (a)
13	OHB_7	-	-	-	- (a)
14	$O-Co-M_1$	-	-	-	- (a)
15	$O-Co-M_2$	-	-	-	- (a)

(a) Insoluble in DMF.

Table-57

Viscosity data of Co-polymers of 4-hydroxybenzoic acid and 3-hydroxybenzoic acid: Poly(4-Co-3-oxybenzoates) (Table-18):

(i) Solvent : DMSO.

(ii) Concentration : 0.5 %.

(iii) Temperature : 30°C.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	P-Co-M_1	-	-	-	- (a)
2	P-Co-M_2	-	-	-	- (a)
3	P-Co-M_3	-	-	-	- (a)
4	P-Co-M_4	-	-	-	- (a)
5	P-Co-M_5	1.073	0.072	0.139	0.141
6	P-Co-M_6	1.059	0.059	0.116	0.117
7	P-Co-M_7	1.059	0.059	0.116	0.117
8	P-Co-M_8	1.040	0.039	0.078	0.078
9	P-Co-M_9	1.040	0.039	0.076	0.078
10	P-Co-M_{10}	1.057	0.057	0.111	0.111

(a) Insoluble in DMSO.

Table-58

Viscosity data of Copolymers of 4-hydroxybenzoic acids and 3-methoxy-4-hydroxybenzoic acid ; Poly(4-oxybenzoates-Co-4'-oxy-(3'-methoxybenzoates) (Table-20):

(i) Solvent : DMSO.

(ii) Concentration : (a) 0.25 % for samples VB_2 and VB_3.
(b) 0.50 % for samples VB_4 to VB_{11}.

(iii) Temperature : 30°C.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	VB_1	-	-	-	- (a)
2	VB_2	1.043	0.044	0.171	0.172
3	VB_3	1.036	0.036	0.142	0.142
4	VB_4	1.071	0.069	0.136	0.138
5	VB_5	1.064	0.064	0.125	0.126
6	VB_6	1.062	0.061	0.119	0.120
7	VB_7	1.051	0.051	0.100	0.101
8	VB_8	1.036	0.036	0.071	0.071
9	VB_9	1.041	0.041	0.080	0.080
10	VB_{10}	1.046	0.046	0.090	0.094
11	VB_{11}	1.052	0.051	0.100	0.100

(a) Insoluble in DMSO.

Table-59

Viscosity data of polyesters obtained from 1,2-bis(4'-carboxy-phenoxy) ethane (Table-34):

i) Solvent : DMSO.

ii) Concentration : 0.5 %.

iii) Temperature : 30°C.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	BE_1	1.0520	0.0513	0.1004	0.1009
2	BE_2	1.0430	0.0439	0.0856	0.0862
3	BE_3(a)	-	-	-	-
4	BE_4	1.1280	0.1282	0.2410	0.2450
5	BE_5	1.1950	0.1949	0.3570	0.3640

(a) Polymer insoluble in DMSO.

Table-60

Viscosity data of polyesters obtained from p-azoxybenzoic acid (Table-35):

i) Solvent : i) p-chloro phenol for polymers (PABC- 1-4,8).
ii) H_2SO_4 (98%) for polymers (PABC 5-7,9-12).
ii) Concentration i) 0.5 %.
ii) 0.35 % for polymer ($PABC_4$).
iii) Temperature : 25°C.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	$PABC_1$	1.092	0.0849	0.1659	0.1743
2	$PABC_2$	1.142	0.1345	0.2658	0.2676
3	$PABC_3$	1.168	0.1660	0.3076	0.3134
4	$PABC_4$	1.163	0.1640	0.4336	0.4424
5	$PABC_5$	1.042	0.0425	0.0829	0.0833
6	$PABC_6$	1.035	0.0331	0.0695	0.0687
7	$PABC_7$	1.046	0.0463	0.0896	0.0905
8	$PABC_8$	1.100	0.1000	0.1900	0.2290
9	$PABC_9$	1.040	0.0395	0.0778	0.0782
10	$PABC_{10}$	1.042	0.0425	0.0829	0.0833
11	$PABC_{11}$	1.056	0.0565	0.1096	0.1105
12	$PABC_{12}$	1.049	0.0490	0.0981	0.0964

Table - 61

Viscosity data of polyesters obtained from 3,3'-dimethoxy-4-4'-dihydroxy benzalazine (Table-36):

i) Solvent : DMSO.

ii) Concentration : 0.5 %.

iii) Temperature : 25°C.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	AZ_1	1.059	0.0588	0.1160	0.1150
2	AZ_2^a	-	-	-	-
3	AZ_3	1.100	0.0995	0.1890	0.1920
4	AZ_4	1.118	0.1177	0.2220	0.2250
5	AZ_5	1.086	0.0857	0.1649	0.1665
6	AZ_6^a	-	-	-	-

(a) : Polymers insoluble in DMSO.

Table-62

Viscosity data of Polyamides obtained from 1,2-bis(4'-carboxy phenoxy) ethane (Tables 38 to 40):

i) Solvent : DMSO.

ii) Concentration: 0.5 %.

iii) Temperature: 25°C.

Sr. No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	BEA_1	1.0410	0.0412	0.0777	0.0803
2	BEA'_1	1.0950	0.0950	0.1815	0.1706
3	BEA''_1	-	-	-	-
4	BEA_2	1.0500	0.0497	0.0919	0.1012
5	BEA'_2	1.0860	0.0857	0.1649	0.1605
6	BEA''_2	1.0730	0.0724	0.1395	0.1414
7	BEA_3	-	-	-	-
8	BEA'_3	1.1130	0.1131	0.2142	0.2122
9	BEA''_3	1.0770	0.0769	0.1390	0.1540
10	BEA_4	-	-	-	- (a)
11	BEA'_4	-	-	-	- (a)
12	BEA''_4	-	-	-	- (a)
13	BEA_5	-	-	-	- (a)
14	BEA'_5	-	-	-	- (a)
15	BEA''_5	-	-	-	- (a)
16	BEA_6	-	-	-	- (a)
17	BEA'_6	-	-	-	- (a)
18	BEA''_6	-	-	-	- (a)

(a): Polymer insoluble in DMSO.

Table-63

Viscosity data of Polyamides obtained from 2,2-bis (4'-carboxy-ethoxy-phenyl) propane (Table-41):

i) Solvent : DMF.
ii) Concentration : 0.5 %.
iii) Temperature : 25°C.

Sr.No.	Polymer	Viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	BP_1	1.0590	0.0588	0.1160	0.1150
2	BP_2	1.0640	0.0633	0.1230	0.1240
3	BP_3	1.0680	0.0673	0.1270	0.1280
4	BP_4	1.1040	0.01041	0.1980	0.2000
5	BP_5	1.0900	0.0905	0.1730	0.1750
6	BP_6	1.1040	0.1041	0.1980	0.2000

Table -64

Viscosity data of copolymers obtained from DMT, EG and Hydroxy aromatic acid (Table-44):

i) Solvent : o-chlorophenol (OCp).

ii) Concentration : 1 %.

iii) Temperature : 25°C.

Sr. No.	Polymer	viscosity			
		η_{rel}	η_{sp}	η_{inh}	$[\eta]$ dl/gm
1	MP_1	1.345	0.345	0.296	0.308
2	MP_2	1.171	0.171	0.158	0.162
3	MP_3	1.212	0.213	0.192	0.198
4	MP_4	1.431	0.431	0.358	0.376
5	MP_5	1.143	0.143	0.133	0.136
6	MP_6	1.207	0.207	0.192	0.214
7	MP_7	1.184	0.183	0.168	0.172
8	MP_8	1.072	0.074	0.071	0.072
9	MP_9	1.198	0.193	0.187	0.179

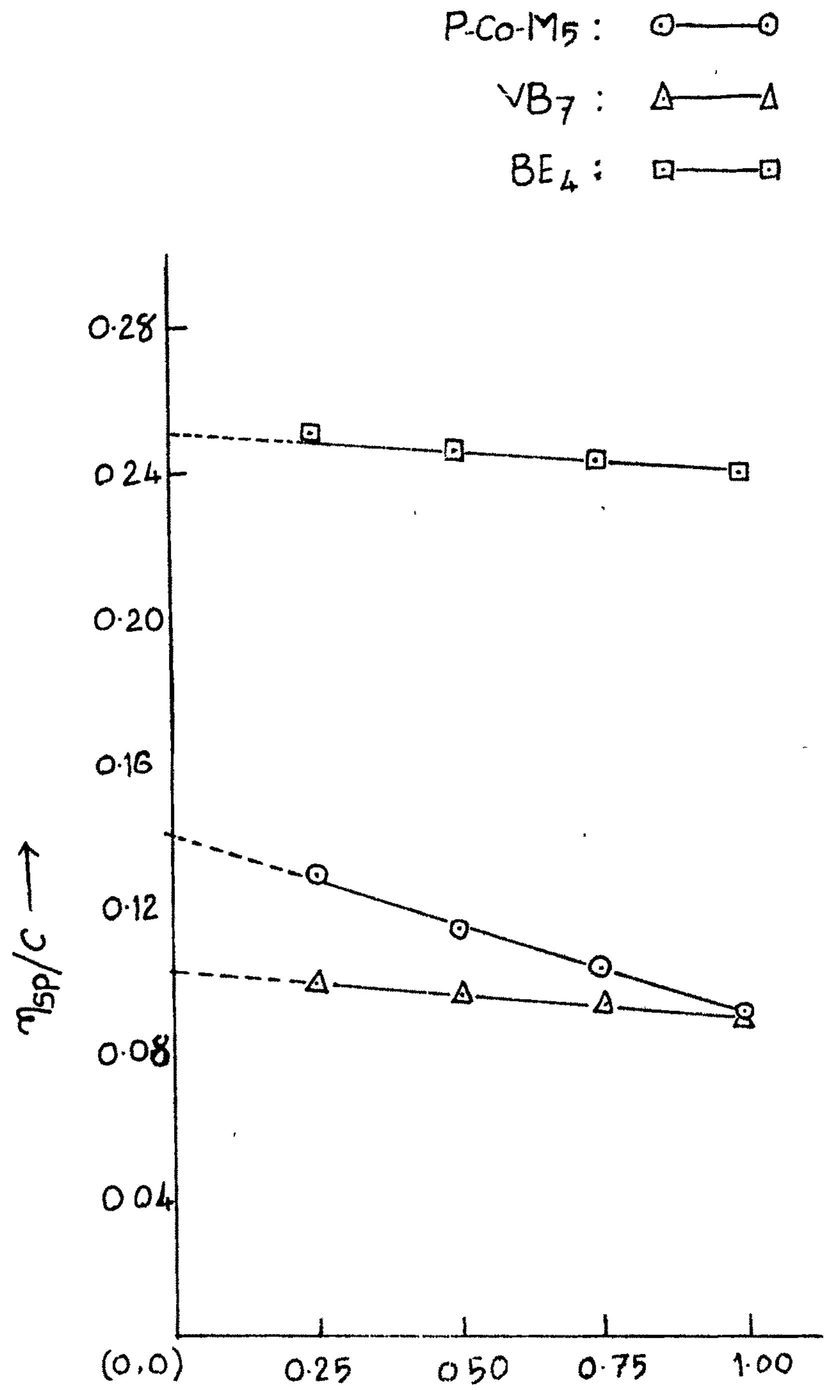


FIG. 20: Viscosity

Table -65

Viscosity of Polymeric Samples with Different Concentrations at constant Temperature :

i) Solvent used : DMSO.

ii) Temperature : 30°C.

Sr. No.	Polymer	Concentration (%) (C)	η_{sp}	η_{sp}/C	$[\eta]$ dl/gm	
					Graphical method	One point method
1	P-Co-M_5	1.00	0.0896	0.0896	0.140	0.141
2	(Table-57)	0.75	0.0771	0.1030		
3		0.50	0.0454	0.1140		
4		0.25	0.0323	0.1290		
5	VB_7	1.00	0.0890	0.0890	0.102	0.101
6	(Table-58)	0.75	0.0696	0.093		
7		0.50	0.0473	0.095		
8		0.25	0.0249	0.099		
9	BE_4	1.00	0.2563	0.240	0.250	0.245
10	(Table-59)	0.75	0.1940	0.243		
11		0.50	0.1318	0.247		
12		0.25	0.0696	0.252		

5.5 Thermogravimetry (391, 392):

5.5.1 Introduction

The thermal analysis technique of thermogravimetry (TG) is one in which the change in sample mass is recorded as a function of temperature. Three modes of thermogravimetry may be described. (a) isothermal or static thermogravimetry in which the sample mass is recorded as a function of time at constant temperature (b) quasistatic thermogravimetry, in which the sample is heated to constant mass at each of a series of increasing temperatures, and (c) dynamic thermogravimetry in which the sample is heated in an environment whose temperature is changing in a predetermined manner, preferably at a linear rate. The studies, discussed here are based on dynamic thermogravimetric analysis.

The resulting mass-change versus temperature curve (Thermograms or thermogravimetric curve) provides information concerning the thermal stability and composition of the initial sample.

Perhaps the greatest number of applications of thermogravimetry during the past ten years has been in the characterization of polymeric materials. These studies have been useful not only in the applied area but also in the theoretical aspects of high polymers. Application of

TG include comparisions of the relative thermal stability, the effect of additives on the thermal stability, moisture and additive contents, studies of degradation kinetics, direct quantitative analysis of various copolymer systems, oxidation stability, and many others.

The thermal stability is defined as a general term indicating the ability of substances to maintain its properties as nearly unchanged as possible on heating. From a practical point of view, thermal stability needs to be considered in terms of the environment to be imposed on the material and the functions it has to perform. The thermobalance is a useful technique for studying the ability of a substance to maintain its mass under variety of conditions.

5.5.2 Experimental:

In the present study twenty one polymer samples were screened for TGA study. Thermogravimetric analysis of the polymer samples have been carried out using Du-Pont-900 Thermal Analyzer. Direct Thermograms and graphs obtained by plotting temperature against % weight loss are shown in Fig. 20 to 31.

5.6 DIFFERENTIAL SCANNING CALORIMETRY (DSC) AND DIFFERENTIAL THERMAL ANALYSIS (DTA) STUDY:

5.6.1 Introduction:

There are two common laboratory methods DTA/DSC of which the polymer chemist avails himself to determine glass

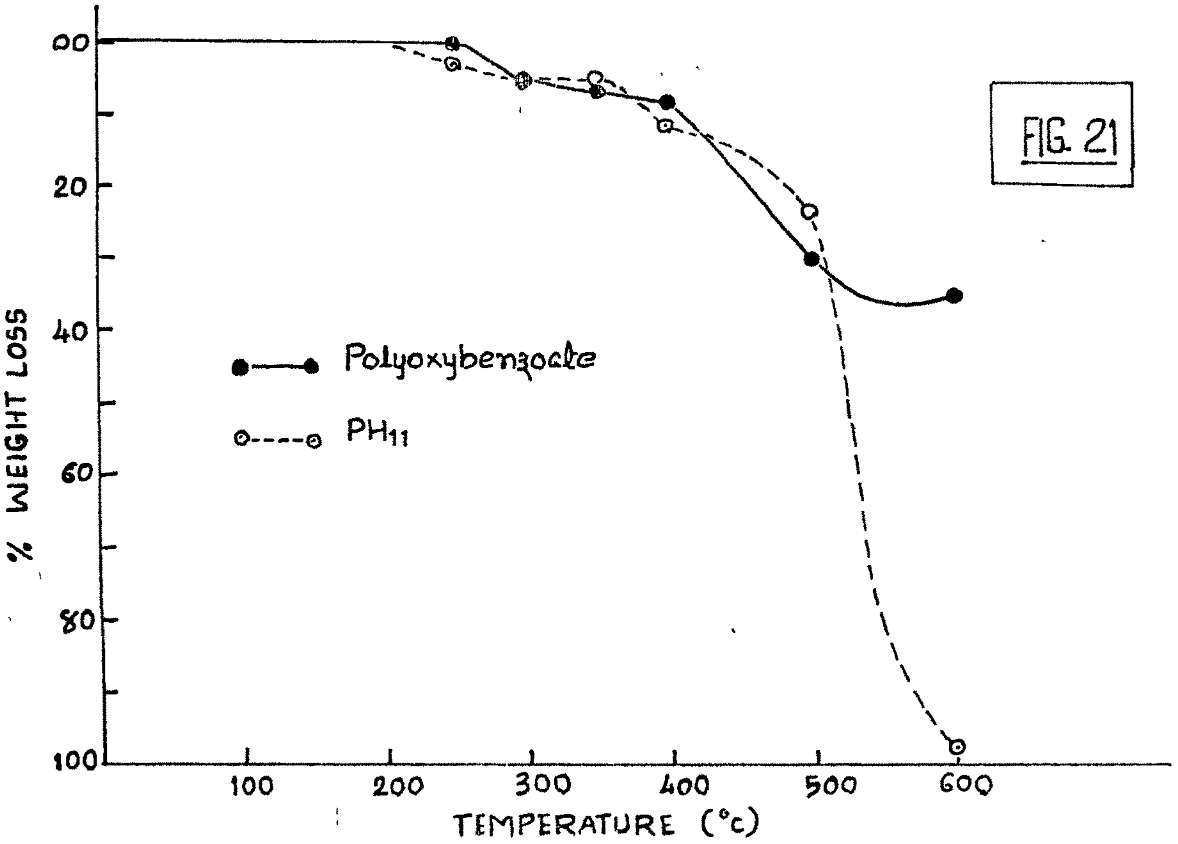


FIG. 21

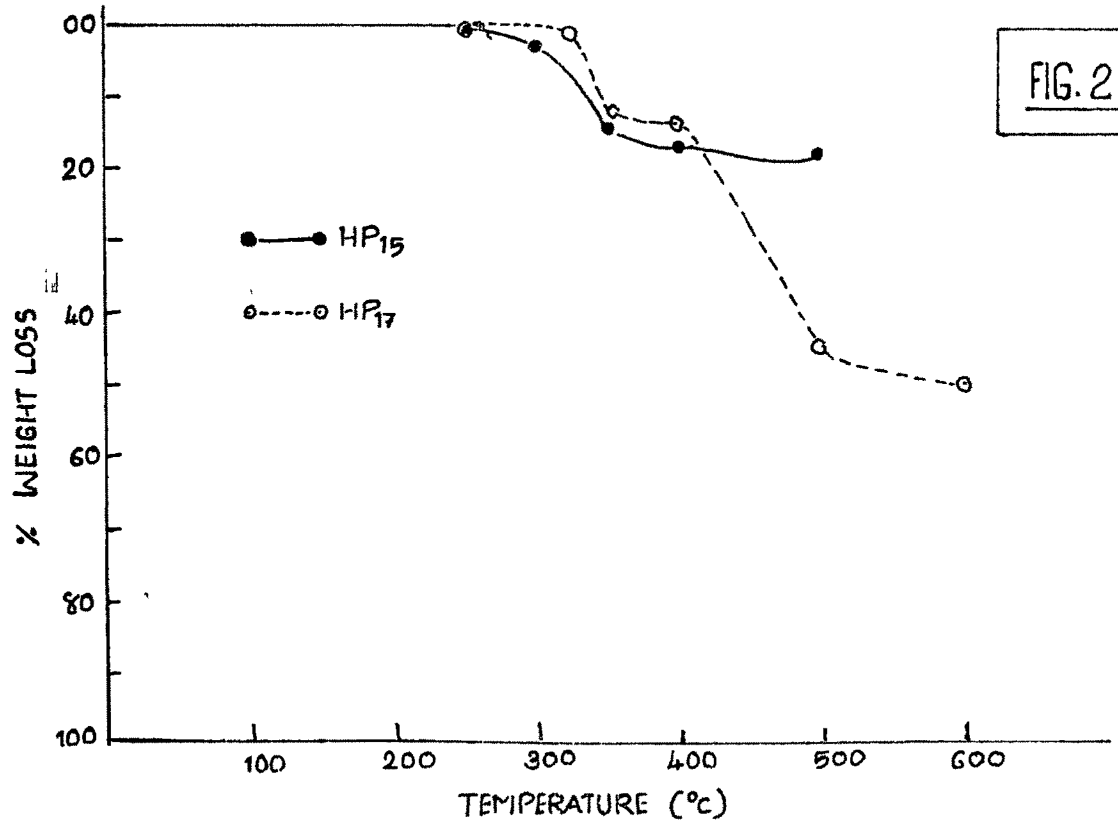


FIG. 22

TGA Thermograms

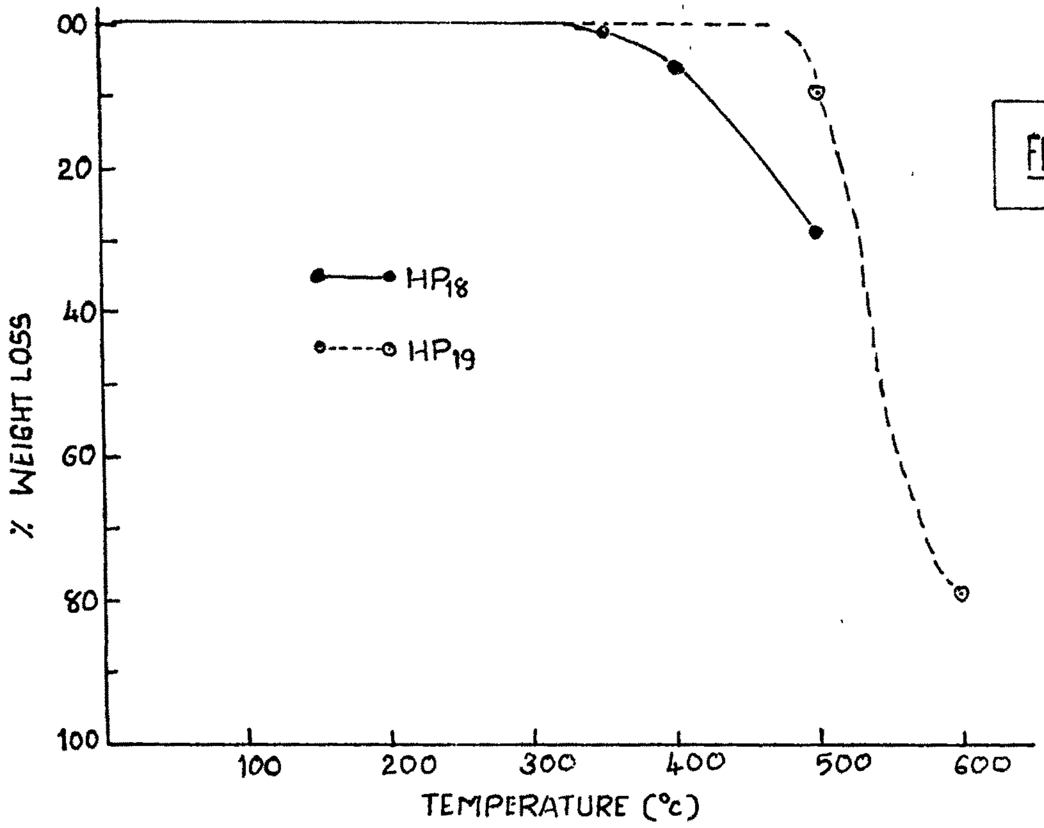


FIG. 23

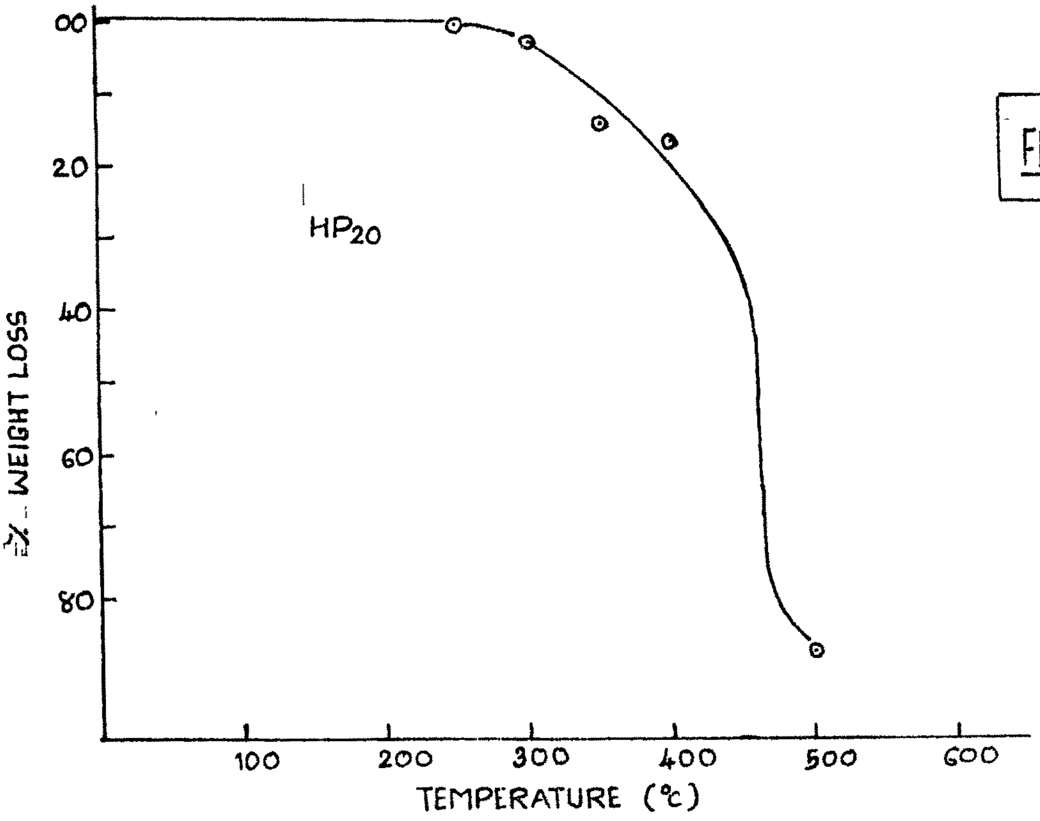


FIG. 24

TGA Thermograms

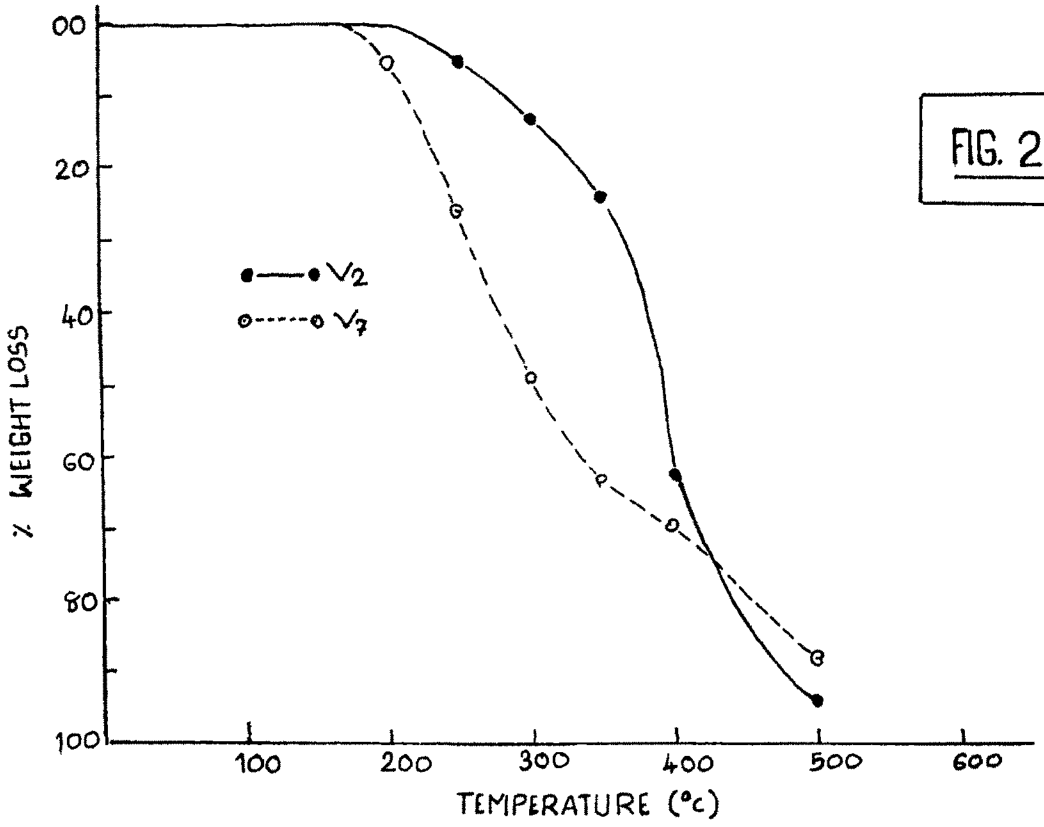


FIG. 25

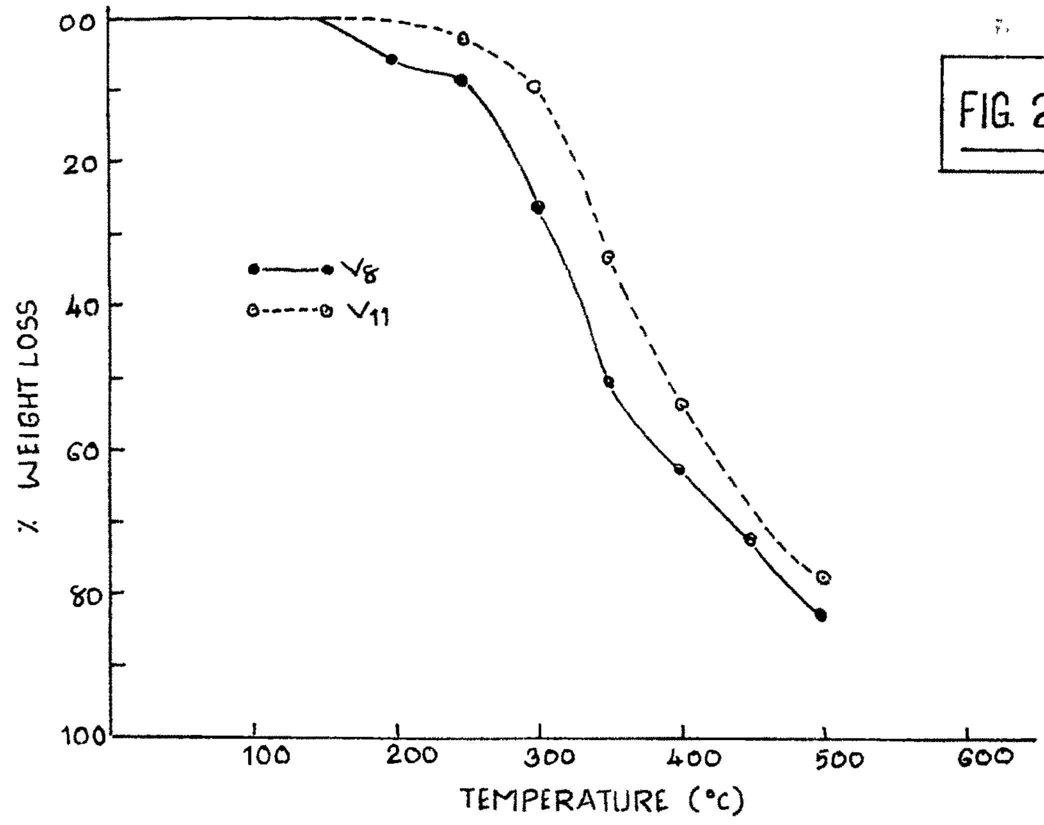


FIG. 26

TGA Thermograms

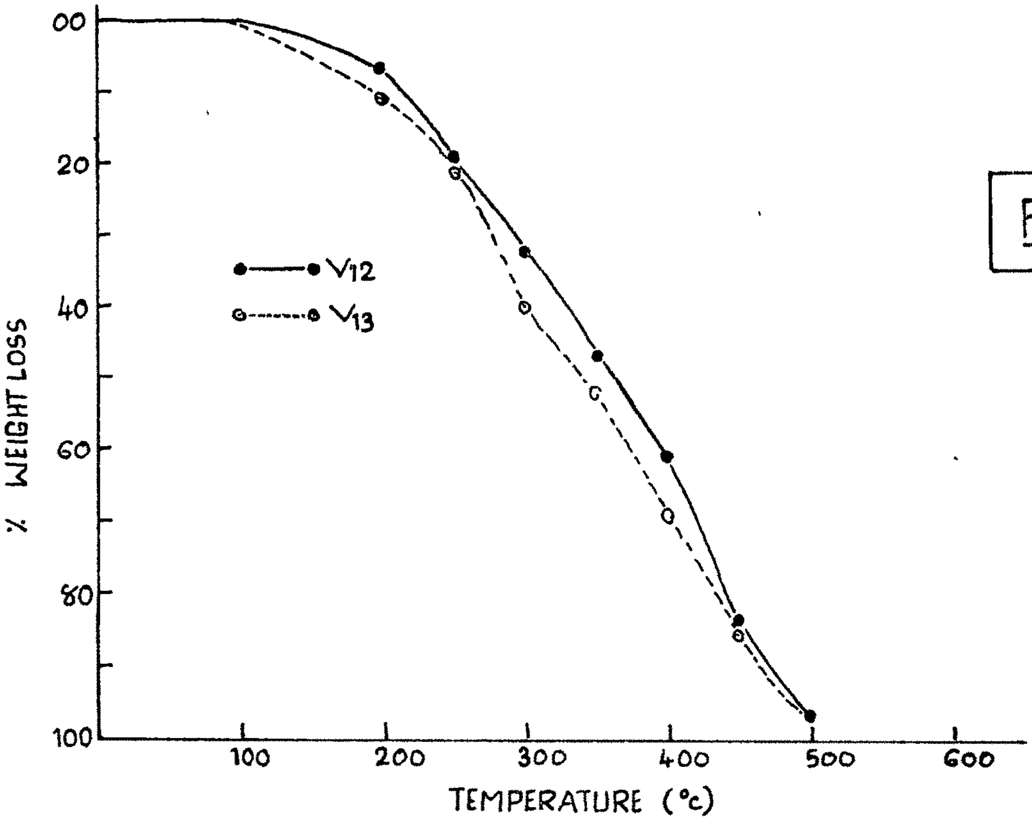


FIG. 27

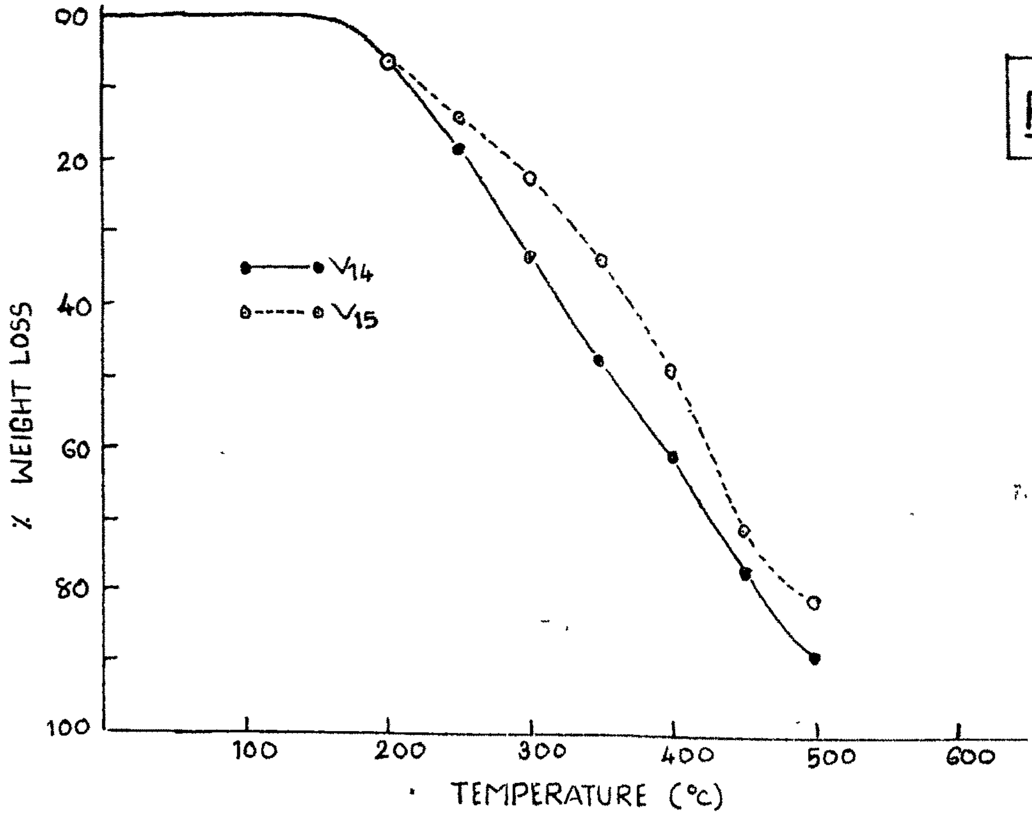


FIG. 28

TGA Thermograms

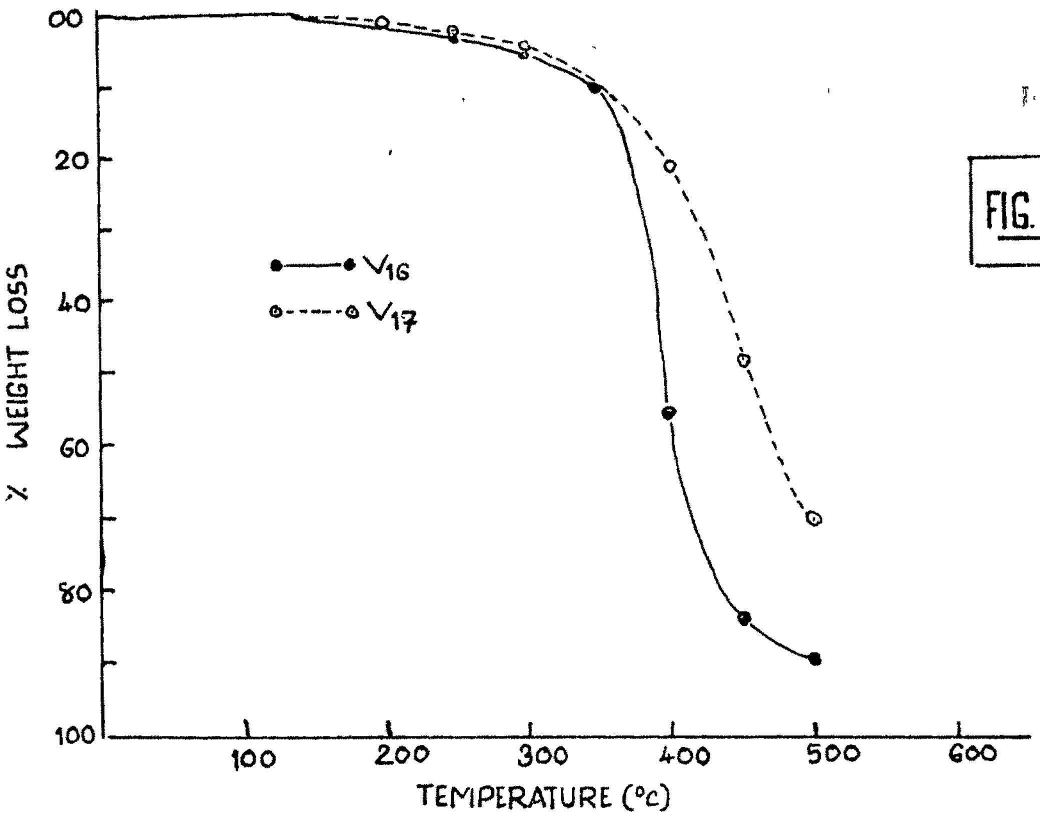


FIG. 29

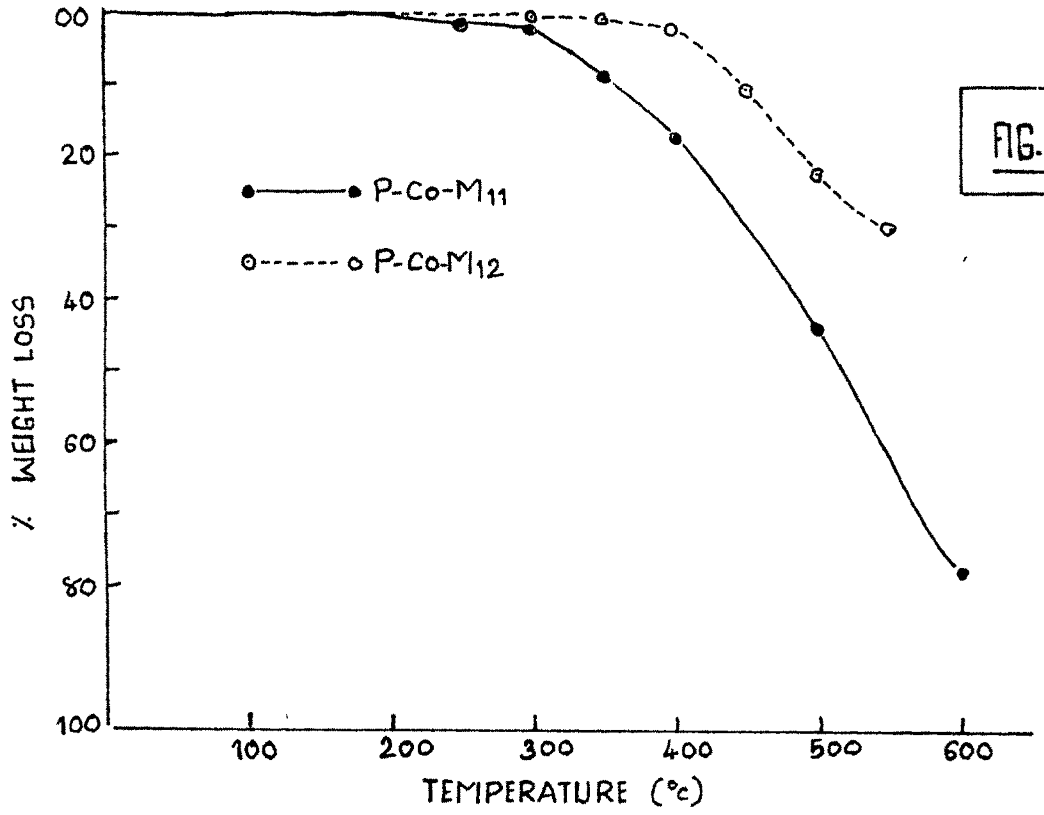


FIG. 30

TGA Thermograms

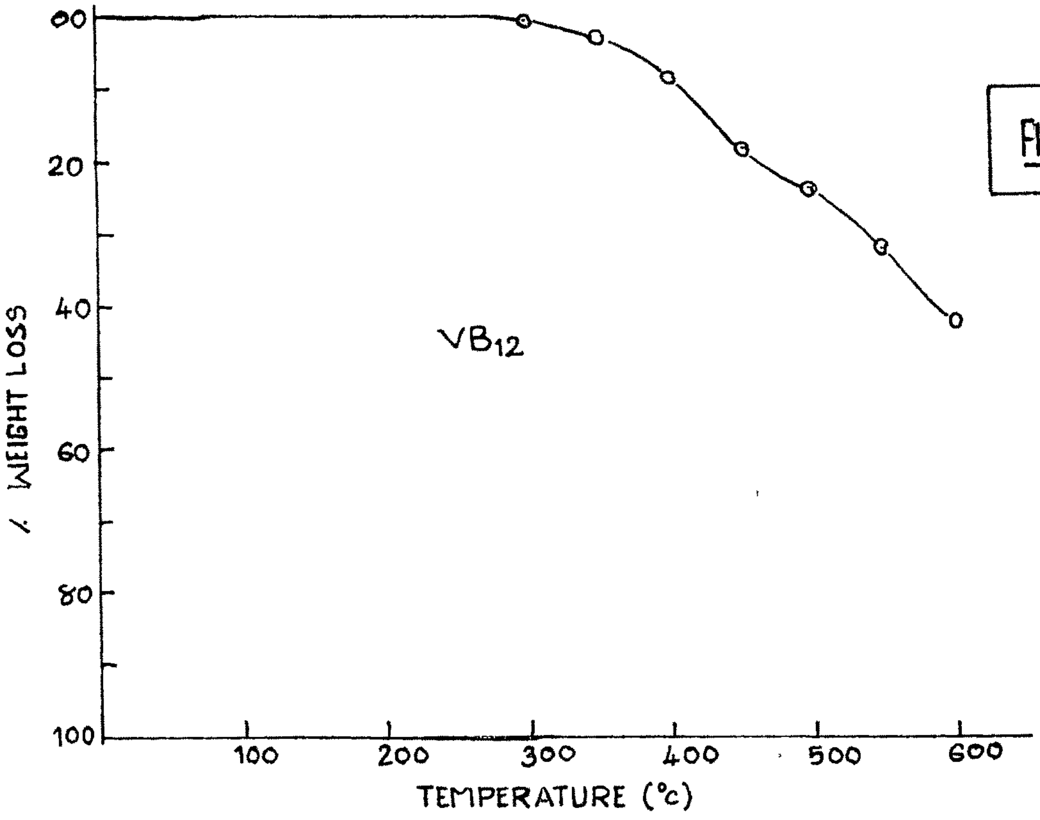


FIG 31

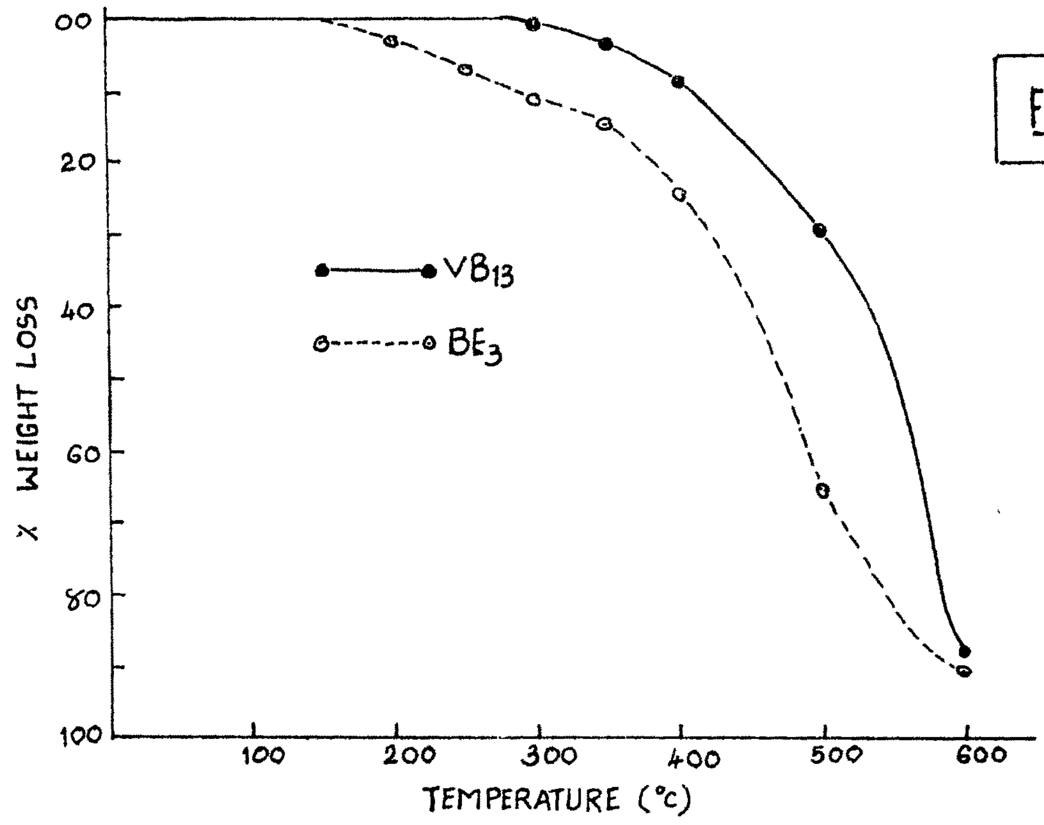


FIG. 32

TGA Thermograms

transition temperature (Tg), Melting Temperature (Tm) and transition temperatures for liquid crystalline polymers. Although both give similar looking graphic results, they are different in the thermal techniques used.

In DTA the observed thermogram is a measure of the difference in temperature between sample and the inert reference materials as the temperature of the common chamber is raised. So, if a material experiences a Tg or Tm, energy is consumed and its temperature lags behind that of the reference, hence a negative slope.

DSC is the technique of nonequilibrium calorimetry in which the heat flows into or from the sample and reference is measured as some function of time or temperature. In present available DSC equipment, the heat flow is measured by keeping the sample and reference thermally balanced by changing a current passing through heaters under two chambers.

An ideal (i.e. one which is never seen in practice) curve demonstrating both Tg and Tm is shown in Fig.33a (392).

The first endothermic break in the curve presents Tg and the sharp endothermic peak, the Tm. Frequently the base line is seen to come back gradually toward the original location after experiencing Tg.

There is another thermodynamic change which is seen occasionally, and that is an exotherm due to crystallization. This occurs between the Tg and Tm, and is due to the fact that the amorphous region may develop crystalline region after it is in its mobile rubbery state. Therefore a slightly more complex figure may present itself with three transitions, the crystallization exotherm just preceding the Tm (Fig.33b) (392).

If one traces the cooling curve of the sample, the crystallization exotherm is readily obtained (only if, of course crystallization occurs). It occurs at a slightly lower temperature then Tm due to some supercooling effect. If the sample is rapidly quenched then no crystallization forms and no exotherm is observed on cooling and no endotherm on reheating the sample.

Reaction may occur with the polymer itself, trace catalyst or impurities to endothermic peaks. An off-gas will produce an endotherm which is irreproducible on recycling the sample. The heating rate is important to visibility of the Tg; 5°C/minute is almost always too slow and 30°C/minute too fast to be able to observe the transition.

DSC is especially useful for studying organic solids and liquids. Liquid crystal systems have been studied by several authors (393-395) with respect to both heats

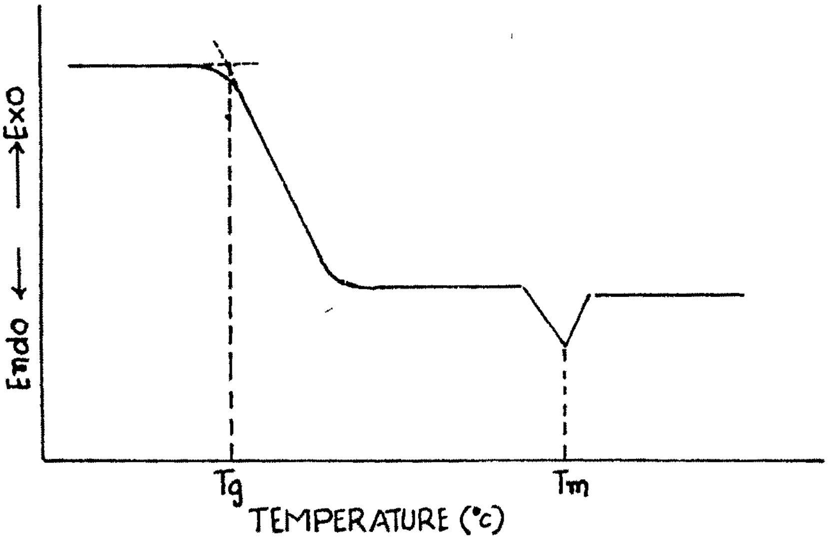


FIG. 33a: An Ideal Representation of Tg and Tm Determination by DSC or DTA (392)

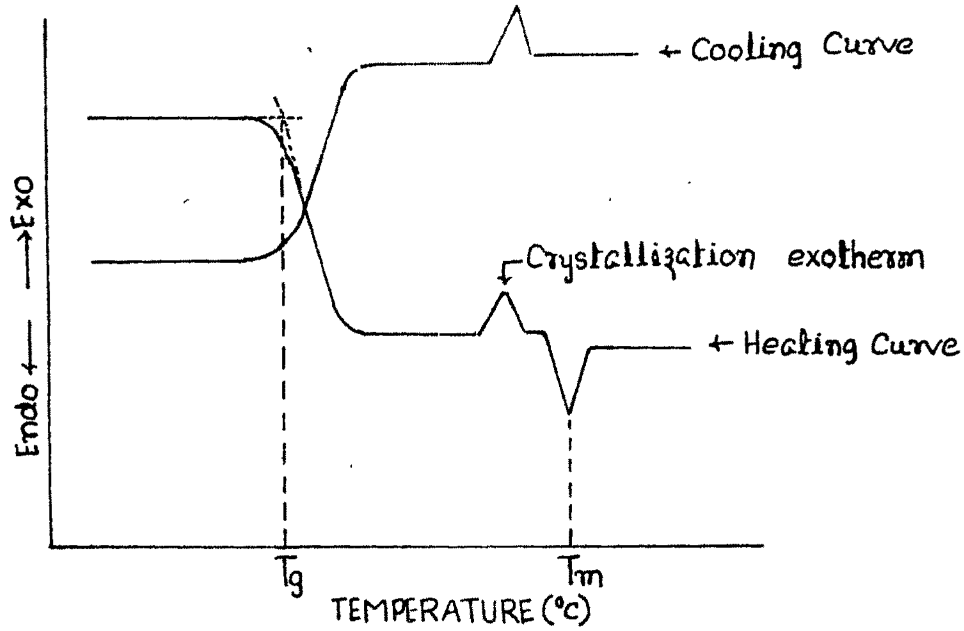


FIG. 33b: An Ideal DSC or DTA Heating and Cooling Curves Showing a Crystallization Exotherm (392)

of transition and specific heats of solid, liquid and mesophases.

Finkelmann (240) has pointed put the essential features of the phase behaviour of liquid crystalline side chain polymers. Usually, DSC trace exhibits a glass transitions, characteristic of the polymer backbone and a first-order transformation from the mesophase to the isotropic phase due to the mesogenic side chains.

The thermal behaviour of liquid crystalline main-chain polymers is more complicated. In most cases, samples show a glass transition, melting (endotherm) and mesophase-mesophase and/or mesophase-isotropic liquid transitions (endotherm). Quickly cooled samples may demonstrate so called cold crystallization (exotherm) when heated above the glass transition (396, 397). However, as observed by Grebowicz and Wunderlich (398) for low molecular weight liquid crystals, the low temperature behaviour depends on the cooling rate: the slower the cooling rate, the smaller are the glass transition and the cold crystallization exotherm. Additional first order transitions may be observed at low temperature (280, 292, 306, 399-402). They may result from

(i) A recrystallization of the polymer chain during the melting of crystalline structure originally formed.

(ii) Fundamental differences in crystal morphologies (for example folded-chain crystals and partially extended chain crystals). The two morphologies are assumed to be so different that no structural changes will occur during thermal scanning in the DSC.

(iii) 'True' Polymorphism.

This makes it difficult to interpret the DSC curves of liquid crystalline main-chain polymers and the nature of the transition can be established only through a combination of optical observations and x-ray investigations.

5.6.2 Experimental:

In present study seven polymer samples were screened for DTA/DSC study. Data were collected with 990 Dupont's Analyzer. The different thermograms are shown in Fig.34-35 and Fig.36-37.

5.7 X-RAY ANALYSIS:

The wide angle x-ray diffractograms were obtained for three polymer samples to observe the crystallinity in the mesogenic polymers.

Philips-x-ray diffractometer, Model No.PW 1390 was used for diffractograms. X-ray diffraction patterns are shown in Fig. 38-39.

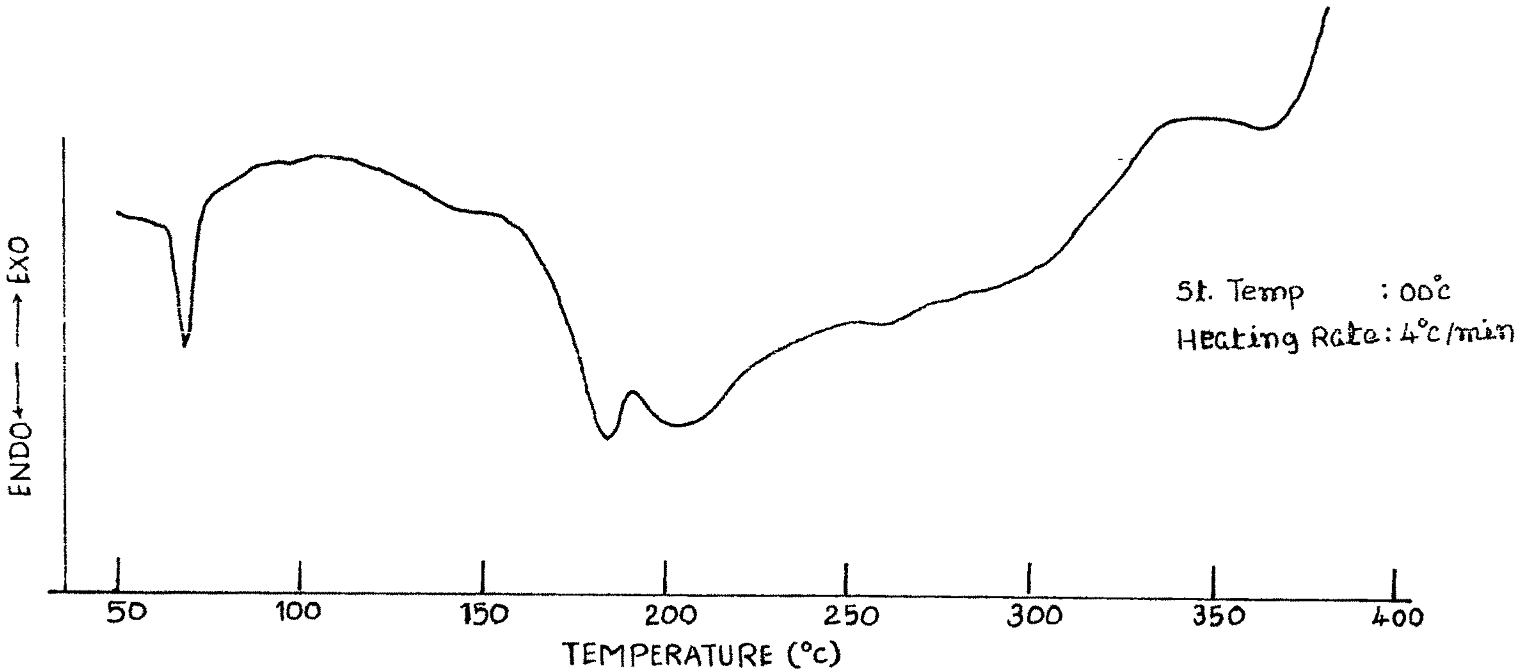


FIG. 34a: DSC Thermogram for Polymer HP_5

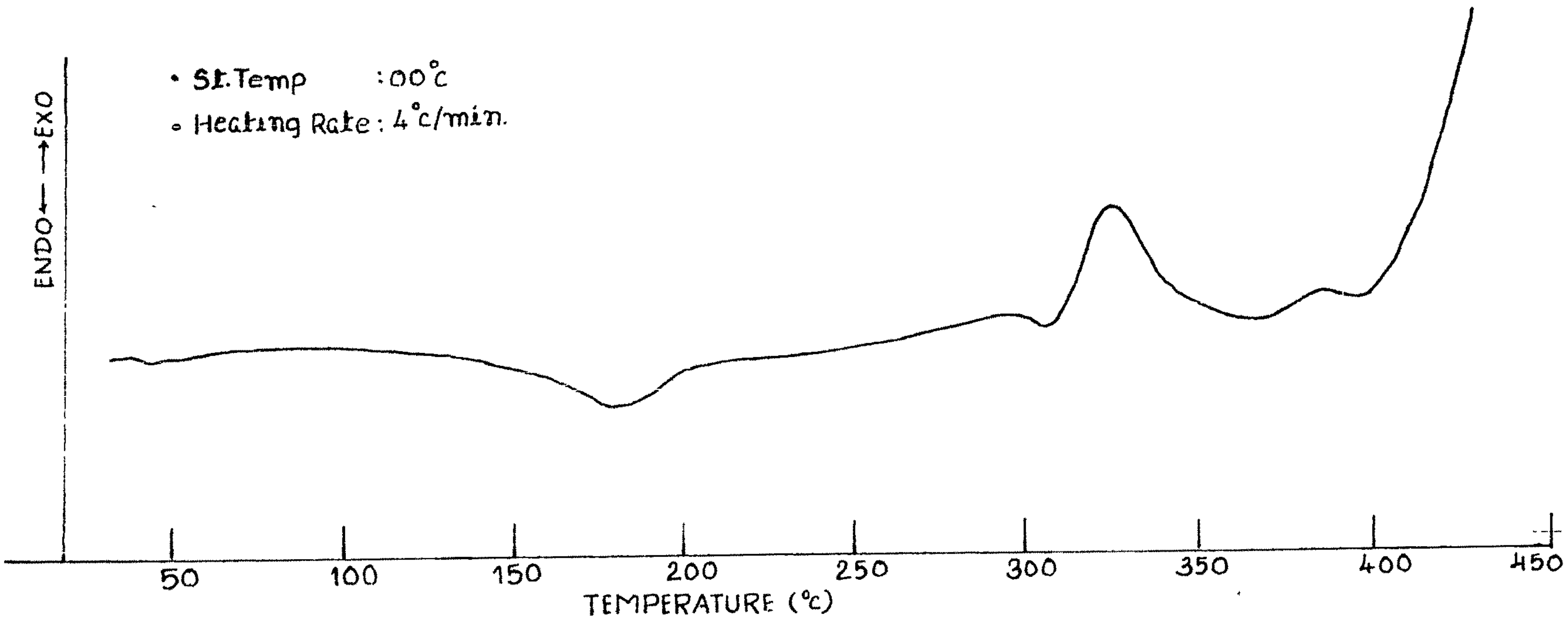


FIG 34b: DSC Thermogram for Polymer HP_3

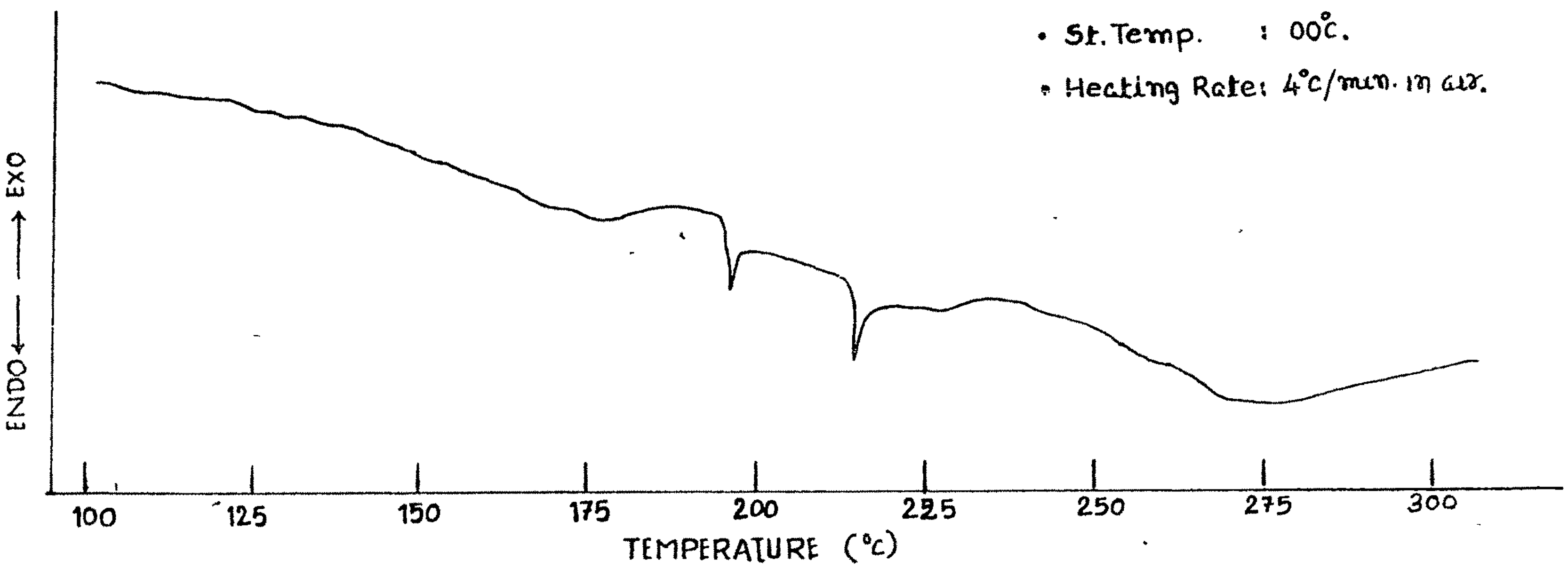


FIG. 35: DSC Thermogram of Polymer Vg

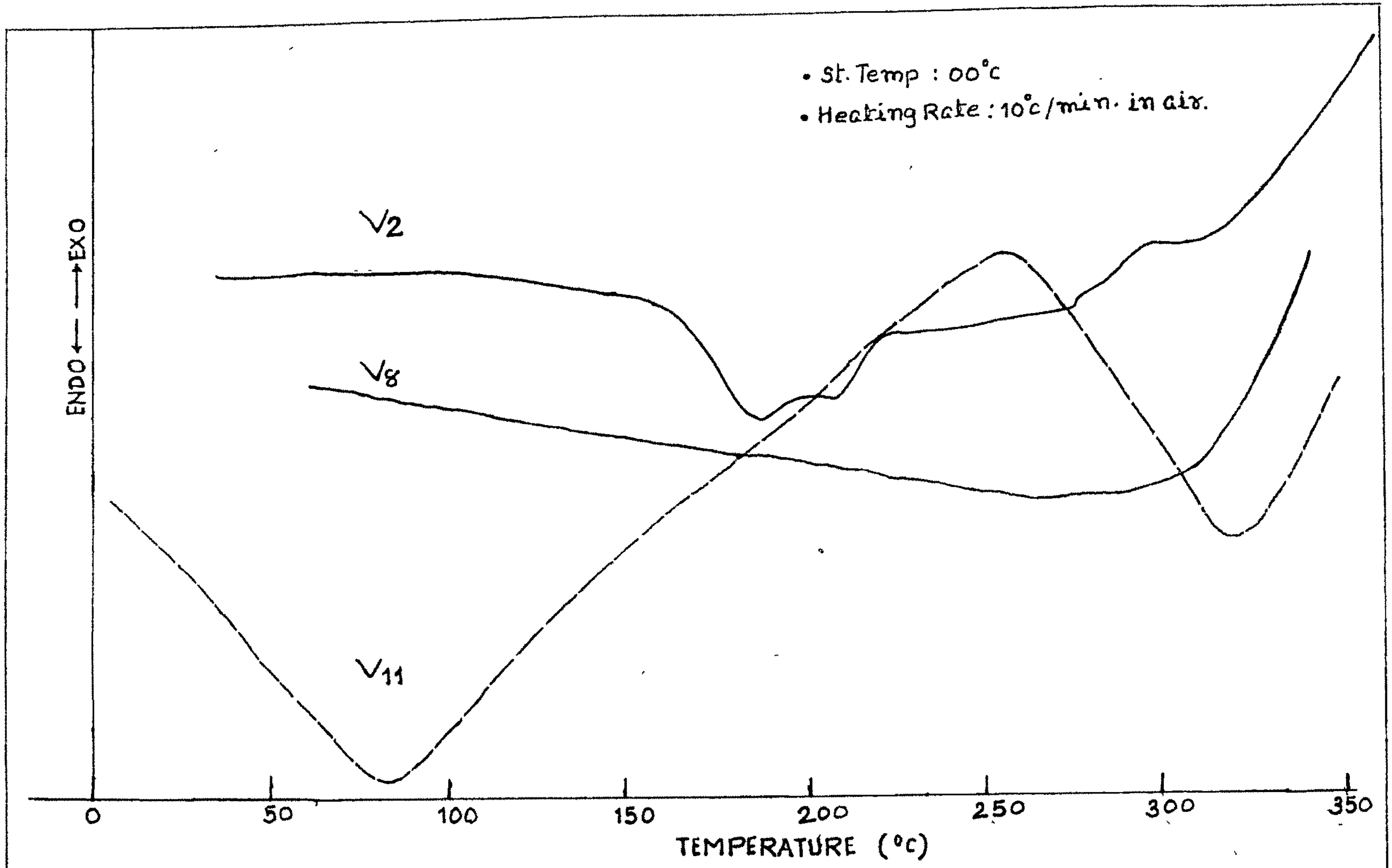


FIG. 36: DTA Thermograms of Polymers V_2, V_8 and V_{11}.

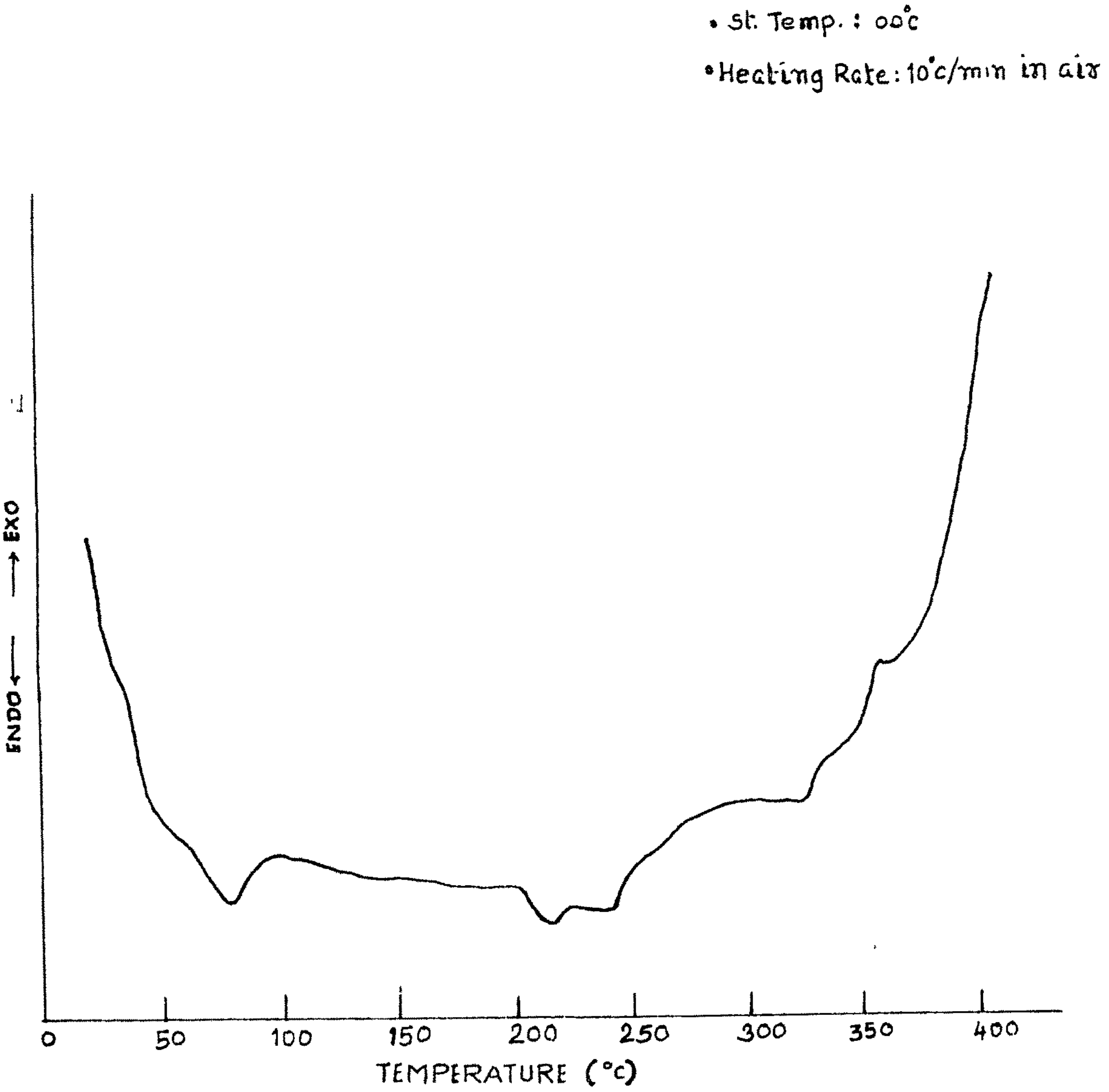


FIG. 37: DTA Thermogram of Polymer BE_3.

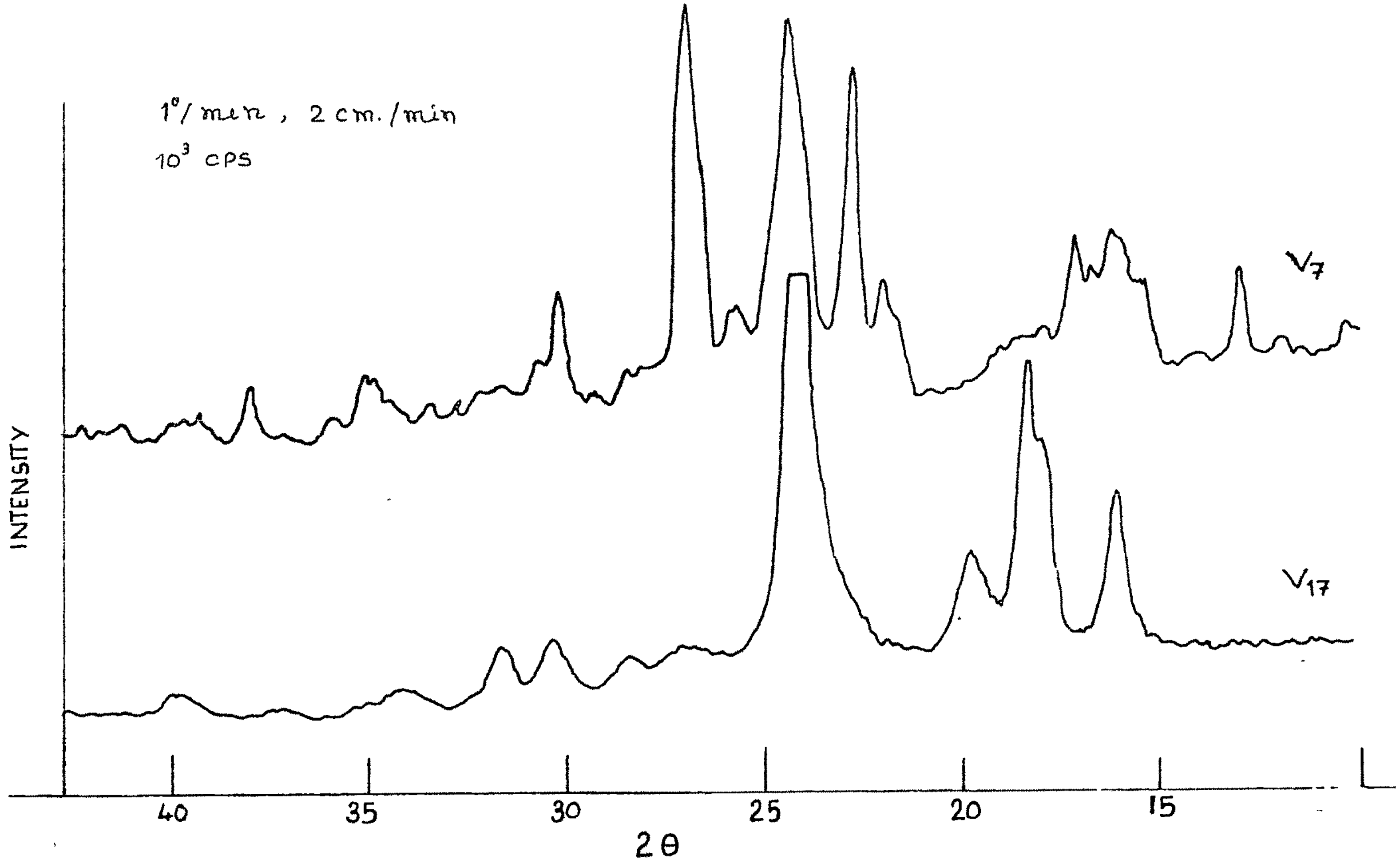


FIG. 38: X-ray Diffraction Patterns for Polymer Samples V$_7$ and V$_{17}$

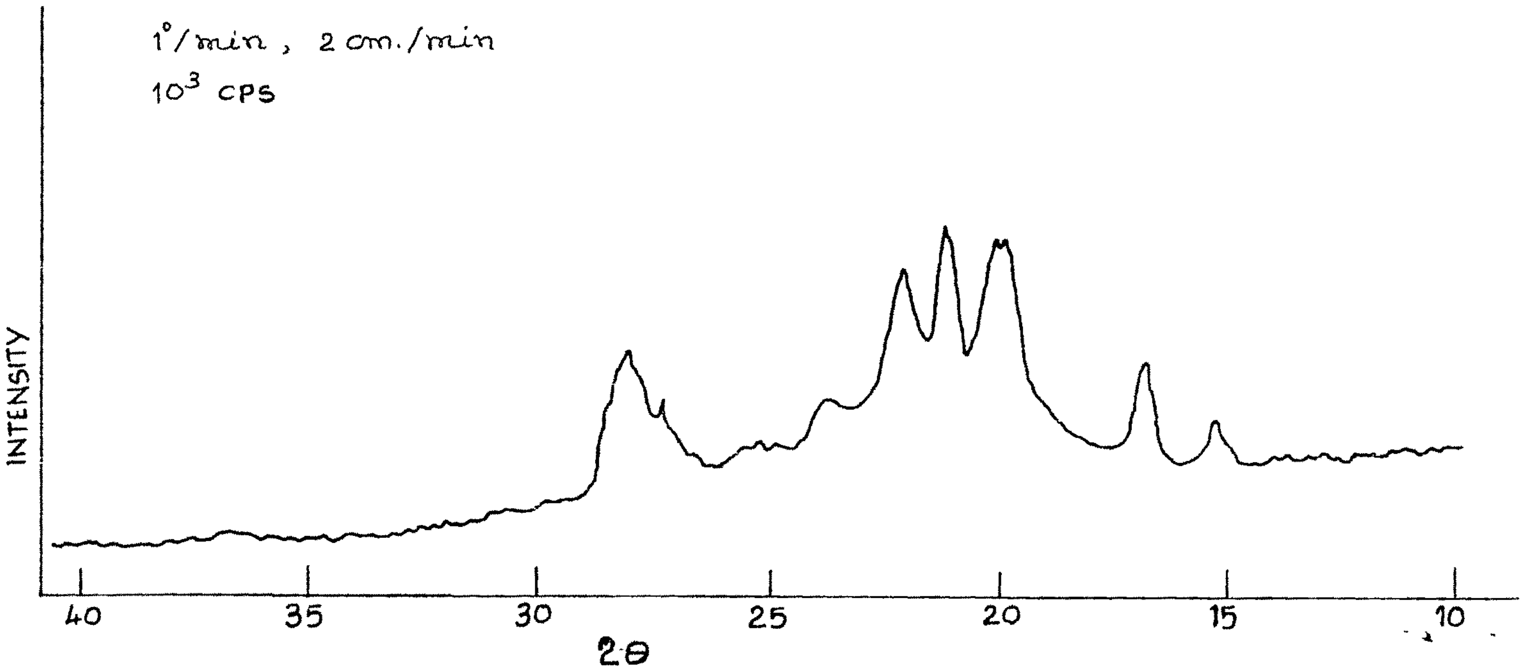


FIG. 39: X-ray Diffraction Pattern for Polymer Sample BE_3