RESULTS AND DISCUSSION

i CHIRAL AND ACHIRAL AMIDO-ESTERS

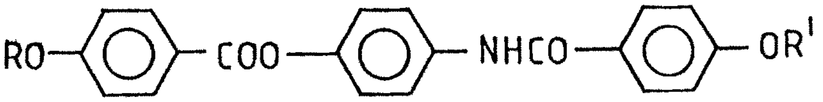
EFFECT OF AMIDE LINKAGE ON MESOMORPHISM

Liquid crystalline homologous series with chiral and achiral molecules having an amide linkage were synthesized.

A number of mesogenic homologous series are reported having -COO-, -CH=N-, -N=N-, -CH=CH-, -CH=CH-COO-, -C=C-, -C≡C- etc groups as central linkages. Many mesogenic homologous series contain two central linkages, both of them may either be ester (315, 316) or azomethine groups (317) or one of them may be ester and the other azomethine (318, 319). However, to the best of our knowledge, the first homologous series containing (-NH-CO) amide group as one of the central linkages was reported from our laboratory by Vora and Gupta (320) in 1981. Soon after that Kalyvas and McIntyre (321) and Vora and Patel (322) reported a symmetrical homologous series having an ester and amido central linkages.

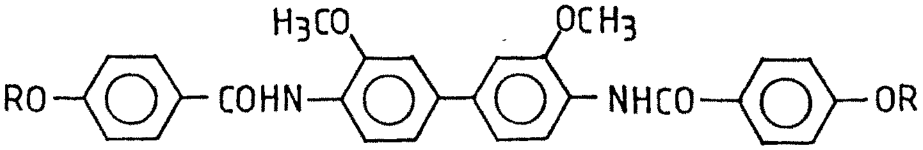
Neither Brown and Shaw (14) in their review on "mesomorphic state" nor Gray (133) in his classical monograph on liquid crystals have suggested amide group to be conducive to mesogenic properties. This may probably be the reasons for rarity of mesogens with amide linkage. Gray (13) in the review of structural requirements for mesogens has expressed the options that if there are more than two benzene rings and one of the middle group is conducive to mesomorphism, 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. Subsequently Brown (9) has also mentioned that compounds with -CONH- may exhibit mesomorphism.

As discussed earlier the liquid crystalline order in polymers is of greater interest and importance. Many of these polymers have amide linkage. Model compounds

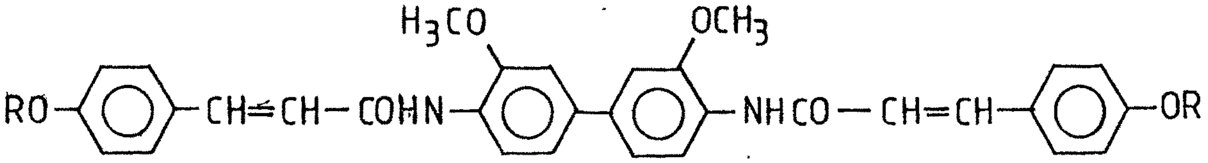


$OR = OR'$ SYMMETRICAL

$OR \neq OR'$ UNSYMMETRICAL



4,4'-bis(4''-n-alkoxybenzoyl)-3,3'-dimethoxybenzidine



4,4'-bis(4''-n-alkoxycinnamoyl)-3,3' dimethoxybenzidine

FIGURE:24

exhibiting mesomorphism and having an amide group would be of interest to understand the mesogenic behaviour of such compounds and of polymers having amide linkage.

Vora et al., (323) and Gupta (324) took up the study of number of mesogenic series with ester and amide central linkages and also of mesogenic series having two amide linkages as reported in Fig.24.

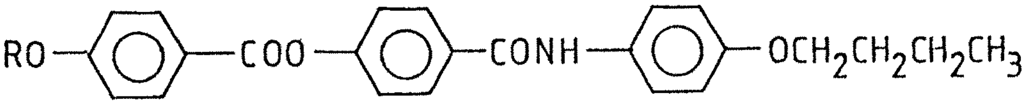
The observation of Vora et al., (323) and Gupta (324) made it clear that compared to an ester and azomethine linkage, amide-central linkage enhances smectic and nematic phases and enhancement is more in case of smectic mesophase.

Vora et al., (325) studied the effect of amide linkage on mesomorphism having a chiral terminal substituent. They have observed that these results further support the earlier findings of Vora et al., (323) that -CONH- linkage enhances smectic mesophase much more compared to nematic mesophase.

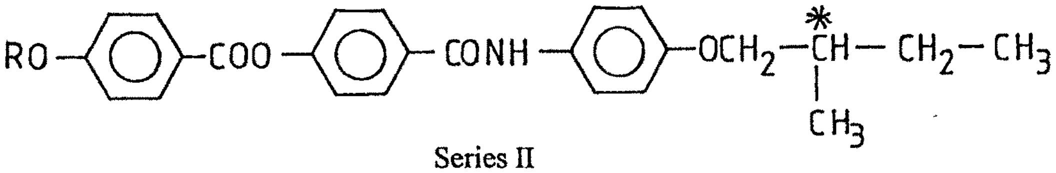
It is interesting to note that in above studies the nitrogen of amide linkage is attached with central phenyl or biphenyl ring as shown in the figure. 24

It has been observed by Griffin (326) and others (321, 344) that reversal of the central linkage exhibits some remarkable differences in liquid crystalline properties. It was thought proper to synthesize a few homologous series having reversal of amide linkage to compare with other similar homologous series reported earlier by our school. Moreover it was thought proper that reversal of the amide linkage may induce smectic C phase in the series which would be highly useful if it is further converted to chiral smectic *C by introducing chiral substituent in the system.

With this in view following two homologous series I and II were synthesized and their mesogenic properties were studied.



Series : I



Series II

Where, R = $(C_n H_{2n+1})$

n = 1 to 10, 12, 14, 16, 18.

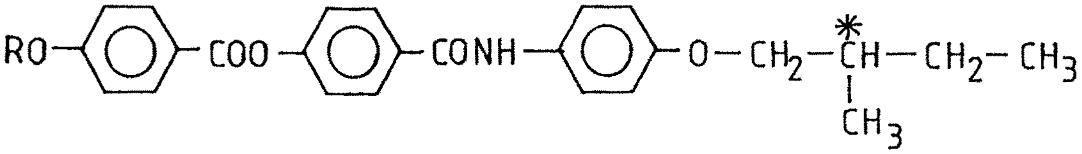
Series - I was synthesized by the route shown in Figure 25

For the synthesis of series I, intermediate 4-n-alkoxy benzoic acids and 4-n-alkoxy benzoyloxy benzoic acids were synthesized, which are mesogenic in nature. The transition temperatures of all the intermediate acids compare well with the literature value with a few exception.

Methyl to n-propyl derivatives of series I exhibit only nematic phases. Smectic mesophase commences from n-butyl derivative. n-Butyl to n-decyl derivatives exhibit smectic and nematic mesophases. n-Dodecyl to n-octadecyl derivatives exhibit only smectic phases. All the smectic homologues exhibit smectic C phases. Middle members exhibit polymorphism of smectic mesophase.

The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits odd-even effect for nematic-isotropic transition temperatures (Fig.26).

Smectic-isotropic transition temperature curve do not exhibit odd-even effect even though smectic-mesophase commences early in the series II.



(4'-n-alkoxy benzoyloxy benzoyl)4"-S-(+)-2-methyl butoxy anilines:

The strong tendency of series I to exhibit smectic-C mesophase prompted us to introduce a chiral tail in the molecule to obtain chiral smectic *C phase which would impart ferroelectric properties to the molecules.

The series is synthesized as indicated in Fig.25 Homologues from n-propyl derivatives onwards exhibit smectic *C and cholesteric mesophase upto n-dodecyl derivative. n-Tetradecyl to hexadecyl derivatives exhibit only smectic *C phases.

The plot of transition temperatures against number of carbon atoms in alkoxy chain for series II exhibits odd-even effect for cholesteric - isotropic transition temperatures as well as for smectic-cholesteric transition temperatures (Fig.29).

The odd-even effect in 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 molecules are continuously in contact with parts of neighbouring molecules. The energy of the system depends on different conformations of molecules, London - Vander Walls dispersive forces between the neighbouring molecules and on steric repulsions between different molecules (327). For the mesogenic homologous series, Gray (328, 329) 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 Vander 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 Fig. 34

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 (133) 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 (133) of the terminal intermolecular cohesions. However, Gray (133) and Maier and Baumgartner (330) 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 chainlength 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 chainlength 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 chainlength, 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 stage, presumably because the terminal intermolecular attractions are inadequate to maintain the parallel molecular orientation, required for the 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 cholesteric 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-alkoxybenzylideneamino-fluorenones and 4-n-alkoxybenzylideaminobiphenyls, having substitution in 2 or 3 positions (317) and 2-methyl-1, 4-phenylene bis (4'-n-alkoxybenzoates), (315) 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., (331-333) have studied a number of naphthylidene Schiff bases and have evaluated the effect 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 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 phase, 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 (133,334-336). 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 alternations of nematic-isotropic transitions (odd-even effect) have been discussed by different workers. Gray (328) 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 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 predominate:

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.

Effects (i) and (ii) would increase the nematic-isotropic transition temperature 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 attractions are

Table 42

Average Thermal Stabilities °C

Series	(I) R'=C_4H_9	(II) R'=*C_5H_{11}	(A) R'=C_4H_9	(B) R=R'	(C) R'=C_7H_{15}	(D) R'=*C_5H_{11}	(E) R'=C_4H_9
Nematic/Chol. to Isotropic (C_1 to C_8)	279.38	307.0 (C_3 - C_8)	256.75	250.94	231.81	200.17	252.5
Sm-Chol./or Nematic/Isotropic (C_6 - C_{16})	237.64	238.0	-	203.43	211.71	199.83 (C_{12},C_{14}, C_{16})	153.5 (C_3 -C_{16})
Commencement of Smectic mesophase	C_4	C_3	-	C_6	C_2	C_{12}	C_7

weak. Gray has explained the alternations 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. 35), then the terminal methyl groups present different faces to one another or to other end groups in the molecules depending on whether the chain is even or odd. The different resultant attractive forces would 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. 35) 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-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.

Maier (337), Maier and Baumagartner (330) 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 (327) 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 carbon atom C_2, increase 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 become longer, their flexibility makes the effect progressively smaller until for long end chains, it becomes unnoticeable. Pines et al, (338) have measured the order parameters in a series of nematic liquid crystals p-n-alkoxy azoxybenzenes by ^{13}C NMR. .The ordering exhibits an odd-even alternation 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 (339) 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.

A typical behaviour of transition temperature curves is observed in the graph (Fig.29). They fall steeply. In the same way solid-mesomorphic transition temperature curve exhibits rising tendency initially, and subsequently falls steeply. Normally mesomorphic homologous series do not exhibit such behaviour. The odd-even effect is already explained in the previous text.

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

Table 42 summerises the average thermal stabilities of different mesogenic homologous series synthesized i.e.

1) 4(4'-n-alkoxy benzoyloxy benzoyl)-4"-n-butoxy anilines (Series - I)

2) 4(4'-n-alkoxy benzoyloxy benzoyl)4"-S(+)-2-methyl butoxy anilines (Series II).

Transition temperatures of Series I and Series II are compared with those of

3) 4(4'-n-alkoxybenzoyloxy)-4"-n-butoxy benzanilides - [A] (340)

4) 1,4-bis (4'-n-alkoxybenzoyloxy) amino phenols [B] (321, 322).

5) 4(4'-n-alkoxy benzoyloxy)4"-n-heptyloxy benzanilides [C] (320)

6) S(+)-4(4'-β-methyl butoxy benzoyloxy)-4"-n-alkoxybenzoyloxy benzanilides - [D] (341)

7) 4(4'-n-alkoxy benzoyloxy) benzylidene-4"-n-butoxy anilines -[E](342).

The reference to the geometry of series I and series A (Fig 36) indicates they are essentially same accept that one of the central linkage amide (-CO-NH-) is reversed in series A as -NH-CO- in the molecules. In the present series the nitrogen of amide linkage is attached to terminal phenyl ring and can take part into group reasonating structures along with terminal n-butoxy group which contribute to polarizability of the molecules of series I. In the case of series A, the nitrogen of amide linkage is attached to central phenyl group which is attached to another phenyl ring via an ester linkage. This would cause difference in the polarizability of molecules of series I and A. This is also reflected in the thermal stabilities of both the homologous series. Nematic-isotropic thermal stabilities of series I are higher compared to those of series II. It is known that increase in polarizability enhances mesophases. However the appearance of smectic phase in series I is from n-butyl derivative which is totally absent in series A. This indicates that a simple reversal of a central linkage has dramatic effect on the appearance of smectic mesophase in a homologous series. Amide central linkage has nitrogen atom which has a lone pair of electron and terminal butoxy group also contributes to reasonating structure. Both these together comtribute in resonating structures which has resulted into the appearance of smectic mesophase in series I.

Molecules of series B are symmetrical and n-alkoxy group is changing at both ends of the molecules from methyl to n-octadecyl derivative. Moreover molecules have reversed amide linkage compared to seris I. Series I has fixed n-butyl group at one end but at the other end alkyl group changes from methyl to n-octadecyl. One would expect that the thermal stabilities of series B would be higher as it possesses symmetrical molecules and alkyl groups are changing at both the ends. However the results indicate that both the thermal stabilities of series I are higher compared to those of series B. This further supports above view that reversal of amide linkage where nitrogen of amide linkage is attached to n-alkoxy phenyl ring contributes towards enhancement of mesophases due to increased polarizability of the series I.

The molecules of series I and series C differ in reversal of amide linkage and in fixed n-alkoxy group at one end which is n-heptyloxy in the case of series C and n-butoxy in the case of series I.

As the molecules of series C have n-heptyloxy group at one end as well as reversal of amide linkage compared to series I, its lower thermal stabilities can easily be explained in lieu of above discussion. This further supports the view that reversal of amide linkage has profound effect on mesogenic behaviour.

Molecules of series D have an optically active linkage 2-methyl butyl at one terminus compared to series I. Naturally α-methyl group in an alkoxy group would adversely affect (343) the mesomorphic character of a homologous series. Compared to series I it has also reverse amide linkage. Both these factors reduce the thermal stabilities of series C to very great extent as reflected in Table 42. Even the commencement of smectic mesophase is delayed in series D which is at dodecyl derivative.

Series I and series II differ only in terminal substituent at one end of the molecules. S (+) 2-methyl butyl group joined to alkoxy group would have steric effect due to α-Methyl substituent compared to the molecules of series I having n-butyl group. However, the α-carbon having asymmetric nature would not have fullest breadth increasing effect. Due to this reason nematic thermal stabilities of series I is little higher compared to series II. However smectic thermal stabilities of series I and II are almost equal. This is quite an interesting observation.

Molecules of series II and series D are almost identical except in the reversal of the amide linkage. It has been pointed out earlier that reversal of amide linkage enhances smectic and nematic thermal stabilities of the system I which has nitrogen of amide linkage with terminal alkoxy phenyl group. The reference to Table 42 clearly indicates that average cholesteric thermal stabilities of series II are much higher than those of series D. However, the difference in the smectic average thermal stabilities of two series is not as high as cholesteric thermal stabilities. Moreover, the commencement of smectic phase in series II is from third member (first two members are not synthesized) whereas in series D smectic phase commences very late in the series i.e. from n-dodecyl derivative. This shows that reversal of amide linkage has profound effect on mesomorphic properties of the systems even if they have α-methyl group in alkoxy chain. The difference between series A and series - II is in the terminal alkoxy chain at one end and in the reversal of amide linkage. The S(+) 2-methyl butyl group at one end does induce smectic tendency in a system, however reversal of amide linkage has made it more pronounced. Series A does not exhibit smectic phase in the homologous series but it commences from the n-propyl derivative in series II.

Forgoing discussion indicate that reversal of the amide linkage has profound effect on the mesogenic behaviour of homologous series.

Danuta et al., (344) have synthesized number of model ester-amide to understand mesogenic behaviour of polyesteramides. Their results indicate that reversal of amide linkage in the model compounds where nitrogen of amide linkage is attached with terminal phenyl ring exhibits higher thermal stability.

The reference to Table 42 shows that nematic and smectic thermal stabilities of series I are higher than those of series E. Difference between the molecules of series I and E is in one of the central linkage. Series I has an amide central linkage whereas series E has the Schiff baselinkage. This indicates that compared to azomethine linkage-CH=N-, amide linkage enhances nematic and smectic thermal stabilities. This is attributed to higher polarizability and hydrogen bonding effect of amide linkage. The increase in smectic thermal stabilities is much higher in series I compared to nematic thermal stabilities vis a vis series E. This indicates that amide linkage enhances smectic mesophase more than the nematic mesophase.

Two members (C_{12} and C_{14} of Series II) were screened by DSC method. Both the members exhibit prominent endothermic peaks for solid-mesogenic transitions, small peaks for smectic-cholesteric and mesogenic-isotropic transition. Both members are showing endothermic peaks for phase transitions. Enthalpy and entropy values are recorded in Table 35.a. Both members are showing endothermic peaks as well as exothermic peaks on heating and cooling, respectively in Figure 33.a and 33.b.

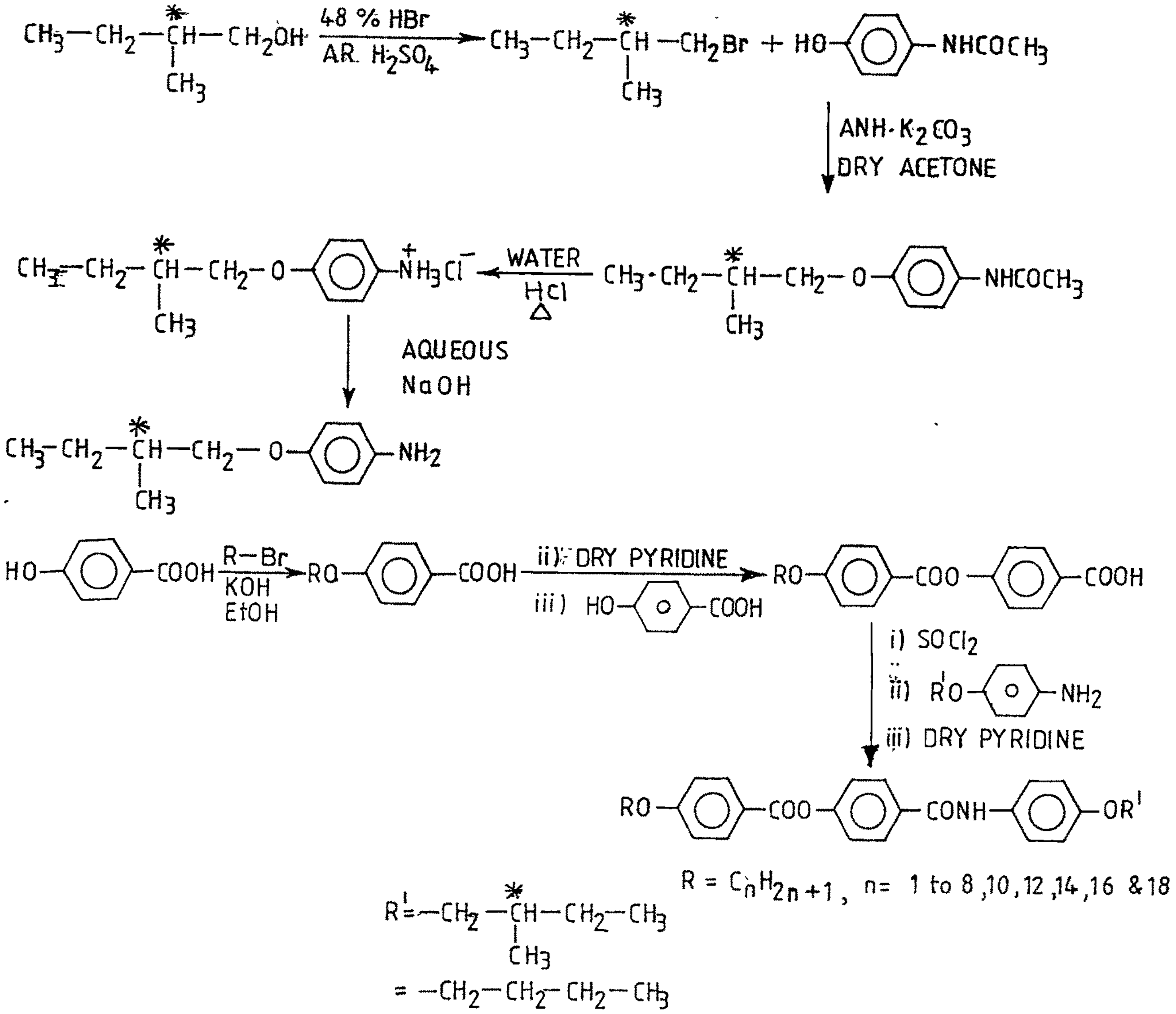


FIGURE :25 SYNTHETIC ROUTE TO SERIES I AND II

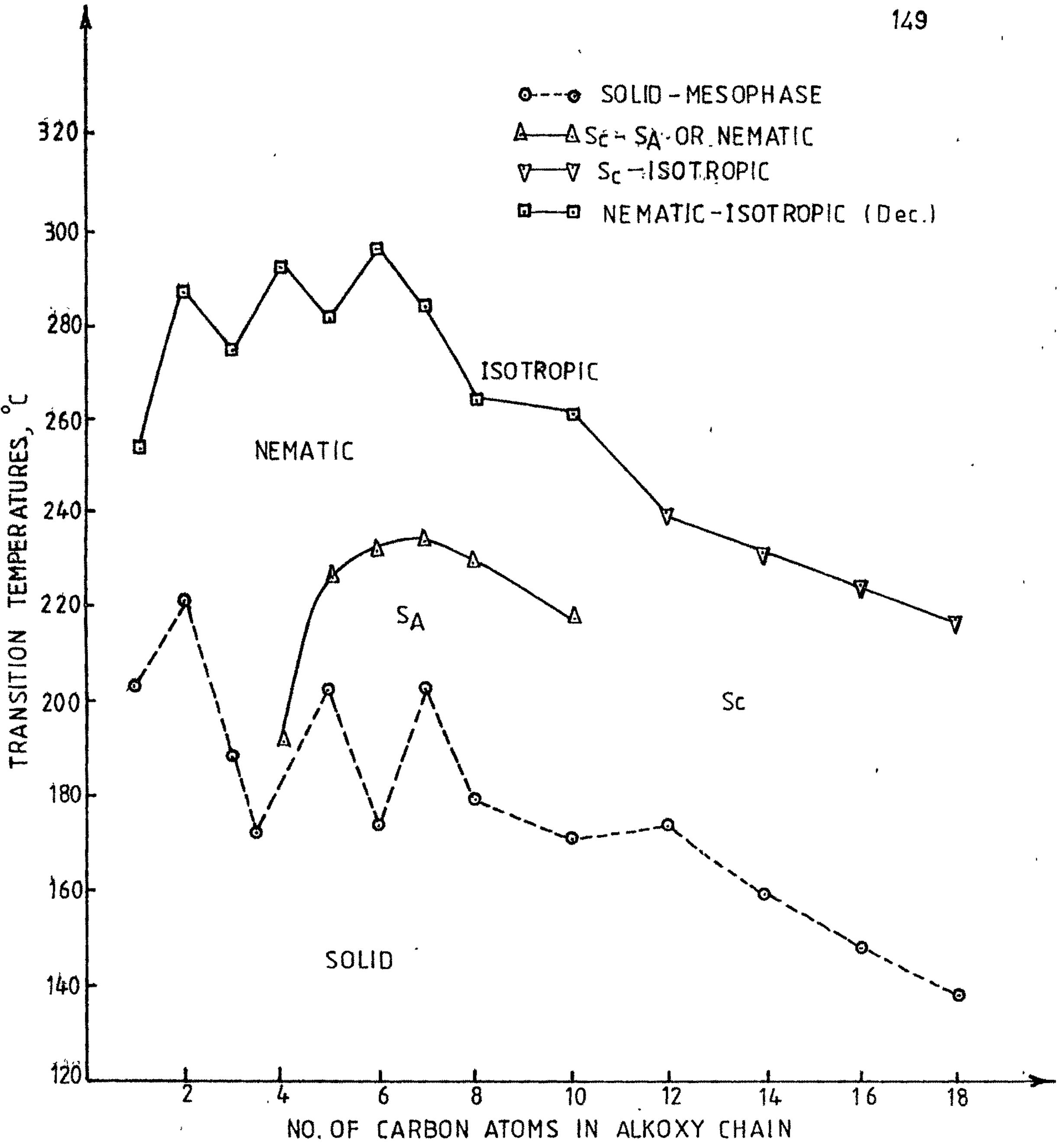


FIGURE : 26 4 (4'- n- ALKOXY BENZOYLOXY BENZOYL) 4''- n- BUTOXY ANILINES (SERIES - I).

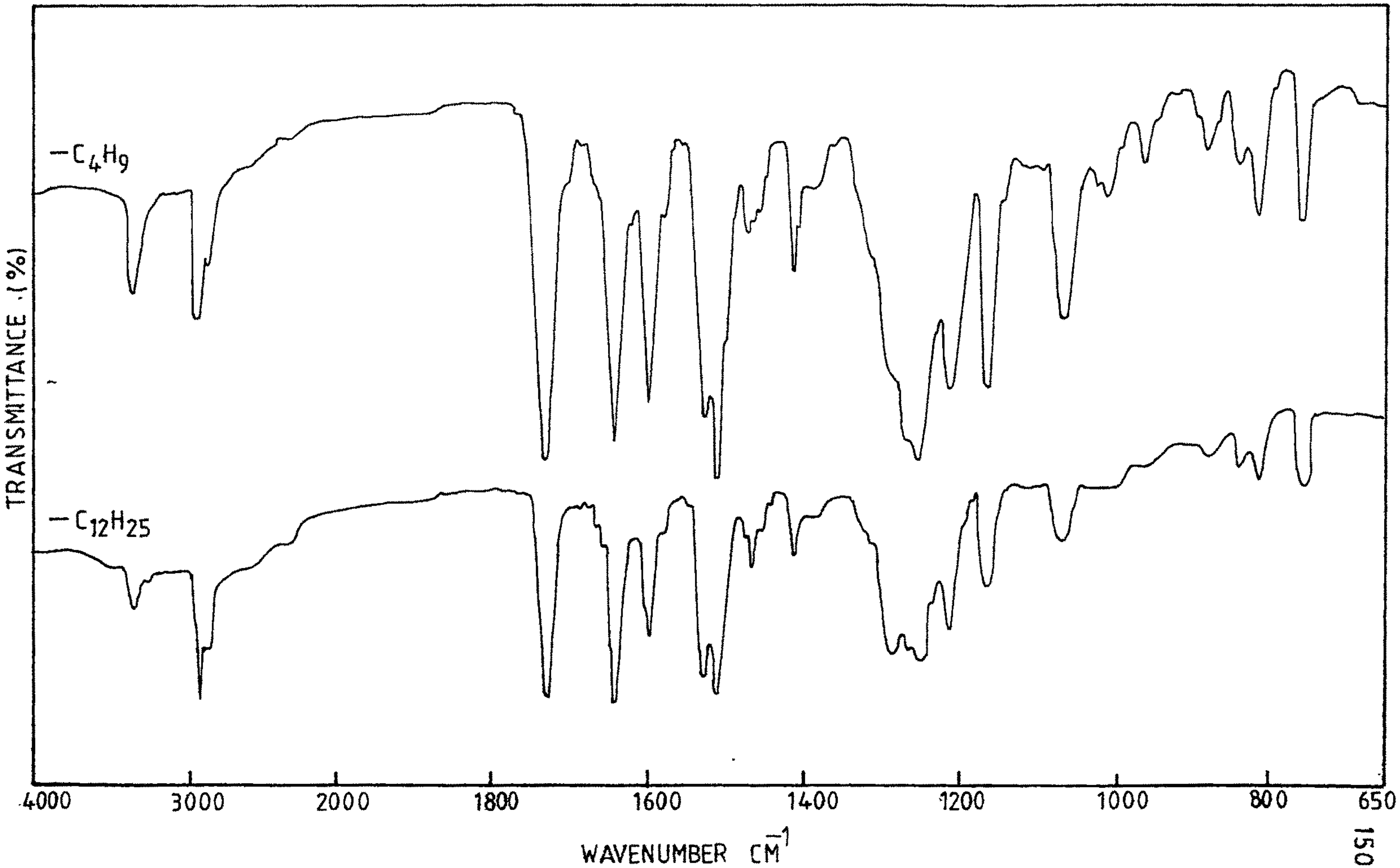


FIGURE:27a.IR SPECTRA OF MESOGENS OF SERIES-I

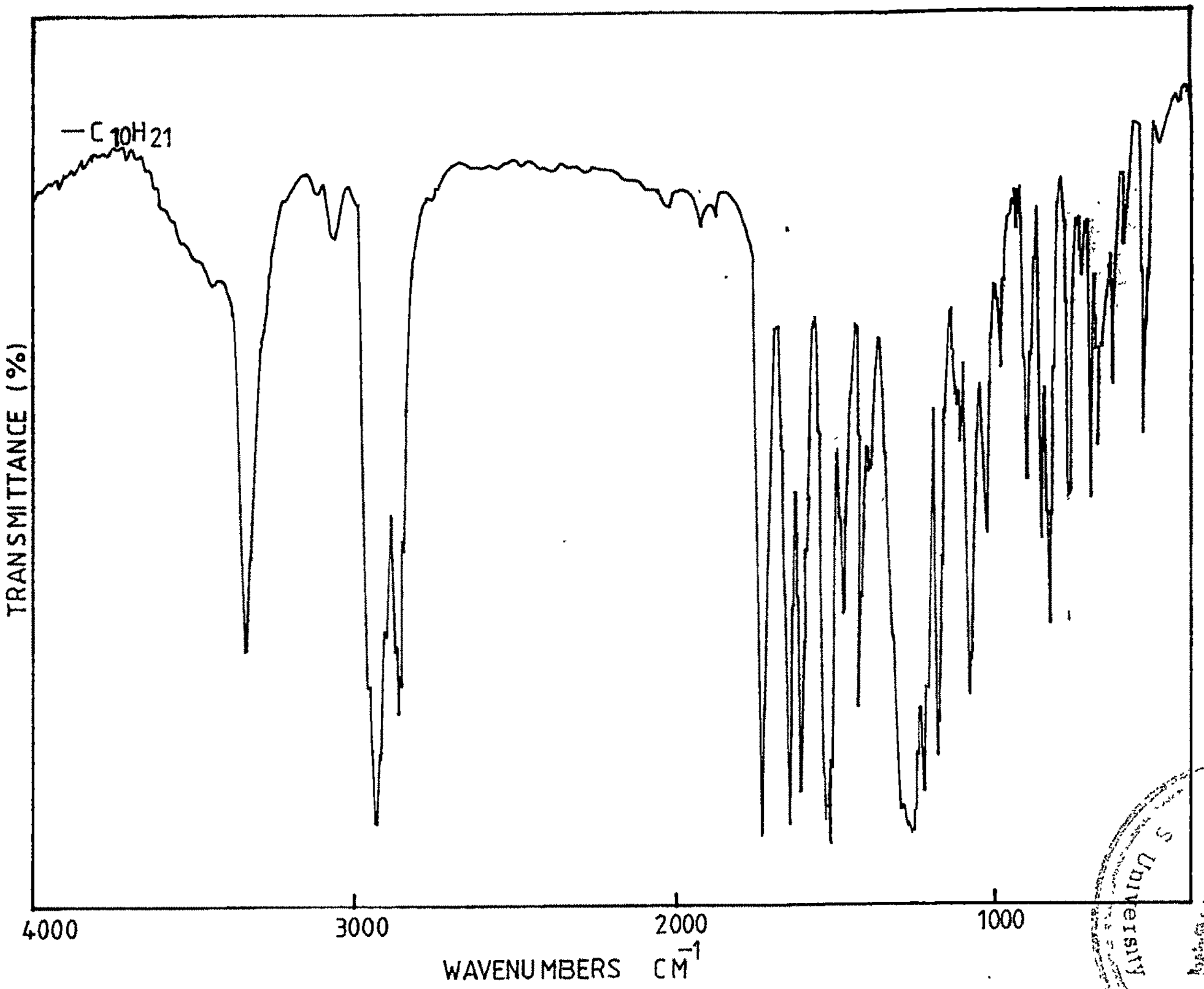


FIG.:27b. FTIR SPECTRUM OF MESOGEN OF SERIES I

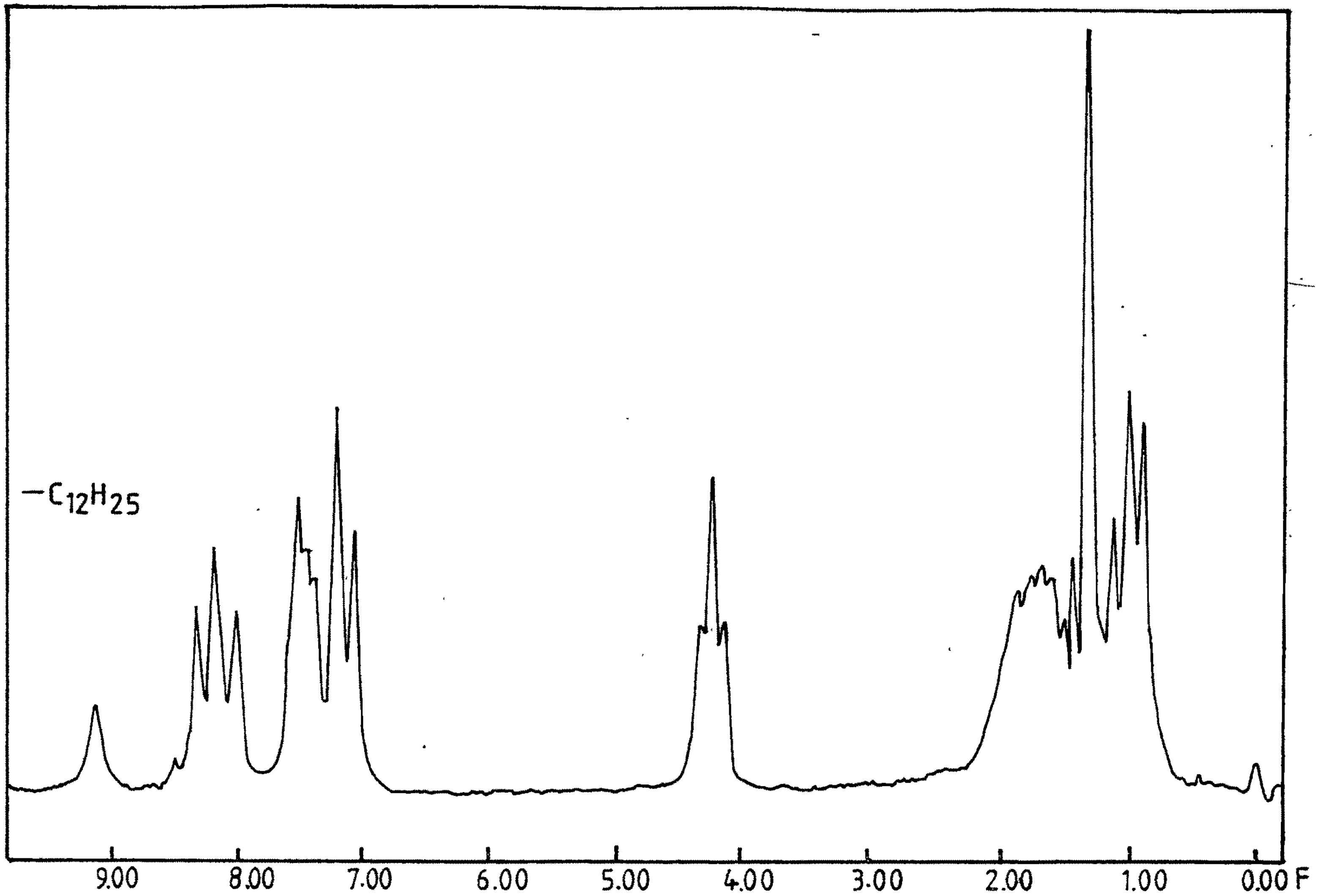


FIGURE:2a NMR SPECTRA OF MESOGEN OF SERIES-I

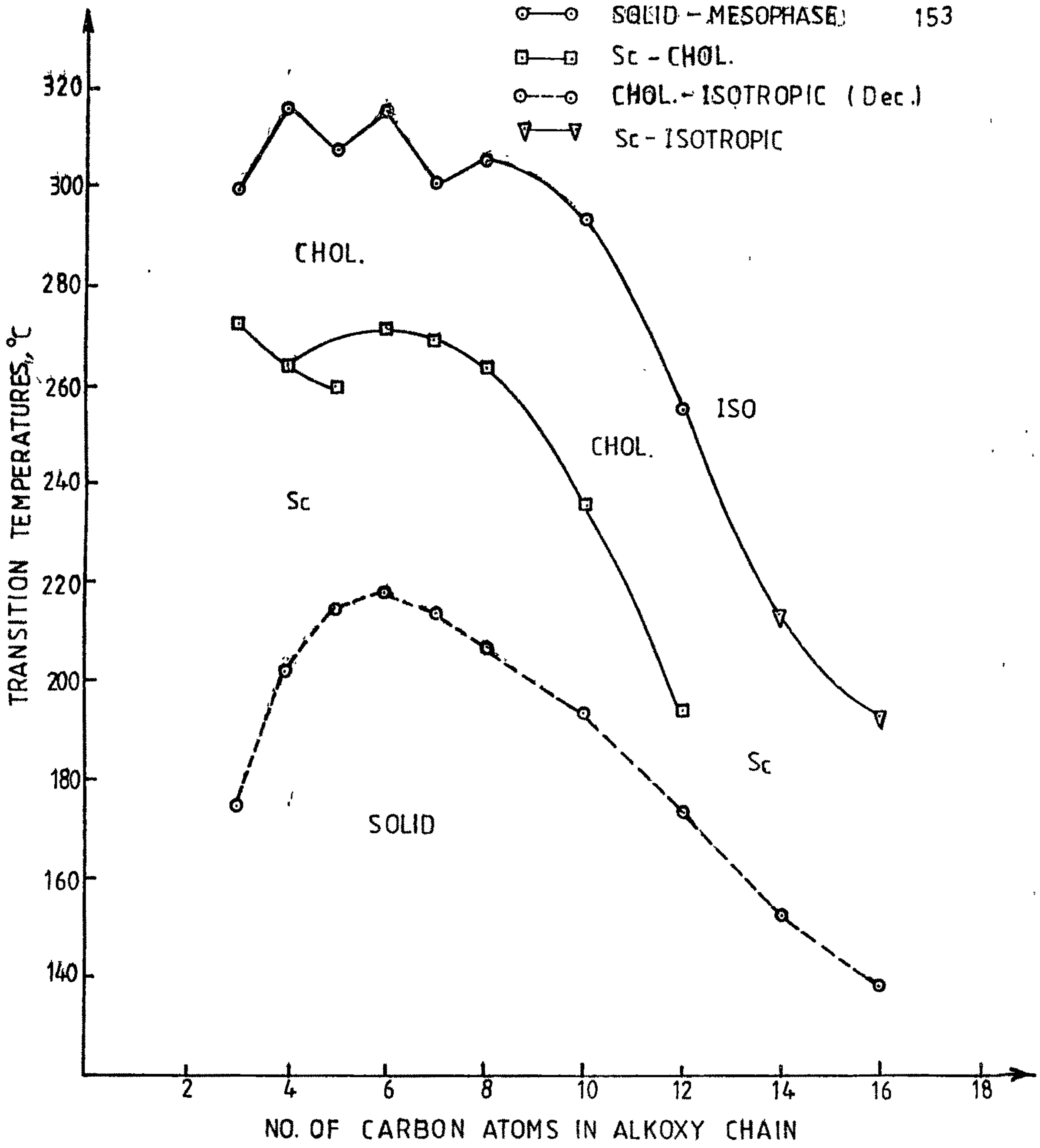


FIGURE: 29 4(4'-n-ALKOXY BENZOYLOXY BENZOYL) 4''- S (+) - 2 - METHYL BUTOXY ANILINES (SERIES - II).

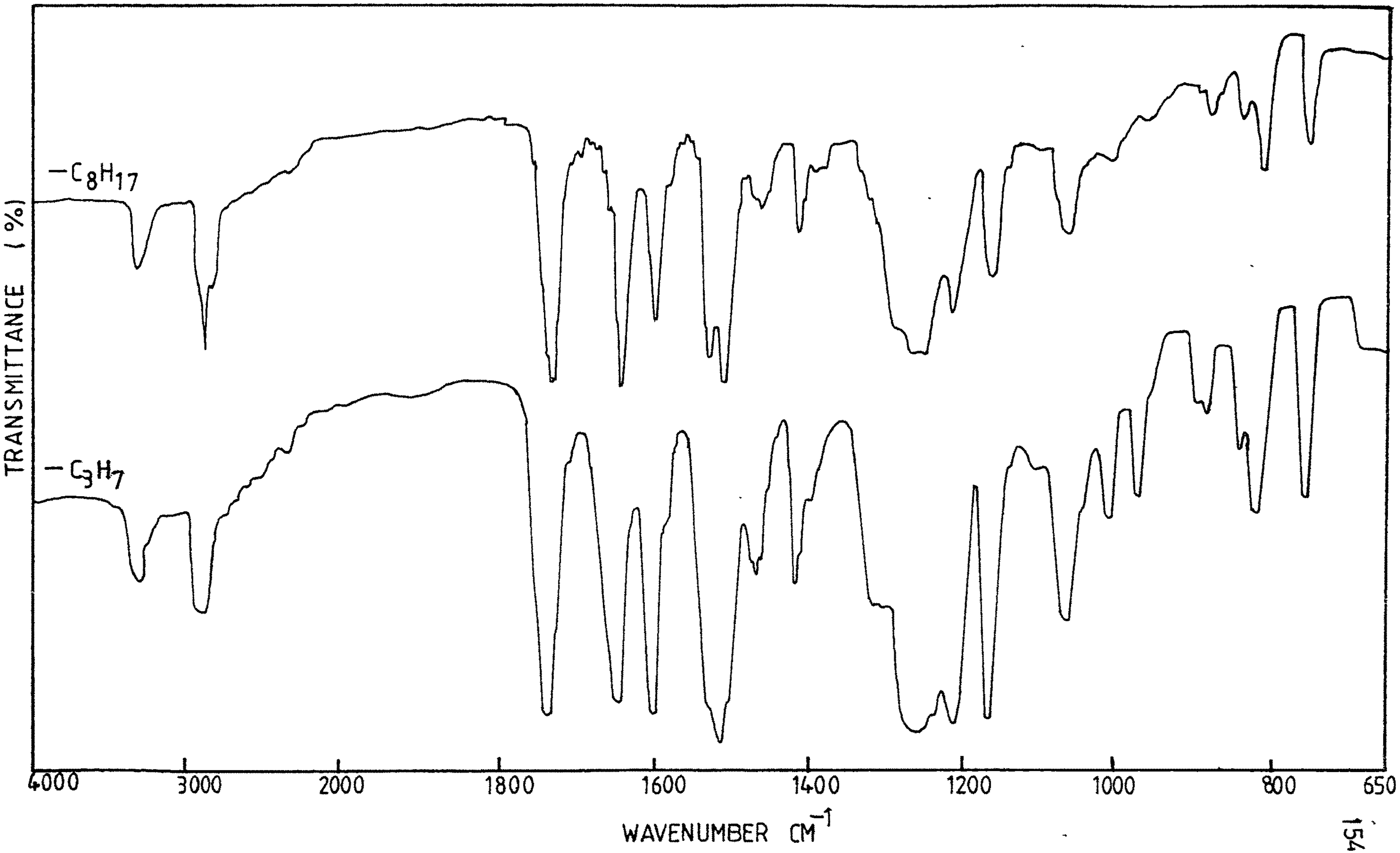


FIGURE :30 IR SPECTRA OF MESOGENS OF SERIES - II

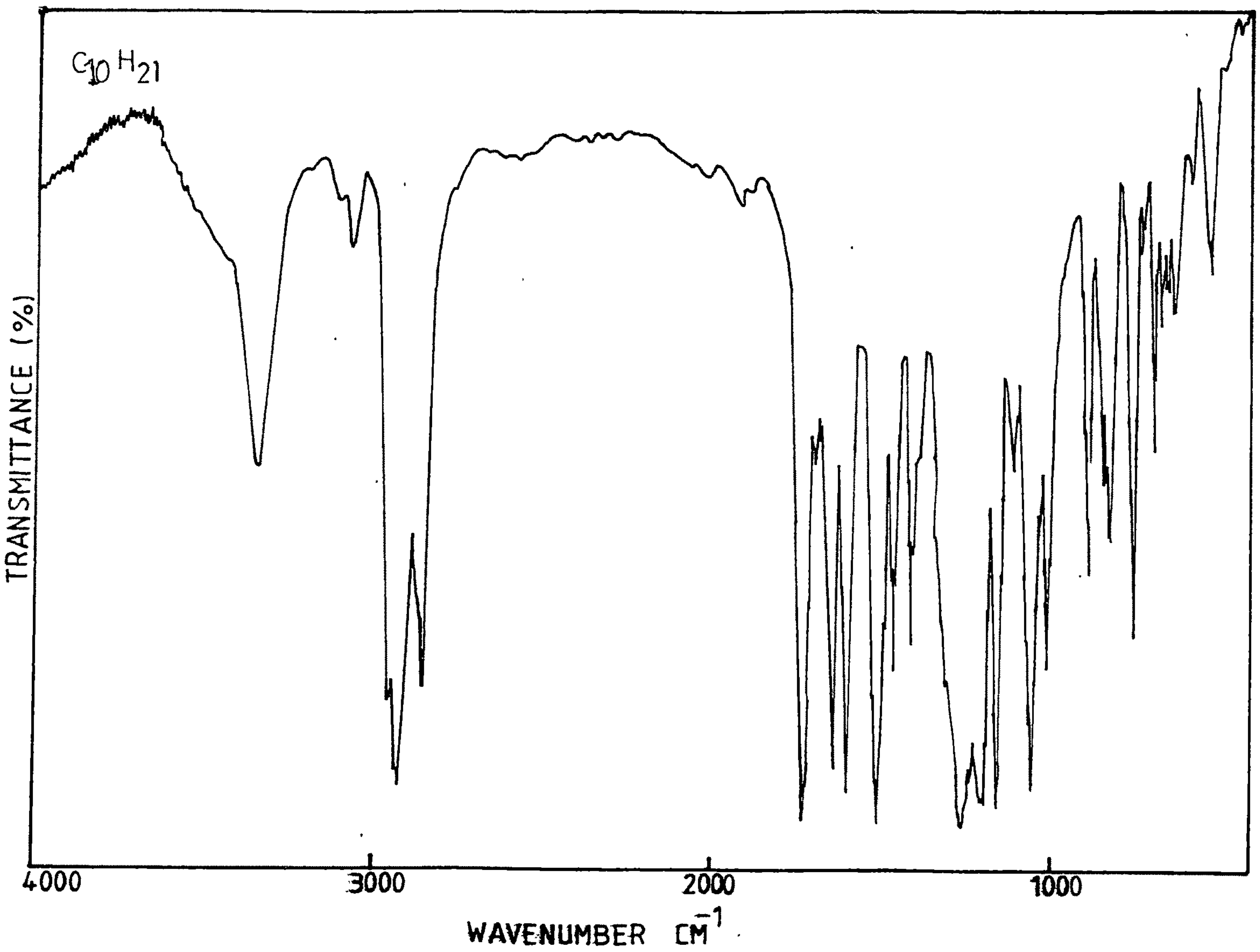


FIG. 31 : FTIR SPECTRUM OF MESOGEN OF SERIES II

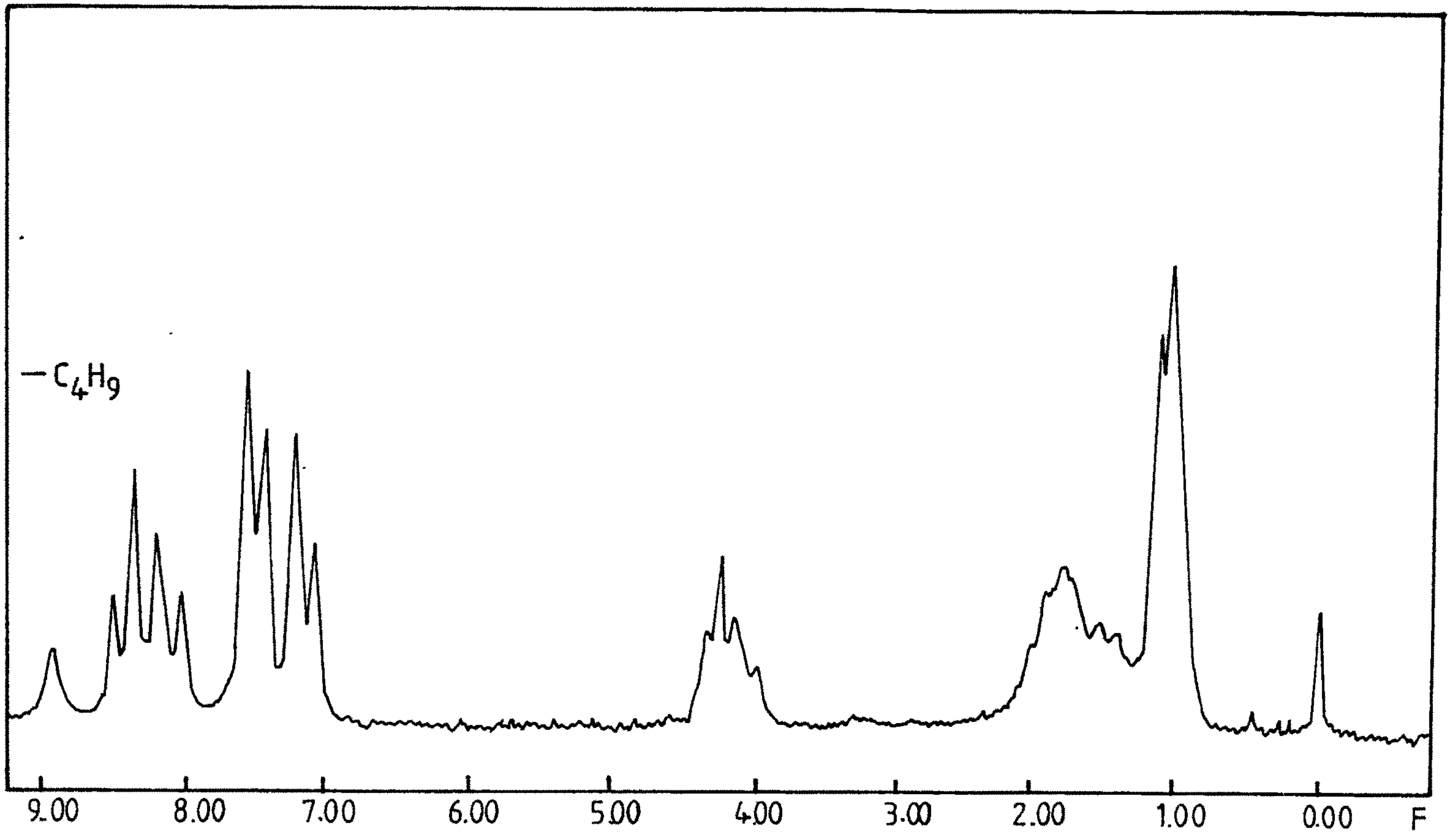


FIGURE: 32 NMR SPECTRA OF MESOGEN OF SERIES-II

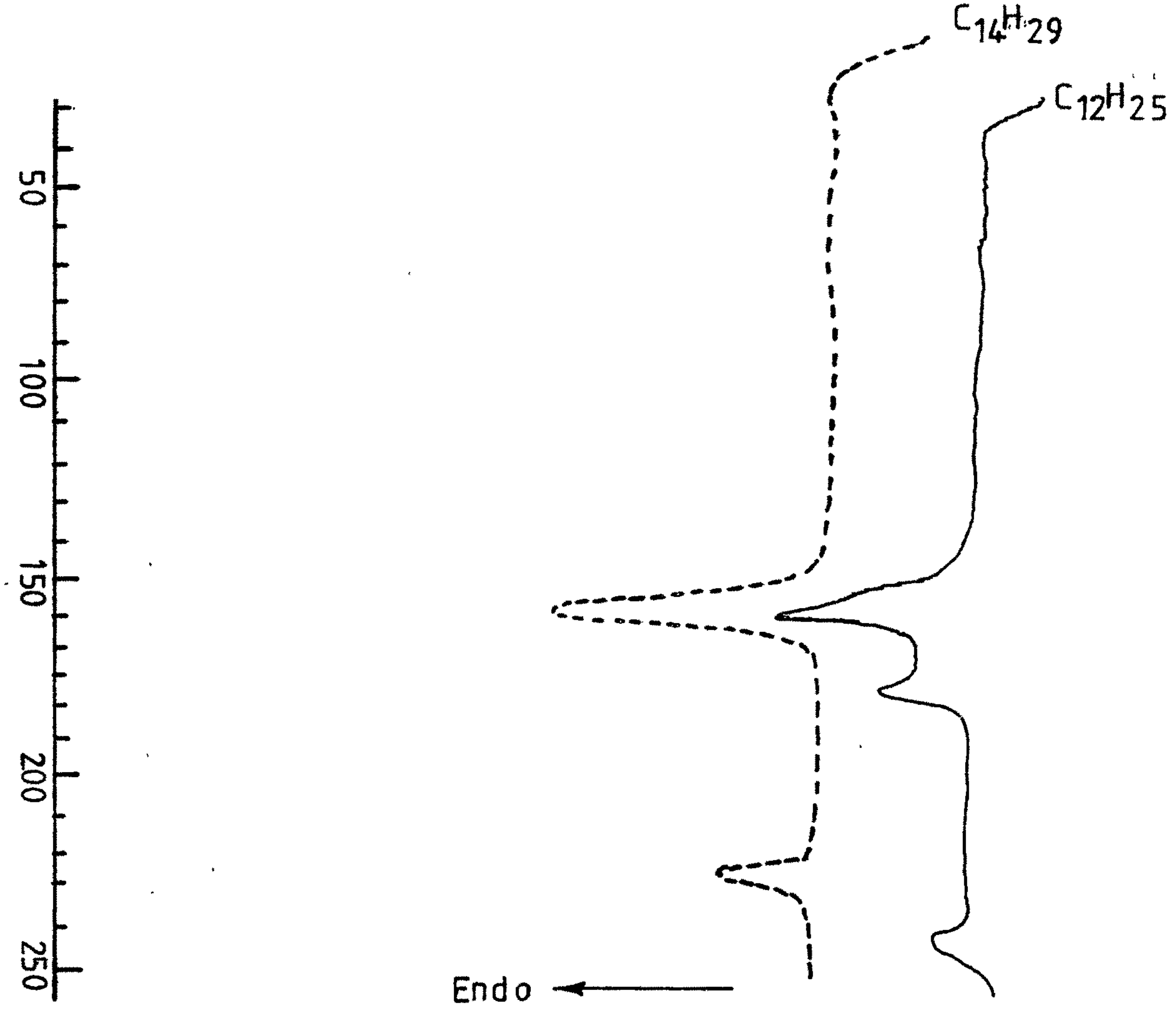


FIGURE: 33a. **DSC** THERMOGRAMS OF SERIES II

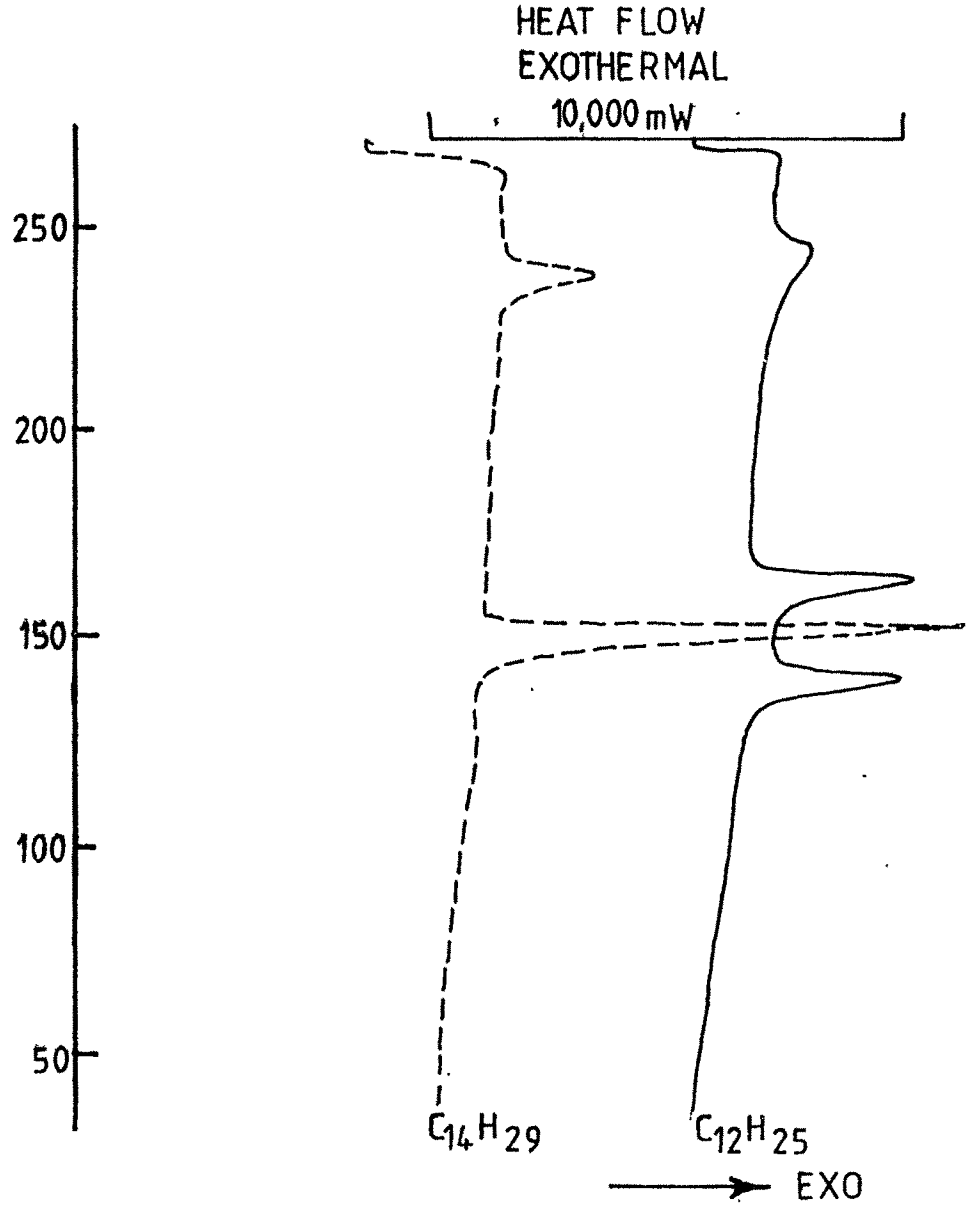


FIG. 33b. **DSC** THERMOGRAMS OF SERIES II

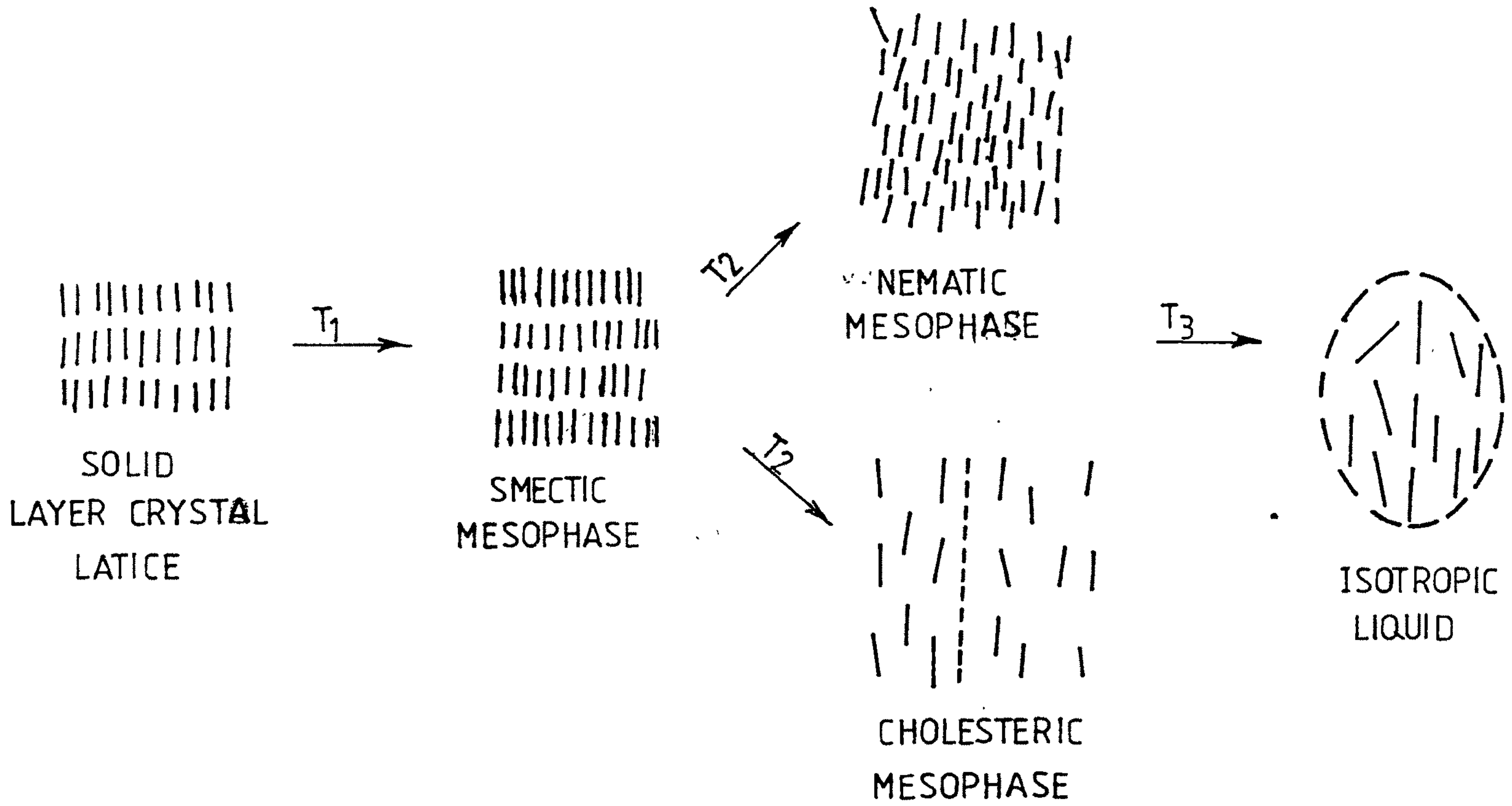

SOLID
LAYER CRYSTAL
LATICE
T_1
SMECTIC
MESOPHASE
T2
NEMATIC
MESOPHASE
T2
CHOLESTERIC
MESOPHASE
T_3
ISOTROPIC
LIQUID

FIG. 34

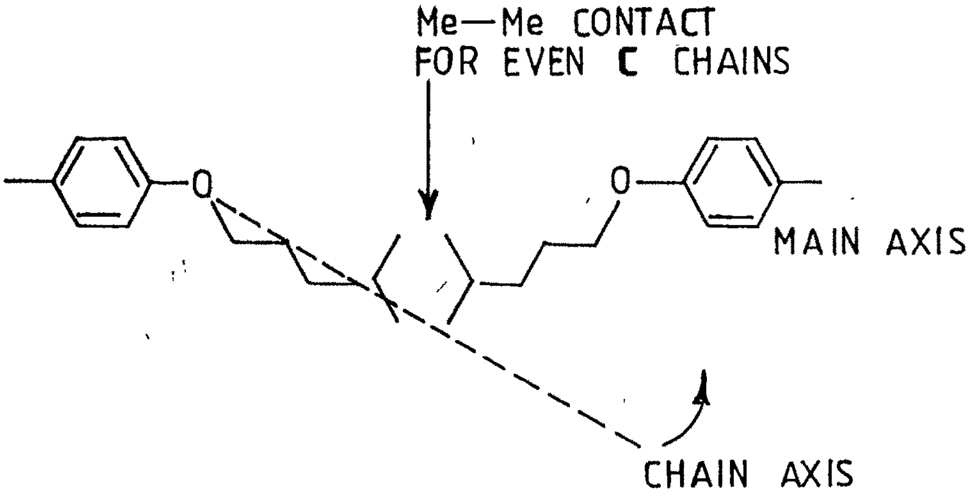
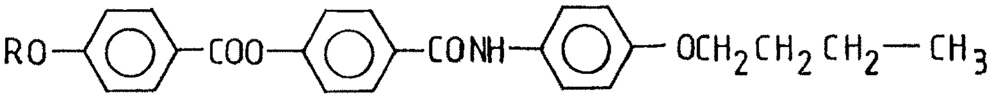
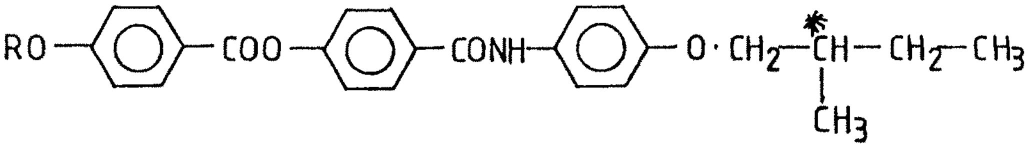


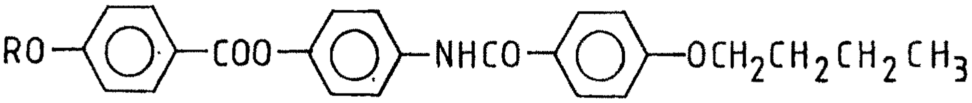
FIGURE: 35



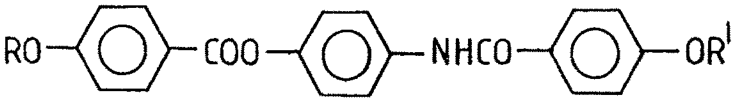
[I]



[II]

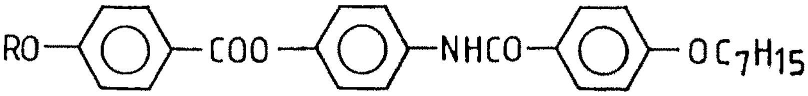


[A]

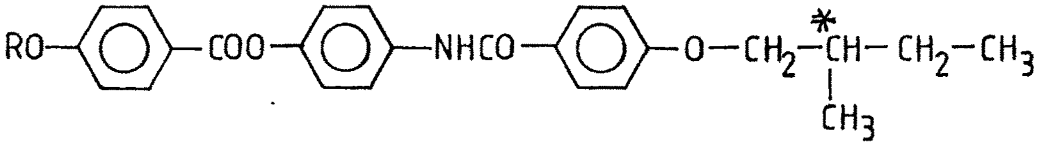


[B]

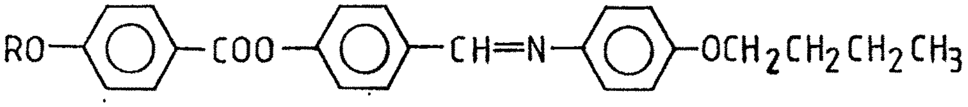
Where , $R = R'$



[C]



[D]



[E]

FIGURE :-36

ii CHOLESTERYL DERIVATIVES

Cholesteryl 4(4'-n-alkoxy benzoyl) amino benzoates: (series III)

Gray (345) and Dave and Vora (272) have reported aliphatic and aromatic esters of Cholesterol. Cholesteryl carbonates and thio-carbonates are already reported in the literature (346, 347). Vora and Teckchandani have reported Choleseryl dicarbonates with rigid and flexible spacers (348) and Dicholesteryl imide esters and carbonates with flexible spacers (349). To evaluate the effect of chemical constitution on cholesteric mesophase and to search new cholesteric and chiral smectic mesophases Vora and Teckchandani (350) studied cholesteric homologous series cholesteryl 4-n-alkoxy carbamates

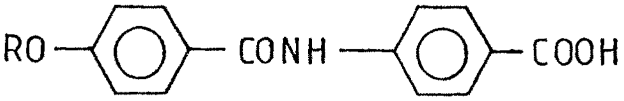
We were looking forward to synthesize a homologous series which gives smectogenic tendencies, moreover it would be quite interesting to further evaluate the effect of amide central linkage on cholesteric systems with this in view homologous series III was synthesized and its liquid crystalline properties were evaluated.

The homologous series was synthesized by following route. 4-n-Alkoxy benzoic acids were synthesized from 4-n-hydroxy benzoic acid and alkyl halides. 4-(4'-n-alkoxybenzoyl)-amino benzoic acid were synthesized by condensing 4-n-alkoxy benzoyl chlorides with 4-amino benzoic acid. N-Methyl-2-Pyrrolidone proved to be better solvent for getting higher yields.

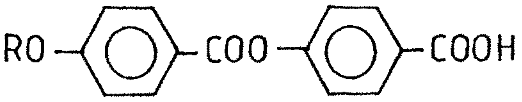
4-(4'-n-Alkoxy benzoyl)-amino benzoic acids:

Thirteen acids were synthesized by condensing 4-n-alkoxy benzoyl chlorides with 4-amino benzoic acid. None of the acids exhibit liquid crystalline properties. All members have very high melting points.

One would expect that these acids should exhibit liquid crystalline properties as 4(4'-n-alkoxybenzoyloxy)benzoic acids (274, 275, 351) exhibit mesomorphism.



Series : a



Series : b

Both the series 'a' and 'b' have difference of amide and ester central linkages. Earlier studies of Vora et al., Mckenlyre et al and Gupta have suggested that amide linkage is more conducive to mesomorphism but in this case the results are otherwise.

It seems that the secondary hydrogen bonding generated by the central linkage of molecules of 'a' which impart high melting properties might be responsible for the non-mesomorphism of these compounds.

Cholesteryl 4(4'-n-alkoxy benzoyl)-amino benzoates:

Thirteen homologues are synthesized by condensing 4(4'-n-alkoxy benzoyl)-amino benzoyl chlorides with cholesterol. Methyl to n-hexyl derivatives exhibit only cholesteric mesophases. n-Heptyl to n-dodecyl derivatives exhibit Sc and cholesteric phases. n-Tetradecyl derivative to n-octadecyl derivatives exhibit Sc, S_A and cholesteric phases. Series III was synthesized by the route shown in Figure. 37

The characterization of smectic phases is done based on their texture. However it would require to be further characterized by other physical methods to designate them as S_C and S_A phases .

The observation of the microscope slide of n-hexadecyl derivative exhibit curved lines typical to SmE phase at around ~ 224°C (Photograph K). In the case of n-octadecyl derivative texture similar to chiral SmA (fine lines, Photograph L) was observed. However, exact transition temperatures could not be determined as phase appears for a small tempeature range and compounds exhibit slight decomposition on repeated heatings.

The transition temperatures versus number of carbon atoms in the alkyl chain are plotted in Fig. 38 The cholesteric-isotropic transition temperature curve exhibits falling tendency and usual odd-even effect. The curve for the even members lies over the odd members. The Sc - cholesteric transition temperature curve rises to the maximum and then falls off. S_A to cholesteric transition temperature curve rises but does not merge with the falling cholesteric-isotropic transition temperature curve even in the n-octadecyl member.

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

Table 43 summerises the average thermal stabilities of different mesomorphic homologous series synthesized i.e.

1) Cholesteryl 4(4'-n-alkoxy benzoyl) amino benzoates (Series : III) and are compared with those of

(2) Cholesteryl 4-n-alkoxybenzylidene-4'-amino benzoates (Series A) (352)

(3) Cholesteryl 4-n-alkyl benzoyl benzoates (Series B) (353)

(4) Cholesteryl 4-n-alkoxy phenyl carbamates (Series C) (354)

The geometry of above homologous series is given in Fig. 41. Reference to table shows that cholesteric thermal stabilities of series III are slightly higher than

Table 43

Average Thermal Stabilities °C

Series	(III)	(A)	(B)	(C)
Cholesteric-Isotropic (C_1-C_6)	327.9	321.0	175.6	178.5 (C_1-C_4)
Smectic-Cholesteric/Iso. (C_7-C_{18})	252.71	226.25	137.37	167.43
Commencement of smectic mesophase	C_7	C_7	C_1	C_1

those of series A. Series : III and Series A differ only in central linkage. Series III has an amide central linkage whereas series A has an azomethine central linkage. An amide linkage is more polar compared to an azomethine linkage hence one would expect higher thermal stabilities of cholesteric phase in series III, however the increase is not as expected. Smectic thermal stability of series III are also higher than those of series A. This confirms further that amide linkage is more conducive to mesomorphism compared to azomethine linkage and enhancement is more in smectic phase compared to nematic or cholesteric phase.

The smectic and cholesteric thermal stabilities of series B is much lower compared to those of series III. Molecules of series B have keto group (>C=0) as one of the central linkage, whereas in series III central linkage is an amide group. The keto group will impart acoplanarity and even 'Kink' in the structure of molecules of series B.

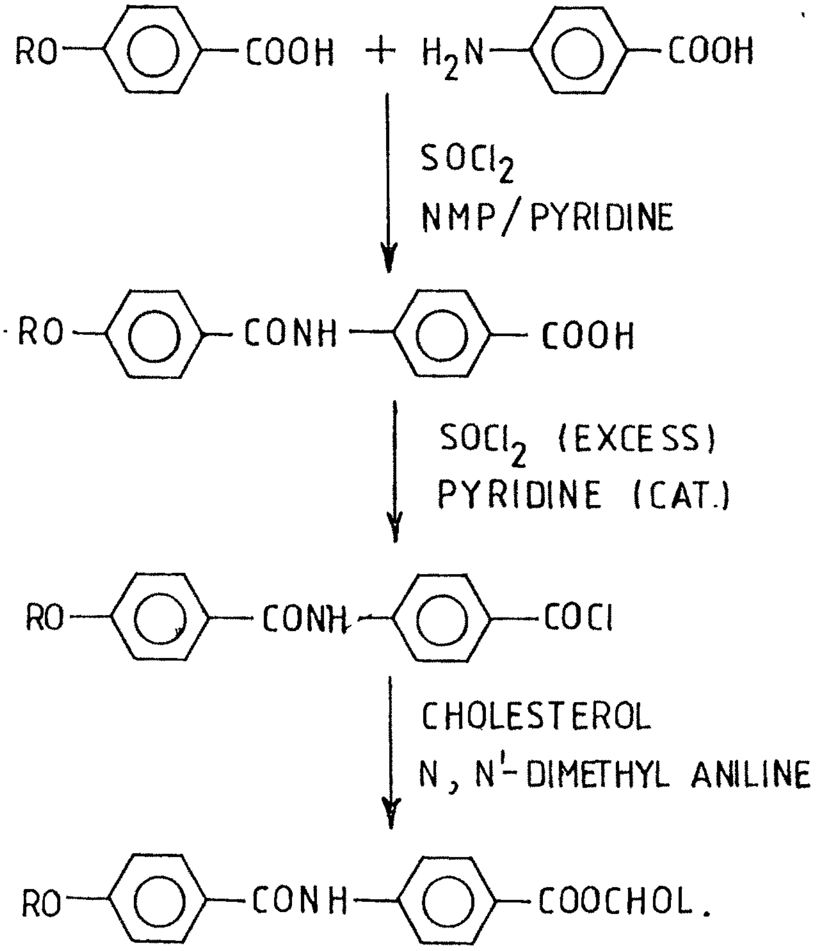
Both these factors will affect the cholesteric and smectic thermal stabilities of series B as observed in the comparison of the two series.

The molecules of series C have only one phenyl ring attached to cholesterol via urethane linkage.

The cholesteric and smectic thermal stabilities of series C are much lower compared to those of series III. This is understandable as molecules of series: C have one phenyl ring and a central linkage less compared to molecules of series III. However, smectogenic tendencies of series C is very high. Smectic phase commence from n-heptyl derivative in series III whereas it commences from the very first member of series C. The cholesteric phase is eliminated from the system from n-pentyl member. All these aspects indicate that carbamate linkage enhances smectogenic tendencies of the system much more compared to amide linkage

It is worth noting that cholesteric phase persists up to the last member of the series as observed by Dave and Vora (355). This was attributed to the effect of broad cholesteryl moiety which outways polarizability effect of higher alkyl chain in the system. It needs strong polar group or a central linkage in the case with series C to eliminate cholesteric phase from the higher homologues. This is observed in normal nematogenic systems of rod-like molecules (13).

The liquid crystalline behaviour of the series has further supported the view that amide central linkage enhances liquid crystalline properties of the system and enhancement is more in smectic phase thermal stabilities compared to schiff base or a keto central linkage. Compounds exhibit cholesteric phases at very high temperatures and can be good candidates for high temperature thermography. Smectic phases are characterized by textures.



$R = C_nH_{2n+1}$, n= 1 to 8,10,12,14,16,18

CHOL. = CHOLESTERYL GROUP

FIGURE:37 SYNTHETIC ROUTE TO SERIES III

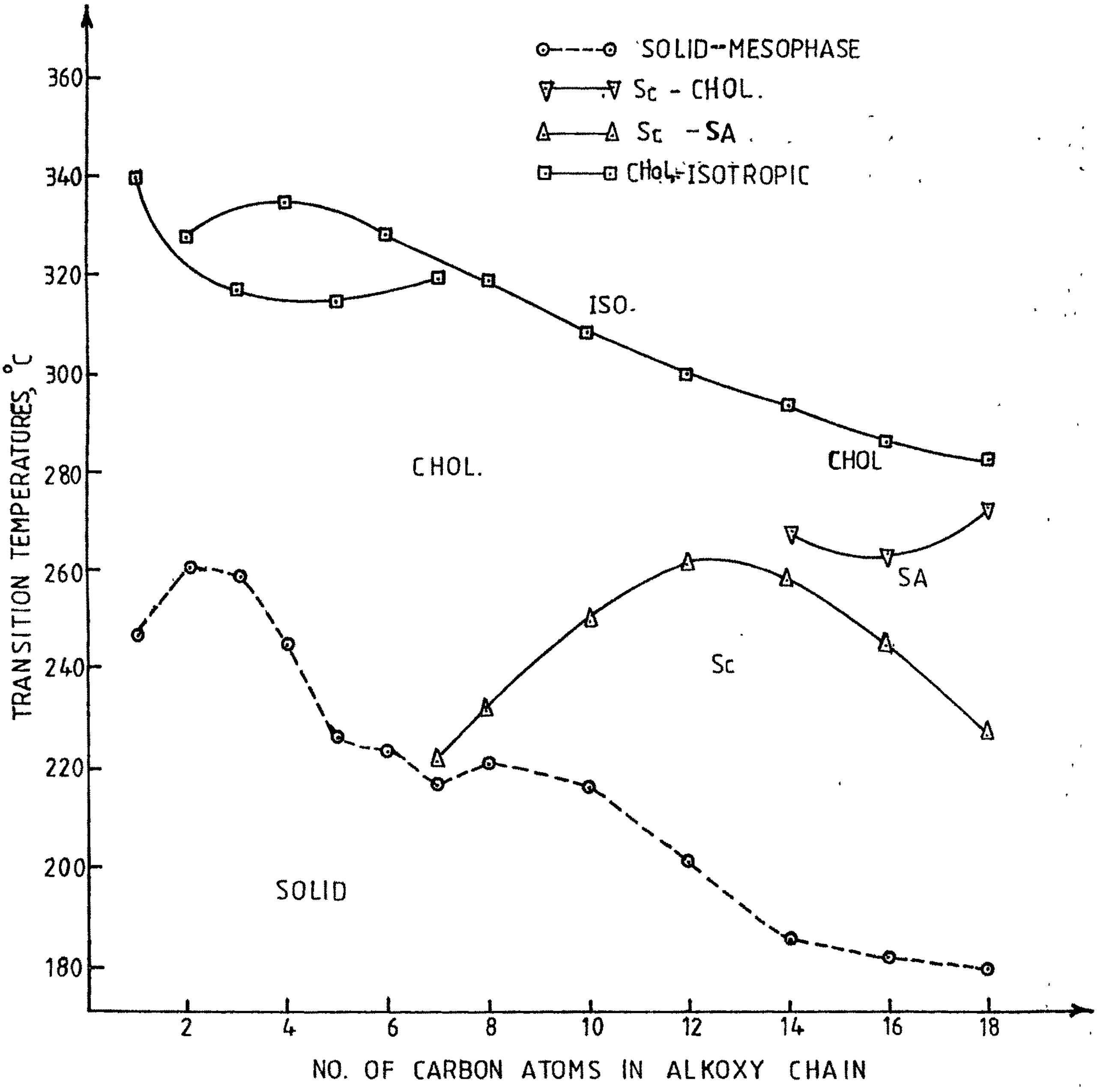


FIGURE :38 CHOLESTERYL 4 (4'-n-ALKOXY BENZOYL) BENZOATES (SERIES-III)

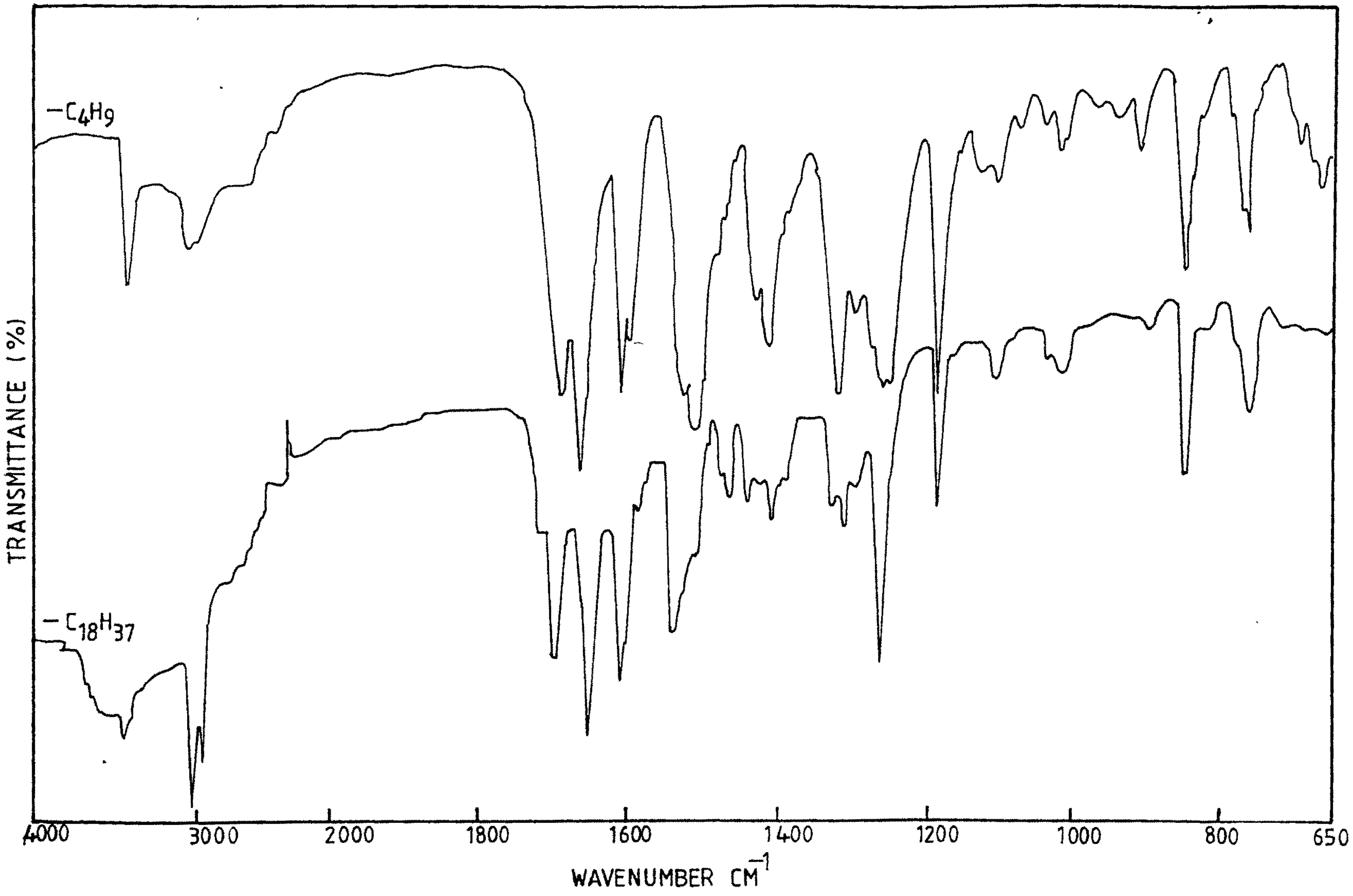


FIGURE:39a IR SPECTRA OF COMPOUNDS OF SERIES III

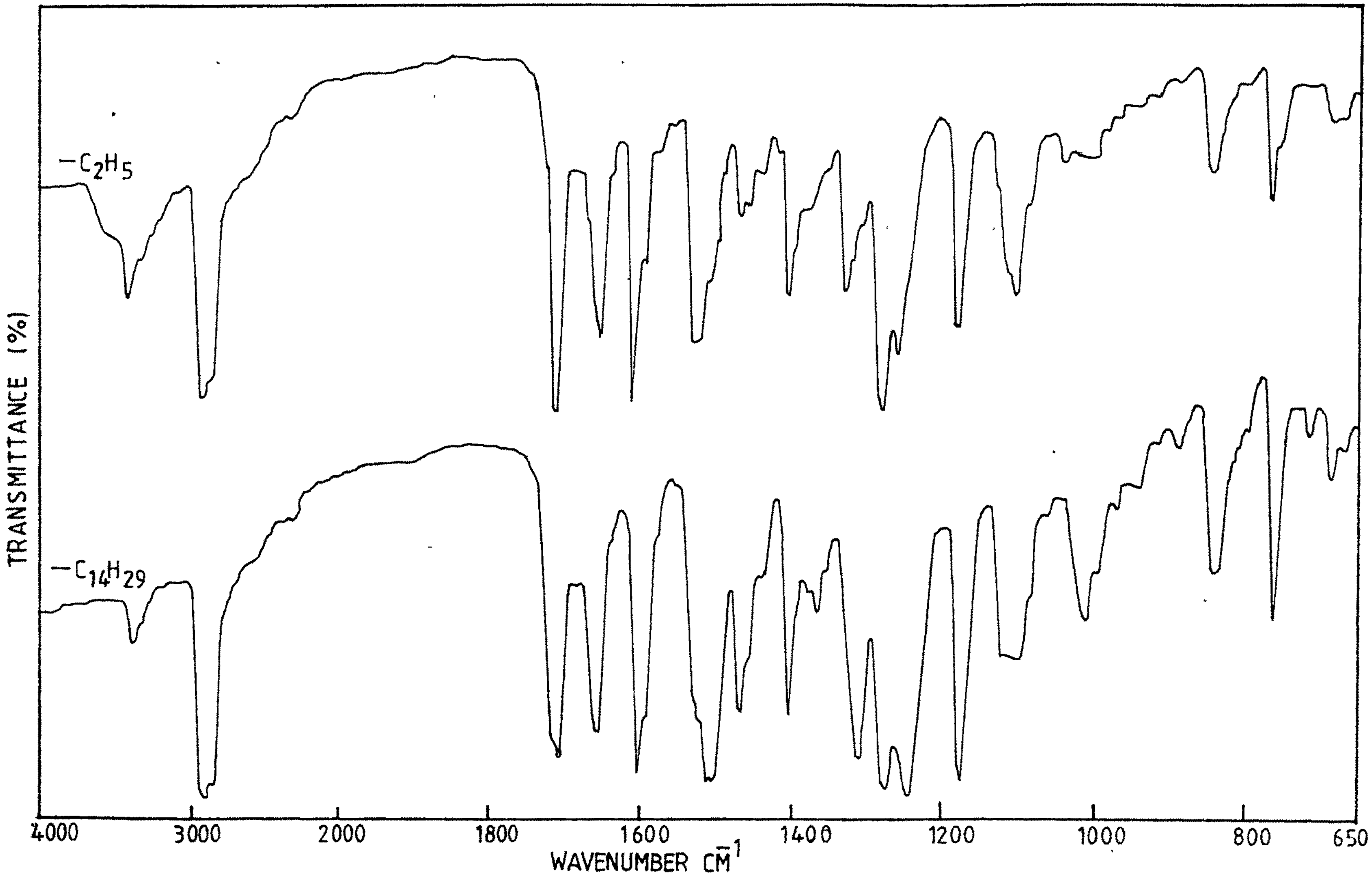


FIGURE :39b. IR SPECTRA OF MESOGENS OF SERIES-III

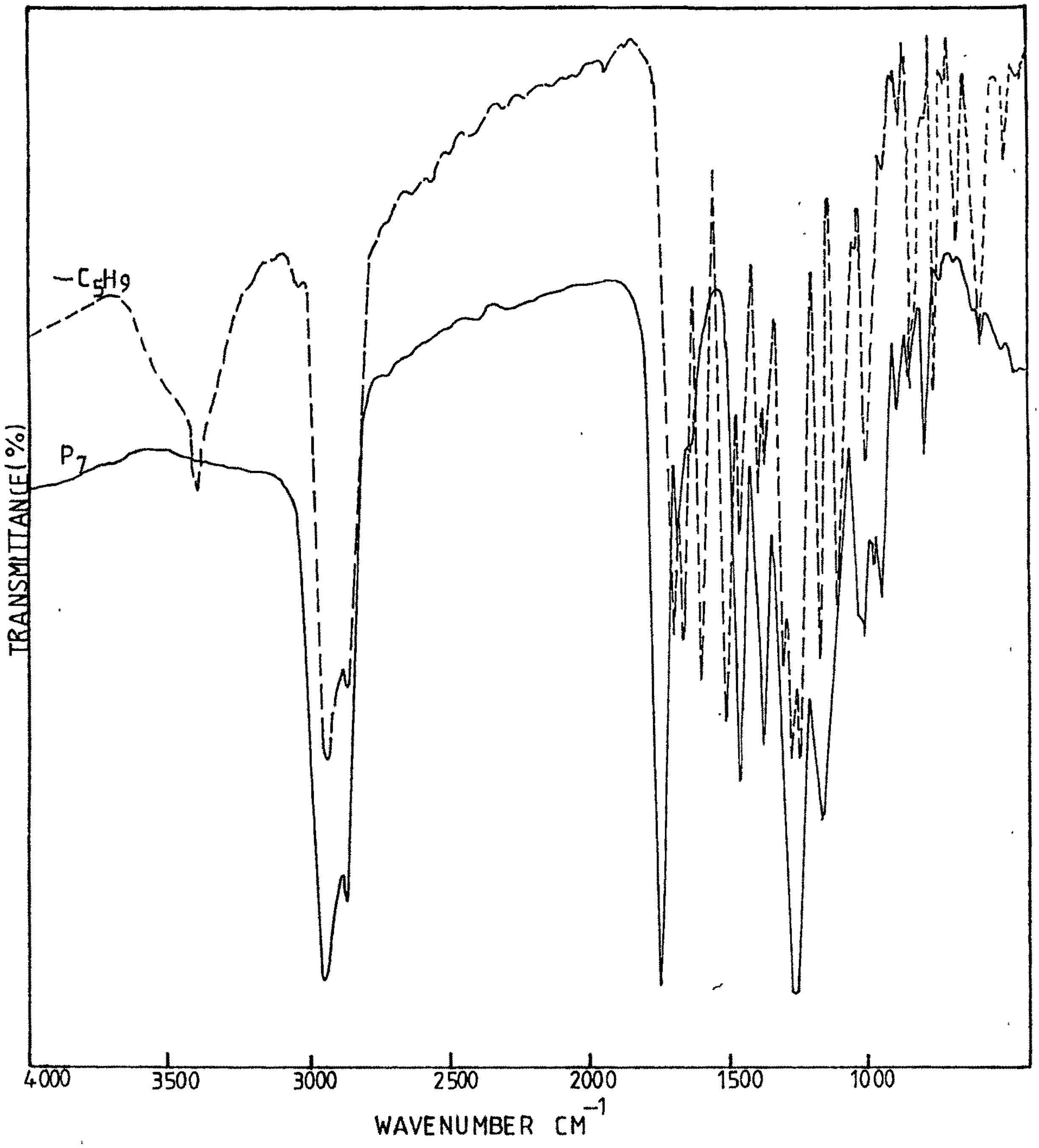


FIG. 39c. FTIR SPECTRUM OF MESOGENS OF SERIES III AND POLYMER

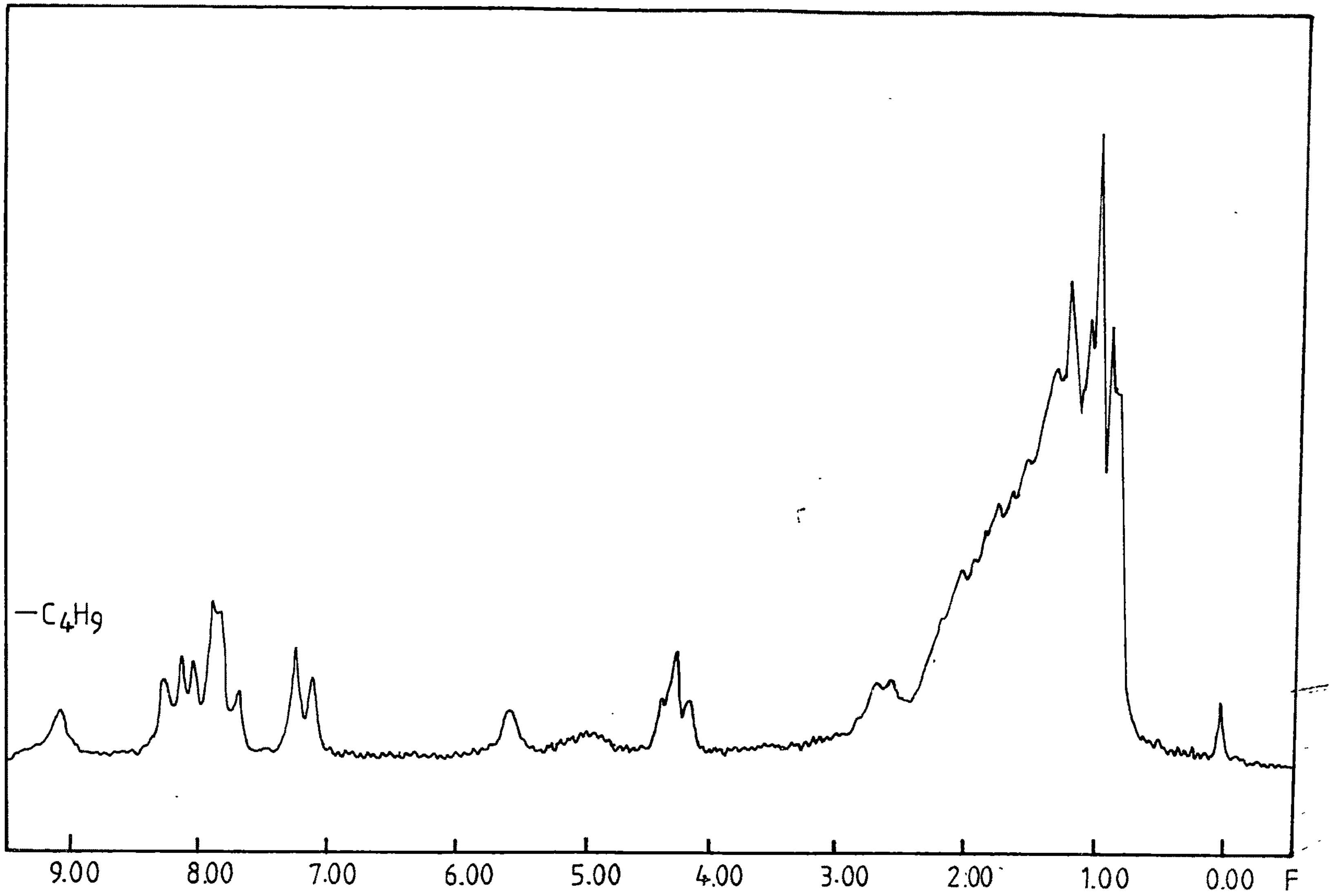
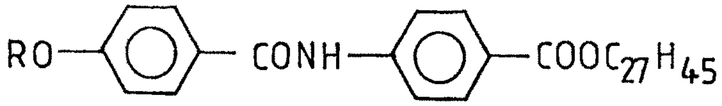
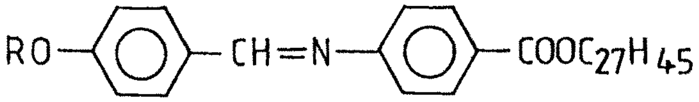


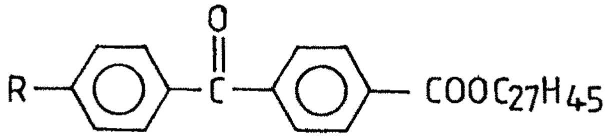
FIGURE :40 NMR SPECTRA OF MESOGEN OF SERIES-III



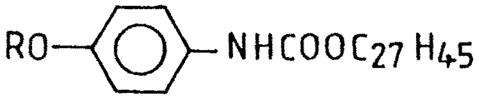
[III]



[A]



[B]



[C]

Figure : 41

iii OTHER MESOGENIC COMPOUNDS

Other Mesogenic Compounds:

Mesogenic compounds having - NO_2 group at both the terminus : It will be quite interesting to study the effect of nitro group present at both the terminus of a mesogenic molecules.

Two compounds of such structures are synthesized (Figure 42a)

i) Bis (4-nitrobiphenyl) adipate (AC-1)

ii) Bis (4-nitrobiphenyl) terephthalate (AC-2)

Both compounds exhibit nematic mesophase, compound AC-1 having four flexible methylene units exhibit nematic mesophase, compound AC-2 having two biphenylene units and central phenylene group also exhibit nematic mesophase at very high temperature. This is as expected because of total aromatic nature of molecules of AC-2 having central rigid p-phenylene ring. One would expect that such a compound may exhibit smectic mesophase. It's surprising that compound AC-2 does not exhibit smectic phase. Two terminal nitro groups might generate repulsion in close packing of the molecules, which may not allow ordered smectic phase to exist. If on one of the terminus alkoxy group exists then the molecules may exhibit smectic phase.

A few cholesteric derivatives with special features:

Flexibility plays an important role in mesomorphic properties. In many mesogenic compounds introduction of flexibility either eliminates mesophase or renders it to monotropic in nature. It also lowers melting points as well as mesogenic-isotropic transition temperatures.

Cholesteric compounds with large mesophase range and higher transition temperatures are useful in applications in non-destructive testing devices.

With this in view and to initiate the study in this direction two cholesteric derivatives are synthesized. (Figure . 42 b)

4-n-Alkoxy benzoyl glycine:

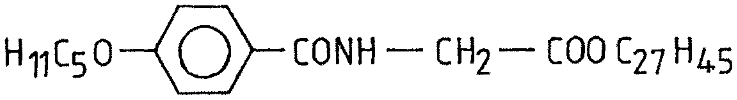
4-n-Butoxy and 4-n-pentyloxy benzoyl glycine were synthesized by known methods (281). Both are analyzed, their melting points are as under:

i)	4-n-butoxybenzoyl glycine	M.P. 145.0°C
ii)	4-n-pentyloxy benzoyl glycine	M.P. 126.0°C.

Recent reference indicate that hydrogen bonding induces mesomorphism in simple organic compounds (355 a,b,c). However in the present study both the glycine derivatives are non-mesogenic, may be because of secondary hydrogen bonding resulting out of amide linkage.

Cholesteryl 4-n-alkoxybenzoyl gylcines:

Cholesteryl 4-n-butoxy benzoyl glycine (GC-1)



Cholesteryl 4-n-pentyloxy benzoyl glycine (GC-2)

Both the compounds exhibit cholesteric phase of broad range and high transition temperatures. Cholesteric phase shows its classical textures like focal-conic and plane texture. Normally plane texture exhibits vivid colours. None of them exhibit blue phase.

As mentioned earlier flexibility has decreased solid-cholesteric transition temperatures but decrease in cholesteric-isotropic transition temperature is not marked one. It seems cholesterol moiety with a flexible chain having amide linkage exhibits higher cholesteric thermal stability. These compounds can be used with other cholesterics for high temperature detection.

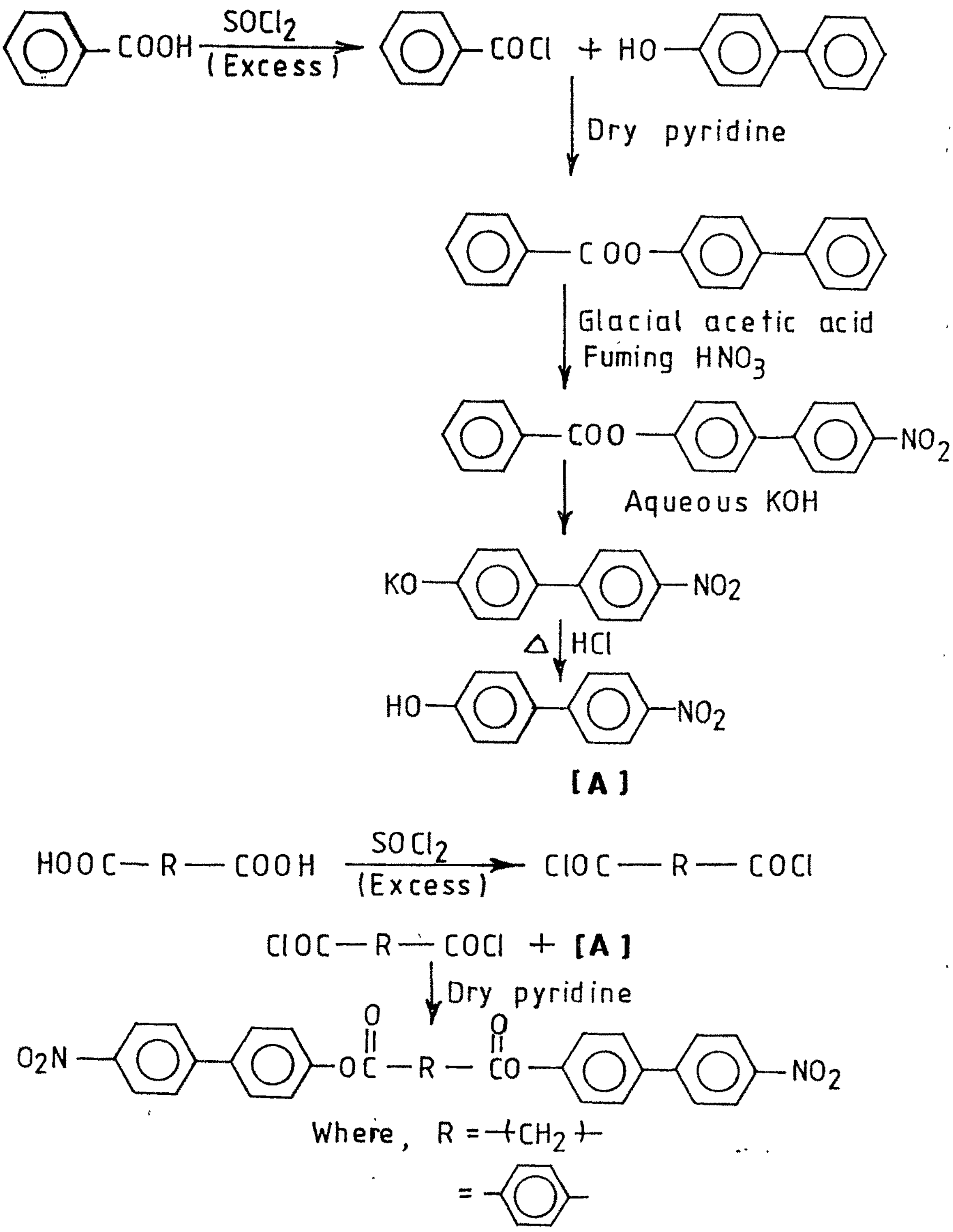
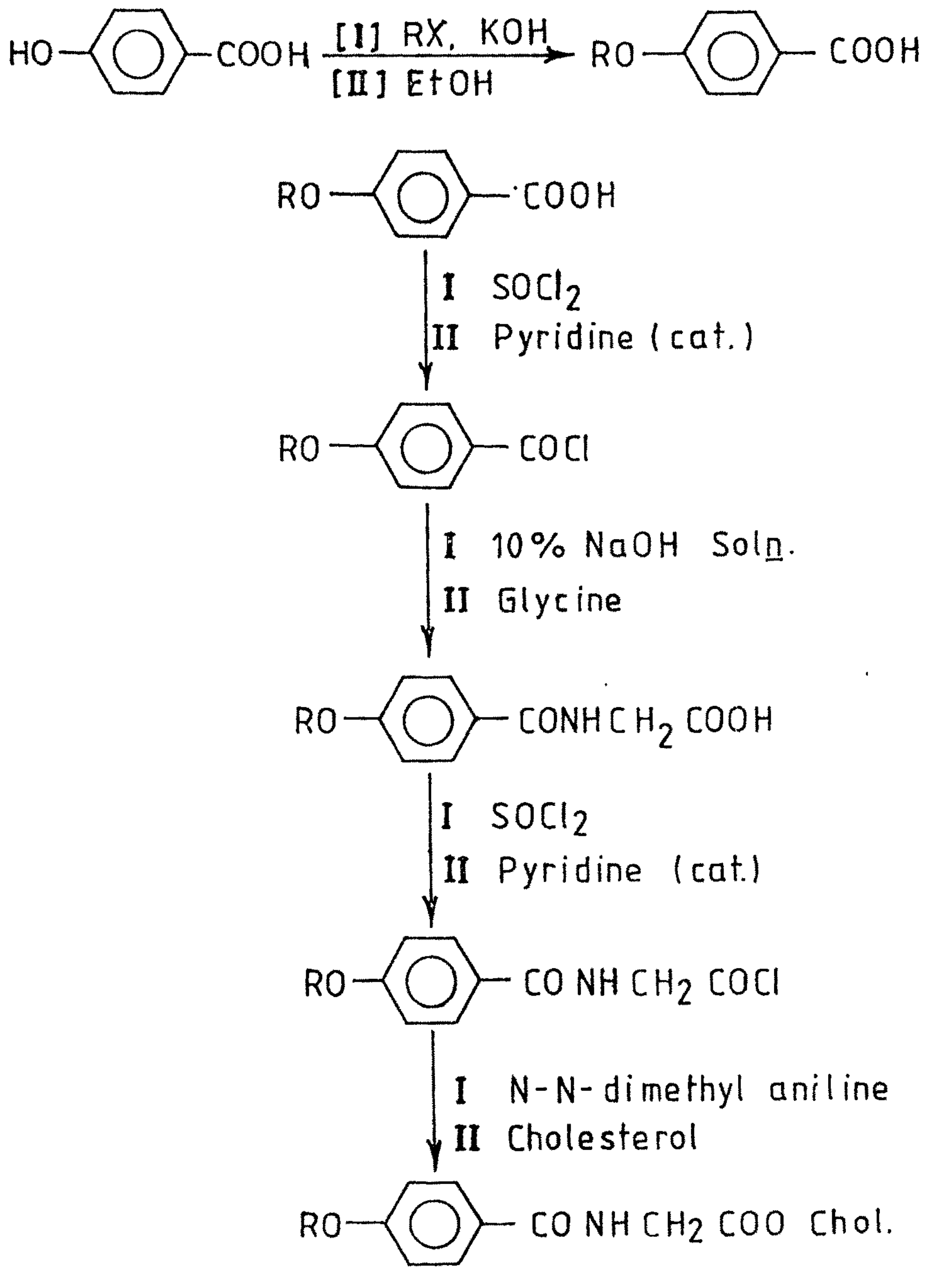


FIGURE: 42a. SYNTHETIC ROUTE OF OTHER MESOGENIC COMPOUNDS.



R = $-C_4H_9$
$-C_5H_{11}$

Chol. = Cholesteryl Group

FIGURE:42b SYNTHETIC ROUTE OF OTHER MESOGENIC COMPOUNDS.

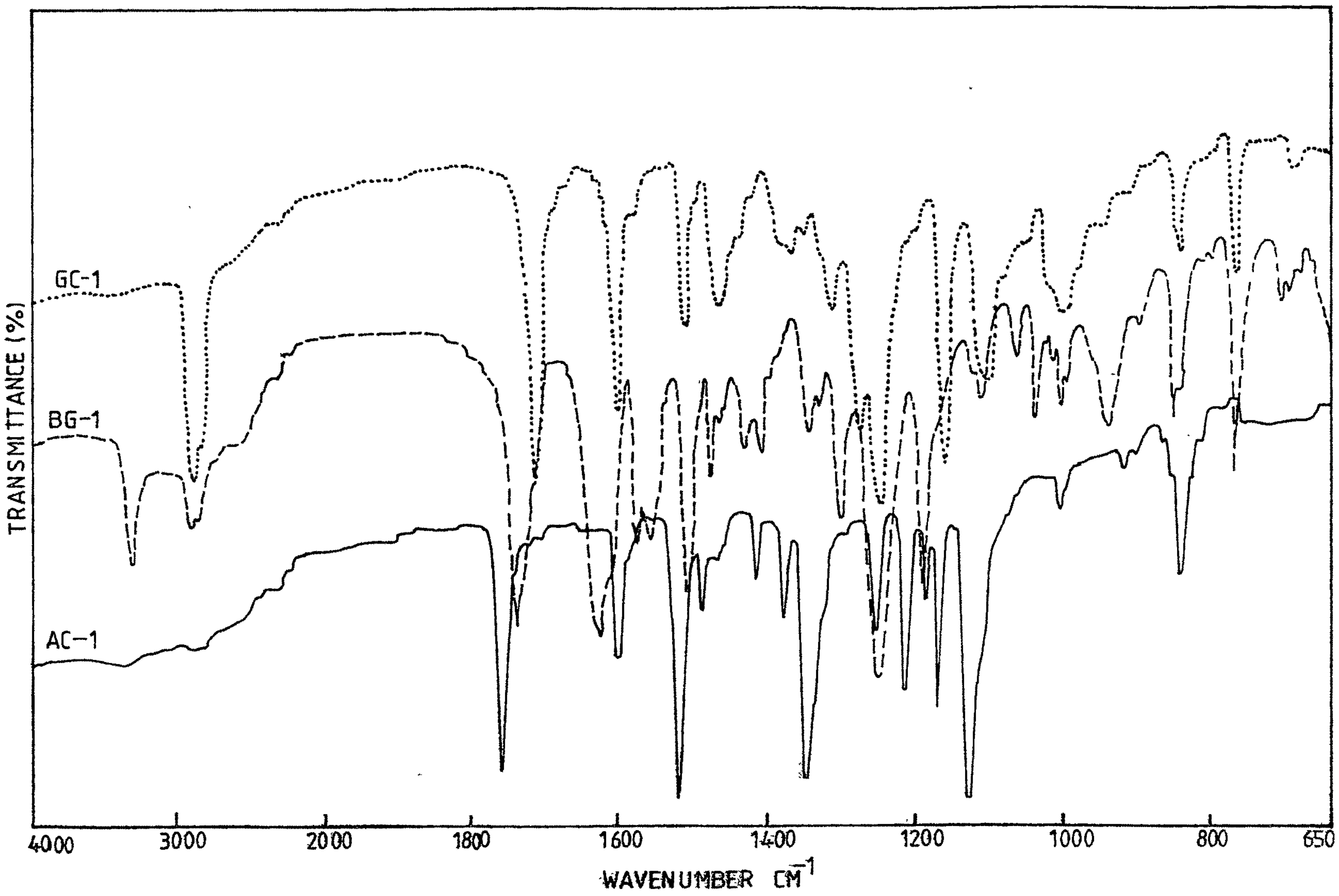


FIG. 43 IR SPECTRA OF OTHER MESOGENIC COMPOUNDS

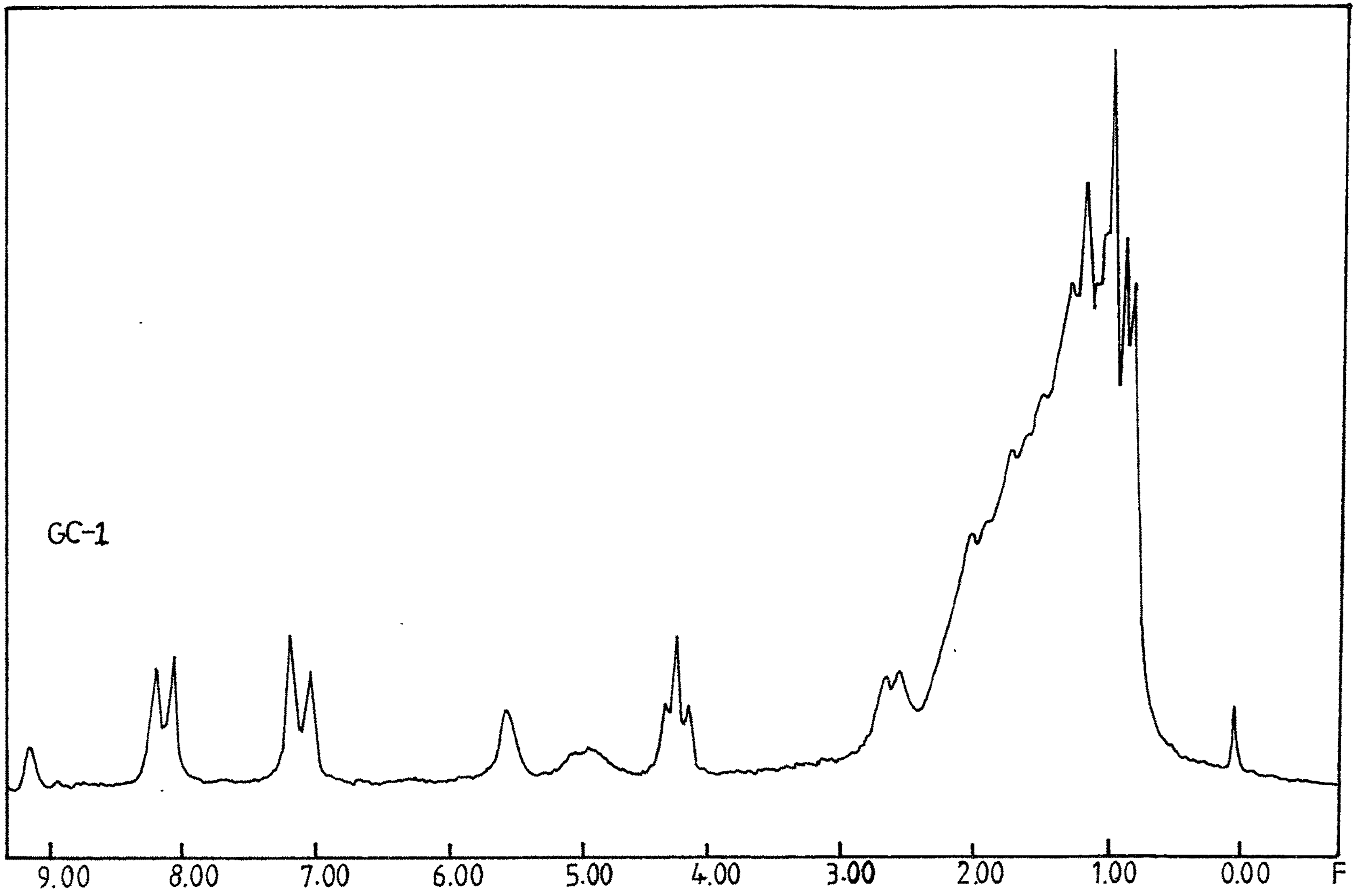


FIGURE:44 NMR SPECTRA OF MESOGEN OF OTHER COMPOUND

iv SIDE CHAIN MESOGENIC POLYMERS

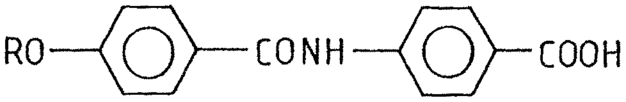
Side Chain Liquid Crystalline Polymers:

For many years, liquid crystalline side chain polymers have been investigated intensively for their scientific and technical potential (199,356-359). Side chain polymers with flexible spacers exhibit mesomorphism. The concept of flexible spacer was originally proposed by Finkelmann et al., (360). However, it has been pointed out that without flexible spacers side chain polymers can exhibit mesomorphism (361, 362). Even polymers exhibiting mesomorphism with main chain having a broad segment as side chain have been reported (363). Our school got interested in main chain polymers with amide and ester-amide linkages. To understand the mesogenic properties of polyesteramides and polyamides number of mesogenic systems, model compounds and homologous series with esteramides and only amide linkages were studied (181, 364, 365)

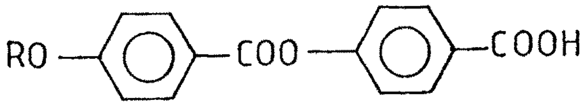
Monomers and polymers are synthesized as described in the experimental section. The synthetic route is given in Figure 45. The melting of monomers and transition temperatures are recorded in experimental section. The monomers and polymers are characterized by elemental analysis and IR spectra. Polymers were further evaluated by using viscosity, TGA, GPC, Fluorescence spectra, conductivity, and x-ray study.

Shibaev et al., (366) studied thermotropic LC polymers having an amide linkage. Gallot et al, (367) reported polyacrylamide segment containing LC polymers. This shows interest in Liquid Crystalline polymers with amide linkage is increasing. Number of polyacrylates and polymethacrylates having side chain with ester linkages and mesogenic pendant groups are reported (356, 357, 368-370).

The mesogenic segment of polymers from P_1 to P_6 is amidoacids. Similar compounds with an ester linkage exhibit liquid crystalline properties.



(i) Non-Mesogenic



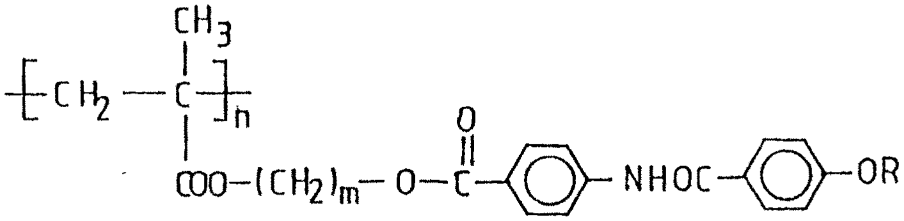
(ii) Mesogenic

Earlier studies have shown that amide linkage enhanced mesomorphic behaviour of a system (181, 364, 365). In the present study 4-(4'-n-Alkoxy benzoyl)-amino benzoic acids have been synthesized. The data in section 2.4.1.2 indicates that none of the monomers exhibit mesomorphism It seems that the amide linkage might be inducing intermolecular hydrogen bonding which would be non-conducive to mesomorphism. Monomers having ester linkage with similar structures exhibit mesomorphism.

As some of the side chain polymers having an amide linkage exhibit liquid crystalline properties it was imperative that polymers P1 to P6 (Table 17) having meso phase conducive groups will exhibit mesomorphism. In the present study it has been found except polymer P_4, all the five polymers exhibit birefringence on cooling the melt with the shear force. In the case of polymer P_4, birefringence is observed on cooling as well as on heating. It seems, the melt results in homeotropic arrangement hence classical structure of nematic or smectic phase is not observed However shearing

Table 17

Transition Temperatures of Polymethacrylates:



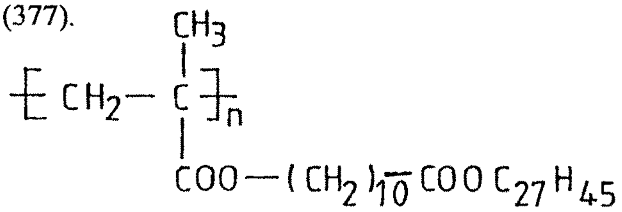
Sr. No.	Code	R n-alkyl group	m	Transition Temperatures °C
1	P_1	Butyl	2	$K \xrightarrow[{[102]^*}]{140} \text{Iso}^{+}$
2	P_2	Octyl	2	$K \xrightarrow[{[97]^*}]{120} \text{Iso}^{+}$
3	P_3	Dodecyl	2	$K \xrightarrow[{[84]^*}]{105} \text{Iso}^{+}$
4	P_4	Butyl	6	$K \xrightarrow[{[106]^*}]{125} \text{Iso}^{++}$
5	P_5	Octyl	6	$K \xrightarrow[{[54]^*}]{104} \text{Iso}^{+}$
6	P_6	Dodecyl	6	$K \xrightarrow[{[43]^*}]{97} \text{Iso}^{+}$

\+ Melt exhibits birefringence on cooling

++ Melt exhibits intense birefringence when disturbed on heating as well as cooling gives birefringence and nematic type texture for a moment. Removal of shear stress again results into homeotropy.

Results indicate that side chain polymethacrylates having ester and amide linkage have high tendency to give homeotropic phases.

Polymers exhibiting cholesteric optical properties have been prepared and elegantly characterized by Finkelmann in collaboration with Ringsdorf and Rehage (209, 213, 371, 372). Shibaev et al., (373, 374) have synthesized three varieties of poly cholesteryl ω-methacryloyloxyalkanoates (flexible spacer, n=5,10 and 14) and have reported on the existance of a liquid crystalline phase and its structure. Shannon (375) has synthesized methacrylate and acrylate monomers of cholesteric esters via Phase-Transfer catalysis. Methacrylate monomers (n=3,4,5,10) exhibit mesomorphism. Thermal study on liquid crystalline side-chain polymers containing the cholesteryl group is carried out by Yamaguchi et al., (376). Abrikosov phases (smectic A*) have been detected in optically active polymeric side chain liquid crystalline polymers. For example, the chiral polymer of the structure shown below was found to exhibit a twisted smectic A* phase (377).



$$\left[CH_2-\underset{COO-(CH_2)_{10}-COOC_{27}H_{45}}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} \right]_n$$

When this polymer forms a liquid crystalline phase it is thought that the main chain of the polymer prevents a cholesteric phase from forming and instead induces the formation of smectic A phase. However, the strong chirality of the side group forces the layers to twist to give an abrikosov phase. In the present study we report solution polymerization of cholesteryl carbonates having vinyl group. They exhibit mesomorphism.

Monomers and polymers are synthesized as described in the experimental section. The synthetic route is given in figure 47. The monomers and polymers are characterized by elemental analysis and IR spectra. Polymers were further evaluated by using viscosity, TGA, GPC, Fluorescent spectra, conductivity and X-ray study.

Both the monomers having flexible methylene spacers 2 (M_7) and 6 (M_8) exhibit monotropic cholesteric phases. The solution polymerization of both the monomers resulted into oligomeric cholesteric compounds P_7 and P_8. Both their oligomers exhibit smectic mesophase having texture like Sm*C phase. Mesogenic oligomers on cooling exhibit Sm*C phase upto room temperature indicating high super cooling tendency.

A Co-polymer of M_7 i.e. cholesteryl carbonate with ω-Hydroxyethyl methacrylate and butyl methacrylate in (80:20 ratio) respectively was synthesized The resulting polymer also exhibits smectic *C phase of good thermal stability. Polymers also exhibit good fluorescence behaviour. Co-polymer exhibits maximum fluorescence. The polymers have less fluorescence properties compared to respective monomers.

As mentioned earlier all the monomers and polymers (oligomers) exhibit mesomorphism. The oligomers will be tested for their application aspect.

The polymer P_7 was screened by DSC method at a scan rate 10°C/min. and 20°C/min. (Fig 49). Both DSC results indicate that polymer P_7 exhibits endothermic peak on heating for solid-cholesteric transition but does not exhibit endothermic peak for cholesteric-isotropic transition. Enthalpy and Entropy values are recorded in Table 35.b.

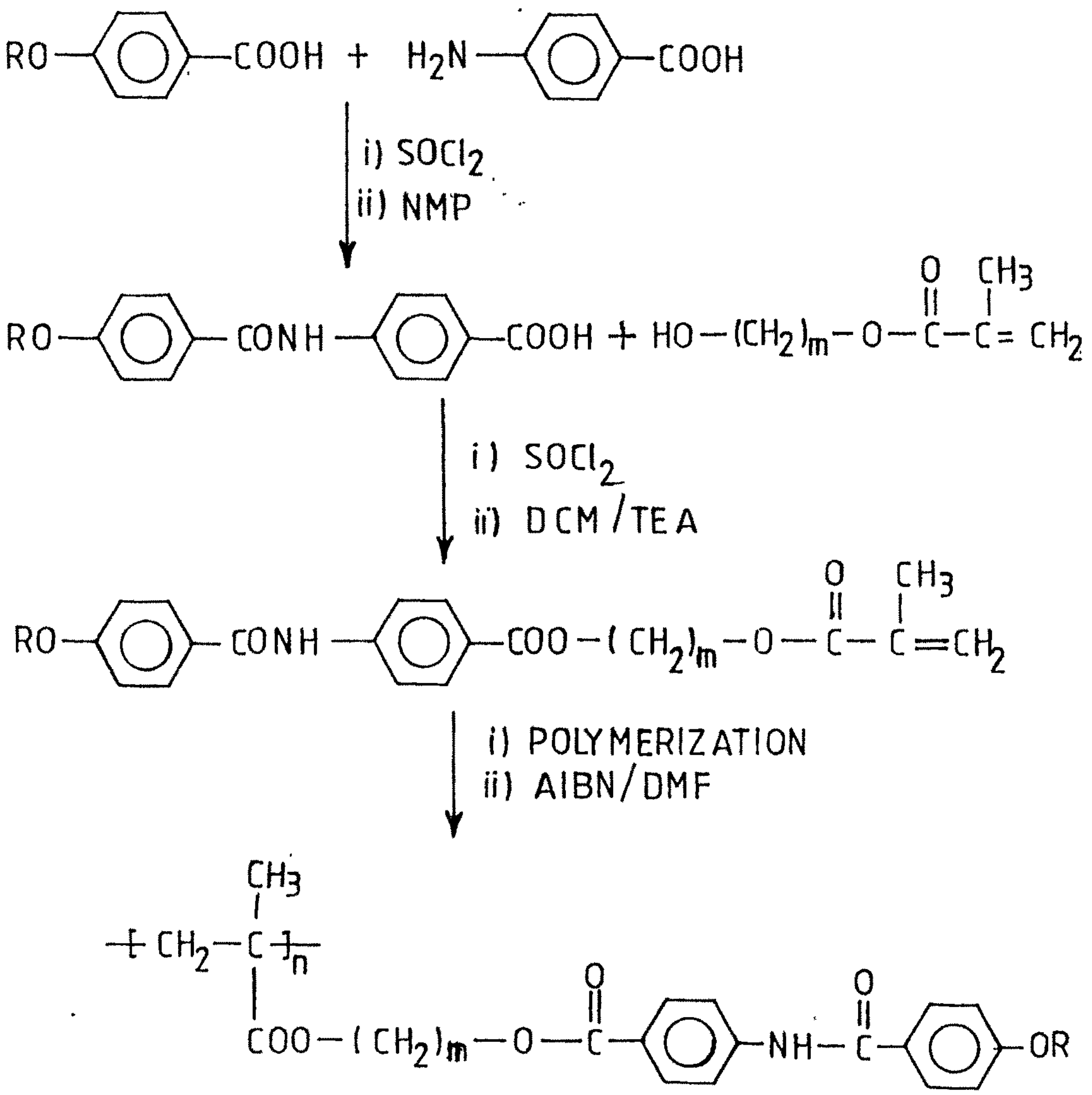
Table 21.a

Transition temperatures of Monomers, Polymers and Co-polymer having Carbonate linakage

Code	m	Transition Temperatures °C		
		Sc	Chol.	Isotropic
M_7	2	-	(40.0)	79.0
M_8	6	-	(49.0)	59.0
P_7	2	89.0	-	131.0
P_8	6	58.0	-	72.0
CP	-	95.0	-	119.0

( ) Indicates monotropic transition temperatures

CP = Co-polymer (P_7 +Butyl Methacrylate)
(80:20)



WHERE, R = C_4H_9, C_8H_{17}, AND, $C_{12}H_{25}$

m = 2 AND 6

FIGURE: 45 SYNTHETIC ROUTE OF POLYMETHACRYLATES

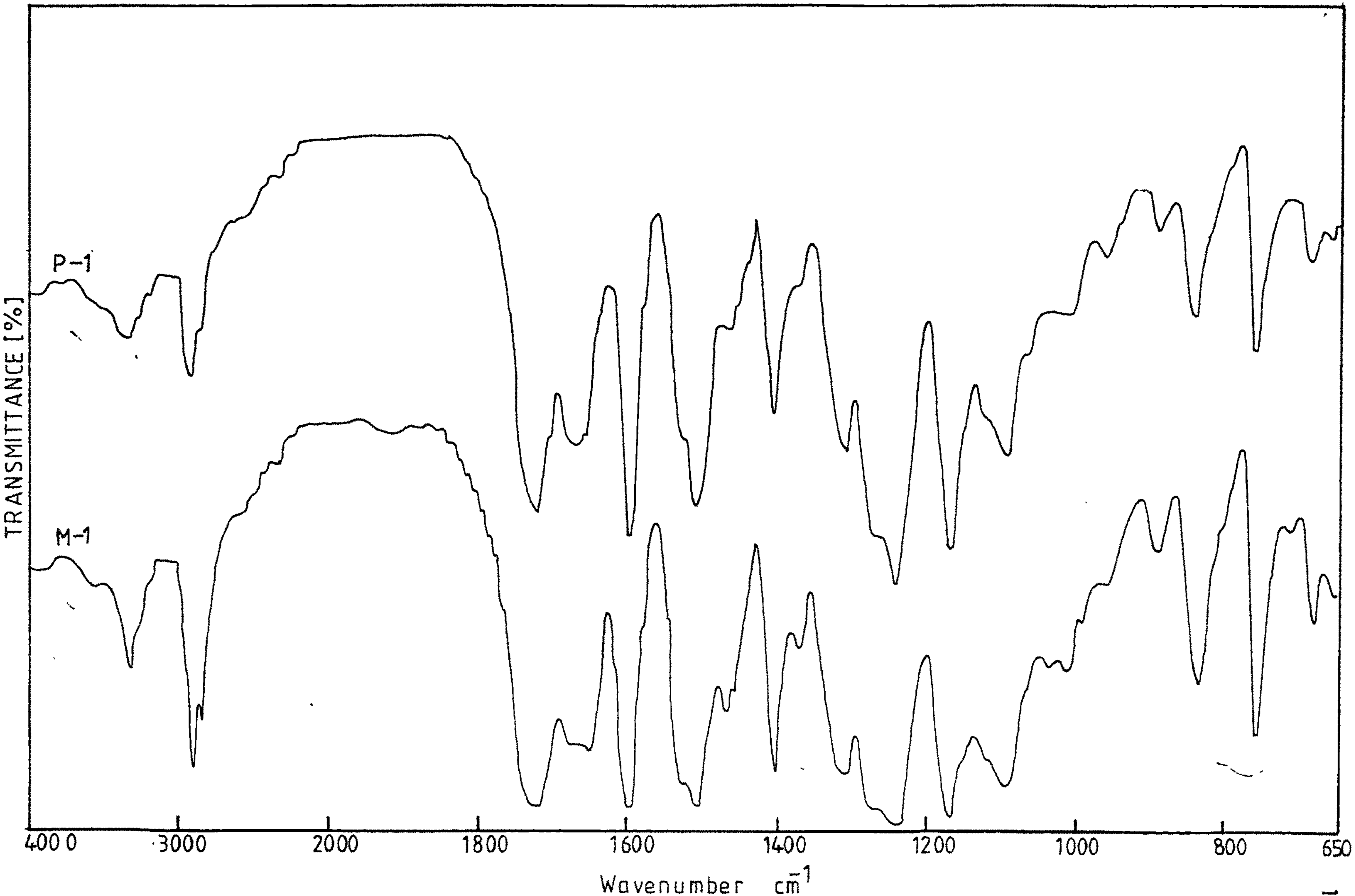


FIGURE:46a IR SPECTRA OF MONOMER AND POLYMER

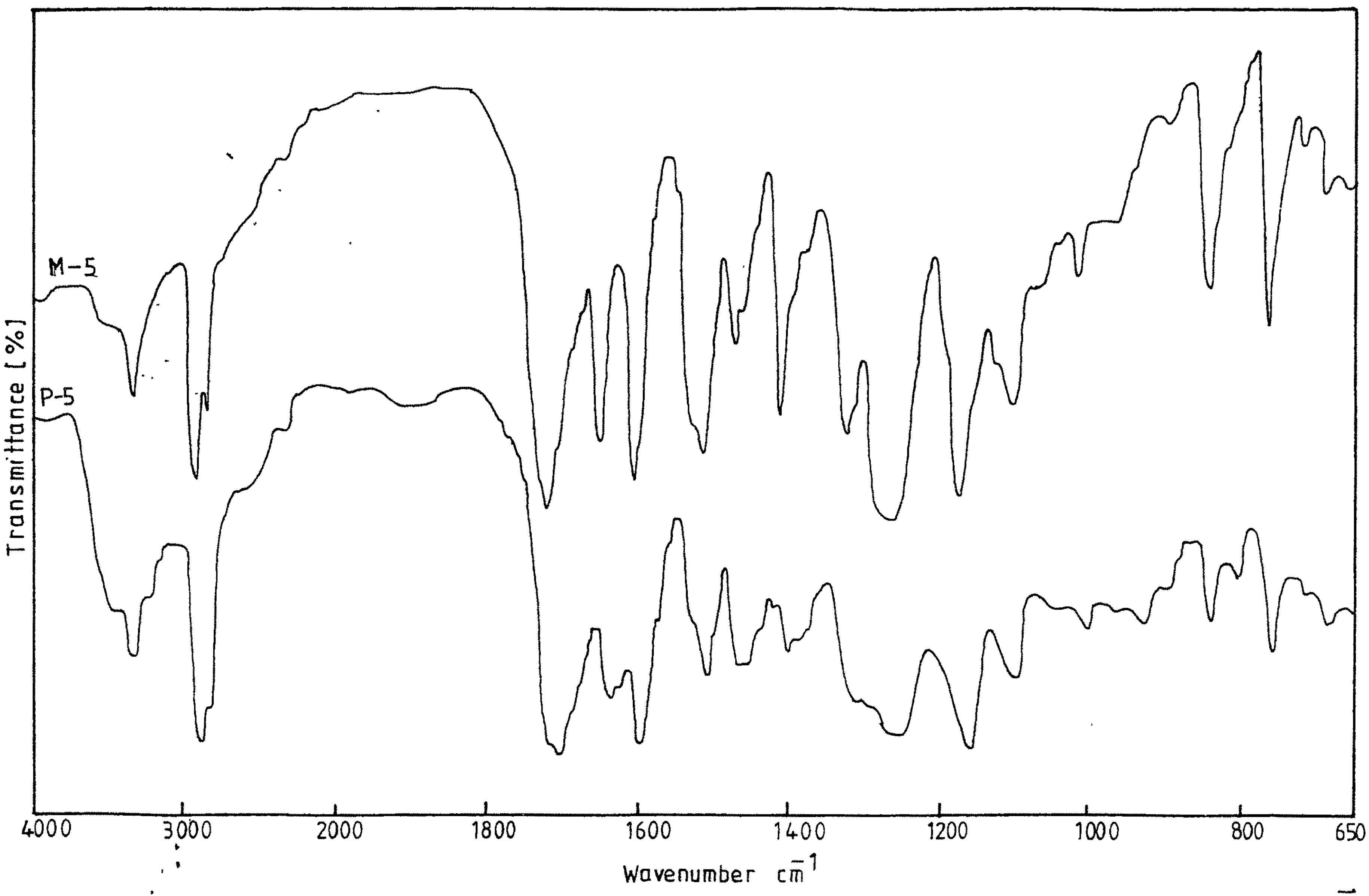
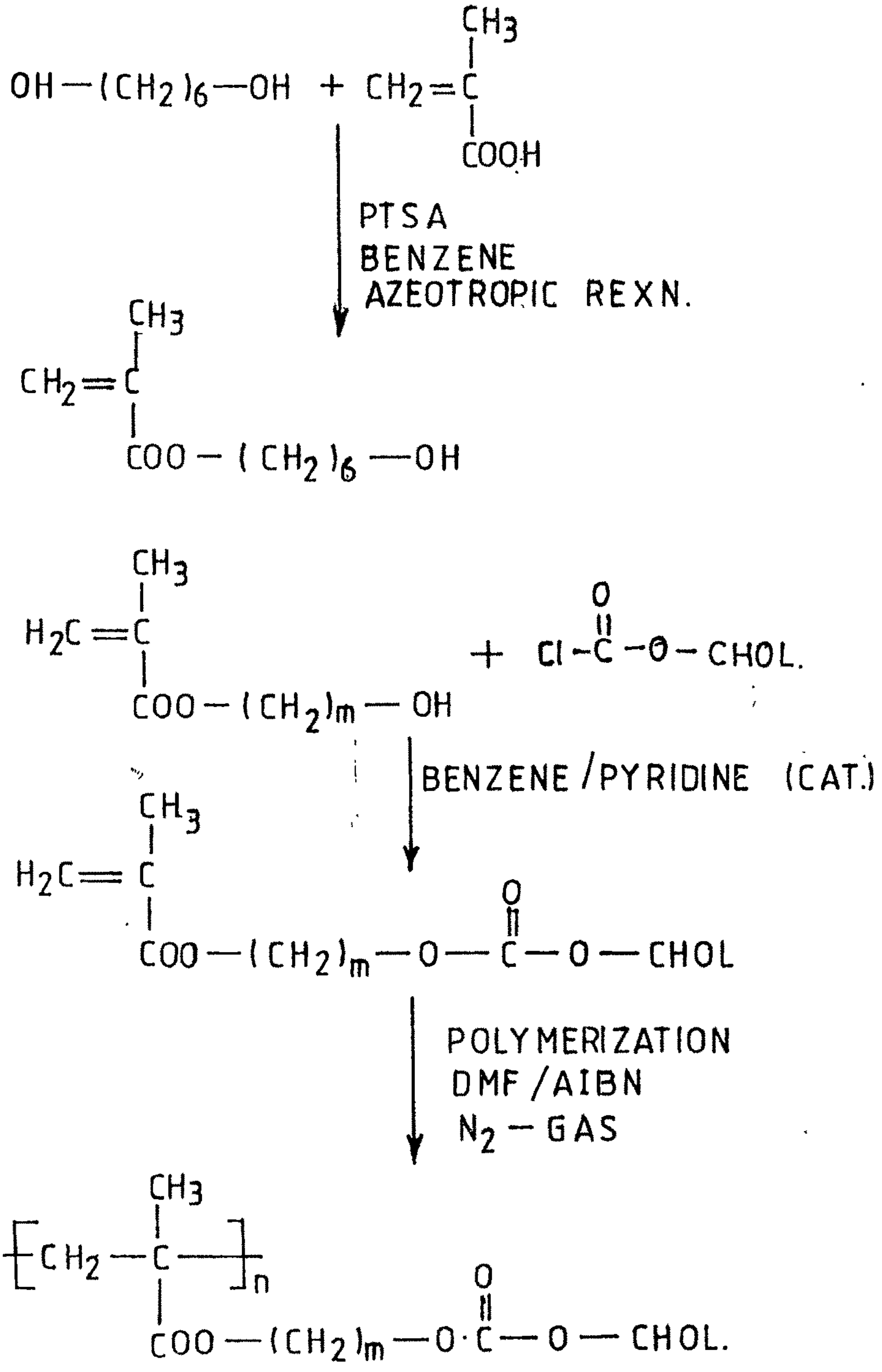


FIGURE 4.6: IR SPECTRA OF MONOMER AND POLYMER



CHOL. = CHOLESTERYL GROUP ; m = 2 AND 6

FIG. 47 SYNTHETIC ROUTE OF POLYMERS.

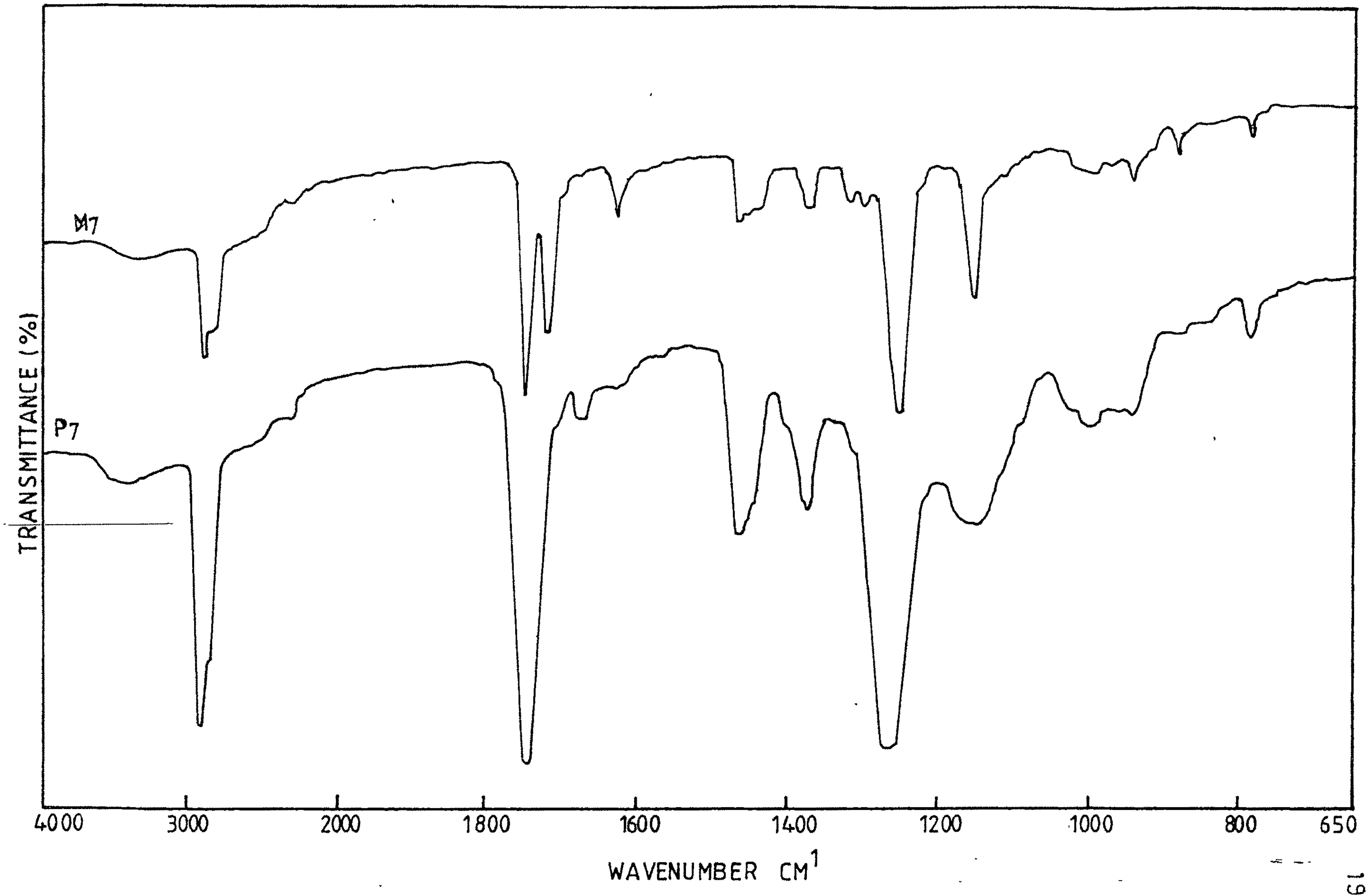


FIG. 48 IR SPECTRA OF MONOMER AND POLYMER

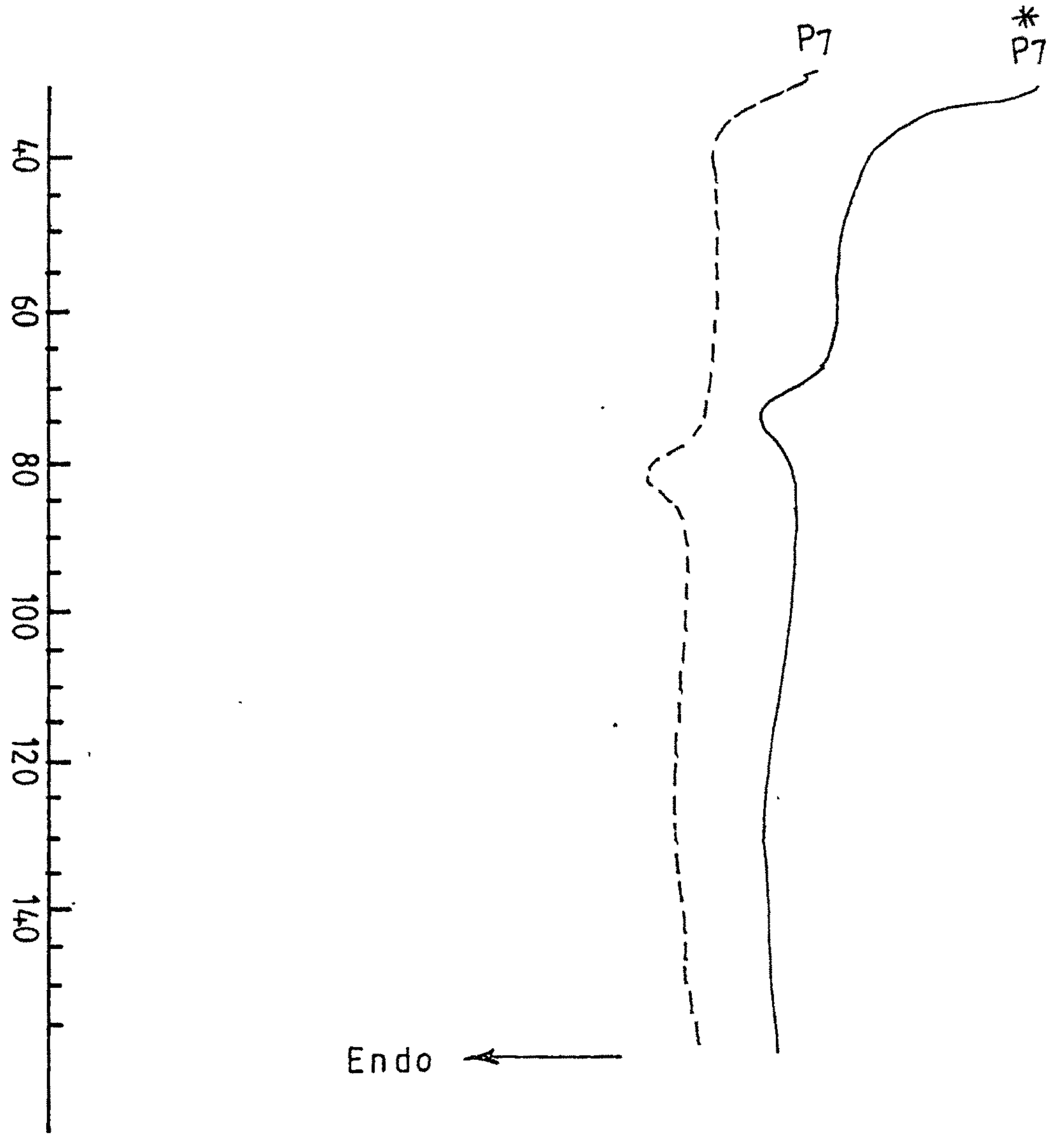


FIGURE:49 DSC THERMOGRAMS OF POLYMER P_7

V MAIN CHAIN MESOGENIC POLYMERS

Condensation Polymers

Polychalcones

Chalcone linkage offers many advantage over other linkages in polymers as it endows the system with fluorescent properties, can be reacted to obtain cyclic rings (378) and polymers can also be used as chelating polymers (379). It means polymers containing chalcone linkage can be designated as reactive polymers. Mesogens with chalcone linkage are rare. Vora and Sheth (380) had prepared polymers with chalcone linkage which exhibited mesomorphism. However, polymers exhibited relatively higher transition temperatures. These polymers exhibited fluorescent properties Encouraged by these results Vora and Teckchandani (381) increased the flexibility of the dicarboxylic acid moiety in the system by introducing 'oxyethylene spacers' in the place of methylene spacers. Solid to mesomorphic and mesomorphic to isotropic transition temperatures were drastically reduced but fluorescent behaviour was not affected. One striking feature of "oxyethylene spacer" polymers was that smectic mesophase was eliminated. This prompted us to investigate polymeric ester and esteramide having chalcone linkage with increased flexibility by increasing number of methylene spacers to 6 and 10 i.e. $-(CH_2)_6$ and $-(CH_2)_{10}$ With this in view polyester-amides and polyesters were synthesized by the route given in Fig.50.

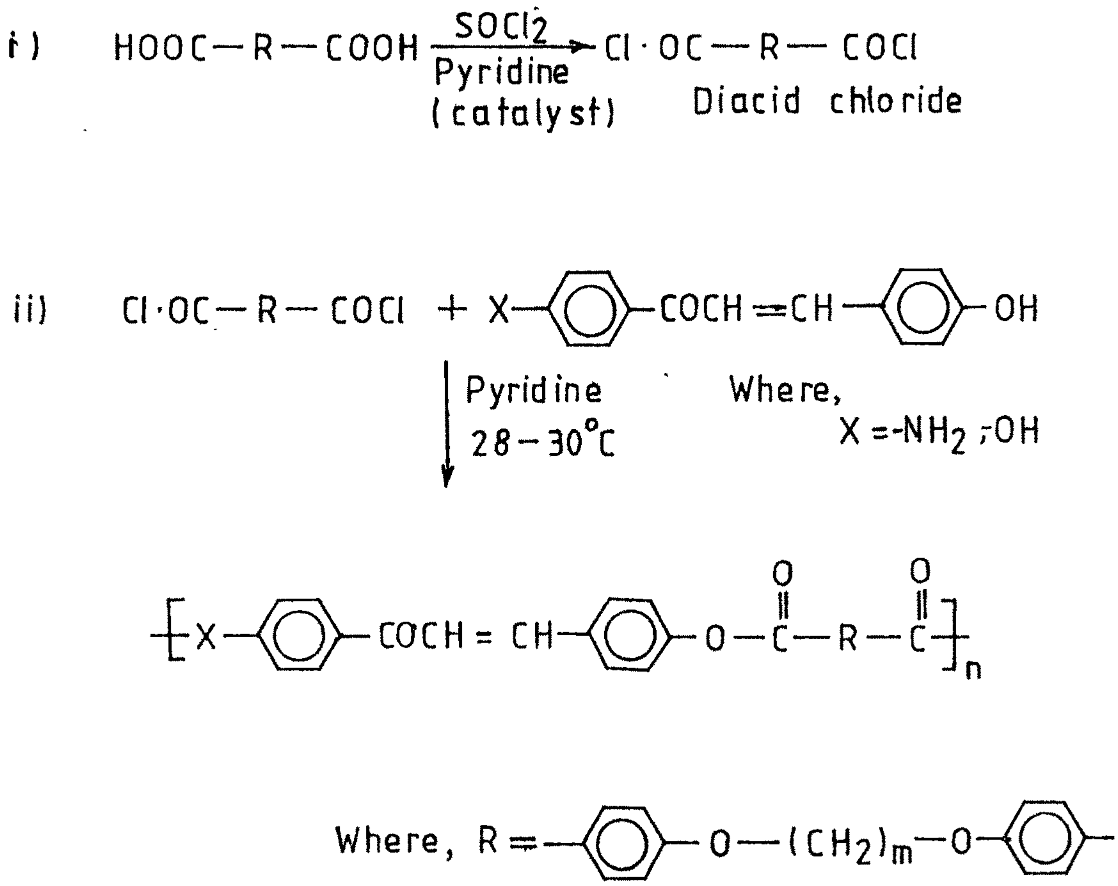
Four condensation polymers EP-1 to EP-4 are synthesized and they are characterized by IR (Table 26) Viscosity (Table 27), Calorimetry data (Table 35b). The transition temperatures are recorded in Table 24. The molecular weight of polymer (EP-1) was determined by GPC method (Table 37).

Reference to table 24 shows that the polymers EP-1 to EP-4 exhibit nematic mesophases.

The comparison of mesogenic properties of different polymers is a difficult task as the mesogenic properties of polymers depend not only on the chemical constitution but also on the molecular weight and polydispersity of the system. In the present study the structures of all the four polymers vary uniformly hence intrinsic viscosity values [η] are taken to compare the properties of polymers.

The Nematic.-Isotropic. transitions do not differ much in the case of EP-1 and EP-3 eventhough -0- is replaced by - NH - in EP-3. However, the transition temperature of EP-2 is much higher compared to all the other three polymers which is difficult to explain. A little difference can be explained on viscosity results, but here difference is large enough. Molecular weight and polydispersity data can through some light which could be obtained for EP-1 (molecular weight 2028) only. An interesting aspect worth noting is that polymer EP-3, even after cooling exhibits nematic texture. This trend is not observed in other similar polymers. The intrinsic viscosity obtained by using one point method (313), indicates that this procedure can be used . The procedure followed by condensation polymerisation gives consistant data. Intrinsic viscosity does not defer markedly from EP-1 to EP-4.

DSC Results (Table 35.b, Figure 52 a.b) indicate typical behaviour. Except polymer EP-1 none of the polymers exhibit endotherm for Nem.-Isotropic transition temperatures. In the case of polymer EP-3 an extra peak not matching with microscopic results is observed at 67°C. Reexamination of the slide of polymer EP-3 indicated that there is no phase change at this temperature. This indicates that the endothermic peak at 67°C in the case of EP-3 may be due to Cryst. I - Cryst. II transition.



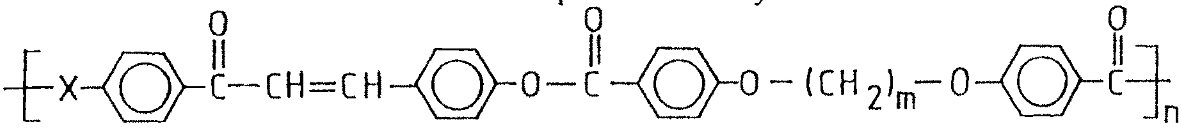
m = 6 and 10

X = NH, O

FIG. 50. SYNTHETIC ROUTE OF POLYCHALCONES

Table 24

Transition Temperatures of Polychalcones



Sr. No.	Code	X	m	Transition Temperatures °C	
				Nematic	Isotropic
1	EP1	-0-	6	140.0	190.0
2	EP2	-0-	10	150.0	256.0
3	EP3	-NH-	6	124.0	190.0
4	EP4	-NH-	10	141.0	169.0

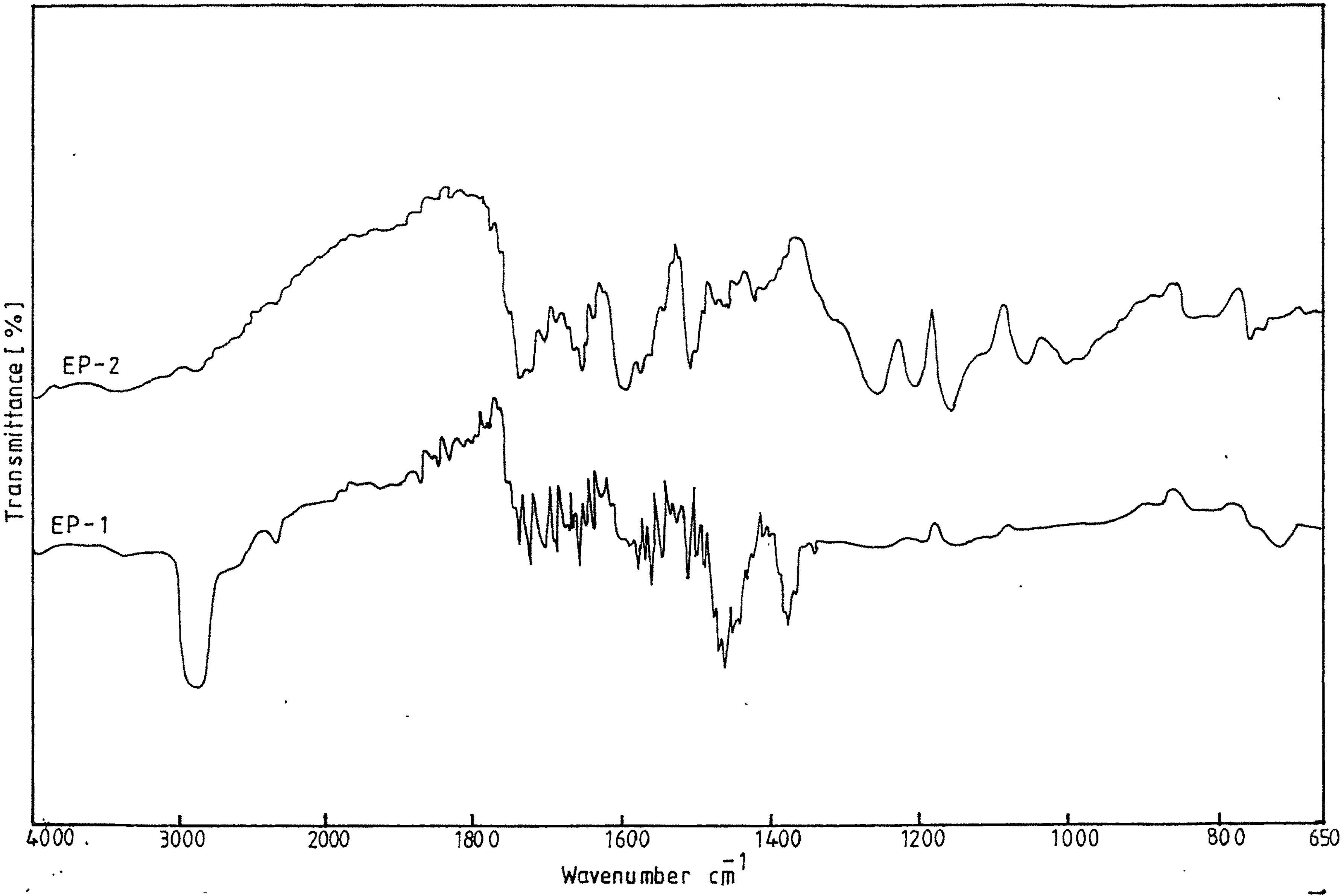


FIGURE:51a. IR SPECTRA OF POLYMERS

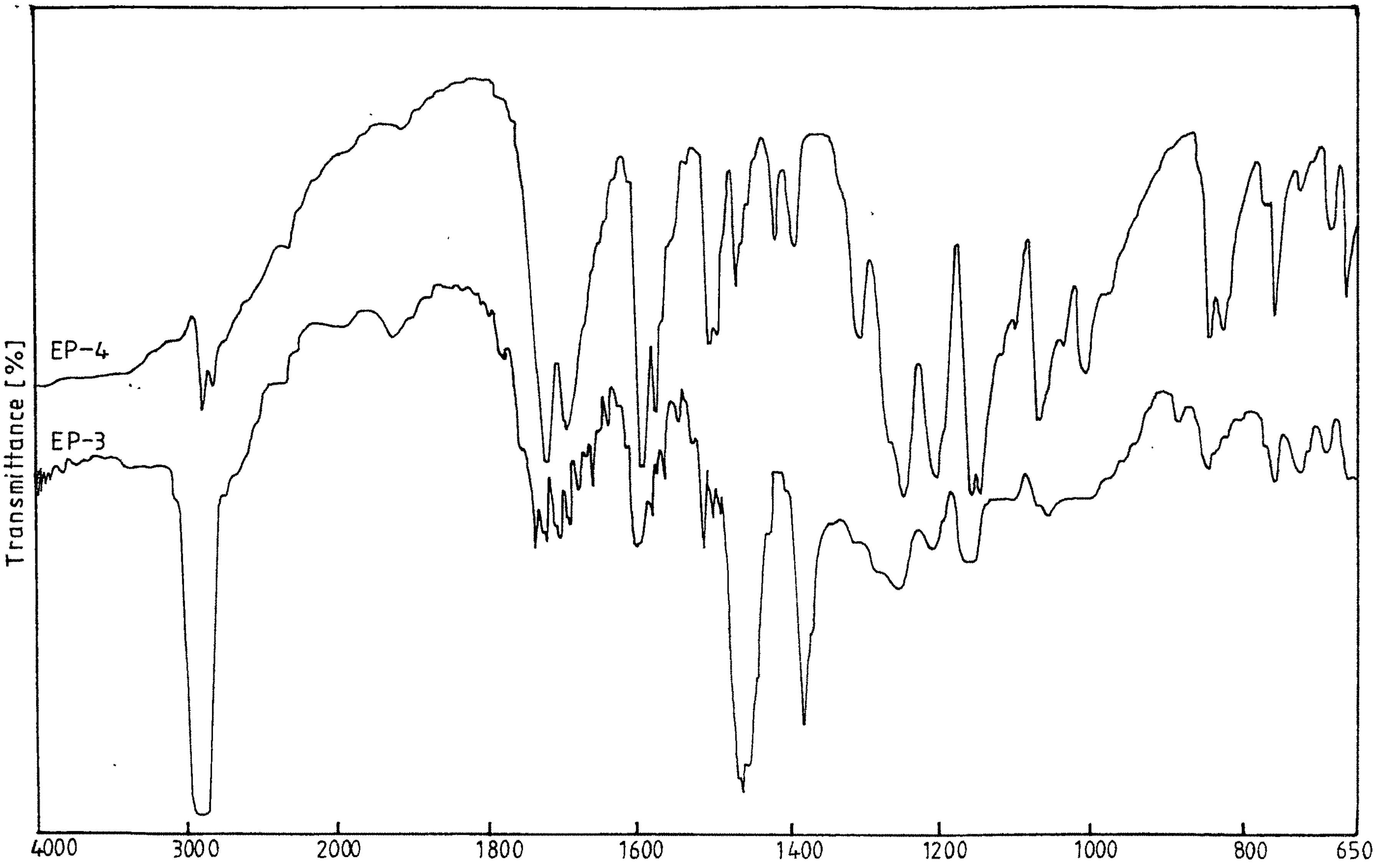


FIGURE:51b.IR SPECTRA OF POLYMERS

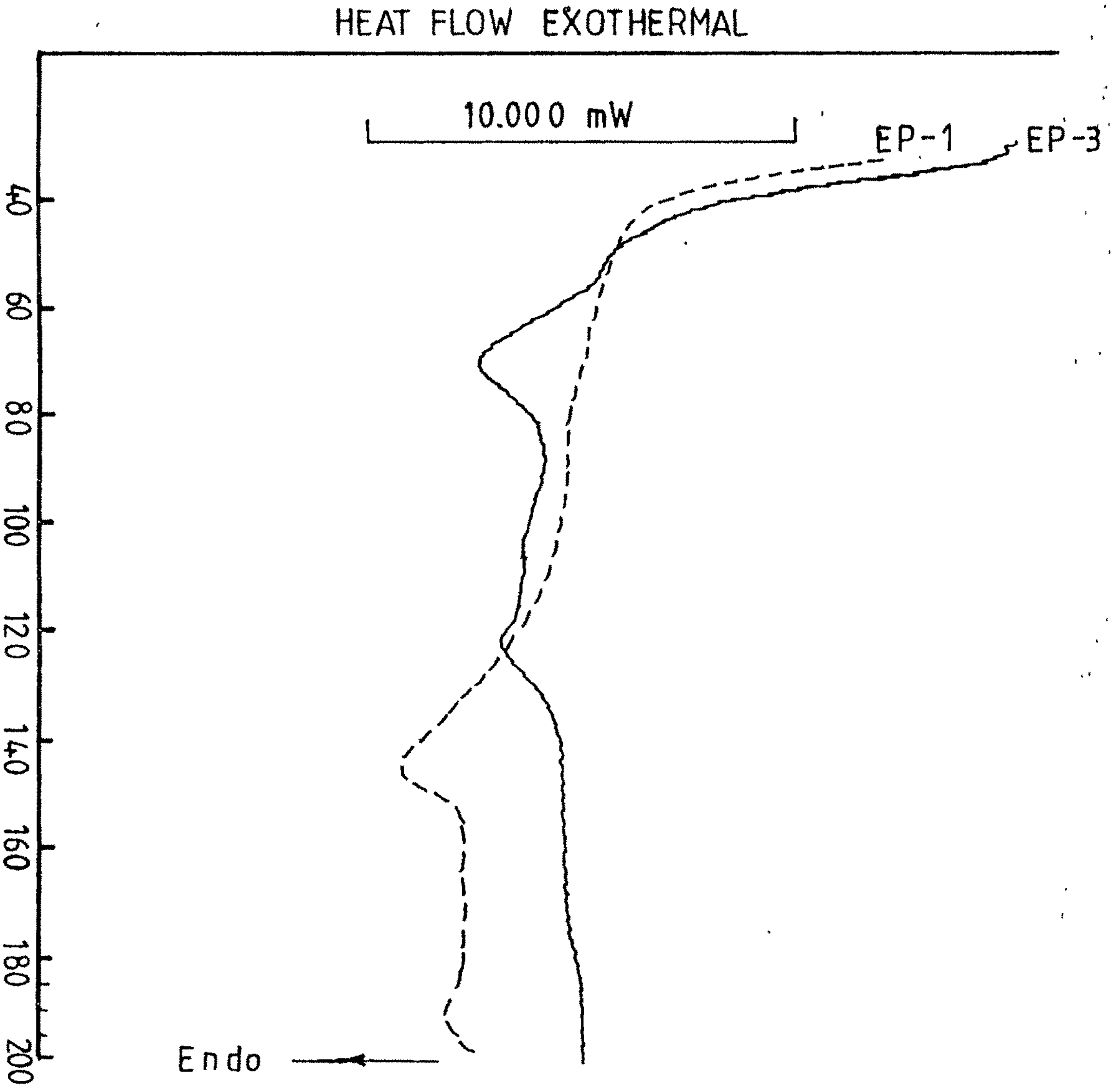


FIGURE 52a. DSC THERMOGRAM OF POLYMERS

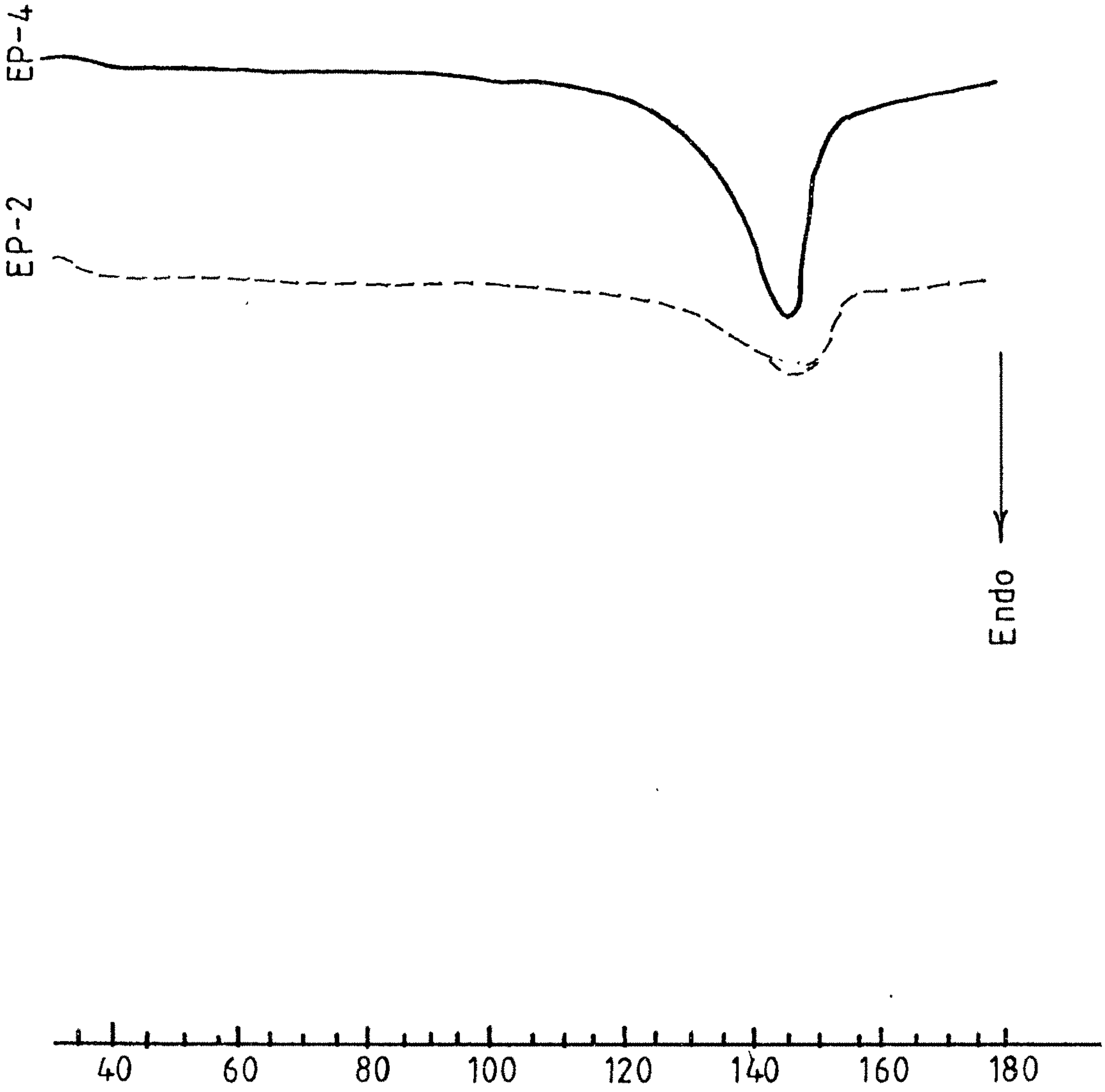


FIGURE : 52b.**DSC** THERMOGRAMS OF POLYMERS.

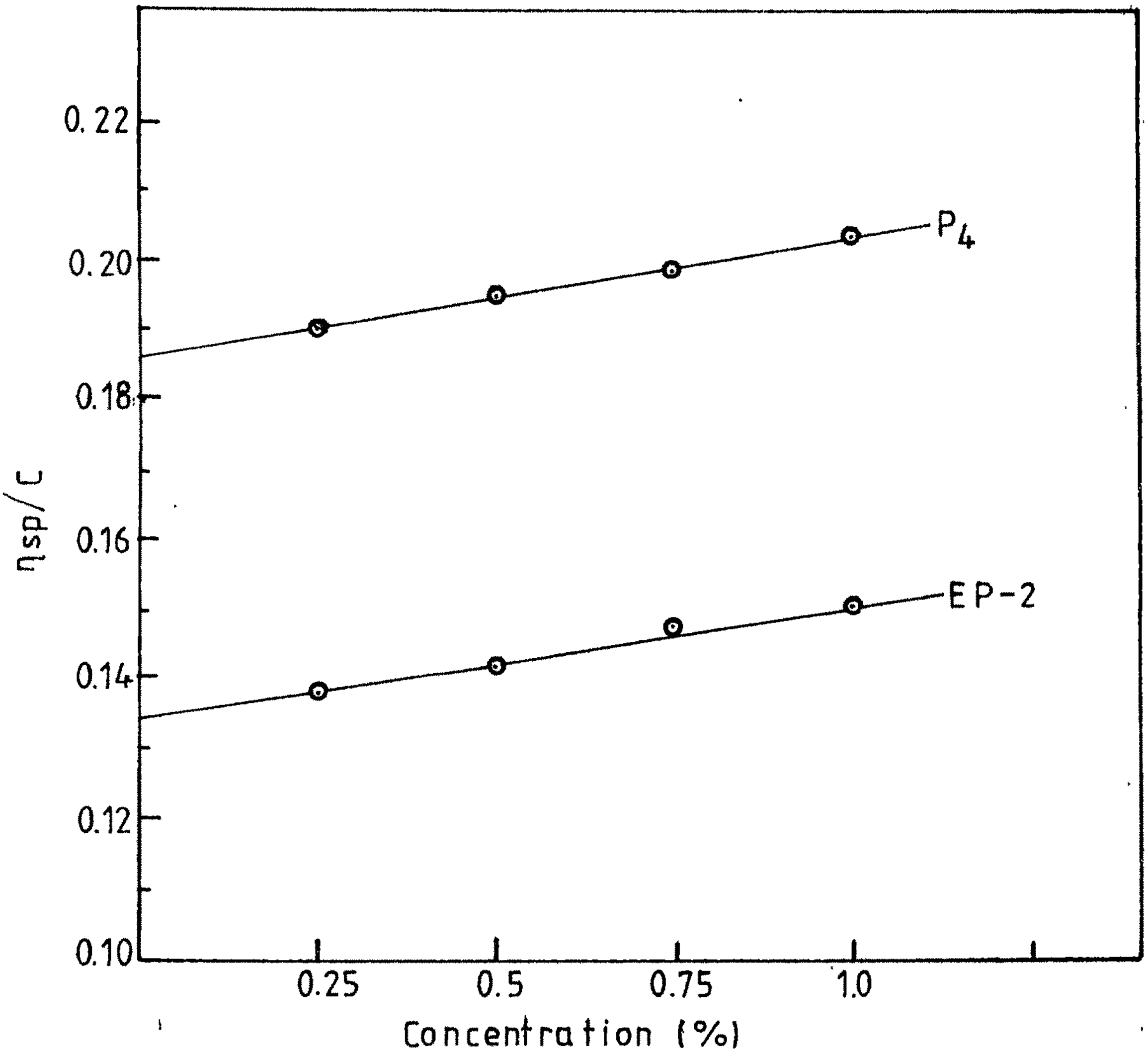


FIG. 53 PLOT OF η_{sp}/c VERSUS CONCENTRATION

Enthalpy change in polyesters EP-2 to EP-4 from Solid-Nematic differs and is higher for EP-4. However in the case of EP-3 the ΔH value (J/g) is much less due to second crystalline modification. The major enthalpy change in cryst. I to Cryst. II phase change in EP-3 suggests that it might be a highly ordered phase. Only X-ray study can through some light on this aspect.

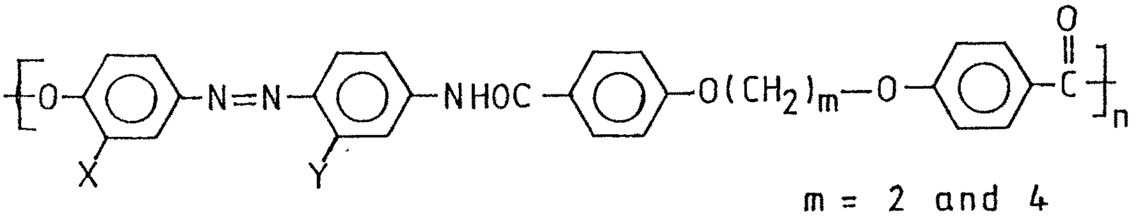
Polyesteramides:

Aromatic polyamides exhibiting lyotropic mesogenic properties are extensively studied due to their technological applications. They possess rigid rod-like structure which help to exhibit lyotropic mesomorphism.Theoretical prediction by de Gennes (382), and DiMarzio (383) that incorporation of flexible spacers in the rigid polymer back-bone would act as solvents and polymers with flexible spacers are expected to exhibit thermotropic liquid crystalline properties lead to the synthesis of thermotropic liquid crystalline polymers with flexible spacers. Number of polyesters were synthesized with flexible spacers and their mesogenic properties were evaluated (233, 384-387).

Polyesters with all rigid molecules exhibited mesomorphism at very high temperatures (228, 388, 389) making it difficult for the processing of these polymers. The polyesters with flexible spacers exhibited mesomorphism at relatively lower temperatures and fibres were drawn from the anisotropic melt with all round good physical properties (200, 227, 387).

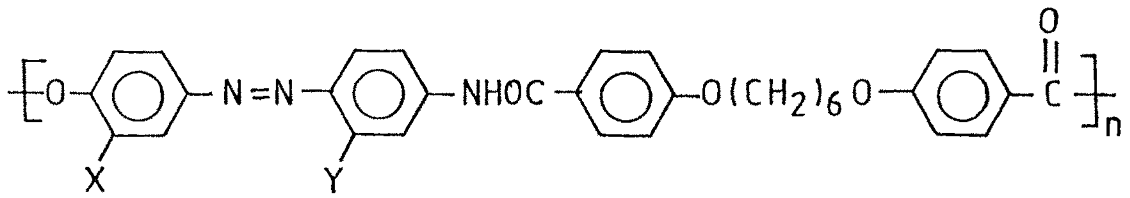
Number of lyotropic polyamides and thermotropic polyesters were synthesized and studied. The literature survey revealed that polyesteramides are rarely studied which exhibited mesomorphism. Vora et al., (322, 340, 365) studied different low molecular weight mesogens with ester and amide linkages and observed that compared to ester and Schiff base linkages, amide linkage enhances mesomorphism, though enhancement in smectic phase is greater than the nematic phases.

Based on the observations of Vora et al., (210, 322, 365) on the role of amide central linkage in the enhancement of mesophases, Vora and Sheth (390) synthesized number of polymeric azomesogens having ester and amide central linkages. Polyesteramides exhibited mesophases between 128-280°C Solid-nematic transition temperatures. The molecules had following structures:



m = 2 and 4

All the polymers had two or four methylene spacers in the acid moiety. It was thought of interest to increase the flexibility further to six methylene units and observe the effect of increased flexibility on mesomorphic behaviour of resultant polyesteramides having an azo linkage. In the present study three polyesteramides are synthesized having six methylene spacers. All the three polymers are characterized by IR and elemental analysis.



All the three polymers exhibit nematic mesophase. All the three polymers on heating further polymerize at higher temperatures hence nematic-isotropic transition temperatures could not be recorded. In many such polymers post polymerization occurs on heating in the mesogenic system which leads to solidification. Two of the polymers start decomposition also during post polymerization. All the three polymers were synthesized by the route shown in Fig. 55.

It has been pointed out earlier that its difficult to compare mesogenic properties of polymers quantitatively as number of factors affect their mesogenic properties over and above their chemical constitution.

The solution viscosity of all the polymers was evaluated by using Ubbelohde viscometer. The intrinsic viscosity was calculated by using one point method (313).

Comparison of transition temperatures of PEA-1 to PEA-3 with the polymers reported by Vora and Sheth would give some understanding about the effect of chemical constitution on mesomorphism.

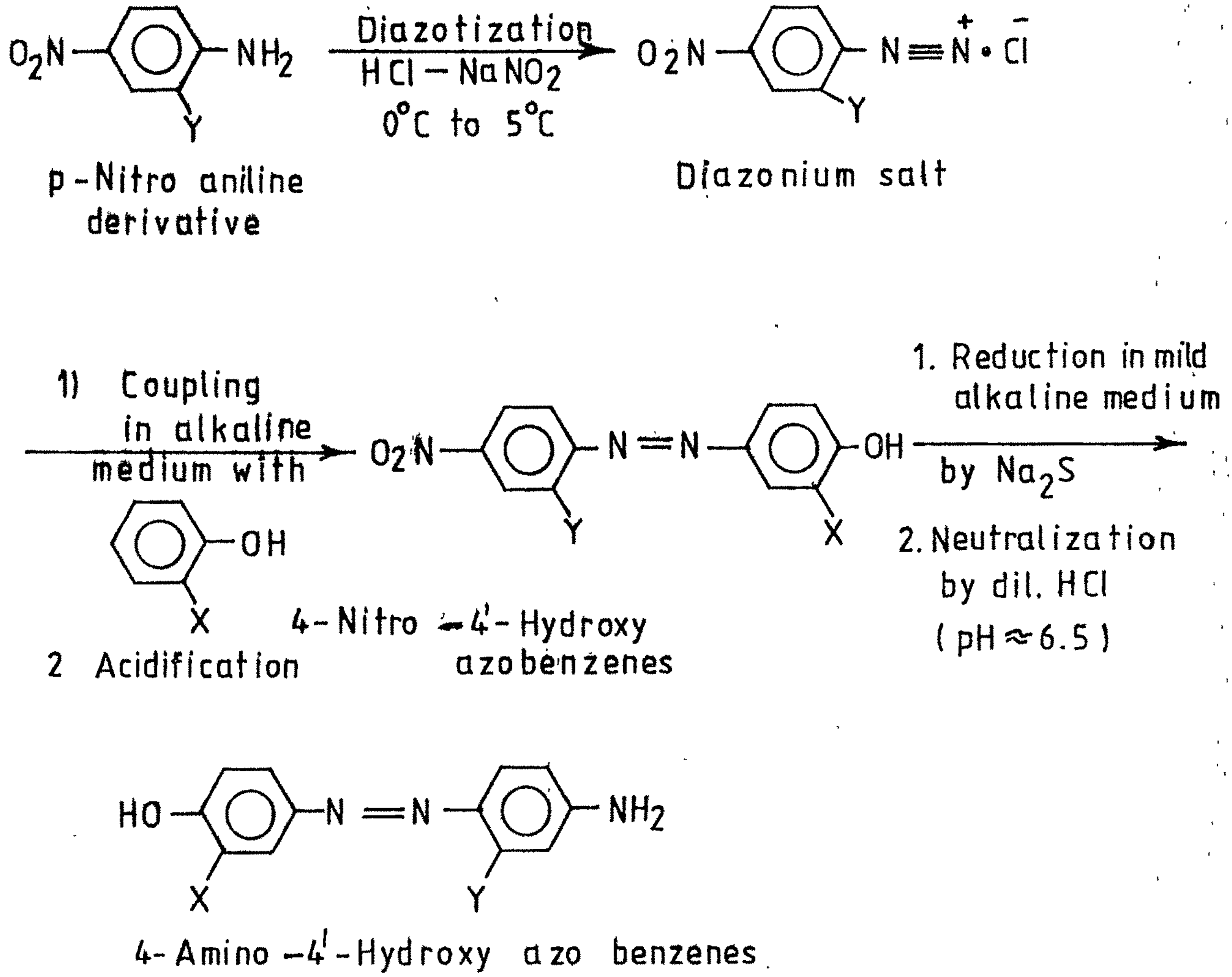
Increase in the length of flexible spacers may lead to smectic mesophase and/or decrease in transition temperature especially solid-mesomorphic transition.

The comparison of transition temperatures of PEA-1 to PEA-3 with reported similar polymers having difference in flexible chain length (391) indicates that solid-nematic transition temperatures of PEA-1 and PEA-2 are higher compared to similar polymers having methylene flexible spacers 2 and 4. Post polymerization temperatures do not differ much in the case of polymer with two methylene flexible spacers whereas polymer with four methylene flexible spacers has much lower nematic isotropic transition temperature.

In the case of PEA-3 the solid-nematic transition temperatures are much higher compared to polymers with lesser flexibility (391). This is difficult to explain. The difference in structure compared to PEA-1 and PEA-2 is that both polymers have lateral chloro-substituent (PEA-3 and Chp-1a, 2a).

The thermogravimetric results will be discussed along with other polymers.

Present study indicates that the system may exhibit notable reduction in transition temperatures if flexibility is increased to a greater extent.

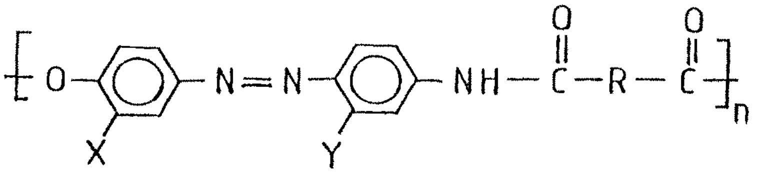


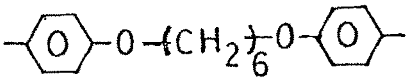
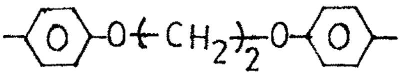
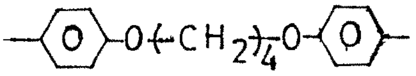
Where, $X = H$ $Y = H$
$= CH_3$ $= H$
$= H$ $= Cl$

FIG. 54 SYNTHETIC ROUTE OF AZOBENZENES (SUBSTITUTED)

Table 28

Transition temperatures of Polyesteramides



Code	X	Y	R	Transition Temperatures °C	
				Nematic	Isotropic
PEA1	H	H		285	290 (P)
PEA2	CH_3	H	"	233	295 (P)
PEA3	H	Cl	"	270	>300 (P)
Chp-1a	Cl	H		149	267(P)
Chp-2a	Cl	H		152	257(P)

(P) = Sample post polymerizes and become solid

Chp-1a & Chp-2a synthesized by Vora and Sheth

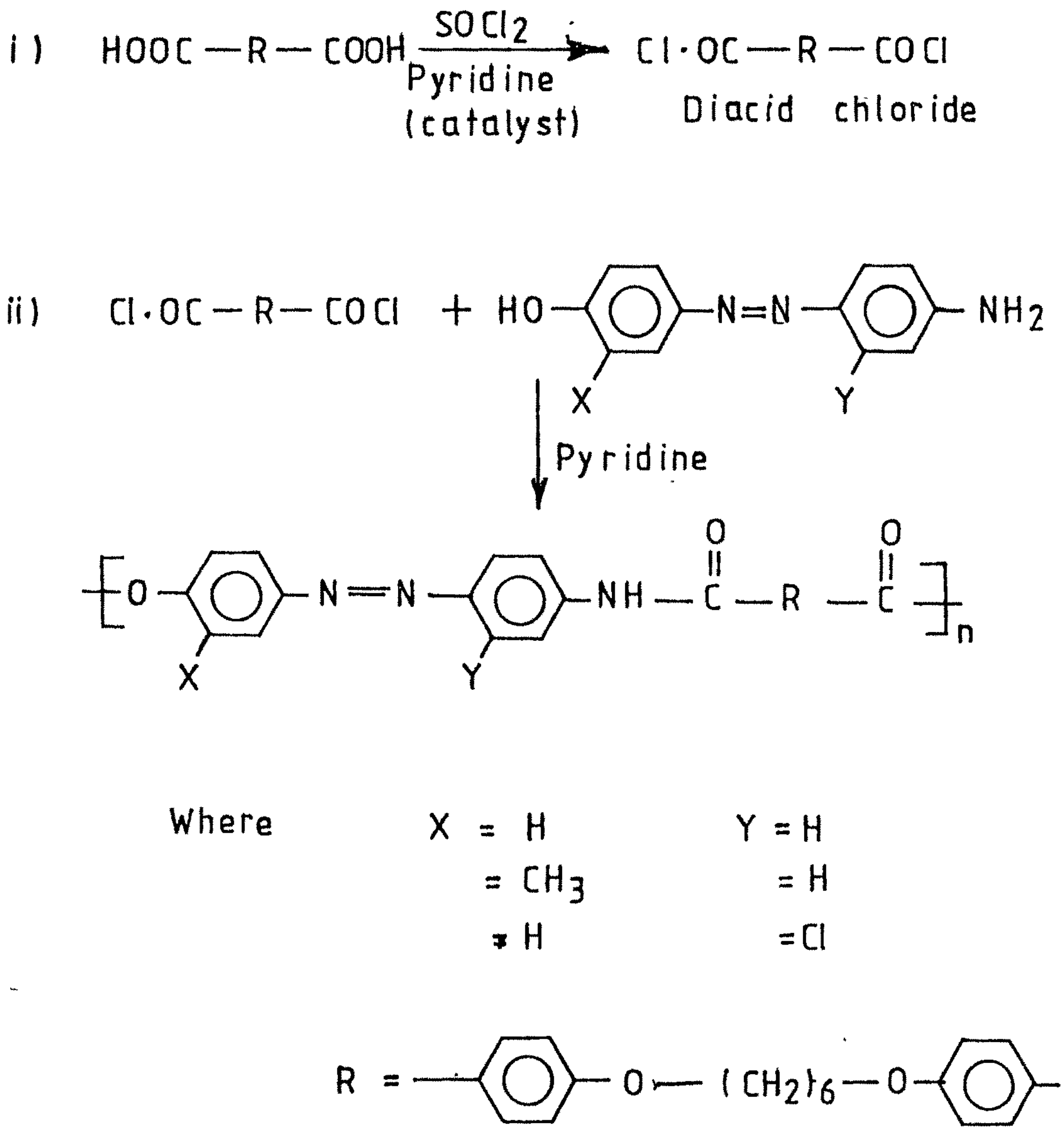


FIG. 55 SYNTHETIC ROUTE OF POLYMERIC AZOMESOGENS.

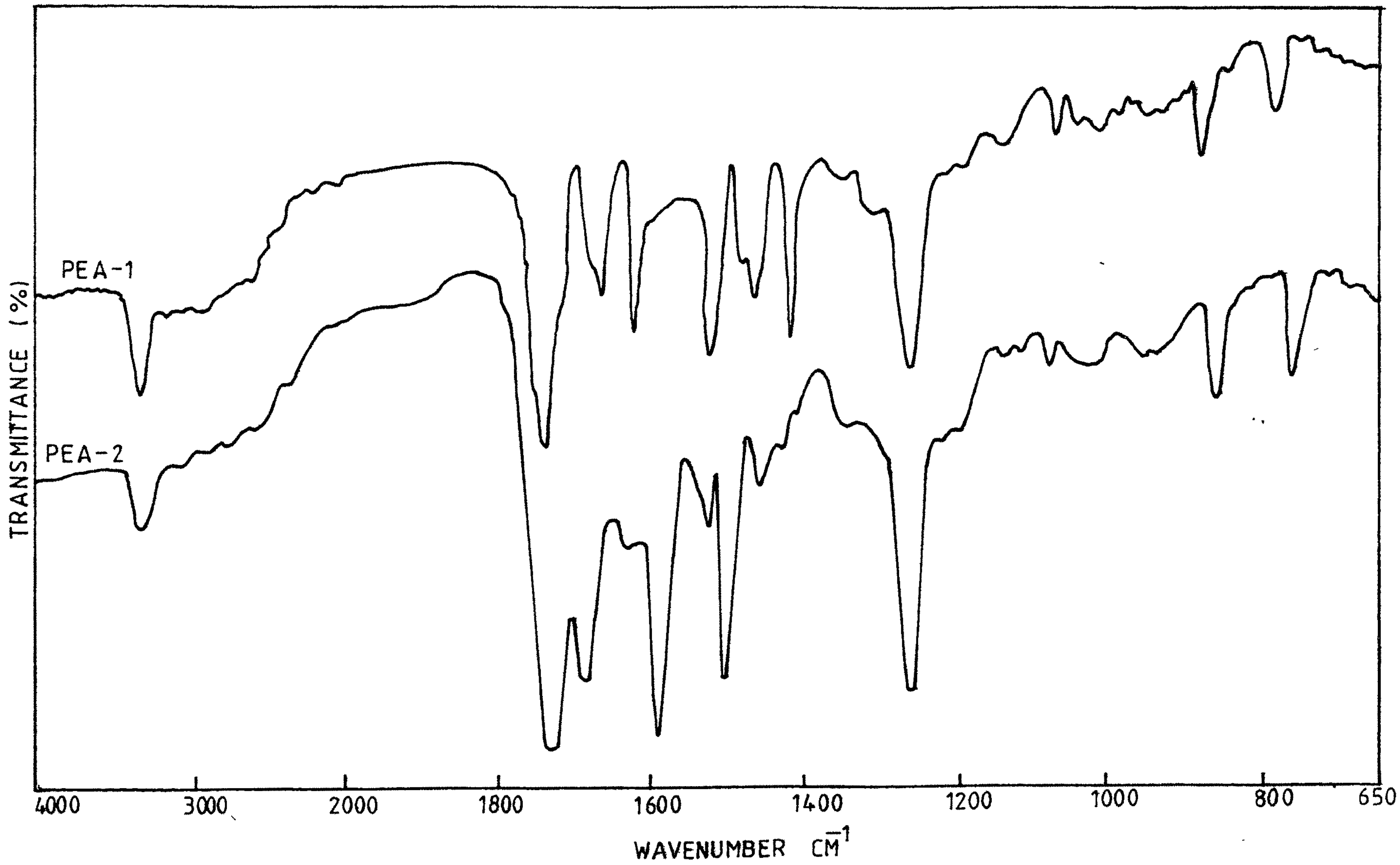


FIGURE : 56 IR SPECTRA OF POLYESTERAMIDES

vi MODEL COMPOUNDS

Model Compounds:

To corelate the mesogenic behaviour of polymers it is normal practice to synthesize model compounds, and evaluate their mesogenic properties.

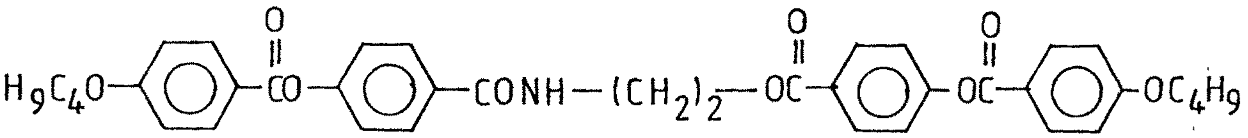
In the present study models involving central flexible or rigid core with amide and ester group or diester group with terminal alkoxy group are synthesized and their mesogenic properties are evaluated.

Model compounds with central ester-amide linkage:

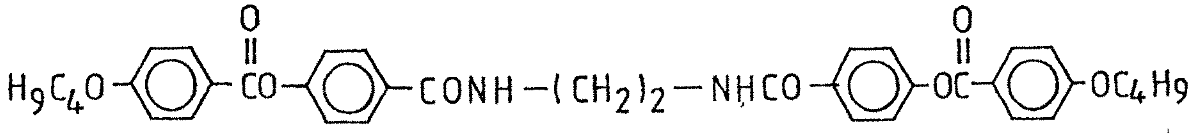
AE-1 to AE-4, four compounds have been synthesized. Reference to Table 32 indicates that central rigid core of 1,4 phenylene group imparts very high nematic ranges. However, flexible linkages exhibit lower nematic-isotropic transition temperatures. This is further supporting to the observation that if liquid crystalline polymers have high transition temperatures, increase in the flexibility reduce the mesogenic-isotropic transition temperatures.

AE-4 exhibits smectic mesophase which is absent in other all the three compounds. This is quite an interesting observation. It is known that increase in end alkoxy chain induces smectic phases in the LC polymer system, but here the AE-2 exhibits only nematic phase, though structurally conducive phenylene spacer should favour smectic phase. It seems steric factors might be prevailing in the AE-2 compared to in AE-4 which has a flexible spacer hence AE-4 additionally exhibits smectic phase.

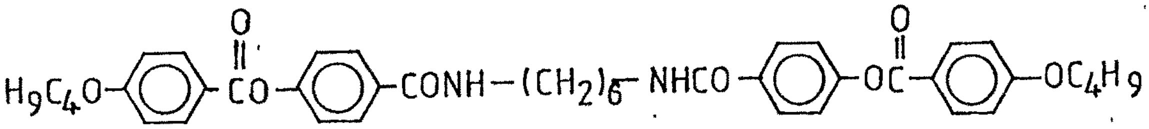
One compound isomeric to compound AE-5 was synthesized having central two amide linkages with flexible spacers.



1,2 Bis(4-n-butoxybenzoyloxy benzoyl) amino ethanol (AE-3)
(Mesogenic)



1,2 Bis(4-n-butoxy benzoyloxy benzoyl) diamino ethane (AE-5) (Melting point >300°C)
(Non-Mesogenic)



1,6 Bis(4-n-butoxy benzoyloxy benzoyl) diamino hexane (AE-6) (Melting point 247°C)
(Non-Mesogenic)

It is quite interesting to note that compound AE-5 with two amide central linkages with flexible spacers does not melt up to 300°C.

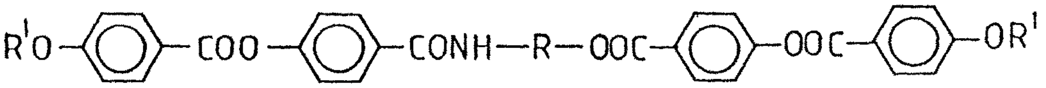
If one considers high melting as the reason for non-mesomorphism, increase in flexibility may decrease the isotropization temperature. With this in view, flexible spacer length was increased to $(-CH_2-)_6$, compound (AE-6) melts at 247°C but does not exhibit mesomorphism. Strong intermolecular hydrogen bonding due to two central amide linkage may be responsible for the non-mesomorphism in these two compounds.

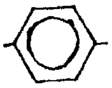
Model compounds with central diester linkages with flexible chain:

AZ-1 to AZ-3 (Fig. 57a)all the compounds exhibit nematic phases. This indicates that polymers involving "azobenzene" nucleus will be quite conducive to obtain LC polyesters (Table 33.a).

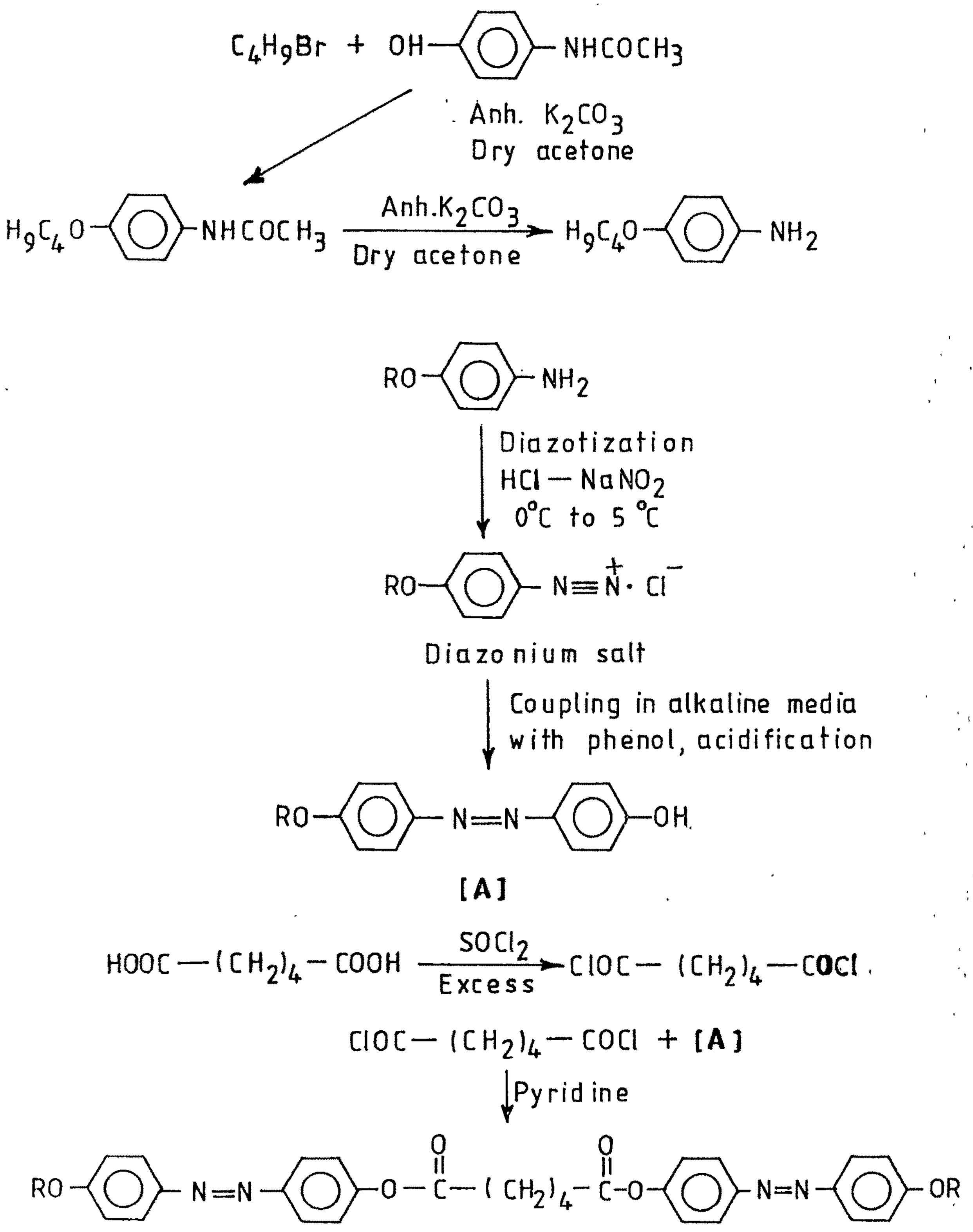
Table 32

Transition Temperatures of Amido-Esters:



Code	R' n-alkyl gr.	R	Transition Temperatures °C		
			Sc	Nematic	Isotropic
AE1	Butyl		-	225	300 (d)
AE2	Octyl	"	-	220	278 (d)
AE3	Butyl	$-(CH_2)_2-$	-	188	203
AE4	Octyl	$-(CH_2)_2-$	120	168	190

d = decomposition



Where R = $-CH_3$, $-C_2H_5$, $-C_4H_9$,

FIGURE :57a SYNTHETIC ROUTE OF MODEL COMPOUNDS

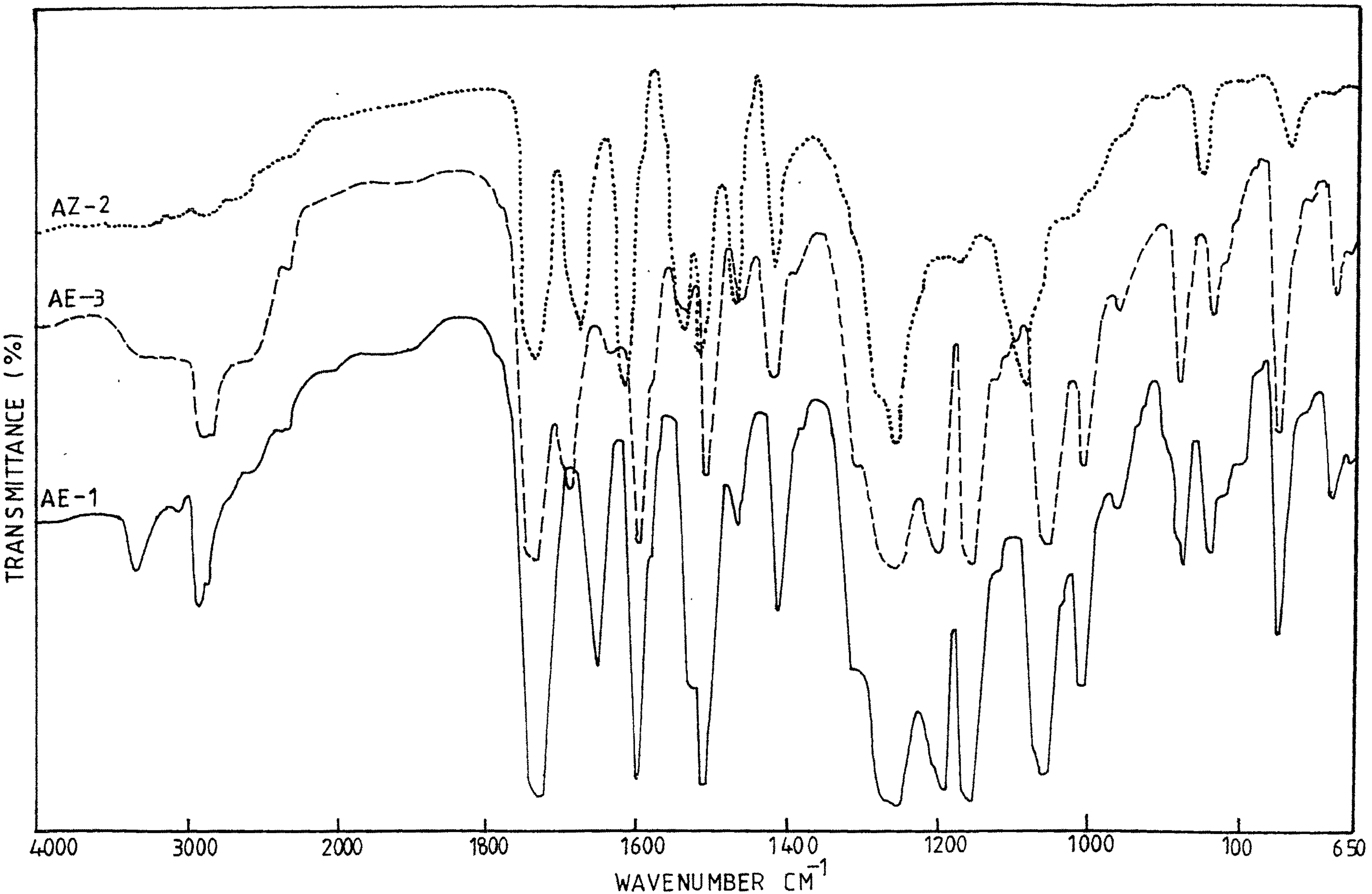


FIG. 57b IR SPECTRA OF MODEL COMPOUNDS

vii EVALUATION OF DIFFERENT MESOGENIC COMPOUNDS

Evaluation of Different Mesogenic Compounds:

7.1 Molecular Weight Determinations:

In the present study four polymer samples were screened for GPC study. The graphs are shown in Figure 58. The samples have low molecular weight that indicates they are oligomeric mesogen(Table 37).

7.2 X-Ray Diffraction Analysis:

The X-ray diffraction profiles of the polymers (P_1, P_2, P_7 and P_8) are shown in Figure 59. Polymers P_7 and P_8 show slight crystallinity but largely the polymers are amorphous. The diffractograms of polymer P_1 shows no peaks and hence indicates a highly amorphous structure In contrast, the diffractogram of polymer P_2 shows strong peaks indicating the crystalline nature of this compound. Polymer P_2 shows highly intense peaks in the region $2\theta = 18^\circ$ to 28° and small peaks in the region $2\theta = 10^\circ$ to 15°.

The unit cell has been found to be tetragonal with lattice constants a = 7.9274 A°, c = 31.3595 and V = 1970.75 A° for polymer P_2. The cell parameters have been calculated by Ritwelt analysis. The values of Sin 2θ and the corresponding hkl, in all cases are in good agreement with observed Sin 2θ values (Table 38.b).

7.3 Conductivity Study:

The conductivity (σ) versus temperature T (°K) (heating as well as cooling) for the polymers (P_2 and P_7) are plotted in Figures 60.a and 60.b and the graphs of log σVs 1/T ($^\circ K^{-1}$) are plotted in Figure 61 for all polymers (Table 39a,b).

At lower temperature the conductivity decreases with increase in temperature and on cooling conductivity increases with decrease in temperature. The increase in conductivity or decrease in resistivity with decrease in temperature indicates that these polymers behave like semiconductors.

The activation energy of polymers (Table 39.c) for conductance was calculated by using the following equation

$$\sigma = \sigma o \,.\, e^{Ea/KT}$$

$$Ea = 2.303 \times K \times slop$$

7.4 Fluorescent Spectra:

The fluorescence of coumarin, their derivatives and other polymers have been studied (392, 393). They have reported that the chromophores (C=0,C=C) directly or indirectly helps in exhibition of luminescence from the polymers. Danuta et al., (394) reported that the fluorescence yield of the polymer may be caused by molecular interaction between carbonyl groups of the compound and acetone molecule. The chalcone compounds have also been studied for its luminescence properties (395). They believed that the fluorescence emission in polymer and monomer is due to photon-photon interaction. One of the common molecular transition is an electronic transition (396). The $n \rightarrow \pi^*$ transition corresponds to single chromophoric group (C=0, C=C). In the present work the fluorescence properties have been studied for the monomers, polymers and co-polymer (polymer A, B, C and co-polymer D). The data of IR study reveals that C=0 (Ketone) groups called chromophores are present in all monomers and polymers. From the present understanding (393) it is suggested that the principal emission at 440 nm and 430nm, for the corresponding excitations is associated with the presence of the above mentioned chromophores (figure 62.a,b and 62c). It is also believed that the $n \rightarrow \pi^*$ of ketone (C=0) group corresponding with chromophoric groups is responsible for observed change in the polymers and monomers emission. A number of repeating unit in long chain in polymer are responsible for the present emission. During the excitation by UV-light the electrons gets excited thereby causing the production of some low energy photons. These photons then interact with the excitation energy (photons). This higher energy can take the electron from n-orbital to the higher state, release the energy which is responsible for the principal emission in the polymers. In the case of monomer no such long chain exists, hence no photons are produced, because of non-availability of the photons in the monomers, such a phenomenon of interaction does not take place and 440 nm band is not observed. From the figure 62.a,b,c it is seen that the fluorescence emission is obtained with the change in the excitation Wavelength corresponds to the different polymers. This can be explained on the basis of the complexes of the groups of the respective polymers from the luminescence centres respectively in the polymers A, B, C and copolymer D(Table 40).

The observed change in exicitation for the corresponding emission in the polymer and monomer due to the significance difference in the nature and location of the chromophore and/or additionally present substituent groups in the respective luminescence centre.

To study the effect of substituents in the monomers and polymers on fluorescence behaviour, the emission spectra were recorded for different excitation wavelengths. The excitation wavelength for which the intensity for emission was found to be maximum, was taken as the excitation wavelength.

Figure 62.a,b,c shows the emission spectra of the monomers, polymers and co-polymer with dominant peak and shoulders at different wavelength. The intensity of

fluorescence, in the case of monomers (M_7 and M_8) are much higher than that of the polymers (P_7 and P_8)

7.5 Thermo Gravimetric Analysis:

Thermal Decomposition Characteristics:

Thermogravimetric curves obtained at a scan rate 10°C/min. for all polymers reported in the present investigation are shown in Figures 63.a,b,. The graphs of ln[ln(1/T)] vs 1/T (°K^{-1}) are plotted in Figures 64a,b,c for all polymers(Table 41 a,b.)

Based on the visual observation of thermograms, an attempt is made to assess the thermal stability of each of the polymers qualitatively. Arbitrary methods for the assessment of thermal stability of polymer for TG traces have been briefly reviewed by Reich and Levi (397). These methods can broadly be classified as qualitative and semiquantitative. Qualitative methods compare stabilities by detailed observations of thermogram.

Thermal degradation of all the polychalcones take place in two distinct steps. A thorough examination of these thermograms reveals that the polychalcones are thermally stable upto 330°C, after that thermal degradation starts upto 353°C temperature. Polymer lose some of its weight.

The polymer EP-1 loses 10% of its weight at 325°C. Polychalcone EP-1 decomposes with a rapid weight loss (40.0% of its weight) in the temperature range 380-475°C. The maximum rate of weight loss occurs at 475°C. Beyond 500°C, the second decomposition step commences with 15% loss of its weight with low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 547°C.

The polymer EP-2 loses 10% of its weight at 355°C. The polymer EP-2 loses 20% of its weight in the temperature range 355-425°C. The maximum rate of weight loss occurs at 400°C. The second decomposition step commences at 550°C with a loss of 5.0% of its weight at low rate of weight loss compared to first step. The maximum weight loss occurs at 555°C.

The polymer EP-3 loses 10% weight at 312°C. The polymer EP-3 loses 40.0% of its weight in the temperature range 315 to 420°C with maximum rate at 395°C. The second decomposition step commences at 450°C with 22% loss of its weight at low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 542°C.

The polymer EP-4 loses 10% of its weight at 320°C. In the temperature range 365-475°C, the polymer sample EP-4 loses 40% of its weight. The maximum rate of weight loss occurs at 430°C. Beyond 500°C the second decomposition step commences with a loss of 20% of its weight, having low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 533°C.

Thermal stability of the polychalcones studied are established on the basis of T_{max} for the first step of decomposition. The thermal stability of polychalcones increase in the following order.

$$\text{EP-3} < \text{EP-1} < \text{EP-2} \approx \text{EP-4}$$

Thermogram of polymethacrylates (P_1,P_2,P_3 and P_5) also exhibits two step decomposition. The polymer P_1 loses 10% of its weight at 470°C. The polymer loses 39% of its weight in the temperature range 480-570°C. The maximum rate of weight loss occurs at 510°C. The second decomposition step commences at 590°C with a loss of 8.5% of its weight at low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 600°C.

The polymer P_2 loses 10% of its weight at 450°C. In the temperature range 450-540°C, the polymer (P_2) sample loses 37% of its weight. The maximum rate of weight loss occurs at 500°C. Beyond 550°C the second decomposition step commences with a loss of 9.5% of its weight having low rate of weight loss comapred to the first step. The maximum rate of weight loss occurs at 580°C.

The polymer P_3 loses 10% of its weight at 430°C. The polymer P_3 loses 38% of its weight in the temperature range 430-520°C. The second decomposition step commences at 540°C with a loss of 8% of its weight at low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 580°C.

Similarly, the overall thermal degradation of P_5 also involves two degradation steps. The polymer P_5 loses 10% of its weight at 430°C. The first step encompassing a temperature range 430-520°C, involves about 43.5% of weight loss. The rate of weight loss reaching a maximum at 480°C. The second step of degradation commences with a loss of 9.5% of its weight, having low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 620°C.

Thermal stability of the polymethacrylates studied are established on the basis of $T_{max}\downarrow$ for the first step of decomposition. The thermal stability of polymethacrylates increase in the following order.

$$P_3 < P_5 < P_2 < P_1$$

Thermogram of polycarbonates (P_7 and P_8) and co-polymer (CP) also undergoes two step decomposition. The polymer P_7 loses 10% of its weight at 390°C. In the range of 390-400°C the sample loses 40% of its weight with a maximum rate at 470°C. Above 490°C, the second step of degradation commences which involves a further weight loss of 11% upto 550°C with a maximum rate of 520°C.

The polymer P_8 loses 10% of its weight at 340°C. In the temperature range 310-400°C, the polymer sample (P_8) loses 33% of its weight. The maximum rate of weight loss occurs at 380°C. Beyond 440°C. the second decomposition step commences with a loss of 12% of its weight, having low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 550°C.

The copolymer (CP) loses 10% of its weight at 330°C. The copolymer (CP) loses 34.5% of its weight in the temperature range 330-430°C. The maximum rate of weight loss occurs at 370°C. The second decomposition step commences at 510°C with a loss of 12% of its weight at low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 580°C.

Thermal stability of the polycarbonates and copolymer studied are established on the basis of $T_{max\downarrow}$ for the first step of decomposition. The thermal stability of polycarbonates increase in the following order.

$$CP < P_8 < P_7$$

Thermogram of polyesteramides PEA-2 and PEA-3 also undergoes two step decomposition. The polymer PEA-2 loses 10% of its weight at 370°C. In the temperature range 430-500°C the sample loses 30% of its weight with a maximum rate at 460°C. Beyond 550°C, the second decomposition step commences with 13% loss of its weight with low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 560°C.

The polymer PEA-3 loses 10% of its weight at 355°C. The polymer PEA-3 loses 39% of its weight in the temperature range 360-460°C. The maximum rate of weight loss occurs at 430°C. Beyond 570°C, the second decomposition step commences with 15%

loss of its weight with low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 640°C.

Thermal stability of polyesteramides studied are established on the basis of Tmax for the first step of decomposition. The thermal stability of polymer PEA-3 is higher than PEA-2.

PEA-2 < PEA-3

Activation energy (Ea) (k.cal/mole) calculated according to Broido method for the first step of the thermal decomposition of different polymers (Table 41.c)

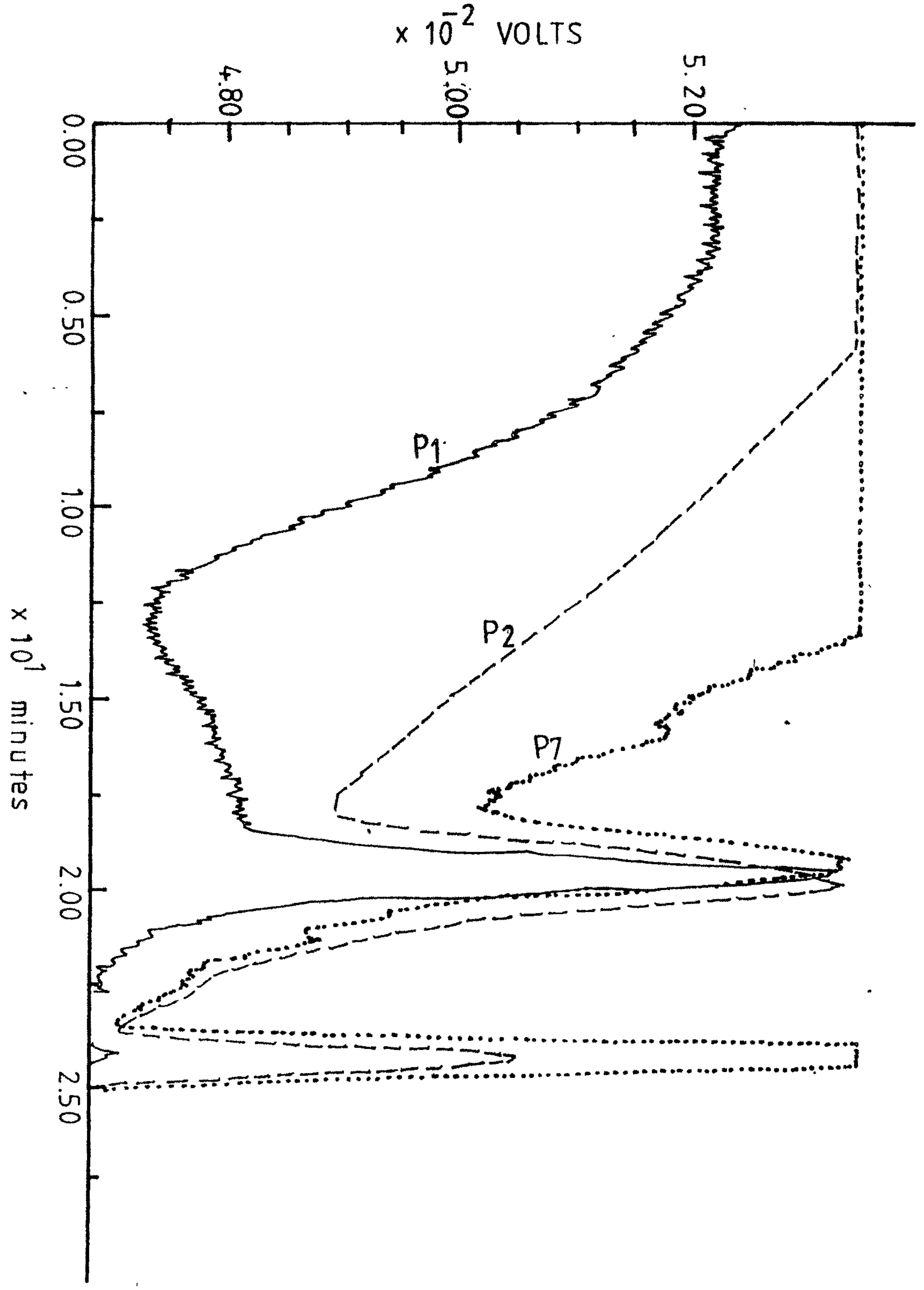


FIGURE:58 GPC THERMOGRAM OF POLYMERS

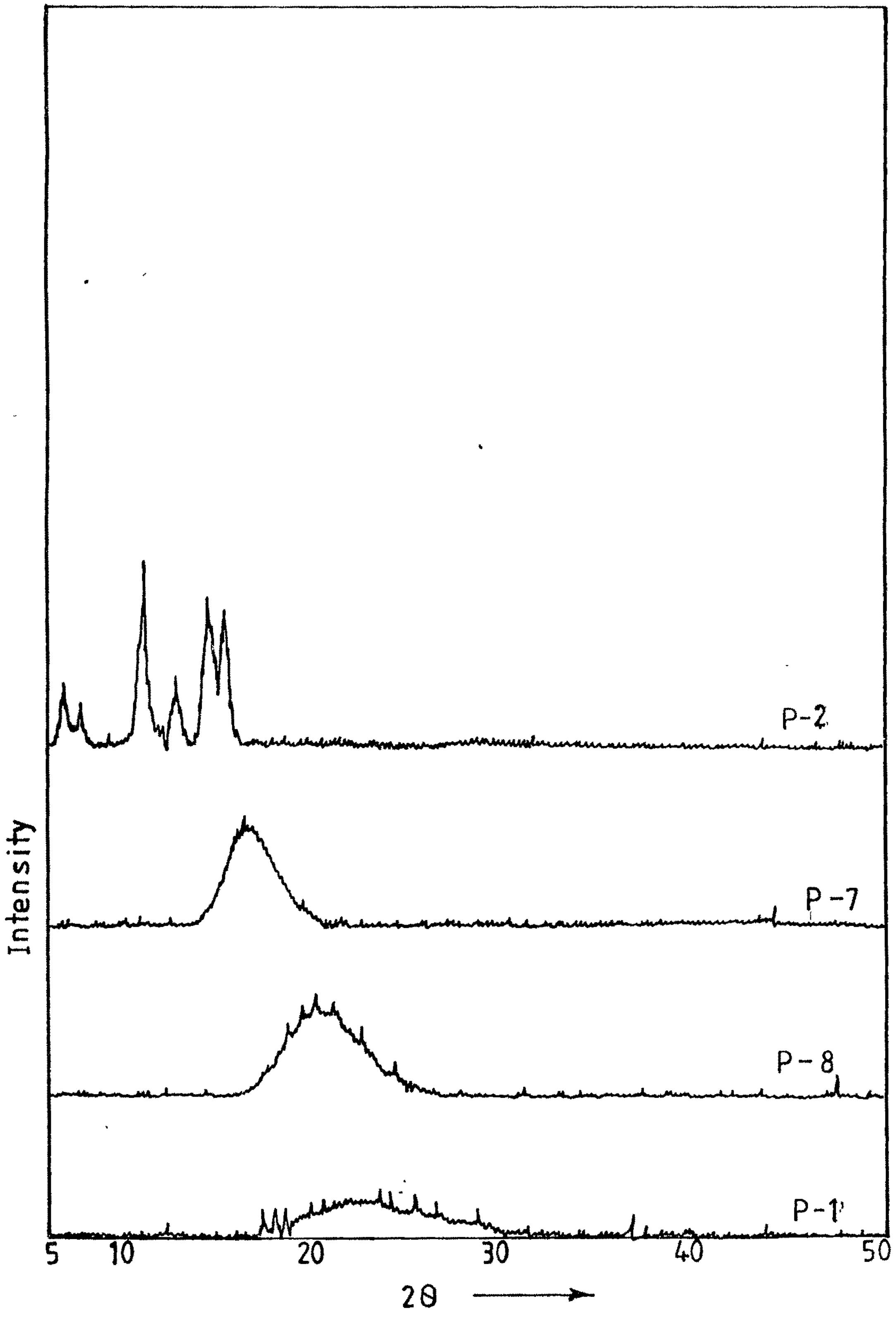
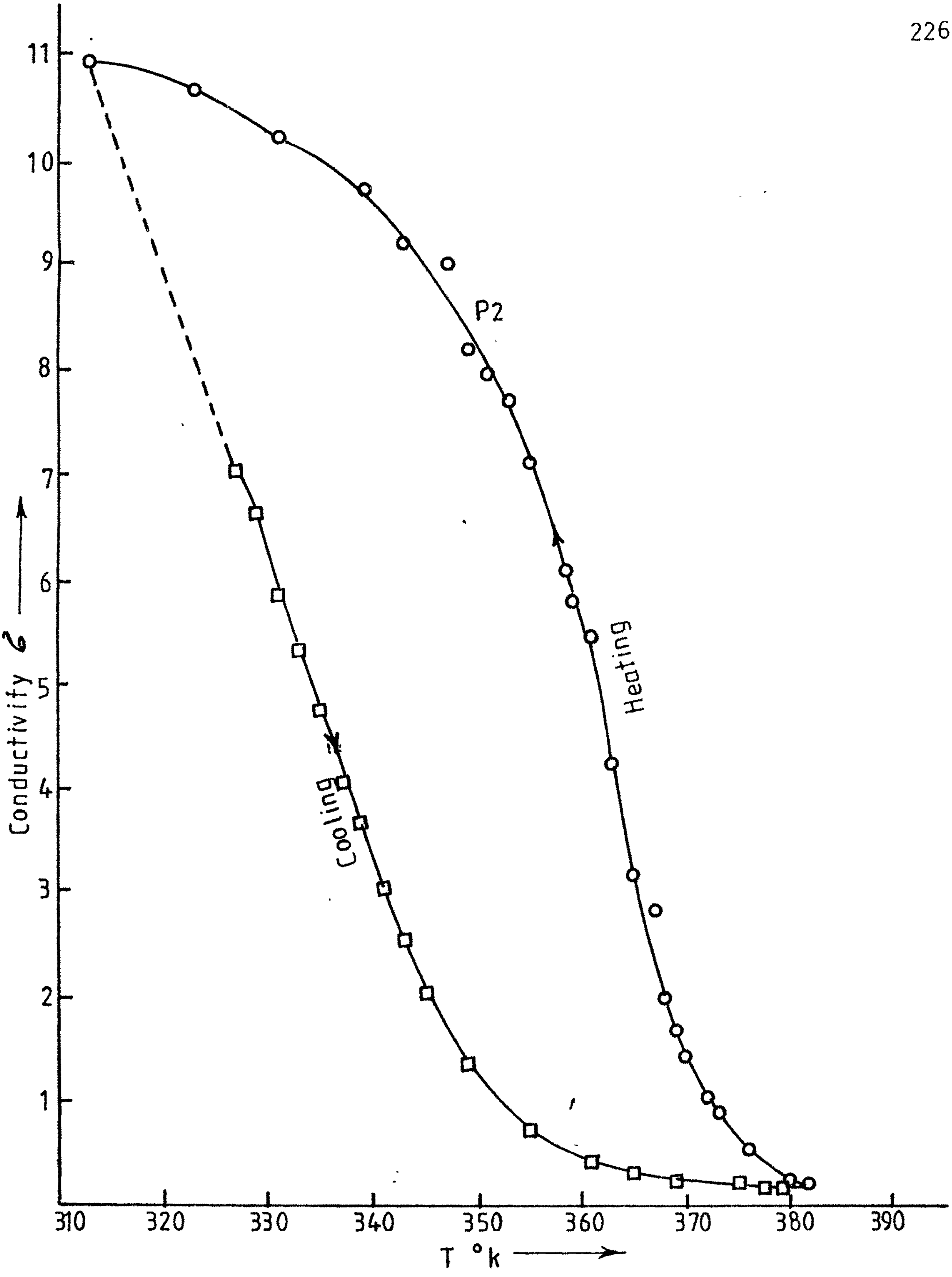


Fig.59 X-Ray diffractogram of the polymers



11
10
9
8
7
6
5
4
3
2
1
Conductivity σ
310
320
330
340
350
360
370
380
390
T °k
P2
Heating
Cooling

FIGURE : 60a.

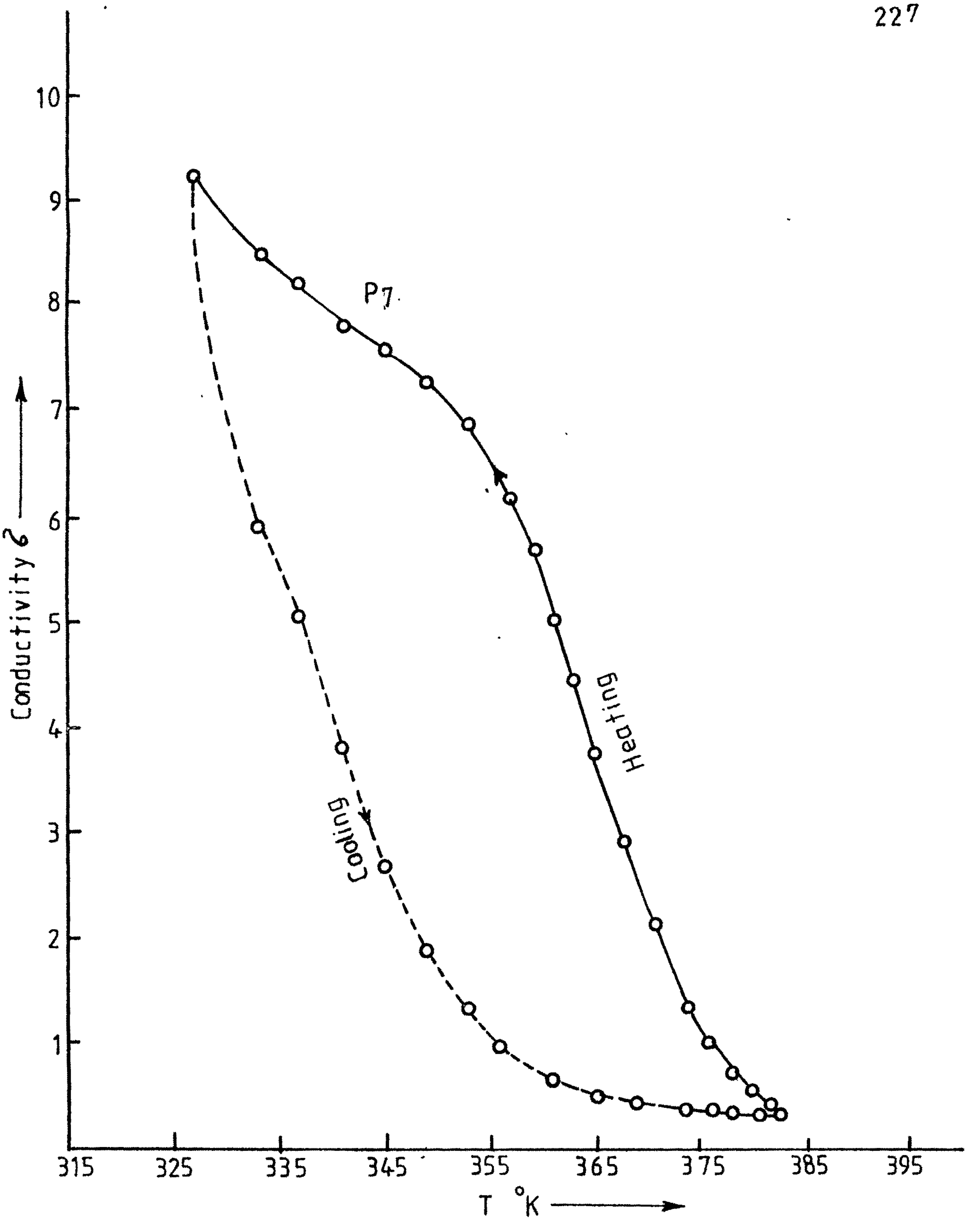

Conductivity σ
10
9
8
7
6
5
4
3
2
1
P7
Heating
Cooling
315
325
335
345
355
365
375
385
395
T °K

FIGURE: 60b.

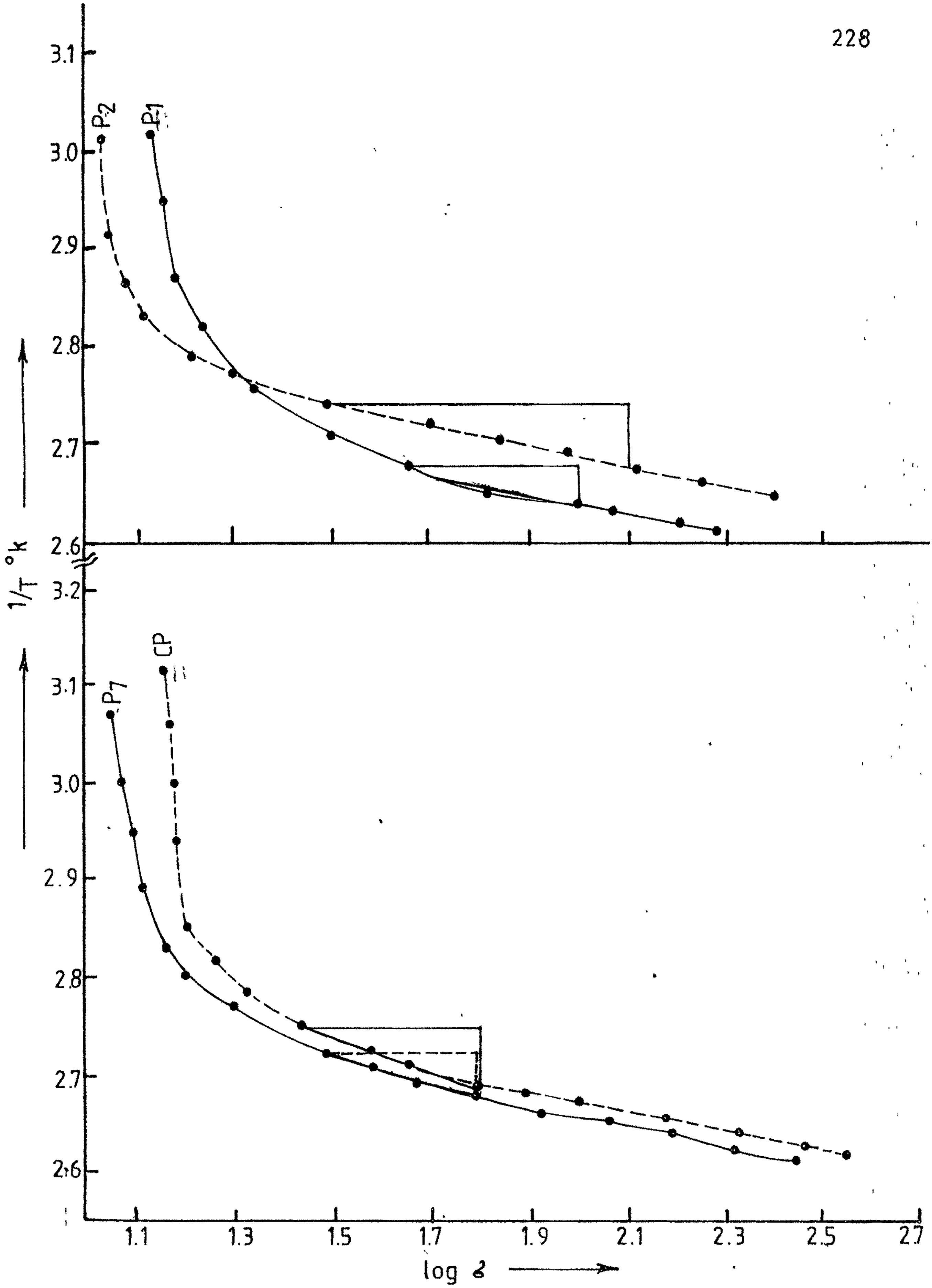


FIGURE : 61 log ∂ Vs. 1/T (°k⁻¹)

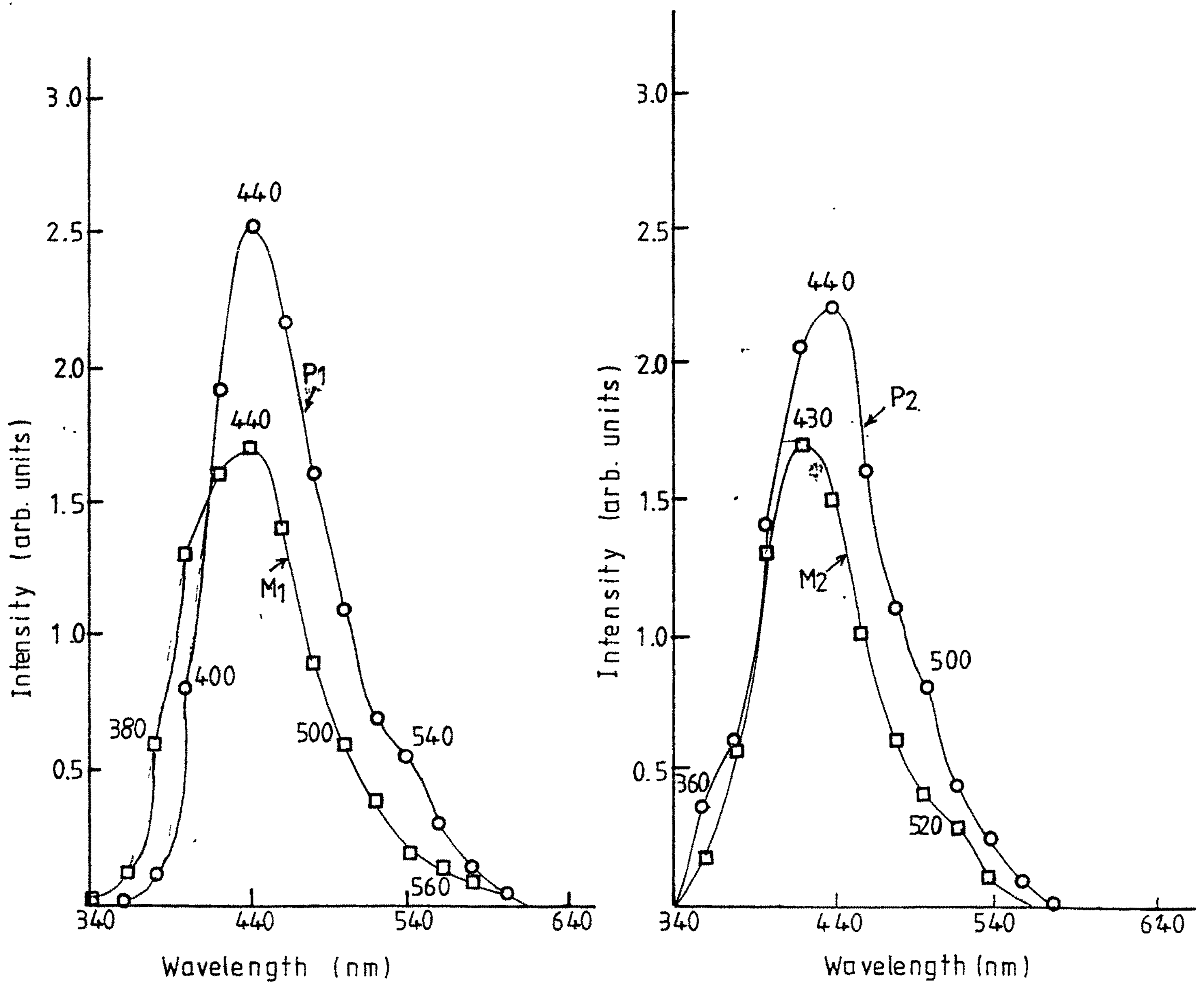


FIGURE : 52a. FLUORESCENT SPECTRA OF MONOMER AND POLYMERS

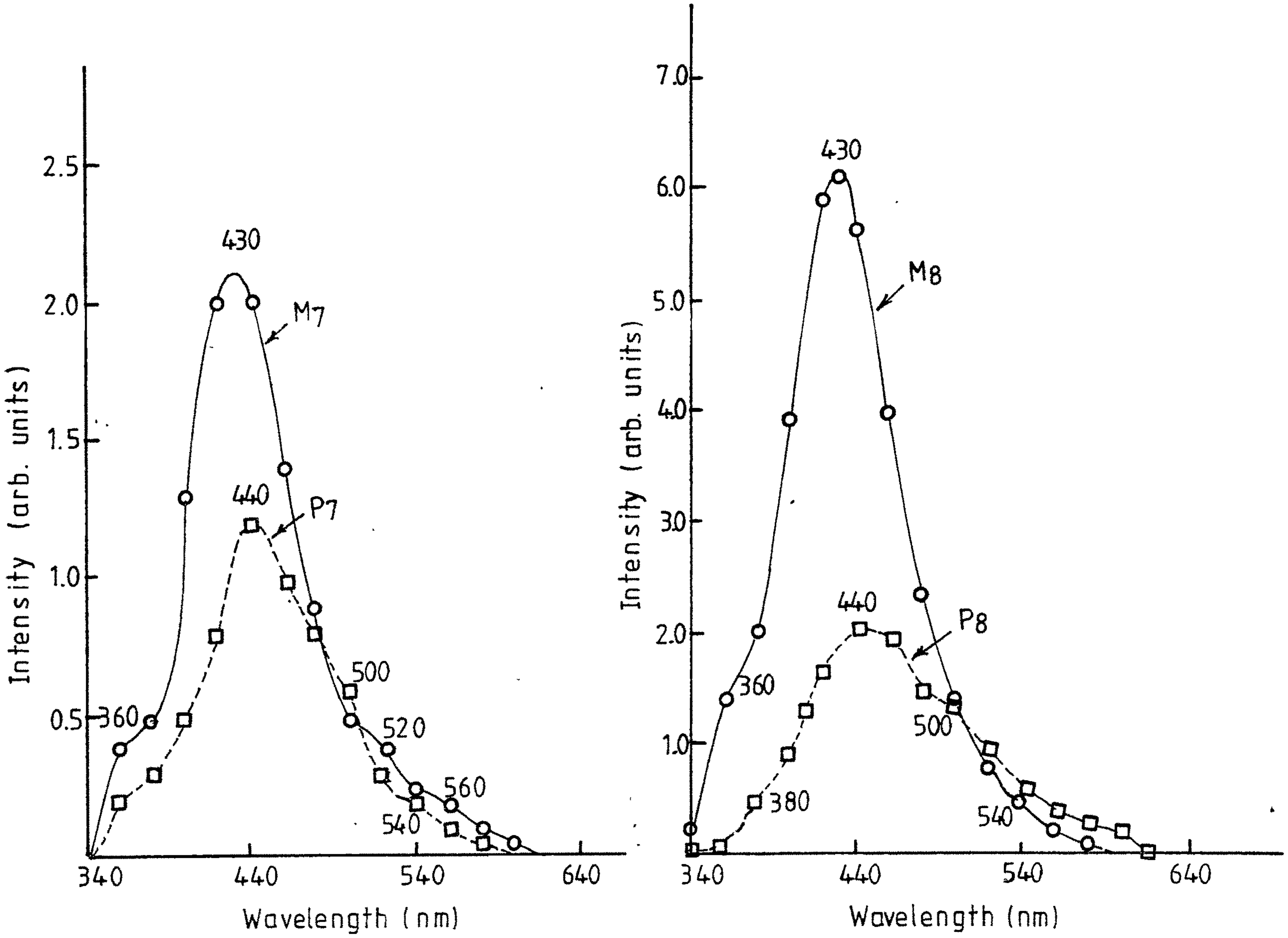


FIGURE:62b. FLUORESCENT SPECTRA OF MONOMERS AND POLYMERS

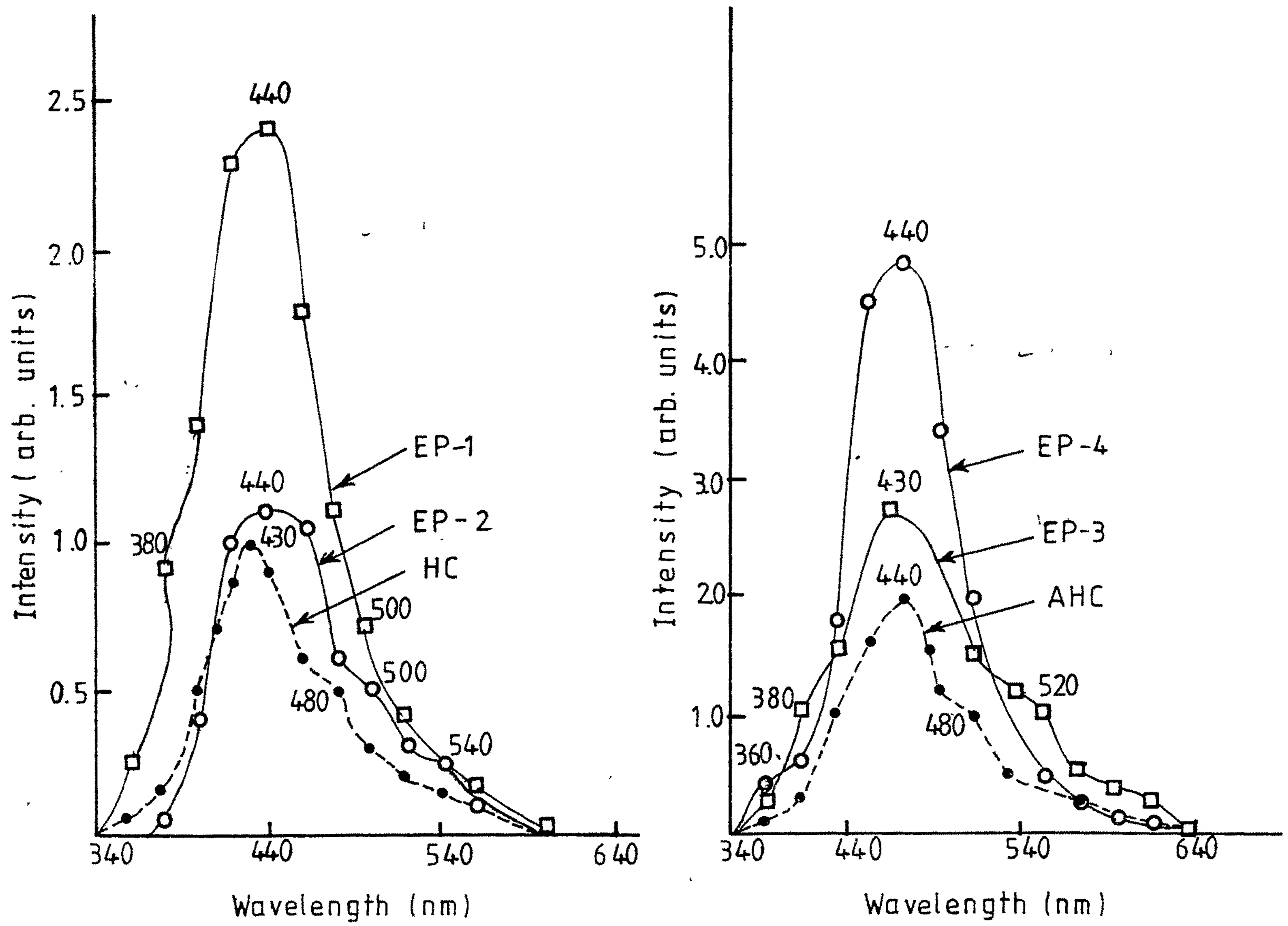


FIGURE :62c. FLUORESCENT SPECTRA OF MONOMERS AND POLYMERS

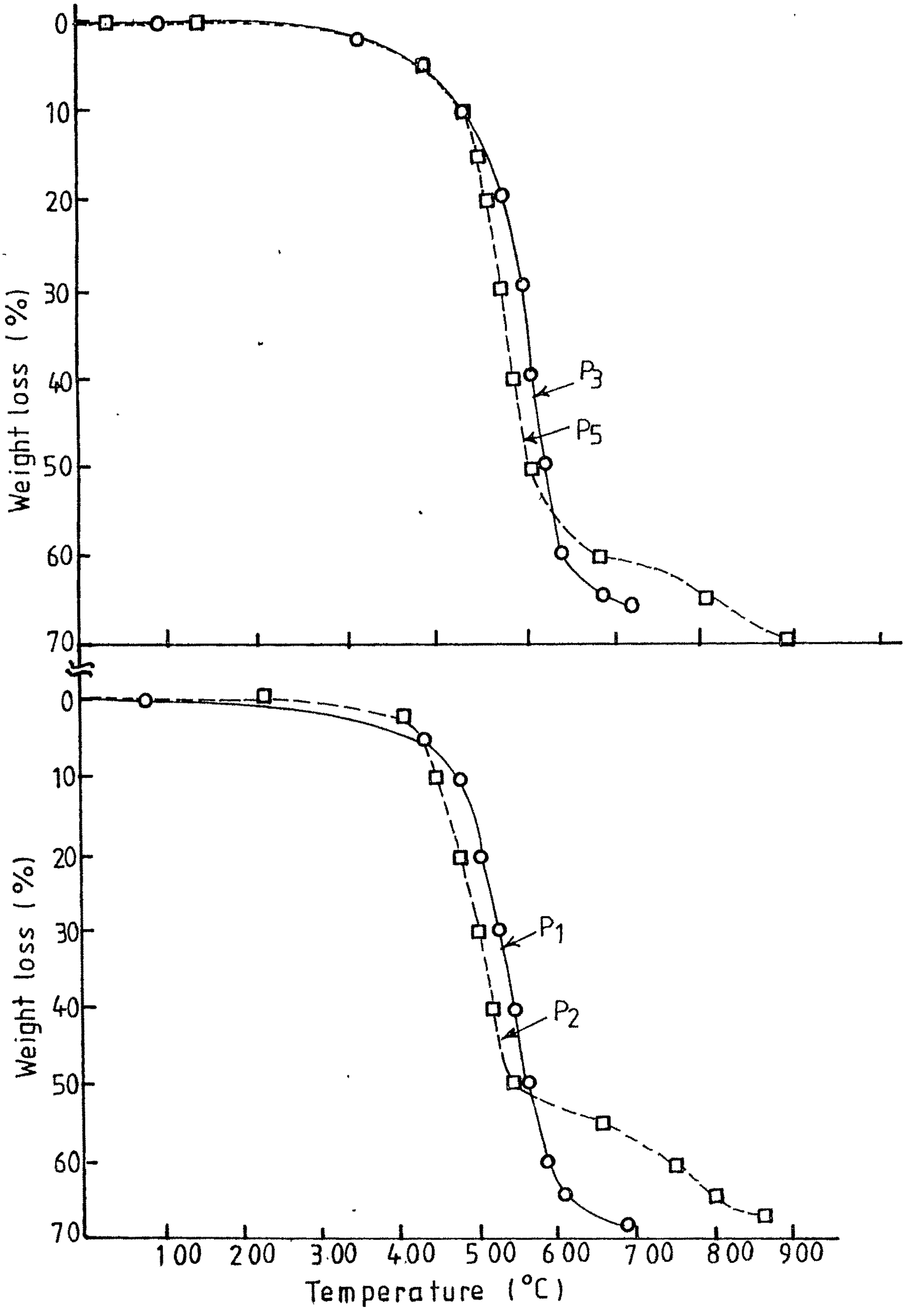


FIGURE:63'a.TGA THERMOGRAM OF POLYMERS

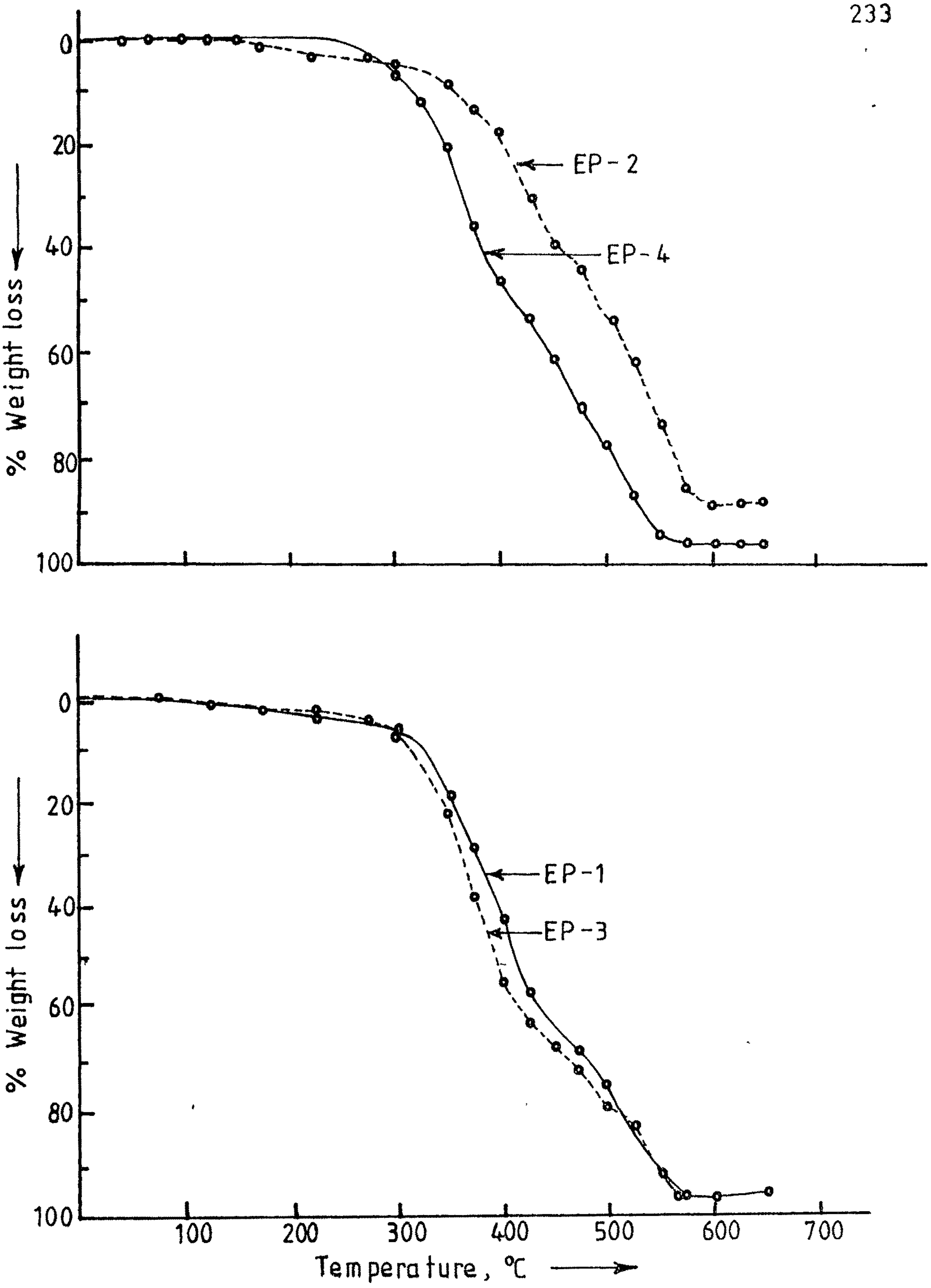


FIGURE:63b.TGA THERMOGRAM OF POLYMERS

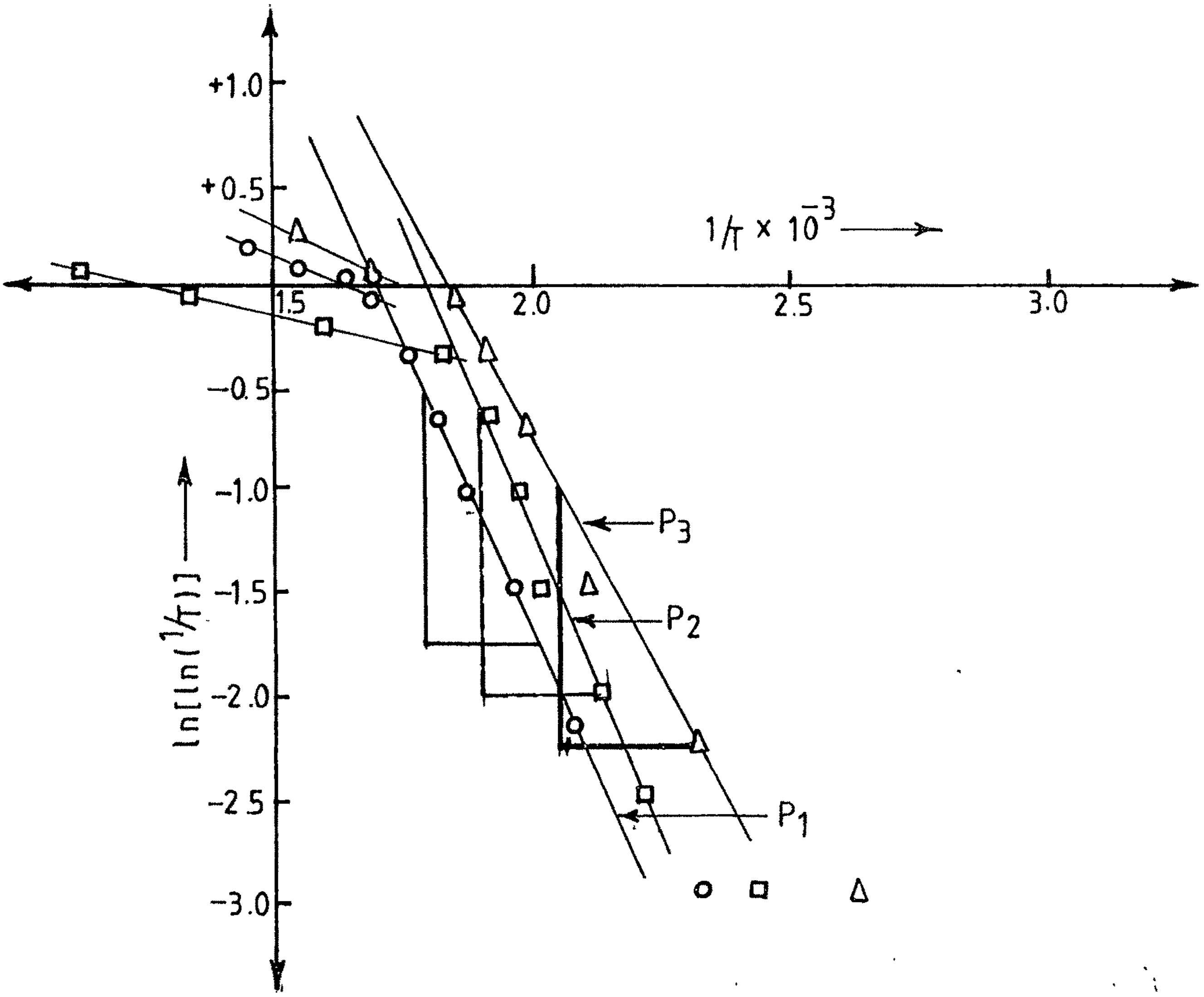


FIGURE:64a. ln[ln(1/T)] Vs. 1/T (°k⁻¹)

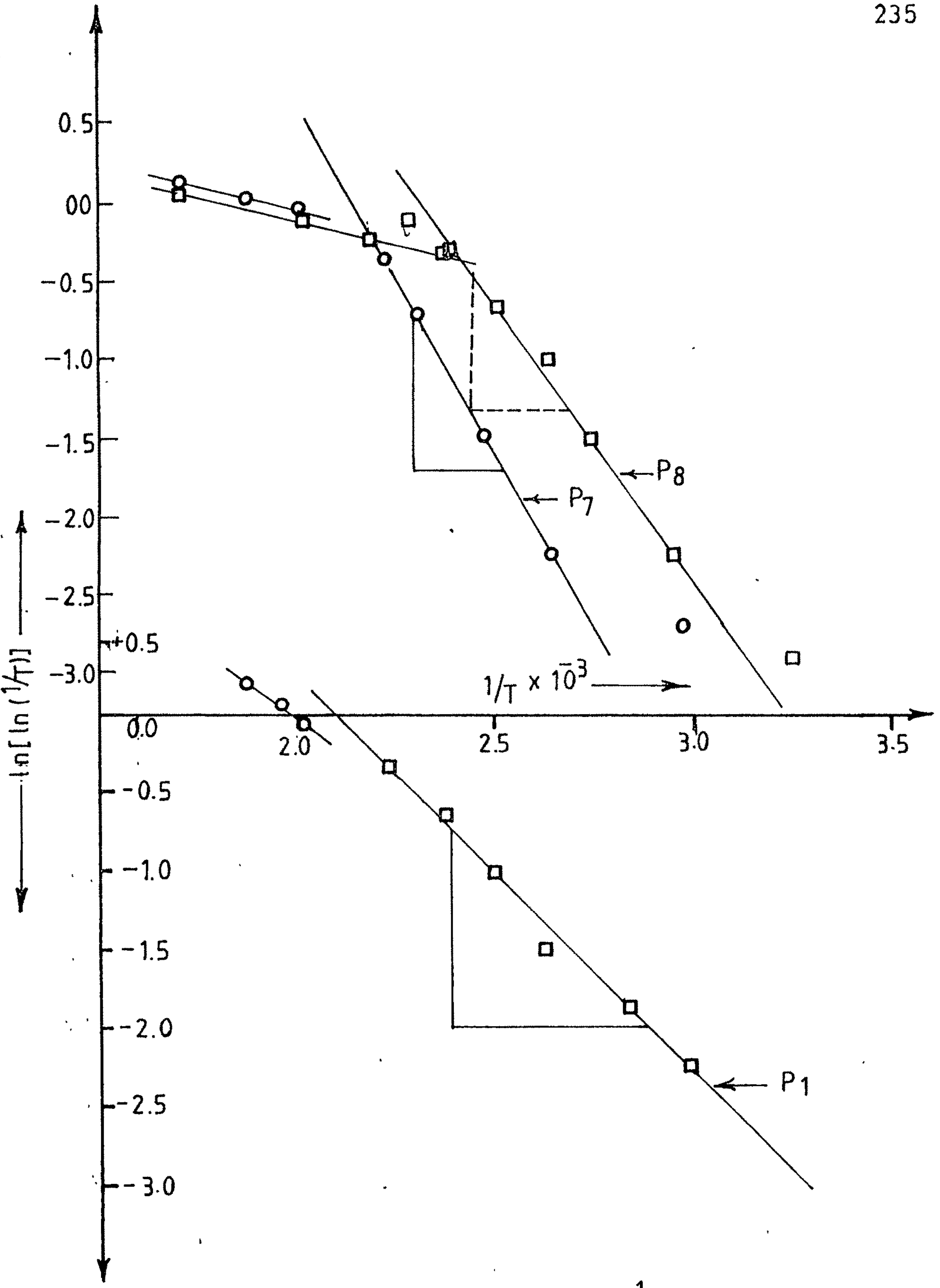


FIGURE : 64 b. $\ln[\ln(1/T)]$ Vs. $1/T$ ($^{\circ}k^{-1}$)

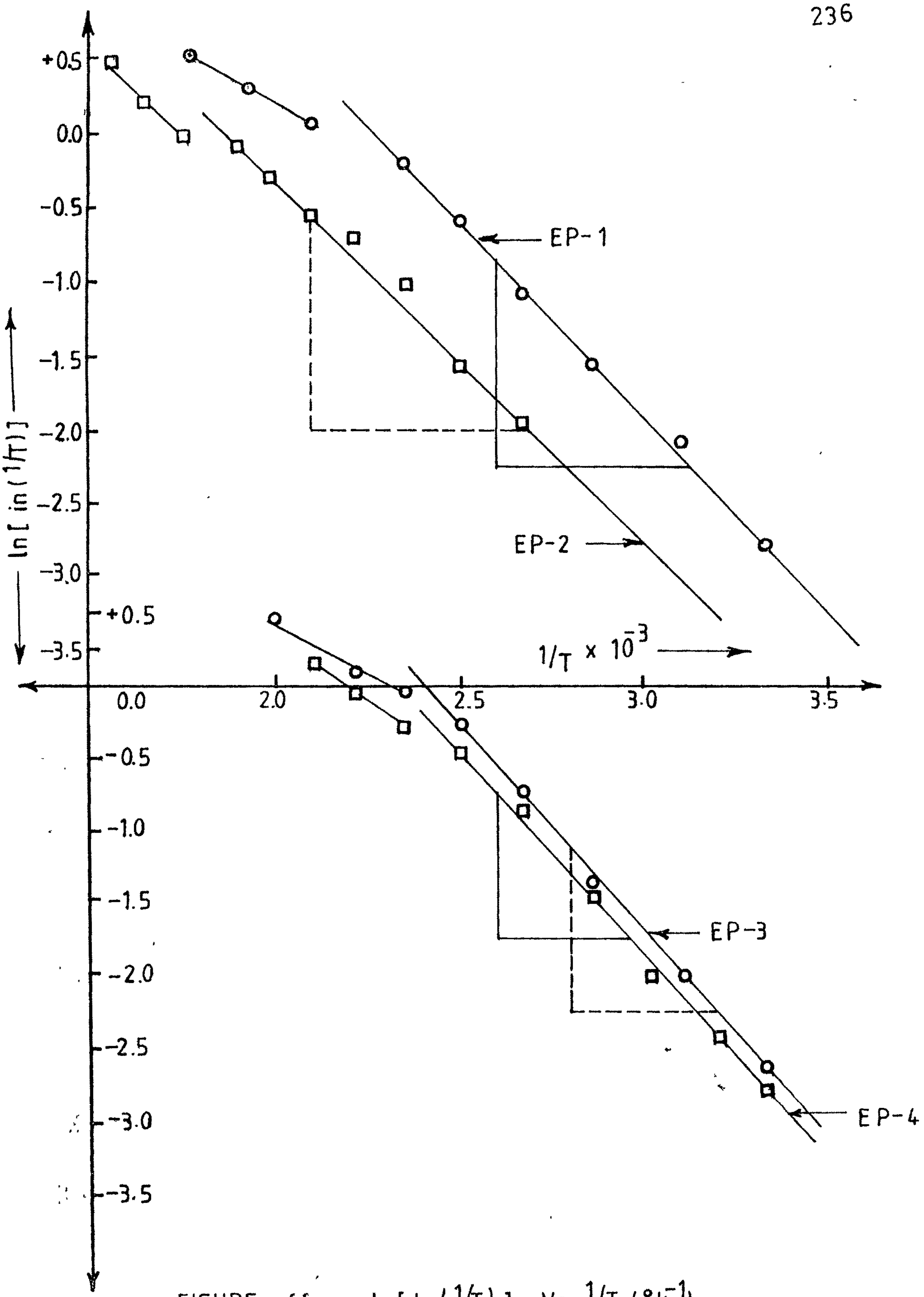


FIGURE : 64c. ln[ln(1/T)] Vs. 1/T (°K⁻¹)

viii TEXTURES OF DIFFERENT PHASES

Textures of different phases and characterization of Smectic Phases:

The microscopic method of characterization is by observing textures of different phases.

i) Cholesteric phase

Classical texture exhibited by cholesteric compounds is focal conic similar to a smectic texture which on slight disturbance or with a pressure on coverslip changes to the plane texture which normally exhibits vivid colours. Many times in cholesteric plane texture, certain typical broad thread like lines are observed which are called oily streaks

The different textures of cholesteric phases exhibited by different compounds prepared in the present work are given in Photographs A,B and C.

Photographs exhibit plane textures including the one exhibiting oily streaks. Some of these compounds exhibit vivid colours which can be seen from the photographs.

ii) Nematic phases

The nematogens exhibit classical threaded texture and the marble texture. The photographs of different nematogens are taken in the nematic phase which exhibits both type of textures.

Textures of smectic and nematic phases observed in polymers.

The classical textures of smectic and nematic phases are difficult to observe in many mesogenic polymers. Many times a slide is kept on the heating stage for a longer period at fixed temperature to develop the classical textures more so for the focal-conic smectic texture.

In the present study polymer P_7 exhibited Sm*C type texture. Photograph J is howing smectic *C phase observed in polymer P_7 and polymers EP-2, EP-3 and PEA-3 exhibited nematic texture. Photographs D, E and F are showing nematic phase observed in PEA-3, EP-2 and EP-3, respectively. Photograph I shows birefringence observed in P_2 obtained by pressing the slide on cooling.

iii) Smectic Phases

In the present study the types of the smectic mesophases are inferred from the textures observed under polarising microscope during heating as well as on cooling.

This smectogens studied in the present work exhibit focal-conic (fan shaped) or broken focal conic texture. Focal conic texture suggest the presence of S_A phase (Photograph M) whereas broken focal conic texture suggest the presence of S_c phase (Photograph O).

Microphotographs of different mesophases:

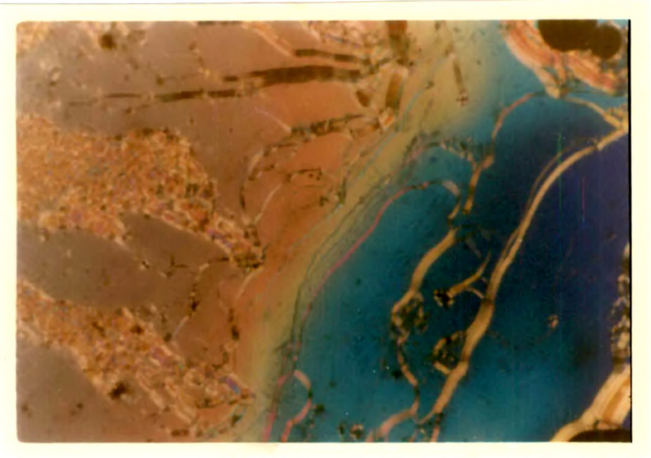
[A] Cholesteric phase with oily stricks of cholesteryl 4-(4'-n-tetradecyloxy benzoyl)-amino benzoate on heating at 265°C.

[B] Cholesteric (chiral Nematic) phase with oily stricks of Cholesteryl 4-(4'-n-decyloxy benzoyl)-amino benzoate on heating at 283°C

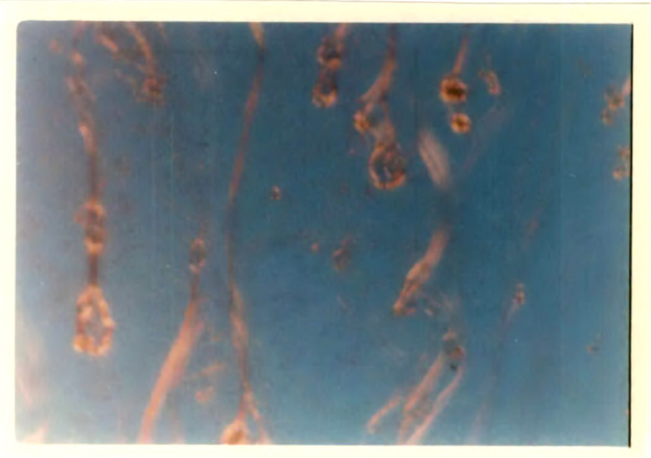
[C] Cholesteric (Chiral nematic) phase with oily stricks of 4(4'-n-decyloxy benzoyloxy benzoyl) 4"-S(+)-2-methyl butoxy aniline on heating at 210°C.

All the photographs taken under cross polarizers

Magnification 20 x 10



A



B

C

[D] Nematic marble texture of 4-(4'-n-pentyloxy benzoyloxy benzoyl)-4"-n-butoxy aniline on cooling at 270°C.

[E] Nematic Schlieren texture of 4(4'-n-hexyloxy benzoyloxy benzoyl)-4"-n-butoxy aniline on heating at 260°C.

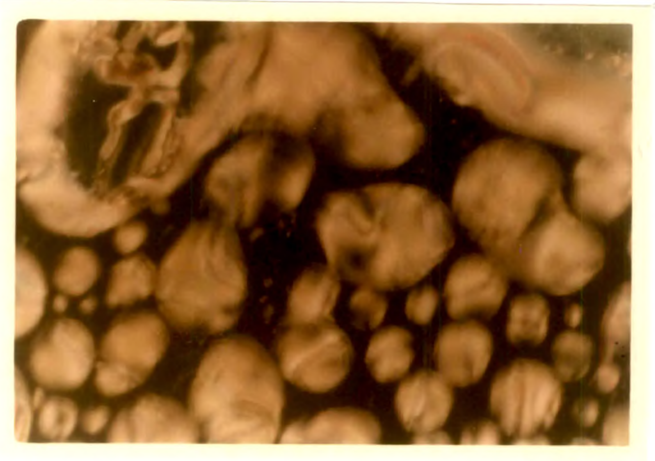
[F] Nematic Schlieren texture of polyestereamide (PEA-3) on heating at 260°C.

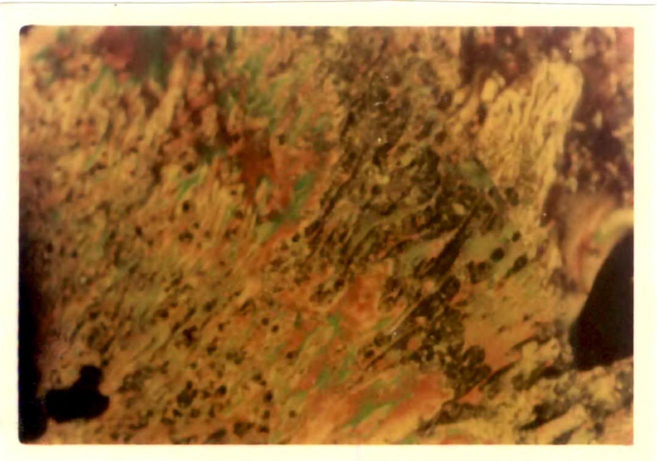
All the photographs taken under cross polarizers.

Magnification 20 x 10.

D

E





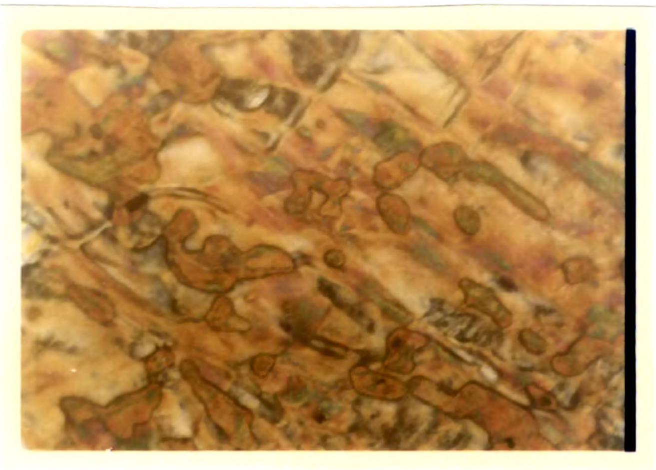
F

[G] Nematic marble texture of polychalcone (EP-2) on heating at 200°C.

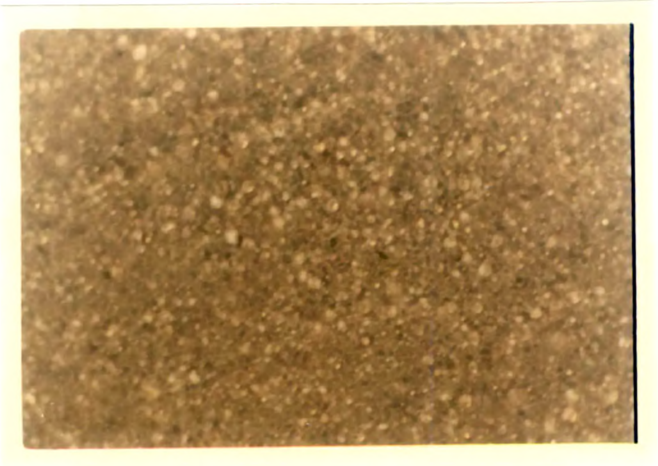
[H] Coalescing droplets of nematic phase of polychalcone (EP-3) on cooling at 180°C.

All the photographs taken under cross polarizers.

Magnification 20 x 10.



G



H

[I] Polymer P_2 showing intense birefringence during cooling at 85°C on pressing the coverslip.

[J] Chiral smectic C phase of polymer P_7 on heating at 95°C.

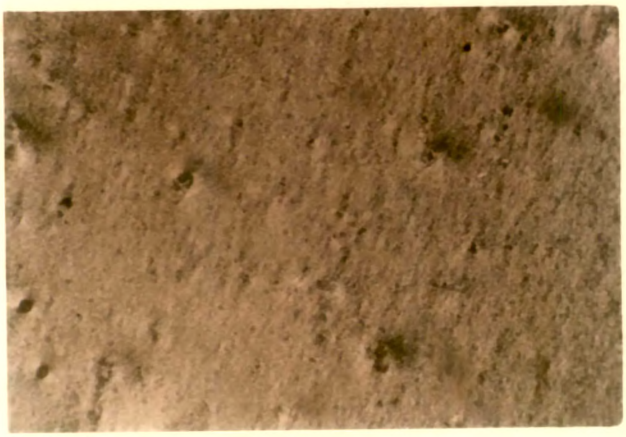
[K] Texture similar to smectic E phase (curved lines) or a typical texture of a smectic phase of Cholesteryl 4(4'-n-hexadecyloxy benzoyl)-amino benzoate on heating at 224°C.

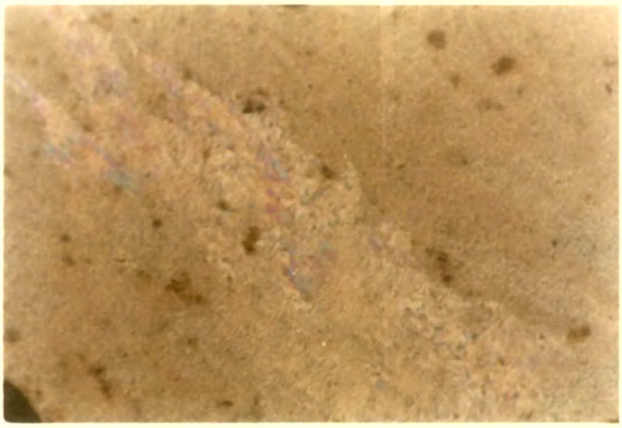
All the photographs taken under cross polarizers

Magnification 20 x 10.

I

J





K

[L] Chiral smectic A phase (fine lines) of Cholesteryl 4(4'-n-octadecyloxy benzoyl)-amino benzoate on heating at 231°C.

[M] Smectic A phase (focal conic) of 4(4'-n-decyloxy benzoyloxy benzoyl)-4"-n-butoxy aniline on heating at 225°C.

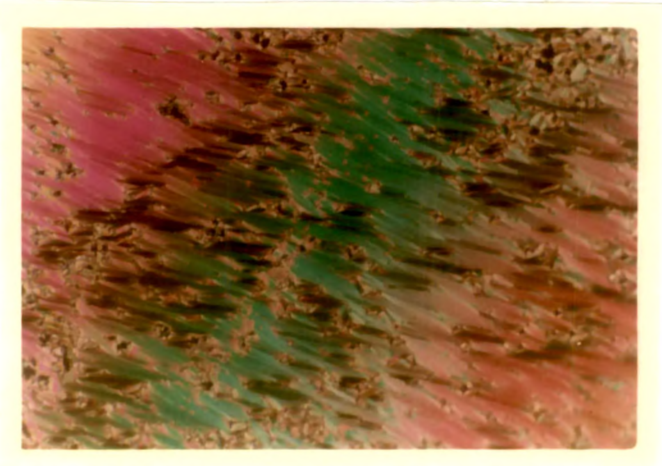
[N] Showing conversion of smectic A to cholesteric phase of Cholesteryl 4(4'-n-textradecyloxy benzoyl)-amino benzoate on heating at 264°C

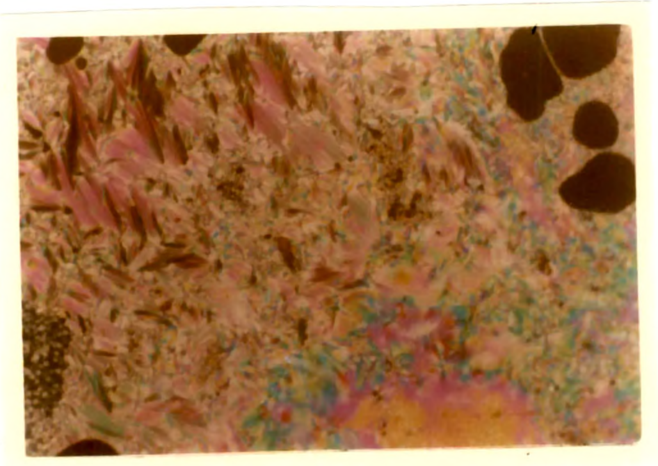
All the photographs taken under cross polarizers

Magnification 20 x 10.

L

M





N

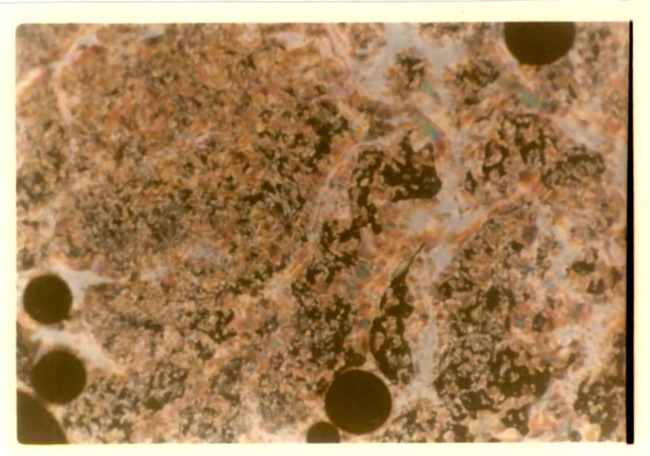
[O] Smectic C phase (broken focal conic) of 4(4'-n-decyloxy benzoyloxy benzoyl)-4"-n-butoxy aniline on heating at 215°C.

[P] Showing conversion of smectic C phase to cholesteric phase of 4(4'-n-decyloxy benzoyloxy benzoyl)-4"-n-butoxy aniline on heating at 232°C.

All the photographs taken under cross polarizers

Magnification 20 x 10.

O



P