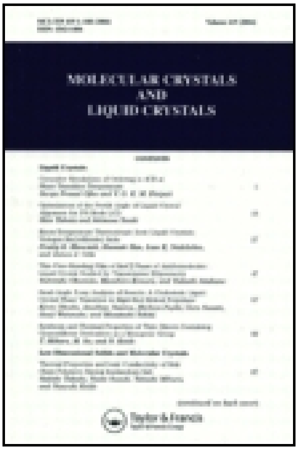

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Mesogenic Polymers with Heterocyclic Moiety: I Polyesters†

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Eight polymers were synthesised by condensing acid chloride of *2,4*-bis(4′-carboxyphenoxy)-*6*-chlorotriazine with different dihydroxy compounds. The polyesters obtained exhibited both nematic and smectic mesophases. The polymers were characterized by elemental analysis and IR spectra. The model compound was also synthesised to correlate the mesogenic properties of polymers with the monomer structure. Even though dihydroxy aromatic monomers like bisphenol-A, phenolphthalein and *1,4*-dihydroxy anthraquinone were used the polymer still exhibited mesogenic properties. This is very interesting because the acid monomer, which is symmetrically substituted and has a flexible ether linkage, would not normally be conducive to mesomophism in polymers with such broad molecules. An attempt has been made to correlate structural aspects with mesogenic properties of polymers.

INTRODUCTION

Liquid crystalline polymers are finding applications in the textile industry.[1–2] A number of addition reaction polymers have been reported which exhibit lyotropic mesomorphism[3,4] and recently a number of condensation reaction polymers exhibiting thermotropic mesomorphism have been synthesized.[5–7] In many cases following the suggestion of de Gennes,[8] the repeating unit consisted of an extended segment and a more flexible segment. Krigbaum *et al.*, have reported mesogenic homopolyesters incorporating different rigid units.[9–11] Roviello and Sirigu,[6] and Blumstein and co-workers[12] have

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used different rigid units with flexible segments. Griffin and Havens[13] prepared polymers having quite long repeating units. We have reported[14-15] homopolyesters of *p*-hydroxy benzoic acid and vanillic acid and have tried to correlate the effect of molecular weight on mesomorphism. The effect of lateral methoxy group has also been evaluated. In the present study it was planned to synthesize reactive polymers by using *2,4*-bis(*4'*-carboxy phenoxy)-*6*-chloro-triazine as one of the monomers. The monomer has a typical flexible segment which contains a symmetrically substituted heterocyclic sym-triazine moiety having flexible ether linkage. It would be quite interesting to observe the mesogenic properties of these polymers and to evaluate the effect of chemical structure on mesomorphism. Here we present for the first time mesogenic polymers incorporating a monomer having a sym-substituted triazine heterocyclic moiety.

EXPERIMENTAL

Benzene, Cyanuric chloride, *p*-hydroxy benzoic acid and other raw materials used in the synthesis of monomer and polymers were of high purity and were further purified by standard methods before their use.

1. *PREPARATION OF POLYMERS:*

1a. *Preparation of monomer: 2,4-bis(4'-carboxyphenoxy-6-chloro-s-triazine: (BCPCT)*

In a flat bottom conical flask provided with a magnetic stirrer 9.25 gm (0.05 mole) cyanuric chloride was added to 50 ml of acetone. After the dispersion of cyanuric chloride a solution of *p*-hydroxy benzoic acid 13.8 gm (0.1 mole) in 100 ml. sodium hydroxide (8.0 gm, 0.2 mole) solution was added gradually to the flask over a period of one hour. The temperature was maintained between 0°–5°C and the stirring was continued for one hour. The temperature was then raised to room temperature, maintaining the pH between 7 to 8, and stirring was further continued for 3 hours. One mole of the *p*-hydroxybenzoic acid was reacted by keeping the temperature between 0–5°C and a second mole reacted at room temperature. At the end, the reaction mass was made acidic to precipitate the monomer which was filtered, re-dissolved in sodium hydroxide solution, filtered to remove unreacted cyanuric chloride and then the filtrate was acidified to obtain precipitates of BCPCT. The precipitates were filtered and washed with alcohol to remove unreacted *p*-hydroxybenzoic acid. The pure dicarboxylic acid monomer (BCPCT) which was dried under vaccum, decomposed at 310°C.

Calculated Analysis: C = 52.645, H = 2.580, N = 10.838, Cl = 9.16.

Found Analysis: C = 51.98, H = 3.430, N = 10.177, Cl = 8.67.

1.b *Preparation of acid chloride of monomer (BCPCT)*

Two to three drops of pyridine were added as a catalyst to 5 gms. of monomer (BCPCT) contained in a round bottom flask. 15 ml of thionyl chloride was added to the flask and refluxed for four to five hours, until evolution of the HCl gas ceased. After completion of the reaction, excess thionyl chloride was distilled off and the diacid chloride obtained used for further reactions.

1.c *Model compound of (BCPCT) with phenol*

One mmole of diacid chloride of monomer BCPCT was condensed with 2 mmoles of phenol in the presence of solvent pyridine at room temperature. After the reaction was over the product was added to 1:1 HCl–ice (mixture), the separated solid was filtered and washed with dilute sodium hydroxide solution to remove unreacted starting materials, then washed with water and finally by alcohol. The final product (MC) was dried in vaccum. Transition temperatures recorded were: K *80* N *330* I.

Calculated Analysis: C = 64.90, H = 3.336, N = 7.7849, Cl = 6.580.

Found Analysis: C = 64.97, H = 3.801, N = 6.647, Cl = 6.23.

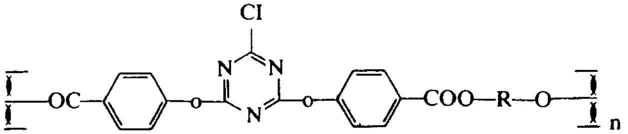
1.d *Synthesis of polyesters*

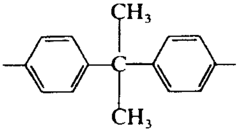
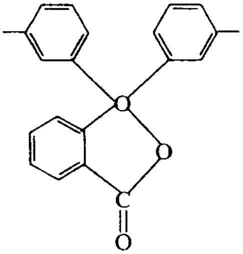
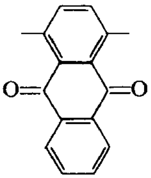
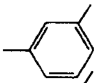
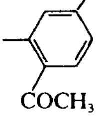
Equimolar amounts of diacid chloride of monomer BCPCT and hydroquinone were added, with stirring, to pyridine at a lower temperature (0°–5°C). After some time the temperature was raised to room temperature, (25°) and then whole mass was stirred at 25°C for 5 to 6 hours. After completion of the reaction the flask contents were poured over 1:1 ice-cold HCl solution. The precipitated polymer was filtered and washed with water followed by alcohol. The product (PE_1) was dried under vaccum.

Similarly a number of other polymers (PE_2 to PE_8) were synthesized by taking different bisphenols shown in Table I.

TABLE I

Transition temperatures and viscosity data of polymers:



Sr.			Transition Temp. °C			η
No.	Polymers	R	S	N	I	dl.g^{-1}
1.	PE_1		161	—	300	0.40
2.	PE_2		—	190	241	0.33
3.	PE_3		—	214	238	0.27
4.	PE_4		—	118	274	0.29
5.	PE_5		174	—	300	0.38
6.	PE_6		198	—	271p	0.26
7.	PE_7	$—(CH_2)_4—$	200	—	290p	0.42
8.	PE_8	$—(CH_2)_2—$	—	141	283p	0.46

p = polymerised under melt condition and solidified.

TABLE II

Elemental analysis

Sr. No.	Polymer	Molecular formula of repeating unit	Calculated C%	Calculated H%	Found C%	Found H%
1.	PE_1	$C_{23}H_{12}N_3O_6Cl$	59.80	2.6	57.40	3.30
2.	PE_2	$C_{32}H_{22}N_3O_6Cl$	66.26	3.79	64.82	4.26
3.	PE_3	$C_{37}H_{20}N_3O_8Cl$	66.32	2.99	64.88	3.959
4.	PE_4	$C_{31}H_{14}N_3O_8Cl$	62.89	2.37	61.77	2.892
5.	PE_5	$C_{23}H_{12}N_3O_6Cl$	59.80	2.6	60.80	3.511
6.	PE_6	$C_{25}H_{14}N_3O_7Cl$	59.58	2.78	58.67	3.558
7.	PE_7	$C_{21}H_{16}N_3O_6Cl$	57.08	3.62	58.18	2.606
8.	PE_8	$C_{19}H_{12}N_3O_6Cl$	55.14	2.9	56.96	3.645

1.e *Purification of polymers*

The polymers were purified by a solvent/non-solvent method. Dimethyl formamide was used as the solvent and ethanol was used as the non-solvent. The polymer was dissolved in dimethyl formamide and filtered. The filtrate was added to the ethanol, stirred and the precipitated polymer was filtered and dried under vaccum. The polymers were all purified in this manner.

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

1.f *Transition temperature measurements*

A polarizing microscope provided with a Mettler FP-2 heating stage was used to observe mesomorphism in the polymeric samples. Some of the polymeric samples on further heating become isotropic while some of the polymeric samples on further heating undergo polymerization in the liquid crystalline phase and become solid and remain unchanged up to 300°C, suggesting that resulting higher polymer is infusible up to 300°C.

1.g *Viscosity measurements*

Viscosity was measured, for a 0.5% solution of polymer in the solvent dimethyl formamide at 30°C, by using an ubbelohde viscometer. Intrinsic viscosity (η) is calculated by using the formula[16] given below;

$$(\eta) = \frac{2\,(\eta_{sp} - \log \eta_{rel})^{1/2}}{c}$$

The viscosity data is recorded in Table I.

1.h *Characterization of mesophases by contact method*

To characterise and ascertain the smectic and nematic mesophases of the polymer samples the following low molecular weight nematogen, methyl 4-(4′-ethoxybenzoyloxy)benzylidene-4″-amino benzoate was used with K 187.0°C N 330.0°C decomposition. This nematogen is continuously miscible with the polymers exhibiting a nematic mesophase in the nematic phase range of the polymer. When this nematogen was heated along with smectogenic polymer samples, two phases were distinctly observed indicating that polymer samples exhibit a smectic phase.

1.i *IR spectra*

Monomer, model compound and polymer samples were screened by using Nujol/KBr pallets in the range of infra-red frequency. The data for these are given in Table III.

TABLE III

IR spectral data for IR stretching vibration.

Monomer BCPCT	Model Compound	Polymer PE_1
1700 Cm^{-1}	1730–40 Cm^{-1}	1720–30 Cm^{-1}
1680 Cm^{-1}	1590 Cm^{-1}	1640 Cm^{-1}
1560–70 Cm^{-1}	1550–60 Cm^{-1}	1580–90 Cm^{-1}
1450 Cm^{-1}	1450–60 Cm^{-1}	1450 Cm^{-1}
1370 Cm^{-1}	1370 Cm^{-1}	1370 Cm^{-1}
1280 Cm^{-1}	1260 Cm^{-1}	1250–60 Cm^{-1}
1200 Cm^{-1}	1190 Cm^{-1}	1190 Cm^{-1}
1160 Cm^{-1}	1150 Cm^{-1}	1150 Cm^{-1}
1090 Cm^{-1}	1050 Cm^{-1}	1040 Cm^{-1}
1000 Cm^{-1}	1000 Cm^{-1}	1000 Cm^{-1}
800 Cm^{-1}	870 Cm^{-1}	870 Cm^{-1}
750 Cm^{-1}	740 Cm^{-1}	740 Cm^{-1}
710 Cm^{-1}	710 Cm^{-1}	710 Cm^{-1}

RESULTS AND DISCUSSION

The polymerization will proceed as indicated in Figure 1.

Reference to Table I shows that all the polyesters exhibit mesomorphism. Polymers PE_1, PE_5, PE_6 and PE_7 exhibit smectic mesophases, whereas polymers PE_2, PE_3, PE_4 and PE_8 exhibit nematic

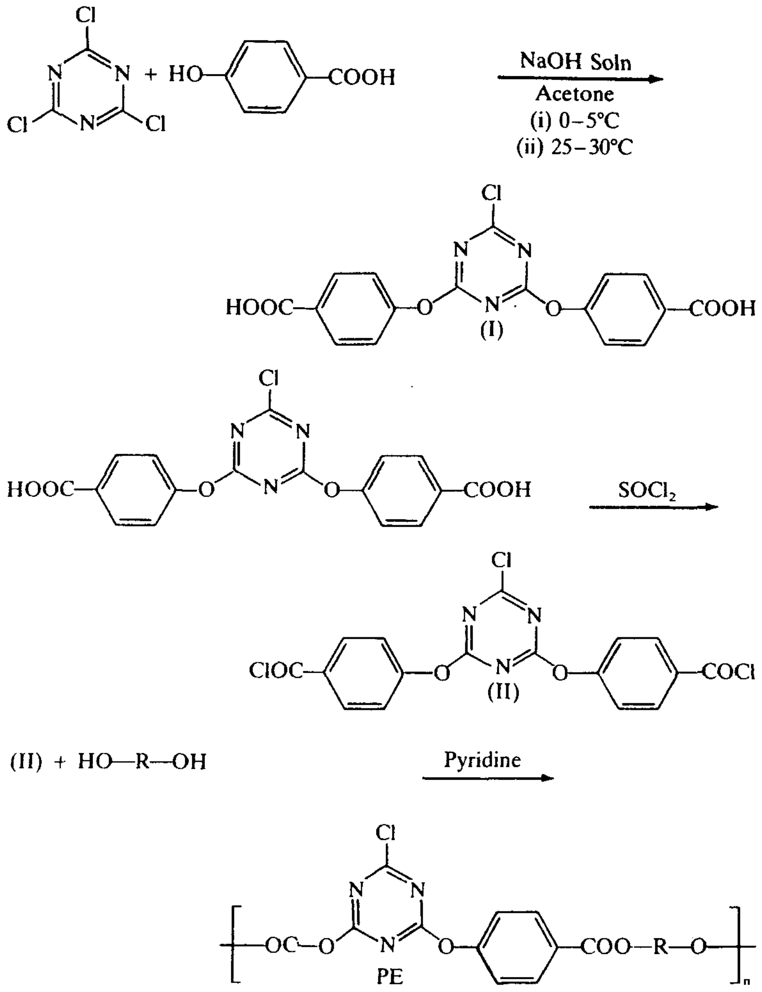


FIGURE 1

mesophases. The polymers PE_2 - PE_4 exhibiting a nematic mesophase are copolyesters with monomer residue having a broad nucleus which repeat in the polymer chain. It has been established[17] for the low molecular weight liquid crystals that an increase in breadth normally affects the smectic mesophase more than nematic mesophase and if the breadth of the molecules increases, the mesophase exhibited will be less ordered i.e. transformation to a nematic phase and further increase of breadth renders the system non-mesogenic.

In a low molecular weight mesogenic system the introduction of broad molecules, like *1,4*-disubstituted anthraquinone or substituted phthalein molecules, will normally eliminate the mesophase completely. It seems that in the polymeric chain the overall breadth to length ratio and geometry of the molecules would be conducive to the formation of a nematic mesophase.

The polymeric systems have some additional aspects compared to low molecular liquid crystal compounds. The type of the mesophases appearing in polymeric system also depends on molecular weight.[14,18] We have observed that an increase in viscosity changes the smectogenic system to nematogenic and finally a higher viscosity value renders the system non-mesogenic. The nematogenic tendency observed in PE_2, PE_3 and PE_4 (Table II) can be attributed to the increase in the breadth of the molecules as the inherent viscosity of these polymers are lower than those of others which exhibit smectic mesophases. As stated above the type of the mesophase observed in the homopolymers of *p*-hydroxy benzoic acid is dependent on the viscosity of that polymeric sample whereas in the copolyesters it is dependent on the structure of co-monomer as shown in the present study. The exhibition of a nematic mesophase by PE_8 is quite interesting. The difference in PE_8 and PE_7 is of the methylene units. The co-monomer in PE_7 has two methylene units more than that of PE_8. It has already been established,[17] that in a nematogenic homologous series as one ascends the series, the middle members exhibit smectic and nematic mesophases and the last members of the series exhibit only smectic mesophases. This is attributed to changes in attractive forces due to the increase of methylene units in the alkoxy chain. In the similar manner, in the polymer chain of PE_7, there will be twice as many methylene units as in polymer PE_8, which might explain the smectogenic tendency of polymer PE_8.

The molecules of co-monomers in PE_1 will be more linear and one would expect a smectogenic tendency in such a polymer as is the case for *1,4*-substitution of benzene nuclei which impart linearity to the system. However, even though polymers PE_5 and PE_6 have 1,3-substituted benzene ring as the co-polymer unit, they exhibit smectic mesophases. Compared to other co-monomers they are less broad and the dipolar acetyl substituent in the copolymer of PE_6 will also contribute towards the side to side attractive forces which are conducive to smectogenic tendencies in a system.

The smectic and nematic mesophases are characterized by using known low molecular weight liquid crystal compounds as mentioned in the experimental section.

To understand the mesogenic properties of the polymers a model compound was synthesized by condensing diacid chloride of BCPCT with phenol. The model compound exhibits a nematic mesophase of broad range (80 *N* 330°C). From the geometry of the model compound (Figure 2) one would not expect it to be mesogenic. Normally compounds with *1,3,5* substituted aromatic nucleus having an ether linkage are considered to be nonconducive to mesomorphism.[19] This mesogenic compound is unique and is one of a new class of compounds which is being reported by us.[20] The exhibition of mesomorphism by the model compound further supports the mesogenic tendencies of polymers derived from the monomer BCPCT.

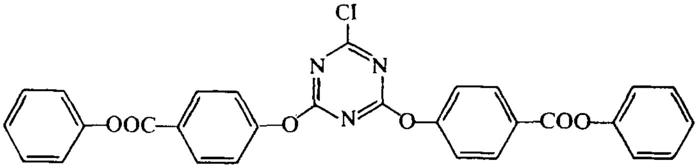


FIGURE 2

One more interesting aspect of these polymers is that they were synthesized as a part of our study in reactive polymers. The chlorine is labile and can be reacted at elevated temperatures (80°C) in alkaline condition with different reagents. This aspect is being investigated and will be presented in due course.

Due to the labile nature of the chlorine all the polymers were prepared, dried and were studied further by taking care that the halogen group does not become hydrolysed.

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