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Synthesis and Properties of Thermotropic Liquid Crystalline Polyesters Based On Anisole Moiety

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Abstract**—**1,6-Di-(p-metoxyphenyl)-1,6-hexanediol (I), was used as starting monomer for preparing new liquid crystalline polyesters. The polyesters were prepared by reacting (I) with adepoyl, suberoyl and sebacoyl dichlorides by interfacial polymerization technique. The resulting polymers had inherent viscosities in the range of 0.86-0.97 g/dl. These polyesters were characterized by elementary and spectral analyses. All of the synthesized polymers exhibited poor solubility in common organic solvents at room temperature, but readily dissolved in aprotic solvents. Thermal behavior of the synthesized polymers was evaluated by TGA analyses and correlated with their structure. The mesomorphic properties were studied as a function of the different dicarboxylate alkanes space length. Analysis by DSC and OPM demonstrated that the polyesters form nematic mesophases over wide temperature range.

Keywords**—**Anisole, Liquid crystal, Polyester, Synthesis, Thermotropic.

I. INTRODUCTION

THERMOTROPIC liquid-crystalline polyesters have drawn a great deal of attention in recent years, focusing their structure–property relationship [1], [2]. Introduction of methylene spacer with long substituents unit as pendent group in the polymer chain can reduce the melting transition temperature while maintaining liquid crystalline properties. However, random distribution of pendent groups in the polymer chain may reduce the mesophase-forming ability as well as thermal transitions due to the repulsive forces, which disrupt close chain packing of the polymers [3]-[5]. Polyesters with an unusual arrangement of the mesogens with respect to the polymer chain as well as combined thermotropic liquid-crystalline polymers are able to form variety of mesophaes [6]-[9]. Many research articles and reviews have been published concerning the combination of mesogenic as pendant group and even number of methylene units in the chains of polyesters [10]-[14]. In this paper, I have described the synthesis and characterization of liquid crystalline polyesters based on anisole moiety as pendant group, aiming to elucidate the influence of methylene spacer and anisole moiety on the stability range of the glass transition temperature and thermotropic mesophase. With the aim of shedding light on certain characteristics, viscosity, solubility and thermal stability were also examined and discussed.

II. EXPERIMENTAL

A. Reagents and Solvents

Anisaldehyde, 1,4-dibromobutane and magnesium metal (Aldrich) were used without purification. Methylene chloride and all other solvents were of high purity but were further purified by standard methods [15].

B. Measurements

Melting points were determined on an Electrothermal IA9100 melting point apparatus and are uncorrected. Elemental analyses were performed on ElementarVario EL III instrument. IR spectra were recorded, as KBr pellets, on Schimadzu IR-200-91527 spectrophotometer and wave numbers are given in cm^{-1}. ^1H NMR spectra, in DMSO solution, were recorded on Bruker DRX-300 spectrophotometer at room temperature using TMS was used as an internal reference. Viscosity measurements were made with a 0.5% (w/v) solution of polymers in DMF at 25°C using an Ubbelohde suspended level viscometer. Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) of the polymers were carried out in air using a DuPont 2000 thermal analyser at a heating rate of 10°C min^{-1} The isotropization temperatures were determined by observing the polymer melts with a polarizing microscope Carl-Zeiss (Jena) equipped with a hot-stage chaixmeca (Nancy, France). The temperature at which initial formation of the isotropic phases occurred was taken as the isotropization temperature (Ti). At the same time, the optical textures of the polymer melts were closely examined to determine the nature of the mesophases. The molecular weights of polyesters were evaluated by following the standard protocol [16].

C. Monomer Syntheses

Synthesis of 1,6-Di-(p-metoxyphenyl)-1,6-hexanediol: A Solution of 1,4-bis(dibromomagnesio)butane **(2)** [synthesized from magnesium (0.25g) and 1,4-dibromobutane **(1)** (1.2g)] in dry ether (50ml) was added to a solution of anisaldehyde (1.37g) in dry ether (10 ml) with stirring under nitrogen gas during the period of 2h. The reaction mixture was stirred at room temperature for 5h and refluxed for 2h, cooled and decomposed by pouring into a saturated ammonium chloride

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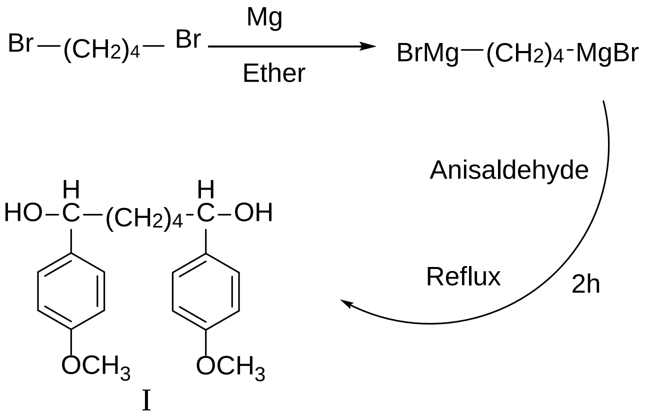
solution (70 ml). The product was extracted with ether and the ether extract was washed with several portions of water, dried and recrystallized from mixture of benzene-petroleum ether (40-60) as yellow needles. Yield 75%, mp.131°C (Lit. mp.132 °C) [17]. Calculated composition of $C_{20}H_{26}O_4$: C, 72.72; H, 7.87 %, Found: C, 72.91; H, 7.24. IR (KBr, ν cm^{-1}): at 2965 cm^{-1} (C-H stretch), at 3420 cm^{-1} (OH stretch).^1H-NMR (DMSO) δ: at 9.4 (s 2H of 2-OH groups), at 6.5-7.1 (m 8H of Ar-H), at 3.7 (s, 6H of $-CH_3$), 1.4 (t, 2H of –CH), at 1.9 (t, 4H of $–CH_2$), at 2.4 (t, 4H of $–CH_2$).



Scheme 1 Synthesis of monomer I.

D. Polymer Synthesis

A typical example of the interfacial polymerization for polyesters **V-VII** is described. A three necked flask equipped with a mechanical stirrer , dry nitrogen inlet and outlet and a dropper was charged with a mixture of 1,6-Di-(p-metoxyphenyl)-1,6-hexanediol (0.01 mol), methylene chloride (25 ml) and a suitable quantity of NaOH. A stoichiometric quantity (0.02 mol) of the NaOH dissolved in water (100ml) was also introduced. After mixing, adipoyl chloride (24 ml) was added in a period of 3 min at 25 °C and vigorously stirred. After complete addition of acid chloride, stirring was continued for 40 min whereby a dark coloured solid separated out, which was filtered, washed with water, hot alcohol and acetone and dried under reduced pressure (1 mm Hg) at 100 °C. The elemental analysis and physical characteristics of polyesters are presented in Table I.

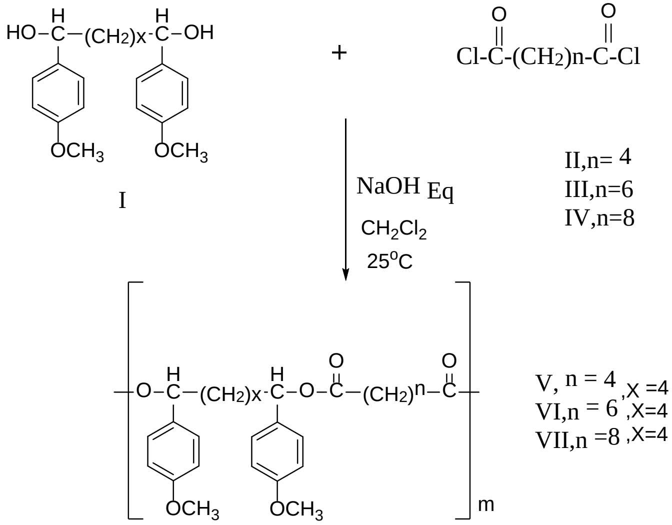
III. Results And Discussion

A. Synthesis of monomer (I)

In the present study, new thermotropic liquid crystalline polyesters based on 1,6-di-(p-metoxyphenyl)-1,6-hexanediol **(I)** was prepared in an appreciable quantity by Grignard reaction, when an organomagnesium bromide (Grignard reagent) was added to 2 moles of anisaldehyde to form secondary alcohol **(I)** in the presence of dry ether as shown in Scheme 1.

B. Synthesis of polymers (V-VII)

An unreported class of polyesters **(V-VII)** based on anisole moiety as a pendent group in the polymer main chain were prepared by treating equimolar quantities of 1,6-Di-(p-metoxyphenyl)-1,6-hexanediol **(I)** with different acids adipoyl, suberoyl and sebacoyl dichloride, as shown in Scheme 2.



Scheme 2 Syntheses of polyesters V–VII.

The structures of polyesters **V-VII** were confirmed by elementary analysis, FT-IR and ^1H-NMR spectra. The IR spectra of all the polyesters showed disappearance of the characteristic absorption band of the –OH group at 3400-3500 cm^{-1} and the appearance of the carbonyl group (C=O) of ester linkage at 1690-1710 cm^{-1}.All the polyesters exhibited approximately similar bands (Fig. 1).

TABLE I
RESULTS OF ELEMENTAL ANALYSES AND SOME PHYSICAL PROPERTIES OF POLYESTERS (V-VII)

Polymer code	Yield %	Mn^a	$\eta_{inh}{}^b$ dIg^{-1}	Molecular formula (mol. wt)	Elemental analyses	C%	H%
V	85	13550	0.97	$C_{26}H_{32}O_6$	Calc.	70.90	7.27
				(440)	Found	71.02	7.65
VI	80	11400	0.86	$C_{28}H_{36}O_6$	Calc.	71.79	7.69
				(468)	Found	71.05	7.42
VII	83	12560	0.91	$C_{30}H_{40}O_6$	Calc.	72.58	8.06
				(496)	Found	73.09	7.91

[a]Measured by end group analysis, [b]Measured for solutions in DMF, with c = 0.5 g/100 mL at 25°C.

The number average molecular weight (Mn) of the unsaturated polyesters was determined using end-group titration techniques, and it ranged between 11400-13550 g/mol. The inherent viscosity (η_{inh}) of polymers was measured in DMF at 25°C and the results are presented in Table I. These results revealed that the polymers were of moderate molecular weight.

C. Solubility

Solubility of the polyesters was determined for powdery samples (0.2 g) in (10 ml) of solvents at 25°C. Most of the polyesters were soluble in aprotic solvents that included dimethylsolfoxide, dimethylformamide, dimethylacetamide and tetrahydrofuran. In common organic solvents and halogenated hydrocarbons, all the polymers were partially soluble (except polymer **VII**, which is soluble in methylene chloride and chloroform). This may be attributed to the

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presence of aliphatic chain with eight methylene groups and the rigid anisole position of the main chain causing increase in solubility.

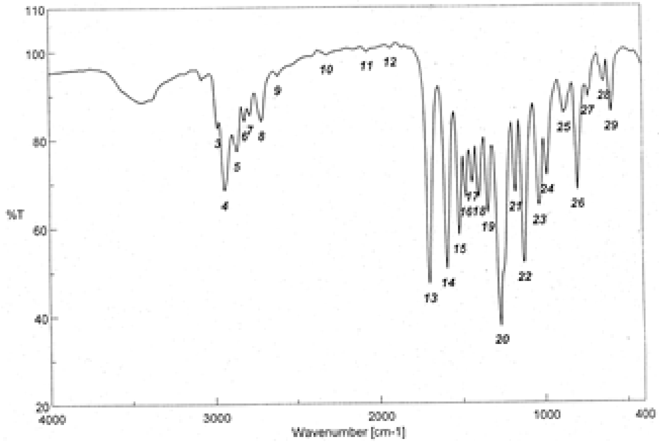

Fig. 1 IR spectra of polymer **V**.

D.TGA Measurements

Thermal behavior of the polyesters (**V–VII**) was evaluated by TGA and DTG in air at a heating rate of 10°C min^{-1}. The thermographs of these polymers are given in Fig. 2, while Table II gives the temperature for various percentages of weight loss. The initial decomposition of polyesters was observed to start at 500°C. The thermographs also indicated in Figure2 that the polymers decompose in two stages and the mass loss is seen to be rapid between ~190-350°C for the polymer **V** in the first region, and between ~250-350°C in the second region. For the polymer **VI**, the mass loss was rapid between ~210-340°C in the first region and between ~340-500°C in the second region.

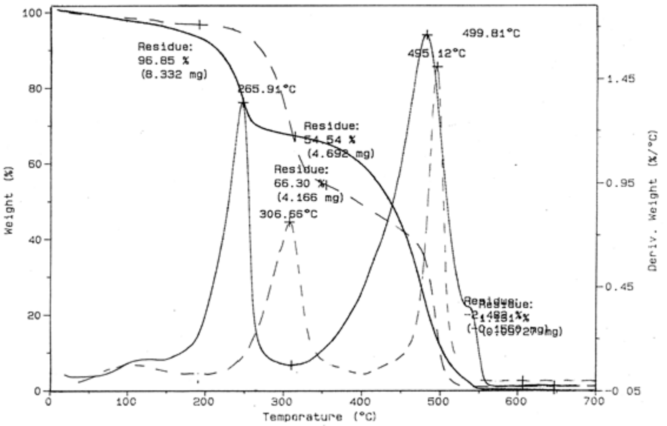

Fig. 2 The TGA and DTG traces of polymers V (–) and VI (- - -) in air at a heating rate of 10 °C/min.

All the studied polymers decompose in the first stage between 190–350°C, whereas in the second stage, they decompose at 350-500°C, which depends on the nature of the polyester. The expected nature of decomposition of these polymers is a pyrolytic oxidation of -C=C- [18], scission of many bonds, in addition to the formation of char as an end product. The temperature for 10% weight loss is considered to be polymer decomposition temperature, and it ranges between 210– 260°C, and the temperature for 50% weight loss was found between 360–440°C. Therefore, the data in Table II indicates that the thermal stabilities of these polymers are in the order **V**> **VI**> **VII**. It should be noted that the inclusion of the anisole moiety as a rigid pendent group into the polymer chain decreases the thermal stability of these polymers.

E. Mesogenic properties of the polyesters

The LC properties of the polyesters were evaluated by differential scanning calorimetry (DSC) with a heating and cooling rate of 10°C/rain and by optical texture observation with a polarizing microscope equipped with a hot stage. All the polyesters (**V-VII**) exhibited melt birefringence and stirred opalescence during polarized microscope observation. The phase transition temperatures of the polyesters are shown in Table II. The isotropic temperature of these polyesters (**V-VII**) was in the range of 250–270°C.

TABLE II
TRANSITION BEHAVIOUR OF POLYESTERS V-VII

No.	*n*	X	Stirred opalescence	Tg (DSC)[a]	Phase transition temperature (°C, microscope)[b]			Weight loss temp. (°C[c])	
					Tm	Ti	ΔT	10%	50%
V	4	2	Strong	150	211	270	59	210	440
VI	6	2	Strong	148	205	263	58	260	370
VII	8	2	Strong	132	202	250	48	210	360

[a]Measured by DSC, [b]Measured usnig a polarizing microscope equipped with a heating stage, [c]From TGA in air with heating rate 10°C min^{-1}. Pendant group in all polymers OCH_3.

In DSC studies, all the polymers revealed multiple endothermic on DSC thermograms, probably due to polymorphism. In some cases, the peaks in DSC are broad, with thermal temperature decomposition. For this reason, isotropization temperatures of the polymers were identified by observing the textures of the melts on a cross-polarizing microscope. The DSC profiles of the polyester **VI** (Fig. 3) revealed multiple endotherms peaks at 148.16 (Tg), 208.25 (Tm), 265.59(Ti) and exotherm peak at 336.71°C, probably due to decompositon. When the sample was cooled after preheating to 419°C, there were no exothermal or endothermal peaks. On second heating cycle, there were two endotherm peaks at 230 and 349°C. This effect might be due to solid-to-solid (Tss), solid-to-mesophase (Tm) and mesophase-to-solid (Ti) transitions, from optical observation by polarizing microscope [19], which is observed from an optical microscope. It should noted that, the phase transition temperature for polymers **V**, **VI** and **VII** (Fig 3 and Table II) respectively, are very close to that temperature of the phase transitions observed by microscopy. The little variance between temperature grades (not more than 5 °C) may be attributed to the observing of the temperatures during the raising in the microscopy [20].

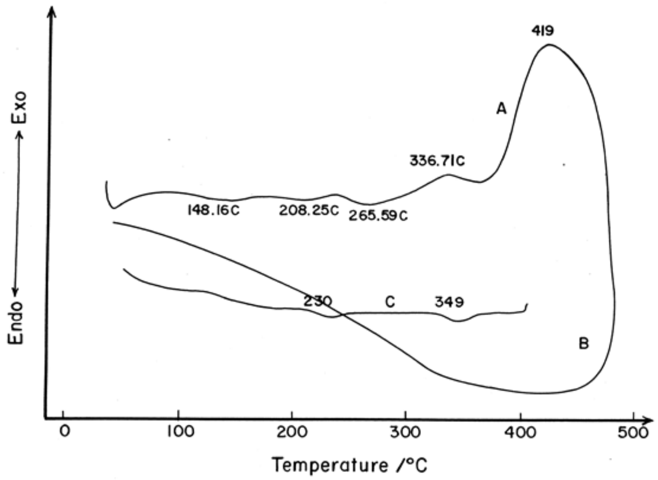

Fig. 3 DSC thermograms of polyestere **VI**: (A) first heating, (B) first cooling and (C) second heating. rate 10 ^{o}C/min.

The effect of spacer length on the thermal properties of the polyesters V, **VI** and **VII** is shown in Table II. Both melting point and isotropization temperature decreases as the length of the flexible aliphatic spacer in the polymer chain increases. The effect of substituents on the thermal properties of the polymers V, **VI** and **VII** is also shown in Table II. Both the melting point and the isotropization temperature were decreased by the introduction of methoxy groups into the polymer main chain [21].

It is known that substituents can reduce the coplanarity of adjacent mesogenic groups and increase the diameter or decrease the axial ratio of the mesogenic units [22]. Thus, the unsubstituted para-linked polyesters is infusible below its decomposition temperature. But fusibility is achieved by the introduction of a methoxy group into the mesogenic moiety lowers the transition temperatures, but of course, also decrease the orientational interactions thereby decreasing the mesophase stability [21]. In DSC measurments, the peaks are broadened some cases, this is attributed to overlapping with thermal decomposition temperature. For this reason, the isotropization temperature of the polymers were obtained by observing the textures of the melt using the polarizing microscope.

F. Texture observation

The characteristic of the texture at a given temperature was fixed by quenching it in liquid nitrogen. Micrographs were then obtained on heating to room temperature (not shown). All the samples **V**, **VI** and **VII** were appeared to have low melt vescosities, indicating, that the presence of a nematic phase is possible. Observation of polyester **VI** in the anisotropic melt displays the typical marbled textures [23] as shown in Fig. 4A at 205°C and Fig. 4B at 263°C (Ti). The other polymer samples (**V** and **VII**) in the mesomorphic state were highly birefringent and they showed stirred opalescence and exhibited typical nematic texture.

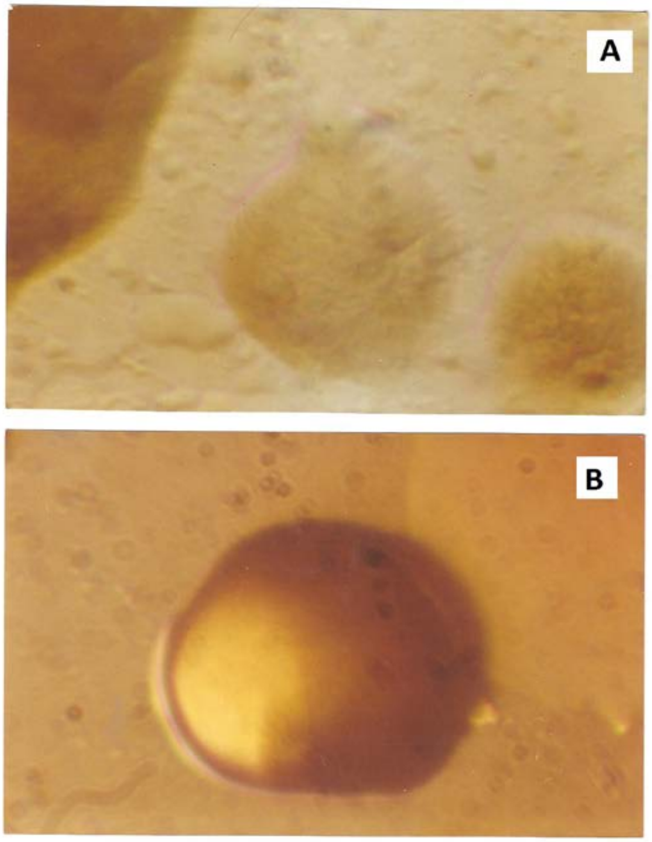

Fig. 4 Photomicrographs of polymer VI in the heating cycle, (A) at 205oC (before melting); (B) 263°C (Ti)

IV. CONCLUSION

A new series of liquid crystalline polyesters containing anisole moiety were synthesized using interfacial polymerization technique at 25°C. The majority of the polymers are soluble in protonic acids. Most of them exhibited melt birefringence and stirred opalesence during polarized microscope observation. Both the Tm and Ti values increased as the length of the flexible alpihatic spacers increased and decreased with the introduction of the methoxy group as a substituent in the polymer main chain.

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