EXPERIMENTAL

2. PREPARATION OF COMPOUNDS:

2.1 Chiral and Achiral Ester-Amide Compounds:

2.1.1 n-Alkyl Halides:

All the alkyl halides (bromides) used were of B.D.H., Fluka or equivalent quality.

2.1.2 Preparation of 4(4'-n-Alkoxy Benzoyloxy Benzoyl)-4"-n-Butoxy Anilines (Series I):

2.1.2a 4-n-Alkoxy Benzoic Acids:

Commercially available 4-methoxy benzoic acid (anisic acid) was used (B.D.H). Number of other methods are known for alkylation of p-hydroxy benzoic acid. However, in the present study, the method developed by Dave and Vora (272) was followed.

4-Hydroxy benzoic acid (0.1 mole), appropriate alkyl halide (0.12 mole) and potassium hydroxide (0.25 mole) were dissolved in 100 ml ethanol and refluxed for 7 to 8 hours. Ten percent aqueous potassium hydroxide solution (25 ml) was added and reflux was continued for two hours to hydrolyse any ester formed. The solution was cooled and acidified with 1:1 cold hydrochloric acid to precipitate the acid. The n-alkoxy acids were crystallized several times from ethanol or acetic acid until constant transition temperatures were obtained. The transition temperatures are in good accordance with the literature (273).

2.1.2b 4-n-Alkoxy Benzoyl Chlorides (272)

4-n-Alkoxy benzoyl chlorides were prepared by reacting the corresponding 4-n-alkoxy benzoic acid with excess of thionyl chloride and heating on a water-bath till the evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using water pump and the acid chloride left behind as a residue was used in next reaction without further purification.

2.1.2c 4-n-Alkoxy Benzoyloxy Benzoic Acids

4-Hydroxy benzoic acid (0.01 mole) was dissolved in dry pyridine (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxy benzoyl chloride (0.01 mole). The mixture was heated on water-bath for half an hour and was allowed to stand for overnight. It was acidified with cold 1:1 hydrochloric acid and the precipitates obtained were filtered, and washed with water followed by cold methanol. The esters recrystallized several times from glacial acetic acid until constant transition temperatures were obtained. The transition temperatures are in good accordance with the literature (274,275).

2.1.2d 4-n-Alkoxy Benzoyloxy Benzoyl Chlorides:

4-n-Alkoxy benzoyloxy benzoyl chlorides were synthesized by the procedure as described above in section 2.1.2b.

2.1.2e Synthesis of 4-n-Butoxy Aniline

4-n-Alkoxy anilines can be synthesized by different routes (276,277). In the present study the following route was followed as it gives over all better yields of 4-n-butoxy aniline (277).

(i) Synthesis of 4-n-Butoxy Acetanilide:

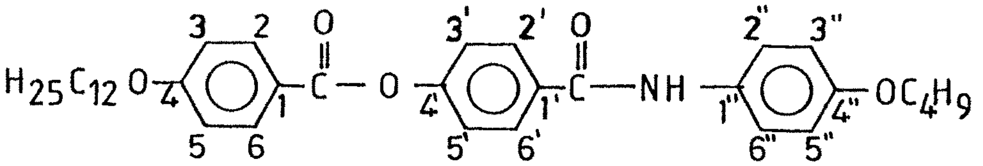
Paracetamol (0.1 mole), anhydrous potassium carbonate (0.15 mole), butyl bromide (0.15 mole) and dry acetone (60 ml) were taken in round bottom flask. The reaction mixture was refluxed on water-bath for 8 to 10 hours. The whole mass was then added to water and the solid obtained was filtered, washed with water and directly used for hydrolysis.

(ii) Hydrolysis of 4-n-Butoxy Acetanilide to 4-n-Butoxy Aniline:

A mixture of 4-n-Butoxy Acetanilide (0.146 mole), water (70 ml) and concentrated hydrochloric acid (45 ml) were stirred for 10 to 12 hours at 90-95°C and then cooled to room temperature. The mixture was made alkaline with 50% sodium hydroxide solution at 20°C. The oily product was extracted with ether. The extract was dried and concentrated at reduced pressure to give an oil which was purified by distillation. Boiling point agree well with the reported value (276,277).

2.1.2f 4-(4'-n-Alkoxy Benzoyloxy Benzoyl) -4"-n-Butoxy Anilines:

Respective 4-n-Alkoxy benzoyloxy benzoyl chloride (0.01 mole) was dissolved in about 5 ml of dry pyridine. The solution of 4-n-butoxy aniline (0.01 mole) in 10 ml of dry pyridine was added slowly to cold solution of acid chloride. The mixture was heated on water-bath for about half an hour and was allowed to stand over night. It was acidified with cold 1:1 hydrochloric acid. Precipitates were filtered and washed with water, dilute sodium hydroxide solution and water. The resulting ester-amides were recrystallized several times from DMF until constant transition temperatures were obtained. The transition temperatures, elemental analysis and IR spectral data are reported in Tables 4, 5 and 6 respectively. NMR spectral data are given below:



NMR (90 MHz, $CDCl_3$)

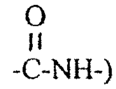
δ 0.9 - 1.7 (m, 30 H of two alkyl chains at C_4 and C_4")

δ 4.25 (t, 4H of two methylene groups in the alkoxy chain at C_4 and C_4")

δ 7.11 (d, 4H at C-3, C-5, C-3" and C-5")

δ 7.45 (BS, 4H at C-3', C-5' and C-2", C-6") δ 8.05 (d, 2H at C-2' and C-6')

δ 8.25 (d, 2H at C-2 and C-6)

δ 9.1 (S, 1H of  $-\overset{\overset{O}{\|}}{C}-NH-$)

2.1.3 Preparation of 4-(4'-n-Alkoxy Benzoyloxy Benzoyl)-4"-S (+) 2-Methyl Butoxy Anilines (Series II):

2.1.3.1 Synthesis of S (+)-2-Methyl Butoxy Aniline:

2 1 3.1a Preparation of S-(+)-1-Bromo-2-Methyl butane from S-(+)-2-Methyl Butanol.

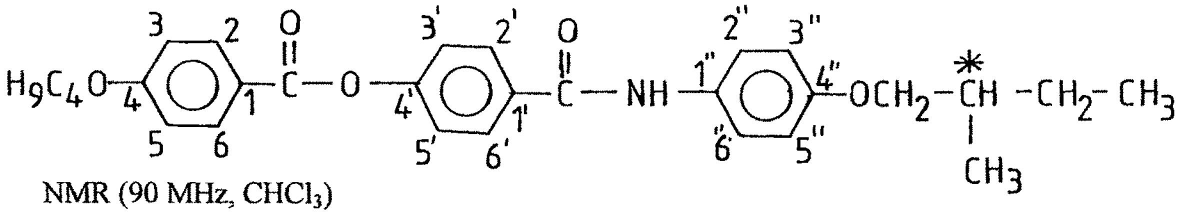
50 grams of hydrobromic acid (48%) was taken in a round bottom flask 15 0 grams of concentrated sulfuric acid was added in portions with constant shaking, 17.6 grams of S(+)-2-methyl-1-butanol was added followed by the addition of 12.0 grams of concentrated sulfuric acid (98%) in portion with shaking. The whole mass was refluxed gently on sand-bath for 3 hours Optically active bromide separated above the acid. The reaction mass was cooled upto room temperature. Bromide layer was separated and washed with water, hydrochloric acid, water, 5% sodium bicarbonate solution and water Bromide was dried over anhydrous calcium chloride and distilled, B P. 120°C Reported 121°C (278)

2.1 3 1b Preparation of S(+)-4(β-Methyl Butoxy) Aniline:

S(+)-4 (β-Methyl butoxy) aniline was synthesized by the procedure described in the preceding section.

2.1.3.2 4(4'-n-Alkoxy Benzoyloxy Benzoyl)4"-S-(+) β-Methyl Butoxy Anilines

4-(4'-n-Alkoxy benzoyloxy benzoyl)4"-S-(+) β-methyl butoxy anilines were synthesized by the procedure described in previous section. The resulting esteramides were recrystallized several times from DMF until constant transition temperatures were obtained. The transition temperatures, elemental analysis and IR spectral data are reported in Tables 7, 8 and 9 respectively. NMR spectral data are given below:



NMR (90 MHz, $CHCl_3$)

1.0-1.79 (m, 16H of alkyl chain at C-4 and C-4");

4.2 (t, 4H of two methylene group in the alkoxy chain at C-4 and C-4")

7.11 (d, 4H at C-3, C-5, C-3" and C-5")

7.46 (d, 4H at C-3', C-5', C-2" and C-6")

8.17 (d, 2H at C-2' and C-6')

8.32 (d, 2H at C-2 and C-6)

8 9 (S, 1H of $-\overset{\overset{O}{\parallel}}{C}-NH-$ of amide linkage)

2.2 Cholesteryl Derivatives

2.2.1 Preparation of Cholesteryl-4(4'-n-Alkoxy Benzoyl)-Amino Benzoates (SeriesIII)

2.2.1a 4-n-Alkoxy Benzoic Acids and 4-n-Alkoxy Benzoyl chlorides:

4-n-Alkoxy benzoic acids and their acid chloride were synthesized by the procedure described in section 2.1.2a and 2.1.2b respectively.

2.2 1b 4-(4'-n-Alkoxy Benzoyl) Amino Benzoic acids

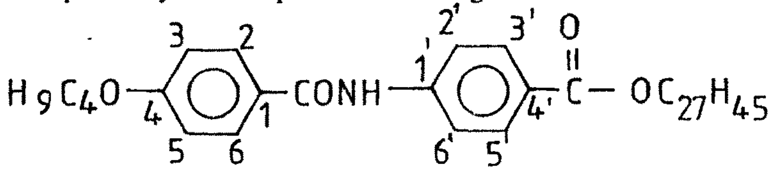
4-Amino benzoic acid (0.01 mole) was dissolved in N-methyl-2-pyrrolidone (10 ml) and was added slowly with constant stirring to cold 4-n-alkoxy benzoyl chloride (0.01 mole). The mixture was heated on water-bath for an hour and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid and the precipitates obtained were filtered and washed with warm water followed by cold ethanol. The lower members recrystallized several times from glacial acetic acid and higher members from dimethyl formamide until constant melting points were obtained. The melting points, elemental analysis and IR spectral data are reported in Tables 10, 11 and 12, respectively.

2.2.1c 4-(4'-n-Alkoxy Benzoyl) Amino Benzoyl Chlorides:

4-(4'-n-Alkoxy benzoyl) amino benzoyl chlorides were synthesized by the procedure described in section 2.1.2.b.

2.2.1d. Cholesteryl 4-(4'-n-Alkoxy Benzoyl) Amino Benzoates: (Series III)

Equimolar proportion (0.01 mole) of cholesterol and appropriate acid chloride of 4-(4'-n-alkoxy-benzoyl) amino benzoic acids were taken in round bottom flask. Freshly distilled N,N-dimethyl aniline (20 ml) was added as a solvent. The whole mass was heated in an oil-bath upto 120°C for two hours. After heating, the whole mass was added to ice-cold water. The blue solid was filtered and washed with dilute alcohol or with acetone (cold) to remove N, N-dimethyl aniline, repeated washings gave a white mass, which was recrystallized from chloroform-acetone mixture till constant transition temperatures were obtained. The transition temperatures, elemental analysis and IR spectral data are reported in Table 13, 14 and 15, respectively. NMR spectral data are given below:



NMR (90 MHz, $CDCl_3$)

0.8-2.0 (m, 52H (for 45 cholesterol protons and as well as 7 propyl group protons at C-4)

4.2 (t, 2H of methylene in the alkoxy chain at C-4);

7.1 (d, 2H at C-3 and C-5);

7.7 (d, 2H at C-2' and C-6');

7.9 (d, 2H at C-2 and C-6);

8.15 (d, 2H at C-3' and C-5')

9 05 (S, 1H of $-\overset{\overset{O}{\|}}{C}-NH-$).

2.3 Other Mesogenic Compounds:

2.3.1 Preparation of Biphenyl Diesters:

Adipic acid and terephthalic acid were commercially obtained. Adipoyl chloride and terephthaloyl chloride were prepared by the method described in section 2.1.2b.

2.3.1a Synthesis of 4-Hydroxy-4'-Nitro Biphenyl (279, 280):

4-Hydroxy-4'-nitrobiphenyl was synthesized by the process reported in the literature. It was synthesized by four step method.

(i) Preparation of Benzoyl Chloride:

Benzoyl chloride was prepared from benzoic acid by the method described in section 2.1.2b.

(ii) Benzoyloxy Biphenyl:

4-Hydroxy biphenyl (0.1 mole) was dissolved in 50 ml of dry pyridine and was added slowly with stirring, to cold benzoyl chloride (0.1 mole) contained in a round bottom flask. The mixture was heated on a water-bath for thirty minutes and was allowed to cool upto room temperature It was acidified with cold 1:1 hydrochloric acid and precipitates obtained were filtered, washed with water and dried. The ester was crystallized from ethanol. Melting point 150°C (Reported 149-150°C) (279, 280).

(iii) 4-Benzoyloxy-4'-Nitrobiphenyl:

4-Benzoyloxy biphenyl (0.145 mole) was taken in round bottom flask, 310 ml of glacial acetic acid was added in the flask and it was heated up to 80-90°C. 100 ml fuming nitric acid was added slowly in such a way that the temperature remained between 80 to 90°C. After complete addition, the reaction mixture was cooled to room temperature. The solid separated was filtered and washed with water and methanol. The product was crystallized from glacial acetic acid. Melting point is in good accordance with the literature (299, 300).

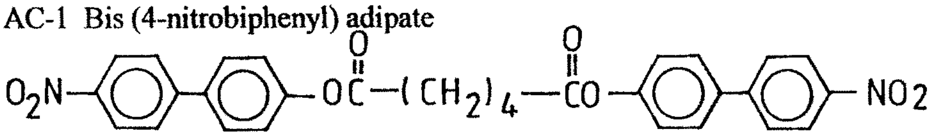
(iv) Hydrolysis of 4-Benzoyloxy-4'-Nitrobiphenyl:

4-Benzoyloxy-4'-nitrobiphenyl (0.18 mole) was taken in round bottom flask, 300 ml of ethanol was added to it and it was heated to reflux An aqueous solution of potassium hydroxide (40 gms of KOH in 100 ml water) was then added dropwise at reflux. After complete addition, the mixture was further refluxed for 30 minutes and cooled over night. Next day, blue crystals of potassium salt were filtered, washed with tetrahydrofuran until wash was colourless. Pure 4-hydroxy-4'-nitrobiphenyl was obtained by dissolving the salt in minimum amount of boiling water and adding 1:1 hydrochloric acid until acidic pH was obtained The yellow solid was filtered, washed with water, dried and crystallized from ethanol. Melting point 203°C. (Reported 203 to 204°C).

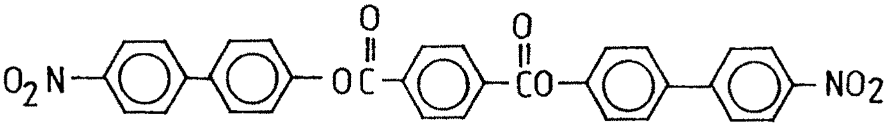
2.3.1b Preparation of Biphenyl Diesters:

4-Hydroxy-4'-nitrobiphenyl (0.01 mole) was dissolved in N-methyl-2-pyrrolidone (10 ml) and was added slowly with constant stirring to cold acid chloride (0.025 mole). The mixture was heated on water-bath for one hour Reaction mass was cooled and then acidified with dilute cold hydrochloric acid. Yellow solid obtained was filtered and washed with water, dried and crystallized from benzene/DMF.

AC-1 Bis (4-nitrobiphenyl) adipate



AC-2 Bis (4-nitrobiphenyl) terephthalate



Transition Temperatures °C

AC-1 $K \xrightarrow{186\ 0^{\circ}C} \text{Nematic} \xrightarrow{208.4^{\circ}C} \text{Isotropic}$

AC-2 $K \xrightarrow{298^{\circ}C} \text{Nematic} \xrightarrow{>330^{\circ}C} \text{Isotropic (d)}$

d - decomposition

Elemental Analysis

	Calculated (%)			Found (%)		
	C(%)	H(%)	N(%)	C(%)	H(C)	N(C)
AC-1	66.67	4.44	5.19	66.23	4.20	5.32
AC-2	68.57	3.57	5.00	68.13	3.49	4.80

IR Spectral data (Bending and Stretching Vibrations) cm^{-1}

AC-1 1750, 1595, 1515, 1480, 1410, 1345, 1250, 1210, 1165, 1120, 1000, 840

2.3.2 Synthesis of Cholesteryl 4-n-Alkoxy Benzoyl Glycine:

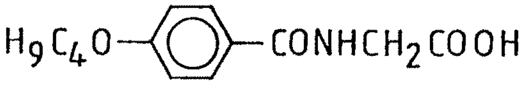
2.3.2a Preparation of 4-n-Alkoxy Benzoic Acids and 4-n-Alkoxy Benzoyl Chlorides

4-n-Alkoxy benzoic acids and its chloride were prepared by the method described in section 2.1.2a and 2.1.2b respectively.

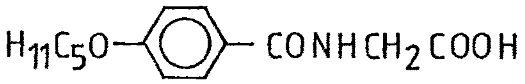
2.3.2b 4-n-Alkoxy Benzoyl Glycine (281)

0.1 mole of glycine was dissolved in 25 ml of 10 percent sodium hydroxide solution contained in a conical flask. Added 0.1 mole of alkoxy benzoyl chloride in two portions to the solution. Stoppered the flask and shook vigorously after each addition until all the chloride was reacted. Transferred the solution to a 100 ml beaker and rinsed conical flask with a little water. Placed a few grams of crushed ice in the solution and added concentrated hydrochloric acid slowly and with stirring until the mixture was acidic to congo red paper. Collected the resulting crystalline precipitate of 4-n-alkoxy benzoyl glycine (4-n-alkoxy benzoyl amino acetic acids), upon a Buchner funnel washed with cold water and drained well. Placed the solid in a 100 ml conical flask with 10 ml of carbon tetrachloride and boiled the mixture gently for 5 minutes. Allowed the mixture to cool slightly, filtered by gentle suction and washed the precipitates, with 5 ml of carbon tetrachloride. The alkoxy benzoyl glycine were recrystallized from aqueous ethanol, until constant melting points were obtained.

BG-1 4-n-Butoxy benzoyl glycine (M.P. 145°C)



BG-2 4-n Pentyloxy benzoyl glycine (M.P. 126°C)



Elemental Analysis

	Calculated (%)			Found (%)		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
BG-1	62.15	6.77	5.58	61.93	6.55	5.63
BG-2	63.40	7.17	5.28	62.96	6.88	5.31

IR Spectral data (Bending and stretching vibrations cm^{-1})

BG-1 3325, 2925, 1740, 1635, 1560, 1510, 1480, 1410, 1300, 1250, 1195, 1040, 945, 860, 770

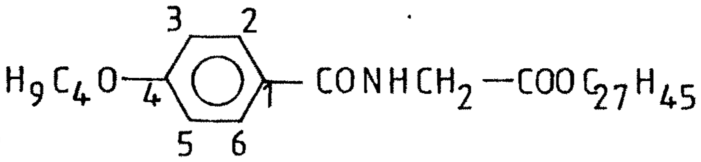
2.3.2c Acid Chloride of 4-n-Alkoxy Benzoyl Glycine

Acid chloride of 4-n-alkoxy benzoyl glycine were synthesized as previously described.

2.3.2d Preparation of Cholesteryl 4-n-Alkoxy Benzoyl Glycine:

Cholesteryl 4-n-alkoxy benzoyl glycine were prepared by the method described in section 2.3.1d.

NMR Spectral Data :



NMR (90,MHz,$CDCl_3$)

δ 0.8 - 2.0 (m, 54H (45H for cholesteryl moiety, 7H for propyl group and 2H for methylene group).

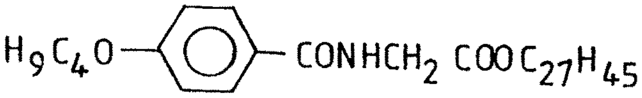
δ 4.3 (t, 2H of methylene in the alkoxy chain at C-4)

δ 7.1 (d, 2H at C-3 and C-5)

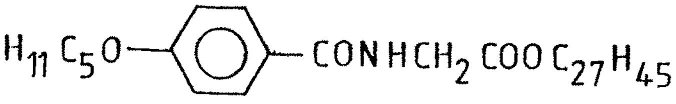
δ 8.2 (d, 2H at C-2 and C-6)

δ 9.1 (S, 1H of $-\overset{\overset{O}{\|}}{C}-NH-$)

GC-1 Cholesteryl 4-n-butoxy benzoyl glycine



GC-2 Cholesteryl 4-n-pentyloxy benzoyl glycine



Transition Temperatures °C

GC-1 $K \xrightarrow{130.0} \text{Chol.} \xrightarrow{256.0} \text{Iso.}$

GC-2 $K \xrightarrow{148.0} \text{Chol.} \xrightarrow{234.0} \text{Iso.}$

Elemental Analysis

	Calculated (%)			Found (%)		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
GC-1	77.54	9.86	2.26	77.24	9.43	2.31
GC-2	77.73	9.95	2.21	77.57	9.83	2.25

IR Spectral data (Bending and Stretching Vibrations) cm^{-1}

GC-1 2900, 1710, 1600, 1510, 1465, 1310, 1250, 1160, 1100, 1000, 840, 765.

2.4 Liquid Crystalline Polymers:

The first thermotropic liquid crystalline polymers (LCPs) were reported in the mid 1970s by Roviello and Sirigu (282) and Jackson and Kuhfuss (283). Since then a large number of LCPs have been reported in literature. In the 1980s, several thermotropic aromatic co-polyesters were commercialized (267,268,283).

Side chain liquid crystalline polymers often have optical properties similar to low molar mass LCs and have generated interest for such applications as non-linear optics, optical filters and in optical storage devices (284).

New thermotropic polymers have been developed with mesogenic cores arranged not only in the main chain or the side chain but with rigid mesogenic groups parallel to the chain (285). Even discotic or disc shaped mesogenic cores have been incorporated in to polymers (286).

Liquid crystalline side-chain polymers have been synthesized by two general processes (199). In the most conventional method, they are obtained by the radical polymerization of appropriate mesogenic monomers such as methacrylates or acrylates. The second possibility starts with "reactive polymers" which can be modified to mesogenic side-chain polymers by using suitable reactive mesogenic compounds. This synthetic method has been used for the preparation of mesogenic polysiloxanes (209,287) obtained by addition of Vinyl-substituted mesogenic compounds to poly(hydrogen-methylsiloxane). However, analogous reactions involving polymers other than polysiloxanes have not been extensively investigated (288,289). In the present work eight monomers with mesogenic side chains were synthesized by multistep synthesis and were polymerized. One co-polymer was also synthesized by using solution polymerization technique.

2.4.1 Preparation of Polymethacrylates Having Side-Chains Containing Amide Groups:

4-n-Alkoxy benzoic acids and its chloride and 4-(4'-n-alkoxy benzoyl)-amino benzoic acids and its chlorides were synthesized as previously described.

2.4.1.1 ω-Hydroxy Alkylene Methacrylates (290-292):

2-Hydroxyl ethyl methacrylate was used as received. 6-hydroxy hexyl methacrylate was synthesized by an azeotropic esterification process. 0.1 mole of methacrylic acid was reacted with 0.12 mole of 1,6 hexanediol together with 2.0 grams of p-toluene sulfonic acid, 0.7 grams of hydroquinone and 100 ml of chloroform for about twenty hours. The reaction mixture was diluted with 250 ml of chloroform, washed with water and concentrated. The remaining oil was purified by column chromatography on silica gel with diethyl ether and hexane (volume ratio 2:1). η_D^{21} : 1.4558

2.4.1.2 Condensation of 4-(4'-n-Alkoxy Benzoyl)-Amino Benzoyl Chloride With ω-Hydroxy Alkylene Methacrylates (M_1-M_6):

In a three necked round bottom flask equipped with droping funnel, stirrer and a thermometer, ω-hydroxy alkylene methacrylates (0.01 mole) were taken in dichloromethane (75 ml) with triethyl amine (35 ml). Appropriate 4-(4'-n-alkoxy benzoyl)-amino benzoyl chloride (0.25 mole) in dichloromethane (45 ml) was added dropwise while maintaining the temperature at 0-5°C. After the completion of the addition, the reaction mixture was stirred for half an hour and was extracted with ether. The etherial solution was treated with saturated sodium bicarbonate solution, followed by water washings. The ether extract was dried. The evaporation of ether resulted in to brown coloured monomers. The final aproduct was recrystallized from dichloromethane till constant melting points (M_1-M_6) were obtained. The elemental analysis and IR spectral data are recorded in Table 16 and 17, respectively (M_1=135.0°C, M_2=125.5°C, M_3=116.0°C, M_4 to M_6 were light brown colour waxy monomers).

2.4.1.3 Polymerization of Monomers (M_1-M_6):

A solution of 0.5 grams of respective monomer, 10 ml of dimethyl formamide and 0.01 gm of N,N-azobisisobutyronitrile were taken in a round bottom flask. The monomer solution was degassed by passing nitrogen for ten minutes and polymerized at 70°C for 42 hours. The polymers obtained were precipitated in methanol, filtered and dissolved again in dichloromethane (DCM) and reprecipitated by adding hexane The purified polymers were dried under reduced pressure. The transition temperatures, elemental analysis, IR spectral data and viscosity data are recorded in Table 17, 18, 19 and 20, respectively.

2.4.2 Preparation of Cholesteryl Carbonate Polymer:

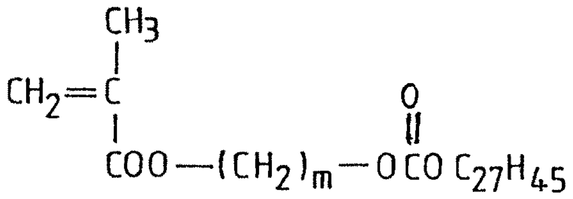
2.4.2.1 ω-Hydroxy Alkylene Methacrylates:

2-Hydroxyethyl methacrylate was used as received. 6-hydroxy hexyl methacrylate was synthesized by an azeotropic esterification It was prepared by the method as described in section 2.4.1.1.

2.4.2.2 Condensation of Cholesteryl Choloroformate With Different ω-Hydroxy Alkylene Methacrylates (Monomers M_7 & M_8).

Cholesteryl Choloroformate (0.01 mole) (recrystallized three times from dry acetone) and 50 ml dry benzene were taken in a quickfit round bottom flask. The contents were rapidly mixed with ω-hydroxy alkylene methacrylate (0.011 mole), 4.0 ml of anhydrous pyridine and 40 ml of dry benzene was added to the reaction mixture. The reaction mixture was stirred for 2-3 hours at about 38-40°C. The mixture was then filtered to separate the precipitates of pyridine hydrochloride and other insoluble materials. The filtrate was concentrated under vacuum to remove excess of benzene, then methanol was added to the solution and the precipitates were crystallized from chloroform-acetone mixture till constant transition temperature were obtained. The transition temperatures, elemental analysis and IR spectral data are recorded in Table 20, 21 and 22, respectively.

General Structure of Monomers:

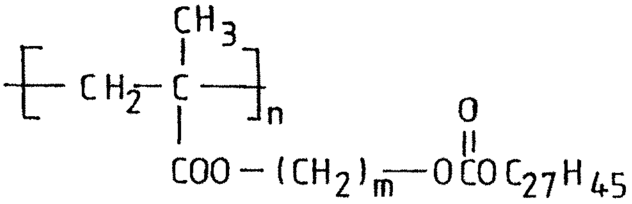


$$CH_2=\overset{CH_3}{\overset{|}{C}}-COO-(CH_2)_m-O\overset{O}{\overset{\|}{C}}O\,C_{27}H_{45}$$

2.4.2.3 Polymerization of Monomers (M_7 & M_8)

Polymerization procedure was followed as described in section 2.5.1.3. The polymers purified by solvent non-solvent method DMF was used as a solvent and methanol used as a non-solvent. Elemental analysis and transition temperatures are recorded in table.The transition temperatures, elemental analysis, IR spectral data and viscosity data are recorded in Table 21a, 21b, 22 and 23, respectively.

General Structure of Polymers:

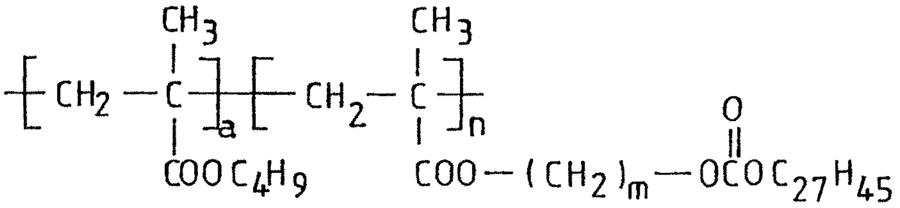


$$-\!\left[CH_2-\overset{CH_3}{\underset{COO-(CH_2)_m-O\overset{O}{\overset{\|}{C}}OC_{27}H_{45}}{C}}\right]_n\!-$$

2.5 Preparation of Co-polymer (CP):

The monomer M_7 and the co-monomer butyl methacrylate with weight ratio 0.8:0.2 was polymerized with N,N-azobisisobutyronitrile as initiator. The procedure of polymerization was the same as followed for homo-polymerization. The co-polymer obtained was precipitated in methanol, filtered and dissolved again in dichloromethane and reprecipitated by adding hexane as a non-solvent. The purified co-polymer was dried under reduced pressure. The transition temperature and viscosity data are recorded in Table 21a and 23.

Structure of Co-polymer:

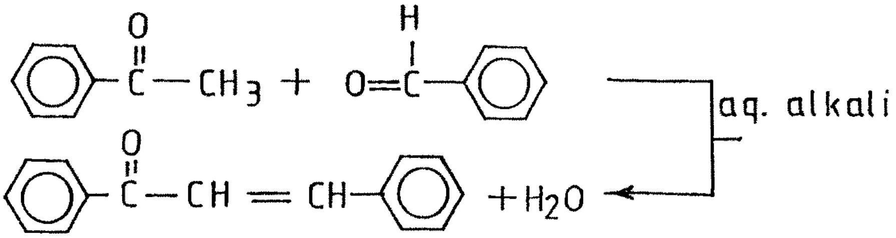


$$-\!\left[CH_2-\overset{CH_3}{\underset{COOC_4H_9}{C}}\right]_a\!\!-\!\left[CH_2-\overset{CH_3}{\underset{COO-(CH_2)_m-O\overset{O}{\overset{\|}{C}}OC_{27}H_{45}}{C}}\right]_n\!-$$

2.6 Synthesis of Fluorescent Thermotropic Polymers having Chalcone Repeating Unit in Main Chain:

Benzylidene acetophenone constitute a class of naturally occurring pigments which are often referred to as "chalcones". The term was first coined by Kostanecki (293) who did pioneering work in the synthesis of natural colouring compounds. An interesting feature of chalcones (poly hydroxylated) is that they serve as starting materials for the synthesis and widely distributed pigments called flavones.

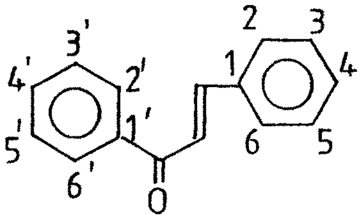
The synthesis of chalcone has been accomplished in a variety of ways but perhaps the simplest method is the one involving the Claisen-Schmidt reaction. This is the reaction of acetophenone with benzaldehyde in the presence of aqueous alkali, resulting in the formation of α, β-unsaturated ketone (294).



The substituted benzylidene acetophenones have like-wise been obtained by condensing the appropriately substituted acetophenones with substituted benzaldehydes in the presence of alkali.

Nomenclature:

Benzylidene acetophenone is the parent member of the chalcone series. The substituents in the benzene rings of chalcone are numbered as shown below and follow the pattern adopted by chemical abstracts.



The alternative name given to chalcone is phenyl styryl ketone, benzalacetophenone, β-phenyl acrylo phenone and α-phenyl-β-benzoyl ethylene (295).

In the present work two different chalcones were synthesized, which were condensed with different diacid chlorides to obtain polymeric chalcones

2.6.1 Preparation of Polychalcones:

2.6.1.1 Preparation of Different Diacids "ω-Bis (4-Carboxy phenoxy) Oligo Ethers"

Following different diacids were used for the synthesis of polymeric chalcones:

a) 1,6-bis (4'-carboxy phenoxy) hexane (DA-I)

b) 1,10-bis (4'-carboxy phenoxy) decane (DA-II)

The diacids (DA-I and DA-II) were synthesized by the same method reported in the literature for synthesis of 1,2-bis (4'-carboxy phenoxy) ethane (296, 297). p-Hydroxy benzoic acid (0.2 mole) was dissolved in 100 ml 22.4% potassium hydroxide solution (0.4 mole) and 30 ml of alcohol in round bottom flask. Appropriate dibromide (0.11 mole) was added to the flask and whole mass was refluxed for 8-10 hours. Reaction mixture was allowed to cool, then acidified with cold 1:1 hydrochloric acid. Solid mass obtained was filtered and washed with water and dilute alcohol. Diacids obtained were recrystallized several times from DMF solvent till constant melting points were obtained.

DA - I : 290°C, Reported 290-292°C (298)

DA - II: 273°C, Reported 273-274°C (298)

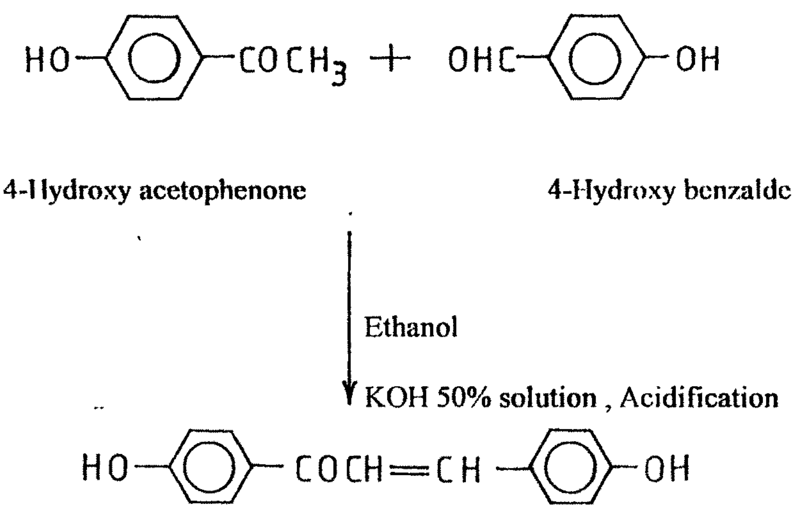
2.6 1 2 Synthesis of Diacid Chlorides of Diacids DA-I and DA-II

Diacid chlorides of appropriate diacids were synthesized as previously described in section 2.1 2b

2.6.1.3 Synthesis of Different Chalcones:

2.6.1.3.a Synthesis of 4,4'-Dihydroxy Chalcone:(4,4'-Dihydroxy Benzylidene Acetophenone) (HC):

4,4'-Dihydroxy Chalcone was synthesized according to the hot condensation process described by Geissman and Clinton (299).



13.6 gms (0.1 mole) 4-hydroxy acetophenone and 13.2 gms (0.1 mole) 4-hydroxy benzaldehyde were dissolved in minimum amount of ethanol, 55 ml of 50% potassium hydroxide was added to the above solution. The flask was heated at 50°C for twenty hours. The solution was acidified by cold 6N HCl solution (congored), Yellow crystalline solid separated, which was filtered and washed with water. It was recrystallized from ethanol M.P. 204°C (Reported 204°C) (299).

2.6.1.3b: Synthesis of 4-Amino-4'-Hydroxy Chalcone: (4-Amino-4'-Hydroxy Benzylidene Acetophenone) (AHC):

4-Amino-4'-hydroxy chalcone was prepared by extending the procedure of Kumar et al., (300) for the para substituted derivative

13.5 gms (0.1 mole) 4-Amino acetophenone, 12.2 gms (0.1 mole) 4-hydroxybenzaldehyde and a few drops of piperidine in absolute ethanol (40 ml) were taken in round bottom flask and were refluxed for twelve hours. The reaction mass was concentrated up to its half the volume and then reaction mass was poured to ice-water mixture with stirring, solid separated, which was filtered, dried and crystallized from ethanol, M.P. 217°C (Reported 217-218°C) (300).

2.6.1.4 Polycondensation of Different Diacid Chloride with Different Chalcones:

The diacid chloride of DA-I and DA-II were condensed with respective chalcones by solution polycondensation reaction, pyridine was used as a solvent. The solution polycondensation reaction can be presented as shown in Figure 24.

The appropriate diacid chloride (0.005 mole) was dissolved in 10 ml dry pyridine and cooled to 0°C in an ice-bath. The solution of respective chalcones (0.005 mole) in 5 ml dry pyridine was added to the diacid chloride with constant stirring. The reaction mixture was guarded against moisture absorption. The temperature of mixture was allowed to rise to room temperature (28-30°C) and stirred for two more hours. It was finally poured into ice-hydrochloric acid mixture and solid separated was filtered, washed with water followed by alcohol to remove unreacted starting materials. Polymers were purified by solvent-non solvent method. DMF was used as a solvent and methanol was used as a non-solvent. The transition temperatures, elemental analysis, IR spectral data and viscosity data are recorded in Table 24, 25, 26 and 27, respectively.

2.7 Synthesis of Polymeric Azomesogens (Synthesis of Polyester Amides):

Azodyes are known from the development of industrial chemistry and are finding newer applications as science progresses The liquid crystal coloured display uses different dichroic dyes dissolved in low molecular weight liquid crystals. Polymeric azo dyes can be a good candidate for the guest-host interaction as well as pigment to colour plastics as they will be more compatible with the polymeric systems.

From a synthetic chemistry standpoint three general strategies can be employed

A The synthesis of monomeric dyes which have polymerizable groups, which are subsequently polymerized by different techniques.

B. The reaction between performed polymers and dyes, where the two components have mutually reactive functional groups resulting in chemical bond formation between the polymer and dye.

C. The synthesis of a polymeric precursor which by appropriate transformation generate the dye structures on the polymer chain

The polymer dyes possess very large molecular size and hence are not suitable for dyeing. Because of their large molecular size, they are slow to diffuse in to the fiber structure but at the same time they possess good washing fastness.

The part of our research deals with the polymeric azomesogens synthesized from polymerizable monomeric azobenzenes Three different azobenzene derivatives were prepared, which were polymerized with diacids to give polymeric azo compounds

The route which was used to synthesize different monomeric azo dyes is represented in Figure 25.

2.7.1 Preparation of Polyesteramides:

2.7.1.1 Synthesis of Substituted 4-Amino -4'-Hydroxy Azobenzenes:

4-Amino-4'-hydroxy azobenzene and its other two derivatives were prepared as described below:

2.7.1.1a Synthesis of Substituted 4-Nitro -4'-Hydroxy Azobenzenes

13.8 gms (0.1 mole) p-nitroaniline was dissolved in 1·1 80 ml dilute hydrochloric acid solution (0.3 mole). The solution was cooled to 0°C in an ice-bath with constant stirring. Sodium nitrite solution obtained by dissolving 7.59 grams (0.11 mole) sodium nitrite in 15 ml water was added slowly to the above solution by maintaining faint positive test on starch iodide paper. It was stirred further for 15 minutes after the addition of sodium nitrite solution. The urea was added to decompose excess of nitrous acid.

In another beaker 9.4 grams (0.1 mole) phenol was dissolved in 100 ml 8% sodium hydroxide solution (0.25 mole) and was cooled to 0-5°C in an ice-bath. The clear solution of diazotized amine was added slowly with constant stirring to the phenolic solution by maintaining temperature 0-5°C and alkaline pH. After the addition of diazonium solution, the whole mass was stirred further for the completion of coupling reaction. The alkaline reaction mixture was acidified to precipitate 4-nitro-4'-hydroxy azobenzene. The scarlet red azo compound was filtered, washed with water and dried. M.P. 184°C (reported 184-185°C) which tellies with the literature (301)

By using above procedure following substituted 4-nitro -4'-hydroxy azo benzenes were synthesized.

Code	X	Y	M.P. °C	
NA-1	H	H	184	(301)
NA-2	CH_3	H	197	(302)
NA-3	H	Cl	209	(302)

2.7.1.1b Synthesis of Substituted 4-Amino -4'-Hydroxy Azobenzenes:

Amino hydroxy azobenzenes were synthesized by the reduction of nitro derivatives synthesized in previous step by using sodium sulfide as a mild reducing agent (303). Strong reducing agent will reduce not only nitro group but the azo linkage also, with the production of p-phenylene diamine and p-amino phenol. Hence sodium sulfide is the best reagent to carry out selective reduction of nitro group and not the azo group.

12.15 grams (0.05 mole) of 4-nitro -4'-hydroxy azobenzene was dissolved in minimum quantity of ethanol and heated to reflux. When it started to reflux, 65 ml 30% w/v (19.5 gms, 0.25 mole) solution of sodium sulfide was added dropwise. The reaction mixture was refluxed until the reduction was completed Completion of reduction was checked by using ferrous sulphate solution for excess of sulphide. After the completion of reaction, the reaction mass was filtered in order to remove insoluble impurities, Filtrate was cooled to 10°C-15°C and was acidified to 6.0-6.5 pH by using dilute hydrochloric acid to separate reduced dye, which was filtered and then washed with cold water. It was recrystallized in aqueous ethanol. M.P. 179°C, (reported 180°C) (301).

By using the same procedure different substituted derivatives of 4-amino - 4'-hydroxy azobenzene were prepared. The data were recorded as under:

M.P. of substituted 4-Amino -4'-hydroxy azobenzenes.

Code	X	Y	M.P. (°C)	
AA-1	H	H	179	(301)
AA-2	CH_3	H	178	(302)
AA-3	H	Cl	170	(302)

2.7.1.2 Preparation of Diacid Chlorides:

Diacid chlorides of DA-I was used for the synthesis of polymeric azomesogens. Synthesis of DA-I is already discussed earlier in the section 2.6.1.1.

2.7.1.3 Polycondensation of Diacid Chlorides and 4-Amino -4'-hydroxy azobenzenes

The diacid chloride (0.005 mole) of DA-I was dissolved in dry 10 ml pyridine, and solution was cooled in an ice bath (5°C-10°C). Substituted 4-amino -4'-hydroxy azobenzene (0.005 mole) in 5 ml dry pyridine was added to the above solution The reaction mixture was stirred and temperature was allowed to rise to room temperature (28°C to 30°C). After that the product was isolated by pouring the reaction mass into 1:1 ice-HCl mixture followed by filtration. The polymer was washed with water and also with hot ethanol to remove unreacted monomers. Polymeric product was purified by solvent - non solvent method. N-methyl-2-pyrrolidone was used as a solvent and ethanol as a non-solvent. The transition temperatures, elemental analysis, IR spectral data and viscosity data are recorded in Table 28, 29, 30 and 31, respectively. The synthesis of polymeric azo mesogens is schematically represented in figure 26.

2.8 Model Compounds :

2.8.1 Preparation of Amido-Esters

2.8.1.1 Condensaation of 4-n-alkoxy benzoyloxy benzoic acids with flexible and rigid hydroxy amines.

2.8.1.1a 4-n-Alkoxy benzoyloxy benzoic acids and its chloride were synthesized as per the procedure given in section 2.1.2c and 2.1.2d.

2.8.1.1b Condensation of 4-n-Alkoxy Benzoyloxy Benzoyl Chloride with p-Amino Phenol and Monoethanol Amine.

Amido-esters were prepared by the condensation of 0.025 mole of 4-n-alkoxy benzoyloxy benzoyl chloride and 0.01 mole of p-amino phenol/monoethanol amine, by the procedure described in section 2.1.2f. All the four compounds were recrystallized from dimethyl formamide. The transition temperatures, elemental analysis and IR spectral data are reported in Table 32, 33 and 34, respectively.

2.8.1.2 Condensation of 4-n-butoxy benzoyloxy benzoic acids with flexible diamines

Amido-esters were prepared by the condensation of 0 025 mole of 4-n-butoxy benzoyloxy benzoyl chloride and 0.01 mole of 1,2-diaminoethane/1,6 diamino hexane by the procedure described in section 2.1.2.f. All the two compounds were recrystallized from dimethyl formamide. The elemental data are recorded in Table 33.

2.8.2 Preparation of Azo-Diesters:

2.8.2.1 Condensation of adipic acid with 4-hydroxy-4'-n-alkoxy azobenzene.

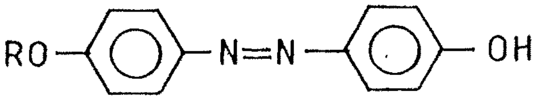
2.8.2.1a Preparation of 4-Hydroxy-4'-n-Alkoxy Azobenzene :

Commercially available adipic acid, 4-methoxy aniline (Anisidine), 4-ethoxy aniline (phenitidine) was used and 4-n-butoxy aniline was prepared by the method described in section 2.1.2e.

4-Hydroxy-4'-n-alkoxy azobenzenes were synthesized by using conventional method of diazotisation and coupling (304).

4-n-Alkoxy aniline (0.1 mole) was dissolved in 1:1 hydrochloric acid (100 ml) and solution was cooled to 0°C. This was diazotized by adding saturated sodium nitrite solution (0.1 mole) with constant stirring, maintaining faint positive test on starch iodide paper. After the completion of diazotization, small quantity of urea was added to decompose excess of nitrous acid. The cold solution of 4-n-alkoxy benzene diazonium chloride was coupled with phenol (0.1 mole) in alkaline condition (0-5°C). After the addition of diazotised solution, the material was stirred for about 15 minutes and then acidified with concentrated hydrochloric acid. The precipitates obtained were filtered and washed with water. It was then dried and recrystallized from aqueous ethanol till constant melting point was obtained (305).

General Structure:



Code	R	M.P. (°C)
AE-1	OCH_3	140.0
AE-2	OC_2H_5	121.0
AE-3	OC_4H_9	108.0

2.8.2.1b Preparation of Adipoyl Chloride:

Adipoyl chloride was prepared from adipic acid by the method described in section 2.1.2b.

2.8.2.1c Preparation of Azo-Diesters :

Azo-diesters were prepared by the condensation of 0.025 mole of 4-hydroxy 4'-n-alkoxy azobenzene and 0.01 mole of adipoyl chloride, by the method described in section 2 1.2f. All compounds were recrystallized from benzene.

General Structure:

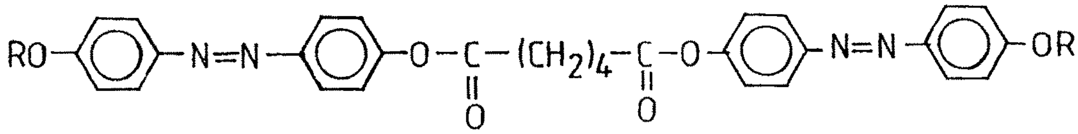


Table 33a&b.

Transition Temperatures (°C)

Code	R =	Transition Temperatures (°C)	
		Nematic	Isotropic
AZ-1	$-CH_3$	165.0	269.0
AZ-2	$-C_2H_5$	192.0	272.0
AZ-3	$-C_4H_9$	178.0	235.0

Elemental Analysis

	Calculated (%)			Found (%)		
	C	H	N	C	H	N
AZ-1	67.85	5.30	9.89	67.10	4.83	9.36
AZ-2	68.69	5.72	9.43	70.13	5.25	8.93
AZ-3	71.64	5.67	8.36	70.93	5.27	7.94

IR Spectral data (cm^{-1})

AZ-2 1725, 1680, 1600, 1530, 1500, 1470, 1430, 1250, 1065, 850, 725.

2.9 Determination of Transition Temperatures:

The transition temperatures were determined by using a polarizing microscope "Leitz Laborlux Microscope" provided with a heating stage.

Slides were prepared by following methods. The substance is taken on a slide and cover slip is placed over it and then compound is heated.

The microscope was standardized by taking melting points and transition temperatures of very pure but known substances like benzoic acid, succinic acid, p-azoxyanisole, vaniline, p-anisal-p-phenetidine, p-azoxyphenetole.

To determine the various transitions a glass slide carrying a thin section of the material with cover slip on it was observed under the microscope. The slide was inserted into the specimen chamber of heating stage and the temperature was raised (5°C/min) to find approximate transition temperatures. The measurements were then repeated and near the transition to be observed the rate of heating was regulated to about 1°C per min. The changing textures over the temperature ranges are carefully observed and recorded as the appearance of focal-conic, plane, homeotropic and threaded structures of smectic and nematic phases emerge under polarised light. All observations were repeated several times in case of any doubt the compounds were purified again and then were subjected to the study under microscope a fresh. Compounds in which decomposition was observed, fresh slide was prepared each time for recording the correct transition temperatures.

2.10 Differential Scanning Calorimetry :

The term differential scanning calorimetry (DSC) was first used by Weston et al., (306) to describe the instrument technique developed by the Perkin-Elmer Corporation. This technique maintained the sample and reference materials isothermal to each other by proper application of electrical energy, as they were heated or cooled at a linear rate. The curve obtained is a recording of heat flow dH/dt, in m.cal/sec. as a function of temperature.

In the true thermodynamic sense, endotherm curve peak is indicated by a peak in the upward direction (increase in enthalpy) while in exotherm peak is recorded in the opposite direction. In all appearances, the DSC curve looks very similar to that of a

DTA curve except for the ordinate axis units. As in DTA the area enclosed by the DSC curve peak is directly proportional to enthalpy change.

$$\text{Area} = K.\ \Delta H_m$$

except that K is independent of temperature.

In the present work, calorimetric study was carried out for number of compounds on Mettler TA 4000 system to study the thermodynamic aspects of mesophases.

The data for enthalpy and entropy changes at different transitions are recorded in Table 35 a,b

2.11 Viscometric Study:

Many methods for measurement of viscosity are reported (307,308) but those which make use of the capillary are well suited for our purpose. It is a unique property that dilute polymer solution has much higher viscosity than that of pure solvent. This is because, the presence of the dissolved macromolecules in the solution increases the energy dissipation in the laminar flow over that for the pure solvent flow by the polymer segments. This large difference in viscosity and various functions derived there from are usually measured to produce information about the nature of micro structure of the polymer under study. It will be proper to define viscosity functions which are being estimated for this purpose.

The ratio of the viscosity of a dilute polymer solution (η) to that of a pure solvent (η_o) of equal density and of equal hydrokinetic pressure is approximately equal to the polymer solvent efflux-time ratio in the capillary viscometer. The latter ratio is designated as the relative viscosity (η_{rel}) or as the viscosity ratio (309).

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

Because $[\eta_{rel}]$ approaches 1 and not zero as the solution become more dilute, the relative viscosity obviously does not denote the polymer's ability to increase the viscosity of the dispersion medium. To compensate for this discrepancy, the relative viscosity is diminished by 1; a new term results that is designated as the specific viscosity $[\eta_{sp}]$.

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

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o}$$

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

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

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

where C is concentration, g/dl.

Viscosity may also be expressed by logarithmic relation (310), termed either the inherent viscosity $[\eta_{inh}]$ or the logarithmic viscosity number and is defined as

$$\eta_{inh} = \ln \eta_{rel}/C$$

where, C is concentration in g/dl.

Usually the reduced and inherent viscosities have different values for a given concentration, the latter being lower. Neither of this term is independent of concentration but they are usually linear functions of concentration in dilute solutions which can be extrapolated to a common intercept as the concentration approaches zero (311). The common limiting value of either of these functions in infinitely dilute solution is called the intrinsic viscosity [η], the limiting viscosity number.

$$[\eta] = [\eta_{sp}/C]\ C\to o$$

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

The linear relationship between the reduced viscosity and the concentration is expressed by the Huggin's equation (312). It is employed to estimate intrinsic viscosity.

$$\eta sp/C = [\eta] + K' [\eta]^2 C$$

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

Similarly Kraemer (310) relationship

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

can be applied to the experimental data and [η] can be determined from the plot of

$\ln \eta_{rel}/C$ Vs C

The methods known as one point methods are also used to calculate intrinsic viscosity [η] which avoids entirely the use of some constants such as K' and K". These one point methods have certain inbuilt limitations. They assume the linear behaviour between C and η_{sp}/C and /or $\ln \eta_{rel}$ Other modifications are also used which involve the constants. In the present study our main interest was the comparison of the viscosity data with the similar polymeric systems, hence, the following equation was used which is recommended for the one point method (313)

$$\eta = \frac{3 \ln \eta_{rel} + \eta_{sp}}{4C}$$

where,C is concentration in g/dl.

Experimental:

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

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

The required amount of well powdered and dried polymer was dissolved in suitable solvent. The clear solution was filtered through G-3 sintered glass funnel. The solution thus prepared was carefully introduced in a viscometer held vertically in the thermostat. It was allowed to attain the thermostat temperature. The flow time was measured atleast three times and the average flow time was noted. From the mean efflux time different viscosities were calculated and are summarized in Tables 20, 23, 27, 31 and 36.

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

η_{sp}/C against C was plotted and the straight line obtained was extrapolated to zero concentration to obtain the value of intrinsic viscosity [η] for the system (Fig.53)

The intrinsic viscosity [η] of the polymer samples obtained from graphical method by taking different concentration of polymer sample tellies with the values obtained by "one point" method as shown in Table 36.

2.12 IR (FTIR) Spectra :

IR Spectral study is highly useful in the characterization of organic materials. All the materials were screened by using Nujol/KBr pellets in the range of Infra-red frequency. The samples were analysed on Perkin-Elmer spectrophotometer and NICOLET, Impact-400 FT-IR. IR (FTIR) Spectra are given in Figs.27a, 27b,30, 31,39a,39b 39c,43, 46a, 46b, 48, 51a,51b,56 & 57b.

2.13 NMR Spectra:

NMR spectra of representative number of series I, II, III and other mesogenic compound using $CDCl_3$ solvent for characterization of synthesized compounds were taken, NMR are given in Fig. 28, 32, 40 & 44.

2.14 Molecular Weight Determination :

The molecular weight of the polymers were determined by Gel Permeation Chromatography (GPC) with Maxima 820 GPC Analyzer by using Tetrahydrofuran (THF) as a solvent. The number average (Mn) and weight average (Mw) molecular weights were determined relative to polystyrene (molecular weight 5000) standards. The data are presented in Table 37.

2.15 X-Ray Diffraction Analysis :

X-Ray diffraction profiles were recorded on a X-ray diffractometer of Rigaku - Japan, using CuKα radiation of 1.5418 A° wavelength The XRD pattern was obtained at a scanning speed of three degree per minute, between 10-35° (2θ) range. The diffraction pattern was indexed for d-spacings planes. The characteristics of X-ray pattern are recorded in Table 38a for polymer P_2.

2.16 Conductivity Study :

Pellets of polymers for measuring the conductivity were prepared in a KBr pellet press. Conductivity was measured by a four probe techniques at various temperatures i.e. from room temperature upto the temperature which is less than transition temperatures of polymers. The pellets were then cooled to room temperature and conductivities were again measured.

The values of conductivity (σ) and log σ were calculated (Table 39a, 39b).

2.17 Fluorescent Spectra :

Fluorescence is light that is emitted from a molecule after the molecule has absorbed light of a different (and shorter) wavelength. One characteristic feature of fluorescent relation is that the fluorescence stops whenever the irradiating light is removed. Though anthracene is colourless but pure sample of it when viewed in ultra violet light gives off blue visible light which is called fluorescence

Aromatic hydrocarbons such as benzene, naphthalene, anthracene and fluorine are called luminophores and are considered as basic fluorescing substances The groups that enhances this fluorescence, or that shift it to the visible region for examples -

-CH=CH-, CO-, CH=CH-COOH, p-Phenylene, -CH=CH-COO-, -CN are called fluorogens. Auxoflores include -NH_2 and -OH groups which enhance fluorescence.

Fluorescence study was carried out using Shimadzo Spectrophotofluorometer F-500. Monomers, polymers and co-polymer were studied in solution form at room temperature. The data are presented in Table 40.

2.18 Thermo Gravimetric Analaysis:

Thermal stability of a polymer provides an important guidelines of its usefulness. Several techniques such as thermogravimetric analysis, differential thermal analysis, differential analysis and thermochemical analysis (314) etc are used for determination of thermal stability. In the present investigation, we have used thermogravimetric analysis technique to determine the thermal stability of polymers, synthesised in the present work. All the polymers have been thermogravimetrically analysed on Shimadzu TG Analyzer in N_2/air atmosphere at heating rate of 10°C/min. The data are recorded in Table 41a,b.

2.18.1 Evaluation of Kinetic Parameters

Thermogravimetric analysis technique has become a useful tool for evaluating kinetic parameter of various reaction and materials (314 a,b,c) which then provide variable technique for evaluation of potentially unstable nature of materials. TGA methods for calculating kinetic parameters (314a) have been proposed (314 c,d,e,f) based on the relationship between weight loss and temperature often utilizing the derivative rather than integral curve. These methods have often been used to evaluate degradation kinetics. The derivation of kinetic data from TGA curve obtained under non-isothermal conditions has received considerable attention and several comprehensive review articles (314 g.h) appeared.

To evaluate activation energy for each step of thermal decomposition of polymers TGA thermograms obtained under non-isothermal (dynamic) conditions have been used. Two types of methods - for treatment of TGA data have been employed to evaluate activation energy (E_a) for each steps of thermal decompositions of polymers:

(i) single heating rate method and

(ii) multiple heating rate method

Among this two methods, single heating rate method is widely used. In present investigation, the same method is used for evaluation of kinetic parameters from TGA data.

Dynamic TGA thermograms have been analysed as per the graphical methods, proposed by Broido (314 i).

Broido Method (314 I): A. Broido has suggested a simple and sensitive graphical method for the treatment of TGA data. According to any time t (W_t) is related to the fraction of initial molecules not yet decomposed (Y) by equation,

$$Y = N/N_o = W_t\text{-}W\alpha \,/W_o\text{-}W\alpha$$

where, W_o is the initial weight of the material and $W\alpha$ is the weight of residue at the end of degradation. For isothermal pyrolysis,

$$d_y/d_t = -K_y^n \qquad \ldots\ldots\ (2)$$

$$\text{If } K = A.e^{-E/RT} \qquad (3)$$

and if T is a linear fraction of time t i e.

$$T = T_o + \beta t \qquad \ldots\ (4)$$

then (2), (3) and (4) may be combined as under:

$d_y/y^n = -(A/\beta)e^{-E/RT}.dT$ ..... (5)

where, $\beta = dT/dt$, the heating rate.

Equation (5) is integrated as,

$d_y/y^n = A/\beta \quad e^{-FRT}.dT$ ..... (6)

For the first order kinetics (n=1), which polymer degradation usually follows,

$d_y/y = -\ln y = \ln(1/y)$ ..... (7)

On integration and taking log of both sides of equation (6), following equation is obtained:

$\ln[\ln(1/y)] = [E/RT_m^{+1}] \ln T + const$ ..... (8)

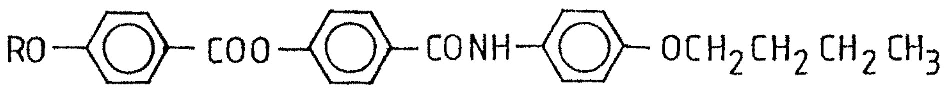
Thus, a plot of ln[ln(1/y)] vs. 1/T yields a straight line, whose slope is related to E. Assumption of $e^{-E/RT}$ $(T_m/T)^2.e^{-E/RT}$ leads to,

$\ln[\ln(1/y)] = -E/R(1/T) + constant$ ..... (9)

Equation (9) is more accurate of two.

Table 4

4(4'-n-Alkoxy benzoyloxy benzoyl)4"-n-butoxy anilines:



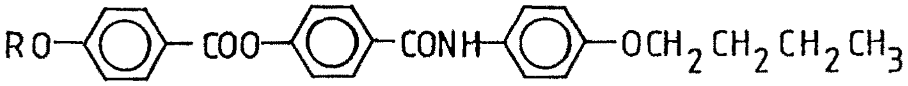
Transition Temperatures (°C)

Sr. No	R n-Alkyl Group	Transition Temperatures °C Smectic-C	Smectic-A	Nematic	Isotropic
1.	Methyl	-	-	207 0	254.0
2.	Ethyl	-	-	242.0	287.0 (d)
3.	Propyl	-	-	210.0	275.0
4.	Butyl	172.0	-	193.0	293.0 (d)
5.	Pentyl	202.0	-	226.0	282.0 (d)
6.	Hexyl	174.0	-	230.0	296.0 (d)
7.	Heptyl	203.0	234.0	259.0	284.0 (d)
8.	Octyl	179.0	227.0	247.0	264.0
9.	Decyl	171.0	218.0	233.5	261.0
10.	Dodecyl	174.0	-	-	239.0
11.	Tetradecyl	159.0	-	-	231 0
12.	Hexadecyl	148.0	-	-	224.0
13.	Octadecyl	138.0	-	-	217.0

(d) Decomposition

Table 5

4(4'-n-Alkoxy benzoyloxy benzoyl)4"-n-butoxy anilines :

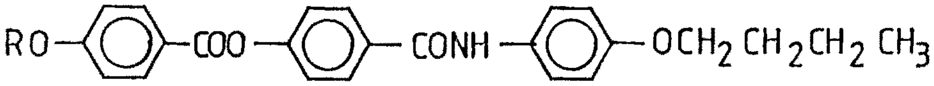


Elemental Analysis :

Sr. No.	R n-Alkyl Group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	71.60	5.97	3.34	71.63	5.87	3.430
2	Ethyl	72.06	6.24	3.23	72.12	6.24	3.153
3	Propyl	72.48	6.49	3.13	72.37	6.44	3.125
4	Butyl	72.88	6.73	3.04	70.85	6.42	3.141
5	Pentyl	73.26	6.95	2.95	72.86	6.85	2.782
6	Hexyl	73.62	7.16	2.86	73.51	7.35	2.830
7	Heptyl	73.96	7.36	2.78	74.12	7.47	2.650
8	Octyl	74.28	7.54	2.71	74.26	7.49	2.73
9	Decyl	74.86	7.89	2.57	74.67	7.93	2.456
10	Dodecyl	75.39	8.20	2.44	75.63	8.16	2.195
11	Tetradecyl	75.88	8.49	2.33	75.79	8.53	2.235
12	Hexadecyl	76.31	8.74	2.23	76.25	8.85	2.13
13	Octadecyl	76.71	8.98	2.13	76.59	8.93	2.204

Table 6

4(4'-n-Alkoxy benzoyloxy benzoyl) 4"-n-butoxy anilines:



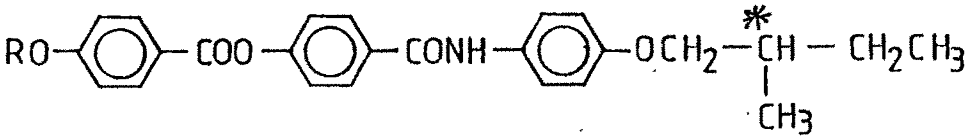
IR Spectral Data

Bending and Stretching Vibrations (cm^{-1})

R = $-C_4H_9$	$-C_{12}H_{25}$	$-C_{10}H_{21}$ (FTIR Data)
3350	3350	3331
2900	2900	2931
1730	1730	2854
1640	1640	1731
1600	1600	1645
1510	1510	1605
1470	1470	1517
1410	1410	1470
1250	1250	1414
1210	1215	1255
1160	1165	1217
1065	1070	1171
810	815	1073
750	755	819
		760

Table 7

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



Transition Temperatures °C

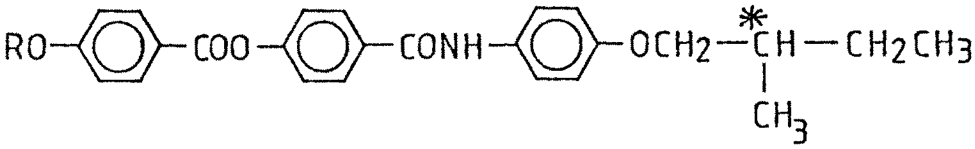
Sr. No	R n-Alkyl Group	Transition Temperatures °C Smectic	Cholesteric	Isotropic
1.	Propyl	175	273	300 (d)
2.	Butyl	202	264	316 (d)
3.	Pentyl	214	260	308 (d)
4.	Hexyl	218	272	315 (d)
5.	Heptyl	214	269	301 (d)
6.	Octyl	207	264	306 (d)
7.	Decyl	194	236	294
8.	Dodecyl	174 (158.3)	193.5 (180.9)	256 (244.7)
9.	Tetradecyl	153 (149.1)	-	213 (203.5)
10.	Hexadecyl	139	-	193

(d) Decomposition

( ) indicates DSC data.

Table 8

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

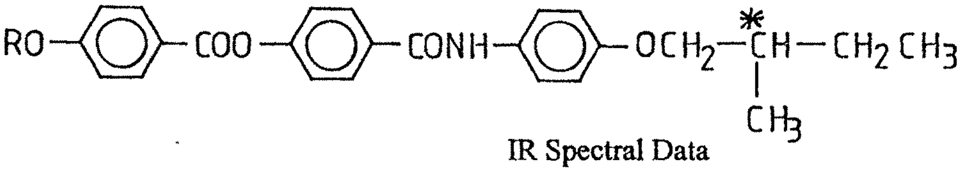


Elemental Analysis :

Sr. No.	R n-Alkyl Group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	72.89	6.72	3.04	72.60	6.78	3.125
2	Ethyl	73.26	6.95	2.95	72.84	7:10	2.868
3	Pentyl	73.62	7.16	2.86	73.51	7.06	2.702
4	Hexyl	73.96	7.36	2.78	73.65	7.14	2.690
5	Heptyl	74.28	7.54	2.71	74.17	7.46	2.660
6	Octyl	74.58	7.72	2.64	74.38	7.08	2 864
7	Decyl	75.13	8.05	2.51	75.34	8.13	2.612
8	Dodecyl	75.64	8.35	2.39	74.79	7.79	2.581
9	Tetradecyl	76.10	8.62	2.28	74.70	8.36	2.310
10	Hexadecyl	76.52	8.87	2.18	76.35	8.90	2.09

Table 9

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



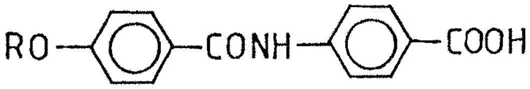
IR Spectral Data

Bending and Stretching Vibrations (cm^{-1})

$R = -C_3H_7$	$R = -C_8H_{17}$	$R = -C_{10}H_{21}$ (FTIR Data)
3325	3325	3346
2900	2900	2924
1730	1730	2854
1645	1640	1735
1600	1600	1648
1510	1515	1604
1415	1410	1514
1210	1210	1414
1165	1165	1317
1060	1070	1206
970	880	1166
820	810	1065
750	750	827
		759
		690

Table 10

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

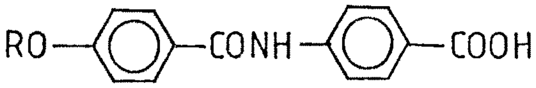


Melting points (°C)

Sr. No.	R n-Alkyl Group	Melting Points (°C)
1	Methyl	338.0
2	Ethyl	324.0
3	Propyl	316.0
4	Butyl	307.0
5	Pentyl	302.0
6	Hexyl	301.0
7	Heptyl	291.0
8	Octyl	286.0
9	Decyl	288.0
10	Dodecyl	283.5
11	Tetradecyl	283.0
12	Hexadecyl	282.4
13	Octadecyl	281.0

Table 11

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

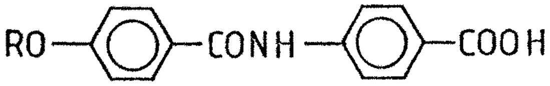


Elemental Analaysis

Sr. No.	R n-alkyl Group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	66.42	4.80	4.17	65.94	4.31	4.87
2	Ethyl	67.37	5.26	4.91	68.23	4.88	5.21
3	Propyl	68.23	5.69	4.68	67.68	5.26	4.45
4	Butyl	69.00	6.07	4 47	68.90	5.92	4.31
5	Pentyl	69.73	6.42	4.28	68.98	6.62	4.35
6	Hexyl	70.38	6.75	4.11	69.29	6.29	3.87
7	Heptyl	70.99	7.04	3.94	69.19	6.81	4.34
8	Octyl	71.55	7.32	3.79	70.86	6.89	3.91
9	Decyl	72.55	7.81	3.53	71.93	7.94	3.74
10	Dodecyl	73.41	8.24	3.29	72.85	7.67	3.10
11	Tetradecyl	74.17	8.61	3.09	73.65	7.94	3.12
12	Hexadecyl	74.84	8.94	2.91	74.28	8 76	2.79
13	Octadecyl	75.44	9.23	2.75	74.74	8 73	2.87

Table 12

4-(4'-n-Alkoxy benzoyl) amino benzoaic acids



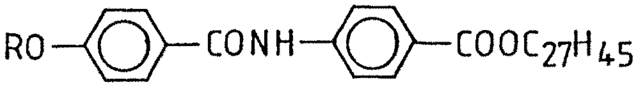
IR Spectral Data

Bending and Stretching vibrations (cm^{-1})

R = - C_4H_9	R = - $C_{18}H_{37}$
3350	3345
2950	2925
1690	1700
1660	1650
1605	1605
1510	1520
1410	1465
1320	1405
1260	1310
1180	1260
850	1180
760	850
	760

Table 13

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



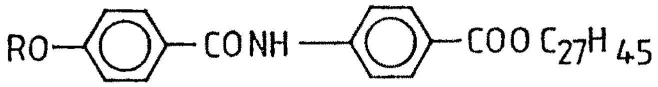
Transition Temperatures

Sr. No.	R n-Alkyl group	Transition Temperatures °C			
		Sc	SA	Cholesteric	Isotropic
1	Methyl	-	-	246	340 (d)
2	Ethyl	-	-	260	328 (d)
3	Propyl	-	-	258	317 (d)
4	Butyl	-	-	245	335 (d)
5	Pentyl	-	-	226	314 (d)
6	Hexyl	-	-	224	328 (d)
7	Heptyl	217	-	223	320
8	Octyl	221	-	232	319
9	Decyl	216	-	251	309
10	Dodecyl	201	-	262	300
11	Tetradecyl	186	258	267	294
12	Hexadecyl	182	245	262	286
13	Octadecyl	179	227	272	282

(d) decomposition

Table 14

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

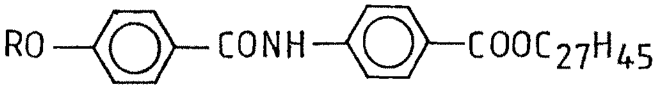


Elemental Analysis

Sr. No	R n-alkyl group	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1	Methyl	78.87	8.92	2.19	78.73	7.61	2.50
2	Ethyl	79.02	9.04	2.14	78.62	8.67	2.51
3	Propyl	79.16	9.15	2.10	78.52	8.62	2.20
4	Butyl	79.29	9.25	2.096	78.91	7.90	2.41
5	Pentyl	79.42	9.35	2.01	78.95	8.94	2.03
6	Hexyl	79.55	9.45	1.98	78.75	8.87	1.89
7	Heptyl	79.67	9.54	1.94	78.78	8.96	1.88
8.	Octyl	79.78	9.63	1.90	78.57	9.04	2.31
9	Decyl	80.00	9.80	1.83	79.46	9.63	1.53
10	Dodecyl	80.20	9.96	1.77	79.72	9.53	1.37
11	Tetradecyl	80.39	10.11	1 71	79.55	9.65	1.81
12	Hexadecyl	80.57	10.25	1.65	79.79	9.75	1.75
13	Octadecyl	80.73	10.38	1.60	79.96	9.85	2.04

Table 15

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



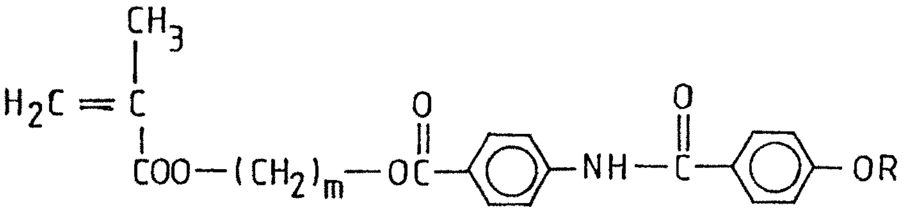
IR (FTIR) Spectral data

Bending and Stretching Vibrations (cm^{-1})

R= $-C_2H_5$	$-C_{14}H_{29}$	$-C_5H_{11}$(FTIR)	$C_{10}H_{21}$(FTIR)
3415	3350	3408	3374
2900	2900	2945	2927
1710	1705	1702	1706
1650	1655	1667	1656
1610	1500	1604	1606
1525	1400	1513	1504
1400	1310	1403	1404
1330	1275	1378	1315
1280	1170	1179	1278
1175	1100	1119	1123
1100	1010	1018	1018
840	840	850	841
765	760	767	768
		694	690

Table 16

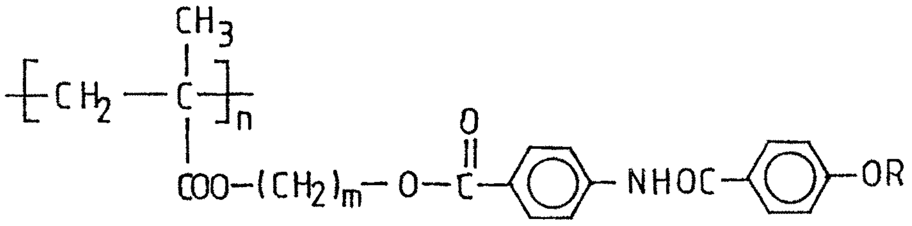
Elemental analysis of Methacrylate Monomers



Sr. No.	Code	R n-alkyl group	m	Calculated (%)			Found (%)		
				C	H	N	C	H	N
1	M_1	Butyl	2	67.76	6.35	3.29	66.92	6.26	3.31
2	M_2	Octyl	2	69.85	7.28	2.91	70.32	7.09	2.85
3	M_3	Dodecyl	2	71.51	8.01	2.61	70.69	7.87	2.52
4	M_4	Butyl	6	69.86	7.28	2.91	69.42	7.42	2.65
5	M_5	Octyl	6	71.51	8.01	2.61	72.47	8.06	2.26
6	M_6	Dodecyl	6	72.85	8.60	2.36	71.95	8.32	2.46

Table 17

Transition Temperatures of Polymethacrylates:



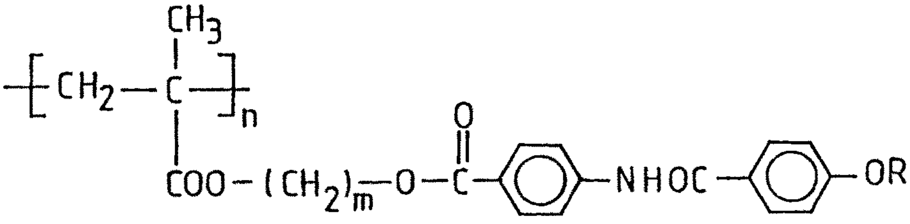
Sr. No.	Code	R n-alkyl group	m	Transition Temperatures °C
1	P_1	Butyl	2	$K \xrightarrow[{[102]^*}]{140} Iso^{+}$
2	P_2	Octyl	2	$K \xrightarrow[{[97]^*}]{120} Iso^{+}$
3	P_3	Dodecyl	2	$K \xrightarrow[{[84]^*}]{105} Iso^{+}$
4	P_4	Butyl	6	$K \xrightarrow[{[106]^*}]{125} Iso^{++}$
5	P_5	Octyl	6	$K \xrightarrow[{[54]^*}]{104}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

\+ Melt exhibits birefringence on cooling

++ Melt exhibits intense birefringence when disturbed on heating as well as cooling

Table 18

Elemental Analaysis of Methacrylate Polymers



Sr. No.	Code	R n-alkyl group	m	Calculated (%)			Found (%)		
				C	H	N	C	H	N
1	P_1	Butyl	2	67.76	6.35	3.29	65.39	7.17	3.14
2	P_2	Octyl	2	69.85	7.28	2.91	68.65	6.44	2.61
3	P_3	Dodecyl	2	71.51	8.01	2.61	68.93	7.13	2.33
4	P_4	Butyl	6	69.85	7.28	2.91	67.83	6.47	3.06
5	P_5	Octyl	6	71.51	8.01	2.61	68.84	7.25	1.98
6	P_6	Dodecyl	6	72.85	8.60	2.36	70.39	7.47	1.96

Table 19

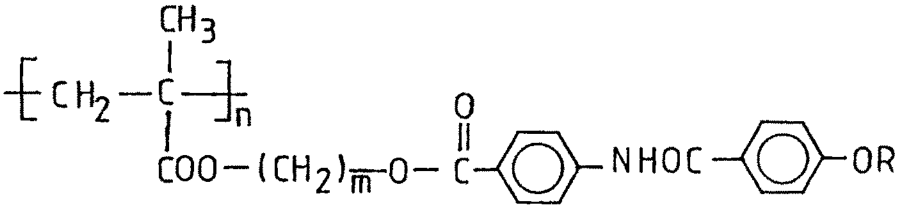
IR Spectral data of the Monomethacrylates and Polymethacrylates

Bending and Stretching Vibrations (cm^{-1})

Monomer (M_1) (KBr)	Polymer (P_1) (KBr)	Monomer (M_5) (KBr)	Polymer (P_5) (KBr)
3350	3350	3350	3350
2900	2925	2900	2900
1715	1720	1715	1710
1600	1600	1640	1600
1505	1510	1600	1505
1465	1405	1510	1400
1405	1310	1465	1250
1245	1240	1405	1160
1160	1170	1315	1100
1090	1090	1250	840
890	845	1170	760
840	760	1100	690
760	690	840	
690	690	760	
		690	

Table 20

Viscosity data of the Polymethacrylates



Solvent N-Methyl-2-Pyrrolidone

Temperature : 33.3°C

Concentration : 0.5%

Polymers	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
P_1	1.0332	0.0332	0.0663	0.0653	0.0656
P_2	1.0521	0.0521	0.1041	0.1015	0.1021
P_3	1.0629	0.0639	0.1185	0.1222	0.1212
P_4	1.0975	0.0975	0.1950	0.1860	0.1885
P_5	1.0708	0.0708	0.1417	0.1369	0.1642
P_6	1.0550	0.0550	0.1100	0.1070	0.1078

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)

Table 21.b

Elemental analysis of Monomers and Polymers having Carbonate linkage

Code	Calculated (%)		Found (%)	
	C	H	C	H
M_7	75.28	9.96	75.10	9.87
M_8	75.28	9.96	74.86	8.36
P_7	76.25	10.37	76.03	10.17
P_8	76.25	10.37	74.45	9.13

Table 22

IR Spectral data of Monomer and Polymers

Bending and Stretching Vibrations (cm^{-1})

M_7 (KBr)	P_7 (KBr)	P_8 (KBr)	P_7 (FTIR) (KBr)
2820	2825	2830	2950
1750	1745	1740.	2871
1720	1670	1675	1743
1640	1470	1470	1675
1470	1380	1370	1463
1380	1260	1250	1378
1250	1150	1160	1265
1155	935	940	1169
940	785	190	890
885			847
790			791
			470

Table 23

Viscosity data of Polymers :

Solvent N-Methyl-2-Pyrrolidone

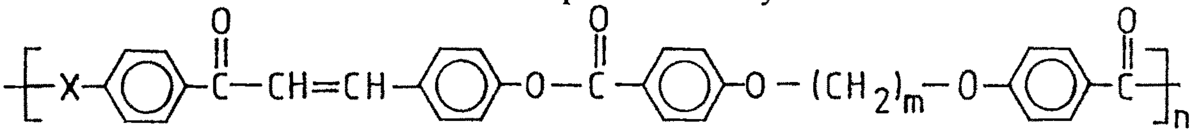
Temperature : 25.0°C

Concentration : 0.5 %

Code	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
P7	1.0201	0.0201	0.0805	0.0796	0.0798
P8	1.0436	0.0436	0.0872	0.0853	0.0858
CP	1.0355	0.0355	0.0709	0.0698	0.0701

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

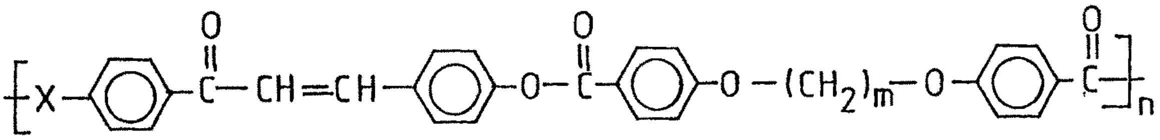
Table 25

Elemental Analysis of the Polychalcones

Sr.No.	Code	Calculated (%)			Found (%)		
		C	H	N	C	H	N
1	EP1	74.73	5.34	-	72.93	4.83	-
2	EP2	75.61	6.30	-	73.45	5.62	-
3	EP3	74.87	5.53	2.50	72.62	4.90	1.90
4	EP4	75.85	6.32	2.27	73.45	5.69	1.87

Table 26

IR spectral data of the Polychalcones

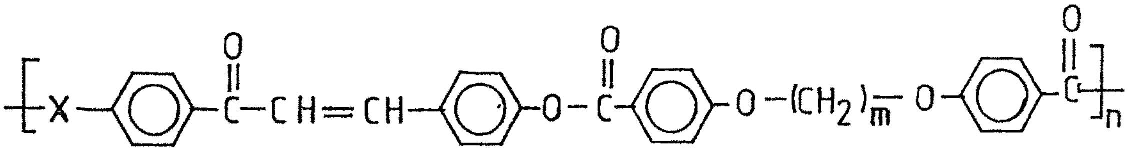


Bending and Stretching Vibrations (cm^{-1})

EP1 (Nujol)	EP2 (KBr)	EP3 (Nujol)	EP4 (KBr)
1720	1740	2900	2900
1690	1655	1740	2830
1660	1600	1691	1720
1580	1510	1660	1690
1560	1420	1600	1590
1460	1250	1510	1575
1370	1150	1460	1500
1140	1050	1380	1470
1045	800	1160	1390
810		845	1140
		760	840
		720	750

Table 27

Viscosity data of the Polychalcones



Solvent: Dimethyl Formamide

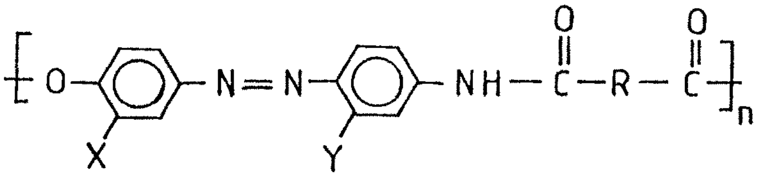
Temperature: 34.4°C

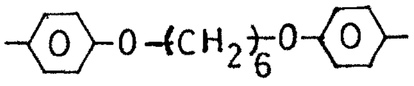
Concentration: 0.5%

Code	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
EP1	1.0665	0.0665	0.1330	0.1288	0.1298
EP2	1.0705	0.0705	0.1410	0.1363	0.1374
EP3	1.0679	0.0679	0.1358	0.1314	0.1325
EP4	1.0724	0.0724	0.1449	0.1397	0.1411

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)

(P) = Sample post polymerizes and become solid

Table 29

Elemental analysis of Polyesteramides

Code	Calculated (%)			Found (%)		
	C	H	N	C	H	N
PEA1	68.38	5.98	11.97	67.32	5.13	10.53
PEA2	69.04	6.30	11.51	68.04	5.28	10.45
PEA3	62.26	5.19	10.90	60.58	6.25	9.86

Table 30

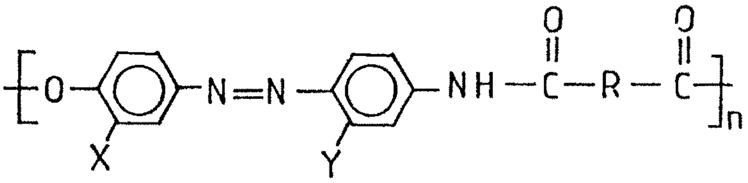
IR spectral data of Polyesteramides

Bending and Stretching Vibrations (cm^{-1})

Monomer AA-1	Polymer PEA-1	Polymer PEA-2
3380	3325	3330
3285	1720	1725
1585	1680	1655
1490	1600	1600
1475	1525	1510
1440	1500	1450
1375	1460	1400
1255	1250	1240
850	1060	1060
	845	885
	725	840
		755

Table 31

Viscosity data of Polyesteramides

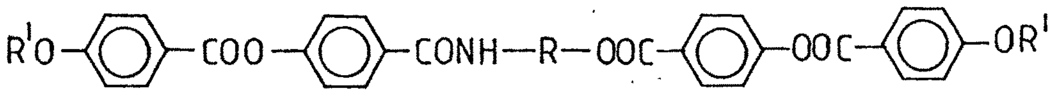


Solvent	N-Methyl-2-Pyrrolidone
Temperature	38.3°C
Concentration	0.5 %

Code	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
PEA1	1.0846	0.0846	0.1692	0.1624	0.1641
PEA2	1.0744	0.0744	0.1487	0.1435	0.1448
PEA3	1.0692	0.0692	0.1385	0.1339	0.1350

Table 32

Transition Temperatures of Amido-Esters:



Code	R' n-alkyl	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

Table 33

Elemental analysis of Amido-Esters

Code	Calculated (%)			Found (%)		
	C	H	N	C	H	N
AE1	71.90	5.56	1.99	71.26	5.19	1.83
AE2	73.80	6.77	1.72	72.96	6.82	1.57
AE3	69.83	5.97	2.14	69.23	5.78	2.03
AE4	72.16	7.19	1.83	71.68	6.89	1.68
AE5	69.94	6.14	4.30	69.26	6.32	3.96
AE6	71.19	6.78	3.96	70.92	7.02	3.75

Table 34

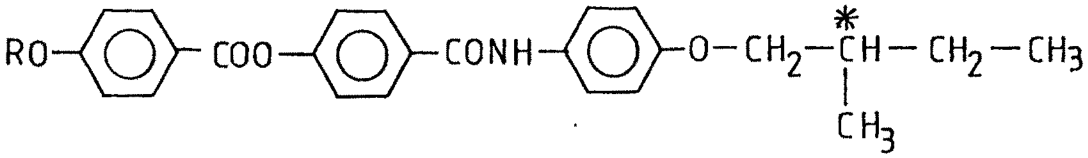
IR spectral data of Amido-Esters

Bending and Stretching Vibrations (cm^{-1})

AE-1	AE-2	AE-3	AE-4
3350	3350	2900	2900
2900	2875	1735	1735
1730	1730	1690	1690
1650	1650	1600	1600
1600	1600	1510	1510
1510	1510	1420	1420
1410	1410	1200	1200
1190	1180	1155	1155
1160	1055	1055	1050
1055	1005	1010	1010
1010	875	880	875
870	840	840	840
840	750	755	750
750			

Table 35a

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



Calorimetric Data

Sr. No.	R n-Alkyl Group	Weight mg.	Transition State	Peak Temps. (microscopic Reading	ΔH J/G	ΔS J/g.°K	Total ΔS J/g.°K
1	Dodecyl	12	K----Sc	158.3 (174.0)	11.70	0.0271	
			Sc ---Chol	180.9(193.5)	2.10	0.00463	0.0389
			Chol---Iso	244.7(256.0)	3.73	0.00721	
2	Tetradecyl	10	K----Sc	149.1(153.0)	24.06	0.057	
			Sc---Iso	203.5(213.0)	4.91	0.0177	0.0747

Table 35.b

Calorimetric data of Polychalcones and Polycarbonates

Heating rate = 10°C

Sr. No.	Poly mer	Wt. mg.	Transition state	Peak Temp.°C (Microscopic Reading)	ΔH J/g	ΔS J/g.°K	Total ΔS J/g.°K
1	EP-1	17	K-Nematic	144.8 (140.0)	2.44	0.00584	
			Nematic-Iso	190.3 (190.0)	0.39	0.00084	0.0067
2	EP-2	17	K-Nematic	141.1(150.0)	4.51	0.0109	
			Nematic-Iso	- (256.0)	-	-	0.0109
3	EP-3	17	Extrapeak	67.0	5.38	0.0158	
			K-Nematic	121.1(124.0)	0.79	0.0020	0.0178
			Nematic-Iso	- (190.0)	-	-	
4	EP-4	10	K-Nematic	143.1 (141.0)	9.09	0.0219	
			Nematic-Iso	- (169.0)	-	-	0.0219
5	P_7	10	K-Sc	81.2 (89.0)	3.02	0.0085	
			Sc-Iso	- (131.0)	-	-	0.00853
6	P_7*	10	K-Chol.	73.9 (89.0)	1.61		
			Chol.-Iso	- (131.0)	-	-	0.00464

Table 36

Viscosity data of Polymers

Solvent	N-Methyl-2-Pyrrolidone for P_4 and DMF for EP-2
Temperature	33.3°C for P_4 and 34.4°C for EP-2

Polymer	Concentration (%)	η_{rel}	η_{sp}	$\eta_{intrinsic}$ (dl/gm)	
				One pt. method	Graphical
P4	1.0	1.2035	0.2035	0.1898	
	0.75	1.1495	0.1495	0.1891	
	0.50	1.0975	0.0975	0.1883	0.1860
	0.25	1.0475	0.0475	0.1867	
EP2	1.0	1.1500	0.1500	0.1423	
	0.75	1.1107	0.1107	0.1419	0.1340
	0.50	1.0705	0.0705	0.1374	
	0.25	1.0345	0.0345	0.1363	

Table 37

GPC Data of the Polymers

Polymer	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$	Molecular weight
P_1	1177	1816	1.543	1716
P_2	340	1721	5.062	1259
P_7	955	2453	2.569	1960
EP-1	633	2100	3.318	2028

Table 38.b

X-ray diffracting data of polymer P_2

Peak	d-spacing (A°)		I/Io	Sin 2 θ		hkl
No.	Obs.	Calc.		Obs.	Calc.	
1	7.9215	7.9274	31	0.1936	0.1934	100
2	7.7757	7.8399	30	0.1971	0.1956	004
3	7.0583	0.0746	18	0.2170	0.2164	102
4	5.1719	5.2266	16	0.2945	0.2915	006

Table 38.a

X-ray diffracting data for polymer P_2

Obs. No.	2-Theta	Int.	Width	d(A°)	I/Io
1	11.160	564	0.210	7.922	31
2	11.370	541	0.210	7.776	30
3	12.530	333	0.195	7.059	18
4	17.130	293	0.180	5.172	16
5	17.360	465	0.180	5.104	26
6	17.450	526	0.165	5.078	29
7	17.680	934	0.165	5.013	51
8	18.010	1812	0.210	4.921	100
9	18.130	1733	0.165	4.889	95
10	18.580	515	0.165	4.772	28
11	20.600	622	0.210	4.308	34
12	20.80	616	0.180	4.267	34
13	21.030	415	0.180	4.221	23
14	22.94	777	0.225	3.874	43
15	23.22	1256	0.210	3.828	69
16	23.47	1454	0.225	3.787	80
17	23.98	900	0.165	3.708	50
18	24.56	1287	0.210	3.622	71
19	24.78	1278	0.210	3.590	70
20	25.01	961	0.270	3.558	53
21	25.30	564	0.180	3.517	31

Table 39.a

Conductivity data of polymer P_7 (on heating)

$2\pi S = 1.2571$, $I = 0.002$ m.amp.

Obs. No.	T(°K)	Voltage (m.volt)	V/I m.volt/m.amp	Resistivity (Ω cm)	Conductivity (σ) (Mho)x10^{-2}	logσ
1	325	0.060	30.0	22.603	8.6189	-1.0646
2	333	0.061	30.5	11.797	8.4767	-1.0718
3	337	0.063	31.5	12.183	8.2082	-1.0858
4	341	0.066	33.0	12.763	7.8351	-1.1060
5	345	0.068	34.0	13.150	7.6046	-1.1190
6	349	0.071	35.5	13.730	7.2833	-1.1377
7	353	0.075	37.5	14.504	6.8946	-1.1615
8	357	0.083	41.5	16.050	6.2305	-1.2055
9	361	0.103	51.5	19.919	5.0203	-1.2993
10	365	0.138	69.0	26.687	3.7471	-1.4263
11	368	0.175	87.5	33.84	2.9549	-1.5295
12	371	0.241	120.5	46.606	2.1456	-1.6684
13	374	0.371	185.5	71.746	1.394	-1.856
14	376	0.502	251.0	97.079	1.030	-1.9872
15	378	0.678	339.0	131.115	0.7627	-2.1177
16	380	0.908	454.0	175.59	0.5695	-2.2445
17	382	1.223	611.5	236.51	0.4228	-2.3739
18	383	1.417	708.5	274.03	0.3649	-2.4378

Table 39.b

Conductivity data of polymer P_1 (on heating)

I = 0.002 m.amp

Obs. No.	T (°K)	Voltage (m.volt)	V/I m.volt/m.amp	Resistivity (Ω cm)	Conductivity (σ) (Mho) x10^{-2}	logσ
1	328	0.053	26.5	14.396	6.944	-1.1584
2	339	0.053	26.5	14.483	6.906	-1.1608
3	347	0.056	28.0	15.303	6.535	-1.1848
4	355	0.063	31.5	17.20	5.814	-1.2355
5	359	0.068	34.0	18.58	5.382	-1.2691
6	363	0.081	40.5	22.135	4.518	-1.3451
7	369	0.118	59.0	32.24	3.102	-1.5084
8	373	0.167	83.5	45.64	2.19	-1.6594
9	375	0.210	105.0	57.39	1.742	-1.7590
10	377	0.276	138.0	75.42	1.326	-1.8775
11	379	0.366	183.0	100.01	1.000	-2.0000
12	381	0.504	252.0	137.72	0.726	-2.1390
13	382	0.591	295.5	161.50	0.6190	-2.2083
14	383	0.705	352.5	192.65	0.519	-2.2848

Table 39.c

Activation energy of conductance of polymers

Polymer	P_1	P_2	P_7	CP
Activation energy (ev)	1.125	1.702	1.231	1.158

Table 40

Fluorescent Spectral data of Monomers and Polymers (at room temperature)

Block	Sr. No.	Code	Emission Monomer/Polymer (nm) $x10^{-6}$	Excitation Monomer/Polymer (nm) $x10^{-6}$	Intensity (arb.units)
[A]	1	M_1	412	398	1.7
	2	P_1	440	398	2.5
	3	M_2	412	370	1.5
	4	P_2	440	370	2.2
	5	M_3	412	360	1.7
	6	P_3	440	360	5.6
[B]	1	M_7	410	370	2.0
	2	P_7	440	370	1.2
	3	M_8	410	370	6.1
	4	P_8	440	370	2.0
[C]	1	HC	400	350	1.0
	2	EP-1	440	380	2.4
	3	EP-2	440	398	1.1
	4	AHC	400	330	2.0
	5	EP-3	440	360	2.75
	6	EP-4	440	370	4.8
[D]	1	CP	440	370	2.7

Table 41.a

TGA data of polymer (P_7) obtained at 10°C/min.

T °K	% Weight present	1/T x10^{-3} (K^{-1})	Y weight	ln [ln(1/Y)]
335	98	2.985	0.98	-3.902
370	95	2.703	0.95	-2.970
390	90	2.564	0.90	-2.250
405	80	2.469	0.80	-1.500
425	70	2.353	0.70	-1.031
435	60	2.299	0.60	-0.672
450	50	2.222	0.50	-0.367
498	40	2.008	0.40	-0.087
535	36	1.869	0.36	+0.021
585	33	1.709	0.33	+0.103
650	32	1.538	0.32	+0.131

Table 41.b

TGA data of polymer (EP-2) obtained at 10°C/min.

T °K	% weight present	1/T x 10^{-3} (K^{-1})	Y Weight	ln [ln(1/Y)]
300	95	3.333	0.95	-2.97
375	87	2.667	0.87	-1.9714
400	81	2.500	0.81	-1.557
425	70	2.353	0.70	-1.0310
450	61	2.222	0.61	-0.7046
475	57	2.105	0.57	-0.5760
500	47	2.000	0.47	-0.2810
525	39	1.9048	0.39	-0.0602
550	27	1.8182	0.27	+0.2695
575	15	1.7391	0.15	+0.6403
587	12	1.7036	0.12	+0.7515
600	12	1.7036	0.12	+0.7515

Table 41.c

Activation energy (K.cal.mole^{-1}) calculated according to Broido method

Obs. No.	Polymer	Energy of Activation (Ea) (K.cal.mole^{-1})
1	P_1	47.24
2	P_2	47.11
3	P_3	38.49
4	P_5	45.73
5	P_7	36.95
6	P_8	31.41
7	CP	20.79
8	EP-1	22.38
9	EP-2	20.79
10	EP-3	25.98
11	EP-4	20.79
12	PEA-2	23.28
13	PEA-3	26.53