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Synthesis and Study of Main Chain Chalcone Polymers Exhibiting Nematic Phases

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Abstract

The mesogenic main chain polymers of general structure-I were synthesized and their different properties are studied. All the polymers exhibit nematic phases. Classical nematic textures are observed in these polymers. None of the dihydroxy, amino-hydroxy or dicarboxy compounds shows liquid crystalline properties. The role of flexible methylene spacers, degree of polymerization and central linkage on exhibition of all the polymers is discussed. All the polymers are characterized by standard methods.

Keywords: : Liquid crystalline polymers, nematic phase, chalcone linkage, crystalline I –crystalline II etc.

Introduction

The rarity of mesogenic compounds having chalcone linkage and potential of polymers with this linkage for application prompted [1] to study the polymers with chalcone linkage. The first mesogenic homologous series with chalcone linkage have been reported [2] and studied polyesters and polyester-amides by varying flexible methylene spacers from –$(CH_2)_2$- to -$(CH_2)_4$- in carboxy phenoxy diacid moiety[3,4]. They also varied the flexibility by using rigid and flexible dicarboxylic acids as co-monomer. The chemistry and physics of high-performance fiber spinning based on main-chain liquid crystal polymer (MCLCP) solutions and melts was discussed, which is the largest industrial application of liquid crystal technology[5]. Recently Schiff-base chalcone linkage thermotropic mesogens have synthesized and study the effect of substituent on liquid crystalline properties[6,7]. The side chain liquid crystalline photoactive polymers with chalcone pandent chalcone moiety were synthesized and characterized[8,9]. However polymers exhibited relatively higher transition temperatures.

The flexibility of the dicarboxylic acid moiety in the system increased by introducing 'oxyethylene spacers' in the place of methylene spacers[10,11]. Solid to mesomorphic and mesomorphic to isotropic transition temperatures were drastically reduced but florescent behavior was not affected. One striking feature of "oxyethylene spacer" polymers was that smectic mesophase was eliminated. This prompted us to investigate polymeric ester and ester-amide 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 containing chalcone linkage were synthesized by the route given in Figure 1.

It was proposed in the present study to concentrate on flexibility of carboxyl phenoxy diacid moiety by increasing flexibility with high number of methylene spacers to evaluate the effect of increased flexibility on mesogenic properties of polymers with this in view polymers were synthesized by route given in figure 1.

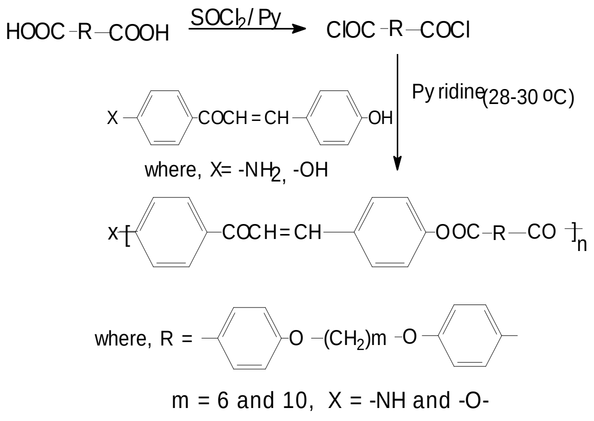

Figure-1
Synthetic route to Polychalcones

Measurements : The synthetic route adopted for the synthesis of polychalcones is shown in Figure:1. Elemental analysis were performed with a Perkin-Elmer 2400, C,H,N analyzer. The IR of polymers was recorded on Perkin-Elmer with KBr pellet. The optical textures of the polymers samples were studied with a Leitz Laborlux 12 Pol (Germany) polarizing microscope fitted with a Kofler heating stage. Ubbelohde Viscometer was used for the measurement of viscosity of polymers in dimethyl formamide as a solvent.

Material and Methods

Preparation of Different Diacids ω-bis (4-carboxy phenoxy) oligo ethers: Following different diacids were used for the synthesis of polymeric chalcones:1,6-bis(4'-carboxy phenoxy) hexane (DA-I),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 [12, 13] for synthesis of 1,2-bis (4'-carboxy phenoxy)ethane. 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. Approximate 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 ^{o}C, Reported 290-292 ^{o}C [12,13], DA-II : 273 ^{o}C, Reported 273-274 ^{o}C [12,13]

Synthesis of Diacid Chlorides of Diacids DA-I and DA-II [14]: Diacid chlorides were prepared by reacting the corresponding diacids 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 vacuum pump and the diacid chlorides left behind as a residue was used in next reaction without further purification.

Synthesis of different Chalcone: Synthesis of 4,4'-dihydroxy chalcone: **4,4'-dihydroxy benzylidene acetophenone** (HC): 4,4'-dihydroxy chalcone was synthesized according to the hot condensation process[17] 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 ^{o}C for twenty hours. The solution was acidified by cold 6 N HCl solution (congored), Yellow crystalline solid separated, which was filtered and washed with water. It was recrystallized from ethanol melting point 204 ^{o}C .

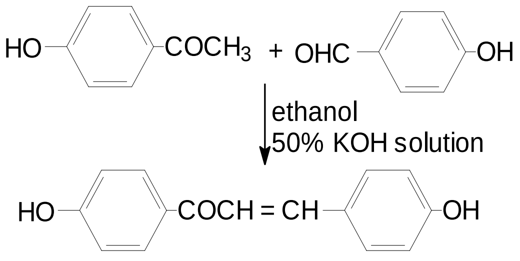

Figure 2
Synthesis of 4,4’-dihydroxy chalcone

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[18] for the para substituted derivative. 13.5 gms (0.1 mole) 4-Amino acetophenone, 12.2 gms (0.1 mole) 4-hydroxy benzaldehyde 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 ^{o}C.

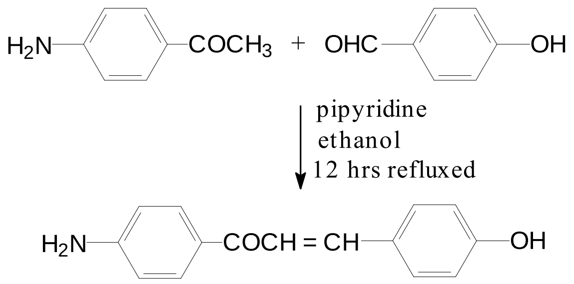

Figure-3
Synthesis of 4-amino-4’-hydroxy chalcone

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 appropriate diacid chloride (0.005 mole) was dissolved in 10 ml dry pyridine and cooled to 0^{o}C in an ice-bath. The solution of respective chalcone (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^{o}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 and viscosity data are recorded in table 1 and 2, respectively.

In the IR spectrum of EP-1 and EP-2, the characteristic keto-ester linkage was observed at 1720 and 1740 cm^{-1}, keto of -CH = CHCO – at 1660 and 1655 cm^{-1}, -CH=CH-Ar at 1560 and 1555 cm^{-1} and $\nu_{C - H}$ bending of alkane at 1460 and 1455 cm^{-1}, respectively and IR spectrum of EP-3 and EP-4 the characteristic keto-ester linkage was observed at 1740 and 1720 cm $^{-1}$, -NH- bending at 1690 and 1690 cm^{-1}, -CONH-R at 1510 and 1500 cm^{-1}, keto of amide at 1600 and 1590 cm^{-1}, -CH=CH-Ar at 1570 and 1575 cm^{-1}, respectively. ν_{C-H} bending of aromatic ring obtained at 760, 750 cm $^{-1}$ etc.

Table-1
Transition temperatures of polychalcones

Code no.	X =	m =	Transition Temperatures ^oC	
			Nematic	Isotropic
EP-1	-O-	6	140.0	190.0
EP-2	-O-	10	150.0	280.0
EP-3	-NH-	6	124.0	190.0
EP-4	-HN-	10	141.0	169.0

Results and Discussion

Reference to table 1 indicates that polymers EP-1 to EP-4 exhibit only 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 structure of all the polymers vary uniformly hence intrinsic viscosity values [η_{int}] are taken to compare the properties of polymers. Due to the solubility parameters of the polymers molecular weight determination could not be done by other method. Number of researchers has studied the effect of increased flexibility of methylene spacers on different polymeric systems[19-22]. A common observation is that the increase in flexibility lowers transition temperatures and induces smectic phases in certain cases[23-25].

Reference to table 1 indicates that increase in flexibility in each system affects solid mesomorphic as well as mesomorphic-isotropic transition temperatures. Compared to EP-1, EP-2 polymers, EP-3 and EP-4 polymers exhibit lower solid-nematic and nematic-isotropic transitions. Normally an amide linkage enhances mesogenic thermal stability. It seems the unsymmetrical linkages (ester and amide) in the repeat unit may be responsible in lowering of solid-nematic and nematic-isotropic transitions of EP-3 and EP-4 polymers. Reference to table:1 further shows that when amide linkage (EP-3 and EP-4), the transition temperatures are severally affected. These results indicate that amide linkage bring down solid-nematic as well as nematic-isotropic transition temperatures.

The polymers exhibit very fine texture similar to nematic phase in small molecules. This is an interesting aspect, normally a good texture is observed after keeping a polymer sample for sometime on the hot stage of the microscope (figure-a and b).

The absence of smectic phase in all the polymers is quite surprising. Even with ten spacers and one of the amide linkage EP-3 and EP-4 do not exhibit smectic mesophase. This may be due to the increased flexibility of the systems.

Polymers EP-1, EP-2 and EP-3 were studied by using Mettler DSC-4000. Polymer EP-1 does not exhibit endothermic peak for nematic-isotropic transition temperature. Only one endothermic peak is obtained for crystalline-nematic transition temperatures. However on cooling the melt an exothermic peak is observed for isotropic-nematic transition temperatures. Polymer EP-2 exhibits one additional endothermic peak between the two recorded transitions Solid-Nematic and Nematic-Isotropic.

It is difficult to account this endothermic peak. However on cooling the melt exothermic peak are not observed for any of the transitions. In the case of polymer EP-3 an endothermic peak for Solid-Nematic transition temperatures is observed. An additional peak between the two transition temperatures is obtained in this polymer also. The DSC results are in conformity with certain unusual mesogenic series [26, 27.]

Reference to table-1 shows that the polymers EP-1 to EP-4 exhibit nematic mesophase only. 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. Transition temperatures do not differ much in the case of EP-1 and EP-3 even though -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) and EP-4 (molecular weight 1960) 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[21], indicates that this procedure can be used. The procedure followed by condensation polymerisation gives consistent data. Intrinsic viscosity does not defer markedly from EP-1 to EP-4.

DSC Results (table 4) indicate typical behavior. Except polymer EP-1 none of the polymers exhibit endothermic for nematic-isotropic transition temperatures. In the case of polymer EP-3 an extra peak not matching with microscopic results is observed at 67^{o}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^{o}C in the case of EP-3 may be due to Crystalline I - crystalline II transition. 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 crystalline-I to crystalline-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.

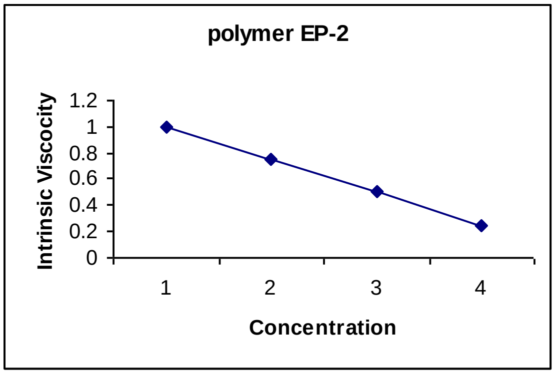

Figure-4
Intrinsic viscosity against different concentration

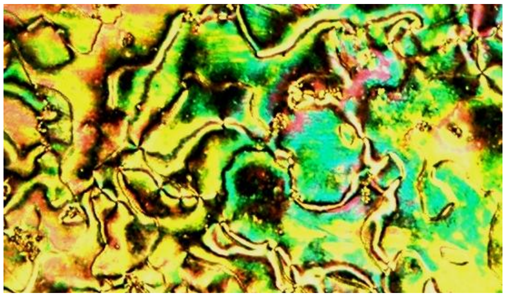

Figure-4
Optical polarized microphotograph of Nematic liquid crystalline phase (Thread like texture) of EP-2 on heating at 245^{0}C

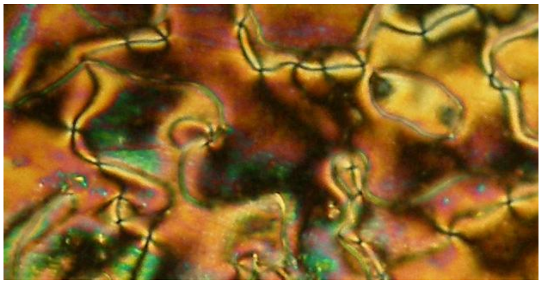

Figure: 5
Optical polarized microphotograph of Nematic liquid crystalline phase (Thread like texture) of EP-4 on cooling at 154^{0}C

Table-2
Viscosity data of the Polychalcones Solvent: Dimethyl Formamide
Concentration: 0.5% **Temperature: 34.4 ^{o}C**

Code	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
EP-1	1.0665	0.0665	0.1330	0.1288	0.1298
EP-2	1.0705	0.0705	0.1410	0.1363	0.1374
EP-3	1.0679	0.0679	0.1358	0.1314	0.1325
EP-4	1.0724	0.0724	0.1449	0.1397	0.1411

Calculated by One Point method (15)

Table- 3
Viscosity data of Polymers Solvent: N-Methyl-2-Pyrrolidone, Temperature: 34.4^{o}C

Polymer	Concentration (%)	η_{rel}	η_{sp}	$\eta_{intrinsic}$ (dl/gm)	
				One pt. method	Graphical
EP-2	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-4
Calorimetric data of Polychalcones and Polycarbonates Heating rate = 10 °C

Sr.No.	Polymer	Wt. mg.	Phases	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

( ) Values indicate microscopic data, K indicates crystalline, Iso. = isotropic

Table-5
GPC Data of the Polymers

Polymer	Mn	Mw	Mw/Mn	Molecular weight
EP-1	633	2100	3.318	2028
EP-4	955	2453	2.569	1960

Conclusion

Polyesters and polyesteramides having chalcone linkage with increased flexibility by increasing number of methylene spacers show higher thermal stability than monomers. All the polymers exhibit nematic mesophases. Except polymer EP-1 none of the polymers exhibit endothermic for Nematic-Isotropic transition temperatures.

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References

1. Vora R.A. and Sheth K.A., *Presented at the International Conference of Liquid Crystal Polymers*, Bordeaux, France, July 20, **(1987)**
2. Chudgar N.K. and Shah S.N., *Liq. Cryst.*, **4(6)**, 661 **(1998)**
3. Gaissman T.A. and Clinton R.O., *J. Am. Chem. Soc*., **68**, 697 **(1984)**
4. Kumar A., Sinha J.,Bhargava K.P.,and Shanker K., *Ind. J. Chem.*, **23**B, 589 **(1999)**
5. Pickena S.J., Sikkemab D.J., Boerstoelc H., Dingemansd T.J. and Van der Zwaagd S., *Liquid Crystals*, **38 (11–12)**, 1591–1605 **(2011)**
6. Thaker B.T., Patel P.H., Vansadiya A.D. and Kanojiya J. B., *Mol. Cryst. Liq. Cryst*. **515**, 135- 147 **(2009)**
7. Thaker B.T. and Kanojiya J.B., *Mol. Cryst. Liq. Cryst.*, **542**, 84-98 **(2011)**
8. Iqbal M. and Dingemans T.J., *Eur. Polym. J., **46***, 2174 **(2010)**
9. Iqbal M., Mendes E. and Dingemans T.J., *J. Polym. Sci..Part A: Polym. Chem.*, **47,** 1368 **(2009)**
10. Jeyashella S. and Subramanian K., *Mol. Cryst. Liq. Cryst.*, **552,** 53–70 (**2012**)
11. Vora R.A., and Techchandani V., Presented at Fourteenth International Conference on Liquid Crystals, Piza, Italy, June **(1992)**
12. Donahoe H.B., Louis E., Benzamin V., Leon F. and Griffin J., *J. Org. Chem.*, **26**, 474 **(1961)**
13. Griffin A.C. and Havens S.J., *Poly. Sci. Polym. Phys. Ed.*, **19**, 951 **(1997)**

14. Dave J.S and Vora R.A., *Pramana Suppl., (***1**), 447 **(1975)**

15. *Techniques and Methods of Polymer Evaluation*, Edt. Slade, P.E. (Jr.) and Marcel, Dekker, Inc., New York, **4 (1975)**

16. Donahoe H.B., Benjamin L. E., Fennoy L. V. and Greiff D., *J. Org. Chem.,* **26**, 474 **(1990)**

17. Geissman T.A. and Clinton R. O., *J. Am. Chem. Soc*., **68**, 697 **(1946)**

18. Kumar A., Sinha J., Bhargava K.P. and Shanker K., *Ind. J. Chem*., **23B**, 589 **(1984)**

19. Blumstein A., Ed. *Liquid Crystalline Order in Polymers*, Academic Press, New York, 334-352 **(1978)**

20. Griffin, A.C. and Havens, S. J., *J. Polym. Sci. Poly. Phys. Ed.,* **19**, 951 **(2004)**

21. Dave J.S. and Vora R.A., *Liquid Crystals and Ordered Fluid*, Edts. Johnson, J. F. and Porter, R. S., Plenum Press, New York, 477 **(1970)**

22. Frenzel J. and Rehaje G., *Macromol. Chem., Repid Commun*., **1**, 129 **(2006)**

23. Kim C., Jorgen K., Kops R. and Jette S., *Macromolecules*, **20**, 2660 **(1987)**

24. Hans R.K. and Ralf P., *Macromolecules,* **21**, 551 **(1988)**

25. Van. L.D. and Strzelecki L., *Polym. J*., **16**, 303 **(1980)**

26. Barrall E.M., Porter R.S. and Johnson J.F., J. *Phys. Chem.,* **71**, 1224 **(1967)**

27. Ellerstein S.M., *Appl. Polym. Symp.*, **2**, 111 **(1966)**

28. *Techniques and Method of Polymer Evaluation*, "Edt. Slade, P.E. (Jr), Marcel Dekker, New York, **4 (1975)**