

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis and Characterization of Thermotropic Liquid Crystalline Polyesters

S. N. Jaisankar^a; K. R. Haridas^a; Ganga Radhakrishnan^a

^a Polymer Division, Central Leather Research Institute, Madras, India

To cite this Article Jaisankar, S. N. , Haridas, K. R. and Radhakrishnan, Ganga(1997) 'Synthesis and Characterization of Thermotropic Liquid Crystalline Polyesters', Journal of Macromolecular Science, Part A, 34: 4, 713 – 723

To link to this Article: DOI: 10.1080/10601329708014997

URL: <http://dx.doi.org/10.1080/10601329708014997>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS

S.N.Jaisankar, K.R.Haridas and Ganga Radhakrishnan*
Polymer Division, Central Leather Research Institute, Adyar,
Madras 600 020, India.

Key words: Thermotropic liquid crystalline polyesters, High temperature X-ray, Differential scanning calorimetry, Spacer and Mesogen.

ABSTRACT

Synthesis and characterization of polyesters of 4,4'-dihydroxy biphenyl with succinic, adipic, suberic and sebacic acids were carried out. Initially the diacids were converted to the corresponding acid chlorides in dimethyl formamide (DMF). 4,4'-dihydroxy biphenyl was prepared from 4-hydroxy biphenyl by bromination and subsequent hydrolysis. The low molecular weight polyesters were prepared by the condensation of diacid chlorides with 4,4'-dihydroxy biphenyl in DMF at appropriate temperature. All the polymers were characterized by ¹H NMR, FT-IR, DSC and hot stage polarizing microscope. Thermotropic liquid crystalline behaviour was established by high temperature X-ray (HTXRD) at various temperature intervals. It was found that among the four compounds prepared, three of them showed nematic phase liquid crystallinity with the exception of the ester of succinic acid.

INTRODUCTION

Interesting studies on thermotropic polymers containing mesogenic units having structures with aromatic and cyclo aliphatic rings connected with or without flexible spacers have been reported in the past two decades [1-9]. Both the molecular structure of the compounds and the manner in which they are assembled can have a great effect on the thermal properties of these polymers [4,5]. In short,

changes in type and direction of these connecting bonds alter the polarizability and geometry of the mesogenic units which in turn alter the liquid crystalline properties. Synthetic routes are available for polymers with well defined arrangements of the mesogenic units in the main chain [6,7] and an interesting series is thermotropic polyesters obtained by in-situ reaction of the mesogen 4,4'-dihydroxy biphenyl. Recently, a few papers have been found in literature regarding the synthesis of mesomorphic compounds based on biphenyl in homo as well as copolyesters [8-10,23,24].

In this paper we have described the synthesis and characterization of liquid crystalline polyesters based on 4,4'-dihydroxy biphenyl and dicarboxylic acids containing even methylene groups. The procedure capable of preparing polyesters directly from hydroxy compounds with acids under mild condition would be a useful one and is very difficult to attain at ordinary conditions [11,18-20]. The common reagents for conversion of acids to acid chlorides, thionyl chloride alone or thionyl chloride in common organic solvents is not effective as the reactant gets charred even below room temperature. We have succeeded in the reaction of thionyl chloride in DMF for the direct polyesterification of hydroxy compounds with acids under mild conditions [21].

MATERIALS AND METHODS

The solvents, chloroform, DMF (AR, S. D. Fine chem., India) were distilled and used. Thionyl chloride (AR, S. D. Fine chem., India) was purified before use by the procedure of Vogel [12a]. The dicarboxylic acids (adipic, succinic) (AR, S. D. Fine chem, India) sebacic (BDH) and suberic (E. Merck) acids were recrystallised before use. 4-hydroxy biphenyl (E. Merck) was recrystallized and used. Bromine (AR, S. D. Fine chem., India) was used as received.

1. Preparation of 4,4'-dihydroxy biphenyl

4-Bromo-4'-hydroxy biphenyl was prepared by the conjugated procedure of Vogel [12 b]. One mole of 4-hydroxy biphenyl was dissolved in 100 mL chloroform in a three necked flask equipped with a dropping funnel and a magnetic stirrer. The contents were then cooled to 0°C by an ice-salt mixture. To this was added drop wise 0.6 moles of bromine in 25 mL chloroform for 2 hours from a dropping funnel and stirred while maintaining the temperature at 0°C. After the addition of the bromine, stirring was continued for an additional hour at the same temperature. Excess bromine was removed by washing the mixture with sodium bisulfate solution (4 g in 25 mL water). The mixture was then twice extracted with water. The organic layer was separated and dried with anhydrous potassium sulphate. Pale white crystalline 4-bromo-4'-hydroxy biphenyl was obtained by the removing the solvent under vacuum. It was recrystallised from chloroform. The substitution of bromine at the para site was confirmed by ¹H NMR and also by the estimation of bromine [13]. The observed value was in good agreement with the calculated value.

Observed bromine value : 32.45%
Calculated bromine value : 32.13%
Yield : 89 %
Melting point : 56°C
TLC : Chloroform : Methanol, 75:25; single spot, rf: 0.5
IR peaks (cm^{-1}) : 3350 (OH stretching), 3025 (aromatic -CH stretching), 1370 (-C-O stretching), 840 (-C-H deformation) 620 (-C-Br stretching).
 ^1H NMR (ppm): 7.32 - 7.25 (multiple peak, biphenyl hydrogens), 4.45 (H of -OH)

4,4'-dihydroxy biphenyl was obtained from the above bromo compound by the following procedure of hydrolysis.

To a solution of 0.8 mol of NaOH in 50 mL water in a beaker, added 0.8 mol of the above bromo compound with stirring. After complete dissolution of the compound, it was boiled for 45 minutes at 100 °C, cooled to room temperature, 50 % of HCl was added drop wise till all the white product precipitated from the solution. The precipitate was washed with water, recrystallised from chloroform and dried in vacuum.

TLC : Chloroform:Methanol, 75:25, single spot, rf:0.5

Yield : 92 %

Melting point : 230°C

IR peaks (cm^{-1}): 3380 (-OH stretching), 3080 (aromatic -CH stretching), 1380 (-C-O stretching) and 830 (-CH deformation)

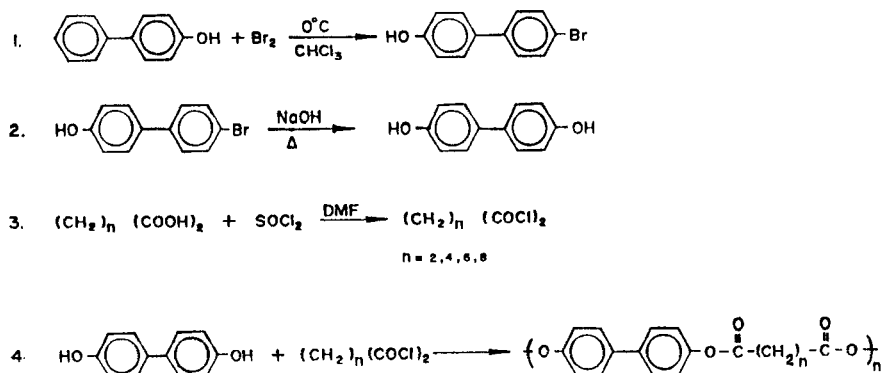
^1H NMR (ppm): 7.4-7.2 (multiple peak, biphenyl hydrogens) and 4.4 (hydrogen of -OH)

Preparation of the polymers

The use of thionyl chloride in DMF is a method for the formation of acyl chlorides from aliphatic carboxylic acids [21-22]. One mole of thionyl chloride was taken in a three necked flask provided with a calcium chloride guard tube and dropping funnel. DMF was added drop by drop at 0°C with stirring till no more sulphur dioxide gas evolved. Then, 0.5 moles of the corresponding acid (succinic, adipic, suberic and sebacic) was added in small quantities with stirring. The temperature was raised slowly to 30°C and the reaction mixture was kept for one hour. Excess thionyl chloride was distilled off. The acid chloride in DMF was then carefully poured into a dry polymerization tube and to this added a solution of 0.5 moles of 4,4'-dihydroxy biphenyl in DMF along with 2 mL of dry pyridine as an acid acceptor. The viscous liquid was then poured into crushed ice when the polymer separates out. The polymer was purified twice by reprecipitation and dried in vacuum (scheme 1).

IR spectra (KBr pellet) were recorded on a Nicolet 20 DX FT-IR spectrometer.

^1H NMR spectra were recorded on a Bruker CXP-90 MHz with DMSO- d_6 or



Scheme 1

CDCl_3 as solvents. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were carried out on a Du Pont 990 thermal analyzer with a 951 TGA and 910 DSC modules respectively. The samples were analyzed in nitrogen atmosphere at a heating rate of 10°C per minute. Optical micrographs were taken on a Reichert-Jung thermogallen hot-stage optical microscope with a magnification of 100X attached with a polarizer and a 35 mm Pentax camera. The X-ray diffraction patterns were recorded on product samples with two different X-ray instruments. Phillips X-ray diffractometer using $\text{CuK}\alpha$ radiation at zero background using a silicone 811 background 289. Rigaku D/Max-C (Japan) diffractometer using nickel filtered $\text{CuK}\alpha$ radiations. The molecular weight of the samples were determined by gel permeation chromatography (GPC) using Waters GPC instrument and a 410 model refractive index detector using THF as solvent.

RESULTS AND DISCUSSION

^1H NMR spectra of all the four polymers prepared (D2 and D4 in CDCl_3 and D6 and D8 in DMSO-d_6). The absence of acid protons indicates that there is no free carboxylic group in these polymers. The multiple peaks at 7.00 - 7.60 ppm are due to the biphenyl ring and peaks at 1.6 - 2.49 ppm indicates that of the methyl hydrogen connected to the ester linkage as well as the hydrogens of $-\text{CH}^2-\text{CH}^2-$ (except in the case of D2). In the FTIR spectrum of the polymer show the peaks at 3028 cm^{-1} (aromatic $-\text{CH}$ stretching), 2920 cm^{-1} (asymmetric $-\text{CH}$ stretching), 1740 cm^{-1} (saturated acyclic $-\text{CO}$ stretching), 1580 and 1500 cm^{-1} ($-\text{C}-\text{C}-$ multiple bonds stretching) and 1380 cm^{-1} ($-\text{CO}$ stretching) confirm the structure of the polymer. Table 2 gives the molecular weight, transition temperatures and decomposition temperatures of the compounds. Table 1 show the polymerization code and polymers code.

TABLE 1 POLYMER COMPOSITION AND POLYMER CODE

S.NO	COMPOSITION	POLYMER CODE
1.	SUCCINYL CHLORIDE/BIPHENOL	D2
2.	ADIPOYL CHLORIDE/BIPHENOL	D4
3.	SUBEROYL CHLORIDE/BIPHENOL	D6
4.	SEBACOYL CHLORIDE/BIPHENOL	D8

TABLE 2 MOLECULAR WEIGHT, TRANSITION TEMPERATURE, DECOMPOSITION TEMPERATURE AND YIELD OF D2,D4,D6,D8

Compounds	$M_n \times 10^{-3}$	Transition Temperature(°C)			Decomposition Temperature (°C)
		1	2	3	
D2	5.2	-	-	146	228
D4	4.8	95	-	280	290
D6	5.1	65	88	123	261
D8	5.2	60	85	118	240

In this paper, we discuss the influence of the spacer length on the liquid crystallinity of biphenyl polyesters. Because of the linear nature of these polymers, it was expected that nematic order would prevail in these thermotropic liquid crystalline polyesters [14]. However, from the DSC spectra, Fig. 1 existence of more than one phase for the two polymer (D6 and D8), is shown, while the polymer of adipic acid with the diol (D4) show only one liquid crystalline phase. It is also clearly seen that all the polymers except (D2) show liquid crystallinity behaviour at a wide range of temperatures. The compound (D2) does not show liquid crystallinity may be due to the lack of spacer to mesogenic ratio in the main chain [14]. Micrograph of this compound near melting temperature does not show any texture in cross polarization which also proves that it is not a liquid crystalline polymer.

Powder X-ray diffraction pattern at the crystalline temperature is very useful in the determination of the structure of the anisotropic melt, because the anisotropic technique is not always be counted as an unambiguous determination of the type

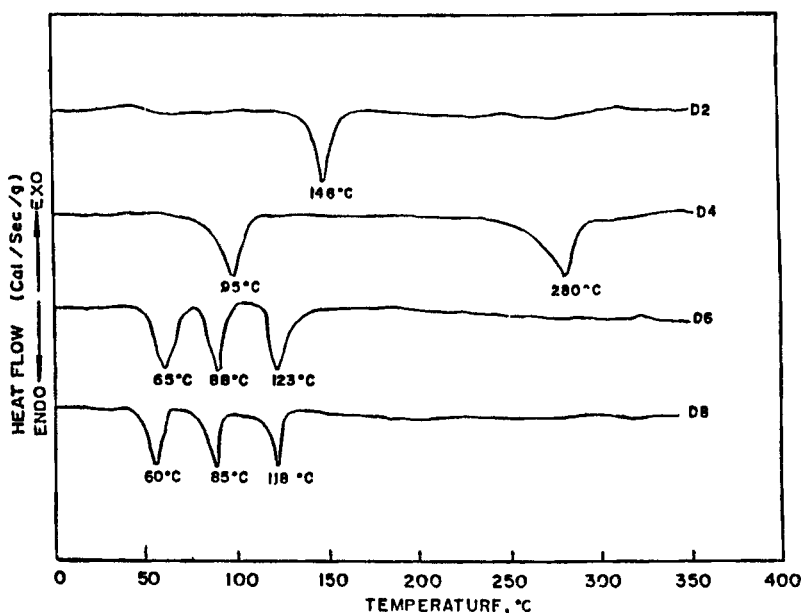


FIG. 1 DSC THERMOGRAMS OF D8, D6, D4, AND D2.

of mesogenic phase present. X-ray diffraction peaks for polyester based liquid crystalline polymer (D8) at different temperature are shown in Fig.2. For (D8) samples, four X-ray diffractometric measurements were performed [16] i) one at room temperature ii) at 85°C iii) crystalline temperature at 118°C and iv) at room temperature after complete heating and cooling cycle. In all the cases, i) and iv) was the same as ii) and iii). From the Fig. 2 the number of peaks distributed at 2Θ values from 8 to 30 degree in the diffraction patten indicate the crystalline nature of the polymers. The liquid crystalline polymer with 2Θ values from 15 to 25 degree confirm the nematic nature as observed from the hot stage optical polarizing microscopy (HOPM) studies. Usually the diffraction pattern from unoriented liquid crystalline state of the polymer shows sharp peak at 2Θ values from 2 to 5 degree. Peak sharpness of the liquid crystalline polyesters increases with increases mesogenic content, suggesting that chain rigidity promotes increase in the order of the polymer samples. The diffractogram of liquid crystalline polymers in the crystalline state contain three sharp reflection of D8 at different temperature levels. From Table 3, 2Θ values from 17 to 25 degree intermolecular spacing of 4.5 to 4.8 °A due to nematic texture and 2.98 °A shows the T_{SA-N} textures already reported [17-20]. There is no difference between the diffractogram of liquid crystalline state after repeated heating and cooling cycles.

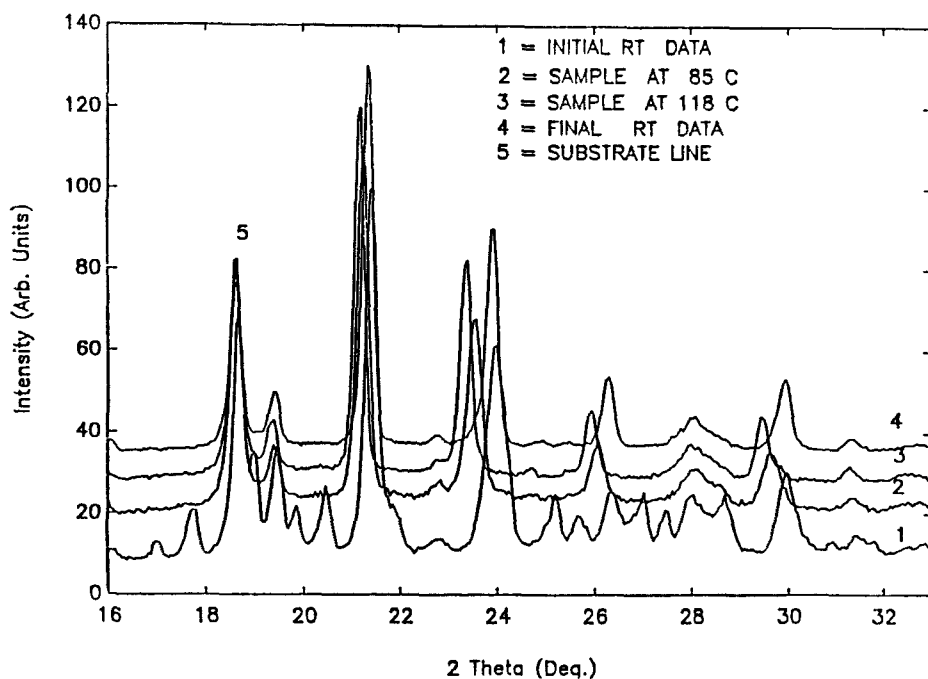


FIG. 2 X-RAY DIFFRACTION DATA OF (D8) SAMPLE.

TGA shown in Table 2 all the four compounds decompose above 200 °C and show only one decomposition. The compounds (D4) are thermally more stable (decompose at 290°C) followed by D6, 265°C, D8, 248°C and D6, 230°C. There is no definite relations between thermal stability and the spacer length of these polymers.

The length of the spacer and nature of mesogenic moiety are important in designing liquid crystalline polymers. It is shown that the crystal to nematic transition temperature decreases with the length of the flexible spacer for a particular mesogen [15], but becomes almost constant when it exceeds a certain value, and finally becomes non-liquid crystalline when it lacks spacer to mesogen ratio. Here, when we use the spacer as ethylene,(D2) there is no liquid crystallinity. The polymer of adipic acid with biphenyl (D4) butyl spacer show a transition temperature to isotropic state at 280°C, while that of suberic and sebacic (D6 and D8) are nearly equal to 150°C.

Fig. 3,4 show the optical micrographs of the polymer (D8) at a magnification of 100X and the temperature of 70, 105°C. The prepared texture seen in the

TABLE 3 X-RAY DIFFRACTION DATA

Experimental				Observed [16-17]	
Temp(°C)	2 Θ	I%	d (°A)	d(°A)	hkl
20	18.68	68.1	4.74	4.5-4.8	112
	18.99	34.2	4.67	4.5-4.8	112
	19.46	35.9	4.55	4.5-4.8	112
	21.42	100	4.14	4.15	212
	21.97	30.2	2.98	2.98	112
85	18.65	73.9	4.76	4.5-4.8	112
	19.40	26.9	4.57	4.5-4.8	112
	21.28	100	4.17	4.15	212
	23.58	58.6	3.77	3.74	004
	29.62	25.5	2.99	2.99	---
118	18.62	59.4	4.76	4.5-4.8	112
	19.39	22.9	4.57	4.5-4.8	112
	21.18	100	4.19	4.15	212
	23.38	61.8	3.8	3.83	102
20	18.63	46.4	4.76	4.5-4.8	112
	19.42	19.8	4.57	4.5-4.8	112
	21.37	100	4.15	4.15	212
	23.92	60.0	3.74	3.74	004
	26.29	23.4	3.39	3.39	122
	29.94	22.8	2.98	2.98	122

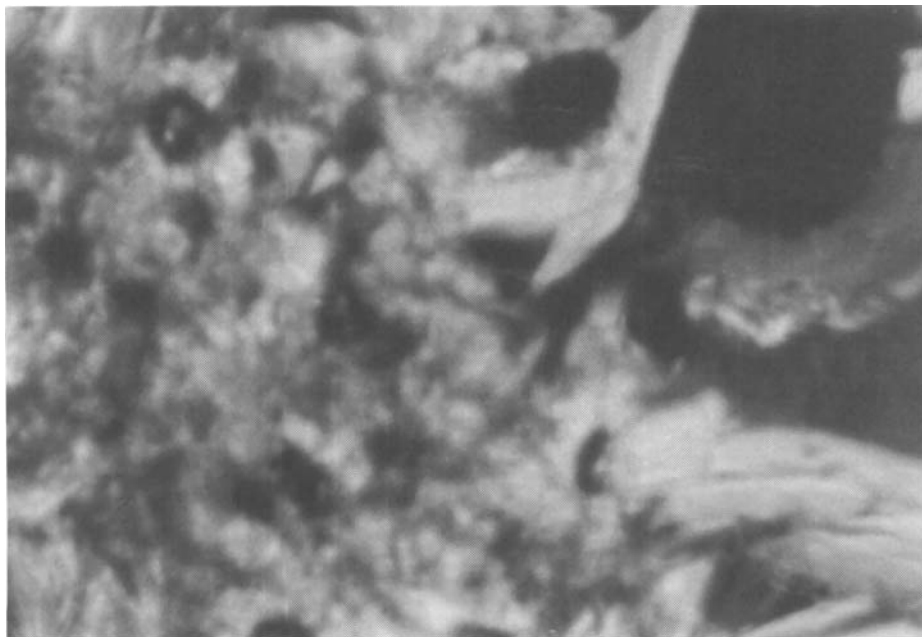


FIG. 3 MICROGRAPH OF (D8) AT 70°C, MAGNIFICATION OF 100X.

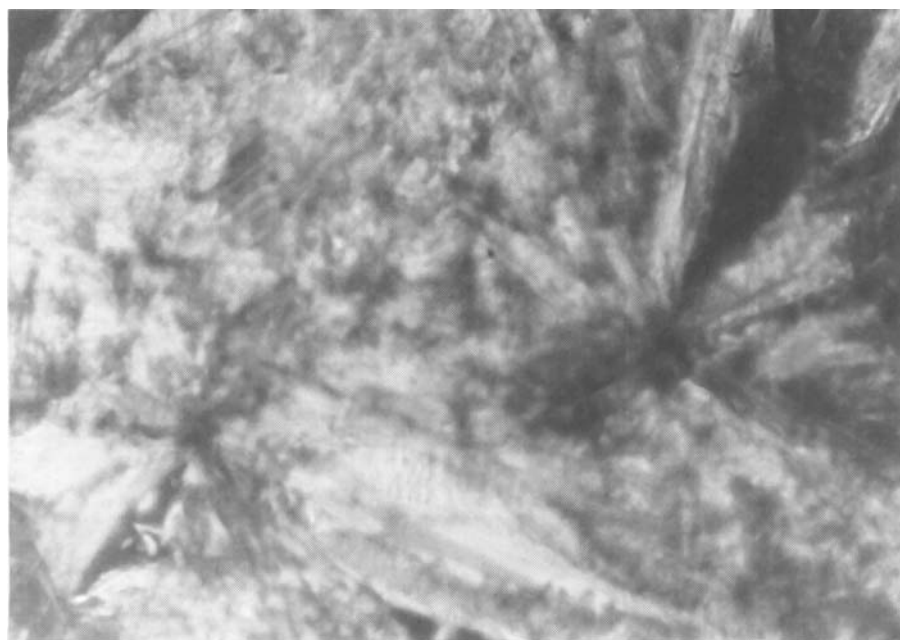


FIG. 4 MICROGRAPH OF (D8) AT 105°C, MAGNIFICATION OF 100X.

polarizing microscope and sequential order of appearance of the mesophase with increasing temperature confirm that the structure obtained for these polymers are nematic phases. The highly ordered one will appear at the lower end of liquid crystalline temperature range.

CONCLUSION

Studies on the liquid crystalline behaviour of polyesters based on 4,4'-dihydroxy biphenyl and aliphatic acid chlorides of varying spacer lengths, 2,4,6 and 8 methylene groups show that all the polymers except the one with spacer length of 2, (methylene group) show highly ordered liquid crystallinity. This polymer shows nematic liquid crystallinity as confirmed by high temperature X-ray studies. Polyesters having a spacer length of 4 methylene group show higher liquid crystalline range while the range and temperature decreases with the length of spacer.

REFERENCES

1. C. Ober, R. W. Lenz, G. Galli and E. Chiellini, *Macromolecules*, **16**, 1034 (1983).
2. K. Clausen, J. Koos, K. Rasmussen, and J. Sonne, *Macromolecules*, **22**, 2660 (1987).
3. H. Finkelmann and G. Rehage, "*Advance Polym. Sci.*" **60/61**, 99 (1984).
4. A. Blumstein, S. Vilasagar, S. Ponrathanam, S. B. Clough and R. B. Blumstein, *J. Polym. Phys. Edn.*, **20**, 877 (1982).
5. G. W. Gray, "Molecular structure and the properties of liquid crystals." Academic Press, London (1962).
6. A. C. Griffin and S. Havens, *J. Mol. Cryst. Liq. Cryst. Let.*, **49**, 239 (1979).
7. A. Roviell and A. Sirigu, *J. Polym. Let. Ed.*, **13**, 455 (1975).
8. W. R. Krigbau, *Macromolecules*, **16**, 1271 (1983).
9. S. L. Kwolek and R. R. Lense, *Macromolecules*, **19**, 1789 (1986).
10. Y. G. Lin and H. Winter, *Macromolecules*, **21**, 2439 (1988).
11. N. B. Lorette and J. H. Brown, *J. Org. Chem.*, **24**, 261 (1959).
12. Vogel's, Text book of practical Organic Chemistry, 4th. Edn. ELBS Publication, London, 1987, a) p484 b) p781.
13. A. Blumstein, K. N. Sivaramkrishnan, R. B. Blumstein and R. S. Clough, *Polymer*, **23**, 47 (1982).
14. C. K. Ober, J. I. Jin, R. W. Lenz, *Advances in Polym. Sci.* Vol.59, Ed. M. Gorden, Springer-Verlag, Heidelberg, 1984, p103.
15. A. Blumstein, K. Sivaramkrishnan, S. Vilasagar, S. B. Clough and R. B. Blumstein, *Springler series of Chem.Phys.*, Ed. W. Helfrich and G. Heppke, Vol.11 1980, p252.
16. Kathleen Van de Velde Marcel Van Beylen, Raoul Ottenburgs and Celest Samyn, *Macromol. Chem. Phys.* **196**, 679 (1995).

17. Bernd Zschke, Willy Frank, *Polymer Bulletin*, **27**, 1 (1991).
18. R. Hoseman and D. L. Fischel, *Mol. Cryst. Liq. Cryst.* **10**, 273 (1970).
19. A. deVries and D. L. Fischel, *Mol. Cryst. Liq. Cryst.*, **16**, 311 (1972).
20. A. Cassolo, M. Foa, D. Dainell, R. Scordamaglia, L. Barino and L. L. Chappy, *Macromolecules*, **24**, 1701 (1991).
21. K. R. Haridas, Ganga Radhakrishnan, *Die Angew. Makromol. Chem.*, **288**, 1 (1995).
22. K. R. Haridas, Ganga Radhakrishnan, *J. Polym. Sci. Part -A Polym. Chem.*, **33**, 901 (1995).
23. P. K. Bhowmik, P. O. Gray, R. W. Lenz, *Macromol. Chem.*, **192**, 415 (1993).
24. V. Percec, D. Thomazos, *Indian J. Tech.*, **31**, 339 (1993).