DISCUSSION

LIQUID CRYSTALLINE HOMOPOLYMERS AND COPOLYMERS OF HYDROXY AROMATIC ACIDS

1. LIQUID CRYSTALLINE HOMOPOLYMERS AND COPOLYMERS OF HYDROXYBENZOIC ACIDS:

The ordered structure of the mesophases can endow a system with many useful properties. Polymers are the materials, whose properties depend on many aspects including the crystallinity and the arrangement of the chains in solid state. If liquid crystalline (mesogenic) order can be induced in polymeric system, host of excellent properties can be visualized. Due to this reason number of polymeric systems conducive to mesomorphism were investigated. Initial studies were in the addition polymers (214-218). Recently, the study of thermotropic mesogenic polymeric materials have attracted more number of scientists due to their structural variations and technological applications (229-232).

Isomeric hydroxybenzoic acids are well exploited as monomers for obtaining thermally stable polymers (403-406).

Homopolymerization of p-hydroxybenzoic acid is extensively studied (407-412). The polymer obtained has very good thermal stability. The polymer was commercialized as thermally stable plastic . The limitation was that the polymer was processed at higher temperature and pressure.

Eventhough poly(oxybenzoate) was extensively studied, only recently, it attracted attention due to the mesogenic behaviour of certain polymers (222-223). One of the patents reveals that first an oligomer was produced from p-hydroxybenzoic acid and then this oligomer was polymerized at 260°C to obtain a highly ordered heat resistant polymer (225).

Recent patent (413) describes aromatic polyesters capable of forming liquid crystalline phase where one of the monomer units is salicylic acid or its derivatives. They claim that the fibres or films have high modulus and strength.

Patel et al. (365) studied homopolymerization and copolymerization by condensing acid chlorides of isomeric hydroxybenzoic acids. They obtained thermally stable polymers.

p-Hydroxybenzoic acid is a starting material for many low molecular weight mesogens, moreover, it induces mesomorphic structure when copolymerized with poly(ethyleneterephthalate). Homopolymerization of p-hydroxybenzoic acid gives thermally stable polymers. All these results enthused us to study the homopolymerization and copolymerization of hydroxy aromatic acids including p-hydroxybenzoic acid.

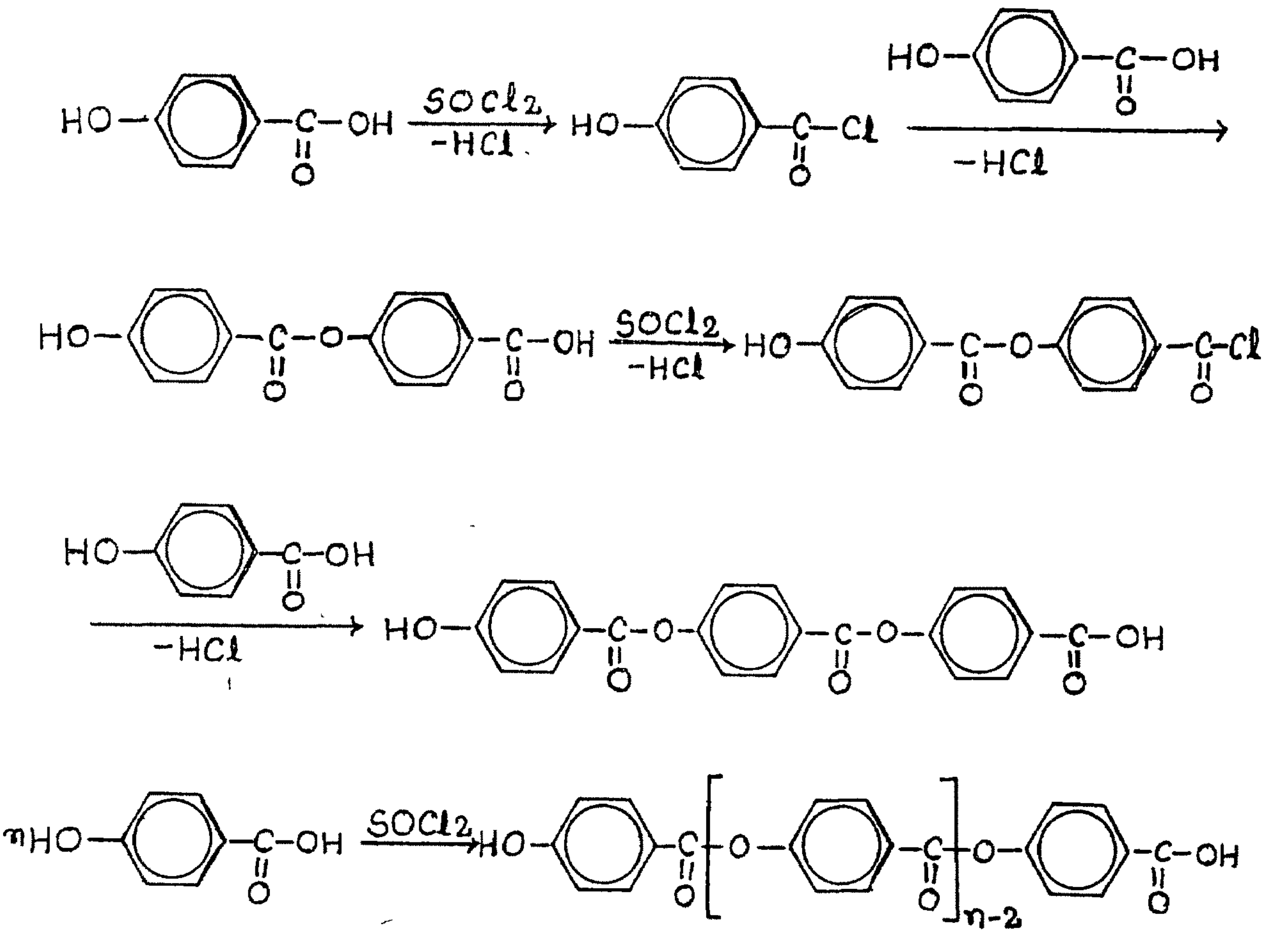
1.1 LIQUID CRYSTALLINE HOMOPOLYMERS:

1.1.1 Poly(4-oxybenzoates):

p-Hydroxybenzoic acid was homopolymerized by using thionyl chloride as condensing agent. No base was used as acid acceptor. The main objective was to obtain polymers with less degree of polymerization to exhibit the possibility of mesomorphism in the poly(4-oxybenzoate). The experimental part records the detailed procedure adopted for the synthesis of homopolymers.

The homopolymerization of p-hydroxybenzoic acid (PHB) will proceed as indicated in Fig.40.

Reference to Table-66 shows that out of fourteen samples prepared by varying different parameters, nine polymeric samples exhibit mesomorphism. Polymer samples HP_1-HP_3 obtained from xylene exhibit smectic mesophase. The polymer sample HP_4 obtained from toluene after one hour heating exhibits smectic mesophase. Sample HP_5 obtained after three hours heating is polymesogenic exhibiting smectic and nematic mesophases. Sample HP_6 obtained after six hours heating is non-mesogenic. The sample HP_7 and HP_8 obtained from benzene after one and three hours heating are smectogenic whereas sample HP_9 obtained after six hours heating is a nematogen. More



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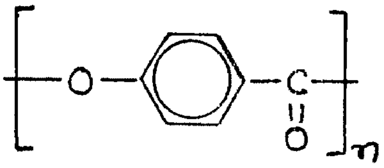
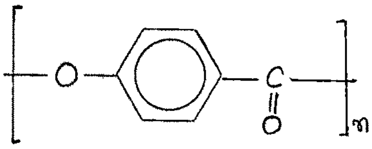


Poly (p-Oxybenzoate)

FIG. 40

Table-66



Poly(4-oxybenzoates)

Transition Temperatures and Viscosity data :

Sr. No.	Polymer	Transition Temperatures (°C)			[η] dl/gm
		Smectic	Nematic	Isotropic	
1	HP_1	306	-	324 P	0.0270
2	HP_2	301	-	318 P	0.0321
3	HP_3	327	-	340 P	0.0402
4	HP_4	274	-	315 P	0.0423
5	HP_5	297	316	325 P	0.0363
6	HP_6	-	-	>350	0.0426
7	HP_7	271	-	313 P	0.0294
8	HP_8	269	-	303 P	0.0355
9	HP_9	-	279	315 P	0.0392
10	HP_{10}	255	-	359 P	0.0363
11	HP_{11}	-	-	>350	0.0534
12	HP_{12}	-	-	>350	0.0592
13	HP_{13}	-	-	>350	0.0492
14	HP_{14}	-	-	>350	0.0463
15	HP_{15}	-	-	>350	0.0474
16	HP_{16}	-	-	>350	0.0453
17	HP_{17}	-	-	>350	0.0644

Table-66 (contd)

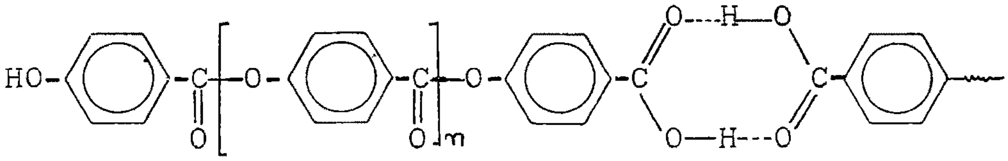
Sr. No.	Polymer	Transition Temperatures (°C)			[η] dl/gm
		Smectic	Nematic	Isotropic	
18	HP_{18}	-	-	>350	0.0679
19	HP_{18}	-	-	>350	0.0736
20	HP_{20}	-	-	>350	0.0429

P : Sample post-polymerizes and becomes solid.

interesting results are obtained when nitrobenzene was used as solvent. When the reaction was stopped within fifteen minutes, the resultant mesogenic polymer HP_{10} was obtained. However, the polymer sample HP_{11} obtained after three hours heating is non-mesogenic. When the homopolymerization was carried out at the boiling point temperature of nitrobenzene, xylene and toluene, then in all the three cases non-mesogenic polymers HP_{12}, HP_{13}, HP_{14} were obtained respectively.

Above results suggest that if milder conditions of temperatures are used during polymerization and the solvent is not highly polar then normally a mesogenic polymer is obtained. In the case of higher temperatures or polar solvents normally a non-mesogenic polymer is obtained.

There is the possibility of dimer formation through hydrogen bonding in the homopolymer as shown under:



This possibility of intermolecular hydrogen bonding is confirmed by IR spectral analysis (Fig. 41; Table-45).

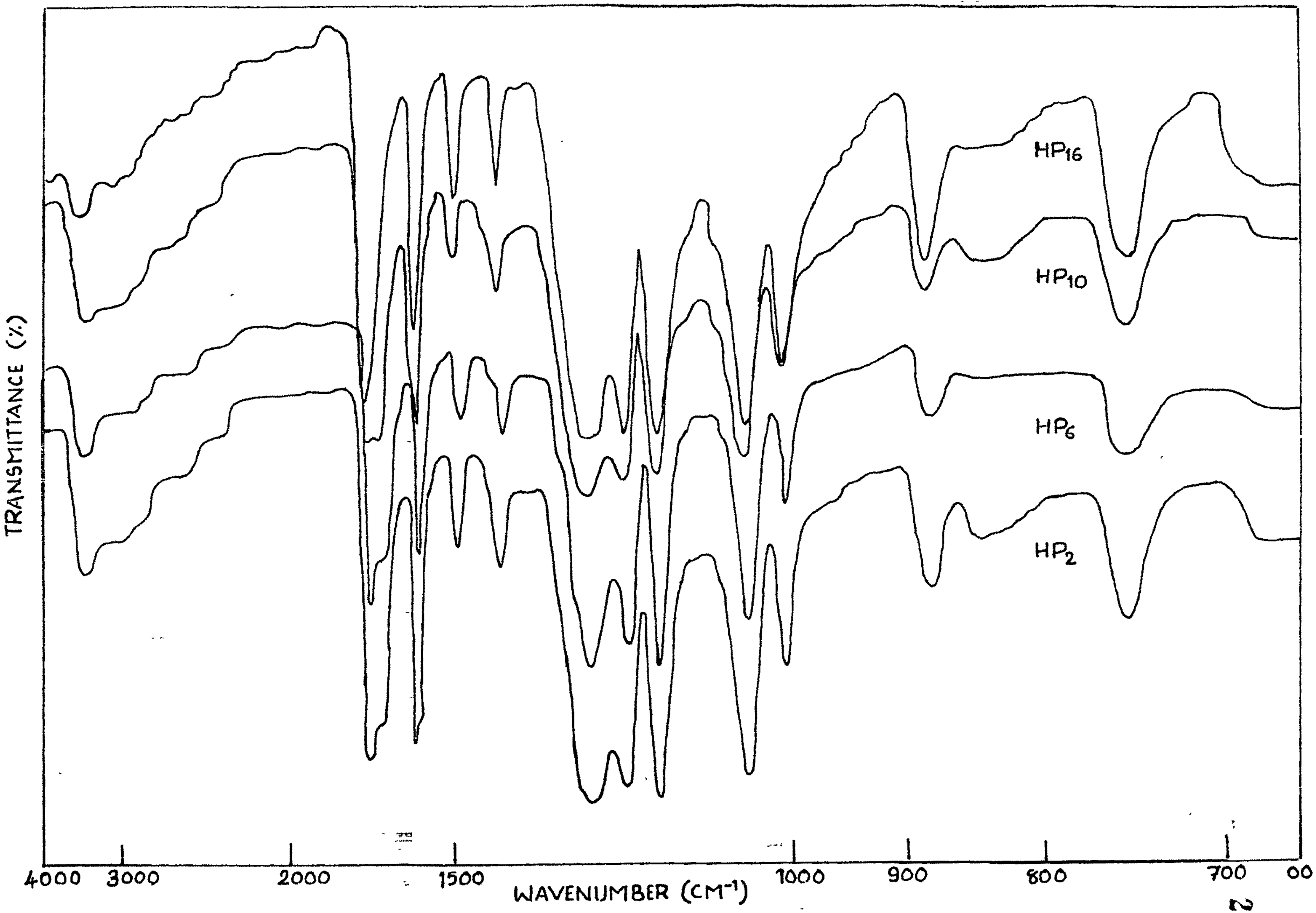


FIG. 41: IR Spectra of Poly(4-oxybenzoates)

Naturally as the degree of polymerization increases, the melting point of the polymer will also be increased and a stage will come that the melting point is increased to such a high degree that polymer remains unaffected upto 350°C. This effect will be doubled as the dimer will have two units of phenyl ring with one more increased phenyl ring in the homopolymer. The resultant polymer may or may not exhibit mesogenic properties at higher temperature. However, normally higher melting points disturb the ordered arrangement in such a way that solid is directly converted to nematic phase or isotropic liquid state. As mentioned in the experimental section, the viscosity measurements were carried out in 98 % H_2SO_4.

Reference to $[\eta]$ values (Table-66) shows that number average molecular weight of these polymers is not very high. Another interesting point worthnoting is that the nematic polymer (HP_9) and the non-mesogenic polymer samples (HP_6, HP_{11}-HP_{14}) have relatively higher intrinsic viscosities $[\eta]$ compared to smectogenic polymers. The viscosity results support the above mentioned assumption that higher molecular weight leads to less ordered mesophase or non-mesogenic character.

The polymer samples obtained at lower heating time are normally smectic in nature whereas the increased heating time results in a polymesogenic or nematogenic polymer in the same solvent. This is difficult to explain without detailed structural study of the polymers in mesogenic state, Reference to Table-66 clearly indicates that progressively longer heating time converts a smectic polymer to a nematic and finally to a non-mesogenic polymer. The non-mesogenic nature of the polymer upto 350°C can be understood as discussed above.

Reference to Table-67 shows that the homopolyesters of p-hydroxybenzoic acid (PHB) have higher solid to mesogenic transitions compared to the homopolymers of trans-4-hydroxycinnamic acid (THCA) (414). The homopolymers of PHB are more smectogenic in nature compared to the homopolyesters of THCA. These results are very typical. One would expect homopolymers of THCA more smectogenic and also exhibiting higher transition temperatures compared to the homopolymers of PHB, as cinnamic acid moiety has a little longer chain length and a little higher polarizability due to the presence of trans-CH=CH- linkage compared to benzoic acid moiety. In absence of detailed X-ray study of both the polymers in different phases it will be difficult to explain above mesogenic systems.

1.1.2 Post-polycondensation of Poly(4-oxybenzoate):

The smectogenic polymer (HP_3) with less degree of polymerization was heated further as reported in the

Table-67

Comparison of Transition Temperatures of Homopolymers of p-Hydroxybenzoic acid (PHB) and Homopolymers of trans-4-Hydroxycinnamic acid (THCA) (414):

Sr. No.	Polymer	Heating hours on water-bath	Transition Temperatures (°C) of Homopolymers of PHB			Polymer	Transition Temperatures (°C) of Homopolymers of THCA		
			Smectic	Nematic	Isotropic		Smectic	Nematic	Isotropic
1	HP_1	1	271	-	313 P	HC_1	190	210	285 P
2	HP_2	3	269	-	303 P	HC_2	185	230	295 P
3	HP_3	6 or 5	-	279	315 P	HC_3	180	235	305 P
4	HP_4	1	274	-	315 P	HC_4	215	245	295 P
5	HP_5	3	297	316	323 P	HC_5	-	210	300 P
6	HP_6	6 or 5	-	-	>350	HC_6	-	235	310 P
7	HP_7	1	306	-	324 P	HC_7	-	215	295 P
8	HP_8	3	301	-	318 P	HC_8	-	230	315 P
9	HP_9	6 or 5	327	-	340 P	HC_9	-	-	350 P
10	HP_{10}	15 minutes or 1	255	-	350 P	H_{10}	-	-	>350
11	HP_{11}	3	-	-	>350	HC_{11}	-	-	>350
12	HP_{12}	3	-	-	>350	HC_{12}	-	-	>350
13	HP_{13}	3	-	-	>350	HC_{13}	-	-	>350
14	HP_{14}	3	-	-	>350	HC_{14}	-	-	>350

P: Sample post-polymerizes and becomes solid.

Sample No.	Solvent	Sample No.	Solvent
1 to 3	Benzene	7 to 9,13	Xylene
4 to 6,14	Toluene	10 to 12	Nitrobenzene

experimental section (Table-23) in the inert atmosphere, in air and under reduced pressure to study the effect of heating on the polymer samples in mesogenic phase. The post-polymerized samples do not exhibit any mesophase up to 350°C and remain unchanged. The solution viscosity results indicate that original intrinsic viscosity $[\eta]$ of HP_3 (0.0.0283) is increased to 0.0474, 0.0453, 0.0644 (Table-66). This increase in viscosity i.e. increase in degree of polymerization explain the non-mesogenic nature due to the increased length of rigid unit of poly(4-oxybenzoate).

It has been reported in a recent patent (415) that the addition of thermotropic mesogenic polymer to poly(ethylene-terephthalate) or in nylon-66 induces mesomorphism in the melt and then fibres of better strength are drawn. Mesogenic materials obtained in the present study can be used to investigate such binary systems which can be potential for industrial applications.

The TGA study is carried out for the samples HP_{11}, HP_{15}, HP_{17-19}. Polymers exhibit good thermal stability. The stability behaviour of the polymers will be discussed simultaneously.

1.2.3 Binary Mixtures With Optically Active d-camphor:

The doping of polymers with optically active compound will be quite interesting, as it induces a cholesteric phase in the system (16, 242, 302). Moreover, chiral compounds on addition to polymers in the nematic state also yield cholesteric phase (220, 267, 416, 417). With this in view two polymers, smectogen (HP_7) (Table-31) and nematogen (HP_9) (Table-32) were mixed with optically active d-camphor in different proportion as given in the experimental section. The mixtures were made homogeneous by first melting both the components together and quenching the mixture. Then mixture was crushed to powder and the melting point and transition temperatures were determined.

The polymers post-polymerized at higher temperature and solidified, hence mesogenic-isotropic transition temperatures could not be determined. The mesogenic-isotropic temperature variations give better insight in the behaviour of binary mixture.

1.1.3a Mixture-1 : Component A + Component B (HP_7+d-camphor):

Reference to Table-31 shows that the smectogen HP_7 on addition of d-camphor exhibits polymesogenic behaviour upto 40 % by weight composition of d-camphor and exhibits smectic and cholesteric phases. Cholesteric phase is clearly identified. It exhibits vivid colour and texture typical of cholesteric phase. However, with 60 % and 80 % by weight of d-camphor, the mixture exhibits only cholesteric phase. The mesogenic-isotropic transition could not be determined as mentioned above. The results indicate that addition of non-mesogenic d-camphor affects the mesophase pattern. This is understandable. It has been observed for low molecular weight liquid crystals that addition of a non-mesogen converts the smectic mesophase to nematic phase at certain concentration (418).

The behaviour of present binary mixture can be understood. Earlier studies (419-420) have indicated that addition of an optically active compound to nematogen gives a cholesteric mesophase. Hence the observation of cholesteric mesophase in the mixture is quite understandable. The solid-mesomorphic temperatures reduced markedly in the binary mixtures compared to pure component A. This also is explainable. Addition of non-mesogenic solutes, non-conducive to mesomorphism always markedly lowers the solid-mesogenic as well as mesogenic-mesogenic and mesogenic-isotropic transition temperatures (421-426).

1.1.3b Mixture-2: Component A + Component B (HP_9+d-camphor):

HP_9 exhibits only nematic mesophase. The addition of d-camphor converts it to cholesteric mesophase as expected from literature reports. Cholesteric mesophase exhibits vivid colours. The textures observed are typical of a cholesteric phase. All the binary mixtures decrease the solid-mesogenic transition temperatures. The mesogenic-isotropic transition temperatures could not be determined as polymer post-polymerizes to infusible polymer (> 350°C).

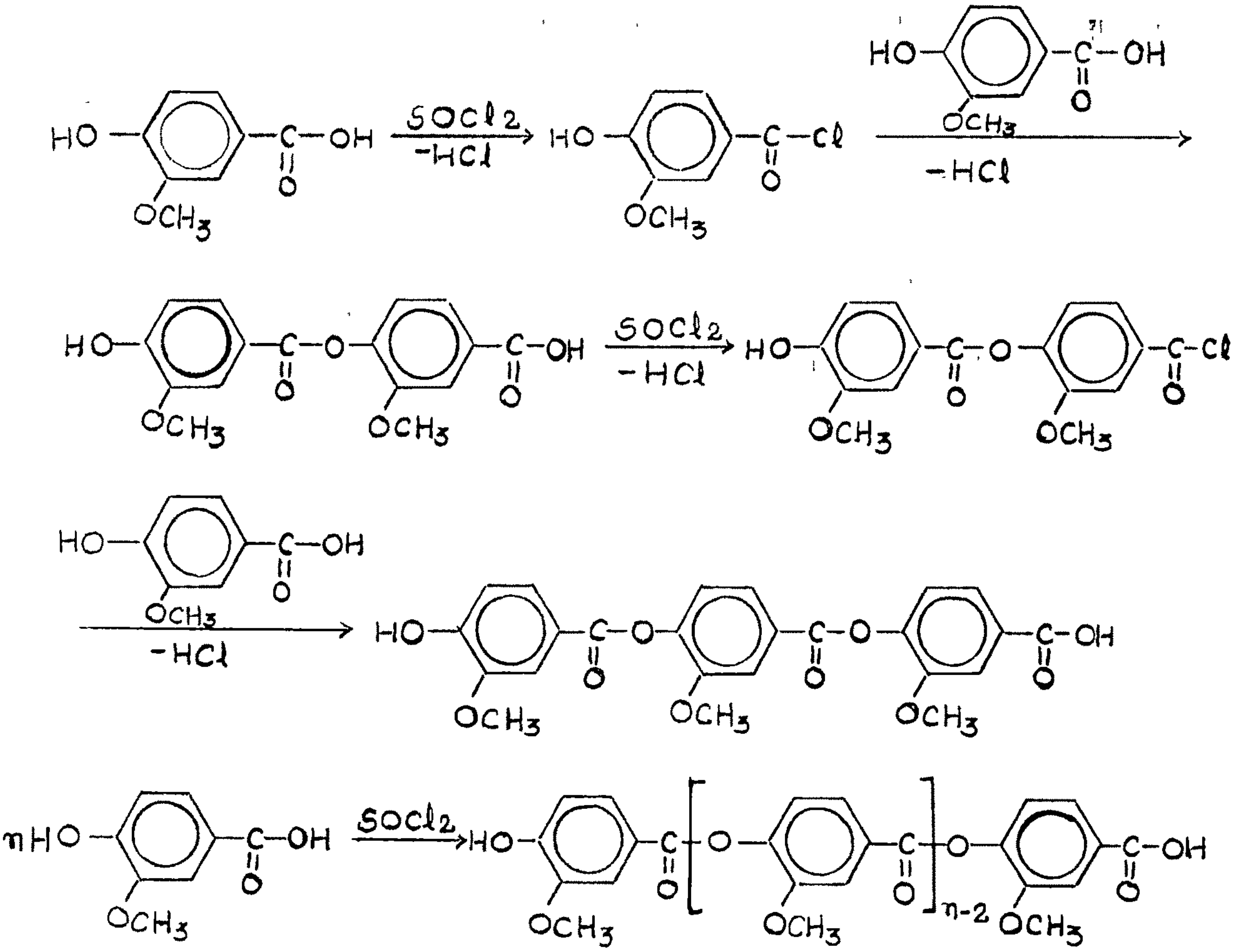
1.1.4 Poly(4-oxy-3-methoxybenzoates):

It is well established that incorporation of a lateral substituent in a mesogenic moiety decreases its solid-mesogenic (or mesogenic-isotropic) transition temperatures (384, 421, 427, 428). Poly(4-oxybenzoates) have very high solid-mesomorphic transition temperatures. They are difficult to process at high temperatures. It was proposed to obtain homopolymers of 4-hydroxy-3-methoxybenzoic acid (vanillic acid) and to evaluate their mesogenic behaviour.

The vanillic acid was synthesized from vanillin (4-hydroxy-3-methoxybenzaldehyde) as described in experimental section. 4-Hydroxy-3-methoxybenzoic acid was homopolymerized in the similar manner as 4-hydroxybenzoic acid by using thionylchloride as condensing agent.

The homopolymerization of 4-hydroxy-3-methoxybenzoic acid (vanillic acid) will proceed as indicated in Fig.42.

Reference to Table-68 shows that out of thirteen samples prepared by varying different parameters, eight



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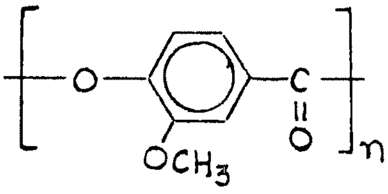
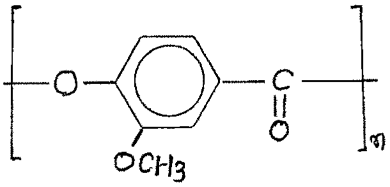


Poly (3-Methoxy-4-oxybenzoate)

FIG. 42

Table-68



Poly(4-oxy-3-methoxybenzoate)

Transition Temperatures and Viscosity Data:

Sr. No.	Polymer	Transition Temperatures (°C)			[η] dl/gm
		Smectic	Nematic	Isotropic	
1	V_1	-	123	224 P	0.0769
2	V_2	-	179	237 P	0.0990
3	V_3	-	-	>350	0.0750
4	V_4	-	215	295 P	0.2178
5	V_5	-	155	265 P	0.0765
6	V_6	-	-	350	0.0825
7	V_7	-	125	238 P	0.1261
8	V_8	-	-	>350	0.0750
9	V_9	125	190	301 P	0.0844
10	V_{10}	-	155	265 P	0.0660
11	V_{11}	-	-	>350	0.0900
12	V_{12}	-	-	>350	0.0597
13	V_{13}	-	164	241 P	0.0273
14	V_{14}	-	-	>350	0.0453
15	V_{15}	-	-	>350	0.0648
16	V_{16}	-	-	>350	0.0708
17	V_{17}	-	-	>350	0.0738

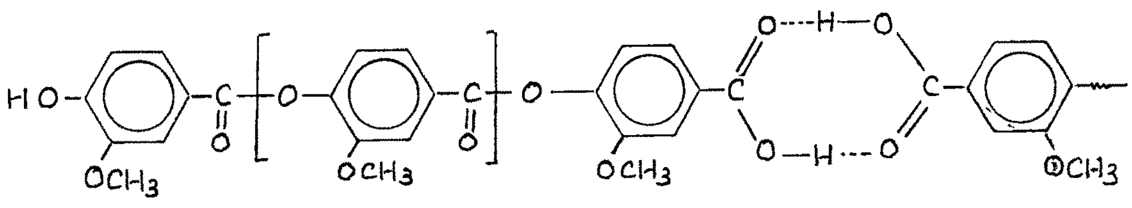
P : Sample post-polymerizes and becomes solid.

polymeric samples exhibit mesomorphism.

Polymers V_1, V_2 obtained from xylene, V_4, V_5 obtained from benzene, V_7 obtained from toluene and V_{13} obtained from nitrobenzene exhibit nematic mesophase. Polymer V_{10} obtained from toluene at high temperature exhibits nematic mesophase, polymer V_9 obtained from toluene at higher temperature and longer reaction time exhibits polymorphism. Polymers V_6 and V_8 obtained from benzene and toluene in six hours heating time are non-mesogenic. Polymers V_3 and V_{12} obtained from solvent xylene and nitrobenzene respectively by heating the monomer at the boiling point of these solvents are non-mesogenic. Polymer V_{11} obtained from nitrobenzene in three hours heating time is also non-mesogenic.

Above results suggest that if milder conditions of temperatures are used during polymerization and the solvent is not highly polar then normally mesogenic polymers are obtained. In the case of higher temperatures and polar solvents normally non-mesogenic polymers are obtained.

There is the possibility of dimer formation through hydrogen bonding in the homopolymer as shown under:



This possibility of intermolecular hydrogen bonding is confirmed by IR spectral analysis (Fig.43, Table-46).

Comparision between the mesogenic tendencies of homopolymers poly(4-oxybenzoates) (Table-66) and poly-(4-oxy-3-methoxybenzoates) (Table-68) shows that poly-(4-oxybenzoates) have smectogenic tendencies compared to poly(4-oxy-3-methoxybenzoates). Moreover, the solid-mesogenic temperatures of poly(4 -oxy-3-methoxybenzoates) are much lower (about 100°C) compared to those of poly(4-oxybenzoates).

The polymeric systems are complex compared to low molecular weight liquid crystal compounds. Straight analogies can not be derived, as in the polymeric systems mesomorphic properties might be affected due to degree of polymerization, nature of packing of macromolecules (coils), the melt viscosity of the polymer and the tacticity of the polymer chain.

The difference in mesogenic behaviour of the two polymeric systems and the lower solid-mesogenic temperatures of poly(4-oxy-3-methoxybenzoates) can be attributed to the structural differences existing between these two polymeric systems. It is established in the

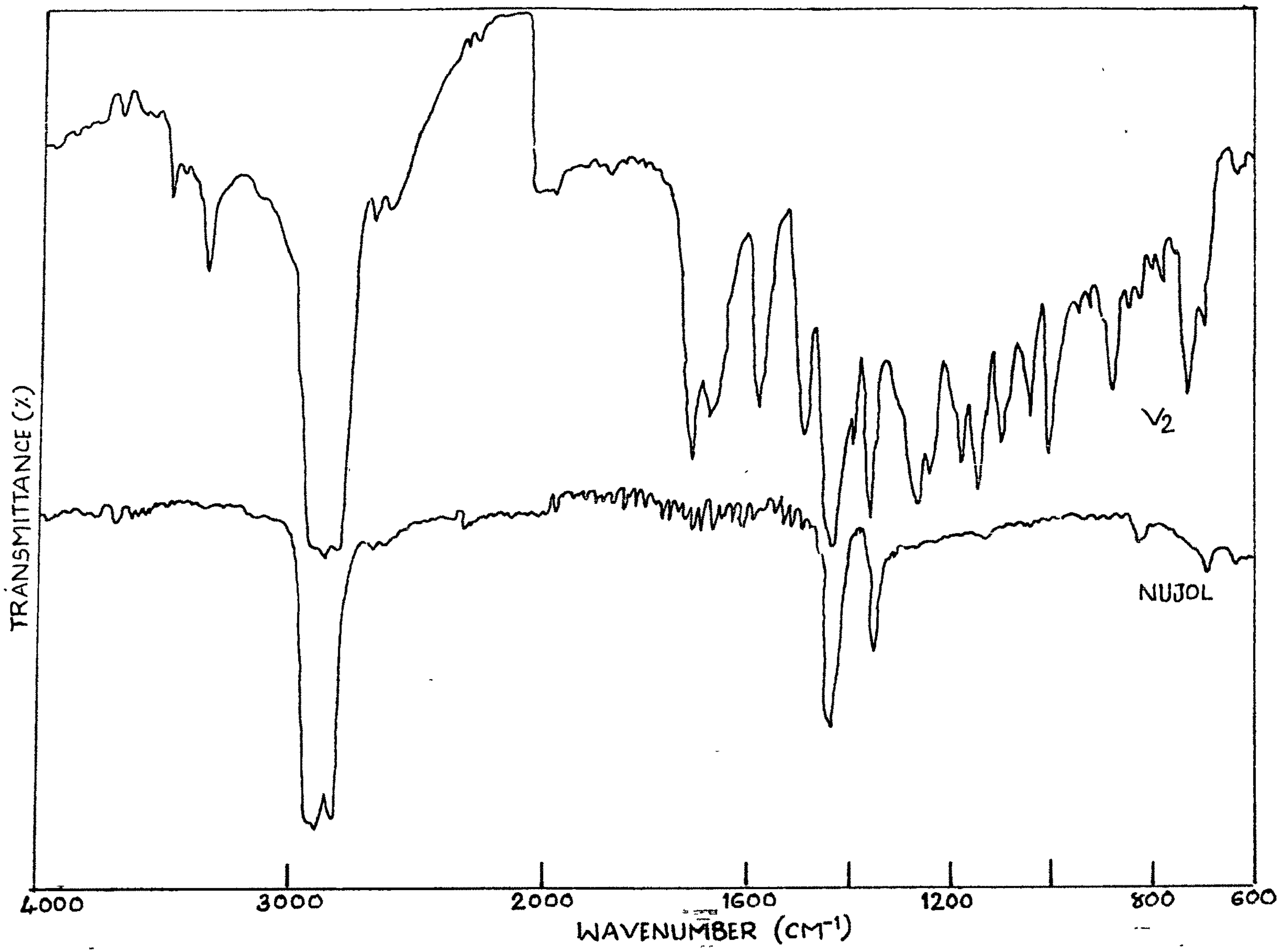
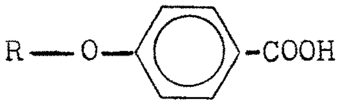


FIG. 43: IR Spectra of Poly (4-oxy-3-methoxybenzoate)

low molecular weight liquid crystals that the increase in the breadth of the molecules decrease solid-mesomorphic and mesomorphic-isotropic transitions as the close packing of the molecules becomes difficult (384, 421, 427-429). The smectic properties are affected more by increase in breadth and acoplanarity in the liquid crystalline systems. The smectic phase may be changed and the whole system becomes nematogenic or non-mesogenic.



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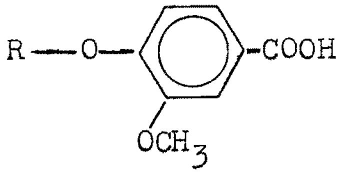


II

System I is mesogenic, whereas system-II is non-mesogenic (430).

Naturally, the molecules of poly(4-oxy-3-methoxybenzoates) will be broader and more acoplanar compared to the molecules of poly(4-oxybenzoates) due to the presence of lateral methoxy group in poly(4-oxy-3-methoxybenzoates).

The solution viscosities of poly(4-oxy-3-methoxybenzoates) is higher than those of poly(4-oxybenzoates). This shows higher degree of polymerization. The viscosity of the some of the homopolymers of poly(4-oxy-3-methoxybenzoates) is measured using DMF as solvent.

The above results indicate that the introduction to a lateral substituent decreases the solid-mesomorphic transitions and is conducive to nematogenic mesophase in polymers which effect is similar to one observed in low molecular weight liquid crystals.

TGA study was carried out for some of the samples. The thermal stability behaviour will be discussed with other polymers.

1.1.5 Post-polycondensation of poly(4-oxy-3-methoxybenzoate):

The nematogenic polymer V_7 (Table-12) was post-polymerized at higher temperature and in different environment as reported in the experimental section (Table-24) to study the effect of different environment and mesogenic state in the resultant polymers. Post-polymerized samples do not exhibit any mesophase upto 350°C and remain unchanged. The value of intrinsic viscosity $[\eta]$ of polymer V_7 is 0.1261, whereas it is 0.0453, 0.0648, 0.708 and 0.0738 for polymers V_{14}, V_{15}, V_{16} and V_{17} respectively (Table-68). The viscosities of post-polymerized samples were measured in conc. H_2SO_4 (98 %) solution whereas the viscosity of sample V_7 was measured in DMF. It is known that conc. H_2SO_4 in the viscosity measurement may cause some decomposition. Even if this is neglected for convenience of interpretation, the viscosity of post-polymerized sample indicates partial degradation of polymer samples during post-polymerization which is difficult to rule out.

1.1.6 Binary mixture of Poly(4-oxy-3-methoxybenzoate) With d-camphor:

As discussed in the beginning it would be quite interesting to dope a mesogenic polymer with an optically active compound to induce cholesteric phase. With this in view one mixture was prepared (Table -33).

Mixture : Component A + Component B
V_2 Polymer + d-comphor

The mixtures exhibit cholesteric mesophases. The trend of solid-mesogenic temperature is the same as observed in previous mixtures, they show decreasing trend as the concentration of d-camphor increases. The cholesteric phase exhibit vivid colours and plane and focal conic texture typical of this phase. The conversion of nematic phase to cholesteric phase is discussed earlier.

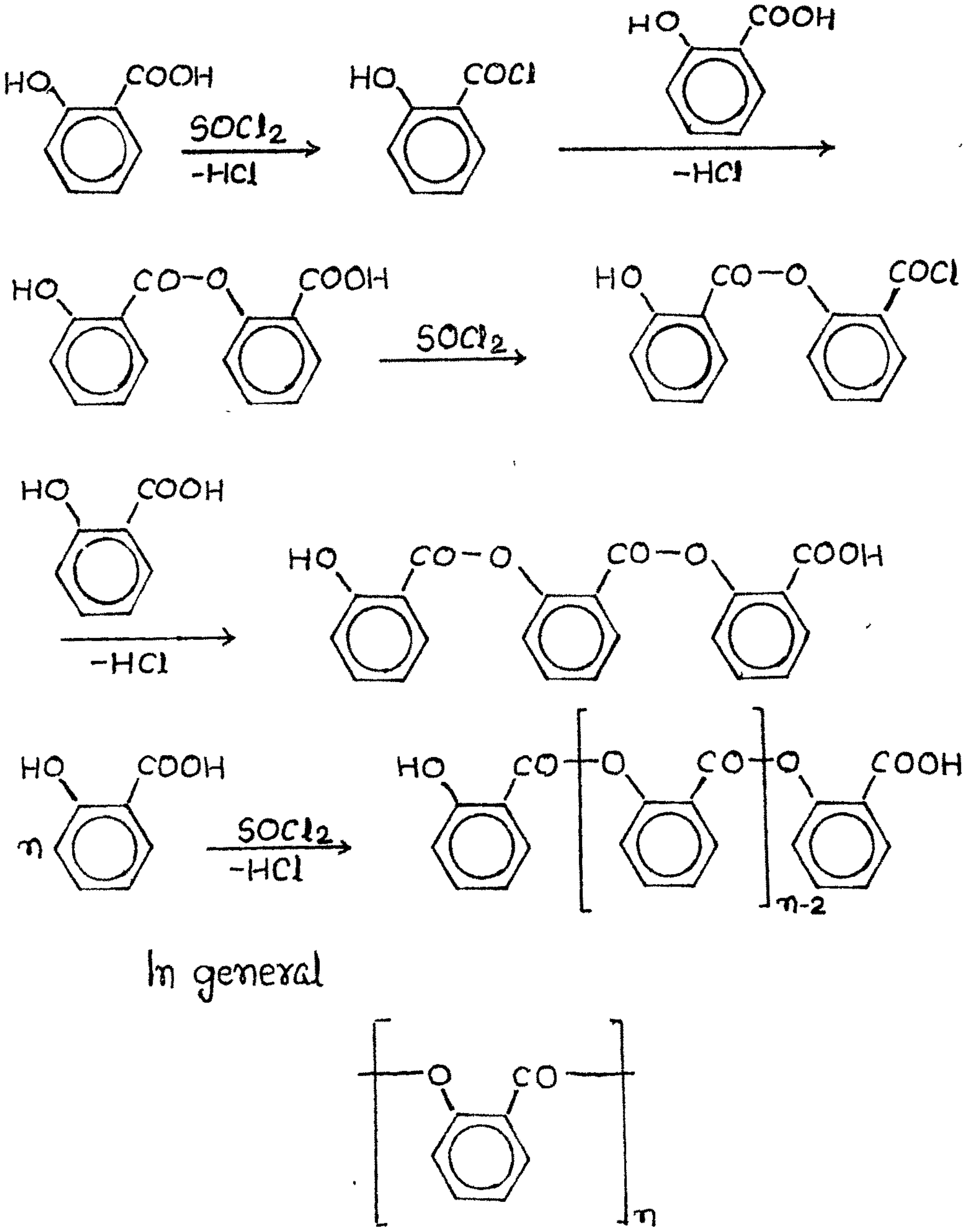
1.1.7 Poly(2-oxybenzoates) and Poly(3-oxybenzoates):

The monomers 2-hydroxybenzoic acid (salicyclic acid) and 3-hydroxybenzoic acid (m-hydroxybenzoic acid) were homopolymerized by using thionyl chloride as condensing agent. 4-hydroxybenzoic acid and its derivative on homopolymerization gave mesogenic polymers. It would be quite interesting to study the homopolymers of ortho- and meta-hydroxybenzoic acid and to evaluate their mesogenic behaviour.

The homopolymerization of 2- and 3-hydroxybenzoic acid will proceed as indicated in Fig.44a,b.

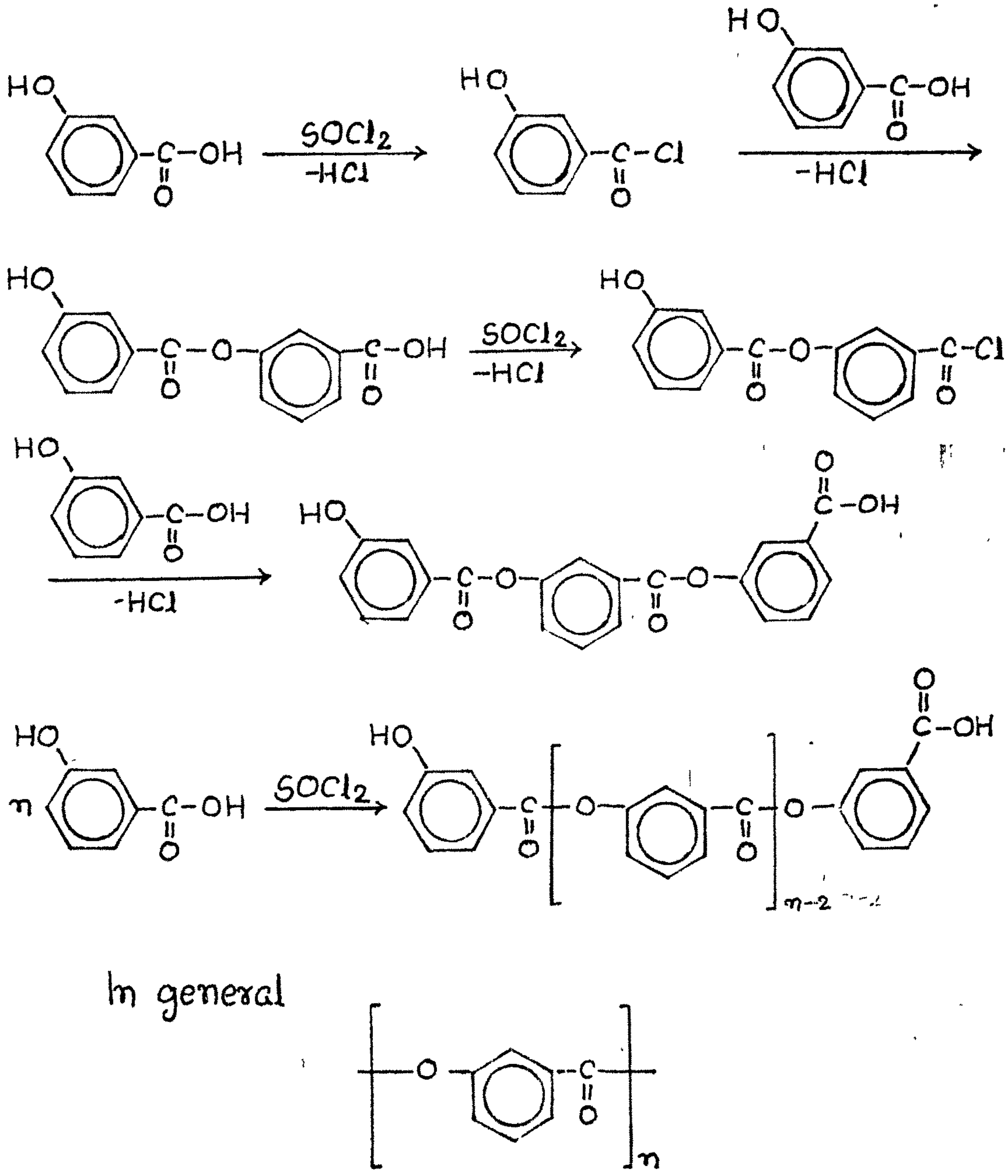
Reference to Table-69 shows that none of the polymers exhibits mesomorphism. The viscosity data indicate that there is a good degree of polymerization. The increase of breadth of the molecules and accoplanarity due to the steric effects in both the polymers are non-conducive to mesomorphism. If one considers models then p-n-alkoxybenzoic acids and their derivatives are reported to be mesogenic, whereas, the derivatives of salicylic acids or 3-hydroxybenzoic acids are not found to be mesomorphic. It is well established in low molecular weight liquid crystals that increase in the breadth of the molecules by a bulky substituents or ortho- or meta - derivatives are non-conducive to mesomorphism.

It has been reported in the introduction chapter that to obtain thermotropic mesomorphic polymers in main chain



Poly (2-oxybenzoate)

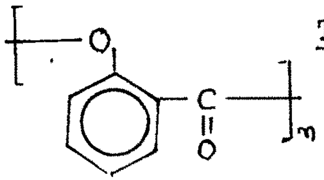
FIG. 44a



Poly (3-oxybenzoate)

FIG. 44b

Table-69



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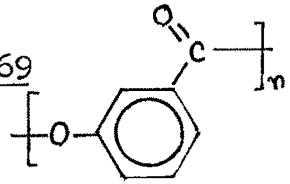


Poly(2-Oxybenzoates) and Poly(3-oxybenzoates)

Transition Temperatures and Viscosity Data:

Sr. No.	Polymer	Transition Temperatures (°C)			$[\eta]$ dl/gm
		Smectic	Nematic	Isotropic	
1	OHB_1	-	-	155	0.253
2	OHB_2	-	-	060	0.216
3	OHB_3	-	-	142	0.253
4	OHB_4	-	-	163	0.327
5	OHB_5	-	-	125	0.309
6	OHB_6	-	-	169	0.381
7	MHB_1	-	-	085	0.264
8	MHB_2	-	-	140	0.235
9	MHB_3	-	-	130	0.288
10	MHB_4	-	-	045	0.158
11	MHB_5	-	-	210	0.434
12	MHB_6	-	-	>350	-
13	OHB_7	-	-	149	-

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

polymers, it is always advisable to use molecules which impart kink or band to the main chain. These to monomers can be quite handy to impart 'kinks' to the main chain which may help to get mesogenic copolyesters with lower solid -mesogenic transition temperatures.

All the homopolymers reported here were characterized by elemental analysis. (Table-16) and by solution viscosity study wherever it dissolved in suitable solvents (Table-69).

1.2 LIQUID CRYSTALLINE COPOLYMERS:

Homopolymerization of 4-hydroxybenzoic acid gave polymers of high thermal stability, whereas the homopolymers of 2-hydroxy and 3-hydroxybenzoic acids are non-mesogenic and have lower thermal stabilities. The copolymers of isomeric hydroxybenzoic acids were studied but there is no reference in these study regarding mesogenic behaviour. We thought it is quite appropriate to synthesize copolyesters of isomeric hydroxybenzoic acid with a view to explore possibility of mesomorphism. Recent patent (413) reports some of the copolymers obtained by melt polymerization of p-hydroxybenzoic acid derivatives and other monomers. In the present study thionyl chloride was used for the copolymerization as described in the experimental section.

1.2.1 Poly(3-Co-2-oxybenzoates):

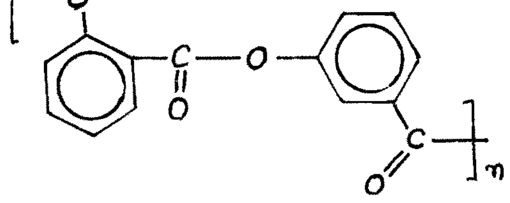
3-Hydroxybenzoic acid (MHB) and 2-hydroxybenzoic acid (OHB) were copolymerized as described in the experimental section by using thionyl chloride as condensing agent. Only two samples were synthesized by varying the ratio of the monomers. Reference to Table-70 shows that both the copolymers are non-mesogenic as expected for such geometry of the polymers.

1.2.2 Poly(3-Co-4-oxybenzoates):

Patel et al. (365) synthesized poly(2-Co-4-oxybenzoates) by condensing acid chlorides of the monomers in a solvent and obtained the polymer of good thermal stability. In the present study, 3-hydroxy- and 4-hydroxybenzoic acids were condensed in the presence of thionyl chloride as described in the experimental section. The ratio of two monomers was varied to study its effect on mesomorphism. The transition temperatures of poly(3-Co-4-oxybenzoates) are reported in Table-71.

Reference to Table-71 shows that all the copolyesters exhibit mesomorphism. Couple of them exhibit polymesomorphism and sample exhibits only smectic mesophase where the ratio of the two monomers is one.

Table-70



Poly(2-Co-3-oxybenzoates)

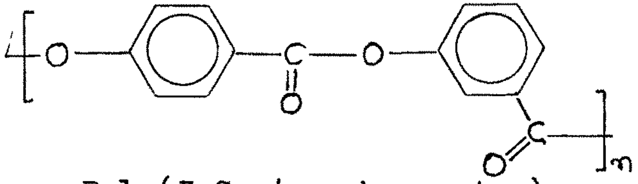
Copolyesters of 2- and 3-hydroxybenzoic acid in air using Thionyl chloride as condensing agent:

Sr. No.	Polymer	Transition Temperatures (°C)		
		Smectic	Nematic	Isotropic
1	$O\text{-}Co\text{-}M_1{}^a$	-	-	228
2	$O\text{-}Co\text{-}M_2{}^b$	-	-	180

a : OHB (0.25 mole) and MHB (1.00 mole).

b : OHB (1 mole) and MHB (1.00 mole).

Table-71



Poly(3-Co-4-oxybenzoates)

Transition Temperatures and Viscosity Data

Sr. No.	Polymer	Transition Temperatures (°C)			[η] dl/gm	Mole ratio PHB/MHB	Phase length (°C)
		Smectic	Nematic	Isotropic			
1	P-Co-M_1	-	150	302 P	-	20.00	152
2	P-Co-M_2	-	150	302 P	-	10.00	152
3	P-Co-M_3	160	225	302 P	-	6.66	142
4	P-Co-M_4	145	231	289 P	-	4.00	144
5	P-Co-M_5	-	190	301 P	0.141	2.00	111
6	P-Co-M_6	-	085	205	0.117	1.25	120
7	P-Co-M_7	056	-	130	0.117	1.00	074
8	P-Co-M_8	-	064	106	0.078	0. 25	042
9	P-Co-M_9	-	062	106	0.078	0.50	044
10	P-Co-M_{10}	-	060	135	0.111	0.80	075
11	P-Co-M_{11}	-	210	265 P	-	-	055
12	P-Co-M_{12}	-	115	305 P	-	-	190

P : Sample post-polymerizes and becomes solid.
PHB: 4-Hydroxybenzoic acid.
MHB : 3-Hydroxybenzoic acid.

1.2.3 Poly(4-oxybenzoate-Co-4'-(3'-methoxy)oxybenzoates):

4-Hydroxybenzoic acid (PHB) and 4-Hydroxy-3-methoxybenzoic acid (VA) were copolymerized by using thionyl chloride as condensing agent as described in experimental section.

Eleven polymers have been synthesized by varying the ratio of two monomers (Table-72). Reference to Table-72 shows that the first polyesters VB_1 where the content of 'VA' is very small exhibits polymesomorphism. All other polyesters exhibit nematic mesophase.

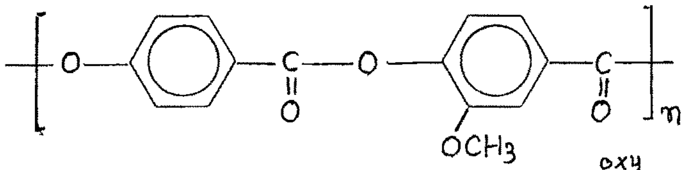
1.2.4 Mesogenic Behaviour of Copolyesters:

The schematic geometry of all the copolyesters is given in Fig.45 and is compared with poly(4-Co-2-oxybenzoates), reported by Vora and Patel (431) and poly(4-oxybenzoates).

Reference to Table-70 shows that both the copolyesters of poly(3-Co-2-oxybenzoates) are non-mesogenic. Reference to Fig. 45 shows that the geometry of polymers A endows non-linearity of the system that it would be difficult for the molecules to pack economically to exhibit mesophases.

All the copolyesters of poly(3-Co-4-oxybenzoates) (B) exhibit mesomorphism (Table-72). Reference to Table-72

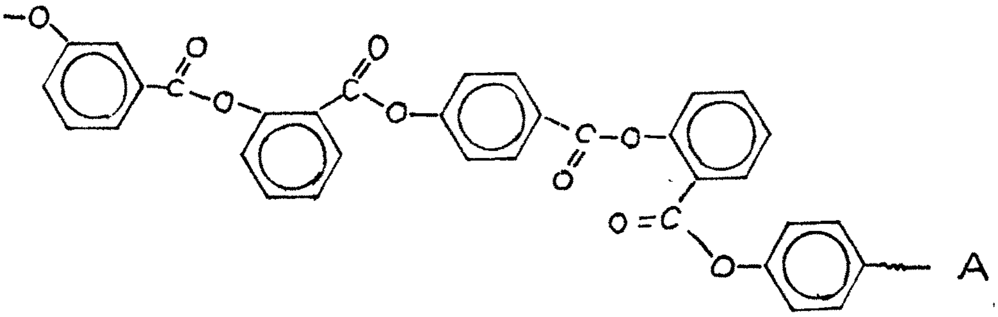
Table-72



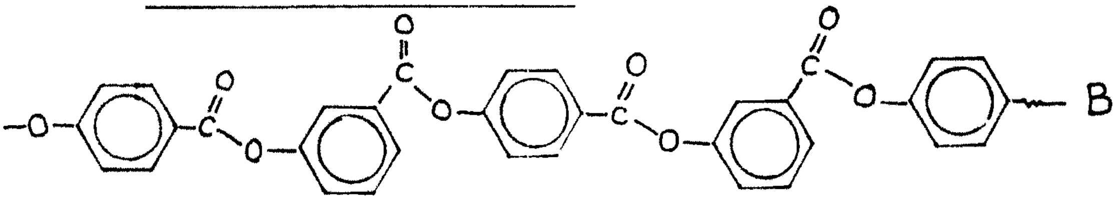
Poly(4-oxybenzoate-Co-4'-(3'-methoxy)oxybenzoates):

Sr. No.	Polymer	Transition Temperatures (°C)			[η] dl/gm	Mole ratio PHB/V	Phase length(°C)
		Smectic	Nematic	Isotropic			
1	VB_1	205	281	303 P	-	200	98
2	VB_2	-	190	285 P	0.172	100	95
3	VB_3	-	145	308 P	0.142	10	163
4	VB_4	-	127	306 P	0.138	05	179
5	VB_5	-	105	311 P	0.126	2.50	206
6	VB_6	-	79	>325	0.120	1.25	>246
7	VB_7	-	99	>325	0.101	1.00	>226
8	VB_8	-	100	159*	0.071	0.10	059
9	VB_9	-	100	159*	0.080	0.20	059
10	VB_{10}	-	100	290	0.094	0.40	130
11	VB_{11}	-	100	321 P	0.100	0.80	221
12	VB_{12}	-	190	308 P	-	-	118
13	VB_{13}	-	-	>325	-	-	-

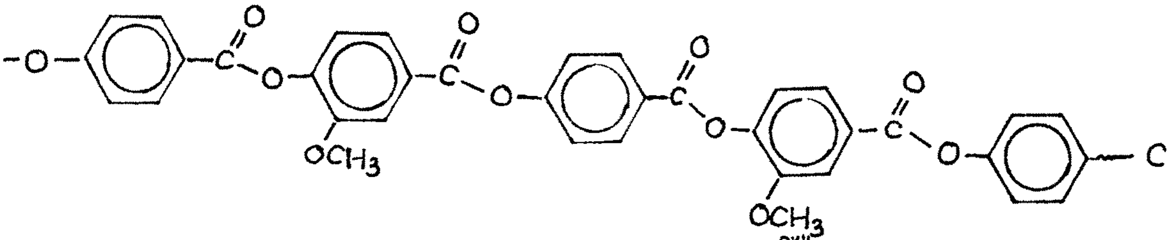
P: Sample post-polymerizes and becomes solid.
PHB: 4-hydroxybenzoic acid.
V : 4-hydroxy-3-methoxybenzoic acid.
* : Nematic phase in second turn.



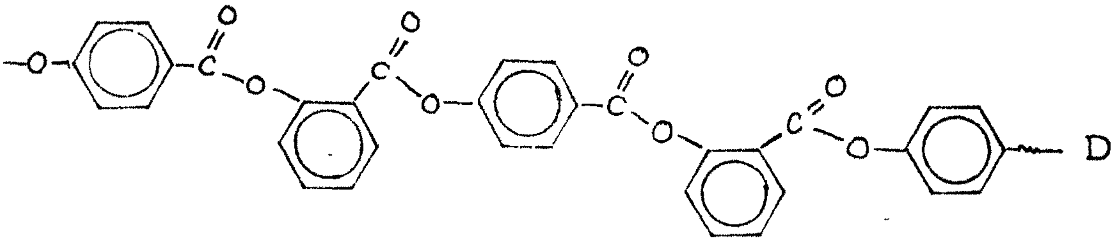
Poly(3-Co-2-oxybenzoate)



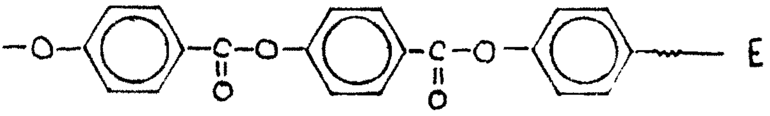
Poly(4-Co-3-oxybenzoate)



Poly[4-oxybenzoate-Co-4'-(3-methoxy)oxybenzoate]



Poly(4-Co-2-oxybenzoate)



Poly(4-oxybenzoate)

FIG. 45

shows that as the content of 3-hydroxybenzoic acid increases the solid-mesomorphic transition temperatures exhibit decreasing tendency. The solid-mesomorphic transitions are much more lower than those of poly(4-oxybenzoates). Mesomorphic-isotropic transition could not be compared as polymers post-polymerize at higher temperatures and become solid. Reference to Fig.45 shows that the geometry of the molecules of the system B will be more non-linear compared to the system E of poly-(4-oxybenzoates). This shows that incorporation of the unit -3-oxybenzoate decreases the linearity of the molecules of the polymer chain (B) thereby causing the reaction in solid-mesomorphic transitions as observed in low molecular weight liquid crystals (260). It is interesting to note that even when the content of 3-oxybenzoate unit is high, the polyester exhibits mesomorphism.

In the copolyesters, poly(4-oxybenzoate-Co-4'-(3'-methoxy)oxybenzoates), the bulky methoxy group will increase the breadth of the molecules (Fig.45; system-C) which will affect the close packing of the molecules compared to poly(4-oxybenzoate) system (Fig.45; system E). Naturally, this will affect the solid-mesomorphic transitions and even the type of the mesophase exhibited by the system. The copolyesters (Table-72, system-C) compared to system E (Table-66); poly(4-oxybenzoate) is nematogenic and the solid-mesomorphic transition temperatures are much lowered. Compared to system B (Table-71, Fig.45), the solid-mesomorphic transitions and mesomorphic-isotropic transitions of system-C (Table-70; Fig.45) are higher and the system-C is more mesogenic.

Comparision of mesomorphic properties of copolyesters A, B and C with poly(4-Co-2-oxybenzoates) (System B) (431) will be quite interesting. All the copolyesters of poly-(4-Co-2-oxybenzoates) are mesogenic except one member where the content of 2-hydroxybenzoic acid (OHB) is very high. Seven members are polymesogenic exhibiting smectic and nematic phases. Only three members having higher content of OHB exhibit nematic mesophase. As mentioned earlier, the polymeric systems are complex compared to low molecular weight liquid crystals hence the comparison of mesomorphic properties will be qualitative and suggest the trend and similarly with the low molecular weight liquid crystal compounds.

The above results indicate that the kink of 2-hydroxybenzoic acid in copolymer with 4-hydroxybenzoic acid gives better mesogenic tendency, indicating typical packing of the molecules in mesogenic form which may find packets as observed in some laterally substituted low molecular weight liquid crystals.

All the copolyesters are characterized by elemental analysis (Table-32), IR spectra (Fig.46), (Table-47).

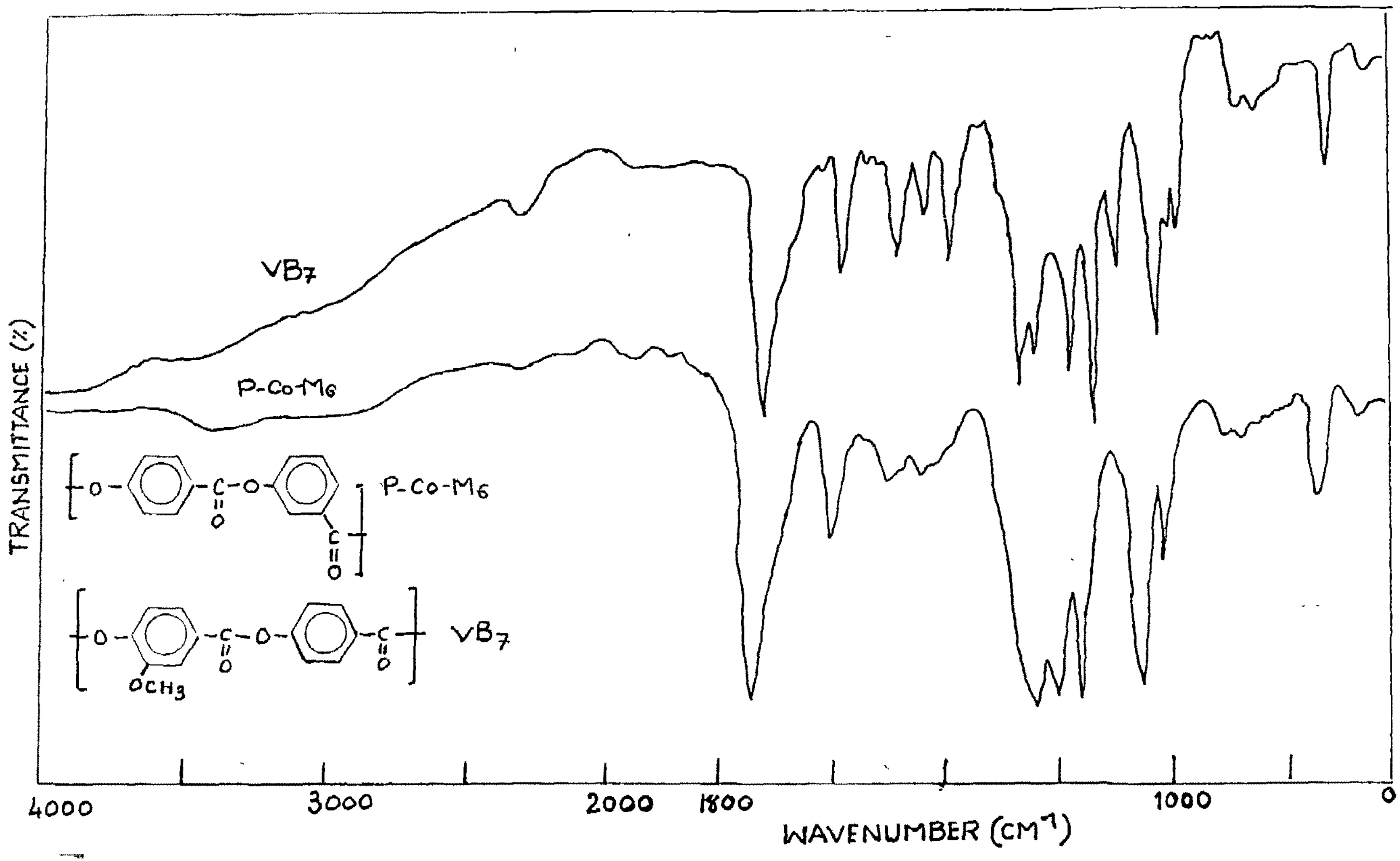


FIG. 46: IR Spectra of P-Co-M_6 and VB_7.

LIQUID CRYSTALLINE POLYESTERS

2. LIQUID CRYSTALLINE POLYESTERS:

2.1 MESOGENIC POLYESTERS WITH FLEXIBLE SPACER:

A number of polymeric systems with rigid and flexible spacers have been studied to evaluate the effect of rigid and flexible spacers on the mesomorphism. The geometry of such polymers is given in Fig.47. This indicates that number of variations have been tried by introducing the flexible spacer in the main chain of the polymer unit.

In the present study number of such variations are tried. The flexible spacer unit is fixed and the geometry of the other monomer unit is varied to evaluate the effect of such variations on mesogenic properties. The solution polycondensation was carried out as described in experimental section by condensing diacid chloride of 1,2-bis(4'-carboxyphenoxy)ethane with different dihydroxy compounds. Route of synthesis is given in Fig.48.

The melting points and transition temperatures of the polyesters (BE) with flexible spacer are recorded in Table-73. Reference to Table-73 shows that all the five polyesters exhibit mesophases.

The polyester BE_1 exhibits only smectic mesophase whereas polyester BE_3 exhibits polymesogenic character.

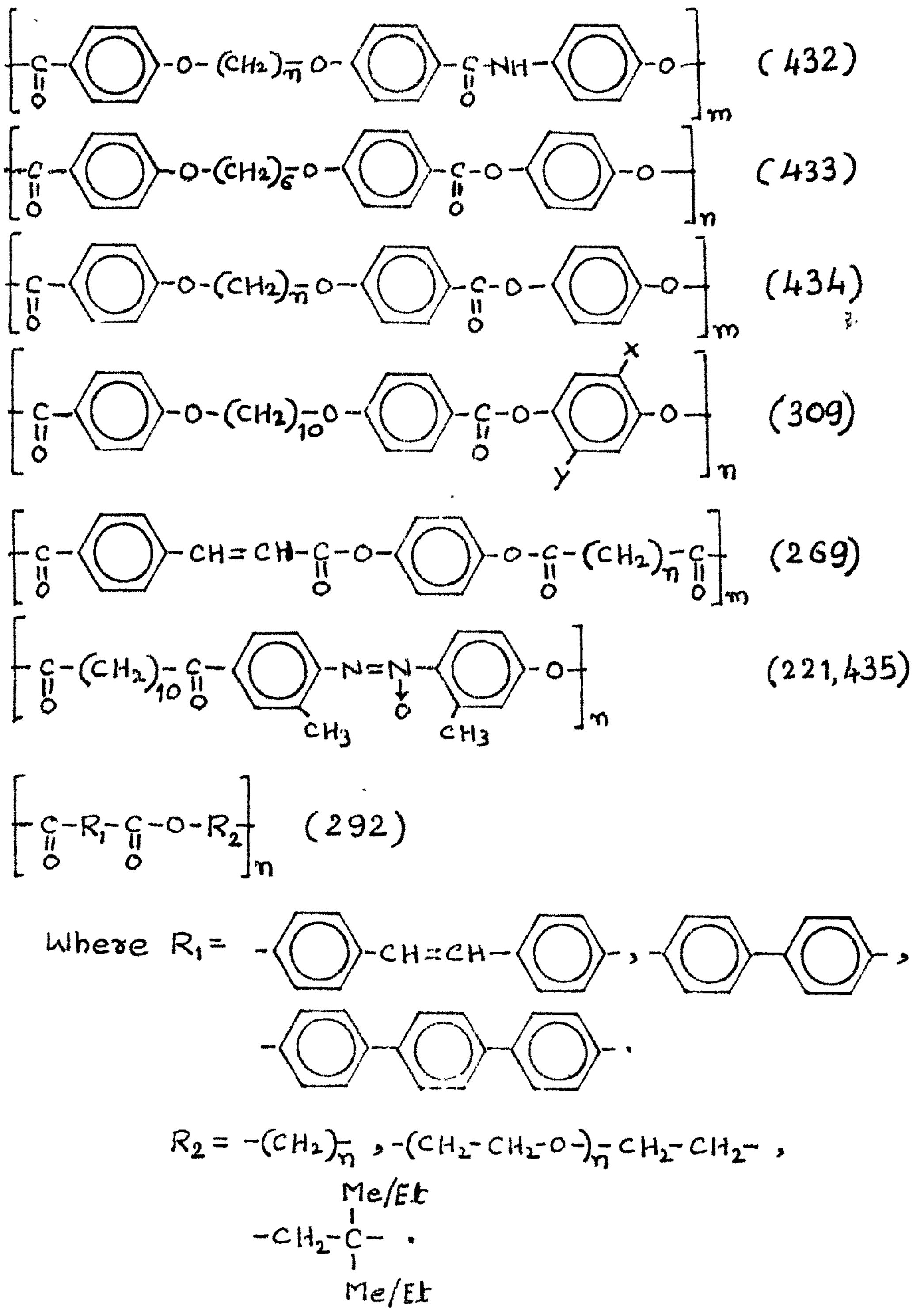

(432)
(433)
(434)
(309)
(269)
(221,435)
(292)
Where R₁ =
R₂ = -(CH₂)ₙ- , -(CH₂-CH₂-O-)ₙ-CH₂-CH₂- ,
-CH₂-C- (Me/Et)(Me/Et) .

FIG.47

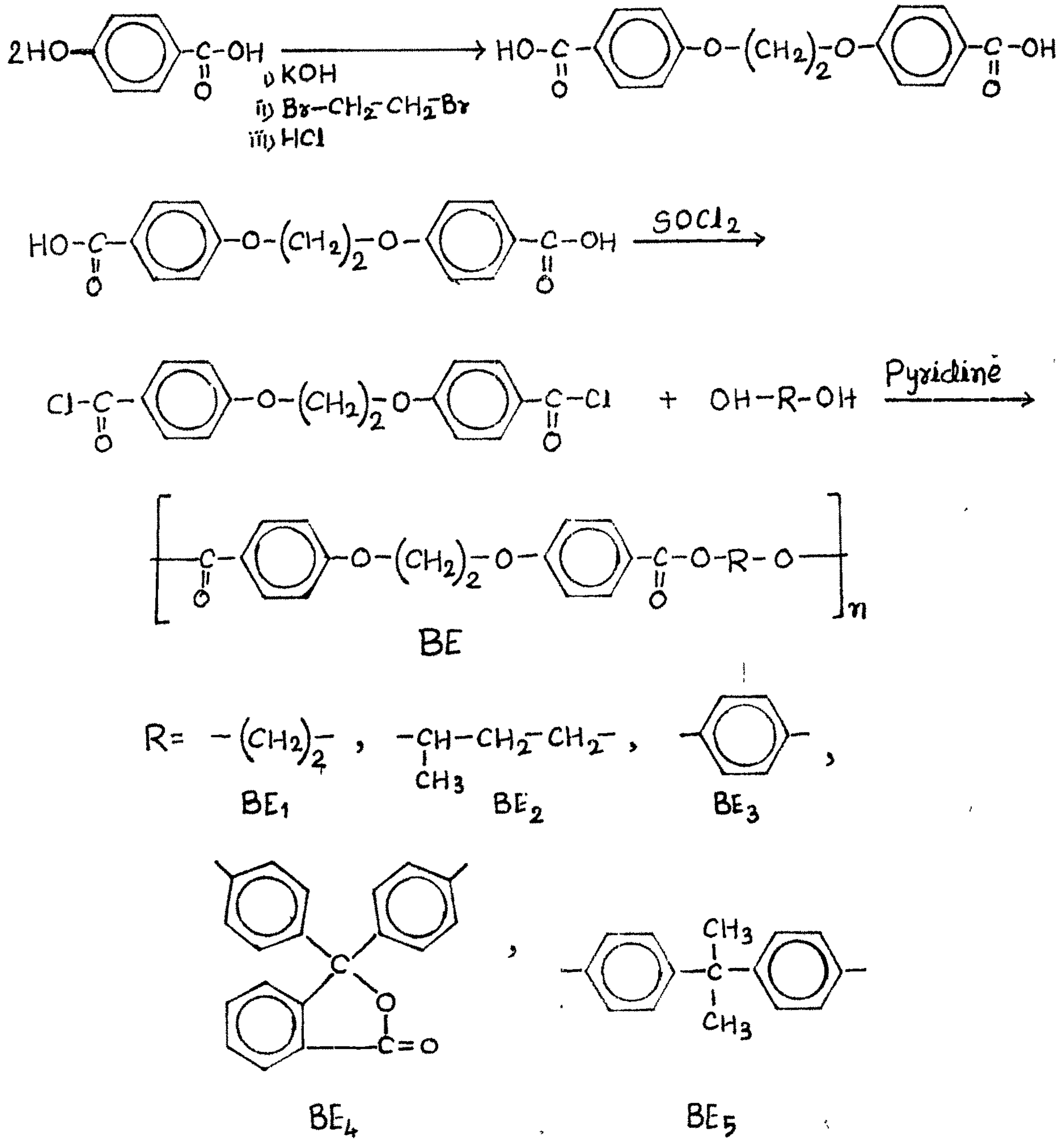
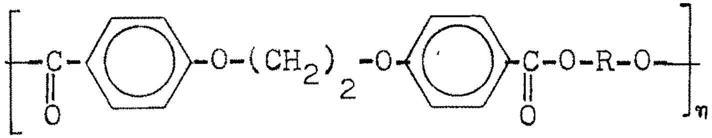
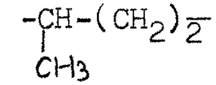
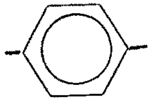
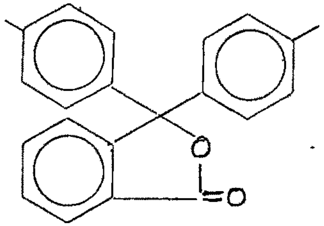
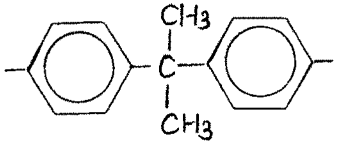


FIG. 48: Route of Synthesis for Polymer System BE

Table-73



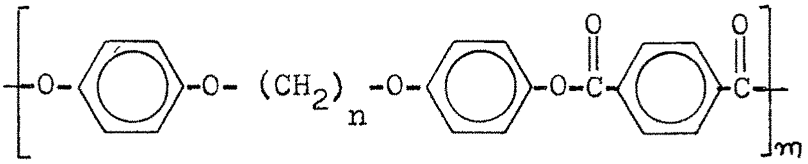
Transition Temperatures and Viscosity Data:

Sr. No.	Polymer	R	Transition Temperatures (°C)			dl/gm $[\eta]$
			Smectic	Nematic	Isotropic	
1	BE_1	$-(CH_2)_2-$	101	-	174	0.1009
2	BE_2	 $-\underset{CH_3}{\underset{\vert}{CH}}-(CH_2)_2-$	-	31	203	0.0862
3	BE_3		215	261	>325	-
4	BE_4		-	147	194	0.2450
5	BE_5		-	136	188	0.3640

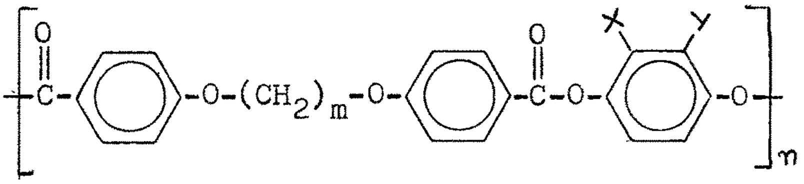
Polyesters BE_2, BE_4 and BE_5 exhibit only nematic mesophases. It is interesting to note that eventhough phenolphthalain (BE_4) and Bisphenol-A (BE_5) will have full breadth increasing effect due to their bulkiness and steric effect, the mesogenic properties are observed in these polymers. The branching and flexibility in the polyester BE_2 has brought down the mesogenic temperature upto room temperature (31°C).

Reference to mesogenic-isotropic temperature (Table-73) clearly shows that phenyl ring (BE_3) enhances thermal stability much more than any other moiety. Polyesters BE_1 and BE_2 have aliphatic flexible spacers over and above one present in diacid residue, naturally, one would expect lowering of mesomorphism (260). In case of polyesters BE_4 and BE_5 though overall polarizability of monomer unit will be more compared to hydroquinone monomer due to the increase in breadth and steric hindrance, mesogenic thermal stabilities will decrease. This indicates that the factors which lower the mesogenic thermal stabilities in low molecular weight liquid crystals are operative in these polymers (260).

To evaluate the effect of chemical constitution on mesomorphism, Antoun et al. (309) studied the following two system:



I



II

Our system is similar to system-II and one of the members of system II is also synthesized by them. They studied the mesogenic system of both the series. They observed that as the flexible chain length increases, the melting point and transition temperatures exhibit the trend of lower melting point and transition temperatures. The decrease follows the definite pattern in system II due to the structural variations as the size of the substituent of hydroquinone increases.

In the present study we observed the similar trend in the liquid crystalline properties of polyesters (BE) with flexible spacer (Table-73). The polymer BE_3 exhibits mesophases with higher thermal stability due to the presence of p-phenylene system of rigid segment. The same polymer is also studied by Strzeleki and Luyen (434). The transition temperatures reported by them are higher than what is observed in present study. They observed only nematic mesophase whereas we observe smectic mesophase also.

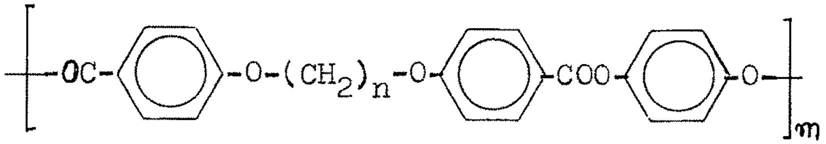
There are number of studies where such variations are observed in polymeric liquid crystalline systems. The liquid crystalline systems are complex and mesophases depend on degree of polymerization and the morphology of polymer obtained, hence one can expect such variations.

Reference to Table-74 shows that the study of the polymer system BE is carried out by three other groups also. Strzeleki and Luyen (434) observed smectic mesophases for the polymers where n = 6 and 10, whereas Noel et al. (433) and Antoun et al. (309) did not observe smectic mesophases. However, Noel et al.(433) reported that the multiple peaks shows that there is a possibility of smectic mesophase after second solid transitions t_2. In the present study, polymer BE_3 exhibits smectic phase. The observation is further confirmed by contact method.

The DTA (Fig.37) also shows two endotherms between 200°C and 300°C supporting the presence of the smectic mesophase.

Antoun et al. (309) has tried to correlate the increase in breadth due to the substitution in p-phenylene system

Table-74



Sr. No.	n	Transition Temperatures (°C)				Ref.
		Smectic I	Smectic II	Nematic	Isotropic	
1	2	-	-	365	290	(434)
2	2	-	215	261	>325	Present study
3	6	-	215	230	300	(434)
4	6	$127t_1$ $256\ t_2$	-	310	347	(433)
5	10	105	215	225	270	(434)
6	10	-	-	236	290	(309)

with melting point and transition temperatures. They have plotted melting point and transition temperatures against substituents (Fig.49) in the p-phenylene system. The melting transitions i.e. mesogenic-isotropic transitions in the series showed a strong dependence on the nature of the substituent. The polymers with monosubstituted or asymmetric hydroquinone units had much lower melting points than that of the unsubstituted polymer or the symmetrically substituted polymer in which both the substituents were -Cl. It was observed that for the monosubstituted polymers larger the size of the substituent, the lower is the melting temperature (mesogenic-isotropic transition).

In present study the solid to mesogenic (melting points) and mesogenic-isotropic transition (melting transitions) temperatures are plotted against the monomer present in the polymer system (Fig.50).

The geometry of monomer fragments present in polyesters BE is given in Fig.51.

Reference to Fig.50 shows that polymer BE_3 exhibits highest solid-mesogenic and mesogenic-isotropic transitions ($>$325°C), indicates the p-phenylene system present in BE_3 enhances liquid crystalline properties due to the polarizability and length of the p-phenylene unit.

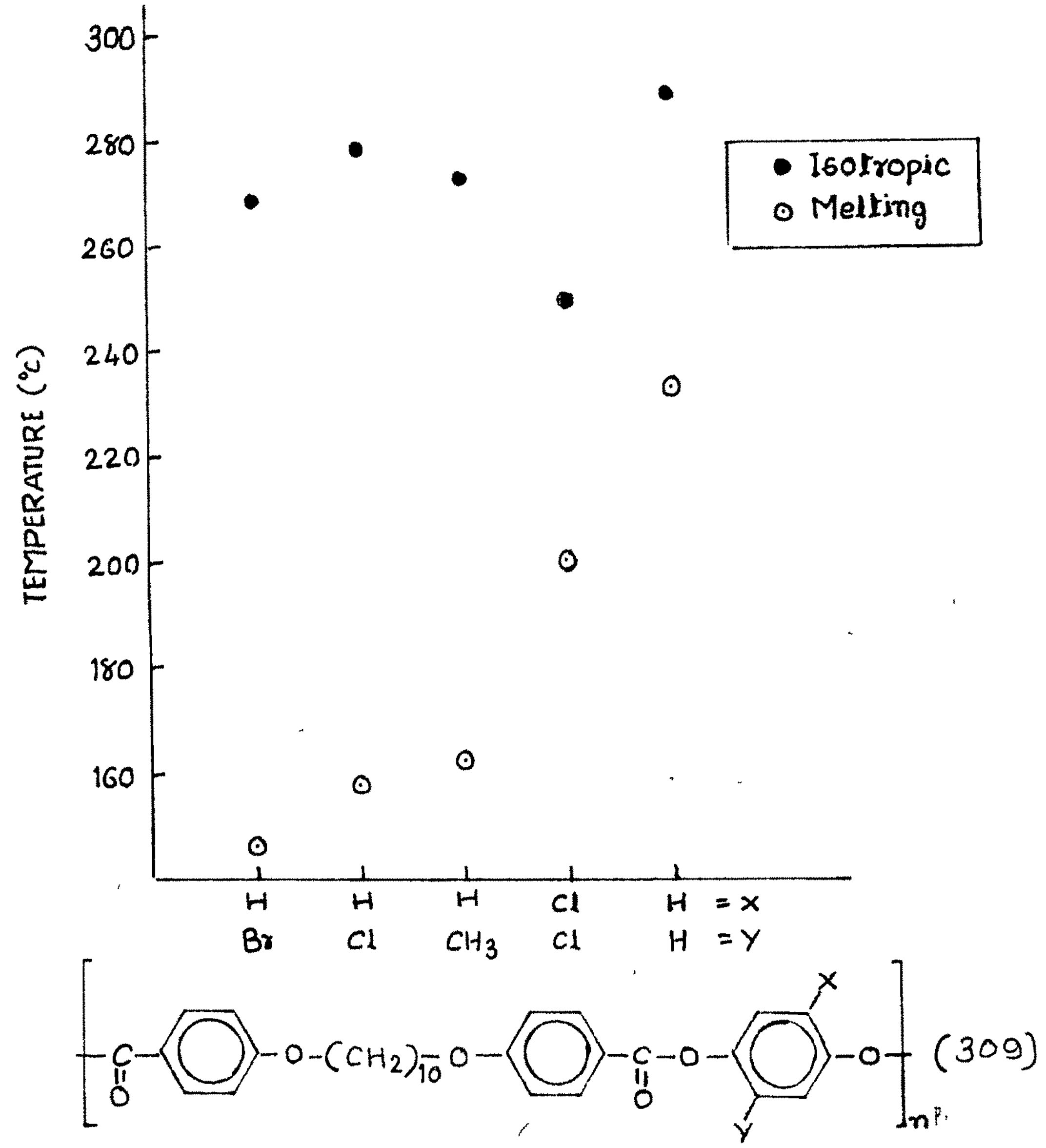
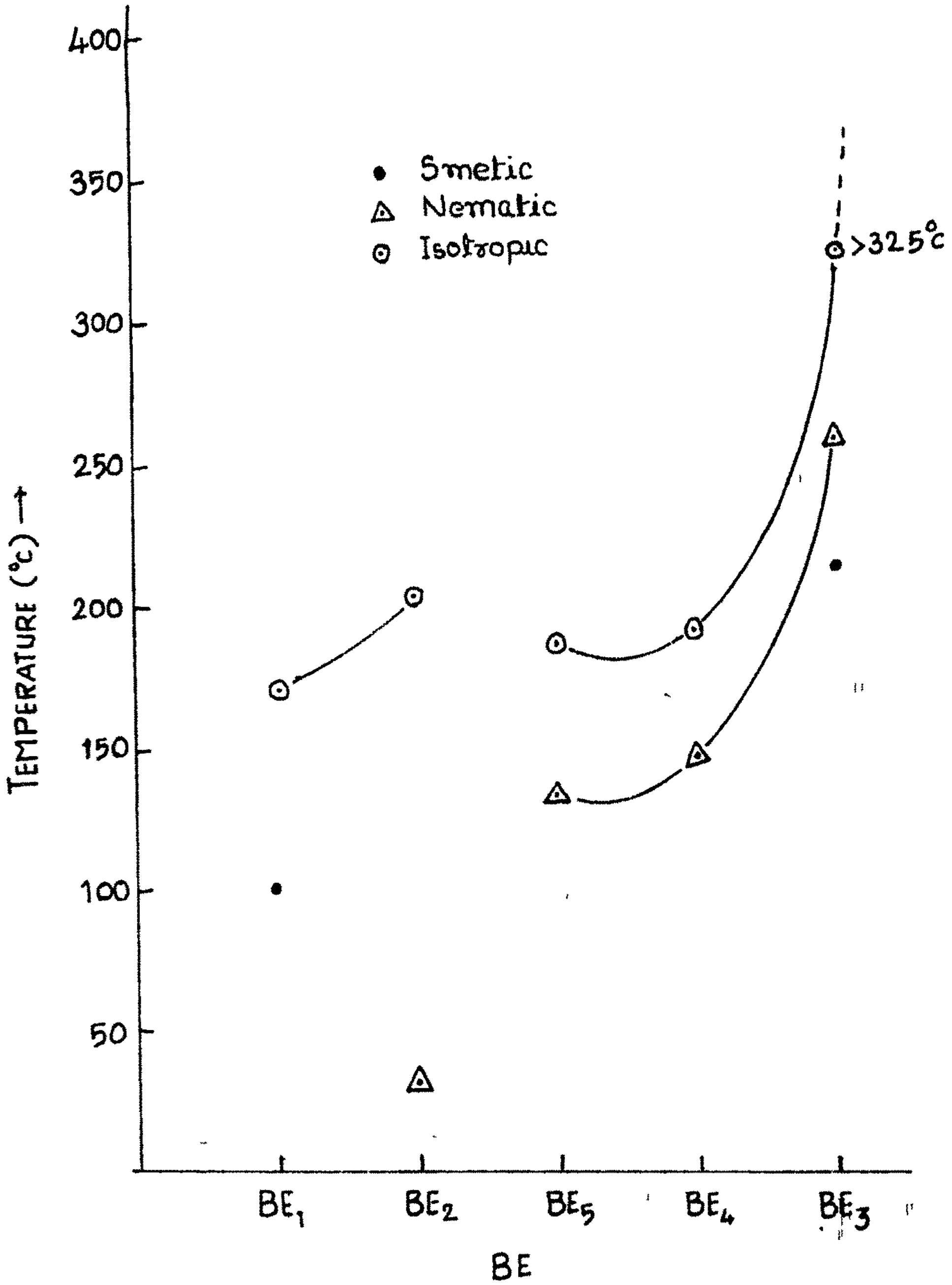


FIG. 49: Dependence of Melting Point and Isotropic Transition Temperature on the Type of Substituent in polymer System (309)



$BE_1 = -(CH_2)_2-$, $BE_2 = -\underset{CH_3}{CH}-(CH_2)_2-$, $BE_5 = -C_6H_4-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_4-$

BE_4 = Phenolphthalein fragment , $BE_3 = -C_6H_4-$

FIG. 50

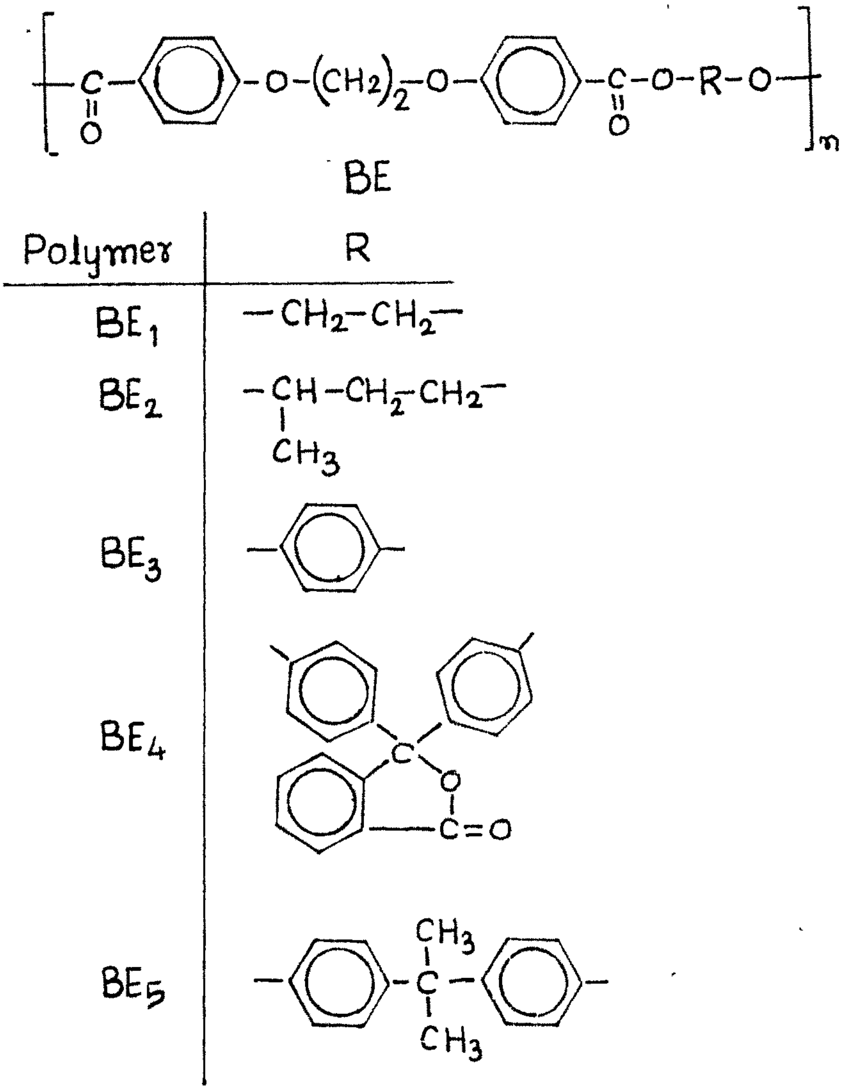


FIG. 51: The Geometry of Monomer Fragment Present in Polymer System BE

Solid-nematic and nematic-isotropic transitions fall as one goes from BE_3 to BE_4 and BE_5. Both these polymers have broad monomer unit, naturally one would expect lower transitions as such behaviours are noted for low molecular weight liquid crystal compounds (260). Interesting point worthnoting is that even though breadth of the molecules of monomer unit present in BE_4 is apparently more than molecules of monomer unit present in BE_5 (Fig.51), the presence of two methyl group in Bisphenol-A molecule due to their steric effect will increase the accoplanarity of the system, hence over and above the size of the molecules, the steric factor plays its role in the mesogenic thermal stability. No such effect would be operative in polymer BE_4. The molecules of monomer unit present in BE_1 and BE_2 are aliphatic and flexible. The solid to mesogenic and mesogenic to isotropic transitions of these polymers are much more lower than those of polymers BE_3 (Table-73). This is understandable as p-phenylene system will enhance polarizability and length of the system much more compared to methylene units. The worthnoting point is that eventhough solid-mesogenic transition temperatures of BE_1 and BE_2 are much lower their nematic isotropic transitions are almost the same or little higher. This indicates that compared to solid-mesomorphic transitions, the mesogenic-isotropic transitions are much affected by the breadth of the monomer units in polymer BE_4 and BE_5.

These observations shows that the effect of chemical constituents shows similar trend to low molecular weight liquid crystals. The mesophase thermal stabilities are affected by increase in the breadth of the system (260).

The polymers are characterized by elemental analysis (Table-37), IR spectra (Fig.52 and Table-48). The mesophases are confirmed by contact method as described in experimental sections. The solution viscosity of the polymers is reported in Table-73.

2.2 MESOGENIC POLYESTERS WITH AZOXY LINKAGE:

Different polyesters were prepared by condensing p-azoxybenzoyl chloride with different aliphatic and aromatic dihydroxy compounds as described in experimental section. The twelve polymers were obtained by condensing six monomers with p-azoxybenzoyl chloride in different conditions. The route of synthesis is given in Fig.53. The melting points of polymers and viscosity are reported in Table-75.

Reference to Table-75 shows that none of the polymers exhibits mesomorphism. Most of them do not melt. Three of them ($PABC_1$, $PABC_{11}$, $PABC_{12}$) do melt but do not exhibit mesomorphism. This is quite surprising. p-Azoxybenzoic acid itself do not melt but its esters are reported to be mesogenic (372). Aliphatic esters exhibit smectic mesophases (372).

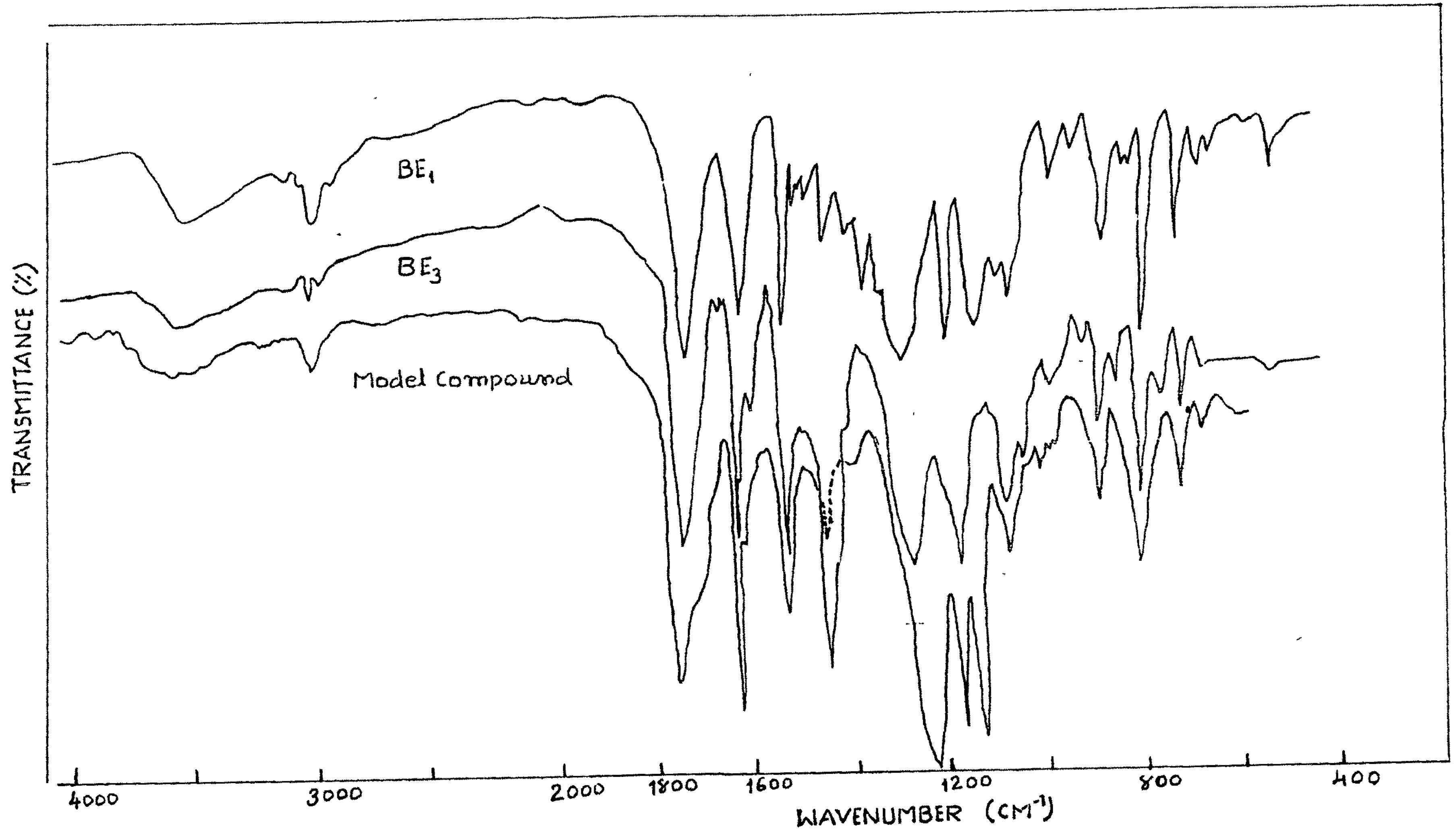


FIG. 52: IR Spectra of Polymer System BE.

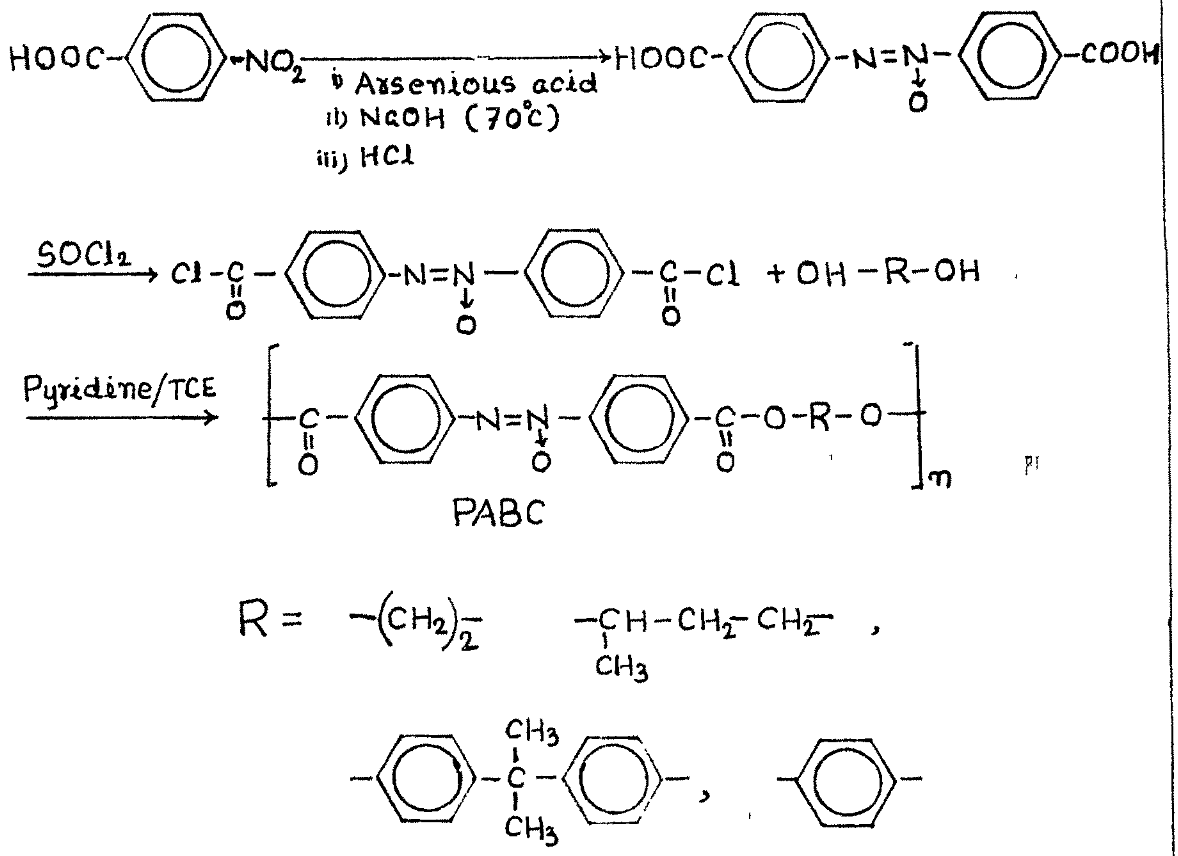
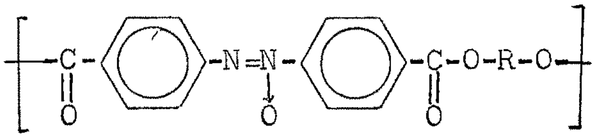


FIG. 53 : Route of Synthesis for Polymer System PABC

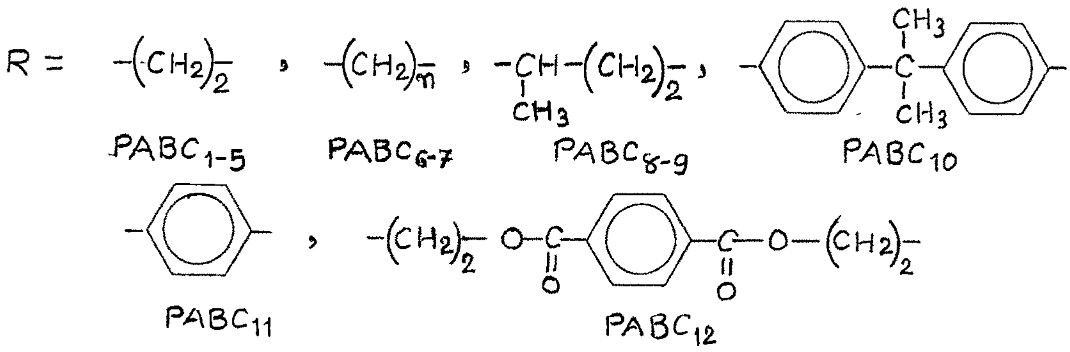
Table-75



Transition Temperatures and Viscosity Data:

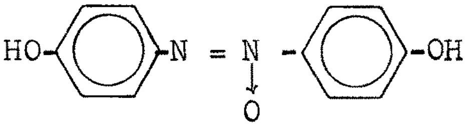
Sr. No.	Polymer	Transition Temperatures (°C)			$[\eta]_{dl/gm}$
		Smectic	Nematic	Isotropic	
1	$PABC_1$	-	-	220*	0.1743
2	$PABC_2$	-	-	>350	0.2676
3	$PABC_3$	-	-	>350	0.3134
4	$PABC_4$	-	-	>350	0.4424
5	$PABC_5$	-	-	>350	0.0833
6	$PABC_6$	-	-	>350	0.0687
7	$PABC_7$	-	-	>350	0.0905
8	$PABC_8$	-	-	>350	0.2290
9	$PABC_9$	-	-	>350	0.0782
10	$PABC_{10}$	-	-	>350	0.0833
11	$PABC_{11}$	-	-	245*	0.1105
12	$PABC_{12}$	-	-	275*	0.0964

* Highly viscous liquid

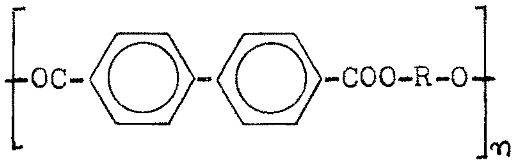


The non-mesomorphism might be exhibited by the polymers which do not melt upto 300°C. In absence of such facilities to examine them at higher temperature under the polarizing microscope or DSC thermogram, it is difficult to say whether they exhibit mesomorphism or otherwise. The polymer samples which melt have aliphatic and aromatic systems conducive to mesomorphism even then mesophases are not observed in this system.

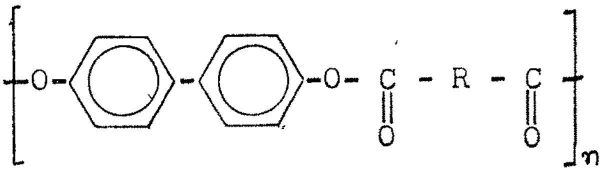
Blumstein et al.(436) have reported mesogenic polymers having the same structural unit but with phenolic group and lateral substitutent:



Krigbaum et al.(231) have reported that out of system I and II, system I exhibits smectic mesophases, whereas system II exhibits nematic mesophases due to the lateral cohesive forces arising out of the geometry of two systems.

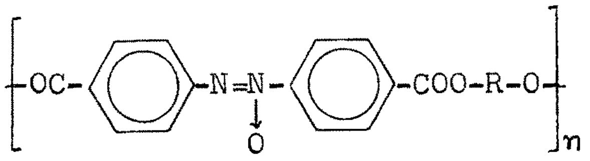


I

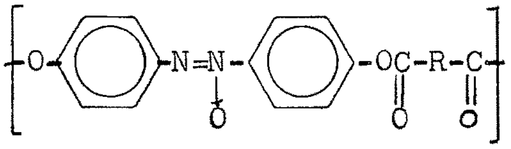


II

In the same manner the system I is similar to the one reported here (Ia) and the system II is similar one reported by Blumstein et al.(IIb) (436).



Ia



II b

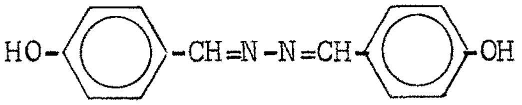
The exhibition of smectic phase by system I indicates that mesophases are more ordered than system II. In the case of system Ia, the attractive forces arising out of the ester linkage are so high that most of the polymers do not melt. This indicates that compared to system II and IIa, the attractive forces arizing out of preferred geometrical arrangements, system I and Ia exhibit higher thermal stabilities. The absence of mesophases in the three polymers which melt is difficult to explain.

Model compounds of p-azoxybenzoic acid, diethyl ester and diphenyl ester exhibit mesomorphism. However, polymers do not exhibit mesomorphism.

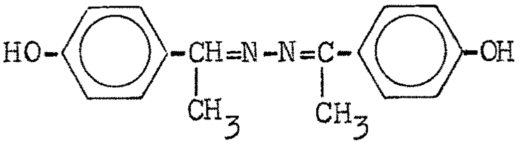
The polymers are characterized by elemental analysis (Table-37), IR spectra (Fig. 54, Table-49). The solution viscosity was measured and the data is given in Table-75.

2.3 MESOGENIC POLYESTERS WITH AZINE LINKAGE:

Roviello and Sirigu (280) reported thermotropic mesomorphic polyesters by using aromatic molecules like 4,4'-dihydroxybenzalazine (I) and dihydroxy-2-α-α'-dimethyl benzalazine (II).



I



II

They have also studied the aliphatic esters of both the systems as model mesogenic compounds to interpret the mesogenic behaviour of polymers. Aliphatic esters of both the series exhibit mesomorphism. The esters exhibit polymorphism of solid phase. The solid-mesomorphic and mesomorphic-isotropic transitions of esters of II are much lower than those of series I. Polymers also exhibit mesomorphism.

It was proposed to investigate more polymers of azine linkage with methoxy lateral substituent to evaluate its

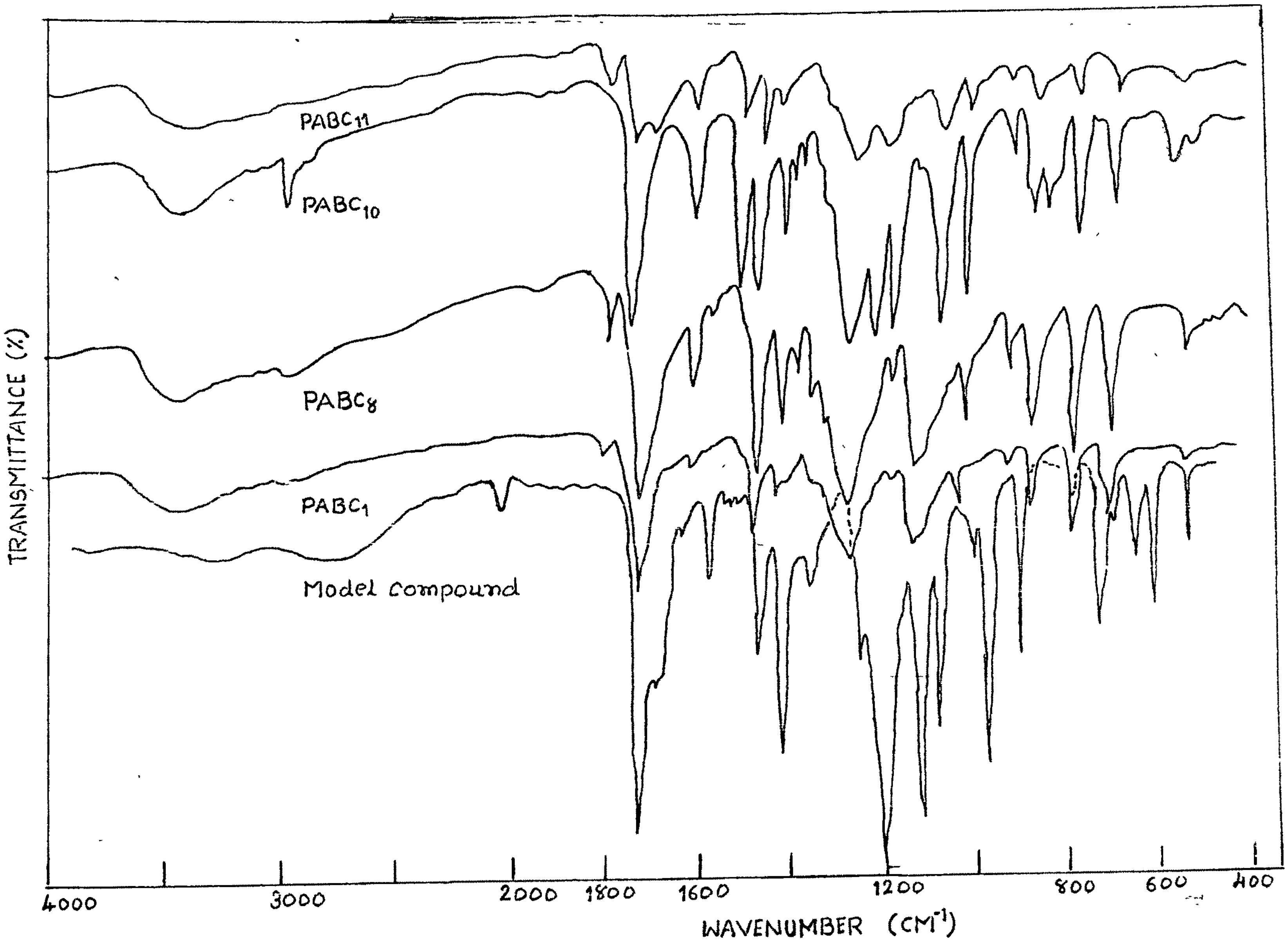


FIG. 54: IR Spectra of Polymer System PABC.

effect on mesomorphism. With this in view a polymer system was investigated having methoxy group as lateral substituted group and azine alinkage in polymeric system. Route of synthesis is given in Fig.55.

The synthesis of monomer and polymers is described in the experimental section. The melting point and transition temperatures are recorded in Table-76.

Reference to Table-76 shows that polymer AZ_1 having aliphatic fraction does not exhibit mesomorphism. Polymer AZ_2 having p-phenylene unit does not melt upto 350°C, hence mesophase could not be observed in this polymer linkage. AZ_3 and AZ_4 having iso-phenylene linkage and flexible acid linkage, respectively exhibit nematic mesophase. Polymer AZ_5 having Bisphenol-A derivative, does not exhibit mesomorphism. Polymer AZ_6 having p-azoxybenzoyl unit exhibits smectic mesophase.

The above observations indicate that in the case of non-mesogenic AZ_1, the flexibility of $-(CH_2)_4-$ is not adequate to induce mesomorphism eventhough "azine" moiety is conducive to mesomorphism. Polymer AZ_2 does not melt, here p-phenylene unit, a rigid core along with rigid "azine" moiety, raises melting point beyond 350°C, hence mesophase could not be observed.

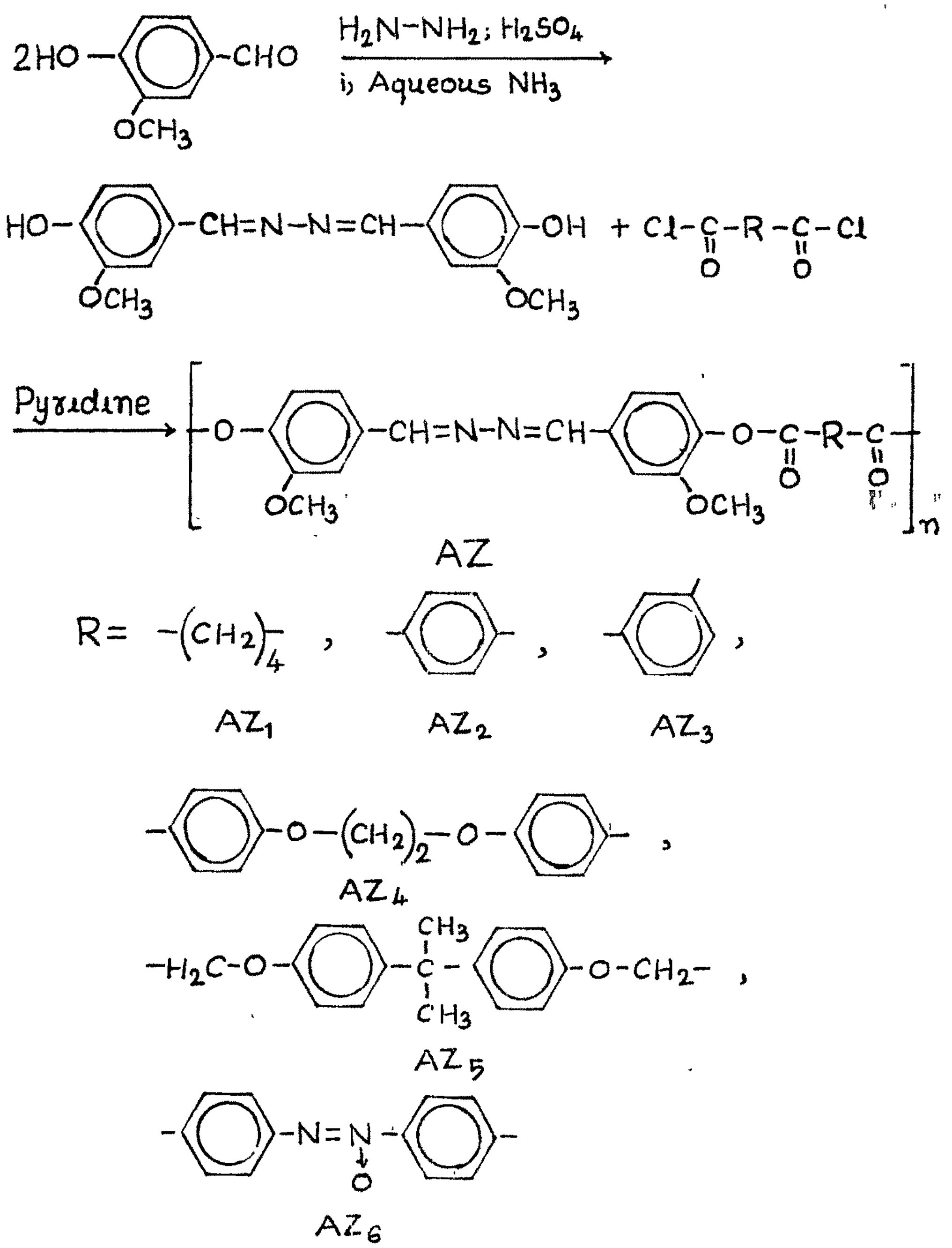
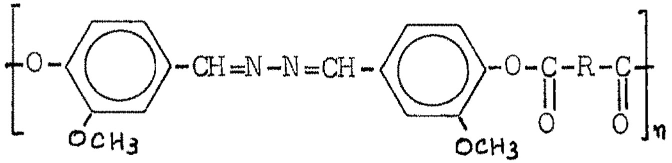
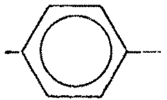
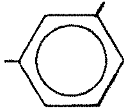
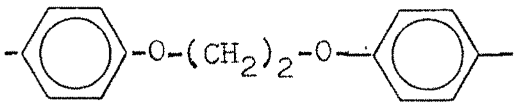
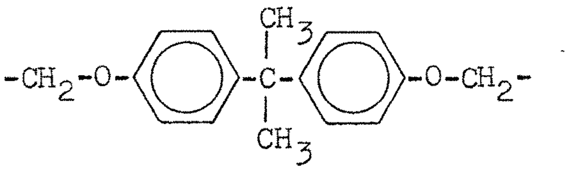
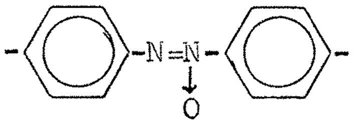


FIG. 55 : Route of Synthesis for Polymer System AZ

Table-76



Transition Temperatures and Viscosity Data:

Sr. No.	Polymer	R	Transition Temperatures(°C)			[η]dl/gm
			Smectic	Nematic	Isotropic	
1	AZ_1	$-(CH_2)_4-$	-	-	155	0.1150
2	AZ_2		-	-	350	-
3	AZ_3		-	190	230	0.1920
4	AZ_4		-	127	296P	0.2250
5	AZ_5		-	-	130	0.1665
6	AZ_6		240	-	290	-

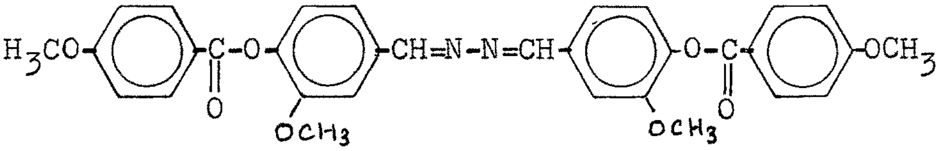
P : Sample post-polymerizes and becomes solid

It seems that meta-linkage of isophthalic acid (AZ_3) and flexible spacers of 1,2-bis(4'-carboxy-phenoxy)ethane, brings down the melting point and transition temperatures and as expected endows the system with mesomorphic properties. It is observed that mesomorphic properties can be induced in a polymeric system having rigid segments by incorporating a flexible spacer or a kink, bend or methylene units of sufficient length. The above results support this statement. Non-mesomorphism of polymer AZ_5 can be attributed to steric factor and increased flexibility due to the presence of two $-O-CH_2-$ linkages. We have noted that in earlier study most of the polyesters of p-azoxybenzoic acid do not exhibit mesomorphism but polyester of it with 'azine' having lateral substituents exhibits mesomorphism. It seems that two bulky lateral methoxy group present in "azine" moiety does not allow melting point to rise beyond 300°C. Due to this reason polymer AZ_6 exhibits mesomorphism. It has been pointed out earlier that polyesters of p-azoxybenzoic acid would exhibit smectic mesophase as the dipole of the ester groups will be acting across the longer axis of the molecules.

Above results indicate that if flexibility is increased beyond certain limit or rigidity is more, mesomorphic properties could not be observed in the polymer system.

Polymers were characterized by elemental analysis (Table-37), IR spectra (Table-50) Fig.56) and solution viscosity (Table-76).

A model compound was obtained by synthesizing dianisoyl ester of 3,3'-dimethoxy-4,4'-dihydroxy benzalanine. The model exhibits nematic mesophase of high thermal stability. The behaviour of model suggests that rigid segment as monomer will raise melting point very high, which is the case observed in polymer AZ_2.



k 258°C N 280°C I

Model Compound

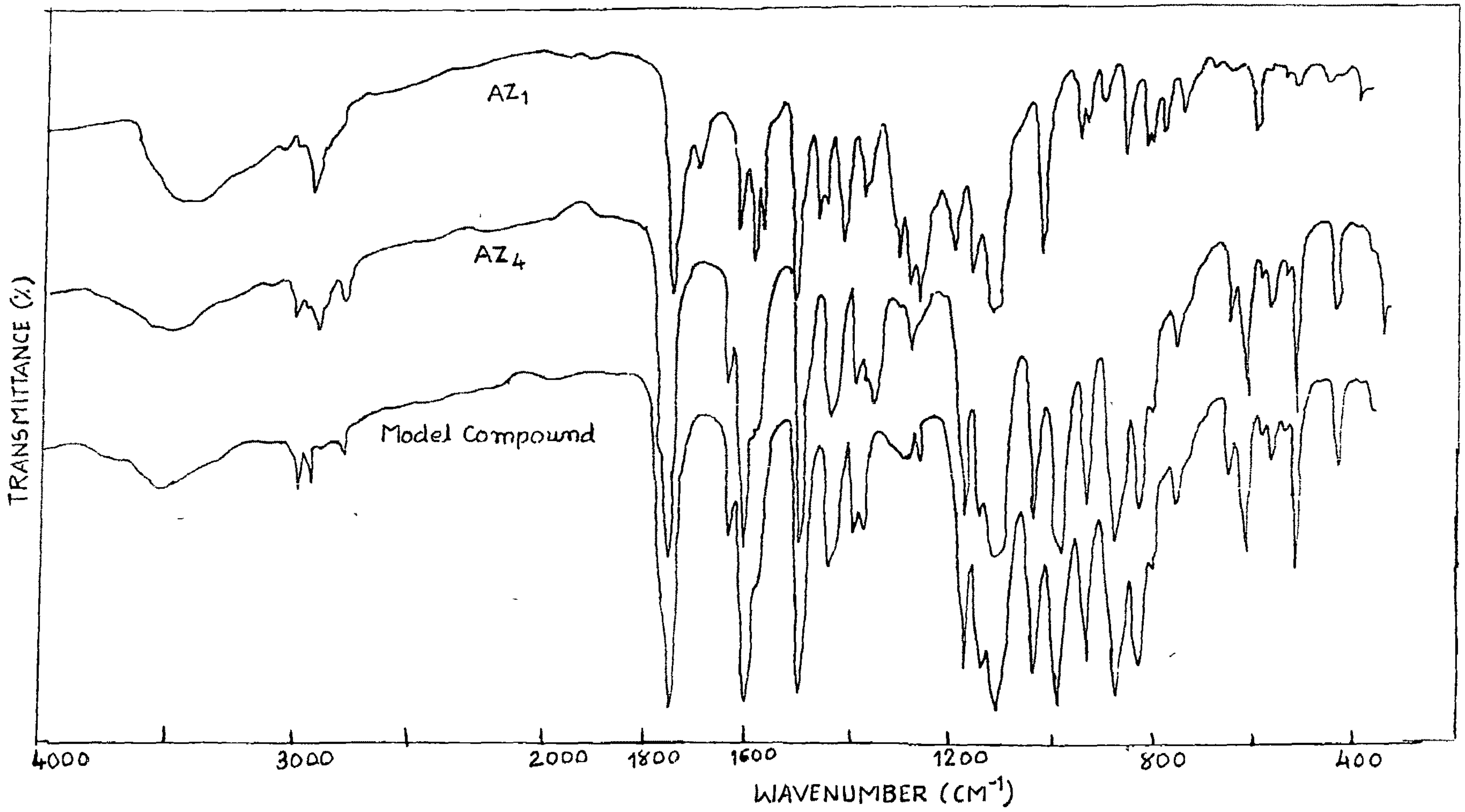


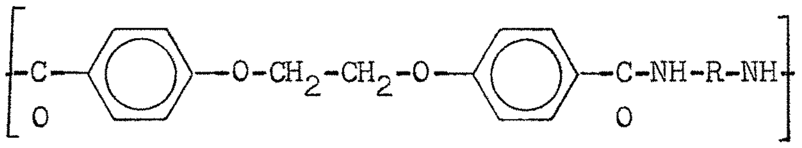
FIG. 56: IR Spctra of Polymer System AZ.

LIQUID CRYSTALLINE POLYAMIDES

3. LIQUID CRYSTALLINE POLYAMIDES:

3.1.MESOGENIC POLYAMIDE -I

Number of polyesters exhibiting thermotropic liquid crystalline properties are reported (309, 433-435). Our earlier study also are on polyesters and many of them exhibit mesomorphism. Polyamides were of greater interest as they exhibited lyotropic mesomorphism and gave high strength high modulus fibres (437). Search was going on for thermotropic liquid crystalline polyamides to facilitate the application aspect as anitrosopic polymer melt can be controlled better for the processing purposes (437). Khan et al.(432) synthesized polyesteramides to bring down the melting point, and observed thermotropic mesomorphism. It was proposed to synthesize polyamides by incorporating flexible spacer as a constant unit and condensing it with different diamines having flexible or rigid structure to evaluate the effect of these parameters on mesogenic properties. With this in view following polymer system was synthesized and studied. The route of synthesis is given in Fig. 57.



BEA

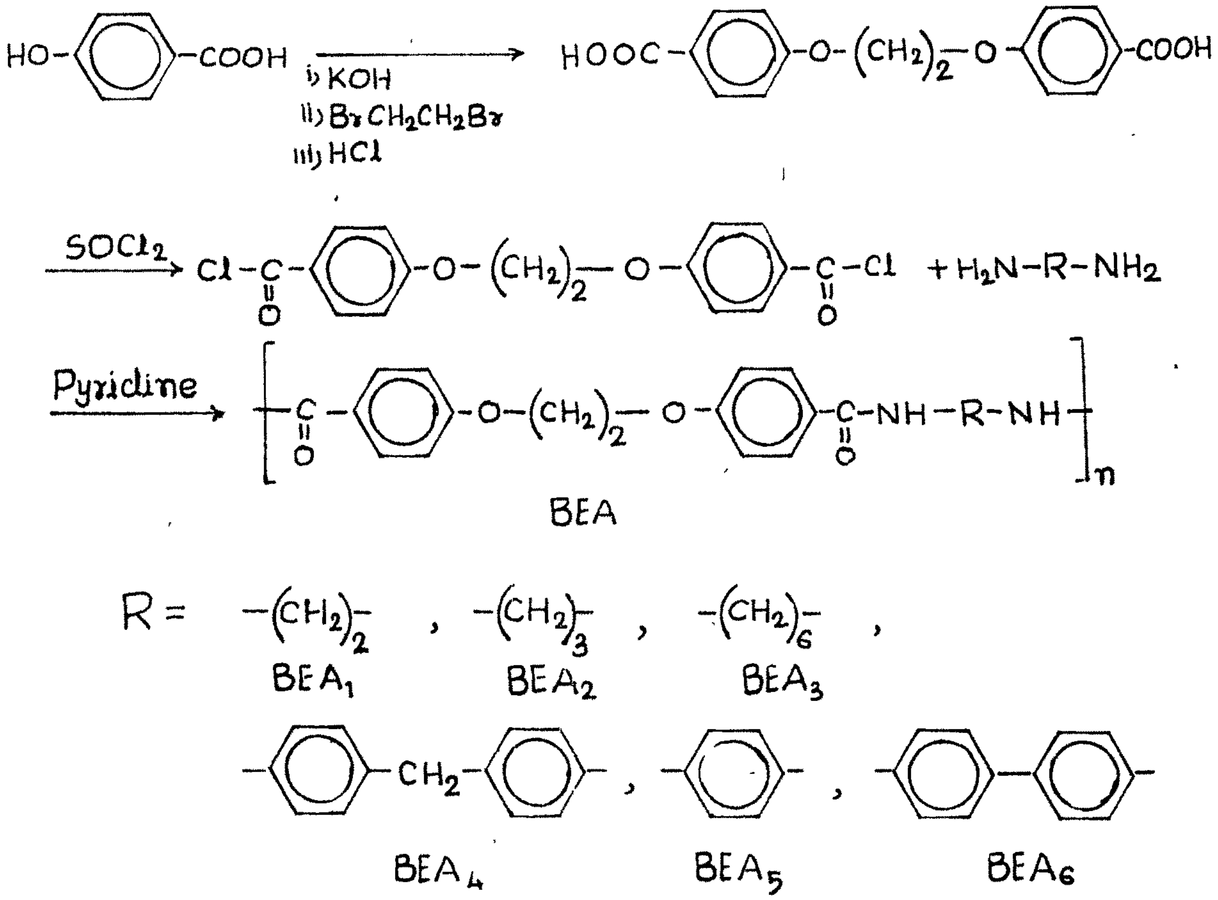


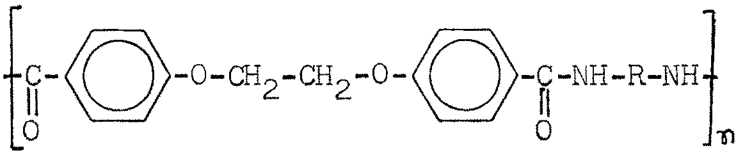
FIG. 57: Route of Synthesis for Polymer System BEA

The synthesis of polyamide is described in the experimental section. The degree of polymerization in the case of polyamides depend also on the temperature and time period during condensation reaction. To evaluate these parameters the polyamides are also synthesized by three different methods. The condensation is carried out at 0-5°C and in 1½ hours, at 23°C and in 1½ hours and at 23°C and in twelve hours. The polyamides obtained by above three methods are studied in detail. Melting points and transition temperatures of polyamides are reported in Table-77.

Reference to Table-77 shows that polyamides having aliphatic diamines as monomers exhibit nematic mesophases, whereas aromatic diamines raise the melting point of polyamide beyond the limit of microscope. It would be interesting to observe these polyamides at higher temperatures to examine whether they exhibit mesomorphism. In absence of DSC apparatus or a hot stage of higher temperature range, it was not possible in the present study.

Comparison of polyesters and polyamides studied in the present investigation will be quite interesting.

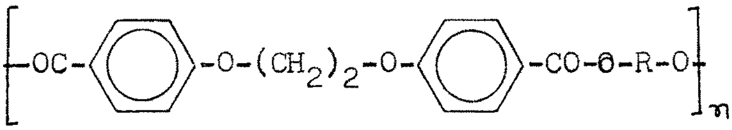
Table-77

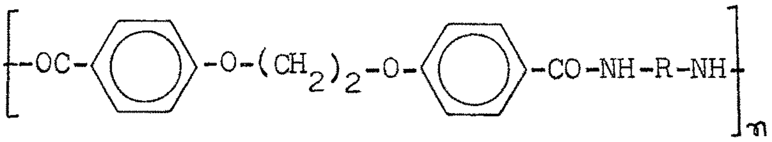


Transition Temperatures and Viscosity Data;

Sr. No.	Polymer	R	Transition Temperatures(°C)			[η] dl/gm
			Smectic	Nematic	Isotropic	
1	BEA_1	$-(CH_2)_2-$	-	160	288	0.0803
2	BEA'_1		-	-	325	0.1706
3	BEA''_1		-	-	285	-
4	BEA_2	$-(CH_2)_3-$	-	138	281	0.1012
5	BEA'_2		155	-	230	0.1605
6	BEA''_2		-	-	233	0.1414
7	BEA_3	$-(CH_2)_6-$	(275)*	280	-	
8	BEA'_3		-	240	272	0.2122
9	BEA''_3		215	-	270	0.1540
10	BEA_4	P-C_6H_4-CH_2-C_6H_4-P	-	-	>325	-
11	BEA'_4		-	-	>325	-
12	BEA''_4		-	-	>325	-
13	BEA_5	-C_6H_4-P	-	-	>325	-
14	BEA'_5		-	-	>325	-
15	BEA''_5		-	-	>325	-
16	BEA_6	P'-C_6H_4-C_6H_4-P	-	-	>325	-
17	BEA'_6		-	-	>325	-
18	BEA''_6		-	-	>325	-

*: Mesophase observed during cooling


I


II

All the polyesters I reported in section (experimental section 2.1.3) (Table-76), whether aliphatic or aromatic, exhibit mesomorphism, whereas polyamides II having the same acid monomer exhibit mesomorphism only when aliphatic diamine is the second monomer. Most of the aromatic polyamides do not melt up to 325°C. Khan et al.(432) have reported polyesteramide having a flexible spacer and a rigid unit, however these polyesteramides exhibit mesomorphism at very high temperatures (> 350°C) where the length of spacer group is short (n=2). This indidates that from polyester to polyamide high melting tendencies of amide linkage hinders the onset of mesomorphism. In earlier study (438) we have reported low molecular mesogenic esteramides which exhibit higher thermal stabilities compared to ester linkages in similar compounds. The higher thermal stabilities of these low molecular weight compounds are attributed to the linear structure of polyamide and higher polarizability compared to ester linkage. This explains the high melting behaviour and non-mesomorphism of polyamides having aromatic moiety.

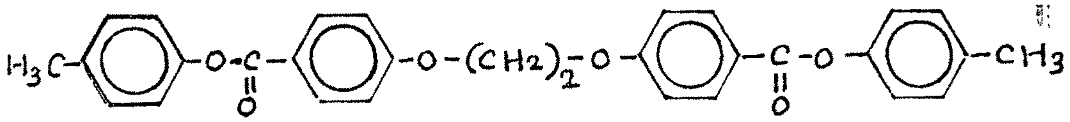
To understand further the behaviour of polyamides compared to polyesters, model compounds were synthesized (Fig.58).

Reference to Fig.58 shows that even the model amides are infusible whereas model esters exhibit mesomorphism. The behaviour of model compounds explain the non-mesomorphism and infusible nature of polyamides compared to polyesters.

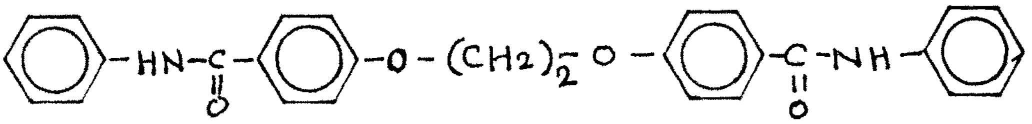
Polyamides were synthesized by using same solvent but changing the reaction temperature and time as described in the experimental section.

Sr.No.	Polymer	Reaction Temperature (°C)	Time (hour)	Solvent
1	BEA_1 to BEA_6	0-5	$1\frac{1}{2}$	Pyridine
2	BEA'_1 to BEA'_6	23	$1\frac{1}{2}$	Pyridine
3	BEA''_1 to BEA''_6	23	12	Pyridine

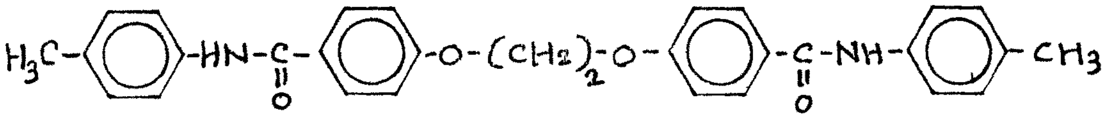
Polyamide BEA_1 is mesogenic, BEA'_1 and BEA''_1 are non-mesogenic. Non-mesomorphism of BEA'_1 can be understood as it does not melt and has much higher viscosity $[\eta]$ value than polyamide BEA_1. The non-mesogenic behaviour of polyamide BEA''_1 is difficult to explain bexause melting point is almost the same as that of isotropic transition of BEA_1.



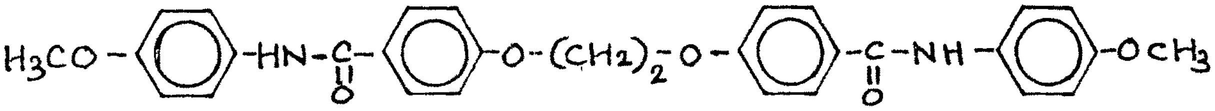
K 212°c I (185°c) N.



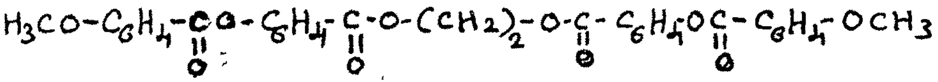
M. P. >300°c.



M.P. >300°c.



M.P. >300°c.



$H_3CO-C_6H_4-\underset{\overset{\|}{O}}{C}O-C_6H_4-\underset{\overset{\|}{O}}{C}-O-(CH_2)_2-O-\underset{\overset{\|}{O}}{C}-C_6H_4-O\underset{\overset{\|}{O}}{C}-C_6H_4-OCH_3$ (439)

K 99°c S >300°c d.

FIG. 58 : Model Compounds.

Polyamide BEA_2 is nematic, BEA'_2 is smectic. This behaviour is as expected, but here again the non-mesomorphism of BEA''_2 is difficult to explain. In both of these cases, stirring period of twelve hours at room temperature (23°C) brings such a change that polymers with the same chemical structure as the BEA series do not exhibit mesomorphism.

In the case of BEA_3, BEA'_3 and BEA''_3 , all the three polyamide samples exhibit mesomorphism. BEA_3 exhibits smectic mesophase.

It can be seen from the above discussion that even a minor variation in the reaction condition affects the exhibition of mesomorphism in polymeric system.

Polyamides are characterized by elemental analysis (Table-42), IR spectra (Table-51; Fig.59) and by solution viscosity study (Table-77).

3.2 MESOGENIC POLYAMIDES - II

Looking to the non-mesogenic behaviour of polyamides-I, especially due to the tendency of polyamides to remain unaffected upto 325°C, it was proposed to synthesize polyamides having flexibility and steric effect on one of the monomers. With this in view following polymer system

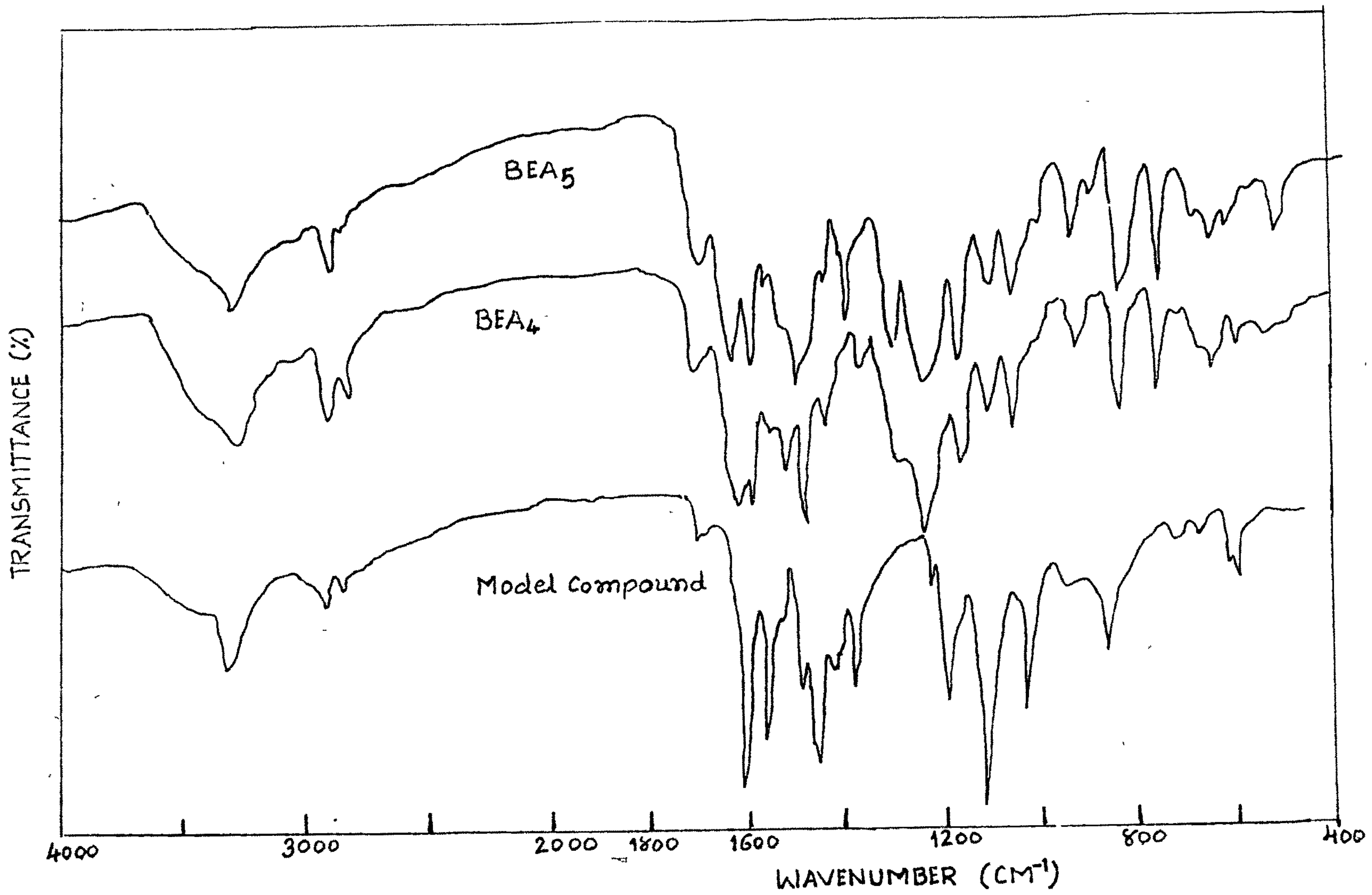
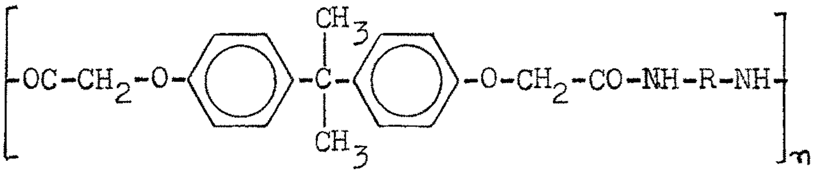


FIG. 59: IR Spectra of Polymer System BEA.

was synthesized and studied. The route of synthesis is given in Fig.60.



BP

Melting points, transitions temperatures and viscosity data are recorded in Table-78.

Reference to Table-78 shows that none of the polyamides exhibits mesomorphism except polyamide BP_6. However all the polyamides-II melt at lower temperature compared to polyamide-I. Polyamide BP_6 having benzidine as one of the monomers exhibits nematic mesophase. This indicates that when steric factors are deterrent and flexibility is incorporated in the monomer, the second monomer with aliphatic and aromatic system (with one benzene nucleus) does not exhibit any mesomorphism.

The results indicate that adequate attractive forces are needed to exhibit mesomorphism. It is necessary to bring down the melting point of polyamide to exhibit mesomorphism, but incorporation of substituents which disturb attractive forces more adversely, then necessary mesophase will not be observed.

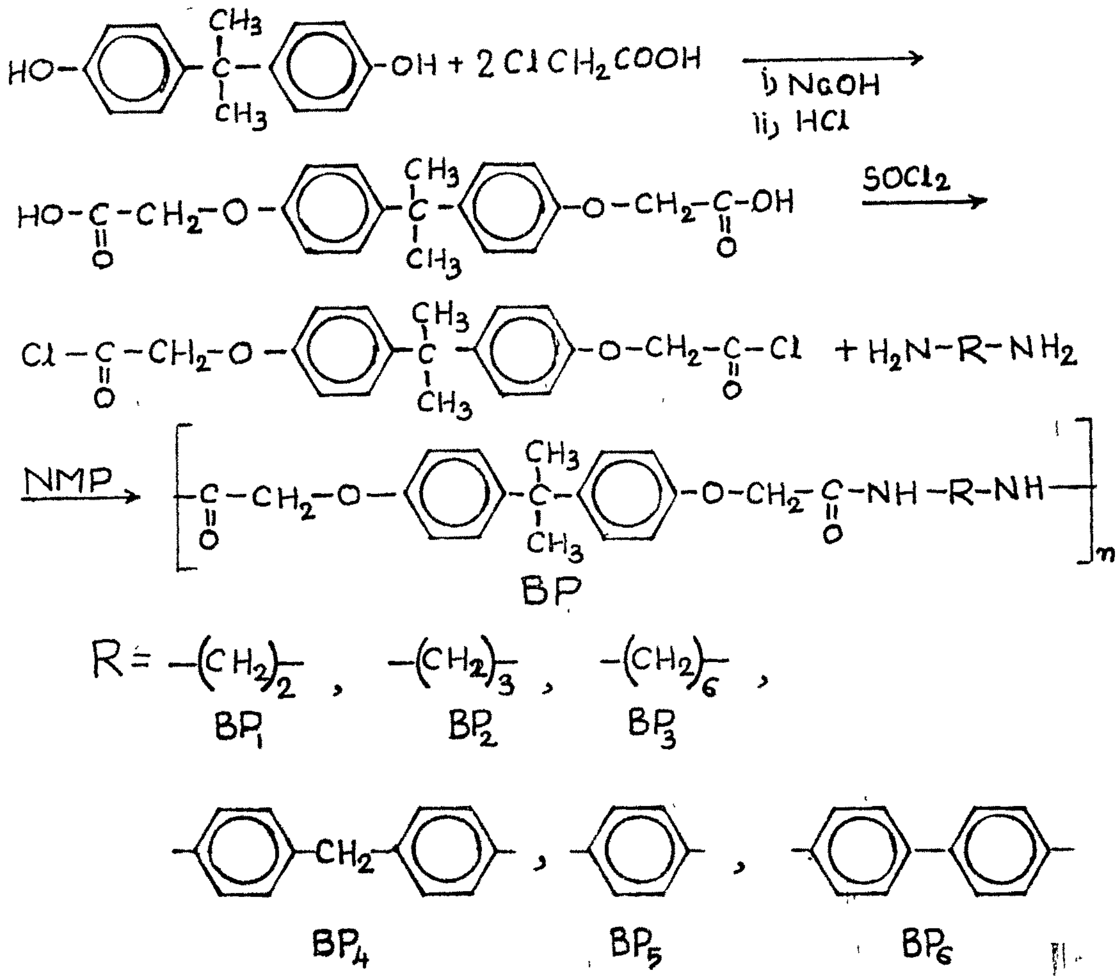
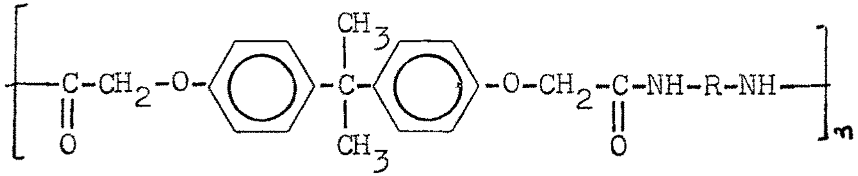
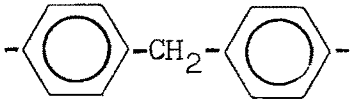
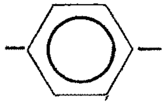
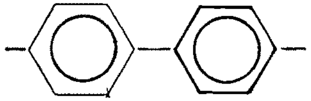


FIG. 60 : Route of Synthesis for Polymer System BP.

Table-78

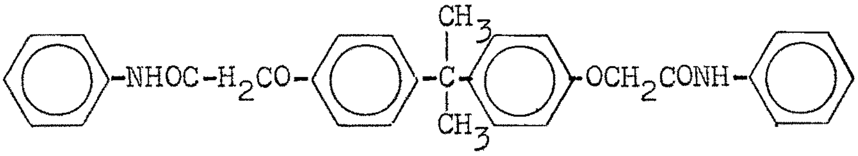


Transition Temperatures and Viscosity Data:

Sr. No.	Polymer	R	Transition Temperatures(°C) Smectic	Nematic	Isotropic	$[\eta]$ dl/gm
1	BP_1	$-(CH_2)_2-$	-	-	104	0.115
2	BP_2	$-(CH_2)_3-$	-	-	097	0.124
3	BP_3	$-(CH_2)_6-$	-	-	100	0.128
4	BP_4		-	-	149	0.200
5	BP_5		-	-	195	0.175
6	BP_6		-	145	256	0.200

All the polymers were characterized by elemental analysis (Table-42) and IR spectra (Table-52, Fig.61).The solution viscosity (Table-78) was measured as described in the experimental section.

A model compound with the following structure was synthesized which does not exhibit mesomorphism.



M.P. 163°C

This shows that polyamides may or may not exhibit mesomorphism. However, model compounds obtained from flexible acids do not melt.

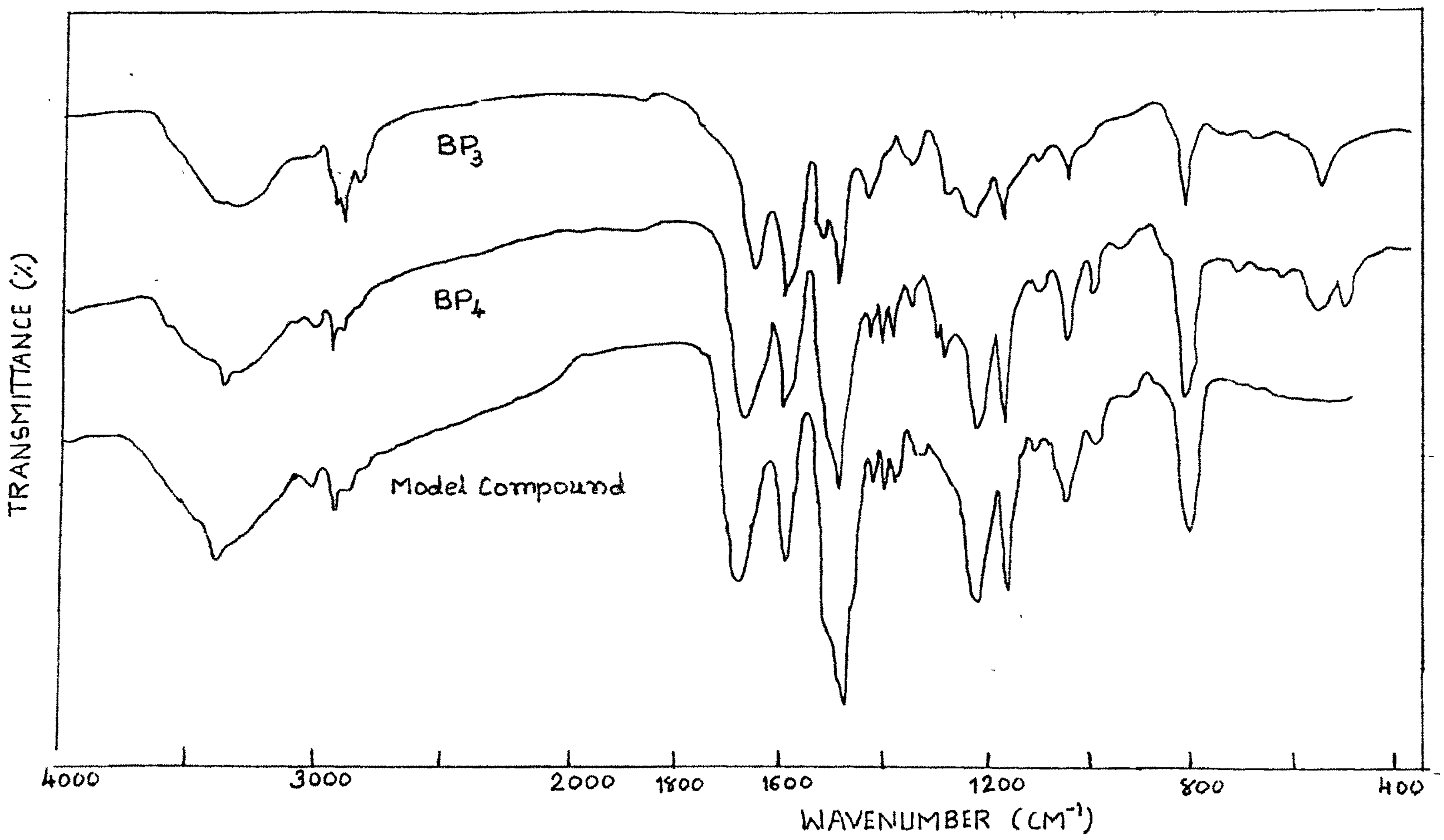


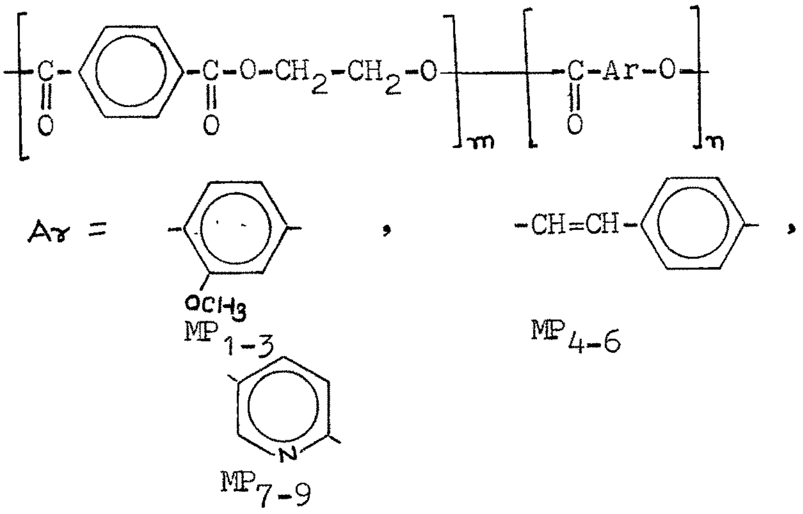
FIG. 61: IR Spectra of Polymer System BP.

LIQUID CRYSTALLINE COPCLYESTERS

4. LIQUID CRYSTALLINE COPOLYESTERS:

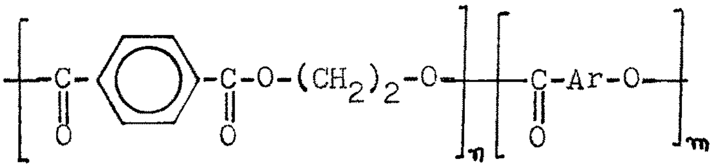
Number of mesogenic polyesters are obtained by condensing terephthalic acid, ethylene glycol and hydroxy aromatic acids or their derivatives. It is known that cross esterification of polyethylene terephthalate with p-acetoxybenzoic acid gives mesogenic polymers (222-225, 440). In the present study laterally substituted 4-acetoxy-3-methoxybenzoic acid, p-acetoxycinnamic acid and 6-hydroxy necotinic acid were copolymerized with dimethyl-terephthalate and ethylene glycol as described in the experimental section by varying molar ratios.

The polymer has the structure as under:



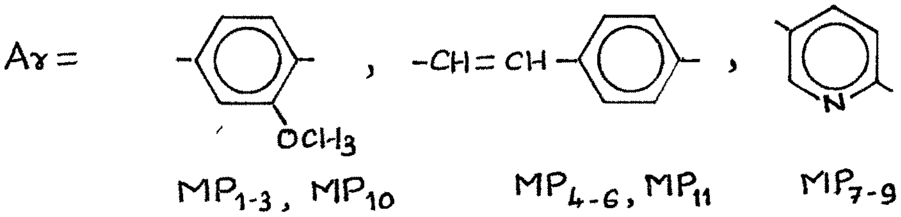
The transition temperatures and viscosity data are recorded in Table-79.

Table-79



Transition Temperatures and Viscosity Data:

Sr.No.	Polymer	Transition Temperatures (°C)			[η] dl/gm
		Smectic	Nematic	Isotropic	
1	MP_1	107	-	161	0.308
2	MP_2	110	-	165	0.162
3	MP_3	135	-	165	0.198
4	MP_4	188	-	241	0.376
5	MP_5	099	-	184	0.136
6	MP_6	155	-	198	0.214
7	MP_7	129	-	205	0.172
8	MP_8	118	-	165	0.072
9	MP_9	121	-	156	0.179
10	MP_{10}	-	-	190	-
11	MP_{11}	-	-	250	-



Reference to Table-79 shows that all the polymers MP_1 to MP_9 exhibit smectic mesophases. The variations in the ratio of oxyaromatic residue to ethylene glycol affects the mesophase transition temperatures.

However, it is difficult to generalize or correlate structural features with mesomorphic tendency because the intrinsic viscosity $[\eta]$ also changes with the change in molar ratios of the two monomers.

Number of research papers (222-225) on thermal behaviour of Co-poly(ethylene terephthalate)-p-oxy-benzoate indicate that when molar concentration of p-hydroxybenzoic acid is 30 to 60 % it exhibits nematic properties. Number of other copolyesters are reported where hydroxyaromatic acids are nephthalene derivatives, (440-443). The systems also exhibit mesomorphism. However, in the present study the polyesters obtained exhibit smectic mesophases even when the concentration is much less (11 %).

In the present investigation the vanillic acid residue will increase the breadth of the molecules of the polymer, whereas other two aromatic hydroxy acid residue will favour the smectic arrangement by increasing over all polarizability of the system. The comparison of the exhibition of mesophase of the present polymeric systems with the exhibition of nematic phases by Copoly (ethylene-terephthalate)-p-oxybenzoate (ETB) can not be made as intrinsic viscosity $[\eta]$ differs substantially (0.308 MP_1, 0.97 ETB). We have observed in our earlier study (444) that within the same polymeric system, increase in the value of intrinsic viscosity $[\eta]$ converts the smectic mesophase to nematic and further increase makes it non-mesogenic. The results of present systems and its comparison with the ETB system further confirms this observations.

It is interesting to note that homopolymers of 6-hydroxynicotic acid do not exhibit mesomorphism whereas homopolymers of p-hydroxycinnamic acid and 4-hydroxy-3-methoxybenzoic acid exhibit mesomorphism.

Monomers were synthesized by different known methods. Synthesis of 6-hydroxynicotinic acid involved number of steps. The polymers were characterized by IR spectra (Table-53, Fig.62). The solution viscosity (Table-79) of all the polymers was studied by using Ubbelohde viscometer at constant temperature.

Polymers MP_2 and MP_5 were post-polymerized in different environments (experimental section 4.2.1) and post-polymerized samples MP_{10} and MP_{11} (Table-44) were obtained respectively. Post-polymerized samples do not exhibit mesomorphism.

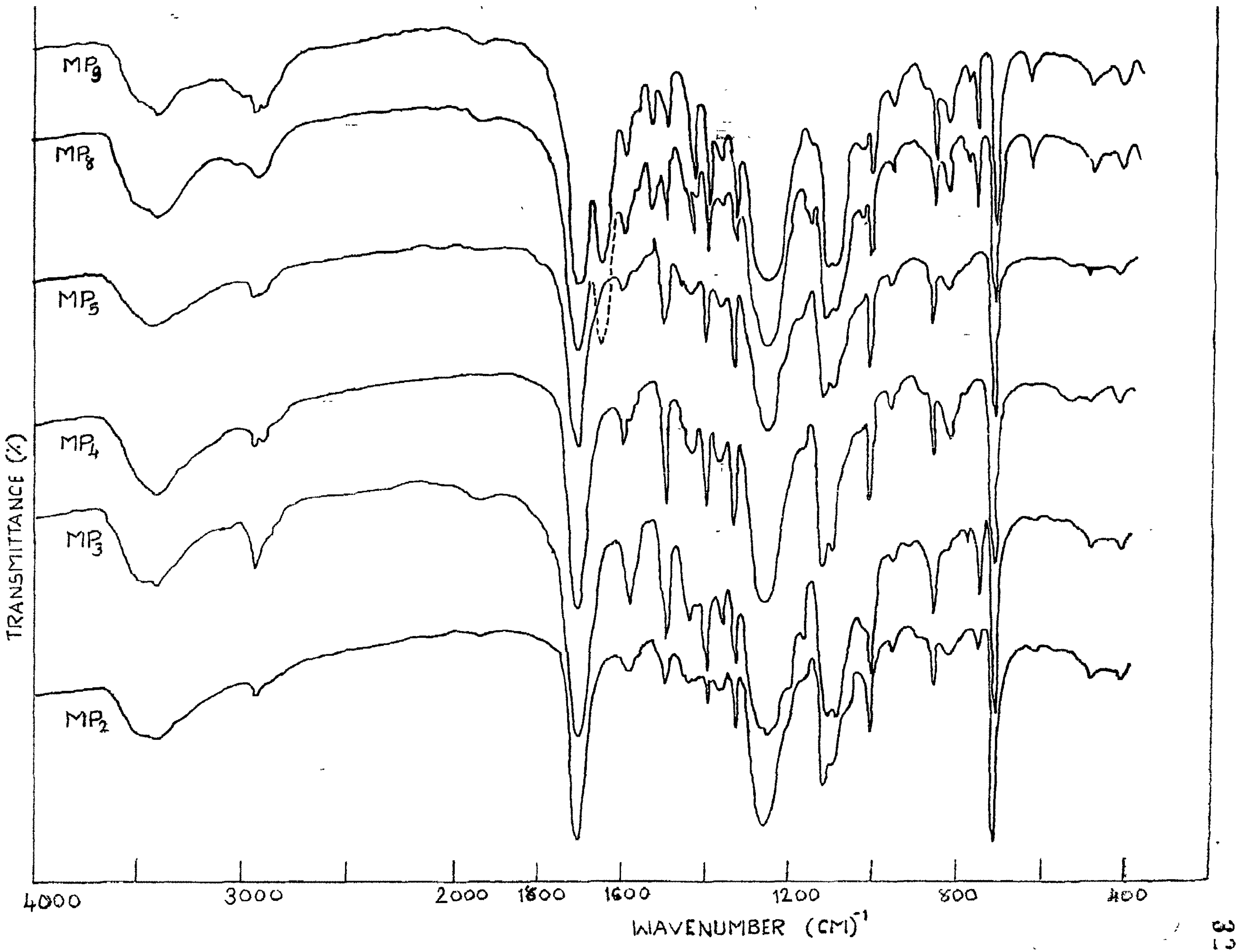


FIG. 62: IR Spectra of Polymer System MP.

The results provide a few more new copolyester systems which can further be exploited for the detailed study for obtaining higher viscosity and commercial feasibility aspects.

DIFFERENT STUDIES ON POLYMERS

5. DIFFERENT STUDIES ON LIQUID CRYSTALLINE POLYMERS:

5.1 CHARACTERIZATION OF MESOPHASES:

As described in the experimental section the mesophases of polymers are characterized by their classical textures observed under the microscope during heating. Care is taken to characterize smectic mesophase, as high viscosity of polymers may not have high fluidity of nematic phase compared to low melting nematogen, moreover, the classical focal conic texture of smectic mesophase may not be observed in many cases.

The characterization of mesophases by texture observation is further supported by contact method. As described in experimental section known low melting mesogens (smectic, nematic) were taken and by contact method respective smectic or nematic mesophases were further confirmed by miscibility rule.

5.2 IR SPECTRA:

IR spectra were taken for model compounds and polymers. The characteristic frequencies for the respective linkages were observed and confirmed the formation of models and polymers.

Table -80

TGA Results

Homopolyesters of p-hydroxy benzoic acid : Poly(4-oxybenzoates):

Loss at various Temperatures. (Heating rate 10°C per minute in air).

Sr.No.	Polymer	% weight loss					
		250°C	300°C	350°C	400°C	500°C	600°C
1	Poly (p-oxy-benzoate) (365)	-	5.0	6.0	8.0	30.0	35.0
2	HP_{11}	2.97	4.80	5.0	11.45	22.9	98.43
3	HP_{15}	0.625	2.5	14.4	16.5	17.5	-
4	HP_{17}	-	1.0	12.5	13.0	45.0	50.0
5	HP_{18}	-	-	0.51	5.1	28.05	-
6	HP_{19}	-	-	-	-	8.4	78.6
7	HP_{20}	0.625	2.5	14.40	16.5	87.5	-

Table -81

TGA Results

Homopolyesters of Vanillic acid : Poly(4-oxy-(3-methoxy)-benzoates) :

Loss at various Temperatures.

(Heating rate 10°C per minute in air).

Sr. No.	Polymer	% weight loss				
		250°C	300°C	350°C	400°C	500°C
1	V_2	5.17	13.16	24.14	62.56	94.32
2	V_7	26.00	49.00	63.00	69.50	88.00
3	V_8	8.33	26.00	50.55	62.38	83.82
4	V_{11}	2.50	19.00	33.00	53.00	77.20
5	V_{12}	19.00	32.50	47.00	61.00	97.00
6	V_{13}	21.11	40.22	51.98	69.63	97.46
7	V_{14}	18.00	33.00	47.50	61.00	89.00
8	V_{15}	14.00	22.00	33.50	49.00	81.00
9	V_{16}	3.00	5.00	9.50	55.00	89.00
10	V_{17}	2.50	4.00	9.50	21.00	70.00

Table -82

TGA Results

Copolymers and polyester:

Loss at various Temperatures.

(Heating rate 10°C per minute in air).

Sr.No.	Polymer	% weight loss					
		250°C	300°C	350°C	400°C	500°C	600°C
1	P-Co-M_{11} (Table-27)	1.5	2.0	9.0	17.5	44.0	78.0
2	P-Co-M_{12} (Table-27)	-	0.187	0.56	1.87	22.4	-
3	VB_{12} (Table-29)	-	1.0	3.0	8.25	23.94	42.56
4	VB_{13} (Table-29)	-	0.50	3.0	8.00	29.0	88.00
5	BE_3 (Table-34)	6.86	10.78	14.21	24.50	65.21	90.16

stability up to 400°C but beyond 500°C it decomposes rapidly. The thermal stability of high molecular weight polymer studied by Patel et al. (365) was compared with present results (Table-80). To study the effect of post-polymerization on the thermal stability of the polymers, poly(p-oxybenzoate) HP_3 was post-polymerized in different conditions (Table-80) and the resultant polymers HP_{15-19} were evaluated for their thermal stabilities. The polymer sample HP_3 heated for 20 minutes at 310°C to 330°C under reduced pressure (77 mm. of Hg) exhibits good thermal stability (12.5 % degradation at 350°C). Encouraged with this result, another samples were prepared from HP_3 by post-polymerizing it at the same temperature under reduced pressure (77 mm. and 0.5 mm. of Hg) (HP_{18} and HP_{19}) (Table-23). The thermal degradation is less in HP_{18} upto 500°C compared to the reported data for high molecular weight poly(p-oxybenzoate) (365). In the case of HP_{19}, the stability is far better than the reported polymer at 500°C.

These results suggest that liquid crystalline low molecular weight poly(p-oxybenzoates) can be processed at lower temperatures and when subjected to lower temperature and when subjected to high temperature treatment under vacuum for short duration, highly thermally stable polymers are obtained. The thermal stability of post-polymerized poly(p-oxybenzoates) is higher than those of poly(p-oxy-cinnamates) (414). The presence of -CH=CH- linkage in cinnamate will render it more susceptible to decomposition.

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

Ten polymers were analysed (Table-81). The polymers V_2, V_8 and V_{11} obtained after six hours condensation time exhibit higher thermal stabilities compared to polymers V_7, V_{12} and V_{13} and which are obtained by condensing the monomer for shorter duration. Homopolymer V_7 was post-polymerized as indicated in Table-24 to obtain polymer samples V_{14} to V_{17} in different environments.

Reference to Table-81 shows that polymers V_{16} and V_{17} exhibit better thermal stability compared to V_7, V_{14} and V_{15} as they are obtained by post-polymerizing V_7 under reduced pressure. The thermal stability of post-polymerized poly-(4-oxy-3-methoxybenzoates) is much less than those of poly(4-oxybenzoates). This shows that lateral methoxy group plays its role in the early decomposition in poly(4-oxy-3-methoxybenzoates).

5.4.3 Poly(4-Co-3-oxybenzoates):

Copolymers of para- and meta-hydroxybenzoic acid P-Co-M_5 and P-Co-M_6 (Table-27) were post-polymerized and studied for their thermal stabilities. Reference to Table-82 shows that copolymer P-Co-M_{11} and P-Co-M_{12} exhibit good thermal stability but P-Co-M_{12} exhibits much higher thermal stabilities than that of P-Co-M_{11}. The difference between the two polymers is in the ratio of acids. The results show that the ratio of isomeric hydroxybenzoic acids affects the thermal stability of post-polymerized copolymers.

5.4.4 Poly(4-oxybenzoate-Co-4'-oxy(3'-methoxy)benzoates):

Copolymers VB_4 and VB_7 (Table-29) were post-polymerized in different environments. The resultant post-polymers VB_{12} and VB_{13} were evaluated for their thermal stabilities (Table-82). Both the copolyesters exhibit good thermal stabilities.

5.4.5 Polyester with Flexible Spacer:

Polyester obtained by condensing diacid chloride of 1,2-bis(4'-carboxyphenoxy)ethane and hydroquinone (BE_3) (Table-73) was evaluated for thermal stability (Table-82). It exhibits good thermal stability but it is much less compared to post-polymerized homopolymers and copolymers of different hydroxybenzoic acids.

5.5 DTA/DSC Study:

It would have been very interesting to study polymer samples by DTA/DSC method. Especially by heating/cooling runs to understand the mesophases further and enthalpy, entropy changes involved in phase transitions. However, in absence of such facilities we could get analysed a few samples from other institutions.

5.5.1 Poly(4-oxybenzoates) (Table-66):

5.5.1a Polymber HP_3:

Thermogram (Fig.34b) indicates as endotherm at 180°C which can be attributed to glass transition temperature (Tg) as microscope readings indicate melting at 237°C;

K 237°C Sm 340°C P

An endotherm at 207°C followed by an exotherm makes the transition endotherm which could have been observed otherwise at 327°C. Exothermic peak can be due to post-polymerization phenomena. On heating, an observation under microscope indicates that at 340°C polymer solidifies from mesophase.

5.5.1b Polymer HP_5:

Thermogram (Fig.34a) shows an endothermic peak at 65°C. This can be attributed to some solid-solid transition at this temperature. The transition temperatures obtained for poly(4-oxybenzoate) (HP_5) are as under ;

K 297°C Sm 316°C N 323 P

However, two endothermic peaks (Fig.34a) are obtained between 202°C and 260°C. No phase transitions are obtained in these temperature ranges. It may be due to the different crystalline modifications or changes which are not detectable under the microscope. Normally, better results are obtained after pre-heating the sample and studying its thermal stability.

However, the endotherms for transitions which should be observed at 297°C and 316°C are missing. The shifting of the base line is due to the exothermic nature of post-polymerization during heating. The post-polymerization seems to be maximum at 330°C, where an exothermic peak is obtained. The heating under microscope also confirms the post-polymerization process.

5.5.2 Poly(4-oxy-3-methoxybenzoates) (Table-68):

5.5.2a Polymer V_2 :

Microscope reading : K 179°C N 237°C P

An endothermic peak is observed at 185°C (Fig.36) indicating smectic-nematic change but it is followed by another endotherm. No phase change could be observed at that temperature. On further heating the thermogram exhibits exothermic reaction i.e. post-polymerization, followed by decomposition and melting.

5.5.2b Polymer V_8 :

Microscope reading: Does not melt upto 350°C.

The thermogram (Fig.36) indicates melting at very high temperature (390°C).

5.5.2c Polymer V_9:

Thermogram (Fig.35) of poly(4-oxy-3-methoxybenzoate) (V_9) shows two endothermic peaks at 195°C and 215°C, The microscope readings are as under:

K 125°C Sm 190°C N 301 P

This shows that solid to mesomorphic peak is missing though little curvature is seen in the thermogram. The peak at 215°C shows a phase change which is not observed under the microscope. There is a possibility that a change from smectic I to smectic II might have been missed in microscope if texture difference is not detectable. However, it is difficult to interpret as DSC of polymer systems show many peaks for crystallization or different polymorphism of crystals. Details study only can throw some light on this.

5.5.2 Polymer V_{11}:

Microscope reading : Does not melt upto 350°C

An endotherm observed at 100°C (Fig.36) can be attributed to solid-solid transition. However, it may be due to moisture also. Polymer was dried then that possibility is less likely.

An exotherm at 270°C suggests polymerization. The melting begins after 300°C.

Above results suggest that with single run of virgin polymer sample, it is difficult to precisely interpret endothermic transitions. Couple of heating and cooling runs, connecting of the sample and studying its DTA/DSC would throw some light on the transitions of the polymers and its correlation with behaviour observed under microscope.

5.6 X-RAY STUDY

X-ray diffractrograms were obtained for three polymers to have information regarding crystallinity of polymers.

5.6.1 Polyester (BE_3) (Table-73):

Reference to diffractogram (Fig.39) shows good degree of crystallinity in the polymer. Number of peaks are observed.

5.6.2 Poly(4-oxy-3-methoxybenzoate)(Table-68):

Polymer V_7:

Diffractogram (Fig.38) shows good degree of crystallinity.

5.6.3 Polymer V_{17}:

Polymer V_{17} was post-polymerized to obtain V_{17}. The diffractogram (Fig.38) of V_{17} shows that intensity of peak is increased. This indicates that degree of crystallinity is increased by post-polymerization of V_7.

The diffractograms of a few polymers indicate good degree of crystallinity in the polymers.