SYNTHESIS AND CHARACTERIZATION OF SOME CONTROLLED STRUCTURE THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS

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ABSTRACT

Four sequentially ordered co-polyesters have been synthesized. In order to preclude any possibility of sequence randomization, a typical plycondensation method has been developed to carry the reaction out at room temperature in presence of a phosphorilating agent. The method consisted of synthesis of a symmetric trimeric compound with a predesigned monomer sequence and its polymerization with a second monomer. The effect of reaction parameters for the synthesis of these polymers, viz. temperature, reaction time, monomer concentration and solvent, on the yield and molecular weight of the polymers have been studied by carrying out the polycondensation process under different reaction conditions. Qualitative structure analysis of the polymers has been carried out by FTIR spectroscopy. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were adopted for thermal analysis of the polymers. Three dimensional molecular structures of the polymers were studied by Wide Angle X-ray Diffraction (WAXD) technique. Texture of liquid crystal polymers were identified by the photomicrographs obtained from optical microscopy. Mesomorphic nature of the polymers would be interpreted by a combination of WAXD and the thermal treatment of the polymers.

Keywords: *Mesogen; mesophase; morphology; nematic; poloycondensation; smectic.*

1. INTRODUCTION

Syntheses of most liquid crystal polymers (LCP) involve a high reaction temperature and a long reaction time. The synthesis of the polyesteramides from p-acetamidobenzoic acid and polyethyleneterephthalate was carried out at 275^0C for 4 hours as was reported by Jackson and kuhfuss[1]. Khan et al. synthesised polyestramides from p-acetamidophenyl acetate and bis(p-carboxyphenoxy) alkane at 282^0C under reduced pressure[2]. A typical method for preparation of polyamide and polyester involved a reaction temperature of 100^0C in the presence of triphenyl phosphine according to the direct polycondensation technique developed by Higashi[3]. Some typical polycondensation methods have also been followed to carry the polymerization reaction under mild conditions[4]. Some phosphorilating agents have been chosen for this purpose. Triphenylphosphine or triphenylphosphine dichloride could initiate direct polycondensation at ambient temperature to produce either polyester or polyamide. Ogata[5] reported the synthesis of polyamides and polyesters using triphenylphosphine and hexachloroethane as initiator system by a low temperature polycondensation method. Ober et al[6] synthesized polyesters from dihydroxy compounds by polymerizing diacid chlorides at 50^0C for 24 hours in inert atmosphere using pyridine as proton acceptor.LC polyesters were prepared by C .Ramireddy and coworkers[7] by using pyridine as catalyst and HCl scavenger,which was produced as a byproduct of the esterification reaction with acid chlorides. The reaction was allowed to proceed for 48 hours at room temperature in dry nitrogen. Polyesteramides with exact desired structure can be synthesised from monomers with proper structure and functional groups. Danuta Sek et al[8] synthesised monomers and carried out the polymerization reactions in boiling chlorobenzene at 130^0C in presence of pyridine in argon atmosphere .The reaction variables have strong influence on molecular weight of the polymers as was observed by James Economy[9].

Since the reaction parameters have prominent influence on the rate of reaction and molecular weight of the polymers, the polycondensation reaction was carried out at different temperature with varying monomer concentration in different solvent system over a range of reaction period, and the yield and the molecular weight of the resulting polymers were studied.The polymers, synthesized by the condensation of aromatic diols and diacids

through a low temperature procedure, were subjected to Fourior Transform Infra Red (FTIR) spectroscopy to study the chemical constituents of the molecules and the molecular interaction among the polymer chains. The chemical composition of the polymers can be determined by the definite absorption bands in the spectrum.The optical texture of the liquid crystalline materials under a polarizing microscope is characteristic of different mesophases. Schlieren texture appeared in the smectic C and B phases as well as in the nematic phase. The so-called mosaic texture is typically encountered with smectic B phase. Smectic A and C phases were recognized by the typical fan shaped or focal conic texture. Smectic C phases showed the fan texture less distinctly. The analyses of the thermal properties of the polyesters have been made by the help of the thermograms obtained from the TGA studies. In order to examine the thermal decomposition of the polymers in greater details, the temperatures corresponding to 5, 10 and 50% weight loss have to be evaluated. The decomposition temperature for 5 to 10% weight loss represented the thermal resistance of the polymer under the experimental conditions. This has been defined as the temperature of incipient thermal degradation accompanied by the evolution of volatile products[10]. Thermal stability of the thermotropic LCPs mostly depends on the nature of the mesogens and flexible spacers present in the polymer chain. Longer mesogenic units lead to polymers with higher mesophase stability. Thermal stability of two series of LCPs ,both with mesogenic triads connected with aliphatic spacers of varying length, have been studied by C. Ramireddy and his coworkers[7]. According to their result, replacement of the aromatic ring of terephthaleic acid by a tricyclopentane cage led to a very substantial depression in the polymer stability.

LCPs undergo various phase transitions during thermal operations .The phase transition processes have been recorded in DSC studies.

WAXD experiments on liquid crystal polymers are useful for mesophase identification. The combination of X-ray diffraction with thermal data and texture examination under the optical microscope is considered the most effective means of identifying mesophase types. Smectic mesophases have been identified in several main chain LC polymers by X-ray diffraction method. Nematic mesophases were identified for polymers with odd number of methylene units in the spacers while smectic mesophases were observed for polymers with even number methylene units[11,12].

2. EXPERIMENTAL
All chemical used were of AnalaR grade.

2.1. Preparation of acid chlorides
Adipoyl and sebacoyl chloride were prepared by the reaction of Adipic and sebacic acid with thionyl chloride.

2.2. Synthesis of monomers
Condensation of p-hydroxybenzoic acid with adipoyl or sebacoyl chloride produced the monomers with dicarboxylic end groups. The reaction was carried out with (2:1 mol/mol) p-hydroxybenzoic acid and acid chloride in presence of pyridine at 50^0C for 2 hours. The product was precipitated in water and recrystallized from a mixture of methanol and dioxan.

2.3. Synthesis of polymers
The polyesters have been synthesized by following a condensation process under mild reaction conditions. Condensation of presynthesised monomers with hydroquinone and with bisphenol A produced the polyesters. Triphenlyphosphine was used as a phosphorylating agent and hexachloroethane was used as catalyst. The following composition of the materials was followed,

Monomer : Ph_3P : C_2Cl_6

1.0   :   1.2   :1.5

Monomer concentration was 0.5 mol lit $^{-1}$ and pyridine was used as the solvent.
In a solution of monomer and triphenylphosphine in pyridine, hexachloroethane was added with constant stirring. The reaction was allowed to continue for 2 hours at room temperature (30^0C). Within five minutes after the addition of hexachloroethane the reaction mixture become heterogeneous with the separation of solid polymer.The polymer was repeatedly washed with methanol and dried under reduced pressure. Yield was above 60%.
Reduced viscosities of the polymers were measured with 0.5% polymer solution in N-methyl-2-pyrrolidone (NMP) at 30^0C using Ubbelhode viscometer.

2.4. Infrared Spectroscopy (IR)
    IR spectra of the samples were recorded on a perkin-Elmer 1600 series FTIR spectrophotometer, 16 scans at a resolution of 4 cm^{-1} were signal averaged. The sample was used in pelletized form with KBr.

2.5. Optical microscopy

Liquid crystalline texture of the polymers was identified by optical microscopy using crossed polars. A polarizing microscope (Leitz Laborlux 12 pol S) fitted with Leitz MPS 46/52 photoauatomat was used for this purpose.

The sample in powder from was taken over a glass slide and was kept on a hot stage above its melting temperature for 5 minutes to destroy prior thermal history. A thin film was made out of it by pressing a cover slide on the molten sample. The glass slide was taken out of the hot stage and cooled to room temperature gradually.

2.6. Thermo gravimetric analysis (TGA)

TGA was done on a Perkin – Elmer 7 series Thermal Analysis system fitted with a data station. 10-15 mg sample was taken in an aluminium pan and the operation was carried out in nitrogen atmosphere. The sample was heated from 30^0C to 500^0C at a heating rate of 10^0C / min. weight loss of the sample at different temperature was recorded.

2.7. Differential scanning calorimetry (DSC)

A Metler FP84 HT hot stage was used for this purpose. 5-10 mg sample was taken in an aluminium crucible and was heated above its melting temperature. It was kept there for 3 minutes to ensure complete melting and was then cooled to room temperature. The scanning rate was 20^0 C/ min during the cycle.

2.8. Wide angle X-ray diffraction (WAXD)

X-ray diffraction pattern was obtained from a Philips X-ray Diffraction unit. CuK_α target and Ni filter were used and scattering angles (2θ) chosen were 0^0 to 33^0.The degree of crystallinity and the corresponding d values were calculated by Equation 1 and 2 respectively.

3.RESULT AND DISCUSSION

3.1. Synthesis of monomer

In order to synthesise copolyesters having regular sequence, one has to prepare a symmetric trimeric compound with a predesigned monomer sequence and polymerize it with a second monomer(13). Monomers with two aromatic rings with carboxylic acid ends groups connected through ester linkages and separated by polymethylene spacers have been prepared according to the following routes:
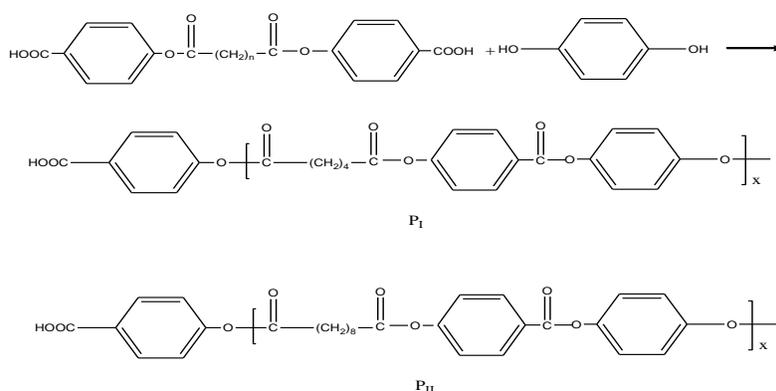

Scheme 1.
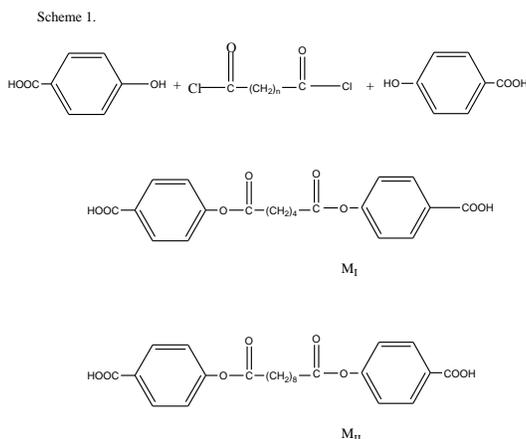
p-hydroxbenzoic acid was condensed with adipolyl and sebacoyl chloride to produce trimeric monomer M_I and M_{II}, varying in spacer lengths, respectively. Pyridine was used as HCl scavenger in this reaction which was necessary in order to achieve increased yield. These trimeric compounds retain their predesigned sequences in the polyesters when polymerized with aromatic diols.

3.2. Synthesis of polymers

It has been established that the properties of copolyesters, including liquid crystallinity are highly dependent not only on their chemical composition, but also on the comonomer sequences ([14]. However, the copolyesters with ordered sequence undergo a rather rapid sequence randomization above their melting points[15], although they seem to be fairly resistant to such randomization below their melting points[16].

In order to preclude any possibility of sequence randomization during polymerization, a typical polycondensation method has been developed to carry the reaction out at room temperature in presence of a phosphorilating agent.

In the present study, triphenylphosphine was used as the phosphorilating agent along with hexachloroethane and pyridine. Solvent effects are less important in phosphine because of the large size of phosphorous atom. Triphenylphosphine is a stronger nucleophile because of greater polarizability of the lone pair electrons than that of nitrogen. The greater rate of reaction with triphenylphosphine is accounted for the greater nucleophilicity of phosphorous atom rather than nitrogen atom. Therefore, in presence of triphenylphosphine, it was not necessary to carry out the condensation reaction in inert atmosphere, because the rate of reaction was only affected by the phosphines and not by nitrogen. Pyridine served the purpose of the catalyst as well as of the HCl scavenger. The reaction was carried out at room temperature for 2 hours. The product obtained was washed with methanol and water to eliminate pyridine and its hydrochloride.

The polymers were prepared using the following reaction sequence.

Scheme 2 A

P_I

P_{II}

Scheme 2 B

P_{III}

P_{IV}
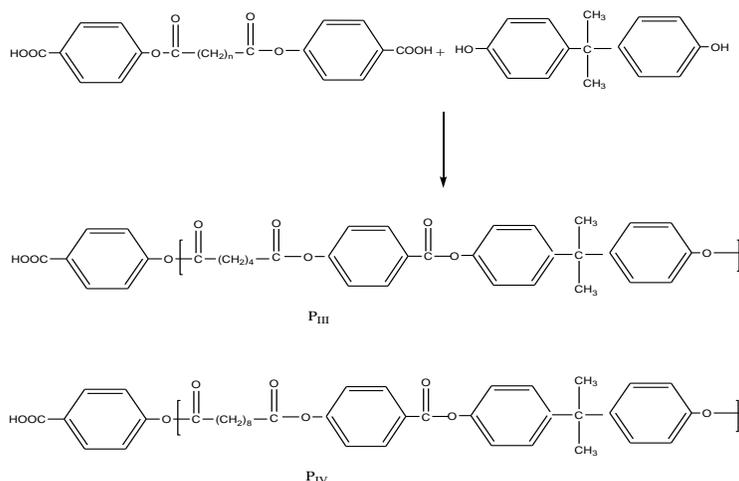
The products appeared in white powder form after purification. The approximate yield of the polyester samples under the specific reaction conditions, mentioned in section 2.3 was 65%. The polyesters showed good solubility in protonic solvents such as sulphuric acid and dichloroacetic acid at room temperature, but were insoluble in dimethyl sulphoxide (DSMO), ethers such as tetrahydrofuran (THF) and chlorinated hydrocarbon like chloroform even on heating. In NMP, solubility of the polymers was found to be higher at room temperature. Reduced viscosity of the polymer was measured in NMP at 30^0C, and was found to be in the range of 0.15 - 0.25 dl/g for all the four samples.

In sulphuric acid, viscosity values were found to be even lower than those in NMP. It may be due to the destruction of polymer chains in the acid solution. The viscosities of the present copolyesters with ordered sequence were lower than those of the random copolyesters prepared in melts.

3.3. Effect of reaction parameters on polycondensation reaction

The reaction parameters are known to have great influence on the rate of the polycondensation reaction. The molecular weight of the products also can be altered by altering the reaction parameters. In order to achieve optimum yield and reasonable molecular weight, the condensation process was carried out at different temperatures, with varying monomer concentrations. The solvent system has also been varied. The reaction was allowed to proceed for different time period. It has been observed that an optimization of molecular weight and yield of polyesters were achieved from a reaction carried out at 50^0C with 1% monomer concentration in pyridine after 8 hours of reaction.

3.4. Characterization of polyesters

It is necessary to analyze the chemical constitution, morphology, thermal properties and crystal structure of the polyesters synthesized in the course of study. In the present study, the polyesters have been characterized by a number of techniques which include FTIR spectroscopy, optical microscopy, TGA, DSC and WAXD.

3.4a. FTIR spectroscopy

The polyesters, synthesized by the condensation of aromatic diols and diacids through a low temperature procedure, were subjected to FTIR spectroscopy and thus permitted identification bands at 2940 cm^{-1} and 730 cm^{-1} associated with methylene spacers and aromatic rings respectively. Bands at 1600 cm^{-1} provided evidences for the existence of C=C stretching. Splitting of the carbonyl region into three distinct bands were also observed (Figure 1).The lowest frequency band at 1686 cm^{-1} assigned to carbonyls involved in hydrogen bonding.
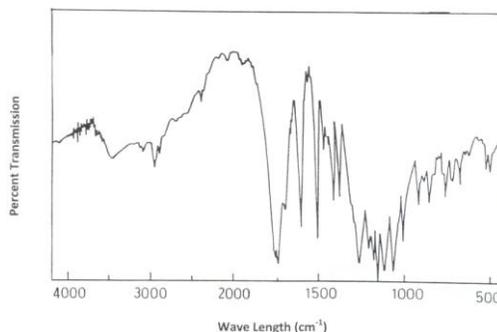

Figure 1. *FTIR scan for polyester P_I.*

The other two higher frequency components at 1734 cm^{-1} and 1750-1760 cm^{-1} were assigned to carbonyls in different environments. For polyesters P_I and P_{II}, absorption at the higher frequency level, i.e. at 1750 cm^{-1} was assigned to carbonyl group attached to phenylene ring on either side. But for P_{III} and P_{IV}, the environment of the carbonyl group was quite different. One side of it was attached to a phenylene ring and the other side was blocked by a 4, 4'-isopropylidene diphenylene group.This carbonyl group would be absorbed at even higher frequency, i.e. at 1760 cm^{-1} because of the hindering effect of the two methyl groups .The frequency component at 1734 cm^{-1} ascribed to ester carbonyl attached to the methylene group on one side and phenylene ring on the other side. A strong band at 1260 cm^{-1} assigned for the C-O stretching, was identified on the spectrograph for each sample.

3.4b. Optical microscopy

The liquid crystalline nature of the polymers was often studied by optical microscopy, which is the most convenient technique for the observation of their textures. LCPs are expected to retain their mesomorphic textures even in the solid films, cast from their melts. Thin films of all four copolyesters were studied under a polarizing microscope in crossed polarized light and were found to possess distinct textures, characteristic for the mesophases.

A thin film of polyester P_I, when studied under a microscope, indicated that the polyester possessed smectic mesophase coexisting with nematic one in its melt. A fan like texture characterized smectic mesophase for polyester P_{II} studied under an optical microscope. Blurred black threads, i.e. grain like texture in thin film of polyester P_{III} indicated that the mesophase it possessed was smectic in nature. The dark areas in the micrographs were the air

bubbles and had no sample in them. Morphology of polyester P_{IV} was found to be quite similar to that of P_{III} and it also exhibited grainy texture, with black areas for air bubbles in its melt cast film. Micrographs for the polyesters are shown in Figure 2 - Figure 5. It has been found[17] that presence of liner polymers having rigid blocks of mesogenic groups interconnected through flexible spacers in the main chain lead to mesophase formation. As the length of flexible spacers increases there is a tendency to form the smectic phase. A longer flexible segment imparts a higher degree of mobility for mesogens to align themselves to form smectic layers. For this reason, small rigid segments of P_I were oriented along both the smectic and nematic layers, where as flexible molecular chains of P_{II} with longer spacers were only aligned to form smectic phase.
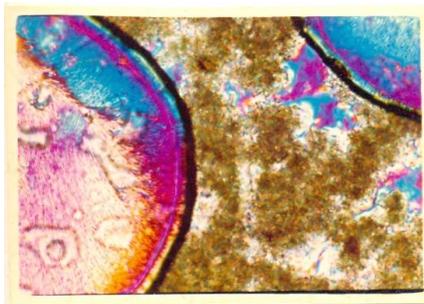

Figure 2. *Optical texture exhibited by thin film of polyester P_I.*
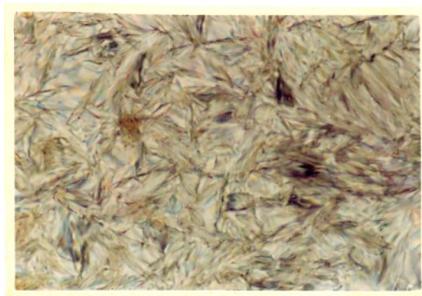

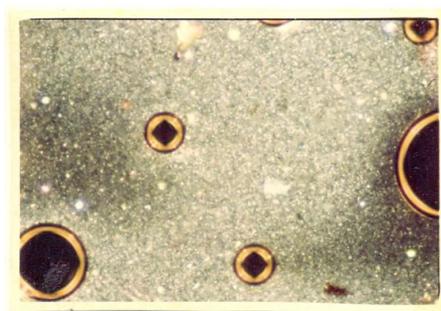Figure 3. *Optical texture exhibited by thin film of polyester P_{II}.*

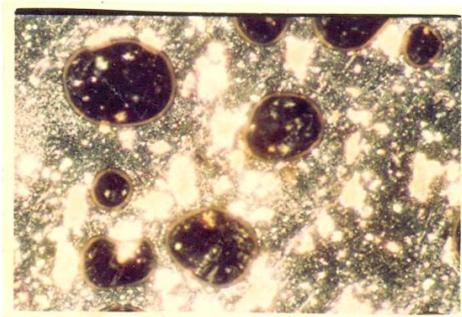Figure 4. *Optical texture exhibited by thin film of polyester P_{III}.*

Figure 5. *Optical texture exhibited by thin film of polyester* P_{IV}.

In polyester P_{III} and P_{IV}, presence of isopropylidene groups, connecting two aromatic rings in bisphenol A (used in the copolymerization process with a trimeric diacid),enhanced close packing of the chains to form smectic layers due to the sterical interlocking of the two methyl groups. Thin films of P_{III} and P_{IV}, when examined under the microscope, exhibited black threads i.e. a sand like texture which characterized smectic mesophase.

3.4c. Thermogravimetric analysis

TGA has been widely used for studying thermal stability of materials. According to the TGA thermograms of the copolyesters, shown in Figure 6, the decomposition was found to be complex. The major decomposition started at about 350^0C and was complete around 500^0C.Vigorous decomposition was preceded by initial degradation step (below 350^0C) in which slight loss in weight (5-10%) was observed. The decomposition temperature for 5-10% weight loss represents the thermal resistance of a polymer under experimental conditions. This has been defined as the temperature of incipient thermal degradation accompanied by the evolution of volatile products[18]. Another proposal has been introduced by Arnold[19]. He used the inflexion temperature of the thermogram as the decomposition temperature of the polymer. Considering the criteria the step is particularly important from the practical point of view. During processing, the copolyesters P_I and P_{II} would be subjected to temperature within the range of 200^0-300^0C in vacuum or under nitrogen and for a very short period in air where as polyester P_{III} and P_{IV} would be subjected to temperature within the range of 225^0-330^0C. Polyesters P_{III} and P_{IV} ,possessing isopropylidene diphenylene ester group as mesogen, were found to degrade initially at higher temperature than polyesters P_I and P_{II} with diphenylene ester group as mesogen.The decomposition of the polymers were found to reach 50% at 385^0- 450^0C depending on the length of the spacers. Polyesters with tetramethylene spacer (P_I and P_{III}) attended 50% weight loss quite earlier (i.e. below 400^0C) compared to the polyesters with octamethylene spacer (P_{III} and P_{IV}). It is evident from the thermal analysis of the polyesters that, though onset of decomposition took place at a temperature irrespective of polymer composition, at the later stage the rate of decomposition was low for the polymers with flexible molecular chains, either possessing longer spacers or having isopropylidene groups connected to the aromatic rings in the mesogen.
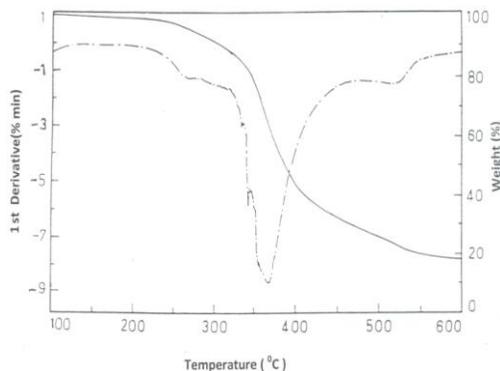

Figure 6. *TGA thermogram for polyester* P_1.

Above 500^0C, a delay in weight loss occurred and finally approached completion. To investigate the thermal decomposition of the copolyesters in more detail, the temperature corresponding to 5,10 and 50% weight loss as well as the mass of volatile products formed at 500^0C were determined and represented in Table 1.

3.4d. Differential scanning calorimetry

The analyses of thermal properties of the copolyesters have been made by the help of their DSC thermograms. Thermogram for polyester P_I is presented in Figure7. Presence of more than one endotherms in the thermograms revealed that the liquid crystal polymers undergo more than one phase transition processes when subjected to thermal treatment[9]. DSC scan for P_I exhibited four major endotherms. The lowest temperature endotherm i.e. the one at 187.6^0C was attributed to the onset of melting with formation of the mesophase. At 266.5^0C the polymer have undergone final melting or isotropization which were preceded by two inner mesophase transitions at 224.5^0C and 237.3^0C.
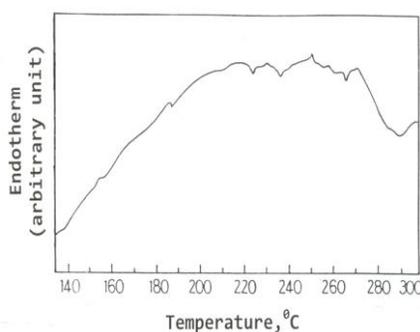
Figure 7. *DSC heating traces for polyester P_I .*

Generally the transition temperatures and the mesophase range decrease with increasing spacer length. Both the melting and isotropization temperature of polyester P_{II} decreased as compared with those of P_I, as the length of the flexible aliphatic segments increased in the polymer chain of polyester P_{II}. For polyester P_{III} and P_{IV}, it was noticed that the melting temperature of P_{IV} with longer spacer decreased, but the mesophase range increased. This is due to the fact that the longer aliphatic chain in flexible element of the macromolecule has a stronger influence on the melting temperature than on the isotropic temperature and caused the mesophase range to be wider.

The stereo geometry of bisphenol A, which was copolymerized with trimeric diacids, played an important role for the formation of the mesophase The isopropylene substituents connecting the two phenolic rings in bisphenopl A caused deviation from linearity and coplanarity of aromatic rings and disrupted the rigid rod like structure of the polymer, thus reducing their thermotropic nature. P_{III} and P_{IV} produced DSC thermograms with three endotherms each, which were attributed to the melting, inner mesophase transition and isotropization of the polymers.They possessed a narrower mesophase range compared to polyester P_I and P_{II}, both having linear rod like mesogens.

A liquid crystal polymer when cooled from its isotropic fluid state, recrystallization to a mesophase would be expected to take place followed by crystallization to solid state.The crystallization temperature could be demonstrated by the exotherms appearing on the thermograms upon cooling. No such noticeable exothermic peak was obtained on the cooling scans for any of the copolyesters under study.

Glass transition temperature (T_g) of the copolyesters could be determined from the heating scan of DSC analysis. T_g of P_I, i.e. 150^0C, was the highest and T_gs of the rest of the polyesters were found in the range of 110^0-115^0C.These values were much higher than those of the random copolyesters, which ranged from 82^0-125^oC .This can be ascribed to lower free volumes for the ordered sequence of the copolyesters than those of their randon sequence counterparts.It clearly demonstrated how strongly the T_g of copolyesters depends on the comonomer sequence. The transition temperatures of the copolyesters are given in Table 2.

3.4e. Wide angle X-ray diffraction

Wide angle X-ray diffraction powder pattern for the synthesised polyesters were collected at ambient temperature. From the corresponding diffractograms, shown in Figure 8, the crystalline behavior of the samples were determined in terms of degree of crystallinity, orientation of the crystals in various direction along the crystal axes and three dimensional lattice structure and the data were summarized in Table 3. Percent crystallinity of the polymers were also calculated.
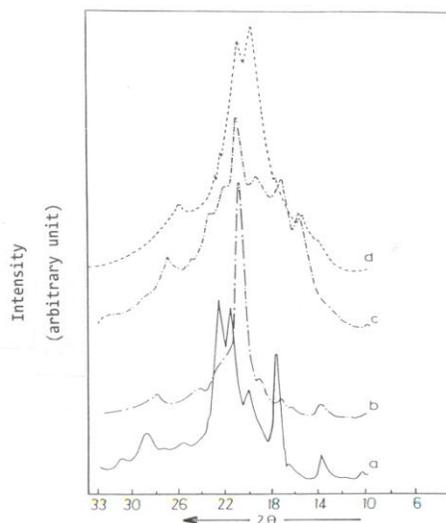
Figure 8. *Wide-angle X-ray powder pattern for*

a.   *Polyester P_I*

b.   *Polyester P_{II}*

c.   *Polyester P_{III}*

d.   *Polyester P_{IV}*

The semicrystalline polyester samples possessed more than 60% crystallinity and degree of crystallinity was found to depend on the rigidity of the molecular chain. Rigid molecules were expected to favour the crystal packing which in turn enhanced the degree of crystallinity.On the light of this concept, the polymer samples under study were compared. Polyester P_I and P_{II} possessed identical molecular structure only differing in spacer length. Due to the presence of tetramethylene spacer,more rigid P_I molecules were expected to pack themselves in more compact crystal lattice and thereby exhibiting higher degree of crystallinity (64.25%) than that of polyester P_{II} (61.19%) having less rigid molecular chains with longer octamethylene spacer. This was also true for the other pair of polyesters, i.e. P_{III} and P_{IV} which were also differing in their spacer length only. P_{III} with tetramethylene spacer exhibited higher degree of crystallinity (67.66%) than that of P_{IV} (64.50%) having octamethylene spacer.

The polyester crystals are orthorhombic in nature and were oriented in different directions along the axes of the orthorhombic plane.The X-ray patterns of the polyester samples showed a number of strong reflections for each of them which provide information about the crystal orientation in three dimensional arrays. Powder pattern of P_I shows strong reflection at $2\theta = 13.8^0$, 17.6^0, 20.2, 21.6^0, 22.8^0, 28.8^0 and 31.2^0 which correspond to the crystal orientation along 101, 011, 110, 111, 200, 201 and 211 planes in orthorhombic form. The orientation was more profound along 011, 111 and 200 plane for P_I crystals. Though the crystals of P_{II} were also oriented along several directions as in P_I , only one strong inter chain peak at $2\theta = 21.2^0$ was identified. It revealed that most of the P_{II} crystals were oriented along 111 planes. Longer molecular chains restricted their arrangement in space in different directions where short rigid rod like molecules were allowed to be oriented along various directions in the crystal plane. Scattering patterns of P_I and P_{II} were in support of this fact. Similarly, X-ray patterns of P_{III} and P_{IV} exhibited several inter chain peaks at different scattering angles which corresponded crystal orientation along various directions. The crystals were mainly oriented along 110 and 111 plane for both the polymers, though few other crystals of P_{III} were oriented along 011 and 002 plane.

Table 1.Thermal decomposition data for the polyesters

Polymer	Temp. at 5% decomposition (^{0}C)	Temp. at 10% decomposition (^{0}C)	Temp. at 50% decomposition (^{0}C)	Decomposition at 500^{0}C (%)	Onset of decomposition (^{0}C)
P_I	262.5	305.0	385.0	75	220.0
P_{II}	265.0	290.0	425.0	85	225.0
P_{III}	281.5	337.5	396.0	75.8	225.0
P_{IV}	325.0	315.0	450.0	83.5	225.0

Table 2.Thermal analysis data for the polyesters

Polymer	crystal→mesophase (^{0}C)	mesophase→mesophase (^{0}C)	mesophase→isotropic (^{0}C)	T_g (^{0}C)
P_I	187.6	224.4 and 237.3	266.5	150
P_{II}	134.4	181.7	216.5	115
P_{III}	140.4	150.3	161.6	110
P_{IV}	135.7	161.2	166.3	115

Table 3. X-ray diffraction data for the polyesters

Polymer		101	011	110	111	200	201	210	211	002
P_I	2θ	13.4	17.6	20.3	21.84	22.6	-	28.8	31.0	-
	d	6.4	5.03	4.36	4.06	3.92	-	3.09	2.88	-
	Intensity	F	S	F	VS	VVS	-	F	VVF	-
P_{II}	2θ	14.0	17.4	19.2	21.2	22.8	24.4	28.2	-	-
	d	6.3	5.1	4.6	4.1	3.89	3.64	3.16	-	-
	Intensity	VF	VVF	VVF	VVS	VF	VVF	VVF	-	-
P_{III}	2θ	-	18.0	20.0	21.5	-	-	27.6	-	16.4
	d	-	4.97	4.43	4.07	-	-	3.22	-	5.39
	Intensity	-	S	S	VVS	-	-	F	-	M
P_{IV}	2θ	-	-	20.0	21.2	-	26.0	-	-	15.5
	d	-	-	4.43	4.18	-	3.42	-	-	5.71
	Intensity	-	-	VVS	VS	-	VF	-	-	VF

VVS → 80-90%, VS → 60-80%, S → 40-60%, F→ 10-20%

4. CONCLUSION

Four controlled structure thermotropic main chain copolyesters have been synthesized. For this purpose, a typical polycondensation process has been followed under mild conditions.The reaction variables, such as temperature, time, monomer concentration, solvent system etc. have been found to have strong influence on the molecular weight of the polymers. Highest molecular weight of the polyesters has been achieved at 50^0C with 1% monomer concentration in pyridine after 8 hours of reaction. Analysis of the FTIR spectra of the polymer samples confirmed the molecular composition of four strictly alternating, highly ordered copolyesters having polymethylene chains as flexible spacers and phenylene or 4,4'-isopropylidene diphenylene groups as the rigid segments.The polyesters samples are semicrystalline and possess more than 60% crystallinity.The polyester crystals are orthorhombic in nature and are oriented in different direction along the axes of the orthorhombic plane. The polymers are thermally stable up to 220^0C without any degradation and only 5-10 % decomposition was noted at 300^0C as obtained from their TGA thermograms.The polymers are found to exhibit more than one phase transitions as approaching their isotropization temperature. Optical micrographs of the polyester films established their smectic mesophases.

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