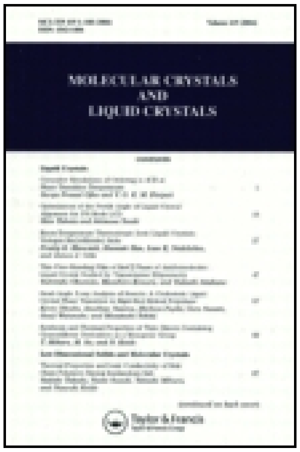

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Mesomorphic Polymers-l: Thermotropic Liquid Crystalline Polymers from p-Hydroxybenzoic Acid†;

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Mesomorphic Polymers-I: Thermotropic Liquid Crystalline Polymers from *p*-Hydroxybenzoic Acid†

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Homopolymerization of *p*-hydroxybenzoic acid was carried out by using thionyl chloride as condensing agent. The Solvent and polymerization temperature were varied to evaluate the effect of these parameters on the resultant homopolymer. The number of polymeric samples obtained by this method exhibit thermotropic nematic and smectic mesophases. The mesomorphic properties are normally obtained when the solvent is non-polar and the polymerization temperature is low. Polar solvents and/or higher polymerization temperatures lead to non-mesogenic character. The viscosity measurements of polymeric samples help to explain the non-mesogenic character of certain polymeric samples. The role of intermolecular hydrogen bonding in the polymeric samples is also discussed.

INTRODUCTION

The ordered structure of the mesophases can endow a system with many useful properties. The polymers exhibiting lyotropic[1] or thermotropic[2-5] mesomorphism provide an ordered polymeric material which can be processed in such a manner that the ordered arrangement is not disturbed. Such ordered polymeric material exhibits higher mechanical strength and has better stability.

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Studies concerning liquid crystalline main chain polymers were originated by Onsager[6] and Ishihara[7] when treating theoretically the packing of rigid rod like molecules. In 1956 Flory[8] extended this theory to concentrated solutions. He proposed that above a critical concentration the macromolecules form a lyotropic liquid crystalline phase.

In 1950 Oster[9] studied polymers with liquid crystalline order in aqueous solutions of tobacco mosaic virus and in 1956 Robinson[1] reported polymeric liquid crystalline solutions of poly (*r*-benzyl-L-glutamate) in various solvents.

The polymerization of a non-mesogenic monomer within liquid crystalline solvents has been reported by Amerik *et al.*[10], Tanaka *et al.*[11] and Blumstein *et al.*[12], organization of the monomer within a mesomorphic solvent was found to have a considerable influence on the kinetics of polymerization and the molecular weight.

Vinyl oleate has been polymerized by different workers in liquid crystalline and isotropic phase.[13,14] Hardy and co-workers[15-17] have studied kinetics of polymerization of cholesteryl acrylate and other monomers. Billard *et al.*[18-20] have studied binary phase diagrams of thermotropic measomorphic polymers with low molecular weight mesogens and have observed miscibility behaviour similar to two low molecular weight mesogens.

Recently the study of thermotropic mesogenic polymeric materials have attracted more number of chemists due to their structural variations and technological applications.[21-24]

The copolymers obtained by condensing terephthalic acid, ethylene glycol and *p*-hydroxybenzoic acid exhibit thermotropic mesomorphism and have improved mechanical and physical properties.[25, 26] These results lead to the synthesis of number of other polymers where *p*-hydroxybenzoic acid is substituted by other hydroxy aromatic acids.[27]

The literature survey reveals that homopolymerization of *p*-hydroxybenzoic acid gives thermally stable polymer.[28-30] One of the patent reveals that first an oligomer was prepared from *p*-hydroxybenzoic acid and then this oligomer was polymerized at 260 °C to obtain a highly ordered heat resistant polymer.[28]

p-Hydroxybenzoic acid (PHB) is a starting material for many low molecular weight mesogens, moreover it induces mesomorphic structure when copolymerized with polyethylene terephthalate. Homopolymerization of PHB gives thermally stable polymers. All these results enthused us to study the homopolymerization of PHB in milder conditions with a hope of getting mesogenic polymeric material.

EXPERIMENTAL

The PHB used was purchased from HPC Co., and was of high purity. It was recrystallized from water and was used for the polycondensation.

(i) Homopolymerization of PHB by using thionyl chloride as condensing agent

2 gms of PHB was taken in a 50 ml R.B. quick fit flask containing 3 ml dry benzene, 3 ml of thionyl chloride was added as condensing agent. The care was taken against moisture absorption by providing calcium chloride guard tube on the condenser. The whole mass was heated on the water-bath by keeping temperature between 80–90 °C for the specific time period. After the reflux period of desired time interval was over, the whole mass was cooled and the ice-cold water was added to the flask and shaken well. The material was then filtered and washed with ice-cold water, followed by ethanol washing to remove unreacted PHB. The solid polymer was dried and the melting point and transition temperatures were determined. The data is recorded in Table I.

To study the effect of temperature, time and the solvent on the homopolymerization of PHB, number of variations were tried. The

TABLE I

Homopolymerization of *p*-hydroxy benzoic acid (PHB) in air using thionyl chloride as condensing agent

Sr. No.	Code No.	Solvent	Heating hours on water-bath	Transition temperature °C		
				Smectic	Nematic	Isotropic
1	HP_1	Xylene	1	306	—	324 *P*
2	HP_2	Xylene	3	301	—	318 *P*
3	HP_3	Xylene	6	327	—	340 *P*
4	HP_4	Toluene	1	274	—	315 *P*
5	HP_5	Toluene	3	297	316	323 *P*
6	HP_6	Toluene	6	—	—	> 350
7	HP_7	Benzene	1	271	—	313 *P*
8	HP_8	Benzene	3	269	—	303 *P*
9	HP_9	Benzene	6	—	279	315 *P*
10	HP_{10}	Nitro benzene	15 minutes	255	—	350 *P*
11	HP_{11}	Nitro benzene	3	—	—	> 350
12	HP_{12}	Nitro benzene	3(210 °C, Oil-bath)	—	—	> 350
13	NP_{13}	Xylene	3(140 °C, Oil-bath)	—	—	> 350
14	HP_{14}	Toluene	3(110 °C, Oil-bath)	—	—	> 350

P = polymerized under melt condition and solidified.

TABLE II

Elemental Analysis

Sr. No.	Polymer	Found	
		C %	H %
1.	HP-2	65.88	3.44
2.	HP-6	68.63	3.92
3.	HP-9	67.85	3.71
4.	HP-10	65.74	4.28
5.	HP-11	68.81	3.74
6.	HP-16	68.78	3.15

Molecular Formula of Repeating Unit : $C_7H_4O_2$
Required : C = 70%; H = 3.33%

Table I summarizes all such variations carried out in the present investigation and the transition temperatures of the resultant polymers.

The elemental analysis of all the polymeric samples was carried out and the results are satisfactory. The analytical data of a few samples are recorded in Table II.

All the polymeric samples are insoluble in common organic solvents like DMF, DMSO, Acetone etc. The polymer is soluble in 98% H_2SO_4.

(ii) Transition temperature measurements

A polarizing microscope provided with mettler FP-2 heating stage was used to observe mesomorphism in the polymeric samples. Most of the polymeric samples on further heating undergo polymerization in liquid crystalline phase and become solid and remain unchanged up to 350 °C, suggesting that resultant higher polymer is infusible up to 350 °C.

(iii) Viscosity measurements

Viscosity was measured by taking 2% solution of polymer in 98% sulphuric acid at 25 °C by using Ubbelohde viscometer. Intrinsic viscosity $[\eta]$ is calculated by using formula[31]:

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

The viscosity data is recorded in Table III.

(iv) Polymerization of low molecular weight polymer by heating in different conditions in the liquid crystalline state

The polymeric sample HP_3 (Table I) exhibiting smectic mesophase was heated as under and the viscosity measurements of the resultant polymer samples were carried out as discussed above (Table III). The thermal behaviour of the resultant polymer sample is also studied.

Polymer HP_3	Heating between 310–330 °C time and environment	Code No. Of resultant polymer
	(a) 20 minutes in nitrogen atmosphere.	HP_{15}
	(b) 1 hour and 20 minutes in nitrogen atmosphere.	HP_{16}
	(c) 20 minutes in nitrogen atmosphere and under reduced pressure (77 mm).	HP_{17}
	(d) 6 hours in nitrogen atmosphere and under reduced pressure (76 mm).	HP_{18}

(v) Characterization of mesophases by contact method

To characterize and ascertain about the smectic and nematic mesophases of the polymer samples following low molecular weight nematogen, Methyl 4-(4′-n-ethoxybenzoyloxy)benzylidene-4″-amino-

TABLE III

Viscosity data for different polymer samples

Sr. No.	Code No.	[η]	Mesogenic Character
1.	HP_2	0.0321	Smectic
2.	HP_3	0.0283	Smectic
3.	HP_5	0.0330	Smectic–Nematic
4.	HP_6	0.0426	Non-mesogenic
5.	HP_8	0.0355	Smectic
6.	HP_9	0.0392	Nematic
7.	HP_{11}	0.0384	Non-mesogenic
8.	HP_{13}	0.0495	Non-mesogenic
9.	HP_{15}	0.0474	Non-mesogenic
10.	HP_{16}	0.0453	Non-mesogenic
11.	HP_{17}	0.0644	Non-mesogenic
12.	HP_{18}	0.0679	Non-mesogenic

TABLE IIIa

IR Spectral Data
IR Streching Vibrations

HP-2	HP-6	HP-10	HP-16
3440 Cm^{-1}	3500 Cm^{-1}	3445 Cm^{-1}	3500 Cm^{-1}
1735 Cm^{-1}	1750 Cm^{-1}	1725 Cm^{-1}	1750 Cm^{-1}
1600 Cm^{-1}	1610 Cm^{-1}	1625 Cm^{-1}	1615 Cm^{-1}
1540 Cm^{-1}	1525 Cm^{-1}	1525 Cm^{-1}	1525 Cm^{-1}
1420 Cm^{-1}	1425 Cm^{-1}	1425 Cm^{-1}	1425 Cm^{-1}
880 Cm^{-1}	885 Cm^{-1}	885 Cm^{-1}	890 Cm^{-1}

benzoate:

$$K \xrightarrow{187.0\,^{\circ}C} N \xrightarrow{330.0\,^{\circ}C} \text{decomposition; was used.}$$

The above nematogen is miscible continuously with the polymers exhibiting nematic mesophase in the nematic phase range. When this nematogen was heated along with smectogenic polymer samples, two phases were distinctly observed indicating that polymer samples exhibit smectic phase.

The characterization of smectic phase by mixing with another labeled smectogen could not be done as the transition temperature of smectic phase is very high in the present polymeric samples.

(vi) IR Spectra

The polymer samples were screened by using KBr Pellets in the range of infrared frequency. The data for four samples are given in Table IIIa.

RESULTS AND DISCUSSION

The homopolymerization of PHB will proceed as indicated in Figure 1.

Reference to Table I shows that out of fourteen samples prepared by varying different parameters nine polymeric samples exhibit mesomorphism. Polymer samples HP_1–HP_3 obtained from xylene exhibit smectic mesophase. The polymer sample HP_4, obtained from toluene after one hour heating exhibits smectic mesophase whereas sample

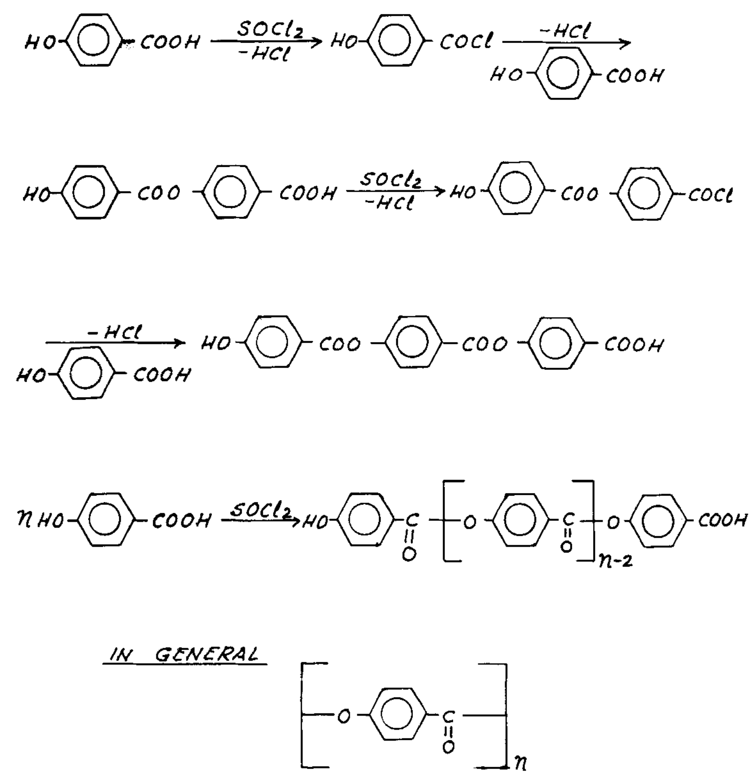
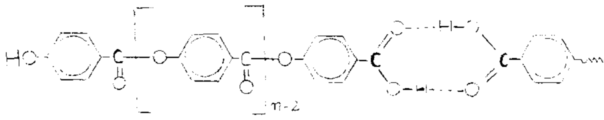


FIGURE 1

HP_5 obtained after three hours heating is polymesogenic exhibiting smectic and nematic mesophases. Sample HP_6 obtained after six hours heating is non-mesogenic. The samples HP_7 and HP_8 obtained from benzene after one and three hours heating are smectogenic whereas sample HP_9 obtained after six hours heating is a nematogen. More interesting results are obtained when nitrobenzene is used as solvent. When the reaction was stopped within fourteen minutes, then the resultant polymer HP_{10} was mesogenic. However, the polymer sample HP_{11} obtained after three hours heating is non-mesogenic. When the homo-polymerization was carried out at the boiling point temperature of nitrobenzene, xylene and toluene respectively, then in all the three cases non-mesogenic polymers HP_{12}, HP_{13} and HP_{14} were obtained.

Above results suggest that if milder conditions of temperatures are used during polymerization and the solvent is not highly polar then normally a mesogenic polymer is obtained. In the case of high temperatures or polar solvent normally a non-mesogenic polymer is obtained.

There is the possibility of dimer formation through hydrogen bonding in the homopolymer as shown under:



This possibility of intermolecular hydrogen bonding is confirmed by IR spectral analysis (Table-IIa). Naturally as the degree of polymerization increases, the melting point of the polymer will also be increased and a stage will come that the melting point is increased to such a high degree that polymer remains unaffected up to 350 °C. This effect will be doubled as the dimer will have two units of phenyl ring with one more increased phenyl ring in the homopolymer. The resultant polymer may or may not exhibit mesogenic properties at higher temperatures. DSC study can throw light on this aspect. However, normally higher melting points disturbs the ordered arrangement in such a way that solid is directly converted to nematic phase or isotropic liquid state. As mentioned earlier the viscosity measurements are carried out in 98% H_2SO_4.

Reference to $[\eta]$ values (Table-III) shows that molecular weight of these polymers is not very high. Another interesting point worth noting is that the nematic (HP_9) and the non-mesogenic polymer samples (HP_6, HP_{11}-HP_{14}) have relatively higher intrinsic viscosities $[\eta]$ compared to smectogenic polymers. The viscosity results support the above mentioned assumption that higher molecular weight leads to less ordered mesophase or non-mesogenic character.

The polymer samples obtained at lower heating time are normally smectic in nature whereas the increased heating time results in a polymesogenic or a nematic polymer in the same solvent. This is difficult to explain without detailed structural study of the polymers in mesogenic state. Reference to Table I clearly indicates that progressively longer heating time converts a smectic polymer to a nematic and finally to a non-mesogenic polymer. The non-mesogenic nature of the polymer up to 350 °C can be understood as discussed above.

The smectogenic low molecular weight polymer sample HP_3 was heated further as reported in experimental section in the inert atmosphere, in air and under reduced pressure to study the effect of heating on the sample in mesogenic phase. The polymer samples obtained do not exhibit any mesophase up to 350 °C and remain unchanged. The viscosity results indicate that the original value of HP_3 (0.0283) is increased to 0.0474, 0.0453 and 0.0644. This increase in viscosity i.e. increase in degree of polymerization explains the non-mesogenic nature due to the increased length of rigid unit of poly(*p*-oxybenzoate).

It has been reported in a recent patent[33] that the addition of thermotropic mesogenic polymer to poly(ethylene terephthalate) or in Nylon-66, induces mesomorphism in the melt and then fibres of better strength are drawn. Mesogenic polymeric materials obtained in the present study can be used to investigate such binary systems which may provide applications.

The TGA results provide very interesting observations. The amorphous polymer decomposes rapidly beyond 500 °C. 22.9% decomposition is at 500 °C. The thermal stability of high molecular weight polymer studied by Patel *et al.*[32] is compared with present results (Table IV). The low molecular weight polymer HP_3 as indicated in experimental section was further polymerized and the thermal degradation of these polymers was studied. The polymer sample (HP_{17}) obtained by heating polymer sample HP_3 for 20 minutes at 310 °–330 °C under reduced pressure (77 mm) exhibited good thermal stability. Encouraged with this result, the polymer sample HP_3 was heated for six hours between 310 °–330 °C at 77 mm pressure (HP_{18}) and another sample of polymer HP_3 was heated between the same temperature but at 0.5 mm pressure (HP_{19}) for 30 minutes. The thermal degradation is less in HP_{18} up to 500 °C compared to the reported data for high molecular weight poly (*p*-oxybenzoate)[32]. In the case of HP_{19}, the stability is far better than the reported polymer at 500 °C. These results suggest that liquid crystalline low molecular

TABLE IV

T G A Results Loss at various temperatures (heating rate 10 ° C per minute)

Sr. No.	Polymer Sample	% Weight loss					
		250 ° C	300 ° C	350 ° C	400 ° C	500 ° C	600 ° C
1.	Poly(p-oxybenzoate) Ref. 32	—	5	6	8	30	35
2.	HP_{11}	2.97	4.80	5	11.45	22.9	98.43
3.	HP_{15}	0.625	2.5	14.4	16.5	87.5	—
4.	HP_{17}	—	1	12.5	13	45.0	50.6
5.	HP_{18}	—	—	0.51	5.1	28.05	—
6.	HP_{19}	—	—	—	—	8.4	78.9

weight poly(*p*-oxybenzoate) can be processed at lower temperature and when subjected to high temperature treatment under vacuum for short duration (30 minutes), thermally stable polymer is obtained.

The two polymer samples HP_7 (smectogen) and HP_9 (nematogen) were doped with optically active camphor. Preliminary results are encouraging. The smectogen gives an additional cholesteric mesophase and nematogen gives a cholesteric phase exhibiting vivid colours. The binary mixture study is contemplated for complete understanding of different molecular forces acting in these systems.

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