SUMMARY

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Polymers are the materials whose properties depend on many aspects including the crystallinity and the arrangement of the chain in solid state. If liquid crystalline (mesogenic) order can be induced in polymeric systems, host of excellent properties can be visualized. Number of polymeric systems conducive to mesomorphism have been investigated and are finding applications in different fields.

Number of liquid crystalline polymers having liquid crystalline properties have been synthesized, characterized and their different properties were evaluated.

(1) Poly(oxybenzoates):

(A) Homopolymers: Different homopolyesters were synthesized by condensing hydroxy aromatic acids by using thionyl chloride as condensing agent in different solvents at varying temperatures and time. Following four hydroxy aromatic acids were used to synthesize homopolymers.

(i) 2-Hydroxybenzoic acid : seven polymers-poly(2-oxybenzoate).
(ii) 4-Hydroxybenzoic acid : Twenty polymers-poly(4-oxybenzoates).
(iii) 3-Hydroxybenzoic acid: Six polymers-poly(3-oxybenzoates).
(iv) 4-Hydroxy-3-methoxybenzoic acid (vanillic acid):
    seventeen polymers-poly(4-oxy-3-methoxybenzoates).

(B) Copolymers: Different types of copolymers were synthesized by using two different hydroxy aromatic acids as monomers in different molar ratios by using thionyl chloride as condensing agent and nitrobenzene/benzene as solvent:

Following copolymers were synthesized:

i) Poly(2-Co-3-oxybenzoates): Two copolymers.
ii) Poly(4-Co-3-oxybenzoates) : Twelve copolymers.
iii) Poly(4-oxybenzoate-Co-4'-oxy-(3'-methoxy)benzoates): Thirteen copolymers.

(C) Post-polymerization:

Some of the homopolymers and copolymers were post-polymerized in liquid crystalline state to evaluate the effect of different parameters like temperature, pressure, time on the resultant polymers and mesogenic properties of the polymers.

(D) Binary mixtures with optically active d-camphor:

Three mixtures were prepared to induce the cholesteric phase in the polymers by varying the percentage weight of optically active d-camphor (component B) in polymers (component A). Following three polymers as component A were used to prepare the mixtures:

i) Poly(4-oxybenzoate) (nematogen).

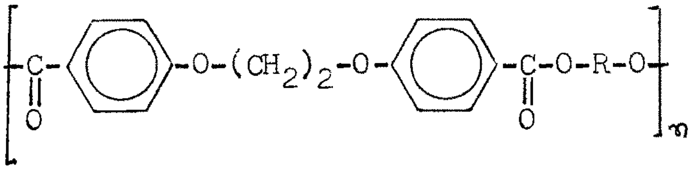
All copolymers exhibit mesomorphism except poly(3-Co-2-oxybenzoates).

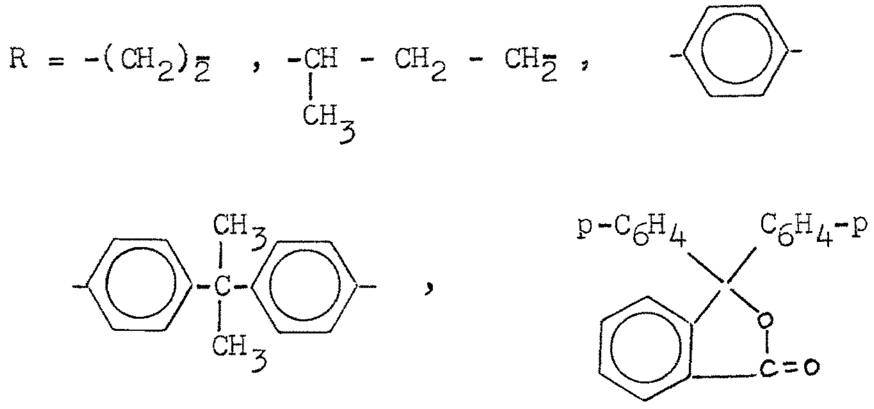
The post-polymerized samples may have higher transition temperatures or they do not exhibit any mesophase up to 350°C indicating the increase in length of rigid unit of poly(oxybenzoate) during the post-polymerization.

The doping of polymers with optically active d-camphor is quite interesting as it induces a cholesteric phase. The solid-mesomorphic temperatures reduced markedly in the binary mixtures compared to pure polymer.

2. Mesogenic Polyesters having flexible spacer:

Five polyesters were synthesized with the general formula BE

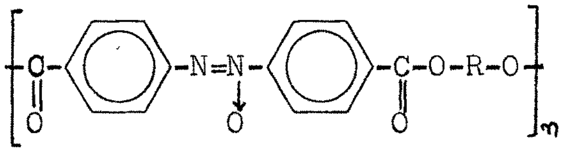


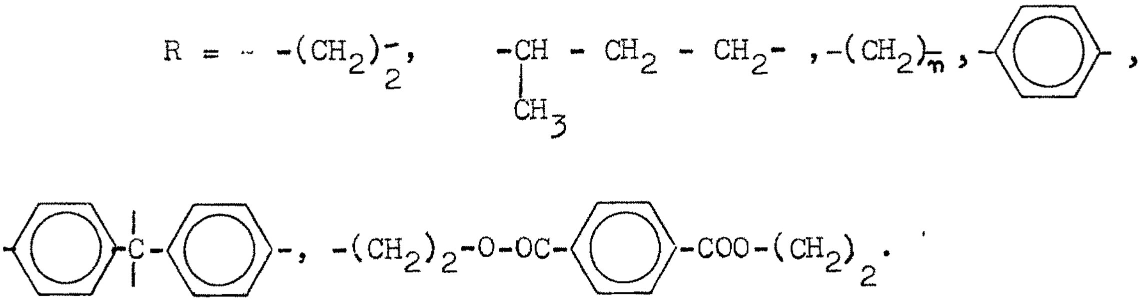


All polymers exhibit mesomorphism. The thermal stability of the polymer having phenyl ring is much more higher than the polymer with aliphatic moiety as observed in low molecular liquid crystalline compounds.

3. Mesogenic Polyesters having "azoxy" linkage :

Twelve polyesters were synthesized with the general formula PABC

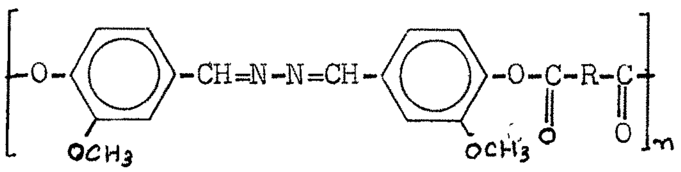


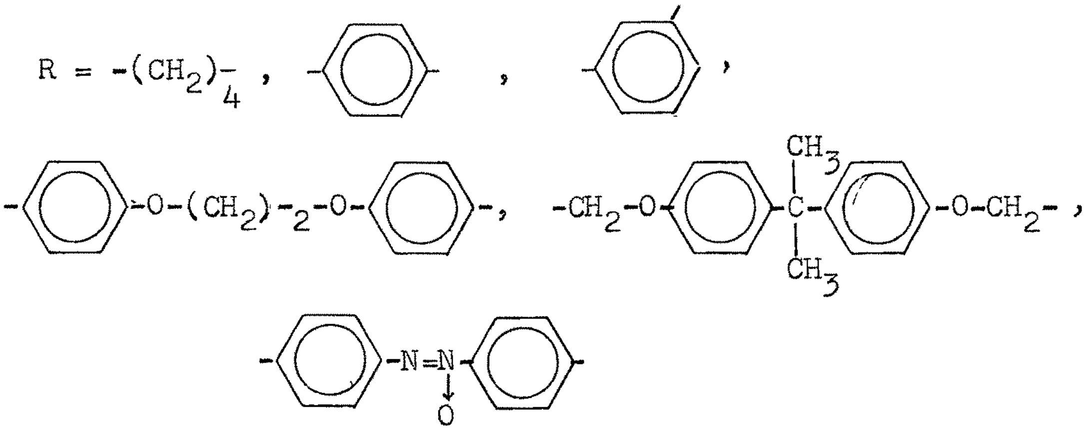


It is surprising to note that none of the polyesters exhibits mesomorphism, though aliphatic or aromatic esters with "azoxy" linkage exhibit mesomorphism. Couple of them melt but do not exhibit mesophases and other are having high melting or transition temperatures.

4. Mesogenic Polyesters having "azine" linkage:

Six polyesters were synthesized with the general formula AZ.



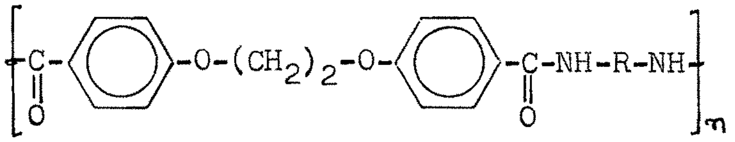


Polymer with flexible chain (-CH$_2$)$_4$ is non-mesogenic and polyesters with p-phenylene ring does not melt while polyesters having rigid-flexible chain and m-phenylene ring exhibit mesomorphism. These results indicates that if flexibility is increased beyond certain limit or rigidity is more, mesomorphic properties could not be observed in the polymer system.

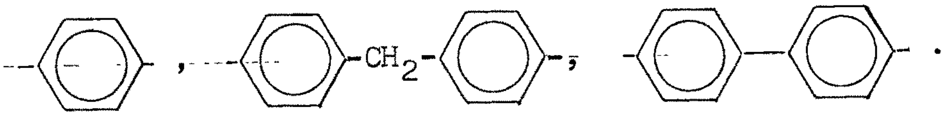
5. Mesogenic polyamides having flexible spacer:

Two polymer systems were synthesized by varying flexible spacer units.

(i) Eighteen polyamides were synthesized with the general formula BEA.

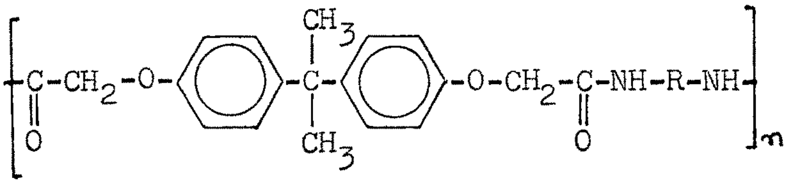


R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)-_6$,



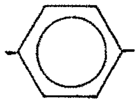
Polyamides having aliphatic diamines as monomers exhibit mesophase whereas aromatic diamines raise the melting point of polyamides and do not melt upto 300°C. This trend of polyamides is similar to that observed in low molecular weight liquid crystalline compounds.

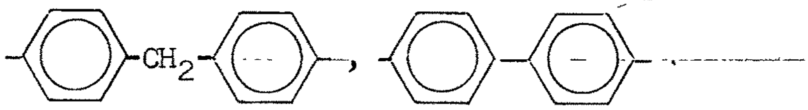
(ii) Six polyamides were synthesized with the general formula BP



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

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





As in the previous system none of the polyamides having aromatic diamine as monomers exhibits mesophase (remain unaffected upto 325°C) in this system flexibility was increased. None of the polyamides exhibits mesomorphism except polyamide having benzidine as one of the monomers. The results indicate that adequate induces nematic properties. In this present study the polyesters obtained exhibit smectic mesophases even when the concentration of mesogenic moiety is much less (11 %).

Two of the polymers were post-polymerized at elevated temperature and under reduced pressure to evaluate the effect of these parameters on the mesogenic properties of polymers. Post-polymerized samples are non-mesogenic in nature.

7. Characterization of Mesophases:

All polymers were screened under polarizing microscope provided with a hot stage for the exhibition of liquid crystalline properties. The characterization of mesophases by texture observation was further confirmed by contact method. Respective low melting nematogens or smectogens were used for the purpose.

8. Model compounds:

Nine model compounds were synthesized to understand the behaviour of polyesters and polyamides. Their structures were confirmed by elemental analysis and IR spectral study.

9. IR Spectral Analysis:

IR spectra were used for the conformation of structure. The presence of ester, amide linkage is confirmed in the respective polymers.

10. Viscosity Measurement:

All the soluble polymers were studied by using Ubbelohde viscometer at constant temperature. Intrinsic viscosity is obtained by using one point method. The study was carried out to correlate the degree of polymerization and mesogenic properties of the polymers. Intrinsic viscosities $[\eta]$ shows that number average molecular weight of these mesogenic polymers is not very high. Nematic polymer and non-mesogenic polymers have relatively higher intrinsic viscosity $[\eta]$ compared to smectogenic polymers. It indicates that higher molecular weight leads to less ordered mesophase or non-mesogenic character.

11. Thermogravimetric analysis (TGA Study):

A number of polymers were analysed and they exhibit good thermal stability. Post-polymerized samples exhibit excellent thermal stabilities.

12. DTA/DSC Study:

Seven polymer samples were analyzed by DTA/DSC study to confirm the transition temperatures of the polymers observed on polarized microscope.

13. X-ray Study:

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

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