PART- I

1. INTRODUCTION

LIQUID CRYSTALS

Liquid crystals is one field which has attracted physicists, chemists, biologist and technologist alike. Liquid crystals is now accepted as the fourth state of matter. Fascination for the field of liquid crystals is primarily due to the theoretical contrast it presented in the discrete behaviour of the intermediate states. The study of mesomorphism gained momentum only during the last two decades because of the expanding horizons of application of liquid crystals to a variety of fields including medicine and electronic industries. Though not every new liquid crystal has turned out to be useful but the potential utility value cannot be denied since more and more usage are being explored thoroughly.

1 DEFINITION AND NOMENCLATURE

Liquid crystals are distinguished from both solids and liquids as non-isotropic turbid and viscous fluid having optical properties such as birefringence usually associated with crystalline solids. Liquid crystalline phase exist in low molecular weight was shown by Austrian botanist Reinitzer (1) in cholesteryl benzoate, being formed with cloudy melting point at 145° C and a clear melting point at 176° C. Only a year later Lehmann's (2) paper confirmed this unique feature as a property of certain compounds to which he gave the name "Flüsige Krystalle" (Liquid crystal) to describe this strange behaviour of the fluid state. After initial discovery of this phenomenon

Lehmann (3,4), Gattermann and Ritschke (5) and Vorlander (6) reported several liquid crystalline compounds, showing liquid crystalline state is truly an intermediate state of matter. Friedel (7) proposed the name "Mesomorphs" for such compounds and the term "mesomorphic state for intermediate phases (as in Greek - Mesos - means intermediate, morphs - form). Other associated terms such as 'mesomorph', mesoform', 'mesophase', 'mesogen' and 'mesomorphism' are also widely used in contemporary literature.

Rinne (8) classified matter as exhibiting either ataxy (disorder or amorphons structure) or eutaxy (an ordered structure). He proposed the name 'para crystals' for the substances exhibiting mesomorphism. Brown and Shaw (9) used the term 'mesomorphism' for the title of their first review. However, the term 'liquid crystals' is still more frequently used in the literature.

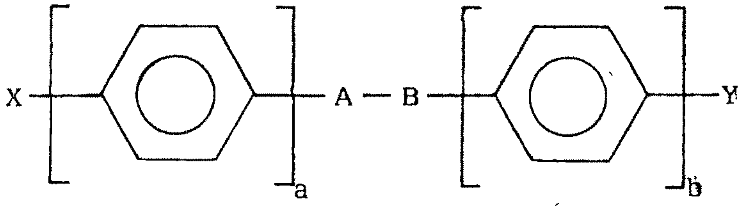
Meso phase may arise as a result of temperature variations, the term 'thermotorpic mesophase' is used for such mesophases. Mesophase may, however, also result from the changes of concentration of solution, for such systems, the term 'Lyotropic liquid crystal' is used. Gray and Winsor (10) preferred the term amphiphilic and non-amphiphilic instead. The amphiphilic mesogens have been called lyotropic i.e. solvent induced mesophases while non-amphiphilic are commonly called thermotropic i.e. temperature induced. A mesomorphic phase characterized by a reversible phase transition is referred to as 'enantiotropic'.

Mesomorphism is essentially a consequence of molecular shape. A necessary (but not sufficient) condition for the formation of mesomorophic state is that the molecules should either be (a) elongated and in some cases flat (possibility of liquid crystallinity) or (b) approximately spheroidal (possibility of plastic crystallinity). A primary determining factor of mesomorphism is the length to breadth ratio of molecular frame, which is denoted by R. If $R \gg 1$, then possibility of liquid crystal formation and if $R \approx 1$, then plastic crystals may formed.

2. CHARACTERISTIC PROPERTIES OF THERMOTROPIC LIQUID CRYSTALS

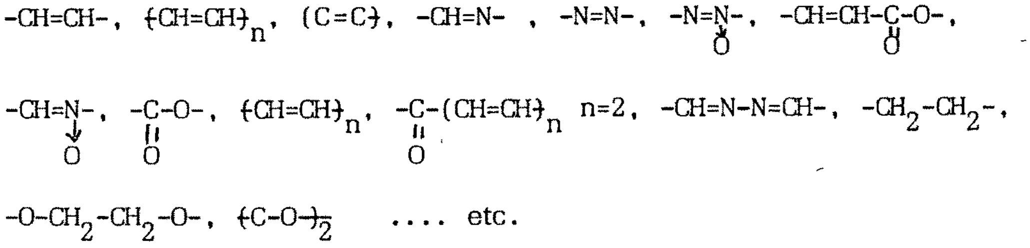
The molecules of liquid crystalline compounds are elongated, rod - or lath shaped, which facilitate to set themselves parallel to one another leading to the closest possible packing. Molecules are held together by local attachment due to polar groups and non-specific Van der Wall's forces. On raising the temperature, the cohesion between the molecules do not break down uniformly in all directions. There may be some residual forces still operating which will tend to hold the molecules together in the groups. Thus for a liquid crystal to be formed, the cohesion forces operating between elongated molecules must be both anisotropic and of suitable magnitude. Another criterion for the formation of liquid crystals is the rigidity of the elongated molecules. The introduction of unsaturation in the chain makes the molecules more rigid due to S_p^2 hybridisation and thus mesomorphism is attained in number of such compounds. Thus liquid crystalline behaviour is observed in systems in which the molecules (7,11,12,13,14) (i) are elongated and rectilinear with 'flat' segments such as benzene rings (ii) are rigid along the long axis with double bonds being common (iii) have strong dipoles along the molecular axis and (iv) have weaker dipolar groups at their ends.

Majority of thermotropic liquid crystals are Aromatic in nature and of general structure I where, x and y are terminal substituents such as alkyl, alkoxy, cyano etc..



(I)

a and b have small integral values. A-B represent the central linkage in the core structure. The usual central linking units are :

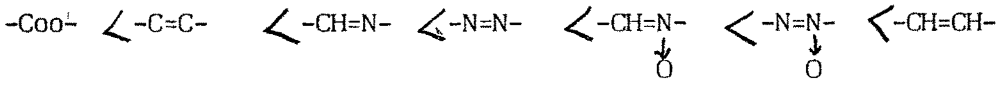


$-CH=CH-$, $(CH=CH)_n$, $(C=C)$, $-CH=N-$, $-N=N-$, $-N=\underset{\overset{\downarrow}{O}}{N}-$, $-CH=CH-\underset{\overset{\parallel}{O}}{C}-O-$,

$-CH=\underset{\overset{\downarrow}{O}}{N}-$, $-\underset{\overset{\parallel}{O}}{C}-O-$, $(CH=CH)_n$, $-\underset{\overset{\parallel}{O}}{C}-(CH=CH)_n$ n=2, $-CH=N-N=CH-$, $-CH_2-CH_2-$,

$-O-CH_2-CH_2-O-$, $(C-O)_2$ .... etc.

Randeau and Collaborators (15) have compared the influence of various functional groups as middle linkages on mesophase thermal stability and have obtained the order as follows :



$$\text{-COO-} < \text{-C=C-} < \text{-CH=N-} < \text{-N=N-} < \text{-CH=}\underset{\overset{\downarrow}{\text{O}}}{\text{N}}\text{-} < \text{-N=}\underset{\overset{\downarrow}{\text{O}}}{\text{N}}\text{-} < \text{-CH=CH-}$$

The linkage between benzene nuclei through ortho - or - meta - positions is not favourable to the liquid crystal formation because the molecules then become non-linear. However, linearity and rigidity are increased by linking up the benzene nuclei directly and thus bi-phenyl system provides a rich source of liquid crystals, which are thermally more stable than the benzene substituted analogues. However, some alicyclic analogues of biphenyl or other aromatic system are reported to be mesomorphic (16). The replacement of aromatic ring by saturated alicyclic ring is found to affect the thermal stability of the system.

The step-wise thermal break-down in "Liquid Crystallines" may be expressed as follows :

$$\begin{array}{c}\text{Crystalline solid}\\\text{state}\end{array} \overset{t_1}{\rightleftharpoons} \begin{array}{c}\text{Liquid Crystalline}\\\text{or Mesomorphic state}\end{array} \overset{t_2}{\rightleftharpoons} \text{Isotropic Liquid State}$$

Transitions t_1 and t_2 take place at sharp definite temperatures and are precisely reversible. But reversal from mesomorphic state into crystalline state is usually accompanied by super cooling. This type of transition in which t_2 is higher than t_1 is referred to as an enantiotropic mesophase. However, in some cases a solid melts to an isotropic liquid at temperature

t_1, but on cooling, super cooling may occur and the temperature may fall considerably below t_1 and mesophase may appear at temperature t_2 before crystallization occurs. This type of mesomorphic state is known as monotropic mesophase. The Schemetic representation for monotropic mesophase is as under :

$$\begin{tikzcd}
\text{Crystalline Solid State} \arrow[rr, "t_1"] & & \text{Isotropic Liquid State} \arrow[dl, shift left] \\
& \text{Mesomorphic State} \arrow[ul] \arrow[ur, shift left, "t_2"'] &
\end{tikzcd}$$

The monotropic temperature t_2 is also reversible and if mesomorphic state is heated, isotropic liquid is obtained at t_2 itself.

2.1 Smectic, Nematic, Cholesteric, Discotic and Condis Liquid Crystals:

The current classification of liquid crystalline state dates back to the work of Friedel (7) in 1922. He carried out detailed optical studies of liquid crystals and conveniently divided them into three types - smectic, nematic and cholesteric. The transition temperatures are always definite and may be represented as :

$$\begin{tikzcd}
\begin{matrix}\text{Crystalline}\\ \text{Solid State}\end{matrix} \arrow[r, shift left, "t_1"] & \begin{matrix}\text{Smectic}\\ \text{mesophase}\end{matrix} \arrow[l, shift left] \arrow[r, shift left, "t_2"] & \begin{matrix}\text{Nematic}\\ \text{mesophase}\\ \text{or}\\ \text{Cholesteric}\\ \text{mesophase}\end{matrix} \arrow[l, shift left] \arrow[r, shift left, "t_3"] & \begin{matrix}\text{Isotropic}\\ \text{liquid state}\end{matrix} \arrow[l, shift left]
\end{tikzcd}$$

The schematic representation of phase transitions in a liquid crystals is given in Fig. 1.

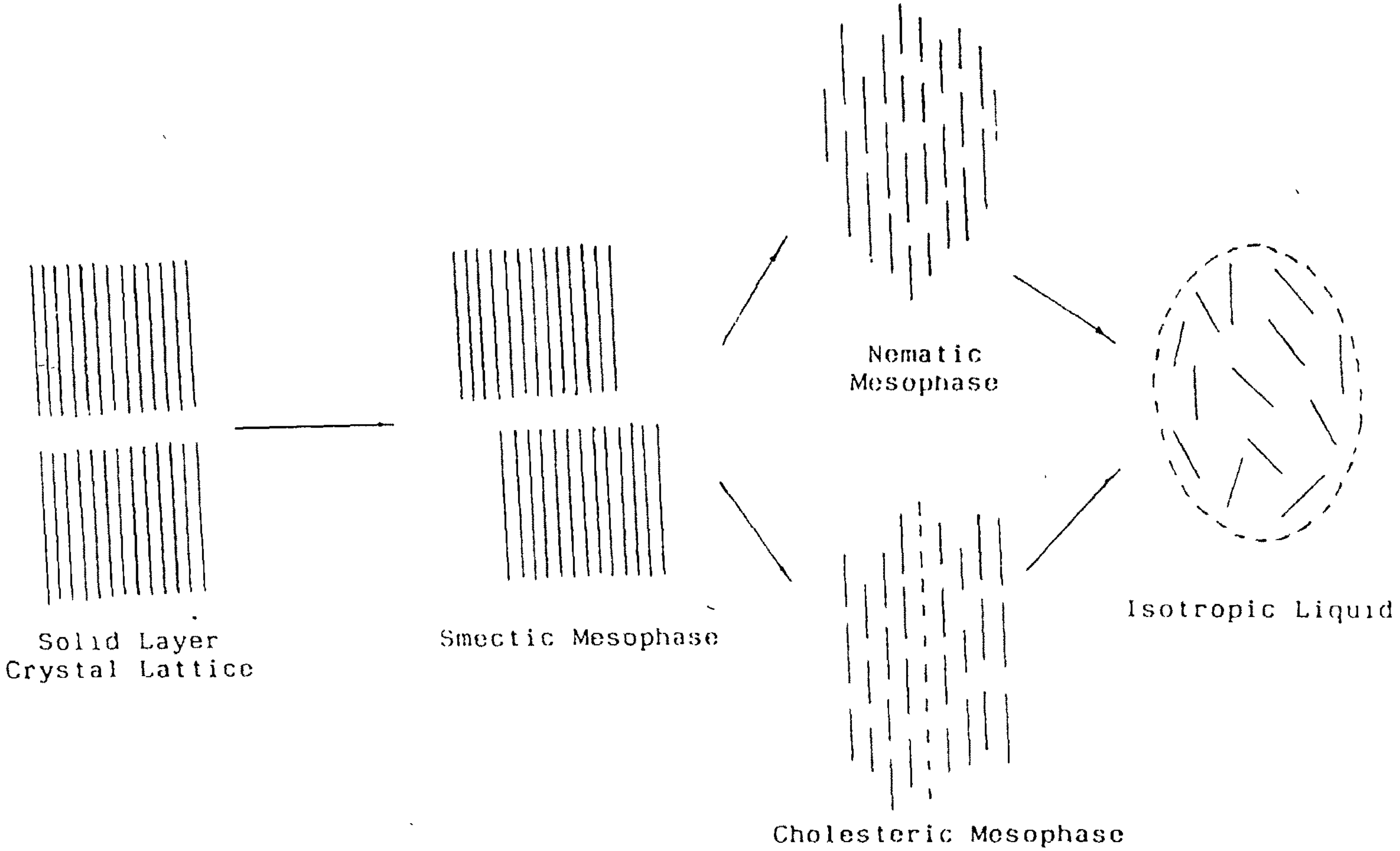


Fig. 1 - Schematic Representation of Phase Transitions

Hence, the transition from completely ordered solid crystal through the smectic and nematic structures to the true liquid may be outlined as follows :

(i) Three dimensional crystal : Apart from vibration the centres of gravity of all latice units are fixed, rotation are not possible.

(ii) Crystals with rotating molecules : The centres of gravity of all the lattice units are fixed, rotations about one or more axes is possible.

(iii) Smectic structure : The centre of gravity of the units are mobile in two directions, rotation about one axis is permitted. Today we recognize that there is a range of smectic structures A,B,C etc., depending upon detailed ordering (e.g. tilting) within the lamellas, which is referred to as polymorphism.

(iv) Nematic structure : The centres of gravity of the units are mobile in three directions, rotation about one axis is permitted.

(v) True or Isotropic liquid : The centres of gravity of the units are mobile in three directions, rotation about three axes perpendicular to one another is possible.

Later development in the field of liquid crystals has added one more new class of liquid crystals commonly known as 'discotic' (columnar) (17) or Cannonic (18) mesophase, exhibited by the disc-like molecules.

2.1.1. Smectic Liquid Crystals :

Smectic mesophase is the most highly ordered of the three phases.

The word 'Smectic' is derived from Greek word 'Smectos' meaning soap like. The molecules are arranged in definite layers in the smectic phase which can slide over one another because the molecules are free to move from side to side, or backward and forward, but not up and down. The best way to represent the molecular arrangement in two planes is as shown in Fig. 2. A film of smectic phase stretched over a small hole in a plate gives the condition of parallel sheets, which is optically extinct and is said to be homeotropic. The homeotropic structure is characterized by the formation of series of strata or terraces, called the Grandjean terraces after their discoverer Grandjean (19). The stratified structure of the smectic phase was inferred from the formation of stepped drops observed under microscope and has been confirmed by X-ray analysis (20). Saupe (21) divided smectic phases into unstructured layers and structured layered on the proposal of Hermann (22).

The extensive work of Sackmann and Demus (23) and de Vries (24) has revealed some of the details of the molecular arrangements of these phases. At least nine different modifications of the smectic mesophases have been identified or proposed (25, 26). Much work on the classification of smectics has been done by Sackmann and Demus (23) and Demus and Richter (27). They classified smectic mesophases according to the texture observed (27) as shown in Table -1.

Depending on the intralayer packing, all smectics can be divided into several classes : smectic - A (Liquid -like order), smectic - B (perfect hexagonal packing), smectic - E (perfect orthorhombic packing) (28-31).

TABLE - 1

Texture classification of Smectic Mesophases :

Type of Smectic Mesophase	Structure	Texture
Smectic A	Planar	i. Stepped drops
		ii. Oily streaks
		iii. Homeotropic.
	Non-Planar (DUPIN cyclides)	i. Simple polygonal texture.
		ii. Simple fan shapped texture.
		iii. Batonnets.
		iv. Bubble texture.
	Cylinders	i. Myelinic texture.
Smectic C	Planar	i. Homogeneous texture.
		ii. Stepped drops.
		iii. Schlieren texture.
	Non-Planar (DUPIN cyclides)	i. Broken polygonal texture.
		ii. Broken fan shaped texture.
		iii. Batonnets.
	Twisted	i. Planar texture.
		ii. Schlieren texture
		iii. Streated fan shapped texture.

Type of Smectic Mesophase	Structure	Texture
Smectic F	Planar	i. Schlieren texture. ii. Stepped drops.
	Non-Planar (DUPIN cyclides)	i. Stripped, broken fan shaped texture.
Smectic B	Hexagonal, Planar	i. Mosaic texture. ii. Homeotropic texture. iii. Stepped drops. iv. Batonnets. v. Ovals. vi. Lancets.
	Non-Planar (DUPIN Cyclides)	Focal conic texture (Paramorphosis).
	Tilted	i. Mosaic texture. ii. Planar texture. (Optically active).
Smectic E	Planar	i. Mosaic texture. ii. Stepped drops.
	Non-Planar	i. Straited ii. Stripped fan shaped texture.
Smectic C	Planar	i. Mosaic texture. ii. Stepped drops.
Smectic D	Cubic	Isotropic
	Bands	Mosaic texture.

Smectic–C is the 'tilted' modification of smectic – A, while smectic – F is the tilted modification of smectic – B. Smectic–D is thought to be packed hexagonally into spherical arrangement, which are then packed in a cubic order. Smectic – G has two different structures. One structure consists of a layer arrangement with a monoclinic unit cell – which is highly ordered state with low molecular mobility (32). The other structure has been found as the same as that of monoclinic smectic B. Smectic – H is tilted analogue of smectic E. Smectic – I exhibits hexagonal direction of tilt of its molecule uniform toward neighbouring molecule.

2.1.2 Interdigited smectics :

This new family with the structure of a highly ordered smectic like phase is recently reported by de Vries (33). The molecules are arranged in layers with their alkyl tails fully interdigited with the tails of molecules of adjacent layers. The currently known smectic phase are therefore suggested to be called as segragated smectics.

2.1.3 Nematic Liquid Crystals :

Nematics are structurally somewhat similar to conventional liquid Nematic is derived from Greek word 'nema' meaning threaded schlieren texture. The molecular arrangement is characterized only by a long range orientational order in longitudinal packing. The molecules exist in form of groups, each group containing about 100000 parallel molecules which are referred to as 'Swarms' proposed by E. Bose (34) in 1909. The optical

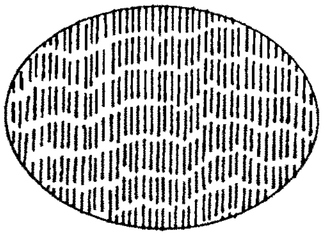


Fig.2

A schematic Representation of Molecular arrangement in

Two Plane smectic strata.

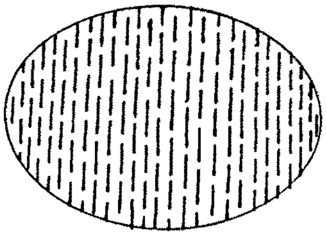


Fig.3

A schematic Representation of Molecular arrangement in nematic phase.

effects of the nematic threads have been studied by Zocher and Birstein (35). Frank (36) has named these lines as disclination. The schematic representation of the order in a Nematic phase is as shown in Fig. 3.

Zocher (37) proposed the distortion hypothesis which is referred to as the continuum theory of liquid crystals. Luckhurst (38) applied both the swarm theory and distortion theories of the nematic mesophase to the study of magnetic resonance experiments and has shown that they lead to isomathematical conclusions.

In contrast to the smectic phase, generally there is considered to be only one nematic phase. de Vries (39) has proposed three types of nematic phases based on X-ray diffraction pattern, and the microscopic studies. These three nematic phases are : (i) skewed cybotactic nematic (ii) normal cybotactic nematic and (iii) the classical nematic phase, as observed in bis-(4'-n-octyloxy-benzal)-2-chloro-1,4-phenylene diamine.

Nematic liquid crystals are optically positive. The nematics can be formed by compounds that are optically inactive or by racemic modification.

Maier and Saupe (40) gave a simple molecular theory of the nematic liquid crystals. They mentioned that nematic isotropic transition temperatures can be determined by calculation of free enthalpies of the phases involved at the transitions.

2.1.4 Cholesteric Liquid Crystal :

The cholesteric phase is the twisted nematic phase as this possess the structure of the nematic liquid crystals twisted about an axis perpendicular to the molecular layers, which results in a helical structure as shown in Fig. 4. This phase is often found in compounds related to cholesterol or sterol type of skeleton. Substances which posses the general requirement of typical nematic structure but are chiral also exhibit cholesteric phase (41-44). The addition of optically active material to nematic liquid crystals also show cholesteric behaviour (45).

The cholesterics although colourless themselves are able to scatter light selectively into different colours. The colour of the reflected light is determined by (a) pitch of the helix (b) the temperature and (c) the angle of the incident beam. Physical effects which wind or unwind the helix, such as temperature mechanical disturbances like pressure or shear and traces of organic vapour result in various colour changes.

Cholesteric phases exhibit typical planar textures with oily streaks, moire fringes and/or Grandjean lines. Some cholesterics yield non planar textures and appear in fan shaped, focal conic or polygonal textures resembling those of smectics. The optically active smectic liquid crystal was reported by Helfrich and Oh (46).

Cholesteric liquid crystals generally have following three textures : (a) Focal-Conic texture - when anisotropic liquid is cooled. (b) Plannar

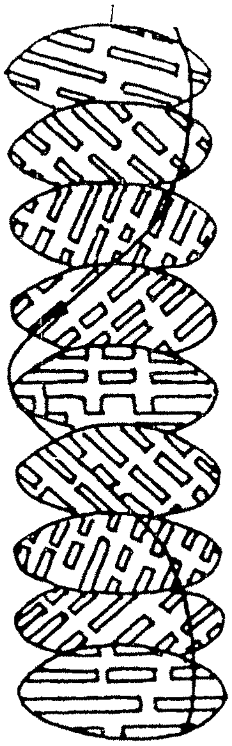


Fig. 4

Probable Organization of Cholesteric Phase.

or plane texture - when sample is uniformly aligned with the twist axis perpendicular to the plane of the film. (c) Blue phase - when cholesteric mesogens are cooled from isotropic liquid, exhibit a phase which is visible to the eyes in reflected light, but not visible microscopically in transmitted light using crossed polaroids. This phase is known as blue phase, which on further cooling changes to a birefringent texture. Researchers (47-55) in this field are trying to establish the molecular structure of the blue phase.

No compound exhibiting both nematic and cholesteric mesophase is known. Only smectic -cholesteric transitions are reported.

2.1.5 Discogens

Number of discogens are now known and seven different columnar phases are clearly identified (56). Disc-like molecules consisting of rigid flat cores such as triphenylene or benzene and of aliphatic side chains have a tendency to display discotic liquid crystalline phases (57,58). The thermodynamical as well as structural properties of such phases have been studied for low molecular weight compounds during the last few years (59-62).

Chandrasekar et al. were first to report discotic phase in the disc-like systems (17). Billard and Destrade (63,64) have reviewed the nature and properties of such phases. Hermann and co-workers (65), have

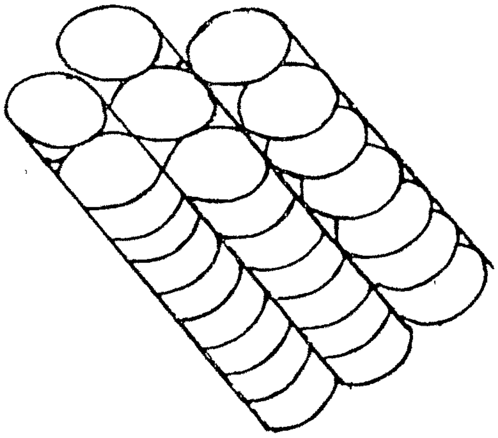


Fig. 5

Schematic Representation of Tilted Columnar Structure.

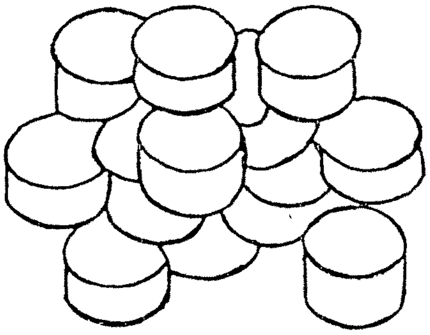


Fig. 6

Schematic Representation of Nematic Phase of Disc-like Molecules.

Schematic Representation of
Nematic Phase of Disc-like Molecules.

smectic phase in a binary mixture at normal pressure. Now it is known that certain cyano compounds with aklyl or alkoxy end groups exhibiting the bilayer smectic A phase also exhibit such re-entrant nematic phase (70,71).

The explanation given is that the anti-parallel association responsible for the bilayer smectic A phase also provide mechanism which accounts for the reappearances of the nematic phase at some lower temperature. This phenomenon was also observed in case of mixtures (72) at atmospheric pressure, at high pressure (73) and at atmospheric pressure in pure compounds (70,71). Number of workers have studied the different aspects of the so called 'Re-entrant' nematic mesophases (74-82).

In general, re-entrant phenomenon is observed in compounds having (i) -CN,NO_2 or -Br polar end group, (ii) at least three phenyl rings in the core and (iii) an electronic distribution such that the maximum electron density is located on the terminal cyano group.

Recently, a new mesomorphic sequence with re-entrant smectic phase is also observed (83). Now this re-entrant behaviour is reported in nematic, smectic, cholesteric, discotic and isotropic phases. Re-entrant isotropic phase is reported (76,84) and re-entrant cholesteric mesophases in polar mesogens are also reported (85,86).

A unique phenomenon of quadruple re-entran of mesophase has been also reported recently (87). The microscopic spin-gas model of a mesogen reproduced mesophases four times.

4. LYOTROPIC LIQUID CRYSTALS

Lyotropic liquid crystals are commonly obtained by action of a solvent on a solid. Ammonium oleate was the first amphiphilic compound reported by Lehmann (88). Mc Bain (89) has discussed the form of mesomorphism in soap solutions. Ostwald (90) has discussed the relationship between these liquid crystalline states and truly colloidal states. Robinson (91) has reported lyotropic cholesteric phase and has discussed similarity between lyotropic cholesteric phase and thermotropic cholesteric phase. The consitutional analogies between amphiphilic, non-amphiphilic and plastic crystals have been discussed in detail by Gray and Winsor (92). Tobacco mosaic virus exhibits this type of mesomorphism (93).

Small et al. (94) have studied lyotropic mesomorphism of ternary and quaternary systems of Lecithin, Cholesterol and Water. Lawson and Flautt (95) have studied NMR spectroscopy of smectic and waxy mesophases in various surfactant system such as sodium palmitate-water system .

5. MESOMORPHISM IN BIOLOGICAL SYSTEMS

Liquid crystals play an important role in nature* Brown and Shaw (9) have pointed out that the mesomorphic modification are of important biological significance. As Bowden (97) has put it, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity. Birefringence in case of muscle was noted by Muralt and

* (96)

Edsall in 1930 (98). The brilliant work of Engstrom and Finean (99), on the structure of nervous tissues shows the presence of two components in optical opposition and in the concentric multi layers of lipid or lipoprotein forming the myelin sheath. From a study of structure of Heamoglobin, Perutz et al. (100) concluded that it could assume liquid crystalline form in red cell. Stewart (101) and Ambrose (102) studied the mesomorphism in biological systems in details and gave reasons and factors controlling mesomorphic states and biological interaction.

Recently Livolant (103) has observed cholesteric phase of DNA in vitro and in vivo.

6. PHYSICAL PROPERTIES OF LIQUID CRYSTALS

Various modern techniques are being used to ascertain the molecular structure and to determine properties of liquid crystals. These techniques are X-rays (104-106), Nuclear magnetic resonance (107), Surface tension (108), Spectroscopy (109-111), Elasticity and viscosity (112), Dielectric constants (113,114), Mössbauer effect (115), Chromatography (116,117), Ultrasonics (118,119), Magnetic succeptibility (120) and Calorimetry (121-125).

Number of books and review papers have discussed the physical properties of liquid crystals and their importance in the different technological applications (126-136). Billard et al. (137) have shown in mössbauer spectroscopy. X-ray studies are useful in understanding different textures and structures of mesophases, while gas chromatography and specific volume studies enable one to achieve purification of chemical substances and to evaluate order of parameters of liquid crystals. Different factors like stability, temperature range, dielectric and refractive index anisotropies (i.e. difference between components, parallel and perpendicular to the director), elastic constants and viscosities of liquid crystal material are all factors which determine its choice for use in various technological applications.

7. APPLICATION OF LIQUID CRYSTALS

Only in the last two decades, intensive studies on liquid crystals has been done to make technological use of the unique properties of liquid crystals. Cholesterics have proven useful as temperature indicators, especially in medicine and the non-destructive testing of materials. In addition they can be used with an absorber for the recording of wave field, e.g. microwaves, IR, UV and ultrasonic waves. Nematics are more important for imaging systems although image storage is better realized with cholesterics. The various technical applications have been discussed in series of review articles (138-150) and some books (151,152).

The application of liquid crystal compounds are over a wide range like in optical memory, light filters, optoelectronic gates, polarizer, temperature stress, pressure and chemical composition indicators, TV receivers, displays and light panels (cholesteric and smectic materials)

Liquid Crystal Displays (LCD) have very low power consumption, ability to withstand high levels of light (Liquid crystal scatter light rather than generate their own light) and low cost. Most of the commerically available LCD's use an electric field effect in a twisted nematic liquid crystal whose dielectric constant parallel to the direction is greater than that perpendicular to it (positive dielectric anisotropy).

7.1 Thermographic Applications

Cholesteric liquid crystals are thermally very sensitive and are widely used for detection of vascular diseases and subcutaneous tumors (153-158) and alergies to chemical substances introduced in the blood stream (159). Liquid crystal thermography assisted in the difficult diagnosis of various intra-abdominal abscessesl and some other diseases (160-163).

Liquid crystals are also used in non-destructive testing as to detect cracks in metallic surfaces and coating (164), to locate stress areas and potential fracture sites in metal (165), in testing insulation in refrigeration and cooling units.

Now liquid crystals are also used for coating decorative fabric. The colour of this fabric changed from yellow to various shades of green at temperatures ranging from 6° to 38° C (166).

7.2 Display devices

Gray (167) has reviewed the current state of art of dyes used with liquid crystals for electro-optical display devices.

Cholesteric liquid crystals encapsulated or incorporated in a thin sheet are used to make common devices like liquid crystal thermometer (168) temperature limit indicator (169), voltage and current meters (170,171), flat screen televisions, storage displays (172) and other display devices (173-175).

7.3. Active Matrix Adressed LCDS

Active substrates such as arrays of amorphous thin-film silicon transistors (TFTS) are used to provide a sharp threshold allowing higher information content than multiplexed twisted nematic LCDS. Such TFTS are used with twisted nematic displays of the pocket colour TV made by Sanyo and Seiko.

7.4. Guest Host Displays

A pleochroic dye is added to a nematic host and the dye molecule gets oriented parallel to the host molecules. Since the colour of the dye depends on the orientation of the dye molecule, an electric field causing reorientation in the nematic host will cause a colour change. Guest-host displays find their use in military air crafts.

Liquid crystal windows were also prepared to control the solar energy by fabricating it with phase change guest-host mixtures (176). Liquid crystal glass cover is used to control the transmitance on the light incident side of the solar cell. Solar cells having this cover maintain constant output voltage under varying load situation (177).

7.5. Chromatographic Separation by LC :

Work in gas chromatography using liquid crystals as stationary phases began in 1960. Because of rod-like shape and ordered arrangements of their molecules, liquid crystals exhibit interesting and useful solvent properties. These act selectively as separation solvents due to molecular shape. The more rod-like a molecule is, the easier it will fit into the liquid crystal 'Lattice' and hence greater its solubility (and the longer its GLC retention time). Detailed application of chromatographic separation is discussed in the second part of the thesis.

LIQUID CRYSTALLINE POLYMERS

1. GENERAL

Because of the direct industrial application possible in ever increasing polymers and plastic technology, scientists are in continuous search of liquid crystallinity to be obtained in the synthetic polymers (178). Recently (179) it is emphasized that how the companies are profiting from polymer research and the unused potential of thermoplastic. Liquid crystal polymer (LCP) is being recognised, which laid dormat till late 1960's. Liquid crystalline order in polymers is of great interest and one of the fascinating area of current research, especially by the development of Kevlar fibers, which has stimulated research due to its additional high modulus and high strength.

In 1950 Oster (180) studied polymers with liquid crystalline order in aqueous solution of tobacco mosaic virus and in 1956 Robinson (180 a) reported polymer liquid crystalline solutions of poly-(r-benzyl-L-glutamate) in various solvents. Recently number of synthetic polymers exhibiting liquid crystalline behaviour have been reported (181-185).

The liquid crystalline order has been found to occur in many proteins and synthetic polymer (186). Number of patents and reports claiming the production of fibers from polymer solutions existing in liquid crystalline state are now known (187-189) which are greater in magnitude than those reported for steel.

Recent books on "Liquid Crystalline Order in Polymers" edited by Blumstein (190), "Polymer Liquid Crystals", eidted by A. Ciferri et al. (191) and "Recent Advances in Liquid Crystalline Polymers", edited by L.L. Chapoy (192) provide detail account of mesomorphic polymers.

Vinyl oleate has been polymerized by different workers in Liquid Crystalline and isotropic phases (193,194). Studies on kinetics of polymerisation of cholesteryl acrylate (195-197) and binary phase diagrams of thermotropic mesomorphic polymers with low molecular weight mesogens (198-200) have been reported.

Co-polymer obtained by condensing terepthalic acid, ethylene glycol and p-hydroxy benzoic acid (p-HBA) exhibits thermotropic mesomorphism and have improved mechanical and physical properties (201,202). Other polymers where p-HBA is substituted by other hydroxy aromatic acids (203) were synthesized. Homopolymerisation of p-HBA gives thermally stable polymers (204-206) which are highly heat resistant.

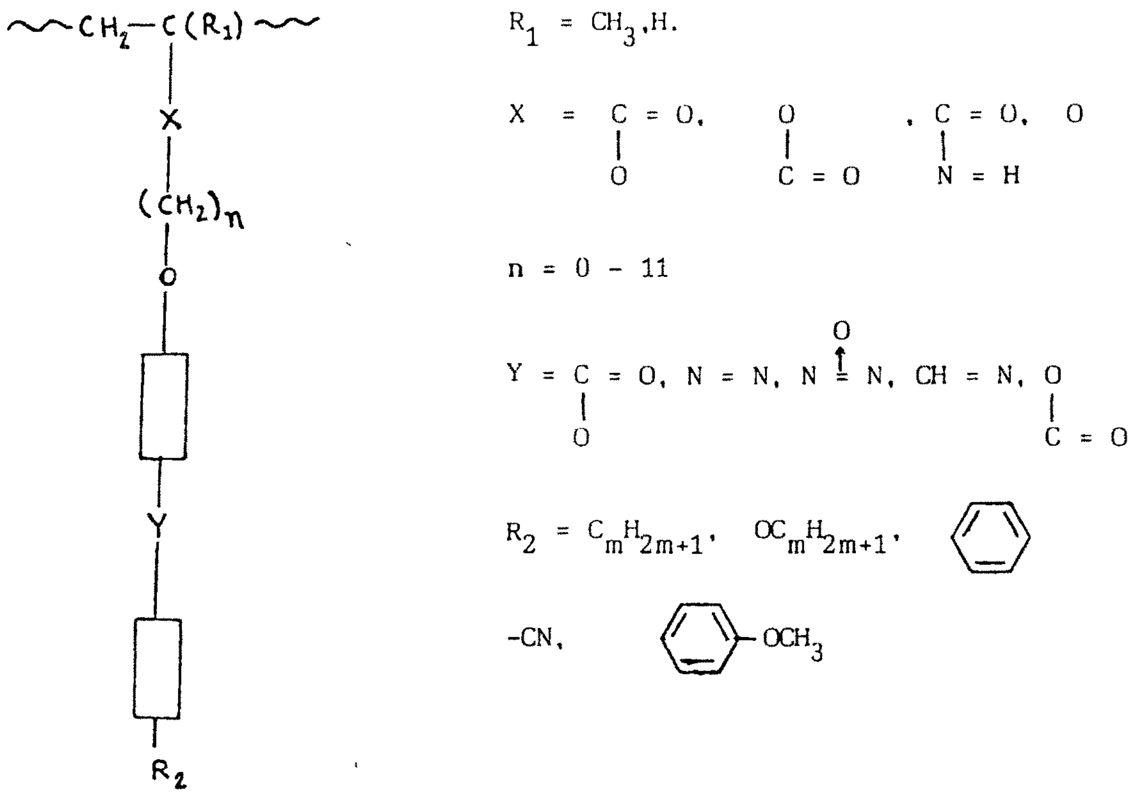
2. CHEMISTRY OF LIQUID CRYSTALLINE POLYMERS: (LCPS)

In the first publication on synthesis of mesogenic polymers, it was believed that an ordered monomer was the necessary condition for the formation of mesomorphic structure in polymers (193). Recently number of condensation polymers exhibiting thermotropic mesomorphism have been synthesized (207-211). In many cases the repeating unit consists of an extended segment and a more flexible segment, following the suggestion of de Gennes (212), Krigbaum et al (213-215) have reported mesogenic homopolyesters incorporating different rigid units. Roviello and Sirigu (209) and Blumstein et al. (216) used different rigid units with flexible segments. Griffin and Havens (217) prepared polymers having quite long repeating units. The rod like structure causes anisotropic packing of macromolecules as predicted theoretically by Flory et al. (218).

2.1 Monomers

Monomers bearing "Liquid crystalline groups" (mesogenic moiety) with subsequent polymerization or addition of molecules of a low molecular mesogenic compound yield mesomorphism in polymers. The most frequently used monomers for the synthesis of mesomorphic polymers are listed in Figs. 7 and 8. Polymerization of non-mesogenic monomer within liquid crystalline solvent have been reported by AmeriK and et al. (219), Tanaka et al. (220) and Blumstein et al. (221).

The polymerization of liquid crystalline monomers have also been obtained (222) and the structure as well as the thermotropic liquid crystalline behaviour of the resulting polymers were studied by Perplies et al. (223) and Wendorff et al. (224). The polymers obtained were thermotropic in nature. Polymerization of non-mesogenic monomers having conducive side chain may result in a polymer with thermotropic liquid crystalline properties (225-227).



$R_1 = CH_3, H.$

$X = \underset{\overset{|}{O}}{C = O}, \quad \underset{C = O}{\overset{O}{|}}, \quad \underset{\overset{|}{N = H}}{C = O}, \quad O$

$n = 0 - 11$

$Y = \underset{\overset{|}{O}}{C = O}, \; N = N, \; N \overset{\overset{O}{\uparrow}}{=} N, \; CH = N, \; \underset{C = O}{\overset{O}{|}}$

$R_2 = C_mH_{2m+1}, \; OC_mH_{2m+1},$

$-CN, \; -OCH_3$

Fig. 7

General Structure of Monomeric Units in Polymers with Mesogenic Side Groups.

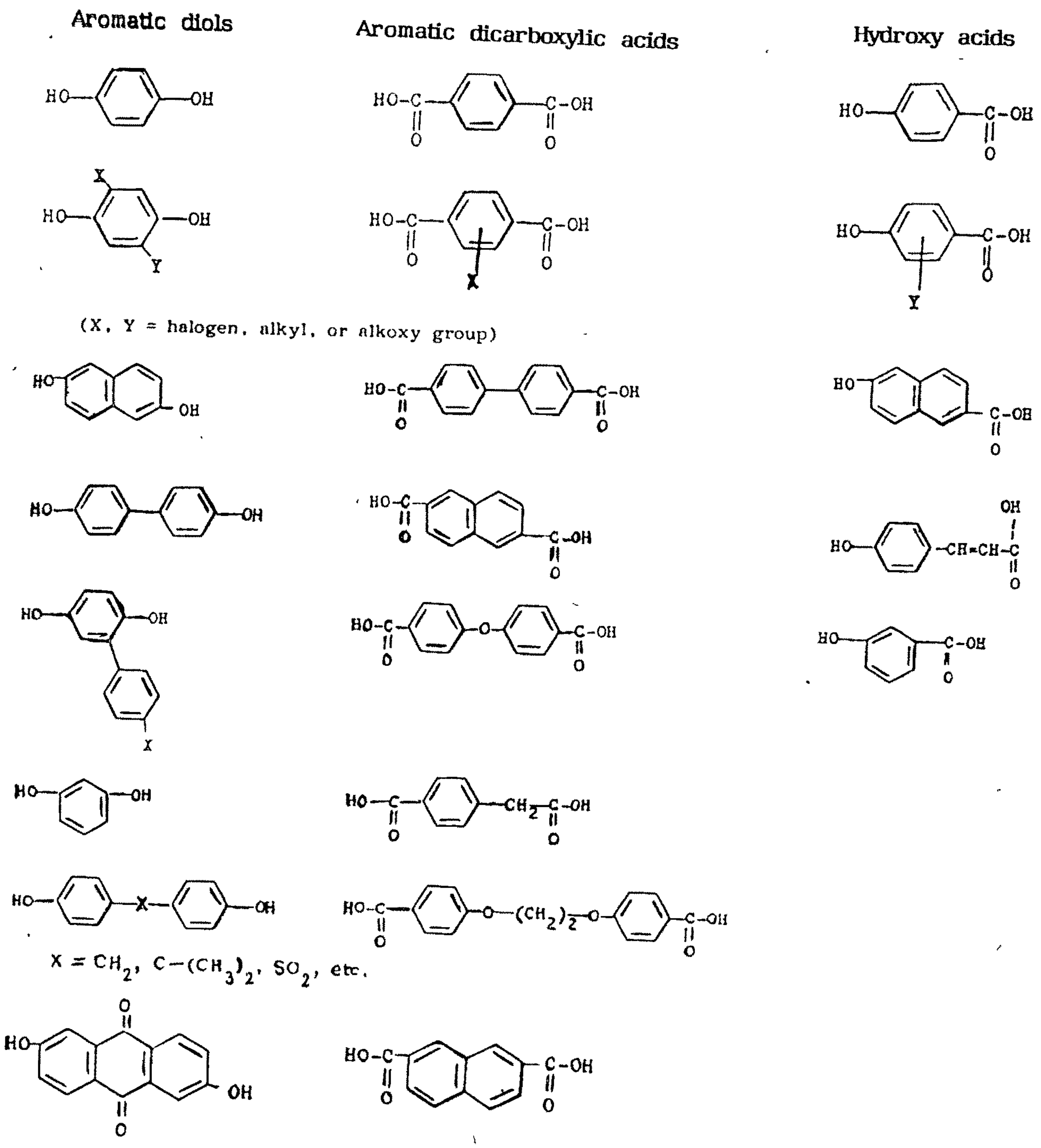


Fig. : 8

Monomers Used in the Synthesis of Liquid Crystal Aromatic Polyesters

For the first time Vora and Patel (228) have reported mesogenic polymers incorporating a monomer having symmetrically substituted triazine heterocyclic moiety and evaluated the effect of chemical structure on mesomorphism.

3. MESOMORPHIC STRUCTURE AND POSSIBLE WAYS TO OBTAIN LIQUID CRYSTALLINE POLYMER

The phase behaviour and characteristic molecular structure of liquid crystalline polymers is given by Finkelmann (229). He stated that if solid polymers with ordered structures are excluded and only homogeneous phases are considered that are in liquid crystalline state. Mesogenic polymers can be sub-divided into the scheme given in Fig. 9. Thus monomer unit can be either amphiphilic or non-amphiphilic. Subsequently one can distinguish whether the mesogenic moiety forms a part of the polymer main chain or is attached to the side chain. A system can be lyotropic or thermotropic, depending upon whether mesophase is observed by variation of solvent or by temperature changes. Some papers are summerized by Kelker (230), Elias (231) and Finkelmann (232). On polymers having lyotropic repeating units, Soil (233) has investigated polymerization of amphiphilic monomers.

Non-amphiphilic monomer units are characterized by their rod-like molecular structure. Anisotropy of polymer is dependent on the nature of incorporation of the mesogenic groups may be directly incorporated into the main chain Fig. 10 a; or may be linked to the main polymer chain as side groups forming a 'Comblike' structure Fig. 10 b. Recently, Kreuder

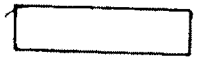
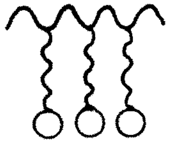
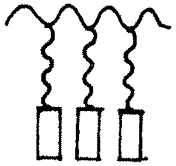
Monomer Unit	 Amphiphilic		 Non-amphiphilic	
Polymer	 Side-chain	 Main-chain	 Side-chain	 Main -Chain
Phase Behaviour	Lyotropic		Thermotropic	Thermotropic, Lyotropic

Fig. 9
Classification of Mesogenic Polymers

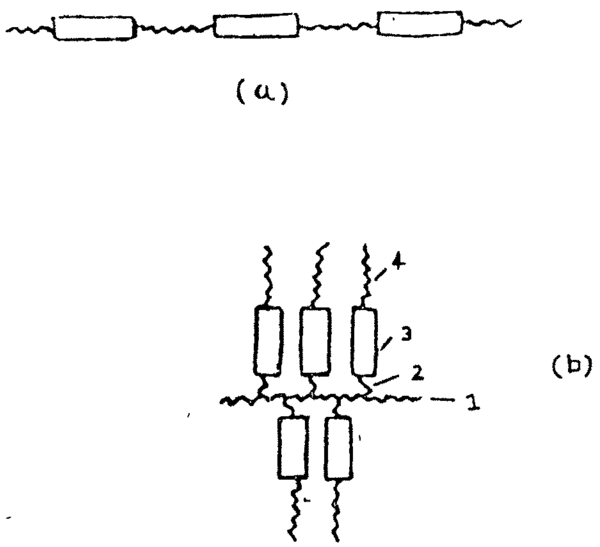


Fig. : 10

Scheme of the macromolecular structure of LC polymers.

(a) Mesogenic groups in the main chain.

(b) Mesogenic side groups.

(1) Main chain

(2) flexible spacer groups

(3) rigid moiety of the mesogenic groups.

(4) flexible tails.

and Ringsdorff (234) classified these 'comblike' polymers into two different classes, depending on the nature of the side mesogenic moieties attached to the main chain polymers.

(a) When mesogenic groups are linear rigid chains Fig. 11 a.

(b) The mesogenic moieties are disc-like called "discotic" liquid crystalline polymers Fig. 11 b.

The molecular features responsible for mesomorphic thermotropic polymers are :

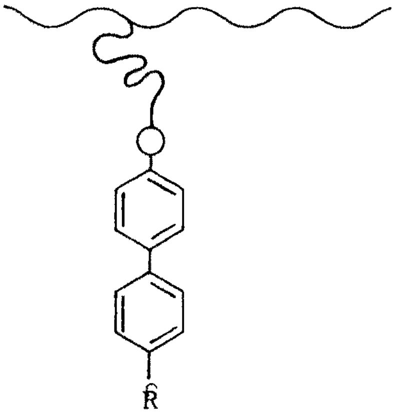
(1) Introduction of the mesogenic groups into a polymer backbone leads to main chain liquid crystalline polymers (190, 234-236).

(2) Attaching mesogenic groups directly to a polymer backbone or though some flexible aliphatic chains leads to side chain LCPS (237-240).

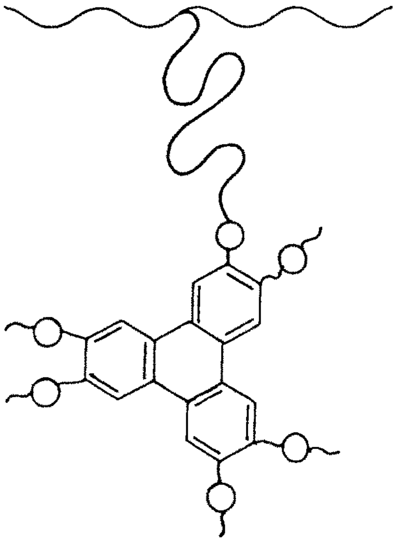
(3) By blending of low molecular weight optically active molecules into the polymer.

4. THERMOTROPIC POLYMERS BASED ON MESOGENIC GROUPS ATTACHED TO THE POLYMER BACKBONE AS PENDENT

These types of polymers can be prepared by three different routes as specified in Fig. 12. Thus, mesogenic polymers can be obtained by using suitable reactive mesogenic monomers (241-247).



(a) ROD LIKE MESOGENS



(b) DISC LIKE MESOGENS

Fig.11

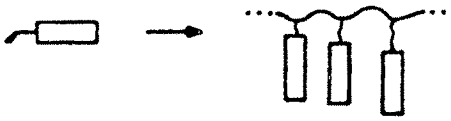
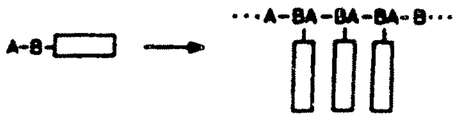
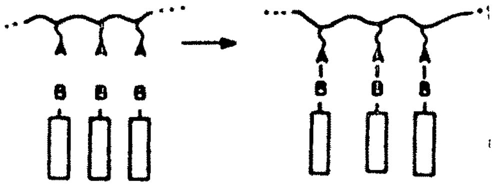
PRINCIPLES		EXAMPLES
ADDITION POLYMERIZATION		POLYACRYLATES POLYMETHACRYLATES POLYSTYRENE DERIVATIVES
CONDENSATION POLYMERIZATION		
MODIFICATION OF POLYMERS		POLYSILOXANES.

Fig. : 12

Scheme for Liquid Crystalline polymers based on mesogenic moieties attached to polymer backbone as pendent.

5. THERMOTROPIC POLYMERS BASED ON MESOGENIC GROUP IN THE MAIN CHAIN OF THE POLYMER BACKBONE

For the synthesis of macromolecules which are expected to be liquid crystalline, a simple concept can be followed by using suitable mesogenic monomers which are able to build up a liquid crystalline phase. If the mesogenic group of these molecules is substituted with appropriate functional group A & B, macromolecules can be synthesized as shown in Fig. 13.

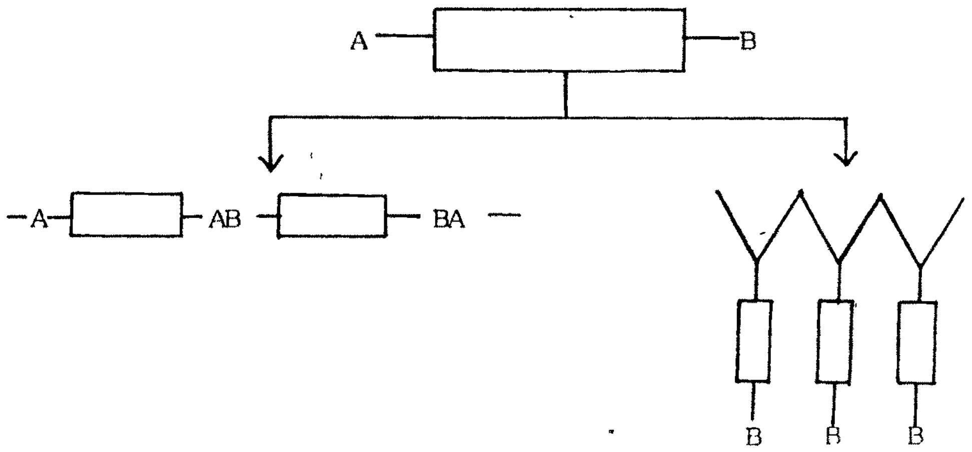


Fig. 13

Polymerisation of mesogenic monomers
(Symbol ▭ indicates mesogenic core)

(1) If A & B are able to perform a condensation reaction, the mesogenic groups built up the polymer main chain forming "Liquid Crystalline Main Chain Polymers".

(2) If A is capable of performing an addition polymerization reaction, the polymer chain build up by A and the mesogenic groups are fixed like side chains to the polymer main chain forming "Liquid Crystalline Side Chain Polymers".

From the reports by Blumstein et al., (248) and Lenz et al., (249) the following factors affecting the type and stability of mesophase of thermotropic, rigid-flexible main chain polymers can be drawn :

(1) The chemical structure and stereo geometry of the macromolecular chain.

(2) The length of the rigid (mesogenic) and flexible segments as well as the type of the groups linking these units together.

(3) The molecular weight and the molecular weight distribution of the polymer.

Lenz et al. (250-253), extensively studied different types of polyesters with terephthaloyl, oxybenzoyl and a flexible spacer ($-CH_2-$) units incorporated

5.1 Different Main Chain Mesogenic Polymers

These can be divided into three sub-groups.

(1) Rigid homopolyesters,

(2) Semi-rigid homopolyesters,

(3) Co-polymers.

5.1.1 Rigid Homopolyesters

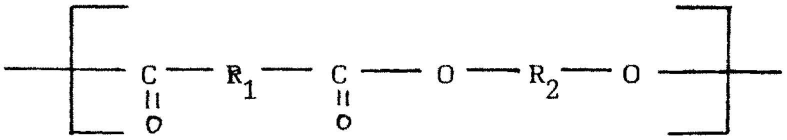
Dupont patents (254) describe rigid homopolyesters in which unsymmetrical monomers have been used to reduce the melting temperatures.

The melting point of poly (p-hydroxy benzoic acid) has been lowered while maintaining the widest possible mesophase above the melting point (255).

5.1.2 Semi-rigid Homopolyesters

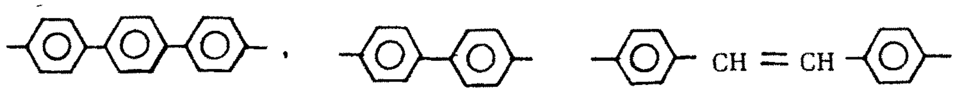
The transition temperatures of these can be controlled by varying the number of methylene units in the flexible segments (217, 256).

In 1980, Jin et al. (257) and Meurisse et al (258) presented a series of mesomorphic polyesters containing flexible spacers having following structure :



$$-\!\!\left[\, \underset{\underset{O}{\|}}{C} - R_1 - \underset{\underset{O}{\|}}{C} - O - R_2 - O \,\right]\!\!-$$

R_1 =



$$R_2 = -CH_2-CH_2-\left[O-CH_2-CH_2-O\right]-CH_2-CH_2-$$

Jin et al. (259) and other scientists found that the thermal properties and capability of mesophase formation depends not only on the structure of central group of mesogenic units, but also on the order of ester linkages.

Krigbaum et al. (210) have reported some homopolyesters of p-p'-bibenzoic acid with aliphatic diols. They also investigated homopolyesters containing an α- methyl stilbene unit (260).

5.1.3 Co-polymers

Co-polymers amides were also prepared using p-acetamido benzoic acid in place of p-acetoxy benzoic acid (261). Wolksen et al (262) described co-polymers containing blocks of biphenyl terephthalate and p-oxybenzoate. An ICI patent (263) shows anistropic melts of co-polymers of p-hydroxy benzoic acid having 50% o-oxybenzoate residues.

The effect of solvent and temperature on mesomorphic characteristics of polymer of p-hydroxy benzoic acid have been studied by Vora et al. (264).

6. LIQUID CRYSTALLINE ORDERING IN POLYMERIC MESOPHASES

On basis of molecular layers arrangements, three main types of liquid crystalline materials (mesophases) can be distinguished : (i) Smectic, (ii) Nematic, (iii) Cholesterics.

The majority of the polymers obtained are characterized by layered structure (265-267), but compared with low molecular weight liquid crystals, smectic polymers are mainly presented by modification with a liquid like intra-layer order, i.e. Smectic A, or C (266-268). Roviello and Sirugu have observed a Schlieren smectic texture indicative of S_B or S_C phase (269). Smectic C phases have also been reported to form 'broken' focal conic textures (270-271). The smectic textures are often obscure and observable only with difficulty because of the high viscosities of the smectic melts (272).

The nematic liquid crystalline state is one of relatively low order in which the molecules or the repeating units of polymers are arranged in a parallel but not lateral order. Polymers of low molecular weight may exhibit Schlieren texture. Upon cooling an isotropic melt, the nematic phase begins to separate at clearing point in form of typical droplets which after further cooling, grow and coalesce to form large domains (273). Quenching the polymer from the nematic phase to room temperature succeeds in 'freezing in" the nematic like textures (274-277).

Number of workers have studied the different aspects of the "Re-entrant" nematic mesophases. The first example of a nematic re-entrance in a mixture of a side chain liquid crystalline polymer with a low molecular weight nematogen, is described by Sigaud et al. (278).

The cholesteric mesophase was realized in polymeric liquid crystals through directed "designing" of the macromolecules containing cholesteric side groups and side groups with asymmetric centres (245, 279, 280). Cholesteric polymers have been described in which mesogenic side chain contains an asymmetric carbon atom (281). Furthermore, a co-polymer containing monomer capable of forming a nematogenic homopolymer and a second optically active monomer is expected to exhibit a cholesteric phase. Cholesteric phases can also be achieved using the well known concept of "Induced cholesteric phase" (282).

Recently discotic polymers have been synthesized containing plate-like chemical groups. These groups are either attached as side groups to a flexible polymer chain or incorporated into the backbone of the chain separated by flexible spacer groups (283-285). It is not known today in which way the incorporation of these groups into a polymer backbone changes the structural and thermodynamical properties of the discotic phases. The light scatter data of the polyester containing tri-phenylene as a core unit along the backbone has shown that the polymer displays a discotic hexagonal phase (Dho). The structural arrangement of Dho phase of polymer is schematically represented in Fig. 14.

7. IDENTIFICATION OF THE TYPES OF MESOPHASE FOR THE THERMOTROPIC POLYMERS

7.1 Optical microscopy

The polymeric system of low molecular weight generally exhibit a homogeneous birefringent field interrupted by threads that represented defect structures. Polymeric cholesteric phases have been identified by the pattern "Oily streaks" in planar textures (199, 258, 280, 286) and by fan-like textures (210, 258, 272,, 280 , 287) in non-planar texture. Batonnets (210, 258,, 272) are characteristic of smectic A and C phases. The Batonents may eventually coalesce to form either a focal conic (272, 280) or a fan shaped texture (272, 287).

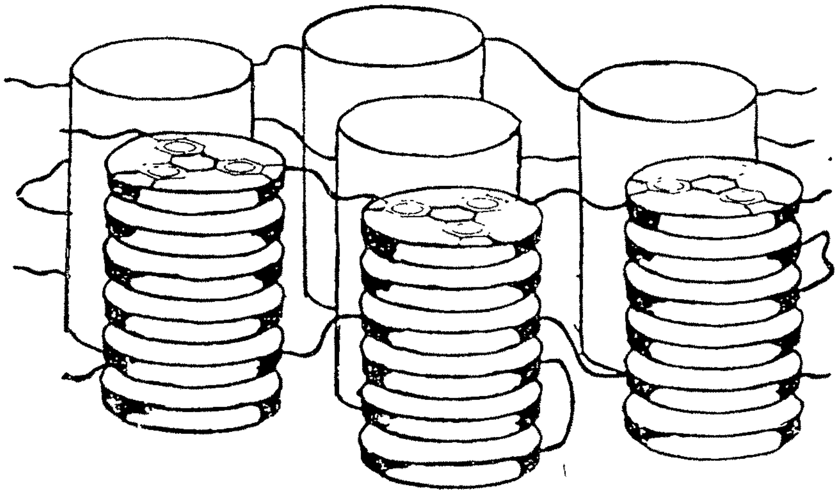


Fig. 14

A schematic Representation of the

D_{ho} Phase of Polymer

(D_{ho} = Discotic hexagonal ordered phase)

7.2 Mutual Miscibility with known Mesogens

In view of the lower solubility of polymer, however, in applying mutual miscibility for the recognition of polymeric mesophases, problems are anticipated. Nevertheless, it has been used successfully to identify a polymeric nematic phase in several instances (272, 288, 289). Ringsdorff, Schmidt and Schneller (290) and Cas-grande, Veyessie and Finkelmann (291) reported that the nematic phases of some polymers bearing mesogenic side chains are immiscible with a low molecular weight nematic phase. This indicates that polymeric nematic phases have a microphase structure with clusters of nematogenic side chains embedded in a continuous phase formed by the polymer backbone.

Mutual miscibility has also been applied to identify the two smectic phases of low order, S_A & S_C. Fayolle, Noel and Billard (199) have identified the smectic - C phase of the polyester by constructing the binary system. Jin et al. (292) have published the experimental study on the miscibility of semiflexible liquid crystalline polymers following phase diagrams covering whole range of composition of mixtures. The use of "Contact method" allows great rapidity in the assessment of the phase diagram (293). George, Porter & Griffin (294) have also studied the phase behaviour of liquid crystalline polymers combined with low molecular weight mesogens.

7.3 X-ray Diffraction

X-ray diffraction is the only route to the identification of the more highly ordered polymeric smectic phases. The x-ray pattern may provide information concerning the lateral packing of molecules and degree of order. Krigbaum and Watanabe (272) were able to classify the smectic phase of poly (4,4'-hexamethylene bibenzoate) as a normal phase by diffraction studies performed for an oriented sample.

X-ray diffraction patterns for liquid crystalline polymers reported were analysed according to de Vries classification (295) based on small molecules i.e. the smectic phase should exhibit a very sharp small angle diffraction pattern from which the sequential length of the mesogenic moiety could be deduced and another at a wider angle which gave information on the average interchain distance. In contrast, the nematic phase is expected to show only a weak, diffused inner ring and strong diffusion at longer angles.

8. APPLICATION OF POLYMERIC LIQUID CRYSTALS

8.1 Ultra high modulus and ultra high strength fibres (235, 296)

Closely packed ensemble parallel extended polymer chains should exhibit the highest achievable specific strength, which are the basis for the technology of ultra high strength organic polymeric fibres. Actually, fibrous structures of significant dimensions that approach their theoretical maximum strength have not yet been prepared inspite of unique characteristic of uniaxially oriented polymers.

It was the discovery of very strong polyaramide fibres produced from anistropic solution, and the realization of the importance of the liquid crystalline state in the preparation of highly ordered extended chain fibres that provide an unprecedented impetus to the research in ultrahigh strength fibres. The stress-strain curves for the ultrahigh strength/high modulus fibres show a strong similarity to those for glass and steel on a specific basis (due to lower specific gravity of the fibres as of rod-like aromatic polymers in comparison to glass and steel).

These fibres are stronger and stiffer than glass and steel and is useful in the reinforcement of rigid and flexible composition. Thus kevlar fibre has been shown to be useful as a tire cord, as replacement of glass and steel belts in bias belted and radial belted tires. Kevlar-49 (297) is competitive with the lower modulus types of graphite fibres and rigid composites. Other specific use applications include conveyor belts, v-belts, ropes and cables, body armor, interior trim, exterior fairings, control surfaces and structural parts in air crafts.

The use of para-oriented fibres for applications where flame resistance and dimensional stability are required include industrial protective clothing, e.g. shirts, coats and smocks for workers in laboratories, foundries, chemical plants and petroleum refineries, welder's clothing and protective shields, fire department turnout coats, pants, jumpsuits for forest fire fighters and for military pilots.

Recently U.S.A. defence department is known to have secret planes which are called 'invisible' planes, means that they can be detected by radar. The reason for non-detection is the kevlar coating or fabrication which is said to absorb microwaves, hence the image of plane cannot be seen on radar.

8.2 Liqid Crystalline Mouldable Resins : (298)

M/s. Dartco Mfg. Inc. (U.S.A.) have developed a self-reinforced liquid crystalline aromatic copolymer that can be moulded on standard injection equipment. Existing tooling designed for conventional engineering thermoplastics can be used for material evaluation and frequently for production. This resin is expected to replace metals, ceramics, glass, composites, thermosets and thermoplastic resins and other materials in such areas as telecommunication equipment, computers, aerospace and auto parts.

The self-reinforcing polymers' major attraction is its outstanding property profile, high strength at elevated temperatures, heat resistance to 354°C, excellent dimensional stability and impact strength at continuous use temperatures of -51°C to 241°C, good burn resistance with minimum smoke. Generation resistance to virtually all chemicals including polar and non-polar solvents and hydrocarbon fuels, resistance to high levels of ionizing and cobalt - 60 radiation, uv resistance, lubricity, machinability and extremely low outgassing. Moreover the thermal stability of these materials is such that it can be used at high regrind ratios.

Injection moulding studies on thermotropic liquid crystal polymers is reported (299). Morphological studies showed that the skin layers of the moulded articles are much more oriented than the core.

8.3 Application of Polymer Dispersed Liquid Crystals (PDLC) : (300)

Uniform liquid crystal droplets in a polymer or liquid crystalline polymer binder can be achieved by several different phase seperation processes making possible electrically switched light shutters with a wide range of applications. These applications include large scale flexible displays that do not require polarizers and are simple to fabricate. Epoxy resins can be used as a polymer binder. These types of displays can provide large display area with nice projection, hence can be used for overhead projection e.g. T.V. Screen, Computer output etc. The PDLC technology can be used to form architectural point of view to prepare window shutters which can provide privacy. PDLC's can also be used in automobile industries to prepare dash board displays, sun-roof, side windows and rear windows.

8.4 Future of Mesogenic Polymers

Liquid crystalline polymers are the latest high growth area based on hydroxy naphthalene or hydroxy benzoic acids or bisphenols - all with a basic aromatic polyester skeleton. LC polymers are new type of product with a strength to weight ratio seven times of steel wire. Their impact strength is very high even in thin sectioned parts.

Dartco's "Ultra 21" is used in dual "Ovenable" cookware due to high heat resistance. The U.S. Air force have developed ATF-Advanced Tactical

Fighters - whose structures will be composed of 50% or more of LC Polymer composite. Thus advanced composite polymers are tomorrow's future for technical revolutions.

The production capacity of U.S. Producers and the trade names and prices of some LC Polymers are listed in "Chemical Business of U.S.A.", July, 1987.

Company	Trade name	Capacity*	Price/lb. Re-inforced
Dartco	Xydar	20-22	$ 7.35
Cllanese	Vector	N.A.	$ 7.35

Consumption		Annual growth
1986*	1991*	27 %
0.3	5.0	

* = Estimated capacity in million pounds a year. N.A. = Not applicable.

Polymer chemists are expanding the frontiers of designing LC Polymers for the toughest and most environmentally resistant products besides the weight advantage.

1. These polymers can be considered as model system for isotropic amorphous polymers where semi ordered regions have been proposed to exist and for drawn amorphous polymers, where by drawing process a high degree of orientational order can be introduced.
2. Polymers that form partially ordered melt or parallel ordered

solution can be processed in such a way that fibres with very high degree of orientational order are obtained. This specific structure leads to superior mechanical properties of the materials.

3. Polymers with ordered melt are of technological importance for the same reason that low molecular weight systems with anisotropic melts are widely used today in technical products, such as electrical displays. Additional advantages are expected for polymer systems, since parameters such as side groups structure formations or co-polymer formation will lead to a large variety of properties of semi ordered melts.

4. If the polymerization is carried out in semi-ordered liquid phase of monomer or in semi-ordered solutions, it is possible to study the polymerization process in ordered system. This will allow a deeper insight to the reaction mechanism. Also, by this procedure macroscopically ordered polymers may be obtained if the monomer phase is macroscopically ordered for instance, due to an external field or due to forces exhibited by specific surfaces. In this case interesting optical properties are expected for the polymeric systems.

In small molecule liquid crystal mesophases, the highly ordered liquid crystalline molecule or ordered solute chromophor shows strong linear dichorism in nematic and smectic phases and circular dichorism effect in cholesteric mesophases (301). Linear and circular dichorism spectra provide information concerning the polarization of electronic . transitions and the detection of hidden transition and they are a probe for monitoring the microscopic environment of the chromophores within polymeric systems.

Liquid crystal induced circular dichorism has been observed for several achiral molecules such as anthracene, dissolved in birefringent concentrated solutions of poly (r-benzyl-L-glutamate) in helix-supporting solvents.

2. AIMS AND OBJECTIVES

AIMS AND OBJECTIVES

Vast technological applications of liquid crystals have made them familiar to common man. The ever increasing applications of liquid crystals and their host of different physical properties have given impetus to the synthetic chemists to produce new materials (small molecules/macromolecules) exhibiting liquid crystalline properties.

Number of structural aspects are considered for the compound to exhibit mesomorphism. It was believed that -NH-CO- linkage is not conducive to mesomorphism. Our school has tried to change this belief by synthesizing mesogenic series with one -NH-CO-linkage. In the present study it was planned to exploit further the strength of -NH-CO- linkage for the exhibition of mesomorphism, when system is non-linear or contains steric hinderance, but two -NH-CO-linkages. Moreover, it was proposed to synthesize mesogens with a terminal group having high dipole moment to give compounds which can exhibit positive dielectric anisotropy.

It was believed initially that discogens need five to six substituents to exhibit mesomorphism. Recent work has changed this belief. It was planned to synthesize discogens with only three substituents and to study their mesogenic behaviour.

Condensation polymers are of great interest. In continuation of earlier work it was planned to synthesize two new polymeric systems, incorporating lateral substituents, broad molecules and odd ethylene spacers to evaluate the effect of these parameters on the mesogenic properties of

3. EXPERIMENTAL

EXPERIMENTAL

1. PREPARATION OF COMPOUNDS

1.1 Synthesis of homologous series with one or two amido central linkages.

1.1 a. Synthesis of 1,3-bis(4'-n-alkoxy benzoyl) amino phenols.

1.1 b. Preparation of 4-n-Alkoxy benzoic acids.

4-n-Alkoxy benzoic acids were prepared by the method of Dave & Vora (302), though other methods (303, 304) are known in the literature as it gave better yield.

4-Hydroxy benzoic acid (0.1 mole), n-alkyl halides (0.12 mole) and potassium hydroxide (0.25 mole) were dissolved in ethanol (100 ml) and refluxed for 7 to 8 hours. 10% Aqueous potassium hydroxide solution (25 ml) was added in the flask after the reaction period, and refluxing was continued for 2 hours to hydrolyse the ester formed. The solution was cooled and acidified with 1:1 cold hydrochloric acid to precepitate the acids. The 4-n-alkoxy benzoic acids were crystallised several times from ethanol or acetic acid until constant transition temperatures were obtained. The transition temperatures are in good accordance with the literature (302, 304).

1.1 c. Preparation of 4-n-Alkoxy benzoyl chlorides (302)

4-n-Alkoxy benzoyl chlorides (0.02 mole) were prepared by reaction of the corresponding 4-n-alkoxy benzoic acids (0.02 mole) with excess of thionyl chloride (2-2.5 mole) and heating on a waterbath till no hydrogen chloride gas was evolved. Excess of thionyl chloride was distilled off under reduced pressure using vacuum pump. The acid chloride left behind as a residue was used in the next reaction without further purification.

1.1 d. Preparation of 1,3-bis(4'-n-alkoxy benzoyl) amino phenols

1,3-bis(4'-n-alkoxy benzoyl) amino phenols were synthesized by condensing two moles of respective 4-n-alkoxy benzoyl chlorides with one mole of m-amino phenol. m-Amino phenol (0.01 mole) was taken in dry pyridine (10-15 ml) and was added slowly with stirring to cold (0-5°C) 4-n-alkoxy benzoyl chloride (0.02 mole). The mixture was heated on a water-bath for an hour and was allowed to stand overnight. The reaction mixture was acidified with cold 1:1 hydrochloric acid and the precipitates were filtered and washed with cold dilute sodium hydroxide solution, followed by cold water and hot alcohol. The esteramides were crystallised from glacial acetic acid until constant melting points were obtained.

The yield was about 65 %.

The melting points and analytical data are given in Table-2 and 3 respectively.

1.2 Synthesis of 1,3-bis(Trans-4'-n-alkoxy cinnamoyl) amino phenols

1.2 a Preparation of 4-n-alkoxy benzaldehydes

Various methods have been described for the preparation of 4-n-alkoxy benzaldehydes (305, 306), but following procedure was adopted in this investigation as it gives better results (307, 308), 4-methoxy benzaldehyde as the first member of the series was bought and purified of (BDH) grade.

0.1 mole of 4-hydroxy benzaldehyde, 0.15 mole of anhydrous potassium carbonate and 0.15 mole of corresponding n-alkyl bromide or iodide were added to dry acetone (60 ml), contained in 250 ml. round bottom flask. The mixture was refluxed in water bath for six to eight hours. The refluxing period was extended to ten to twelve hours in case of higher members. The whole mass was then added to cold water and the aldehydes separated as the form of oily layer were extracted with ether. Ether extract was washed with dilute sodium hydroxide solution to remove unreacted p-hydroxy benzaldehyde followed by water and then dried. Ether was evaporated and 4-n-alkoxy benzaldehydes thus obtained were purified by distilling under reduced pressure. Boiling points were found to be in agreement with those reported in literature (307).

1.2 b. Preparation of trans-4-n-alkoxy-cinnamic acids

Trans-4-n-alkoxy cinnamic acids were prepared by the method of

Gray and Jones (308).

4-n-alkoxy benzaldehyde (0.02 mole), malonic acid (0.04 mole), pyridine (8 ml) and piperidine (3 drops) were mixed and heated at 100°C in a round bottom flask for 3 hours on a steam bath. The mixture was poured in a beaker containing ice (25 gm) and concentrated hydrochloric acid (25 ml). The precipitates were filtered and washed with dilute hydrochloric acid followed by water. The lower members were crystallised from glacial acetic acid. The higher homologues were crystallised twice from benzene and then from acetic acid till constant transition temperatures were obtained. Transition temperatures are in good accordance with the literature (308).

1.2 c. Preparation of Trans-4-n-Alkoxy Cinnamoyl chlorides

Trans-4-n-alkoxy cinnamoyl chlorides were prepared in a similar method as mentioned in section 1.1.c. Corresponding trans-4-n-alkoxy cinnamic acids (0.02 moles) with excess of thionyl chloride (2-2.5 mole) were heated on a water-bath till evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using water pump. The acid chlorides left behind were used for further reaction.

1.2 d. Preparation of 1,3-bis(trans-4'-n-alkoxy cinnamoyl) amino phenols

1,3-bis(trans-4'-n-alkoxy cinnamoyl) amino phenols were synthesized in a similar method as described in section 1.1.d, by taking two moles of trans-4-n-alkoxy cinnamoyl chloride and one mole of m-amino phenol. All the esteramides were crystallized from glacial acetic acid until constant melting points were obtained. The yield was about 62 %.

The melting points and analytical data are given in Table-4 and 5, respectively.

1.3 Synthesis of 3,3'-dimethoxy-4-4'-bis(trans-4-n-alkoxy cinnamoyl) benzidine

1.3 a. Preparation of Trans-4-n-alkoxy cinnamic acids and acid chlorides

Trans-4-n-alkoxy cinnamic acids and cinnamoyl chlorides were synthesized by the method discussed in section 1.2 b and 1.2 c.

1.3 b. Preparation of 3,3'-dimethoxy-4-4'-bis(trans-4-n-alkoxy cinnamoyl) benzidine

3-3'-dimethoxy-4-4'-bis(trans-4-n-alkoxy cinnamoyl) benzidine were synthesized as under :

0.01 mole of 3,3'-dimethoxy benzidine was dissolved in 15 ml pyridine and the solution was added to the round bottom flask containing 0.02 mole of trans-4-n-alkoxy cinnamoyl chloride by maintaining temperature 0-5°C. After that the whole mass was heated on a water bath for an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid and the precipitates were washed with cold water. The amides were crystallised from glacial acetic acid until constant transition temperatures were obtained. The yield was about 68 %.

The transition temperatures are summ rised in Table-6 and the analytical data is given in Table-7.

1.4 Mesogens with positive dielectric anisotropy

1.4.1 Synthesis of 4(4'-Nitro benzoyloxy)-3-methoxy benzylidene-4'-substituted anilines.

1.4.2 Preparation of 4-Nitrobenzoyl chloride

It was prepared as discussed earlier in section 1.1 c. The acid chloride was used in the next reaction without further purification.

1.4.3 Preparation of 4-Nitro benzoyloxy-3-methoxy benzaldehyde.

This was prepared by the method of Vora and Renu (309).

Vanilin (0.01 mole) was dissolved in dry pyridine (10 ml) and slowly added to 4-nitro benzoyl chloride (0.01 mole) with stirring in a round bottom flask in an ice-bath. The mixture was then heated on water bath with occasional stirring for one hour and was allowed to stand over night. It was acidified with cold dilute hydrochloric acid and solid separated was filtered and washed with cold dilute sodium hydroxide solution, followed by water. The aldehyde was crystallized from ethanol until constant melting point was obtained. The melting point was 204°C. The yield was about 68 %.

The analytical data is as under :

	C %	H %	N %
Required	59.80	3.65	4.65
Found	59.68	3.55	4.58

1.4.4 Preparation of 4(4'-nitro benzoyloxy)-3 - methoxy benzylidene-4''-substituted anilines

The equimolar quantities of 4-nitro-benzoyloxy-3-methoxy benzaldehyde (0.01 mole) and different 4-substituted anilines (0.01 mole) were condensed by refluxing them in ethanol (25 ml) for 2 to 3 hours on sand bath. On cooling Schiff bases separated out. They were filtered and crystallized from benzene or benzene-ethanol mixture (1:1), until constant transition temperatures were obtained. The yield was 69-71 % .

Various schiff bases, with transition temperatures are listed in Table-8 and analytical data are summarised in Table-9. IR spectra were taken to confirm the structure.

1.5 Preparation of 4(4'-nitrobenzoyloxy)-3-methoxy benzylidene-2''-chloro anilines

Equimolar quantities of 4-nitro-benzoyloxy-3-methoxy benzaldehyde (0.01 mole) and 2-chloro aniline (0.01 mole) were condensed as mentioned in section 1.4.4. The yield was 60-65 % and melting point was :

$$K \xrightarrow{196°C} I$$

The analytical data is as under :

	C %	H %	N %	Cl %
Required	53.8	3.28	8.37	10.6
Found	52.97	3.06	8.195	

1.6 Discotic Compounds

1.6.1 Preparation of 1,3,5-tri(trans-4'-n-alkoxy cinnamoyloxy benzenes

1.6.2 Preparation of Trans-4-n-alkoxy cinnamic acids and acid chlorides

Trans-4-n-alkoxy cinnamic acids and cinnamoyl chlorides were synthesized by the method discussed in section 1.2 b and 1.2 c.

1.6.3 Preparation of 1,3,5-tri(trans-4'-n-alkoxy cinnamoyloxy benzenes

1,3,5-tri(trans-4'-n-alkoxy cinnamoyloxy benzenes were prepared by condensation of three moles of trans-4-n-alkoxy cinnamoyl chloride with one mole of phloroglucinol in dry pyridine (15 ml). The mixture was heated on a water bath for half an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid, the precipitates obtained were filtered and washed with cold water. The solid was crystallised from the mixture of benzene-ethanol (1:1) until constant transition temperatures were obtained. The transition temperatures and analytical data are recorded in Table 10 and 11 respectively.

1.7 Preparation of Cholesteryl(4-nitrobenzoate) : (310)

4-Nitrobenzoyl chloride was prepared from 4-nitrobenzoic acid, as discussed in section 1.4.2.

Equimolar proportion (.01 mole) of cholesterol and 4-Nitrobenzoyl chloride (.01 mole) were taken in a round bottom flask and N,N'-dimethyl aniline (20 ml) was added as a solvent. The whole mixture was heated at 120°C in an oil-bath for two hours. After heating, the whole mass was added to cold water when the oily mass separates out as solid. The blue mass was filtered and washed with acetone to remove N,N'-dimethyl aniline. The yellow solid was crystallized from chloroform and acetone mixture (1:2), till constant transition temperatures were obtained. The yield of the ester was 60%. The transition temperature of cholesteryl (4-Nitrobenzoate) is as under which tellies with the literature (310).

$$\mathrm{K} \xrightarrow{191.5} \mathrm{ch} \xrightarrow{260.0} \mathrm{I}\ \mathrm{(D)}$$

This compound was used as substrate in the gas chromatographic studies in the work carried out for liquid crystalline compounds used as stationary phase in gas chromatography.

2. MESOGENIC POLYMERS

2.1 Preparation of Co-Polyesters of 4-Hydroxy benzoic acid (P-HBA) and 2-Hydroxy benzoic acid (O-HBA) : (311)

One mole of P-HBA and 0.7 mole of O-HBA as monomers were taken in 50 ml round bottom flask containing 5 ml of benzene as a solvent. 5 ml of thionyl chloride was added as condensing agent. The care was taken against moisture adsorption by providing calcium chloride guard tube, on the dry condensor. The whole mass was heated on the water bath by keeping temperature between 80-90°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 washing to remove unreacted monomers. The solid polymer was dried and transition temperatures were taken.

$$K \xrightarrow{204} S \xrightarrow{216} N \xrightarrow{298} P$$

The polymer was insoluble in alcohol, acetone, benzene glacial acetic acid, but was soluble in DMF, DMSO, NMP, conc. H_2SO_4 and phenols like m-cresol, p-cresol, p-chloro phenol etc. The polymer was purified by solvent, non solvent technique, using DMF as solvent and ethanol as non solvent.

The molecular formula for repeating unit is : $C_{14}H_8O_4$.

The elemental analysis of the polymeric sample was carried out. It can be summarised as follows :

	% C	% H
Required	70.0	3.30
Found	67.80	3.03

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

3,3'-dimethoxy-4,4'-dihydroxy benzalazine was prepared by the method reported in the literature (312).

A mixture of powdered hydrazine sulphate 1.3 gm (.01 mole), 28 ml water and 1.56 ml concentrated aqueous ammonia (d.0.88) were taken in 100 ml. conical flask 3.04 gm (0.02 mole) of vanilin (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 vanilin .

Mixture was further stirred for an hour. Yellow solid mass was separated out, filtered, washed with water and recrystallised from alcohol. Melting point was 189°C.

The yield was about 87%.

The analytical data is as under :

	% C	% H	% N
Required	64.00	5.33	9.33
Found	64.02	5.29	9.29

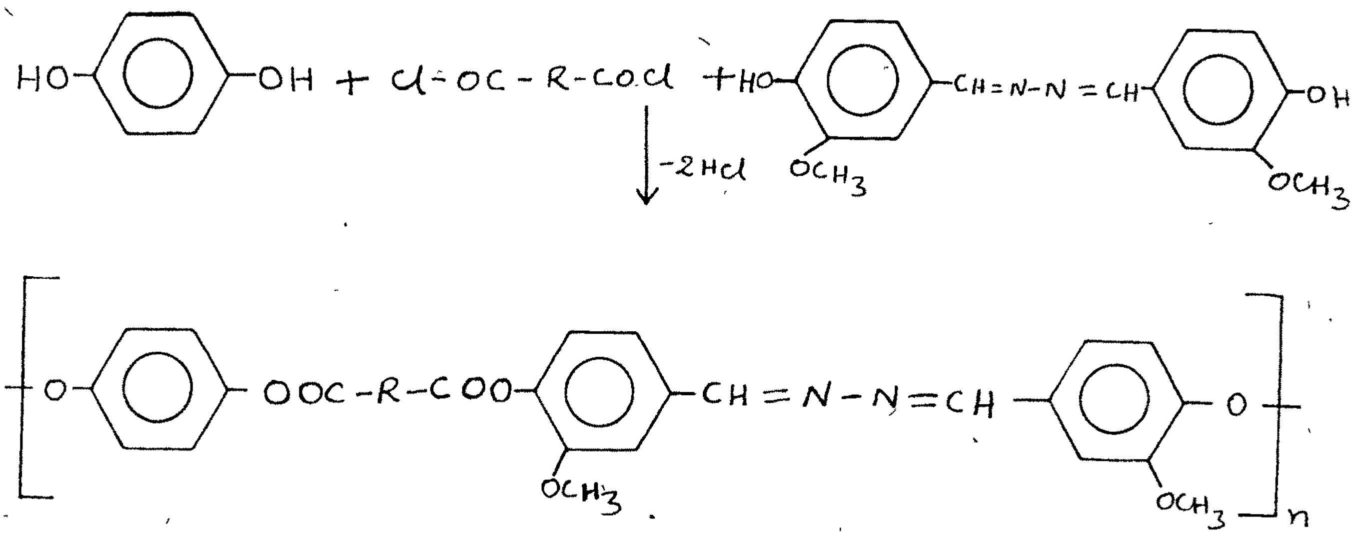
2.2.2 Preparation of diacid chlorides of different aliphatic and aromatic diacids

Diacid chlorides of isophthalic acid and adipic acid were prepared as described in section 1.1.c. In this synthesis, a few drops of pyridine were added as catalyst in preparation of acid chlorides and the reaction time needed was 6-7 hours.

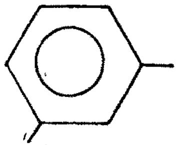
2.2.3 Preparation of polyesters (solution polycondensation)

Co-polyesters were prepared by varying the ratio of three monomers i.e. substituted dihydroxy benzalazine, diacid chloride and hydro-quinone as reported in Table-12. The detail procedure of synthesis is described below.

Definite weighed amount of 3,3'-dimethoxy-4,4'-dihydroxy benzalazine and hydroquinone as per the ratio was dissolved separately in dry pyridine (5 ml each), and was added to 50 ml round bottom flask containing definite amount of diacid chloride required as per the ratio of other two monomers by maintaining temperature 0-5°C. The whole mass was stirred further on magnetic stirrer for one hour at room temperature. After stirring period was over the whole mass was acidified with cold 1 : 1 ice : HCl mixture. The solid product was filtered, washed with dilute HCl followed by washing of water for complete removal of mineral acid. The polyesters were purified by solvent non-solvent method. DMF was used as solvent and alcohol was used as non solvent in purification process.



Where R = $-(CH_2)_4-$,



Transition temperatures, solubility behaviour of polymer and analytical data are summarised in Table 12 and 13 respectively.

2.3 Polyesters from various Dihydroxy naphthalenes

2.3.1 Preparation of 1,3-bis (4'-carboxy phenoxy) propane.

This flexible dicarboxylic acid was prepared by the method reported in literature (313, 314).

6.9 gm of p-hydroxy benzoic acid (0.2 mole) was dissolved in 20 ml, 22.4 % KOH solution (0.4 mole) in 250 ml round bottom flask. 2.56 ml 1,3-dibromopropane (0.1 mole) was added to the flask and the whole mass was refluxed for 3 to 4 hours. Then the reaction mixture was transferred to a beaker and was diluted with water till the sodium salt of acid dissolved completely. The solution was then acidified with dilute hydrochloric acid.

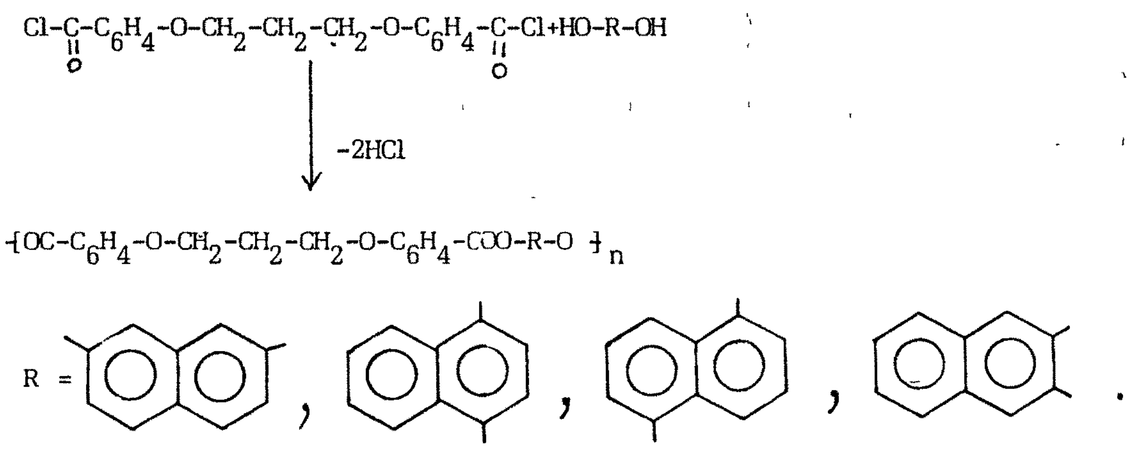
Solid mass was filtered, washed with alcohol to remove unreacted p-hydroxy benzoic acid. Solid mass was redissolved in DMF and reprecipitated by adding excess of alcohol. The process was repeated twice to get pure white product. Melting point was 329°C (reported 326°C) (313, 314). The yield was 80 %.

2.3.2 Preparation of Diacid chloride of 1,3-bis(4'-carboxy phenoxy) propane.

Diacid chloride of 1,3-bis(4'-carboxy phenoxy) propane was prepared as described in section 2.2.2.

2.3.3 Preparation of polyesters (solution polycondensation)

Diacid chloride of 1,3-bis(4'-carboxy phenoxy) propane (DAP) was condensed with different dihydroxy naphthalene (DHN) monomers.



$$\mathrm{Cl{-}\underset{\overset{\|}{O}}{C}{-}C_6H_4{-}O{-}CH_2{-}CH_2{-}CH_2{-}O{-}C_6H_4{-}\underset{\overset{\|}{O}}{C}{-}Cl{+}HO{-}R{-}OH}$$

$$\Big\downarrow \mathrm{-2HCl}$$

$$\mathrm{\{OC{-}C_6H_4{-}O{-}CH_2{-}CH_2{-}CH_2{-}O{-}C_6H_4{-}COO{-}R{-}O\}_n}$$

Dihydroxy naphthalene (0.01 mole) was dissolved in dry pyridine (20 ml) and was added slowly in a quickfit 50 ml round bottom flask containing magnetic needle and a solution of diacid chloride of 1,3-bis(4'-carboxy phenoxy) propane (0.01 mole) in dry pyride (20 ml) with stirring keeping the flask in ice bath. The reaction mixture was stirred continuously with guard tube on the flask at the temperature between 0-5°C for one hour. The temperature was then allowed to rise to 15-20°C and the reaction mixture was stirred at this temperature for further one hour. After that the reaction mixture was stirred at room temperature (30°C) for one more hour. At the end of three hours stirring the whole mass was acidified with cold 1:1 hydrochloric acid. The solid product was filtered, washed with dilute hydrochloric acid followed by washings of water for complete removal of mineral acid. The polymer was washed with hot ethanol to remove unreacted monomer. Polymer was purified by solvent-non solvent technique using DMF as solvent and alcohol as non solvent. The solid polymer was dried and melting points were determined.

The melting points, solubility behaviour and elemental analysis are summarised in Table 14 and 15 respectively.

2.4 Co-Polyester of 4-hydroxy benzoic acid (PHBA) with 2(4-hydroxy benzoyl) benzoic acid (HBBA) (315) :

2.4.1 Preparation of 2(4-hydroxy benzoyl) benzoic acid :

2(4-hydroxy benzoyl) benzoic acid was prepared by the method of Hobacher (316).

Synthesis involves following two stages.

(A) Preparation of phenolphthalein oxime:

In a 500 ml three necked round bottom flask fitted with stirrer and thermometer, were placed 15.9 gm (0.05 mole) of phenolphthalein (m.p. 259-263°C) and 80 ml (0.2 mole) of 2.5 N NaOH. The mixture was heated to 65°C and as soon as the phenolphthalein had dissolved, the flame was removed and a solution of 3.8 gm (0.052 mole) of hydroxylamine hydrochloride (96%) in 15 ml of water was added in one portion.

The solution was stirred for 15 minutes at 75°-80°C and then poured while warm, into 350 ml of 0.5 N sulphuric acid. The yellow precipitates were filtered off and washed with water and pressed in order to squeeze out most of water. For the subsequent step, the wet cake was used.

(B) Preparation of 2(4-hydroxybenzoyl) benzoic acid

The wet yellow cake of "phenolphthalein oxime" was placed into a 500 ml round bottom flask fitted with stirrer and a thermometer.

100 ml 5 N sulphuric acid, prewarmed to 90-104°C was then added into the flask. The mixture was stirred and the yellow slurry was rapidly heated at 100°C for 15 minutes. The dark yellow solution was obtained, which on cooling to 20°C, deposited the sandy crystals of 2(4-hydroxybenzoyl) benzoic acid, which were filtered and washed with three portions of 20 ml of water. After drying at 100-120°c , the acid of moderate greenish yellow colour was obtained. Yield 90 %. Melting point 209-213°C (D).

2.4.2 Co-Polyesters of 4-hydroxybenzoic acid (PHBA) with 2(4-hydroxy benzoyl) benzoic acid (HBBA).

A mixture of PHBA (0.01 mole) and HBBA (0.08 mole) as monomers was taken in 50 ml round bottom quickfit flask containing 5 ml of dry benzene as solvent. 4 ml of thionyl chloride was added as condensing agent. The care was taken against moisture absorption by providing clacium chloride guard tube on the dry condensor. The whole mass was refluxed on water bath for specific time period with frequent stirring. After the reflux period was over, the whole mass was cooled and poured into ice cold water and shaken well. The resultant polymeric material was filtered and washed with water, followed by ethanol washings to remove unreacted monomers. Further, purification was done by washing the polymer with ether. The copolyester was dried in vacuum. The transition temperature was as under, which tellies with the reported one (315).

$$K \xrightarrow{131} S \xrightarrow{206} I$$

This polymer was used as stationary phase in GC for the gas chromatographic studies.

3. CHARACTERIZATION OF LIQUID CRYSTALS AND LIQUID CRYSTALLINE MATERIALS

Elemental analysis of liquid crystals and liquid crystalline polymer samples were performed on Perkin-Elmer model 240 microanalyzer. The results are summarised in the previous sections.

All the liquid crystalline materials were scree ed during heating by using a polarizing microscope to check their melting behaviour and mesogenic character.

Viscometric study of solutions of polymer samples were also carried out. Intinsic viscosity (η) of all soluble polymers was obtained by Graphical method.

Some selected liquid crystals were studied by using DSC apparatus to correlate the transition temperatures obtained by thermal polarizing microscopy and to calculate enthalpy changes and entropy changes.

3.1 Determination of Transition Temperatures

The transition temperatures were determined by using a Leitz Labourlux 12 POL microscope heating stage 350' with an automatic camera.

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

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 textures over the temperature ranges were carefully observed and recorded as the appearance of focal-conic, plane, homeotropic 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 the 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.

The results are recorded in Tables in the earlier sections.

3.2 IR spectral study

Some liquid crystals and liquid crystalline polymers were screened by using Nujol/KBr pellets in the range of infra-red frequency. The samples were analysed on Perkin-Elmer spectrophotometer. The data are given in Tables 16 - 19

3.3 Viscometric study

3.3.1 Introduction

Many methods for the measurements of viscosity are reported (317), but those which make use of the capillary 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 liminar flows 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_o) 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 (318).

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

Because η_{rel} approaches 1 and not zero as the solution becomes more dilute, the relative viscosity obviously does not denote the polymers'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 designated as the specific viscosity (η_{sp}).

The specific viscosity relationship may be expressed by the equivalent form;

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

where η is the viscosity of the solution and η_o is that of 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 (319) termed either the inherent viscosity (η_{inh}) or the logarithmic viscosity number and be defined as $\ln \eta_{rel}/ C$.

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

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 (320). The common limiting value of either of these function in infinitely dilute solution is called the intinsic viscosity $[\eta]$, the limiting viscosity number.

$$[\eta] = [\frac{\eta_{sp}}{C}]_{C\rightarrow 0}$$

The intinsic 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 (321). 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 yield $[\eta]$ and K' is calculated from the value of the slope which is equal to $K'[\eta]$.

Similarly Kraemer (319) relationship

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

can be applied to the experimental data and can be determined from the plot of ln η_{rel}/C 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 $\ln\eta_{rel}$. Other modifications are also used which involve the constants. In the present study the value of $[\eta]$ was obtained by using Huggin's equation. The following equation is recommended for the one point method (322).

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

where C is the concentration g/dl.

3.3.2 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 idependent 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 solutions 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: 20 - 22.

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 were extrapolated to zero concentration to obtain the value of intrinsic viscosity $[\eta]$ for the system, Figures: 15 - 18.

3.4 Differential Scanning Calorimetry

The term "differential scanning calorimetry" has become a source of confusion in thermal analysis in the past several years. This confusion is understandable because at the present time there are two entirely different types of instruments which use the same name. These two instruments are different in designs of which one is actually a differential thermal analysis apparatus. The instruments are :

(a) Differential Scanning Calorimeters which are heat flow recording instruments.

$(dg/dt)_{\Delta T} = 0$, (Perkin-Elmer, Deltatherm and others).

(b) Differential Scanning Calorimeters which are differential temperature recording or DTA instruments. ($\Delta T \neq 0$) (Dupont, Stone Fisher, Linseis and others).

The term diferential scanning calorimetry (DSC) was apparently first used by Waston et al., (323) to describe the instrument technique developed by the Perkin-Elmer Corporation. This technique maintained the sample and reference materials isothermal to each other by proper application of electrical energy, as they were heated or cooled at a linear rate. The curve obtained is a recording of heat flow dH/dt, in mcal/sec, as a function of temperature.

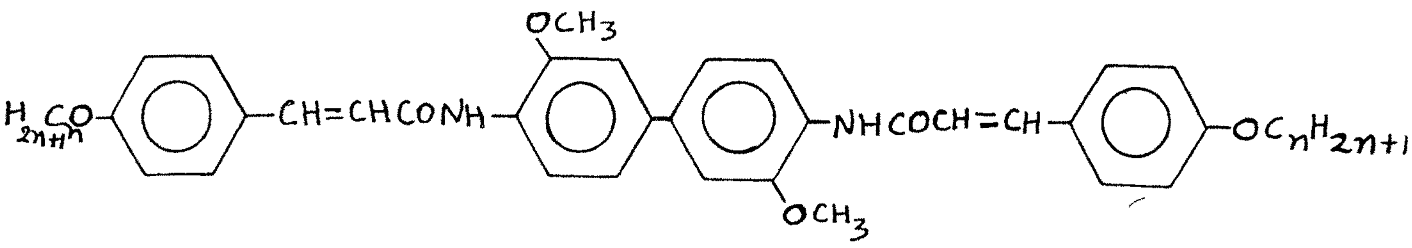
In the true thermodynamic sense, an endothermic curve peak is indicated by a peak in the upward direction (increase in enthalpy while an exothermic peak is recorded in the opposite direction). In all appearances, the DSC curve looks very similar to that of a DTA curve except for the ordinate axis units. As in DTA the area enclosed by the DSC curve peak is directly proportional to enthalpy change.

$$\text{area} = K\Delta Hm.$$

except that K is independent of temperature.

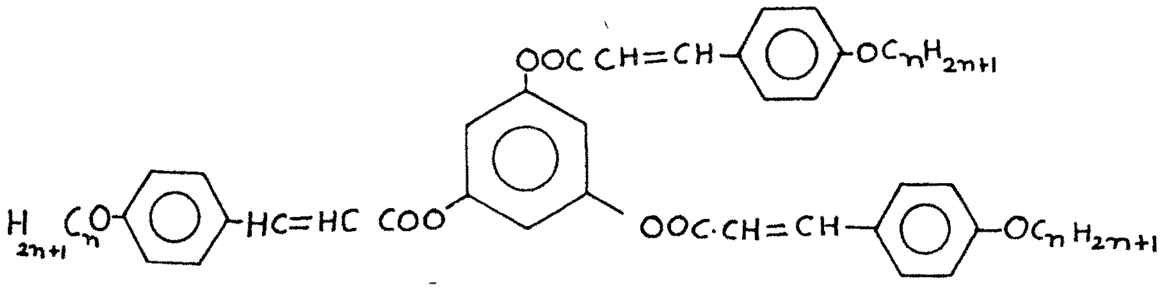
In the present study the homologues of the following mesogenic series were studied.

1. 3,3'-dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl)-benzidines.



n = 4 & 7.

2. 1,3,5-tri(trans-4'-n-alkoxy cinnamoyloxy) benzenes.



n = 4, 8, 16, 18.

3.4.1 Calculation of Enthalpy changes (ΔH) :

The calculations for enthalpy changes (ΔH) at different transitions were carried out by measuring the area of the peaks and applying the equations given in the Mannual of Dupont company.

$$\Delta H = \frac{A}{m} (60 \times B \times E \times \Delta qs \times \text{mol. wt.} \times 10^{-3})$$

where,

ΔH = K cal/mol
A = Area of peak (in^2).
m = weight of the sample (mg).
B = time base setting (min/inch)
E = Cell calibration coefficient
Δqs = y-axis range (m cal/sec/in)
Mol.wt.= molecular weight of the sample.

Entropy changes are also calculated by using equation :

$$\Delta S = \frac{\Delta H}{T}$$

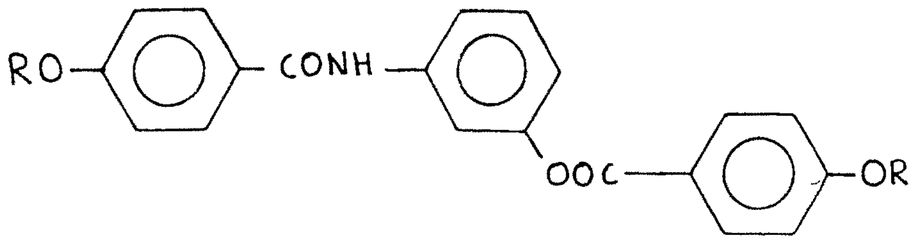
where

ΔS = K cal/mol/^{0}K
T = Temperature in Kelvin.

The data for enthalpy and entropy changes at different transitions are recorded in Tables 23-26, The DSC thermograms are recorded in Figs. 19-20.

TABLE - 2

1,3-Bis(4'-n-Alkoxy benzoyl) Amino phenols

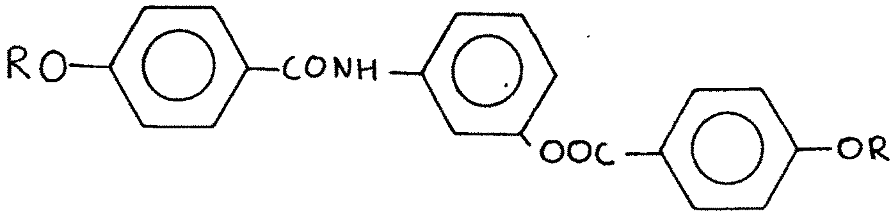


Sr.No.	n-Alkyl Group R	Melting Points °C
1.	Methyl	166
2.	Butyl	172
3.	Pentyl	180 (D)*
4.	Hexyl	210 (D)
5.	Heptyl	182 (D)
6.	Octyl	176
7.	Decyl	145
8.	Dodecyl	95
9.	Tetradecyl	107
10.	Hexadecyl	155

*(D) Decomposition

TABLE - 3

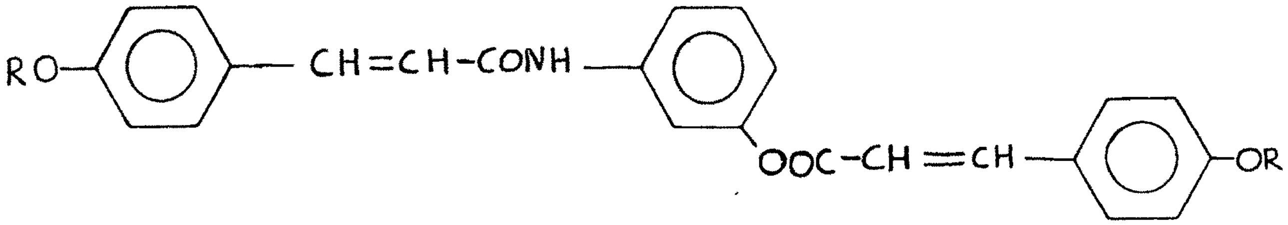
1,3-Bis (4'-n-Alkoxy benzoyl) Amino phenol



Sr. No.	n-Alkyl Group R	Molecular Formula	% Required C	% Required H	% Required N	% Found C	% Found H	% Found N
1.	Methyl	$C_{22}H_{19}O_5N$	70.03	5.04	3.71	69.18	5.0	3.58
2.	Butyl	$C_{28}H_{31}O_5N$	72.88	6.72	3.04	72.81	6.69	3.00
3.	Pentyl	$C_{30}H_{35}O_5N$	73.62	7.16	2.86	73.59	6.99	2.79
4.	Hexyl	$C_{32}H_{39}O_5N$	74.27	7.54	2.71	74.21	7.51	2.69
5.	Heptyl	$C_{34}H_{43}O_5N$	74.86	7.89	2.57	74.80	7.82	2.51
6.	Octyl	$C_{36}H_{47}O_5N$	75.39	8.20	2.44	75.29	8.17	2.39
7.	Decyl	$C_{40}H_{55}O_5N$	76.31	8.74	2.22	76.27	8.71	2.19
8.	Dodecyl	$C_{44}H_{63}O_5N$	77.08	9.19	2.04	76.99	8.97	2.11
9.	Tetradecyl	$C_{48}H_{71}O_5N$	77.73	9.58	1.89	77.69	9.51	1.81
10.	Hexadecyl	$C_{52}H_{79}O_5N$	78.29	9.91	1.76	78.09	9.86	1.69

TABLE - 4

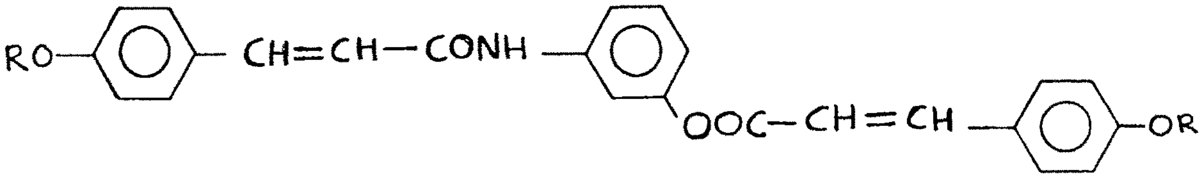
1,3-Bis(Trans-4'-n-Alkoxy Cinnamoyloxy) Amino Phenols



Sr. No.	n-Alkyl Group R	Melting Points °C
1.	Methyl	155
2.	Butyl	149
3.	Octyl	140
4.	Dodecyl	135
5.	Hexadecyl	142

TABLE - 5

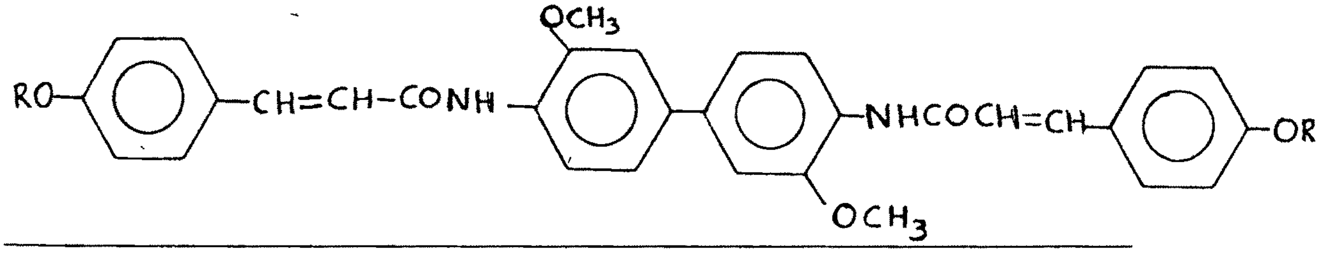
1,3-Bis(Trans-4'-n-Alkoxy Cinnamoyloxy) Amino Phenols



Sr. No.	n-Alkyl Group R	Molecular Formula.	% Required			% Found		
			C	H	N	C	H	N
1.	Methyl	$C_{26}H_{23}O_5N$	72.72	5.36	3.26	72.59	5.29	3.20
2.	Butyl	$C_{32}H_{35}O_5N$	74.85	6.82	2.72	74.78	6.76	2.69
3.	Octyl	$C_{40}H_{51}O_5N$	76.8	8.16	2.24	76.76	8.04	2.19
4.	Dodecyl	$C_{48}H_{67}O_5N$	78.15	9.09	1.89	78.05	9.12	1.80
5.	Hexadecyl	$C_{96}H_{83}O_5N$	79.15	9.77	1.64	79.09	9.69	1.59

TABLE - 6

3,3'-dimethoxy-4,4'-Bis(Trans-4-n-Alkoxy Cinnamoyl) benzidines.

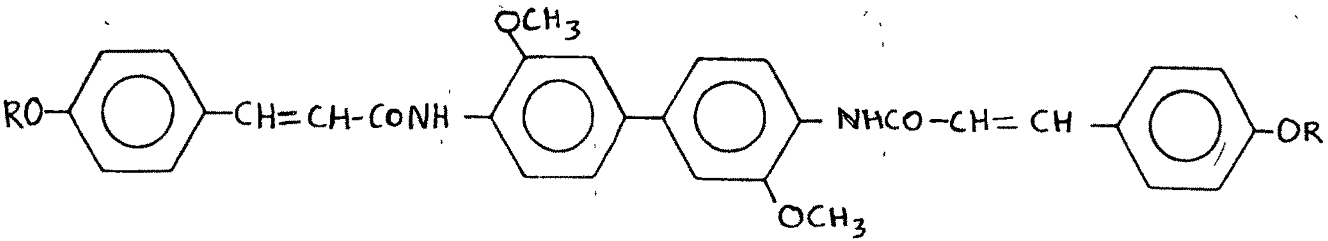


Sr. No.	Alkyl Group R	Transition Temperatures °C		
		Smectic	Nematic	Isotropic
1.	Methyl	-	-	260 (D)
2.	Propyl	-	299	324
3.	Butyl	-	267	321
4.	Pentyl	-	226	298
5.	Hexyl	-	213	289
6.	Heptyl	-	210	271
7.	Octyl	$K_1 \xrightarrow{184} K_2$	206	262
8.	Decyl	161	176	249
9.	Dodecyl	132 S_C 185 S_A	199	239
10.	Hexadecyl	137	170	218

(D) decomposition

TABLE - 7

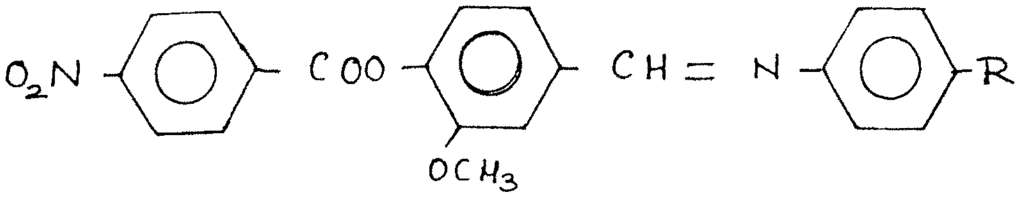
3,3'-dimethoxy-4,4'-Bis(Trans-4-n-Alkoxy Cinnamoyl) benzidine.



Sr No.	n-Alkyl Group	Molecular Formula	% Required			% Found		
	R		C	H	N	C	H	N
1.	Methyl	$C_{34}H_{32}O_6N_2$	72.34	5.67	4.96	72.12	5.72	4.863
2.	Propyl	$C_{38}H_{40}O_6N_2$	73.55	6.45	4.52	73.41	7.24	4.442
3.	Butyl	$C_{40}H_{44}O_6N_2$	74.07	6.79	4.32	74.51	7.001	3.924
4.	Pentyl	$C_{42}H_{48}O_6N_2$	74.56	7.10	4.14	75.00	7.387	3.901
5.	Hexyl	$C_{44}H_{52}O_6N_2$	75.00	7.39	3.98	74.78	7.630	4.095
6.	Heptyl	$C_{46}H_{56}O_6N_2$	75.41	7.65	3.83	75.40	7.44	3.25
7.	Octyl	$C_{48}H_{60}O_6N_2$	75.79	7.89	3.68	75.51	8.255	3.522
8.	Decyl	$C_{52}H_{68}O_6N_2$	76.47	8.33	3.43	76.31	8.29	3.439
9.	Dodecyl	$C_{56}H_{76}O_6N_2$	77.06	8.72	3.21	77.90	8.100	2.972
10.	Hexadecyl	$C_{64}H_{92}O_6N_2$	78.05	9.35	2.85	77.98	9.40	2.818

TABLE - 8

4(4'-n-Nitrobenzoyloxy)-3-methoxy benzylidene 4"-substituted anilines



Sr. No.	R	Transition temperatures °C		
		Smectic	Nematic	Isotropic
1.	$-CH_3$	-	(169)*	192
2.	$-OCH_3$	-	168	205
3.	$-OC_2H_5$	$K_1 \xrightarrow{125} K_2$	150	211
4.	$-CooCH_3$	-	-	202
5.	$-CooC_2H_5$	-	(168)	182
6.	-F	-	-	180
7.	-H	-	-	168
8.	$-NO_2$	-	-	201
9.	-Cl	-	(165)	200

* Values in paranthesis indicate monotropic temperatures.

TABLE - 9

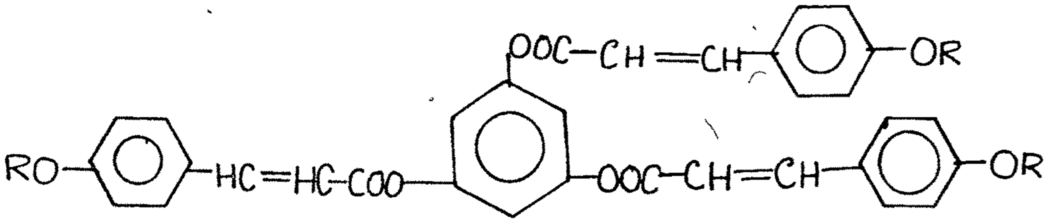
4(4'-n-nitro benzoyloxy)-3-Methoxy benzylidene-4"-substituted Anilines.

$O_2N-C_6H_4CooC_6H_3(OCH_3)CH=N-C_6H_4-R.$

Sr. No.	R	Molecular Formula	% Required			% Found		
			C	H	N	C	H	N
01.	$-CH_3$	$C_{22}H_{18}O_5N_2$	61.15	4.46	8.92	60.80	4.952	7.886
02.	$-OCH_3$	$C_{22}H_{18}O_6N_2$	65.02	4.4	6.9	65.47	4.54	6.89
03.	$-OC_2H_5$	$C_{23}H_{20}O_6N_2$	65.7	4.7	6.7	65.23	4.75	6.97
04.	$-CooCH_3$	$C_{23}H_{18}O_7N_2$	56.98	3.91	7.82	56.00	3.78	7.968
05.	$-CooC_2H_5$	$C_{24}H_{20}O_7N_2$	64.3	4.5	6.3	63.97	4.41	5.905
06.	-F	$C_{21}H_{15}O_5N_2F$	63.95	3.81	7.11	62.98	3.75	6.987
07.	-H	$C_{21}H_{16}O_5N_2$	60.0	4.0	9.3	59.78	3.91	9.058
08.	$-NO_2$	$C_{21}H_{15}O_7N_3$	59.85	3.56	9.97	59.79	3.58	9.635
09.	-Cl	$C_{21}H_{15}O_5N_2Cl$	53.8	3.28	8.37	53.81	3.19	10.779

TABLE - 10

1,3,5-Tri (Trans-4'-n-Alkoxy Cinnamoyloxy) benzenes.



Sr. No.	n- Alkyl Group R	Transition Temperatures °C Nematic	 Isotropic
1.	Butyl	-	159
2.	Hexyl	-	142
3.	Octyl	147.5	175
4.	Decyl	107	147
5.	Dodecyl	116	136
6.	Hexadecyl	112.5	126
7.	Octadecyl	120	138

TABLE - 12

Solution Polycondensation of diacid chloride with 3,3'-Dimethoxy-4,4'-dihydroxy Benzalazine and Hydroquninone

(a) Solvent : Pyridine (b) Reaction period = 1½ hrs. (c) Reaction temp. : 27°C (Room temp.)

Sr. No.	Polymer	Adipoyl chloride	Azine	HQ	Transition Temp. °C		Solubility behaviour				
					N	I	DMF	DMSO	NMP	Benzene	Ethanol
1.	1-AHAZ	1.00	0.5	0.5	-	290	(+)	(+)	(-)	(-)	(-)
2.	8-AHAZ	0.80	0.5	0.3	-	258	(+)	(+)	(±)	(-)	(-)
3.	7-AHAZ	0.70	0.5	0.2	-	240	(+)	(+)	(±)	(-)	(-)
4.	6-AHAZ	0.60	0.5	0.1	-	188	(+)	(+)	(±)	(-)	(-)
		Isophthaloyl Chloride									
1.	1-IHAZ	1.00	0.5	0.5	-	303	(+)	(+)	(±)	(-)	(-)
2.	8-IHAZ	0.80	0.5	0.3	238	289	(+)	(+)	(±)	(-)	(-)
3.	7-IHAZ	0.70	0.5	0.2	-	210	(+)	(+)	(±)	(-)	(-)
4.	6-IHAZ	0.60	0.5	0.1	-	218	(+)	(+)	(±)	(-)	(-)

(+) Soluble (±) Partly soluble (-) insoluble HQ = Hydroquinone

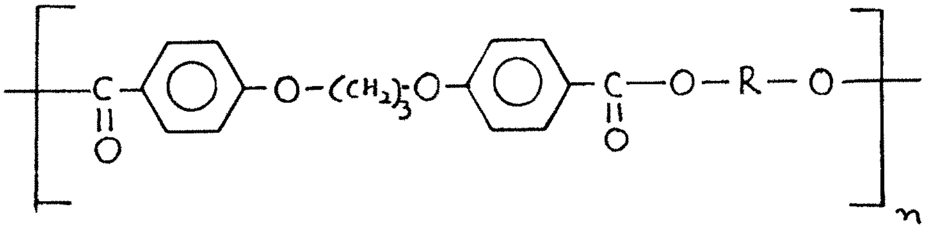
TABLE - 13

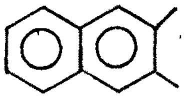
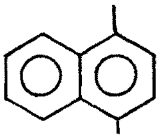
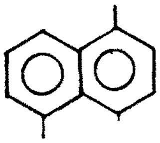
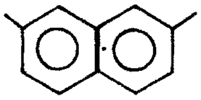
Elemental analysis of Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy benzalazine.

Sr. No.	Polymer	Molecular Formula.	% Required			% Found		
			C	H	N	C	H	N
1.	1-AHAZ	$C_{28}H_{26}O_8N_2$	64.86	5.01	5.41	63.97	4.89	5.27
2.	8-AHAZ	$C_{28}H_{26}O_8N_2$	64.86	5.01	5.41	64.05	4.91	5.31
3.	7-AHAZ	$C_{28}H_{26}O_8N_2$	64.86	5.01	5.41	63.89	4.69	5.29
4.	6-AHAZ	$C_{28}H_{26}O_8N_2$	64.86	5.01	5.41	64.11	4.81	5.39
5.	1-IHAZ	$C_{33}H_{28}O_8N_2$	68.28	4.83	4.83	67.98	4.61	4.75
6.	8-IHAZ	$C_{33}H_{28}O_8N_2$	68.28	4.83	4.83	68.05	4.71	4.79
7.	7-IHAZ	$C_{33}H_{28}O_8N_2$	68.28	4.83	4.83	67.99	4.79	4.75
8.	6-IHAZ	$C_{33}H_{28}O_8N_2$	68.28	4.83	4.83	68.02	4.69	4.71

TABLE - 14

Melting points and solubility behaviour of various Polyesters having Naphthalene nucleus.



Sr. No.	Polymer	R	Melting Point°C	DMF	DMSO	Benzene	Ethanol	Methanol
				Solubility behaviour				
1.	CP-3		146	(+)	(+)	(-)	(-)	(-)
2.	CP-4		240	(+)	(+)	(-)	(-)	(-)
3.	CP-5		338	(+)	(+)	(-)	(-)	(-)
4.	CP-7		291	(+)	(+)	(-)	(-)	(-)

(+) : Soluble (-) : Insoluble

TABLE - 15

Elemental analysis of Polyesters from various Dihydroxy naphthalenes.

Sr. No.	Polymer	Percentages found	
		C %	H %
1.	CP-3	72.97	4.46
2.	CP-4	73.19	4.51
3.	CP-5	73.08	4.38
4.	CP-7	73.68	4.11

Molecular formula of the repeating unit

$C_{27}H_{20}O_6$.

Required C % = 73.64 ; H % = 4.55.

TABLE - 16

I R Vibrations (cm^{-1})

4-CAA	7-CAA
3380 (b)	3450 (b)
2850	3210
2750	2850
1680	2710
1600	1650
1510	1640
1480	1480
1410	1380
1390	1230
1230	1180
1180	1180
1025	1045
990	990
820	820
720	

(b) broad band

TABLE - 17

I R Vibrations (cm^{-1})

4-CPG	16-CPG	18-CPG
2980(b)	2902	2960(b)
2880	2845	1680
1670(b)	1670(b)	1600
1600	1590	1510
1560	1500	1480
1500	1460	1420
1460	1420	1400
1420	1300	1250(b)
1305	1250(b)	1180
1250(b)	1180	1010
1205	1010	980
1170	820	820
1060	720	720
1040		680
1005		
980		
905		
835		
580		

(b) : broad band

TABLE - 18

IR Vibrations (cm^{-1})

1-AHAZ	6-AHAZ	7-AHAZ	8-AHAZ	7-IHAZ
3000-3600 (b)	3000-3380(b)	3000-3380 (b)	2350	2500-2975 (b)
1850	1645	1640	1650	1620
1800	1600	1600	1600	1500
1695	1500	1500	1500	1420
1600	1440	1420	1430	1320
1500	1340	1400	1400	1190
1470	1280	1340	1320	1020
1400	1200	1265	1260	980
1360	1050	1180	810	820
1270	980	1040	750	680
1220	820	830	670	-
1050	750	740	-	-

(b) : broad band

TABLE - 19

IR Vibrations (cm^{-1}).

CP-3	CP-4
3320(b)	3280(b)
1720	1760
1680	1685
1600	1610
1510	1510
1390	1395
1260	1260
1180	1180
1050	1050
1020	1020
840	860
720	730
680	670

(b) : broad band.

TABLE - 20

Viscosity data of Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy benzalazine

Solvent : DMF   Temperature : 29°C

Polymer	Concentration % C	η relative	η specific	η reduced	η inherent	[η] dl/gm Graphical Method
1-AHAZ	1.00	1.587	0.587	0.587	0.462	0.722
	0.67	1.440	0.44	0.658	0.544	
	0.50	1.307	0.307	0.654	0.535	
	0.40	1.267	0.267	0.668	0.5916	
8-AHAZ	1.00	1.23	0.23	0.23	0.207	0.332
	0.67	1.15	0.15	0.22	0.208	
	0.50	1.13	0.13	0.26	0.244	
	0.40	1.11	0.11	0.28	0.261	
7-AHAZ	1.00	1.21	0.21	0.21	0.261	0.239
	0.67	1.14	0.14	0.208	0.156	
	0.50	1.106	0.106	0.212	0.201	
	0.40	1.053	0.053	0.133	0.129	
6-AHAZ	1.00	1.23	0.23	0.23	0.207	0.303
	0.67	1.17	0.17	0.264	0.234	
	0.50	1.12	0.12	0.271	0.227	
	0.40	1.09	0.09	0.225	0.215	

TABLE - 21

Viscosity data of Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy benzalazine

Solvent used : DMF

Temperature °C : 29

Polymer	Concentration % (C)	η relative	η Specific	η reduced	η inherent	[η] dl/g graphical method
1-IHAZ	1.00	1.53	0.53	0.53	0.425	0.572
	0.67	1.38	0.38	0.57	0.481	
	0.50	1.27	0.27	0.54	0.478	
	0.40	1.21	0.21	0.551	0.476	
8-IHAZ	1.00	1.513	0.513	0.513	0.414	0.623
	0.67	1.367	0.367	0.548	0.467	
	0.50	1.26	0.26	0.52	0.462	
	0.40	1.23	0.23	0.575	0.518	
7-IHAZ	1.80	1.213	0.213	0.213	0.193	0.389
	0.67	1.187	0.187	0.279	0.256	
	0.50	1.153	0.153	0.306	0.285	
	0.40	1.133	0.133	0.333	0.312	
6-IHAZ	1.00	1.13	0.13	0.130	0.122	0.169
	0.67	1.09	0.09	0.149	0.128	
	0.50	1.07	0.07	0.146	0.135	
	0.40	1.06	0.06	0.150	0.146	

TABLE - 22

Viscosity data of Polyesters from Naphthalenes.

Solvent used : DMF   Temperature °C : 29

Polymer	Concentration % C	η_{relative}	η_{specific}	η_{reduced}	η_{inherent}	$[\eta]$ dl/gm Graphical Method
CP-3	1.00	1.082	0.082	0.082	0.0788	0.107
	0.67	1.061	0.061	0.091	0.091	
	0.50	1.046	0.046	0.093	0.09	
	0.40	1.038	0.038	0.097	0.086	
CP-4	1.00	1.09	0.09	0.09	0.086	0.164
	0.67	1.073	0.073	0.109	0.105	
	0.50	1.061	0.061	0.122	0.118	
	0.40	1.054	0.054	0.135	0.131	
CP-5	1.00	1.087	0.087	0.087	0.083	0.169
	0.67	1.078	0.078	0.116	0.112	
	0.50	1.064	0.064	0.128	0.124	
	0.40	1.055	0.055	0.138	0.133	
CP-7	1.00	1.081	0.081	0.081	0.780	0.178
	0.67	1.076	0.076	0.113	0.109	
	0.50	1.066	0.066	0.131	0.127	
	0.40	1.053	0.053	0.141	0.055	

TABLE - 23

DSC Results of 3,3'-dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl) benzidines

Sr. No.	Compound	Phase	Tempe-rature °C	Weight of sample mg	Area of peak (sq.in).	Time Base B (min/in)	Cell Coefficient E	ΔqS (mcal/sec/in)	Enthalpy changes ΔH (Kcal/mole)	Entropy changes ΔS (Cal/mole/°K)
1.	4-CAA	K—N	245	3.71	0.53568	5	1	1	28.0691	54.19
		N—I	280		0.010075				0.5277	0.9542
2.	7-CAA	K_1—K_2	57	2.55	0.02976	5	1	1	2.5629	7.7664
		K_2—N	195		0.31248				26.91	57.5
		N— I	245		0.00992				0.8543	1.6492

TABLE - 24

DSC Results and Microscopic results of
3,3'-dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl) benzidines

Sr. No.	Compound	Molecular Formula	Microscopic reading (DSC reading) °C		
			Solid	Nematic	Isotropic
1	4-CAA	$C_{40}H_{44}O_6N_2$	-	267(245)	321(280)
2.	7-CAA	$C_{46}H_{56}O_6N_2$	-(57)	210(195)	271(245)

TABLE - 25

DSC Results of 1,3,5-tri(trans-4-n-alkoxy cinnamoyloxy) benzenes

Sr. No.	Compound	Phase	Temperature °C	Weight of sample mg	Area of peak (sq.in)	Time Base B (min/in)	Cell Coefficient E	q_s (mcal/sec/in.)	Enthalpy changes ΔH (Kcal/mole)	Entropy changes ΔS (cal/mole/°k)
1.	4-CPG	K_1—K_2	75	4.63	0.0248	5	1	1	1.176	3.380
		K_2—K_3	105		0.0264				1.250	3.306
		K_3—I	145		0.439				20.827	50.675
2.	8-CPG	K—N	142.5	5.68	0.343	5	1	1	16.313	39.308
		N—I	169		0.00992				0.472	1.379
3.	16-CPG	K_1—K_2	72	5.28	0.439	5	1	1	30.8632	91.3112
		K_2—N	111		0.536				37.6498	99.0784
		N— I	125		-*				-	-
4.	18-CPG	K_1—K_2	65	4.65	0.2018	5	1	1	17.199	50.886
		K_2—N	112		0.213				18.15	47.267
		N—I	130		0.0101				0.859	2.132

* : Area of peak could not be obtained.

TABLE - 26

DSC and Microscopic Results of
1,3,5-Tri(trans-4-n-alkoxy cinnamoyloxy) benzenes

Sr. No.	Compound	Molecular Formula	Microscopic reading (DSC reading)°C		
			Solid	Nematic	Isotropic
1.	4-CPG	$C_{45}H_{48}O_9$	-(75) (105)	-	159(145)
2.	8-CPG	$C_{57}H_{72}O_9$	-	147.5(142.5)	175(169)
3.	16-CPG	$C_{81}H_{121}O_9$	-(72)	112.5(111)	126(125)
4.	18-CPG	$C_{87}H_{133}O_9$	-(65)	120 (112)	138(130)

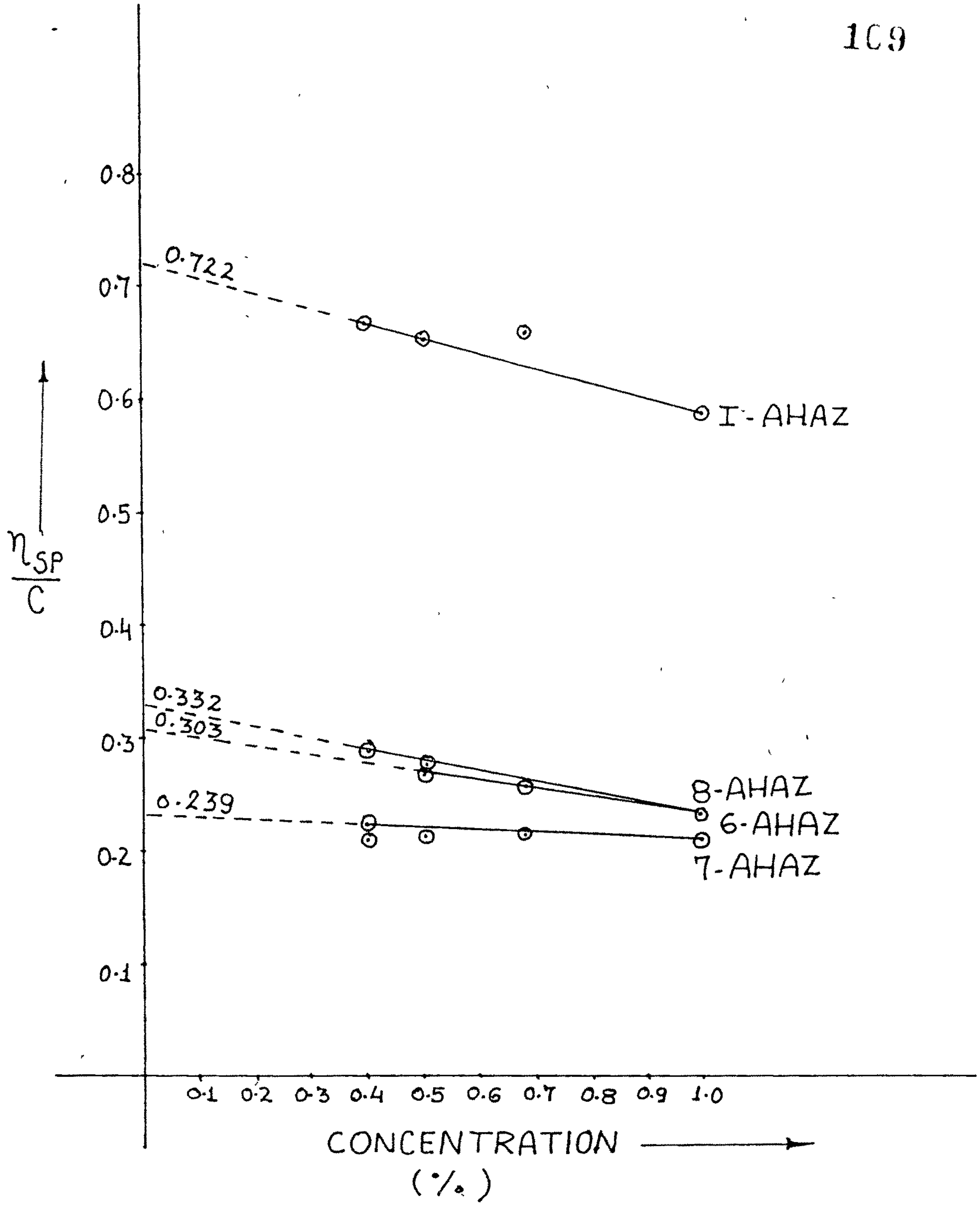


FIG. 15. INTRINSIC VISCOSITY OF POLYMER BY GRAPHICAL METHOD.

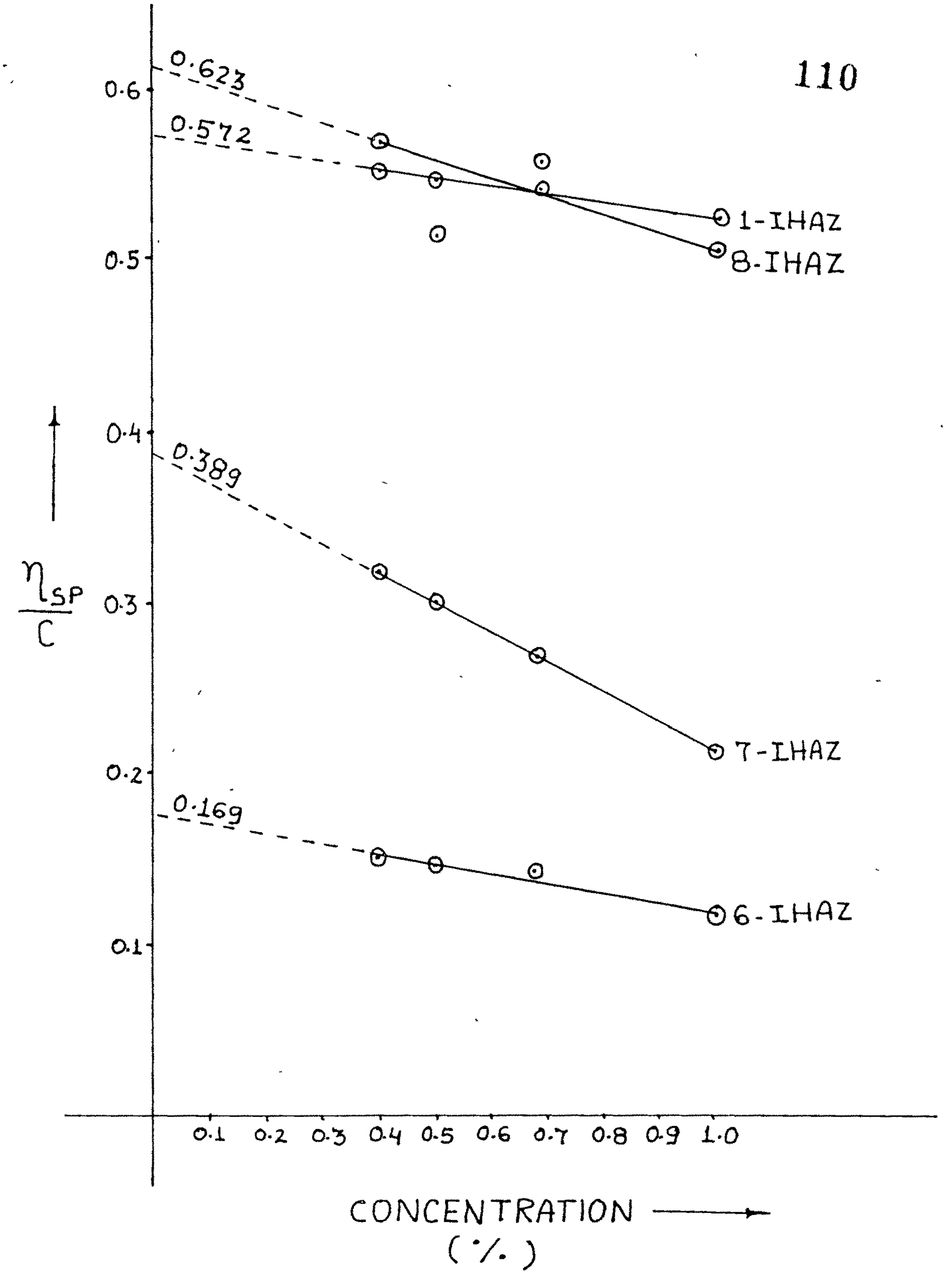
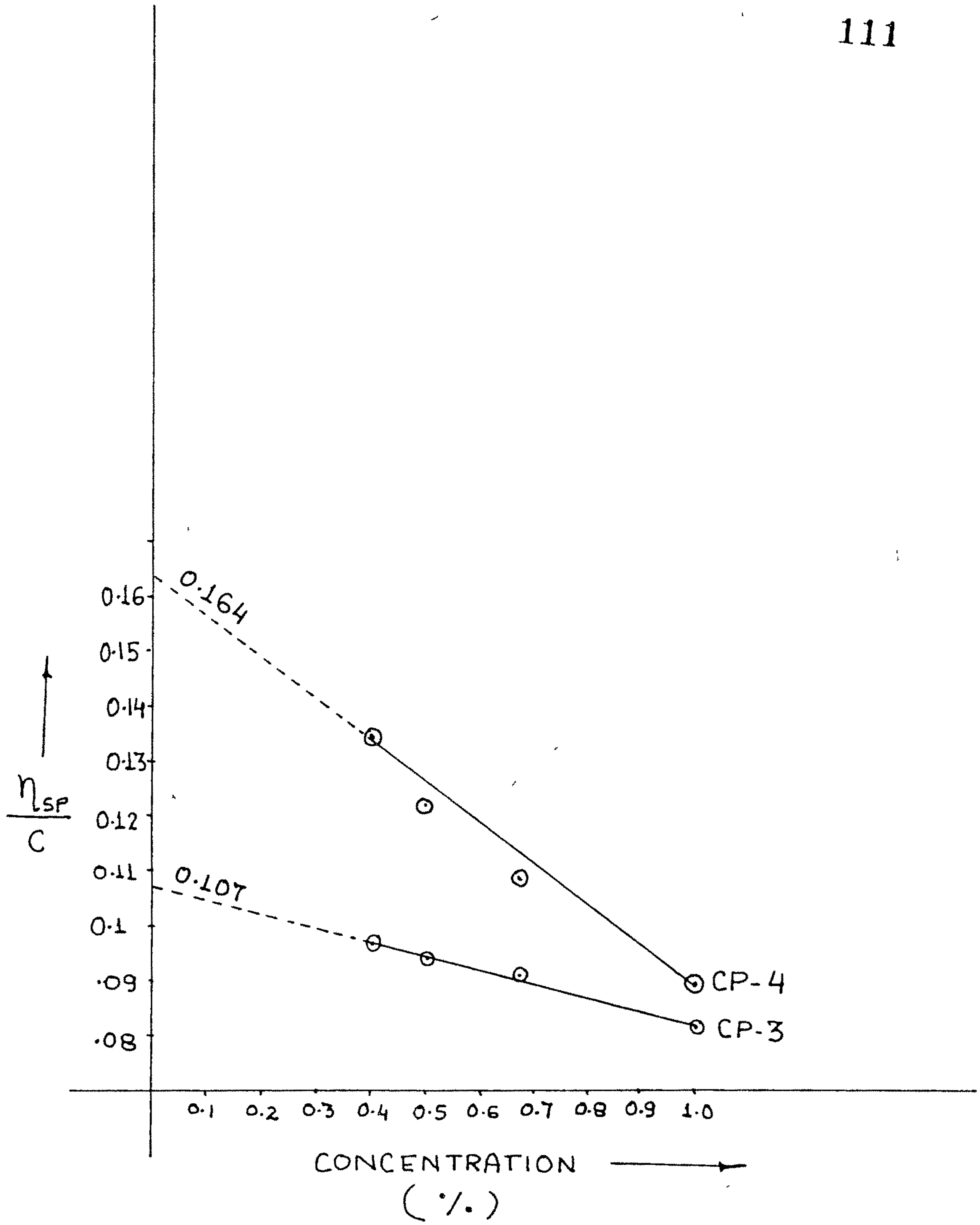


FIG:16. INTRINSIC VISCOSITY OF POLYMER BY GRAPHICAL METHOD



FIG·17 INTRINSIC VISCOSITY OF POLYMER BY GRAPHICAL METHOD

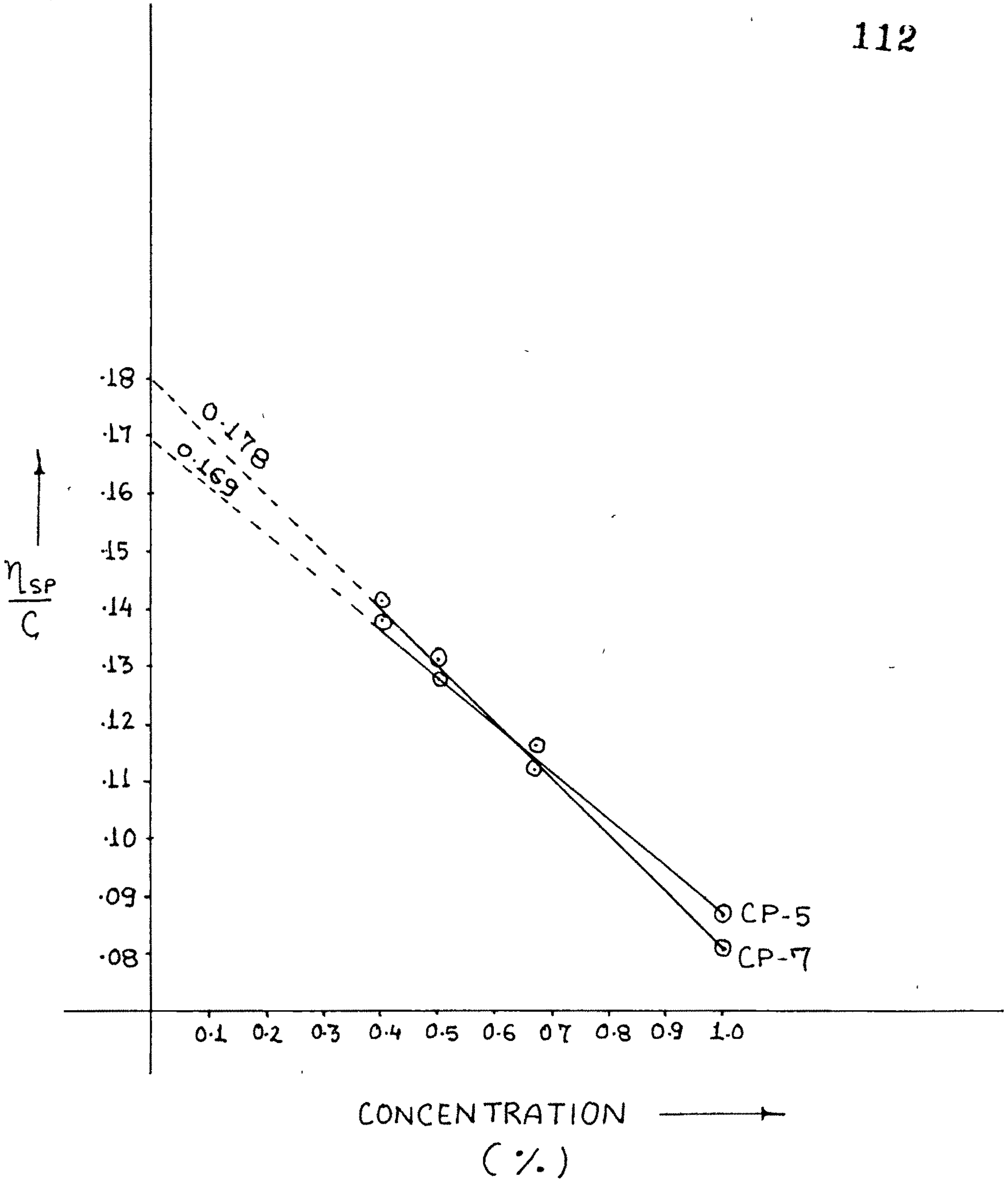
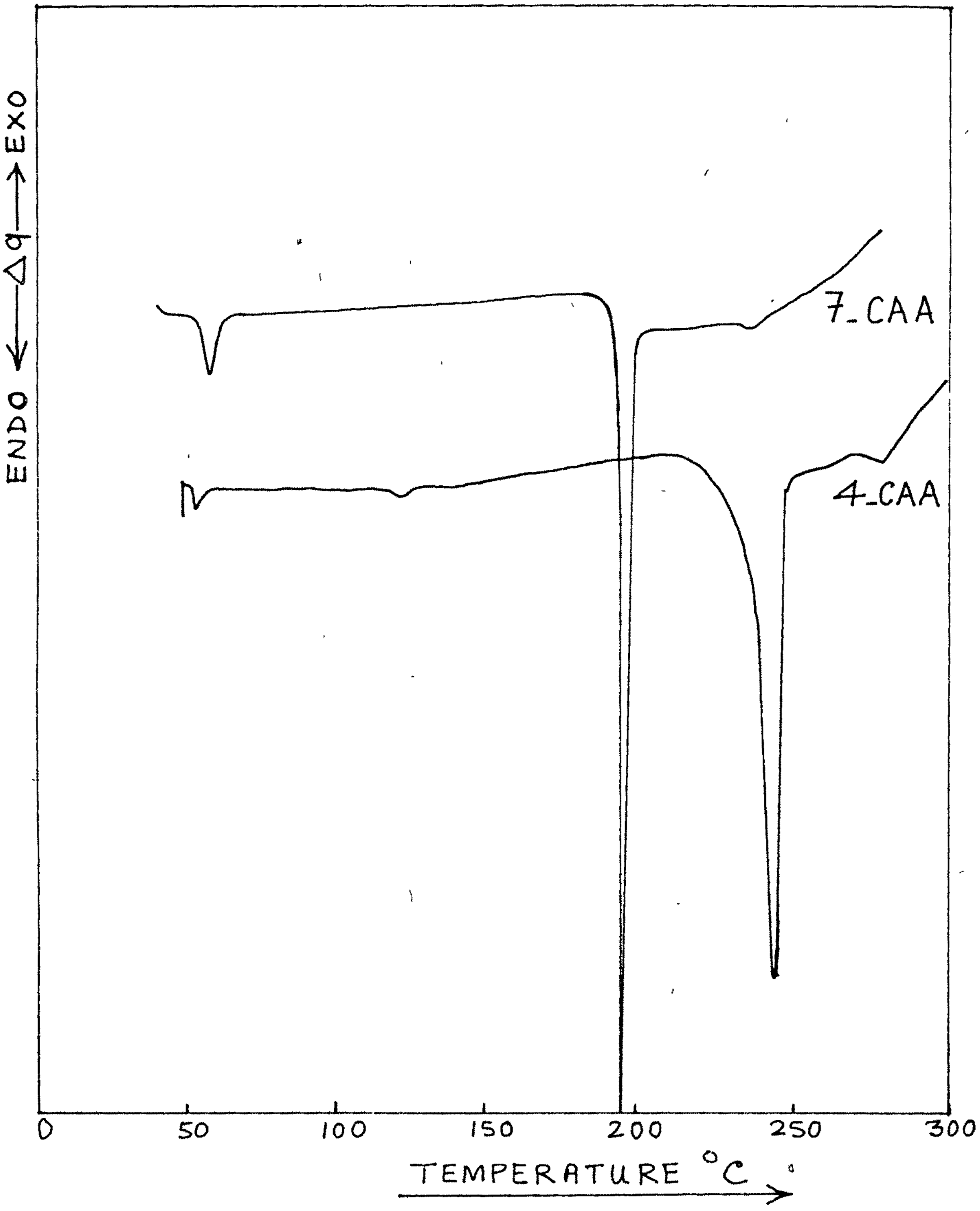
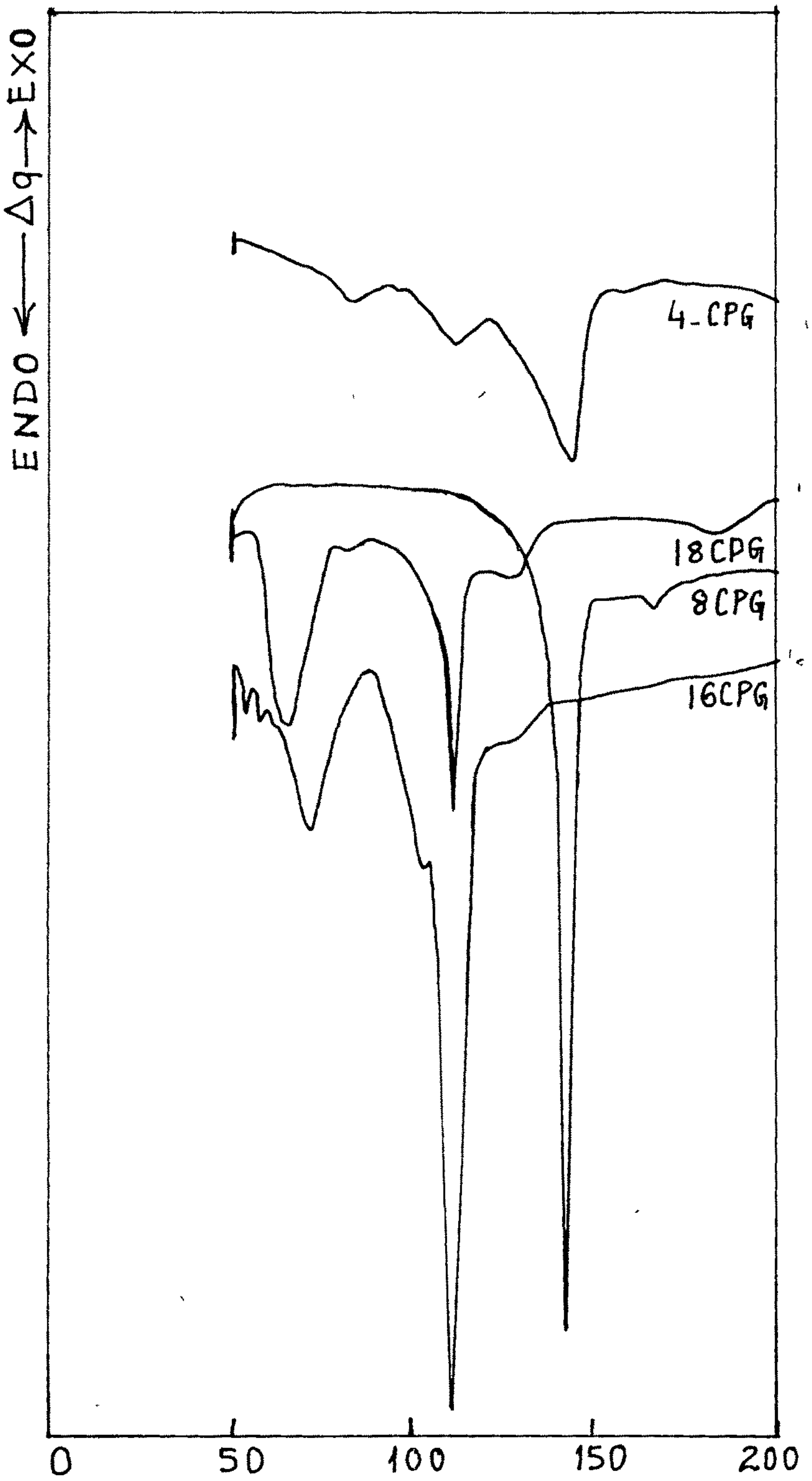


FIG:18 INTRINSIC VISCOSITY OF POLYMER BY GRAPHICAL METHOD



DSC (HEATING RATE 10°C / MIN.)

FIG. 19



DSC (HEATING RATE 10°C/MIN.)

FIG. 20

4. RESULTS AND DISCUSSION

1. HOMOLOGOUS SERIES WITH ONE OR TWO AMIDO CENTRAL LINKAGES

A number of mesogenic homologous series are reported having -COO-, -CH=N-, -N=N-, -CH=CH-, $-N{=}\underset{O}{\underset{\downarrow}{N}}-$, -CH=CH-COO-, -C≡C-, etc. groups as central linkages. Many mesogenic homologous series contain two central linkages, both of them may either be ester (324, 325) or azomethine groups (326) or one of them may be ester and the other azomethine (327, 328).

Many of the mesogens recently reported have central linkages (329, 330) like $-OCH_2-$, $-CH_2-CH_2-$ etc. which were considered to be non-conducive to mesomorphism. The -CO-NH- central linkage was also considered to be non-conducive to mesomorphism. However, from our laboratory, we have earlier reported mesogenic homologous series having amido (-CO-NH-) group as one of the central linkages (311, 331 - 333).

Neither Brown and Shaw (9) in their review on "Mesomorphic State" nor Gray (126) in his classical monograph on liquid crystals have suggested amide group to be conducive to mesogenic properties. This may probably be the reason for rarity of mesogens with amide linkage. Gray (334) in the review of structural requirements for mesogens has expressed the opinion that if there are more than two benzene rings and one of the middle group is conducive to mesogenic structure, then the introduction of a group like -NH-CO- would result in a thermally less stable liquid crystal compared to others where both the middle linkages are conducive to mesogenic character. Brown (129) has also mentioned that compounds with -CONH- may exhibit mesomorphism.

Liquid crystalline order in polymers is of great interest and importance. Many of these polymers are having amide linkage. Model compounds exhibiting mesomorphism and having an amide group would be of interest to understand the mesogenic behaviour of such compounds. Moreover the results of Vora et al., (311, 331, 333) on a mesogenic series having an ester and amide central linkages have shown that contrary to the expectation the smectic and nematic thermal stabilities are increased compared to the homologous series having an ester or an azomethine central linkage, this lead us to synthesize some more series where linearity was changed to assess the strength of amido linkage to induce mesomorphism.

Recently (335) some mesogenic model compounds with amido linkage have been reported. However, the mesogenic series with two amido central linkages are rare as amide linkage will raise the melting point due to its high anistropy. It was also proposed to synthesize homologous series with two amido groups and with bulky lateral substituents to bring down the melting points of the homologues.

Series - I. 1,3-Bis(4'-n-alkoxy benzoyl) amino phenols.

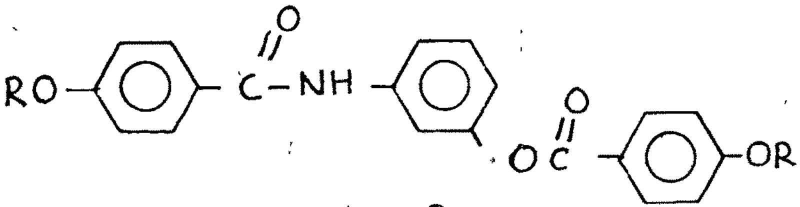
Ten compounds were synthesized by changing the terminal alkoxy group. The central linkage has meta (-1,3-) substitution which imparts non-linearity to the molecules. None of the members exhibit mesomorphism. The compounds have high tendency to crystallize from the melt hence supercooling is not sufficient to induce "monotropic phase".

Series - II 1,3-Bis(trans-4'-n-alkoxy cinnamoyl) amino phenols

Five members were synthesized to varify whether the series exhibits the mesomorphism or not. All the five homologues are non-mesogenic. The compounds were selected in a manner that it covers the range of homologous series.

Common features of Series I and II

The molecules of Series I and II are non-linear as shown in Fig.21


(I)

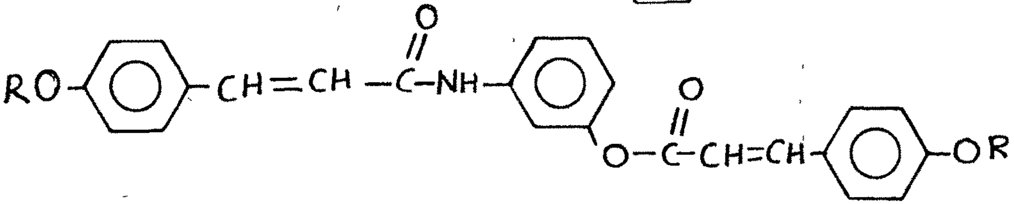
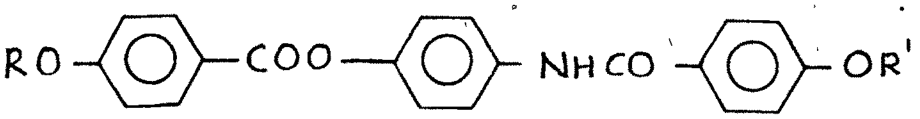

(II)

Fig. 21

Vora et al., have reported (311, 331 - 333) number of mesogenic homologous series with ester and amide linkages with the general structure given in Fig. 22



R & $R' = C_nH_{2n+1}$, Symmetrical and Unsymmetrical

Fig. 22

All these homologous series exhibit rich mesomorphic properties. Encouraged by this it was thought worth trying to synthesize homologous series I and II with unsymmetrical central phenylene unit. However, the non-mesomorphism of series I and II have indicated that non-linearity of the central phenylene unit (1,3-substitution) is highly deterrent to mesomorphism. It might be possible to induce mesomorphism in such non-linear system by introducing more phenylene units.

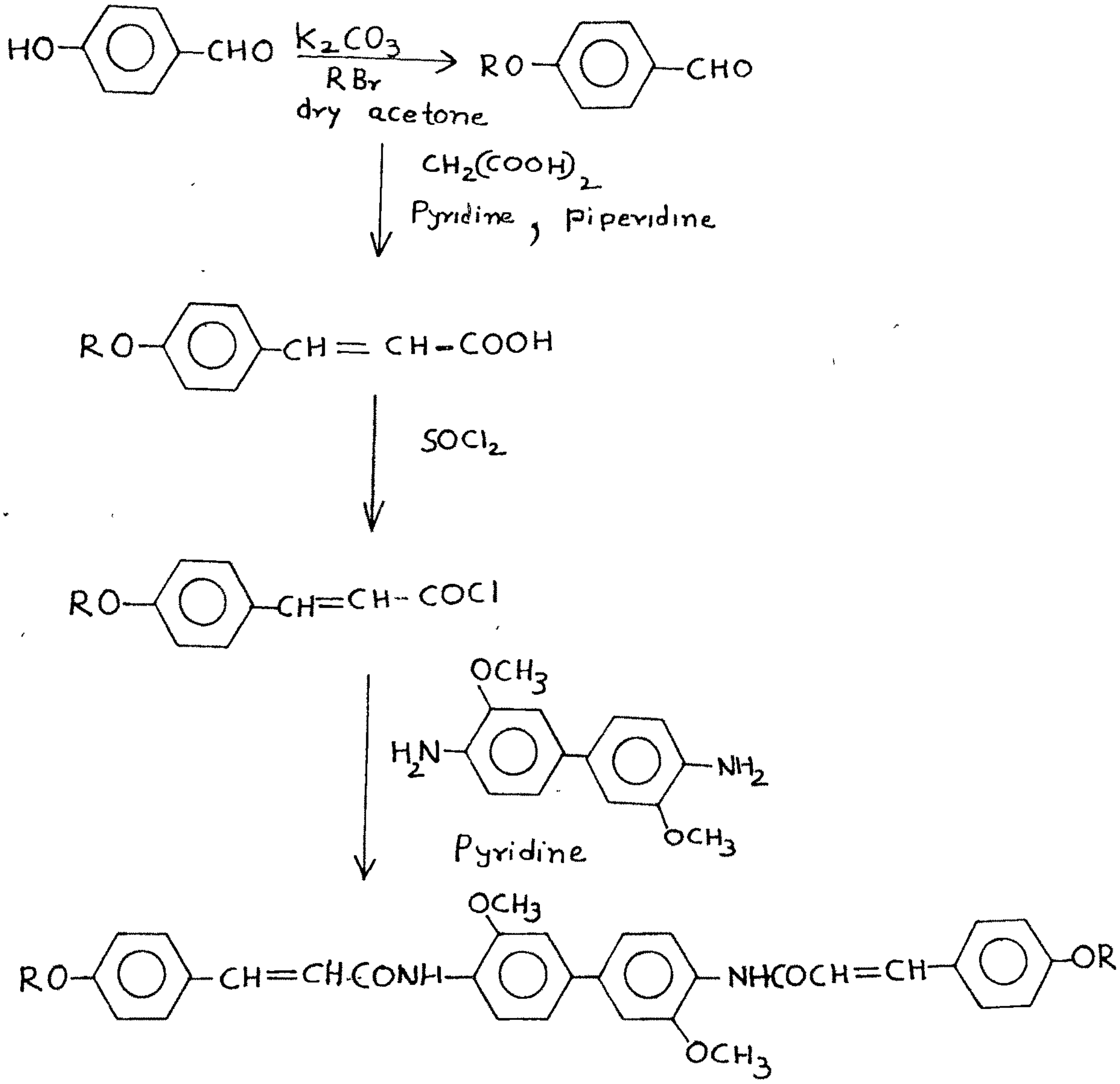
The above discussion explains non-mesomorphism of series I and series II.

Series - III 3,3'-Dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl) benzidines.

Ten members of the homologous series were synthesized by the route as shown in Fig. 23 and their mesomorphic properties were evaluated.

With reference to Table-6 first member starts decomposing from 260 °C. n-propyloxy to octyloxy homologues exhibit nematic phases only. smectic phase commences from decyloxy derivative. The nematic phase persists even upto the hexadecyloxy member. One of the homologues, octyloxy derivative exhibits one crystal-crystal change.

The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (Fig. 24) shows usual odd-even effect for the nematic - isotropic transition temperaturs, where even members fall on the upper nematic-isotropic transition temperature curve. The nematic phase



SERIES-III

FIG. 23

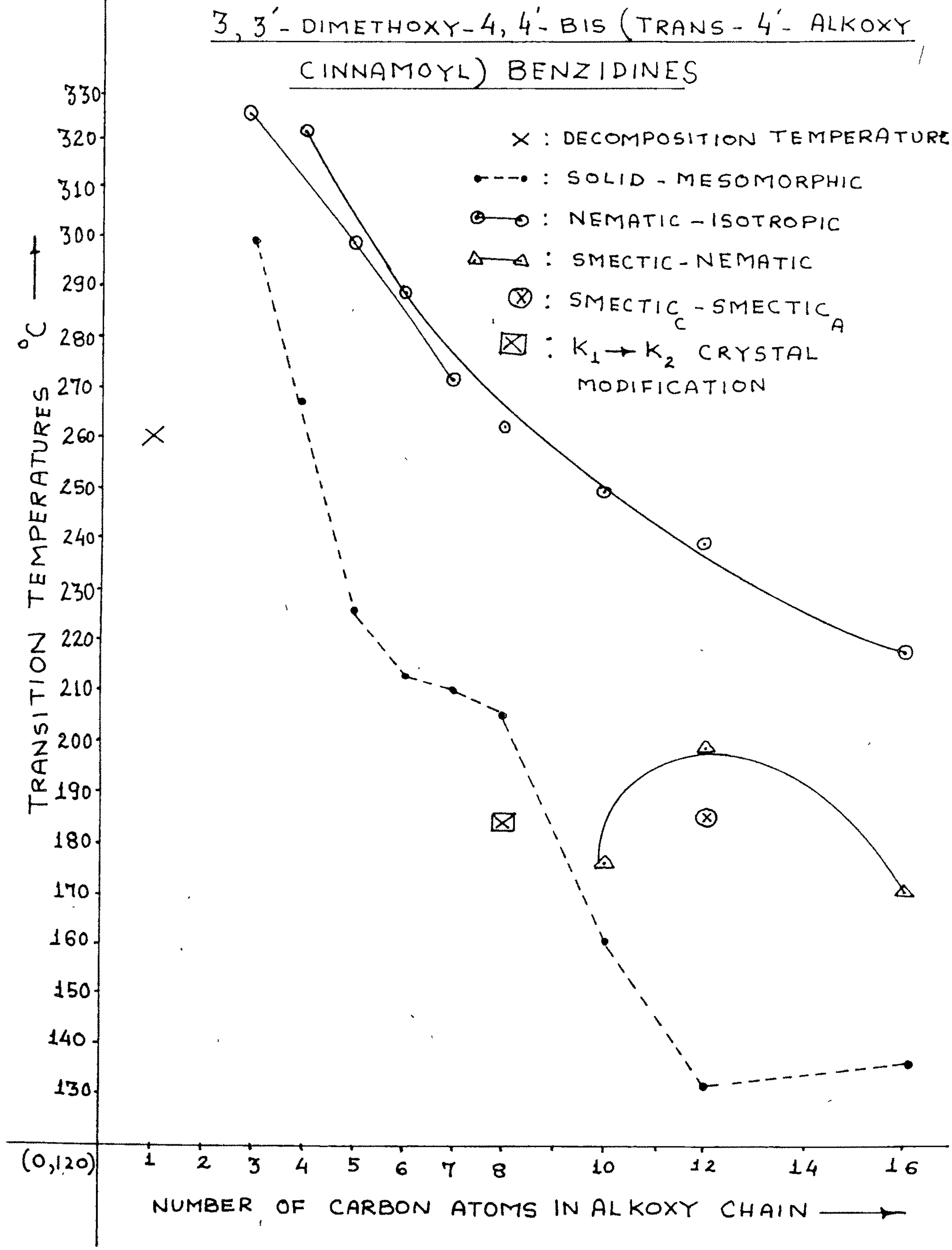

3,3'-DIMETHOXY-4,4'-BIS (TRANS-4'-ALKOXY CINNAMOYL) BENZIDINES
× : DECOMPOSITION TEMPERATURE
•- - -• : SOLID - MESOMORPHIC
⊙—⊙ : NEMATIC - ISOTROPIC
△—△ : SMECTIC - NEMATIC
⊗ : SMECTIC C - SMECTIC A
☒ : K1 → K2 CRYSTAL MODIFICATION
TRANSITION TEMPERATURES °C
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
(0,120)
1
2
3
4
5
6
7
8
10
12
14
16
NUMBER OF CARBON ATOMS IN ALKOXY CHAIN

FIG 24

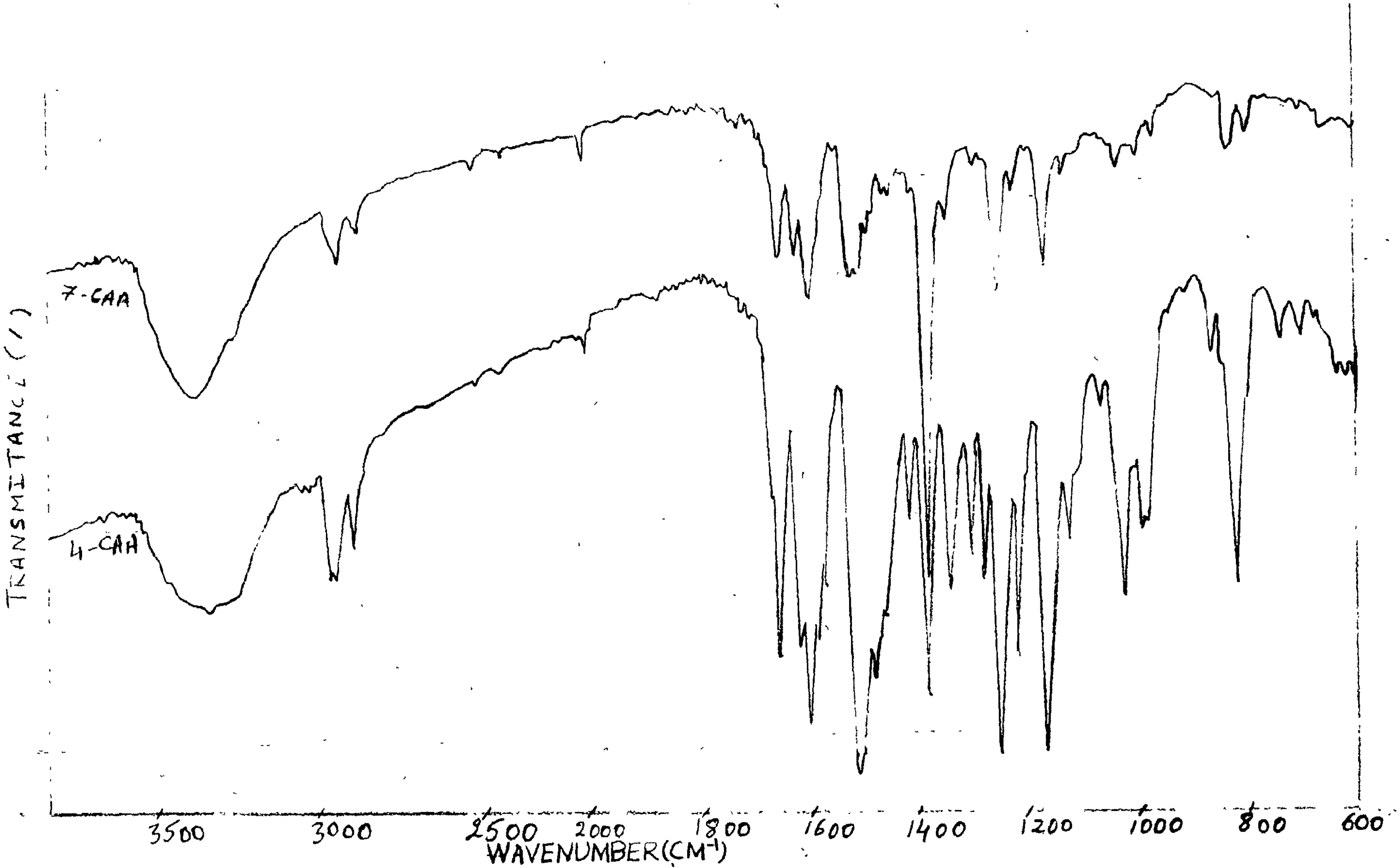


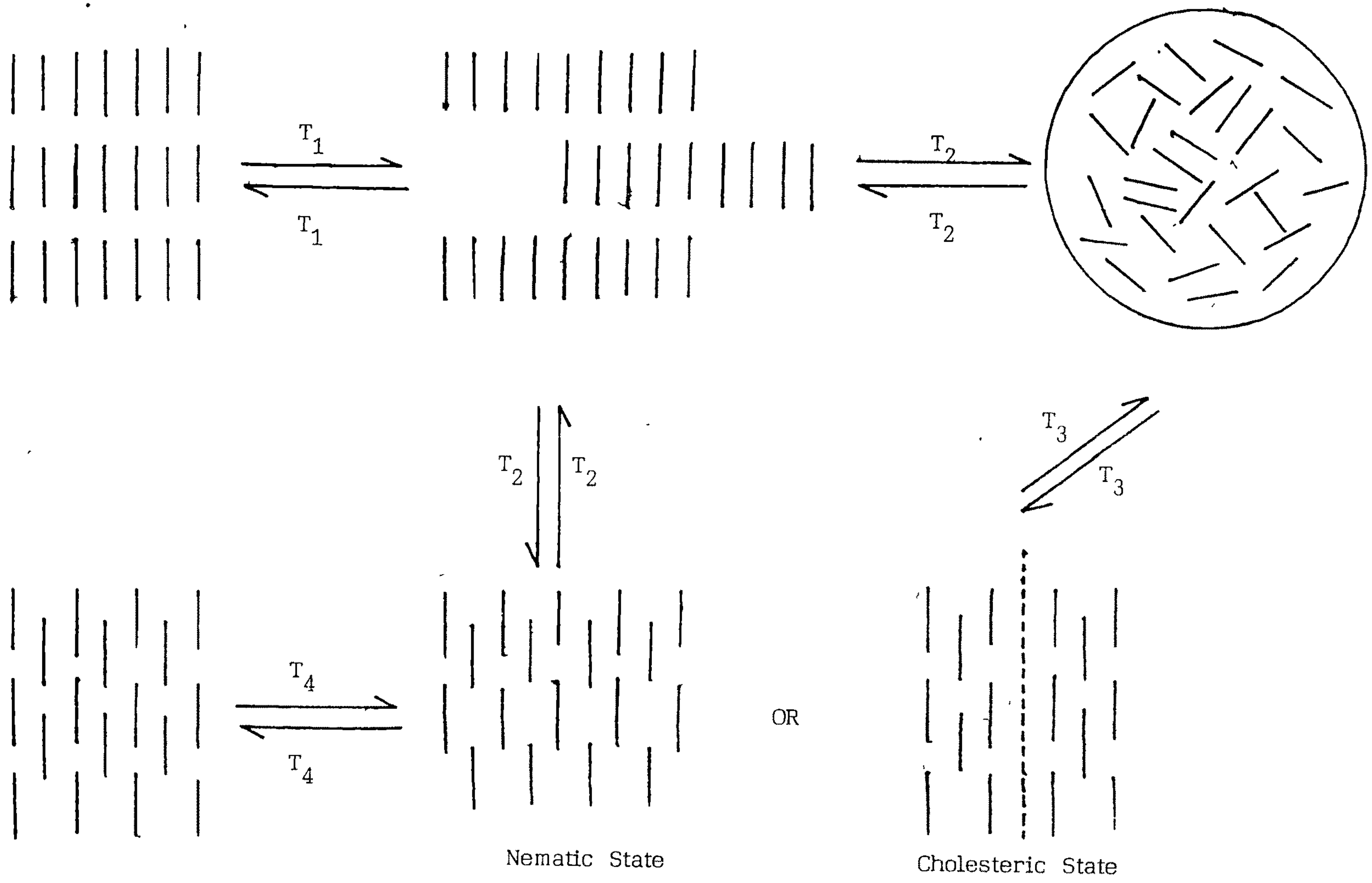
FIG: 24a. IR SPECTRA OF 3,3'-dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl)benzidines persists upto the last member of the series, hence smectic-nematic curve does not merge with nematic-isotropic curve even upto the last members of the series. IR spectra is given in Fig. 24 a.

The nematic-isotropic transition temperature curve exhibits descending tendency as the series is ascended. The smectic-nematic transition temperature curve rises to the maximum and then falls off.

The molecules, forming liquid crystals, generally possess the basic skeleton of relatively rigid aromatic or alicyclic rings with alkoxy or alkyl chains attached to one or both the ends within the isotropic or nematic phases, different regions of each molecule are continuously in contact with parts of neighbouring molecules. The energy of the system depends on different conformations of molecules, London Van der Waals dispersive forces between the neighbouring molecules and on steric repulsions between different molecules (336). For the mesogenic homologous series, Gray (337, 338) has successfully used the concepts of molecular arrangement and complex molecular interactions with lateral and terminal attractions between neighbouring molecules. These ordering forces, which are strongly dependent on molecular separations, have to compete with disordering thermal fluctuations.

Due to the presence of balancing lateral and terminal cohesions and long lath-like molecules, mesogenic compounds melt in stages. They pass through one or more ordered intermediate stages before changing to isotropic liquid phase. The molecular layer structure of the smectic phase occurs in temperature regions where lateral attractions dominate, while the parallel molecular arrangement of nematic phase occurs in a temperature interval with predominant terminal attractions. Thus at the crystal-smectic transition, the primary terminal cohesions of the molecules are overcome and at the smectic-nematic or smectic-cholesteric change, the strong lateral attractions are overcome, and a nematic or cholesteric mesophase is formed. The molecules, either in the nematic or in the cholesteric mesophase are maintained by the residual lateral and terminal cohesions. On further heating all the Van der Walls forces are again broken down and the molecules pass into randomly arranged isotropic liquid state. These changes can be represented schematically as shown in the figure (Fig.25).

In a mesomorphic homologous series, usually the mesomorphic-isotropic transition temperatures change in a regular manner. The increment of each methylene unit brings about regular changes in the transition temperatures of the series. Gray (126) has explained this behaviour by taking into consideration the chain-length of terminal alkyl or alkoxy group. As the alkoxy or alkyl chain is lengthened, the separation of the aromatic centres, which are highly polarizable and have permanent dipolar substituents, is increased; consequently there should be a decrease in the strength of the terminal intermolecular cohesions. However, Gray (126) and Maier and Baumgartner (339) have suggested that the addition of each methylene unit simultaneously increases the overall polarizability of the molecules and the lateral intermolecular attractions. The lower homologues are purely nematic, i.e., for the short chain-length compounds, the separation of the aromatic nuclei is at a minimum and the terminal cohesions are strongest. As we ascend the series, smectic phase commences from the middle members of the series, because as the alkyl chain-length



Arrangement of Lath-like molecules in various states of matter.

Fig. 25

increases, the lateral cohesive forces are also increased and the molecules align themselves in the layered structure before passing to nematic phase. Hence, with increase in the alkyl chain-length, the smectogenic character should predominate at the expense of nematic mesophase. Therefore, in a homologous series, at a certain chain-length of alkyl group, no nematic mesophase would be observed and system would exhibit pure smectic phase. At this stage, smectic mesophase will directly pass into isotropic liquid state, presumably because the terminal intermolecular attractions are inadequate to maintain the parallel molecular orientation, required for the nematic mesophase. This is the general pattern observed for a normal nematogenic homologous series.

A number of other homologous series, however, do not behave exactly as discussed above. In the cholesteric homologous series, the earlier members with shorter alkyl chains exhibit pure cholesteric mesophase, while the higher homologues exhibit both the smectic and cholesteric mesophases. In lower homologues, the terminal cohesive forces are relatively strong, with the increase in alkyl chain-length, the lateral cohesive forces increase and the molecules can align themselves in parallel layered arrangement, before cholesteric mesophase commences at higher temperatures. The cholesteric systems differ from normal nematogenic series in one aspect, i.e., the last members of nematogenic series exhibit purely smectic mesophases, while those of cholesterogenic series exhibit smectic mesophases along with the cholesteric phase. This may be attributed, possibly to the broad and flat cholesterol moiety.

In the case of series 4-n-alkoxybenzylideneaminofluorenones and 4-n-alkoxybenzylideneaminobiphenyls, having substitution in 2 or 3 positions (326) and 2-methyl-1,4-phenylene bis (4'-n-alkoxybenzoates) (324), the last members of the series do not exhibit pure smectic mesophases. In all the above mentioned series, the steric effect increases the thickness of the molecules. This should make it more difficult for the molecules to pack economically side by side in a parallel alignment and should result in a weakening of the lateral intermolecular cohesions. Thus even at the octadecyloxy derivative the smectic-nematic curve does not merge with the nematic-isotropic curve. Dave et al., (340 - 342) have studied a number of napthylidene Schiff bases and have evaluated the affect of broad naphthalene nucleus. They have reported that in all these series, even the last member is not purely smectic, but exhibits polymesomorphism. This can be attributed to the increase in breadth which reduces lateral cohesive forces and to exhibit pure smectic mesophase, the lateral cohesive forces should be much higher than the terminal cohesive forces. In such systems, even in the last member, the molecules are so arranged that on heating, the molecular layers slide over one another and do not get disrupted to the disordered isotropic state, but pass to the nematic mesophase. A nematic phase is thus obtained from the smectic mesophase, on further heating the disruption is complete to give the isotropic liquid. However, there are also a number of homologous series exhibiting pure nematic mesophase upto the last member of the series, without the commencement of the smectic phase (126, 327, 343, 344). All these series contain a lateral substituent, which increases the breadth of the molecules to such an extent that the economical packing of the molecules is not achieved to give a smectic mesophase.

The homologous series reported by Vora et al., (309), have a bulky methoxy group as a lateral substituents, ortho to the ester linkage. Due to the steric interaction, naturally the molecules of these series would be more acoplanar and broad. Decreased planarity and increased breadth of the molecules render three of the series purely nematic, with an exception of a series, where the end ethyl group is a smectogenic group, i.e. it increases the smectogenic tendencies of the homologous series. The octadecyloxy derivative exhibits a monotropic smectic mesophase, in addition to the nematic mesophase.

The alternations of nematic-isotropic transitions (odd-even effect) have been discussed by different workers. Gray (337) has tried to explain such behaviour for nematic-isotropic transitions in terms of the conformation of the alkyl chain. He has considered the Zig-Zag conformation for the alkyl chain, as evidenced from the X-ray studies of crystalline state of some liquid crystalline compounds.

The increase in chain-length will have the following effects and the nematic-isotropic transition temperatures will be determined by those effects which predominates :

(i) The longer molecules will be rotated less readily out of the ordered state.

(ii) The overall polarizability increases with each added methylene unit.

(iii) The frequency with which readily polarizable aromatic parts of the molecules lie next to one another in the fluid nematic melt will decrease i.e., the residual lateral attractions will tend to decrease.

(iv) Each methylene unit forces apart polarizable centres in the molecules and decreases the residual terminal attractions.

Effect (i) and (ii) would increase the nematic-isotropic transition temperatures and (iii) and (iv) would decrease the nematic-isotropic temperatures. Thus rising transition lines are obtained where the effects (i) and (ii) predominate and vice versa. Keeping this in view, the rising mesomorphic-isotropic transition lines are found in the series whose transition temperatures are low, and the residual attraction are weak. Gray has explained the alternation of nematic-isotropic transition temperatures by a diagramatic representation of the possible relative orientations of terminal methyl groups in an end-to-end packing of the molecules of n-alkyl aryl ethers, such as p-n-alkoxybenzoic acids. For short alkyl chains, if the chain extends strictly along its own axis (dotted line in Fig.26), then the terminal methyl groups present different faces to one another or to other groups in the molecules depending on whether the chain is even or odd. The different resultant attractive forces could affect the energy of the system and account for an alternation of the transition temperatures.

With the higher homologues the alkyl chain may be forced (curved arrow in Fig. 26) into line with the main axis defined by the more rigid aromatic parts. Gradually the end groups contact would become the same in nature for odd and even carbon chains, and can explain the petering out of the alternation as the series is ascended. So far, the effects of changes in terminal attractions between the molecules on the nematic-isotropic transition temperatures have been considered, but the effect of residual lateral interactions between the molecules, which would also play some role in determining the thermal stability of the nematic mesophase, has not been discussed.

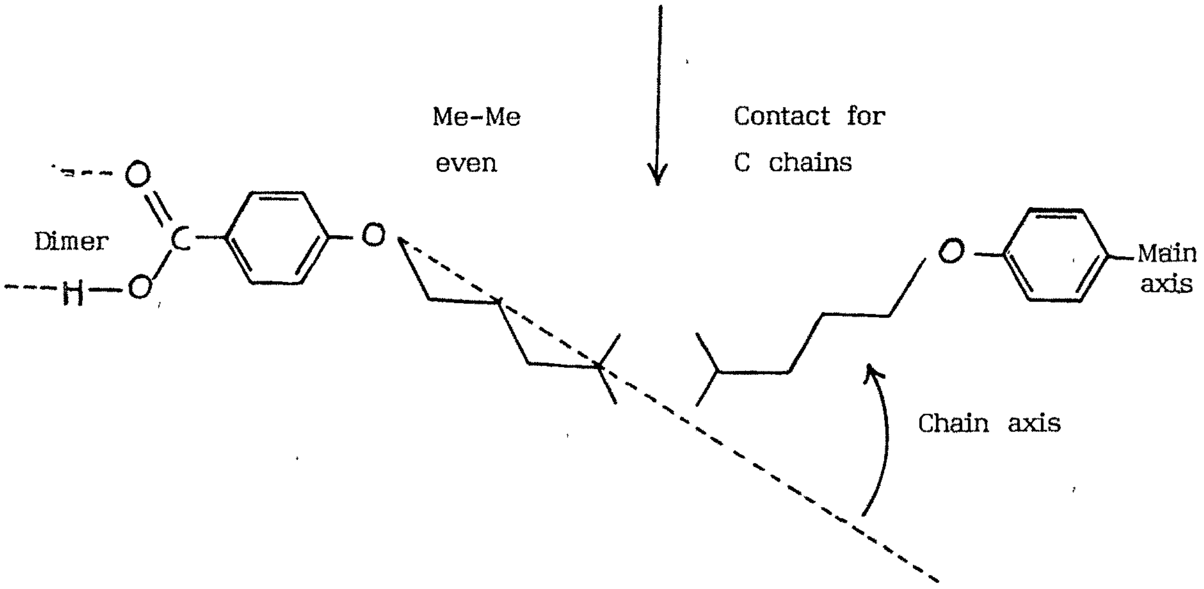


Fig. 26

Maier (345) and Maier and Baumgartner (339) have also tried to explain the alternation effect on the basis of their study of the dipole moment and dielectric anisotropies of a nematogenic homologous series.

Marcelja's (336) theory explains the odd-even effect in isotropic-nematic transition temperatures and entropies. From the geometry of p-P-di-n-alkoxyazoxybenzenes, they have shown that the addition of carobn atom C_2, increases the anisotropy of the molecule and helps the ordering process, subsequent addition of atom C_3 hinders the ordering, atom C_4 helps again, and so on. As the chains becomes longer, their flexibility makes the effect progressively smaller until for long end chains, it becomes unnoticeable. Pines et al., (346) have measured the order parameters in a series of nematic liquid crystals p-alkoxy azoxybenzenes, by ^{13}C NMR. The ordering exhibits an odd-even alteration along the series. They conclude that the benzene rings rotate or flip about the para axes, at a rate greater than 1 KHz for the whole series, throughout the nematic ranges.

de Jeu and Van der Veen (347) have reviewed some experimental results on the variation of the nematic-isotropic transition temperatures T_{NI} and evaluated molecular structure with the aid of expressions for T_{NI}, from molecular statistical theories.

There is a close relationship between mesomorphism and molecular constitution of organic compounds. Hence, the thermal stability - a measure of mesomorphism - can be correlated with the molecular constitution of the compounds.

Table 27 summarizes the average thermal stabilities of :

i) 3,3'-dimethoxy-4-4'-bis(trans-4-n-alkoxy cinnamoyl) benzidines. and are compared with those of: (III)

ii) 3,3'-dimethoxy-4-4'-bis(4-n-alkoxy benzoyl) benzidines (348). (A)

iii) 2,2'-dimethyl-4,4'-bis(4-n-alkoxy-benzylideneamino)-biphenyls (349). (B)

iv) 2,5-dimethyl-4,4'-bis(4-n-alkoxy-benzylideneamino)-biphenyls (349). (C)

TABLE - 27

Average Thermal Stabilities

Series	III	A	B	C	D	E
Nematic-Isotropic C_7 - C_{10}	260.67	216.33	184.75	213.50	217.90	221.67
Smectic-Nematic Or Isotropic C_{10} - C_{12}	187.50	161.50	-	-	-	211.00

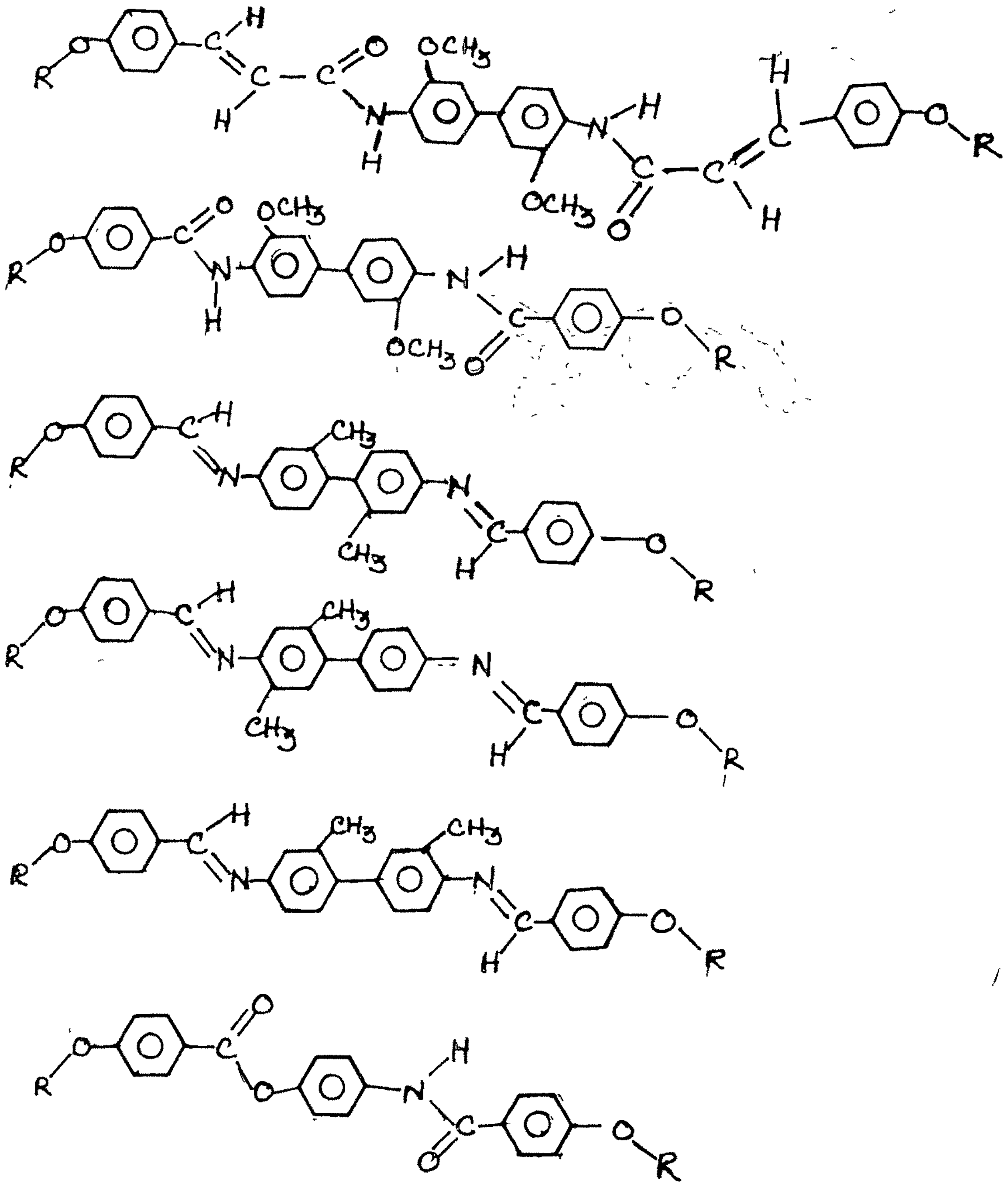
v) 2,3'-dimethyl-4,4'-bis(4-n-alkoxy benzylidene-amino) biphenyls (349). (D)

vi) 1,4-bis(4'-n-alkoxy benzoyl) amino phenols (311). (E)

The geometry of these series are given in Fig. 27

The reference to Table 27 shows that smectic and nematic thermal stabilities of series - III are higher than those of series A. Difference in the two series is in two central linkages (Fig. 27) . Series - III has -CH=CH-CONH- linkages whereas series A has -CO-NH- linkages. The trans -CH=CH- group increases the length and polarizability of the systems. Naturally it will enhance the nematic thermal stability. Vora et al., (311, 331 -333) have observed in number of different systems that eventhough two series differ by trans -CH=CH- group, the difference in the thermal stability is not uniform. Most of these systems contain one -CH=CH- group, whereas series-III has two trans -CH=CH- groups.

The smectic thermal stability of series-III is higher than that of series A. As explained above the molecules of series-III are longer and polarizable due to the presence of trans -CH=CH- group. Naturally, these factors will enhance the smectic thermal stability also. However, the trans- -CH=CH- group will increase little breadth of the molecules which is deterrent to smectic mesophase. Due to this reason the enhancement in nematic thermal stability of series III is of 51°C whereas it is 21.9°C in the case of smectic thermal stability.



[III]

[A]

[B]

[C]

[D]

[E]

FIG. 27

The nematic thermal stability of series B is much lower compared to series - III. Reference to Fig. 27 shows that series-III and A differ in central linkages and in the position and type of the lateral substituents eries III has -CH=CH-CO-NH- linkages, which will enhance nematic stabilities much more compared to -CH=N- linkages due to the high polarizability of the system and possible intermolecular hydrogen bonding as discussed by Vora et al., (33) (Fig. 28). The bulky methoxy lateral substituent in series-III will increase the breadth of the molecules of series III, however, the 3,3'-position of these groups do not impart strain on 1,1'-bond of biphenyl nucleus hence the biphenyl ring remains co-linear. Due to this reason only the breadth increasing effect of $-OCH_3$ lateral substituents will be operative in the molecules of series III. In the case of series B, the lateral $-CH_3$ groups will enhance the breadth of the molecules but the contribution towards increasing the breadth of the molecules will be much less compared to lateral $-OCH_3$ substituents. However, the 2,2'-position of methyl groups will impart strain on 1,1'-bond of biphenyl nucleus. Naturally the acoplanarity of biphenyl nucleus will increase, which will affect the polarizability of the molecules of series B. Over and above that it will increase the thickness of the molecules (126). Both these (126) factors affect nematic as well as smectic thermal stabilities. This explains lower nematic thermal stability of series B compared to series III.

The nematic thermal stability of series C is lower than those of series III. Here again the difference of lateral substituents and the central linkages are similar to series B except the position of lateral $-CH_3$ groups. All the attractive forces discussed above can be applied to this comparison but with one difference. The acoplanarity of bi-phenyl nucleus in series

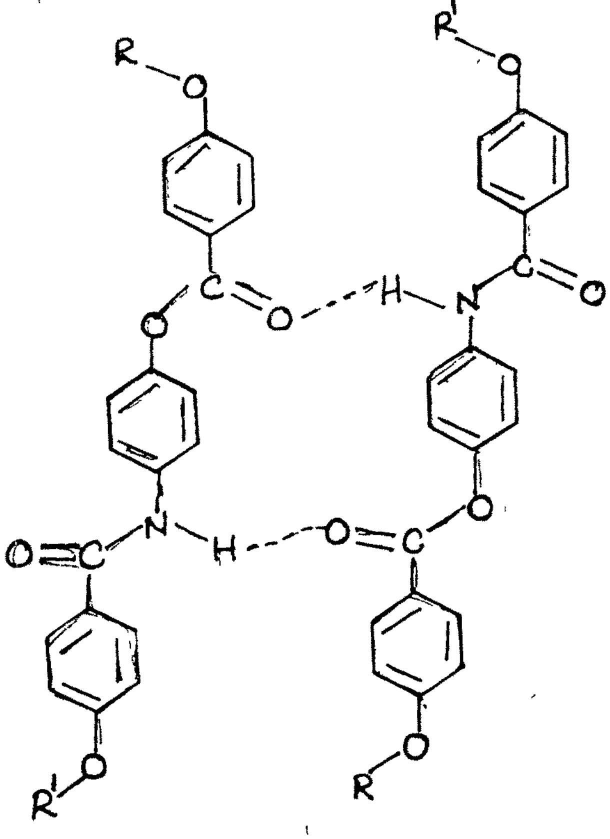


FIG: 28

C will be less compared to series B as the second $-CH_3$ substituents is in position 5, away from the 1,1'-position of biphenyl nucleus. Due to this reason, though the nematic thermal stability of series C is lower than that of series III, but decrease is not as large as is between series III and series B.

The nematic thermal stability of series III and D, differ to almost to the same extent as is with series C. The reference to the geometry (Fig. 27) shows that sereis C and D differ only in the position of one methyl group which is not in 5'-position as is the case with series C but occupies 3'-position. Naturally, the comparison of molecular attractive forces, acoplanarity etc. will be almost the same as is in the case of series C. This explains the difference in thermal stability between series III and D.

The homologues of series B, C and D are known upto the decyloxy member and smectic mesophase does not commence upto the decyloxy member. In the case of series III, smectic mesophase commences from decyloxy member. It has been already pointed out that molecules of series B to D are more acoplanar and thick. The increased acoplanarity and the thickness of molecules affect adversely the smectic mesophase thermal stability as well as the commencement (126), this is the reason for absence of smectic mesophase in series B to D upto decyloxy member.

The nematic thermal stability of series E is lower compared to that of series III. Both the series differ in number of ways. Molecules of series III have two lateral $-OCH_3$ groups, which will increase the breadth of the molecules and will contribute adversely to the mesophase thermal stability. The length and polarizability increase in the molecules of series III due to the presence of two -CH=CH-CONH- groups will be much more compared to -COO- and -CONH$_2$- groups of series E. Out of these two opposing effects, it seems that length and polarizability effects predominate in the molecules of series III, which enhances nematic thermal stability compared to series E.

The smectic thermal stability of series E is higher than those of series III, which is exactly opposite compared to nematic thermal stability. It is known that increase in the breadth of the molecules affect smectic as well as nematic thermal stabilities, but the increase affects more adversely the smectic thermal stability (126). Due to this reason eventhough nematic thermal stability of series III is higher than that of series E, the smectic thermal stability is decreased due to the increase in the breadth of the molecules of series III compared to series E.

The smectic mesophase not only commences from hexyloxy derivative but nematic phase is eliminated from decyloxy derivative in series E. This shows that series E is more smectogenic due to the linear molecules and absence of lateral substituents.

2. MESOGENS WITH POSITIVE DIELECTRIC ANISOTROPY

Compounds with terminal nitro or cyano groups exhibit dielectric anisotropy as their dipole is acting along the long molecular axis. These compounds are finding many applications in display devices (167). Moreover, many compounds with terminal -CN and $-NO_2$ substituents exhibit re-entrant smectic, cholesteric and nematic phases. It was proposed to synthesize some terminally nitro substituted mesogens and to study their mesogenic properties. With this in view different 4(4'-nitrobenzoyloxy)3-methoxy benzylidene -4"-substituted anilines were synthesized and were evaluated for their mesogenic properties.

2.1 4(4'-Nitrobenzoyloxy)3-methoxy benzylidene-4"-substituted anilines.

Nine ester schiff bases were synthesized by changing terminal substituent at one end as shown in Table 8 , out of nine compounds, unsubstituted member and -F, $-NO_2$ and carboxymethyl substituted members are non-mesogenic. Alkoxy, alkyl, carboxyethyl and chloro substituted compounds exhibit mesomorphism.

Number of nitro mesogens are known in the literature. It will be quite interesting to compare the mesogenic behaviour of the schiff bases of the present system with other mesogens having similar structural features to understand the effect of chemical constitution.

TABLE -28

Nematic - Isotropic transition temperatures (°C)

Sr. No.		A	B	C	D	E	F	G	H	I
1.	$-CH_3$	192*	141							
2.	$-OCH_3$	207	–	289*†	201	160	–	–	245	
3.	$-OC_2H_5$	211	–	300*†	222	137	–	123.5		
4.	$-COOCH_3$	202**								
5.	$-COOC_2H_5$	182*					156			264
6.	-F	180**								
7.	-H	168**								
8.	$-NO_2$	201**								
9.	-Cl	200*								

* : Monotropic ; ** : K ⟶ I

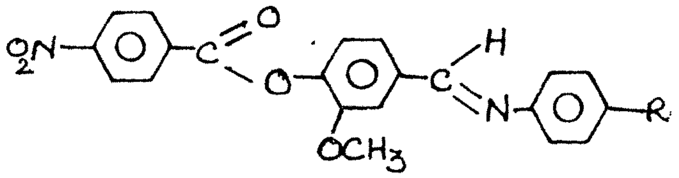
*† : smectic thermal stability (S ⟶ N/ S ⟶ I).

With this in view the smectic/nematic thermal stability of different mesogenic systems are recorded in Table 28 and their geometry is given in Fig. 29.

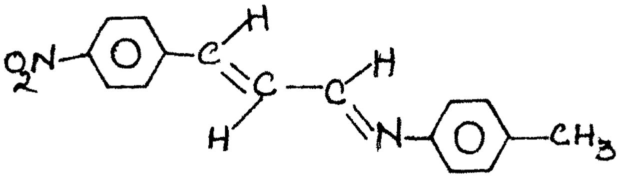
The reference to Table 28 shows that nematic thermal stability of $-CH_3$ substituted mesogen (Sr. No. 1) of present series is higher than that of series B. The reference to the geometry of the molecules of series B (Fig. 29) indicates that present series A has three phenylene units, whereas series B has only two phenylene units. The positive polarizability effect outways the deterrent effects of lateral $-OCH_3$ group of series A, thereby raising the thermal stability (126).

Alkoxy derivatives of series A (Table 28, Sr. No. 2 and 3) exhibit nematic thermal stability whereas the respective members of series C exhibit only smectic phases and of higher thermal stability compared to that of series A. The molecules of series A and C differ only in the lateral substituent and in the positions of terminal groups which are reversed. Naturally, the absence of lateral $-OCH_3$ group in the molecules of series C, imparts it higher thermal stability and smectogenic tendency compared to series A. The lateral $-OCH_3$ group present in series A increases the breadth of the molecules which affects nematic thermal stability (126) as well as the commencement of the smectic phase.

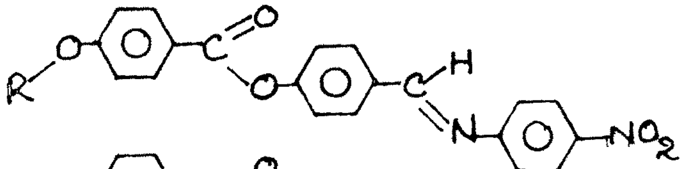
The average nematic thermal stability of alkoxy derivatives of series A (Sr.No.2 and 3) is almost equal to those of series D. Both the series are almost identical, except that the positions of terminal $-NO_2$ and alkoxy



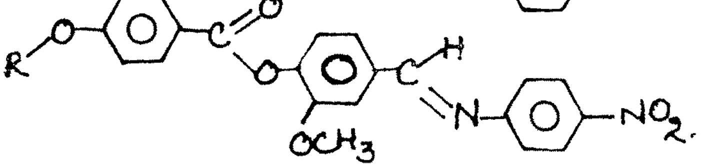
[A]



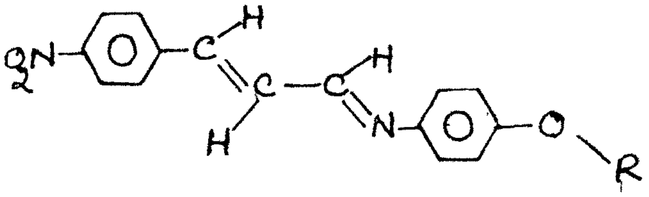
[B]



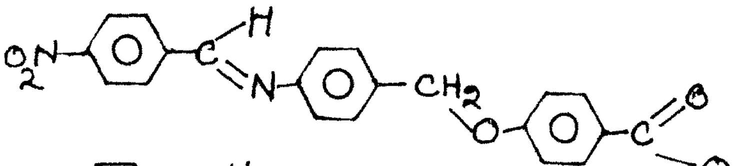
[C]



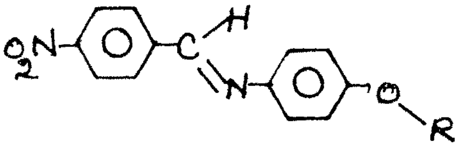
[D]



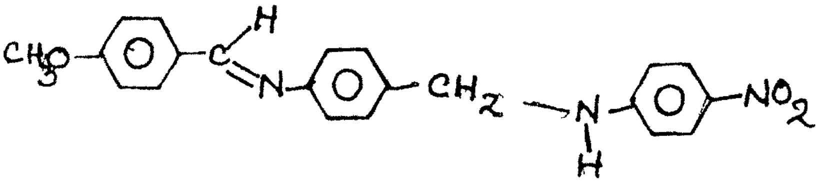
[E]



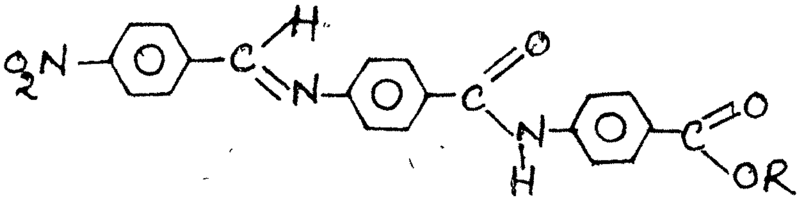
[F]



[G]



[H]



[I]

FIG. 29

groups are reversed. Due to this reason there is a few degree difference in both the members, but the average thermal stability differs by only few degrees.

The nematic thermal stability of methoxy and ethoxy derivatives of series A are higher than those of series E and G. The molecules of series A have one phenylene unit more compared to series E and G, and as discussed above this will enhance nematic thermal stability of series A compared to series E and G, eventhough lateral $-OCH_3$ group is present in series A.

The $-OCH_3$ derivative of series A, exhibits lower nematic thermal stability compared to that of series H. The two series differ in one central group. Series H has $-CH_2-NH-$ group, whereas series A has -COO- central group. The effect of central $-CH_2-NH-$ group is not much known, but the deterrent effect of lateral $-OCH_3$ group on mesomorphism is known. As discussed above this group contributes in the decrease of nematic thermal stability compared to that of series H.

Thermal stability of ethoxy derivative of series A (Sr.No.3) is much higher than that of series G. The molecules of series A are longer by one phenylene unit and -COO-linkage compared to series G. The length of molecules and polarizability will increase the thermal stability of series A compared to series G. It seems that the length and polarizability effects outweighs the deterrent effects of lateral methoxy group.

Out of the carboxy methyl and carboxyethyl derivatives, ethyl derivative gives monotropic phase whereas methyl ester is non-mesogenic. The monotropic transition temperatures observed in compound no. 5 (Table 28) is lower than that of series F (352). Two series differ in one central group and the lateral $-OCH_3$ group. Compound no. 5 of series A contains -COO- central linkage, whereas the member of series F has flexible $-CH_2-O-$ central linkage. It is known that flexible central linkage reduces the mesogenic thermal stability (126). the reduction is quite large explaining the lower thermal stability of series F compared to that of series A.

The molecules of series a have an ester linkage compared to molecules of series I, which possess -CONH- central linkage. It has been known that due to its linearity and high polarizability it enhances mesomorphism of system compared to -CH=N- central linkage. Moreover molecules of series-A have lateral $-OCH_3$ group which reduces the thermal stability. Due to these two negative effects operating in the molecules of series A, the member of series I exhibits much higher thermal stability compared to the member (Sr. No. 5) of series A.

The study has provided mesogens with positive dielectric anistropy and helped to understand the effect of different substituents on mesomorphism.

3. DISCOTIC COMPOUNDS

Number of discotic systems are now known after the first report of discogens by Chnadrasekhar et al., (17) in 1977. For many years it was believed that five to six substituents with mesogenic chains are essential to exhibit mesomorphism. However, Takennaka and Kusabayashi (355) and Vora et al., (356) reported that compounds having three substituents on benzene ring exhibit discotic mesophases. Lateron Matsunaga et al., (357) have reported some more simpler systems exhibiting discotic mesomorphism.

In the present study in the continuation of previous work, one more system having discotic molecules and exhibiting mesomorphism is investigated.

3.1 1,3,5-tri(trans-4'-n-alkoxy cinnamoyloxy) benzenes.

Seven members from butoxy to oxtadecyloxy derivatives were synthesized. Discotic compounds exhibit nematic type phase from octyloxy derivative. Smectic type phase does not appear upto the last member of the series.

The transition temperatures are plotted against the number of carbon atoms in the alkoxy chain (Fig. 30). The nematic-isotropic transition temperature curve falls steeply upto hexyloxy derivative and then rises a little.

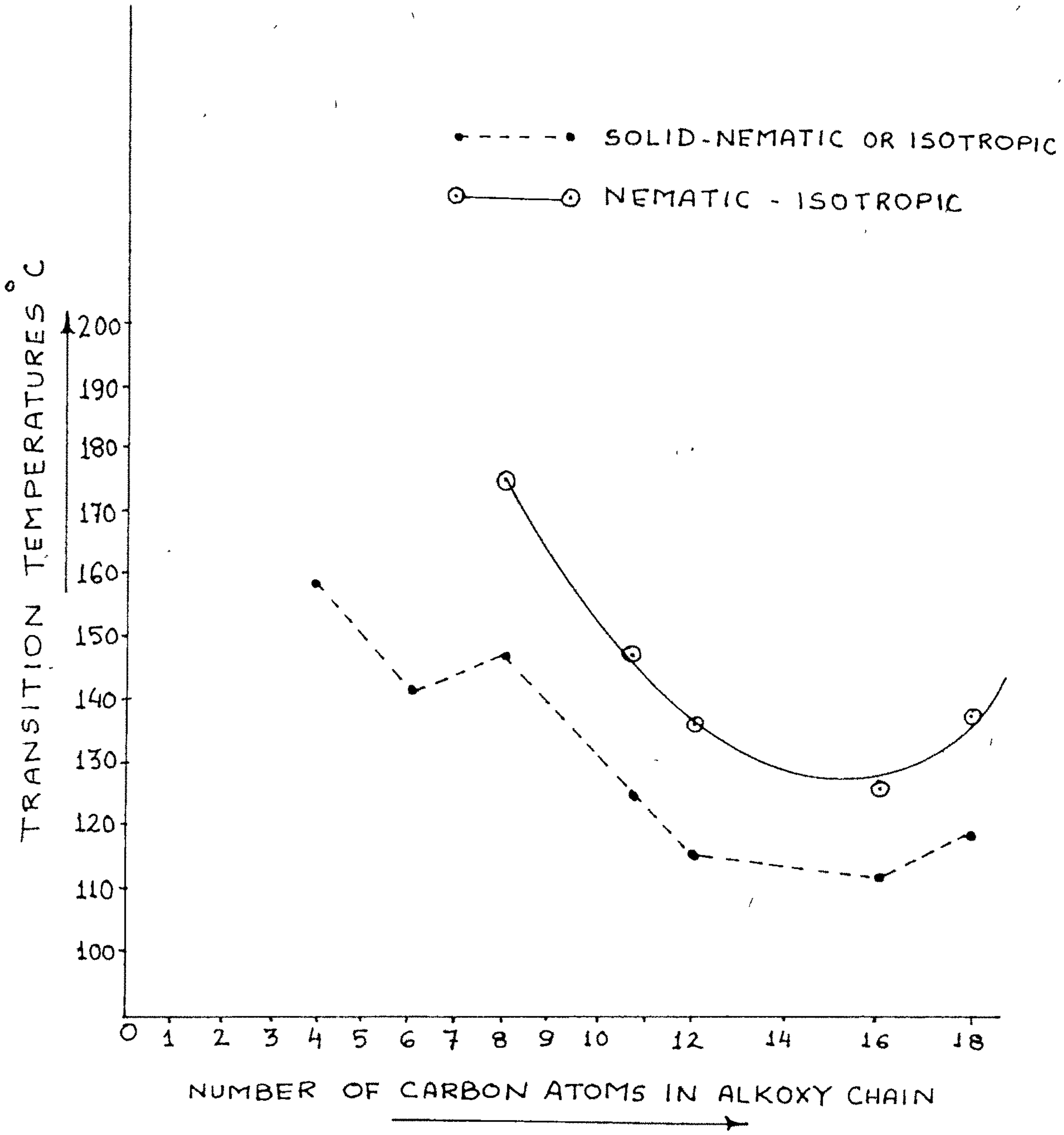


FIG:30
1,3,5-TRI(TRANS-4'-n-ALKOXYCINNAMOYLOXY)
BENZENES

The effect of increase of alkoxy chain on the mesogenic properties of a homologous series with a rod-like molecules has been discussed earlier. Normally increase in the alkoxy chain lowers mesogenic-isotropic transition temperatures as the attractive centres are further separated due to increase in the chain length.

In the case of disc like molecules the trend is the same that as the alkyl/alkoxy chain length increases the mesogenic-isotropic transition temperature decreases. However, it is difficult to interprete without other physical data the effect of chain length quantitatively on the mesogenic tendency of discogens. The general aspect that as the chain lengthens the solid-mesogenic as well as mesogenic-isotropic transition temperatures exhibit decreasing trend holds good. However, in the present system it exhibits a regular falling trend. IR spectra is given in Fig. 30 a.

Comparison of thermal stability of different mesogenic systems provide an understanding regarding the effect of chemical constitution and mesogenic behaviour. Such a comparison in the case of discotic compounds is little difficult, as the exact nature of molecules in different systems are not as straight-forward as in the rod-like molecules. However an attempt is made to correlate the liquid crystalline properties of the present series-I with other related discotic systems.

The nematic discotic phase thermal stability of present series, (Table 29) 1,3,5,-tri(trans-4'-n-alkoxy cinnamoyloxy) benzenes, series-I is compared with other discotic series given in Fig. 31.

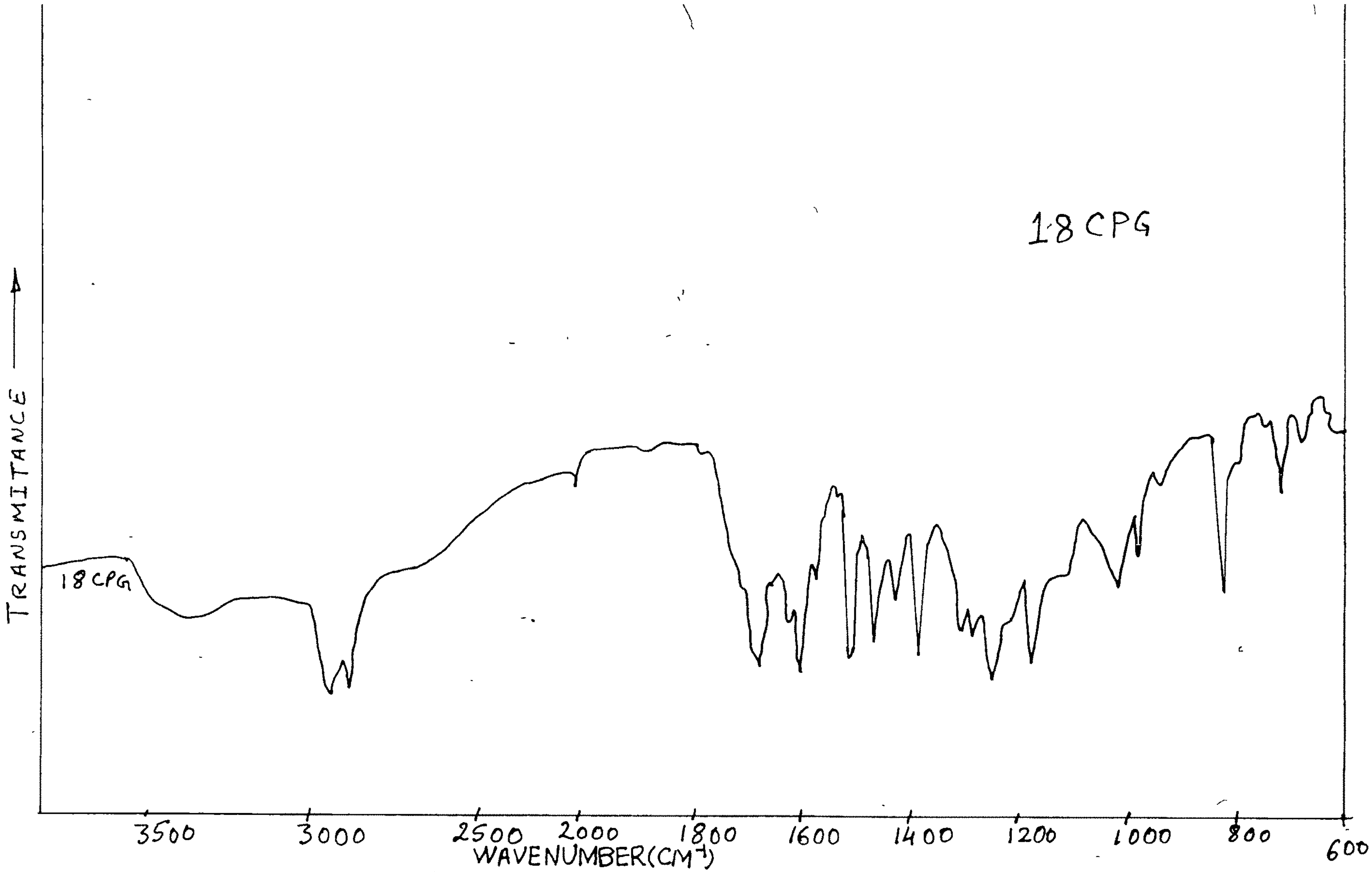

18 CPG
TRANSMITANCE
18 CPG
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
WAVENUMBER(CM⁻¹)

FIG 30 a.

TABLE - 29

NEMATIC-ISOTROPIC TRANSITION THERMAL STABILITY

Series	I	A	D	E	F	G	H	J	K
N-I	161.0	(-22.5)	69.3	83.6	79.15	199	340	121	166
C_8-C_{10}		(C_{10})		(C_5-C_7)	C_8-C_9				(C_8-C_9)

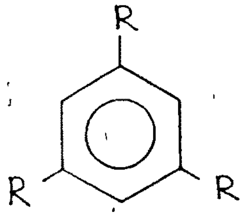
Series B and C are non mesogenic.

Molecules of series-I have identical structure with the molecules of series A,B,C and D, except in the linking groups and the terminal sbustituents.

The molecules of series-I are more polarizable due to the presence of -COO-CH = CH- linkage, which enhances mesomorphism in rod-like molecules (126, 356). The $-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-$ linkage between the central benzene nucleus and substituents provide greater flexibility to adjust or align in orderly manner compared to the molecules of series A, B and D. This is reflected in the mesogenic behaviour of these series. Series-I has higher thermal stability compared to series A and series B is non-mesogenic. However, Vora et al., (356) have reported that higher members of series C are mesogenic in nature and they exhibit little lower thermal stability compared to series-I.

The few homologues of series E and F are mesogenic. Both these series have six substituents on benzene nucleus. Series E has an ether linkage and alkoxy phenylene units whereas series F has aliphatic ester groups. Both these series exhibit lower thermal stability compared to series-I. It seems the steric effect arising out of an ether linkage in series E is responsible for its lower thermal stability compared to series E, which has an ester linkage even though molecules of series E have six substituents (Fig. 31)

In the case of series F, the non-polarizable aliphatic side chain will not contribute much to enhance mesomorphism as compared to polarizable



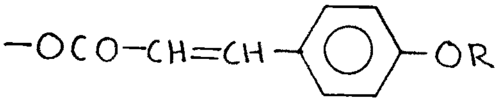
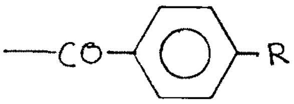
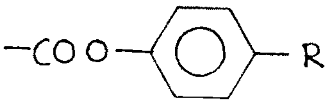
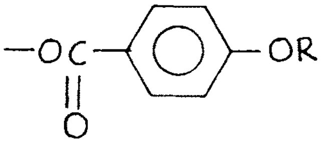
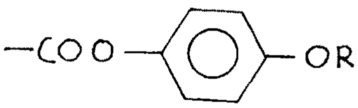
SERIES	R	
I		
A		(355)
B		(355)
C		355)
D		(355)

FIG. 31

Contd---

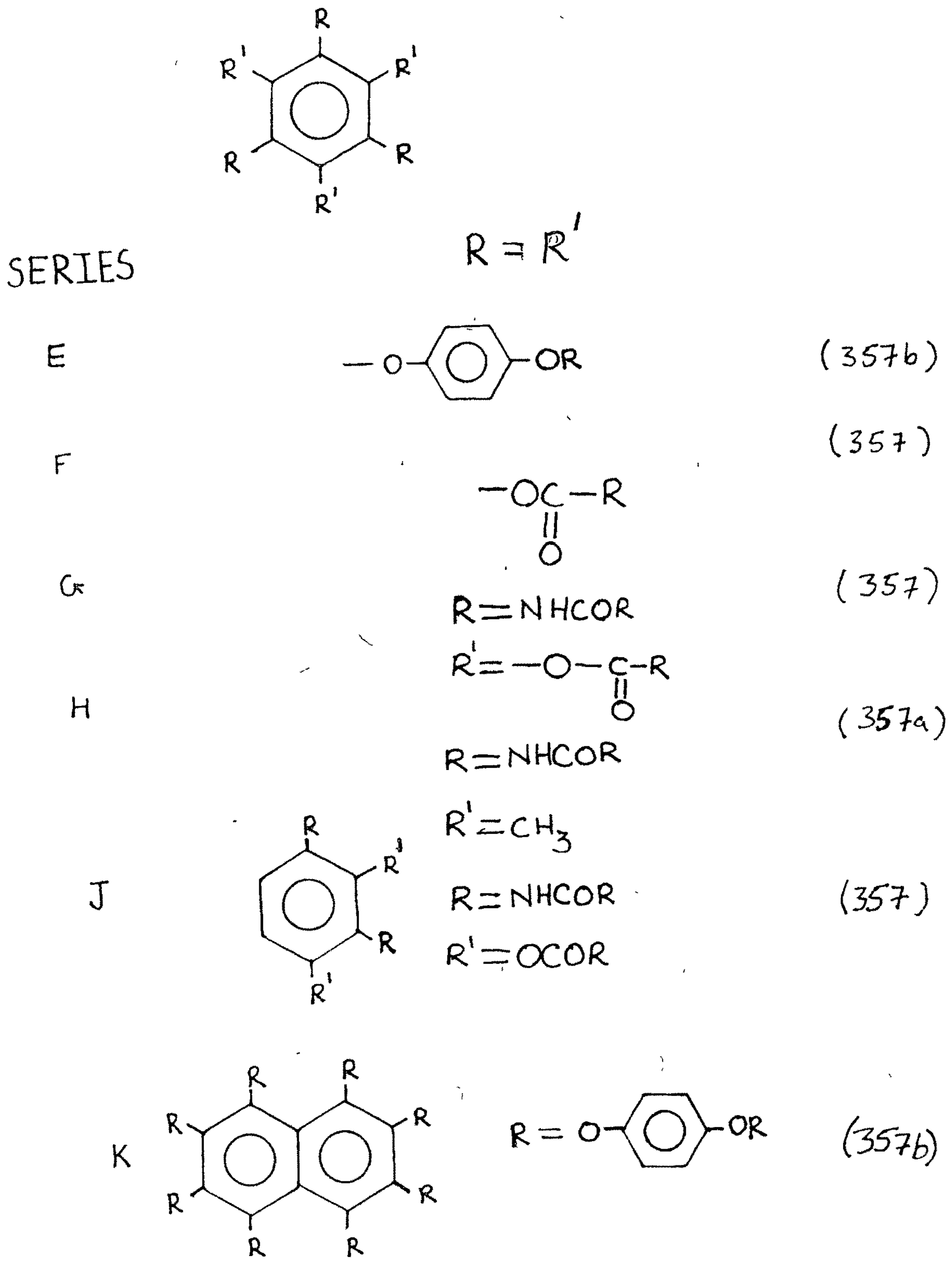

R
R'
R'
R
R
R'
SERIES
R = R'
E
—O—◯—OR
(357b)
F
(357)
—OC—R ‖ O
G
(357)
R = NHCOR
R' = —O—C—R ‖ O
H
(357a)
R = NHCOR
R' = CH₃
J
R = NHCOR
R' = OCOR
(357)
K
R = O—◯—OR
(357b)

FIG: 31

phenylene units of series-I, thereby not contributing towards enhancement of mesomorphism.

The above discussion shows that even small variation in linking groups play an important role in the exhibition of mesomorphism in disc-like compounds.

The molecules of series G and. H exhibit higher thermal stability compared to the molecules of series-I. Series-I has only three substituents whereas molecules of series G and H have six substituents. Naturally the attractive forces between the discs will be much more, which will help in close packing of molecules in the vertical stacks. Moreover, both the systems have -CONH- linkage which will enhance mesogenic character by hydrogen bonding between the molecules.

Thermal stability of series J is much lower compared to series-I. The molecules of series J are unsymmetrical (Fig. 31) having only four substituents whereas, molecules of series I are symmetrical. This must be the reason for the lower thermal stability of series-J

The molecules of series K have naphthalene nucleus and have seven substituents, even then their thermal stability almost coincides with that of series-I. It is very difficult to predict exact geometry of naphthalene nucleus with the substituents with ether linkages. It seems the strain of the ring and the position of the substituents due to ether linkage would have contributed towards the decrease in the thermal stability of series K which coincides with that of series-I.

Above discussion needs further study to quantify different structural aspects by studying appropriate physical properties and structural models.

The structure of discogens were confirmed by standard methods. ^{13}CNMR was taken to confirm the structure of molecules positively (Fig.32 a and b).

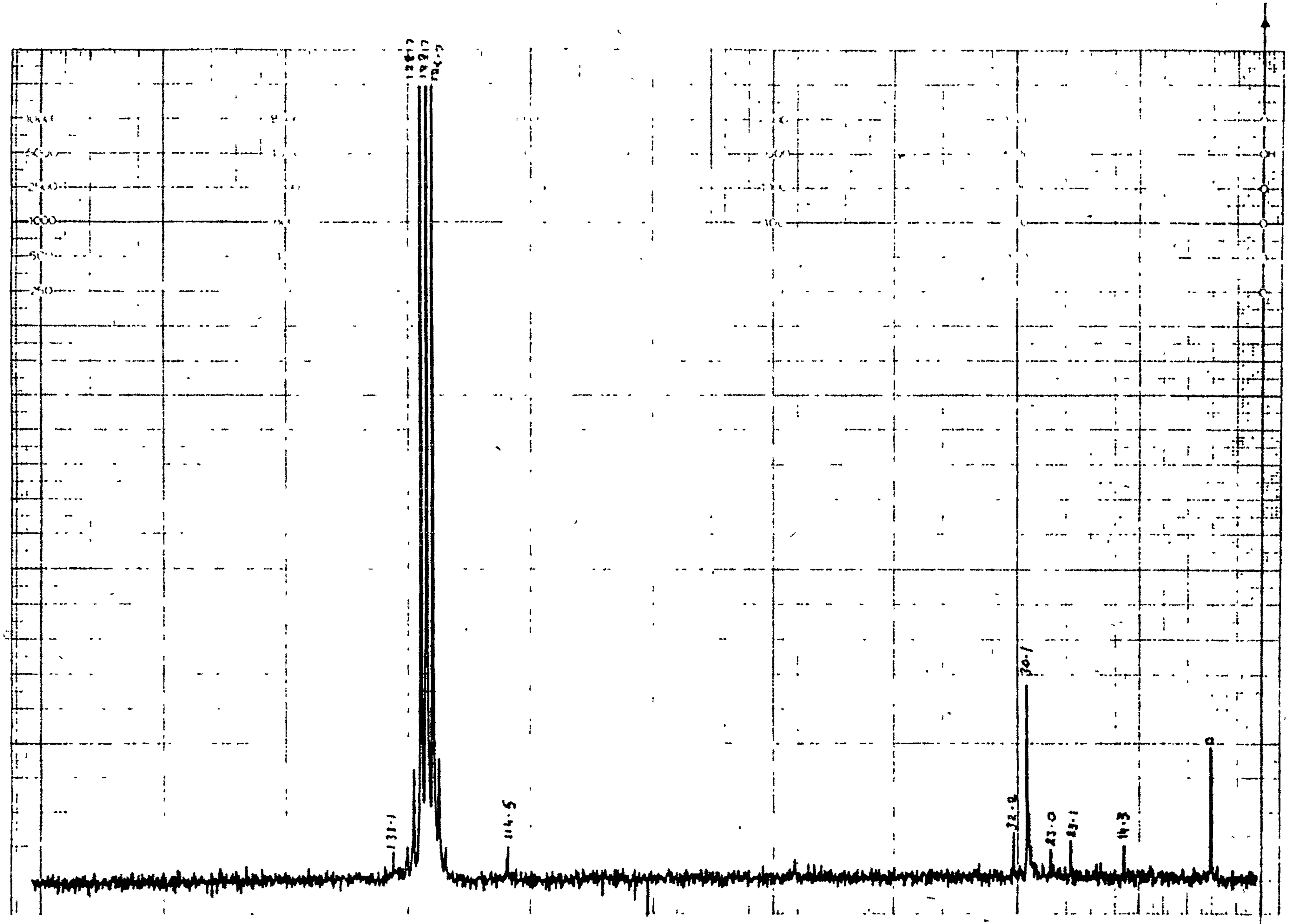


Fig. 32 a

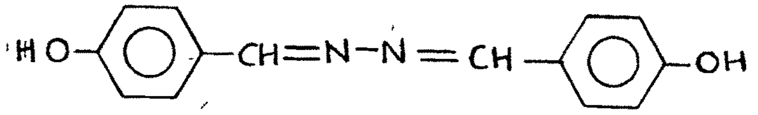
^{13}CNMR of 16-CPG

Fig. 32 b

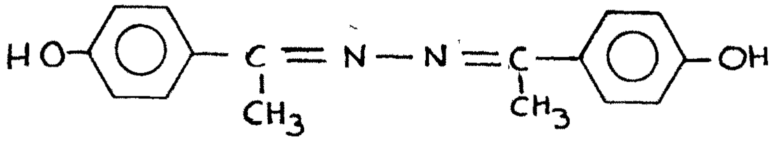
^{13}CNMR of 16-CPG

4. Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy bezalazine

Number of thermotropic mesomorphic polyesters by using aromatic molecules like 4,4'-dihydroxy benzlazine (I) and dihydroxy -α-α'-dimethyl benzalazaine (II), have been reported by Roviello and Sirigu (358).

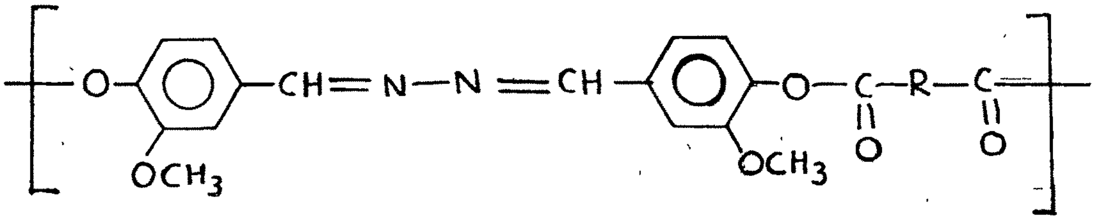


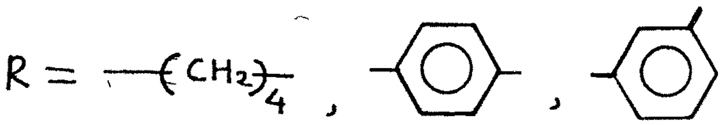
I



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 exhibited mesomorphism. The esters exhibit polymorphism of solid phase. The solid-mesomorphic and solid-isotropic transitions of esters of II are much lower than those of series I. Polymers also exhibit mesomorphism. Lateron Vora and Patel (359) investigated more polymers of azine linkage with methoxy lateral substitution, having the general structure.





etc...

Polymer AZ_1 having aliphatic fraction does not exhibit mesomorphism. Polymer AZ_2 having p-phenylene unit does not melt upto 350°C. AZ_3 having m-phenylene linkage exhibit nematic mesophase.

The above study indicated that aliphatic flexible spacers were not adequate enough to exhibit mesomorphism with azine moiety where as p-phenylene unit increased rigidity to such an extent that polymer does not melt upto 350°C.

It was thought that if aliphatic flexible spacers are kept within the system but the third monomer unit with p-phenylene linkage can be an ideal structure to exhibit mesomorphism.

With this in view, in the present work, co-polyesters were prepared by varying the ratio of two monomers i.e. diacid chloride and hydroquinone, whereas the azine ratio was kept constant as reported in table 12. The route of synthesis is given in Figure 33.

All the polyesters of adipoyl chloride were non-mesogenic showing that aliphatic fraction could not be conducive to exhibit mesomorphism, even with the introduction of p-phenylene unit in the molecule of the polymer unit.

One of the polyesters with isopthaloyl chloride exhibited mesomorphism.

Also in the case of non-mesogens from aliphatic fraction, it is indicated that the flexibility of $\leftarrow CH_2 \rightarrow_4$ is not adequate to induce mesomorphism

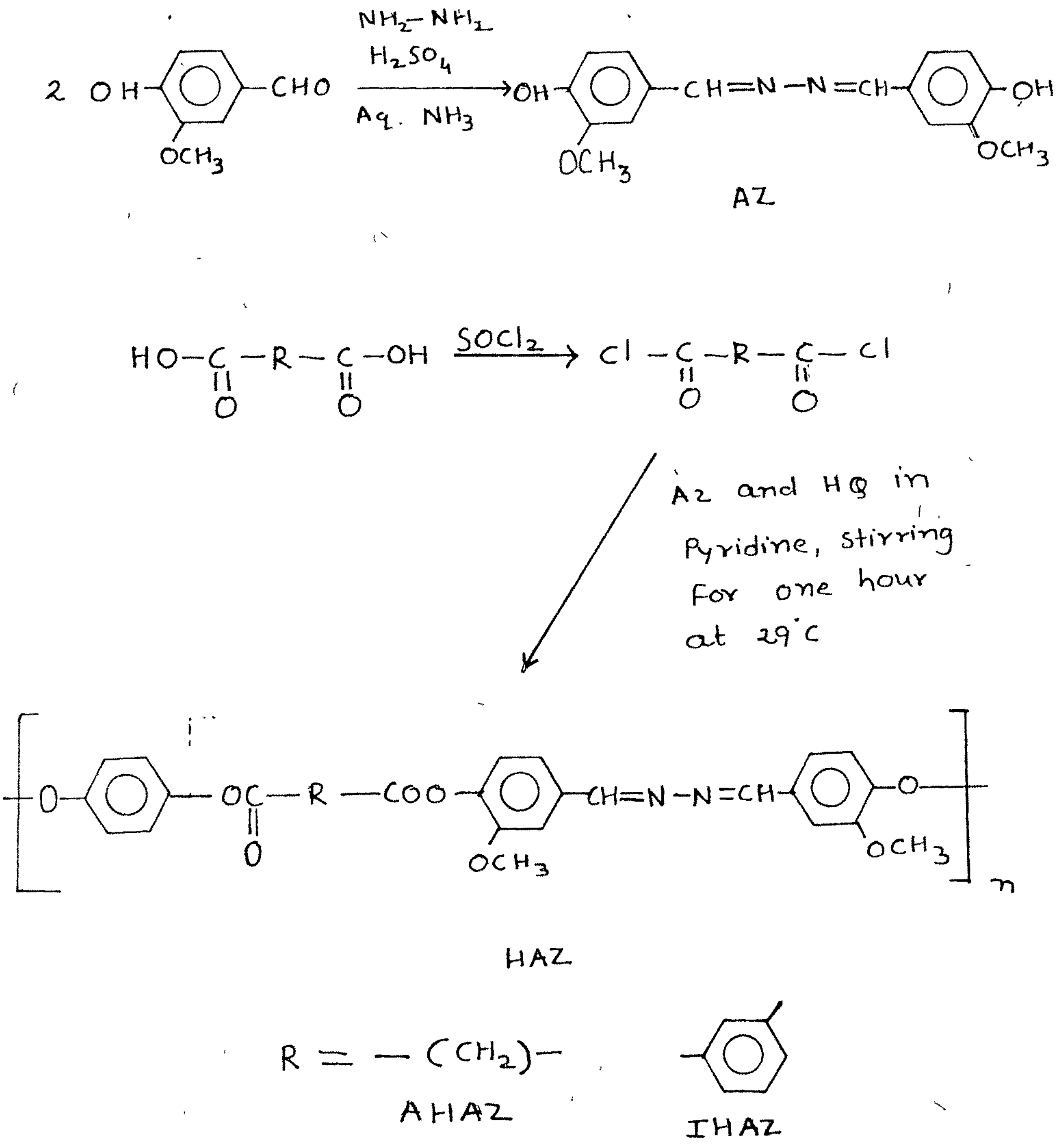

2 OH
CHO
OCH3
NH2-NH2
H2SO4
Aq. NH3
OH
CH=N-N=CH
OH
OCH3
OCH3
AZ
HO-C-R-C-OH
O
O
SOCl2
Cl-C-R-C-Cl
O
O
Az and HQ in Pyridine, stirring For one hour at 29°C
O
OC
R
COO
CH=N-N=CH
O
O
OCH3
OCH3
n
HAZ
R = -(CH2)-
AHAZ
IHAZ

FIG 33

eventhough 'azine' and 'dihydroxy' moieties are conducive to mesomorphism.

It seems that meta-linkage of isophthalic acid (8-IHAZ) endows the system with mesomrophic properties, but the ratio is an important factor which governs the mesomorphism. Hence, the other members though they have all the mesogenic moieties like the aromatic moiety, azine and hydroxy units which are conducive to mesomorphism the polyesters obtained are non-mesogenic.

All the polymers were characterized by elemental analysis (Table 13), IR spectra (Table 18 , Fig. 34) and solution viscosity (Table 20 , 21, Fig. 15, 16).

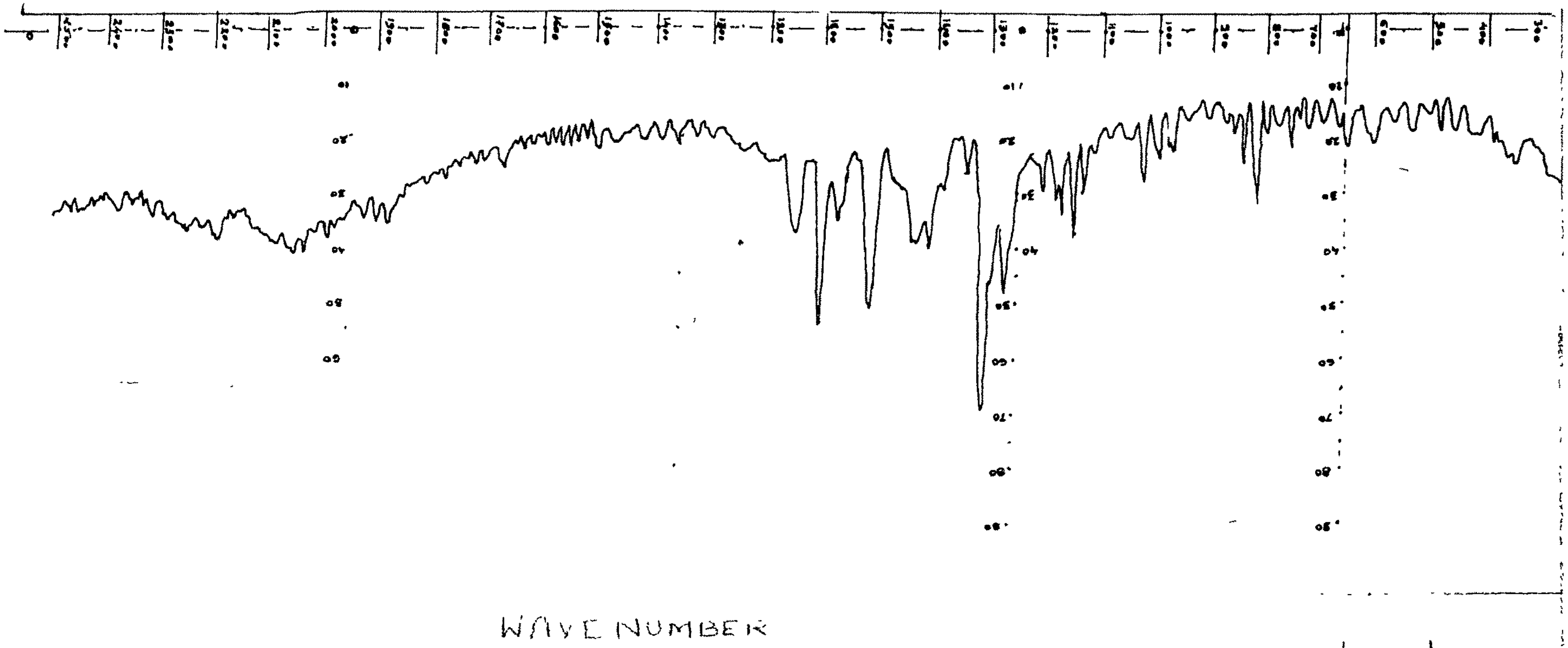
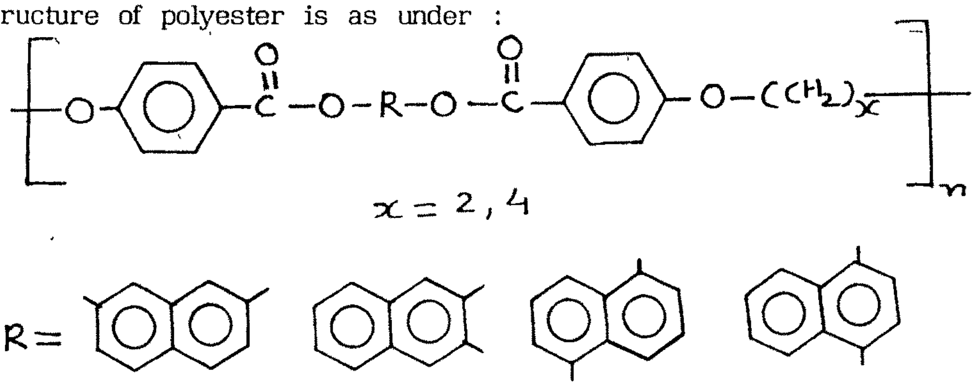


FIG 34 POLYSTERS FROM 3,3'-dimethoxy-4,4'-dihydroxy bezalazine

5. Polyesters with naphthalene nucleus

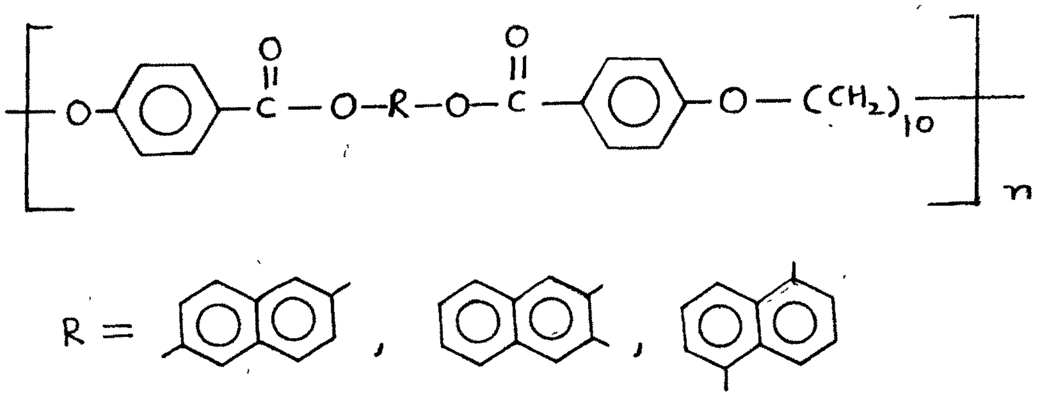
It has been known that proper combination of rigid-rod shaped mesogenic units and flexible spacers lead to thermotropic mesogenic polymer formation. Number of low molecular weight liquid crystals with 1,4-; 1,5-, and 2,6- disubstituted naphthalenes are known to exhibit mesomorphism (360).

Polymerization of diacids with even flexible spacers with different dihydroxy naphthalenes have been known and investigated (361). The general structure of polyester is as under :

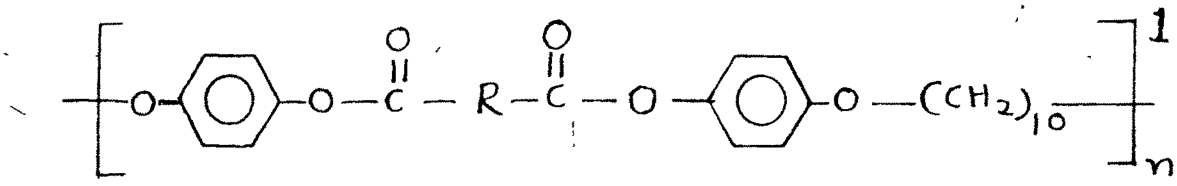


All polymers with flexible spacers x = 2 and 4 exhibit mesomorphism except the two polymers having 1,4-substituted naphthalene moiety. This is quite interesting behaviour.

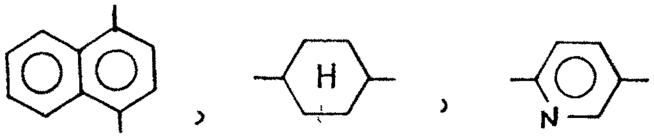
Jin et al., (259) have also reported polyesters of the similar structure with isomeric moiety. They have synthesized two systems with reverse ester linkage.



[I]



[II]



All polymers of series I exhibit nematic mesomorphism. In case of series II, polymers with 1,4-naphthalene unit do not exhibit mesomorphism. The intrinsic viscosity values of both the series are quite high for naphthalene derivatives.

The monomeric diacid studied by Vora and Patel (361) have flexible spacers with even number of carbon atoms($x=2,4$). It is known that odd number of carbon atoms have drastic effect on mesomorphism. In some cases it eliminates mesomorphism. It was planned to synthesize the above system with odd number of flexible spacers having same naphthalene nuclei as reported by Vora and Patel (361).

The synthesis route of polyesters is given in Fig. 35 and other data are recorded in table 30.

The polyesters reported by Vora and Patel (361) and Jin et al., (259) exhibit mesomorphism with few exceptions. However, all the polymers of present series are non-mesogenic. The general structural units of all the three systems are almost identical, except in the spacer length and viscosity. The polyesters reported by Jin et al., exhibit very high viscosity. The polyesters reported above have spacer length of 2,4 and 10. It is the even number in all the three polymers. In the present system the acid

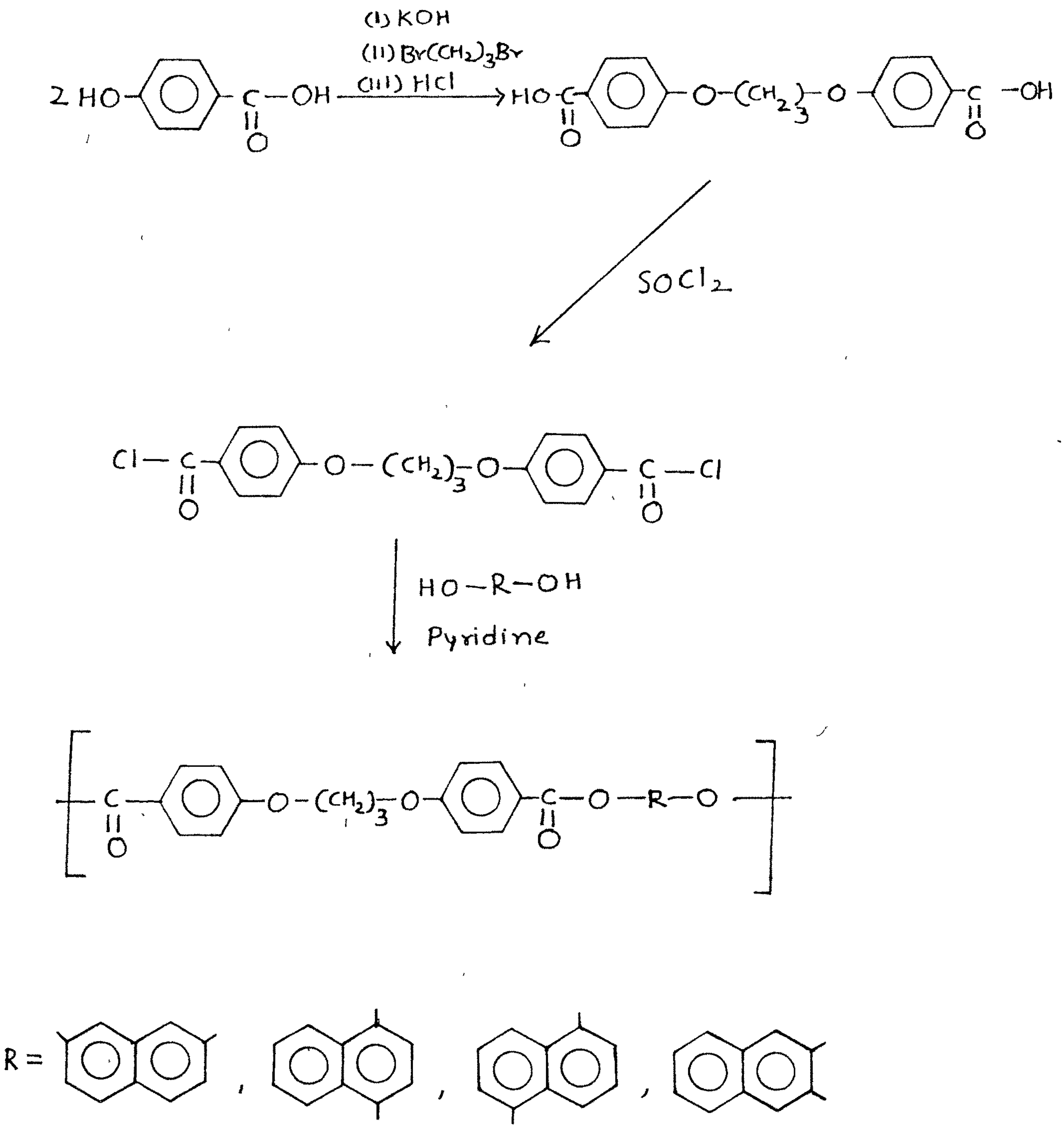

2 HO
C—OH
O
(I) KOH
(II) Br(CH2)3Br
(III) HCl
HO-C
O-(CH2)3-O
C -OH
SOCl2
Cl— C
O—(CH2)3—O
C —Cl
HO—R—OH
Pyridine
C
O-(CH2)3-O
C—O—R—O
R =

FIG: 35

TABLE - 30

Polyesters with Naphthalene Nucleus

Polymer	Diol	Melting point-°C	[n] dl/gm
CP-3	2,3-DHN	146	0.107
CP-4	1,4-DHN	240	0.164
CP-5	1,5-DHN	>338	0.169
CP-7	2,7-DHN	291	0.178

DHN = Dihydroxy naphthalene.

moiety has odd number of flexible spacer. It seems that due to the odd number of methylene units none of the polymer of this class exhibited mesomorphism.

The studies have indicated that even the small variation in the structure can eliminate mesomorphism from the system.

The polyesters were characterised by IR spectra (Table 19 , Fig.36) and elemental analysis (Table 13). Solution viscosity is measured in DMF solvent (Table 12 , Fig. 17 and 18).

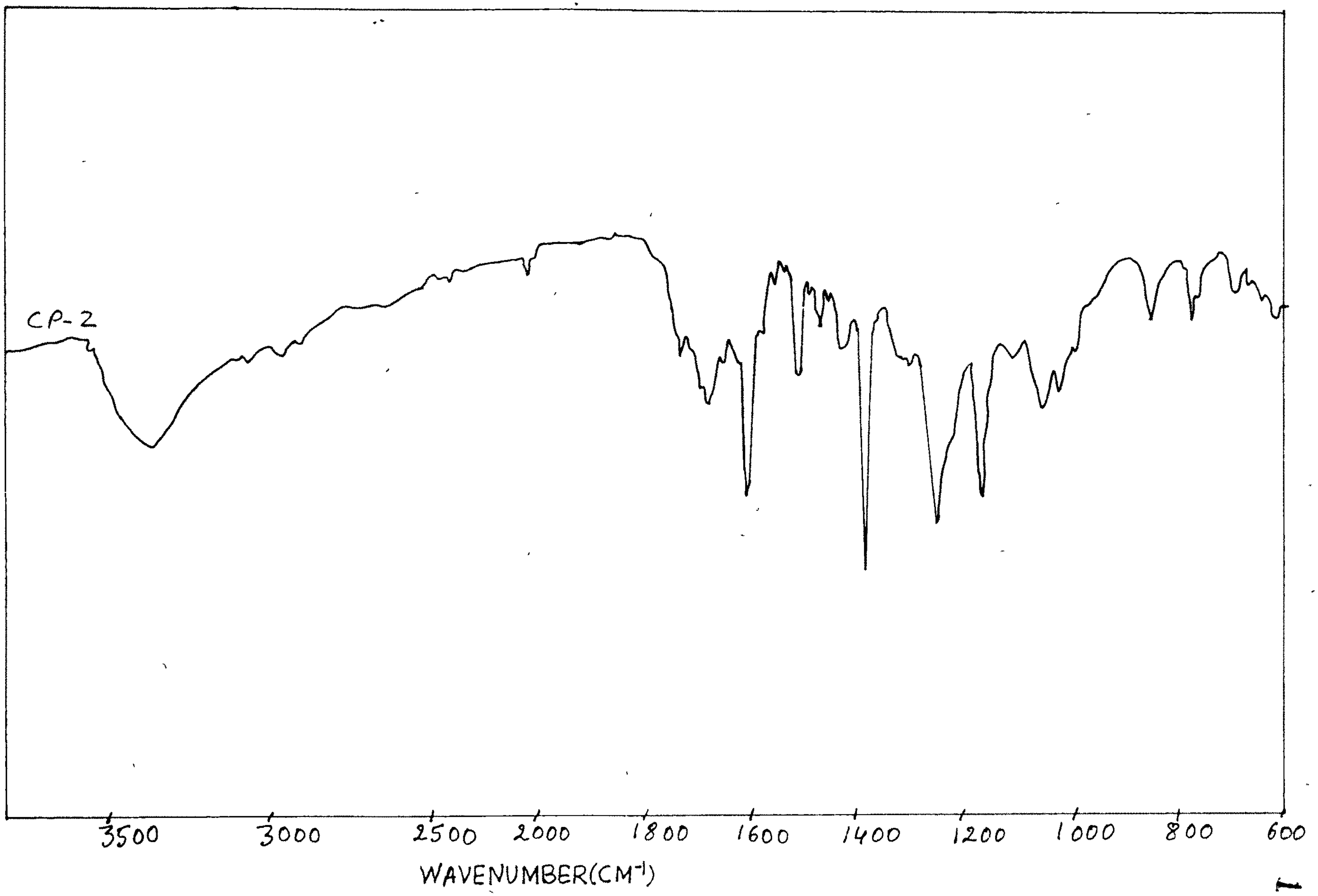


FIG. 36 POLYESTERS WITH NAPHTHALENE NUCLEUS

6. "TEXTURES OF LIQUID CRYSTALLINE MATERIALS"

As described in the experimental section, the mesophases are characterized by their classical textures observed under the microscope during heating. All textures (homogeneous, homeotropic or focal-conic) depend on typical molecular short range order, which in turn is dependent on the molecular structures.

(1) Textures of cholesteric phase exhibited by Ch-PNB liquid crystal

This compound exhibits plane texture. The exhibition of colour is not very intense. The oily stricks can be clearly seen in the cholesteric phase. The photographs A and B show that oily stricks are narrow or broader in the cholesteric phase depending on whether the photograph is taken during heating or cooling.

(2) Textures of smectic phase exhibited by 3,3'-dimethoxy-4,4'-bis(Trans-4-n-alkoxy cinnamoyl) benzidines

The smectic phase of two compound exhibit a focal-conic.(fan shaped) texture which is predominantly found in smectic A phase as shown in photographs C and D.

(3) Textures of nematic phases exhibited by liquid crystalline materials.

Most common and frequently occuring texture of the nematic liquid crystal is the threaded texture. The schlieren texture and marble textures too are commonly observed in nematics. The various textures observed are shown in photographs E through I.

(A) Microphotograph of cholesteric texture with oily stricks of cholesteryl p-nitrobenzoate at 200°C, while heating.

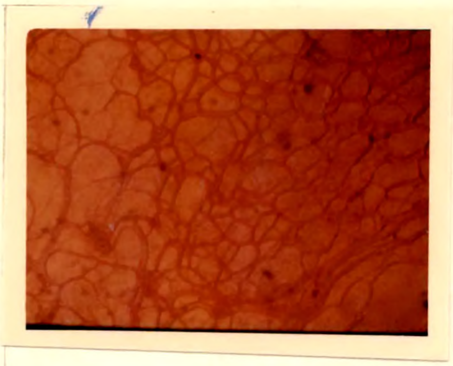
(B) Microphotograph of cholesteric texture with oily stricks of cholesteryl p-nitrobenzoate at 240°C, while cooling.

(C) Microphotograph of smectic A texture of 3,3'-dimethoxy-4,4'-bis(trans-4-n-dodecyloxy cinnamoyl) benzidine, at 170°C, while heating.

(D) Microphotograph of smectic A texture of 3,3'-dimethoxy-4,4'-bis(trans-4-n-dodecyloxy cinnamoyl) benzidine, developing while cooling, at 135°C.

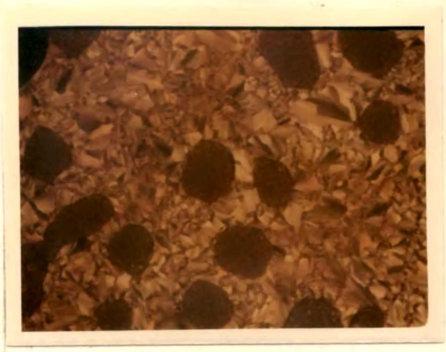
Photographs were taken under crossed polarizers.

Magnification : 20 x 10

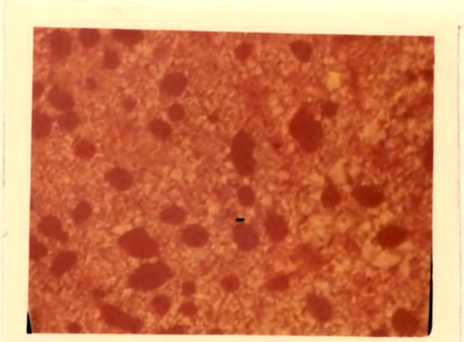


A

B



C



D

(E) Microphotograph of nematic threaded texture with lines of discontinuity of 3,3'-dimethoxy-4,4'-bis(trans-4-n-hexyloxy cinnamoyl) benzidine at 150°C while cooling.

(F) Microphotograph of nematic schlieren texture of 3,3'-dimethoxy-4,4'-bis(trans-4-n-dodecyloxy cinnamoyl) benzidine at 200°C, while heating.

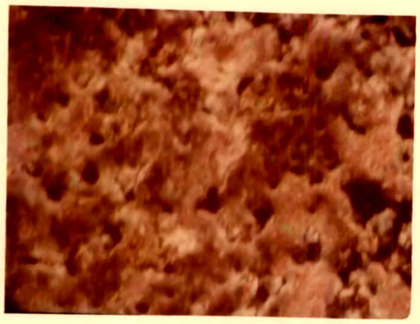
(G) Microphotograph of nematic threaded texture of 4(4'-n-nitrobenzoyloxy)-3-methoy benzylidene-4"-n-methylaniline at 156°C, while cooling.

(H) Microphotograph of nematic marble texture of 1,3,5-tri(trans-4'-
ade
n-hexyloxy cinnamoyloxy) benzene at 111°C.

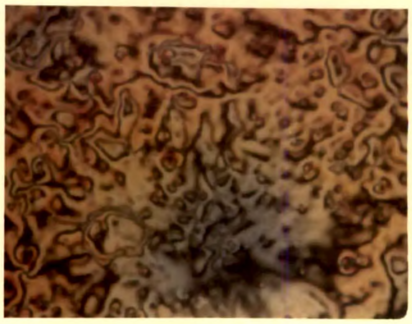
(I) Microphotograph of nematic mesophase at 273°C of Co-polymer of 4-hydroxy benzoic acid and 2-hydroxy benzoic acid.

Photographs were taken under crossed polarizers.

Magnification : 20 x 10

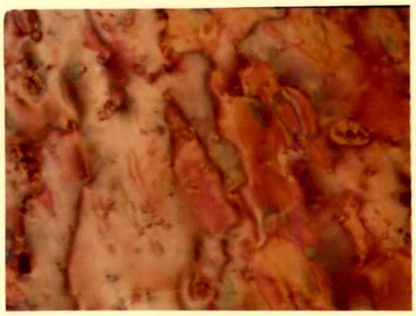


E



F

G



H

I

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