

# Synthesis of Main Chain Liquid Crystalline Polyesters Based on Mesogenic Monomers with Controlled Transition Temperatures

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Received 23 June 2003; accepted 3 January 2004

## ABSTRACT

The structure-property relationships in segmented-chain liquid crystalline polyesters based upon diphenols and aliphatic dibasic acid chloride was studied by differential scanning calorimetry and polarizing optical microscopy. Two mesogenic monomers were synthesized by direct esterification of hydroquinone with *p*-hydroxybenzoic acid in a convenient method. The well-characterized mesogenic monomers incorporated into segmented liquid crystalline polyesters with short linear chain and COOH-end groups. The structure of the monomers and the polymers was studied by FTIR, <sup>1</sup>H NMR, MS. The temperature of transition between the phases and, as a consequence, the range of mesomorphism is highly dependent upon the molecular weight of the polyesters and the length of the mesogenic monomers.

### Key Words:

polyester; mesogenic monomers;  
esterification;  
liquid crystalline polymers.

## INTRODUCTION

Thermotropic liquid crystalline polyesters are well known for their mechanical strength and modulus, stability to chemicals and heat resistance [1-3]. Most current research, in the field of liquid crystalline polyesters, is concerned with liquid crys-

tals formed by main chain polymers [4-5]. These mesogenic polyesters may be divided into three sub-groups: rigid homopolyesters, copolymers and semiflexible homopolymers having both a rigid and flexible segments in the repeat-

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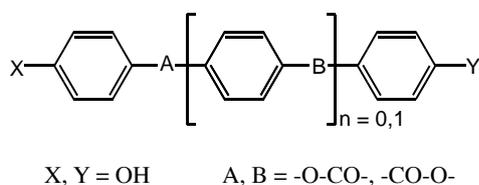
ing unit [6]. In the latter group, also called the segmented main chain liquid crystalline polyesters, the alteration of mesogenic and flexible segments causes an appreciable change in the orientational entropy of the chains and hence in the macroscopic properties of the material [7].

Since the mesogenic segments are generally expensive and it causes concerns regarding the economic benefit for these polymers, synthesis of these segments, by the use of low cost monomers and processes, will help more justification for the development and wider use of these types of materials.

The chemical constitutions of mesogenic units in these liquid crystalline polymers usually have at least two linear substituted cyclic units that may or may not be linked by a short rigid central bridging group [8-9]. The interest of investigators has centered primarily on polymers containing mesogenic groups with ester bridging as internal linkage units. This is because of the scope that is envisaged for practical applications of thermotropic polyesters, as well as the hope that properties of the polymers could be compared with those of widely investigated low molecular liquid crystals containing ester bonds. Although in these mesogenic groups there is no double bond, the electron-rich aryl or phenyl group can slightly shifts its bonding electrons to the carboxyl group; thus, the ester linkage unit owns some double bond character. Therefore, it exhibits a more rigid structure than initially expected [10].

Widespread use of a mesogenic group in the form of an aromatic triad or dyad of 1,4-phenylene unit interconnected by ester bonds has become a feature of the synthesis of the segmented main chain liquid crystalline polyesters [11-17].

In the present work, the main objective has been at first to synthesize mesogenic groups, in a suitable process and from low cost monomers, with the following structures;



and then introduced them into polymer chains along with an aliphatic segment, in a way that the transition temperatures can be controlled.

## EXPERIMENTAL

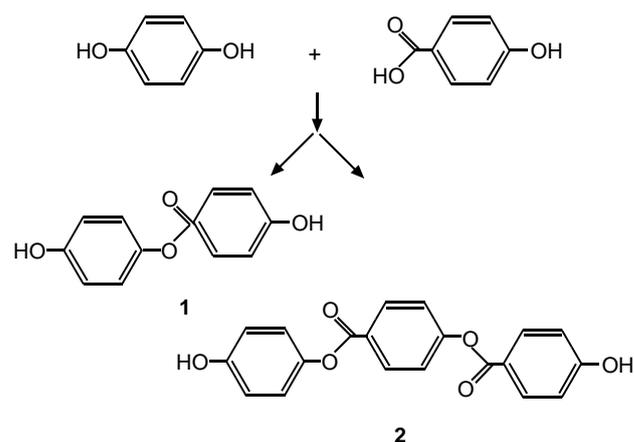
### Chemicals

Hydroquinone, *p*-hydroxybenzoic acid, sebacoyl chloride as monomers were standard grades purchased from Merck (Germany) and used without further purification. Other chemicals include *p*-toluenesulphonic acid, *o*-dichlorobenzene, diphenyl oxide, and pyridine were also purchased from Merck (Germany) and all were used as received.

### Reactions

#### Monomer Preparation

Two types of aromatic diphenol, linked by ester bond as mesogenic monomers were prepared by some modifications of the method described earlier by Jones et al. [18]. The monomers were synthesized by direct esterification of hydroquinone with *p*-hydroxy benzoic acid as given below (Scheme I):



Scheme I

#### Monomer (1)

In a 3-necked round bottom flask equipped with a magnetic bar stirrer, a Dean-Stark trap, a condenser, a thermometer and a  $N_2$  inlet were placed 1.5 g (13 mmol) of hydroquinone, 0.69 g (5 mmol) of *p*-hydroxybenzoic acid, 9 mg of *p*-toluenesulphonic acid and 10 mL of *o*-dichlorobenzene. The flask was flushed with  $N_2$  and was heated with stirring to 180°C. The reaction started to occur at about 160°C as water started to distill out. The reaction was carried out for 2 h, until no more water was evolved. The molten product was quickly poured into a steel container to cool. The solid was ground to a powder and was dissolved to the

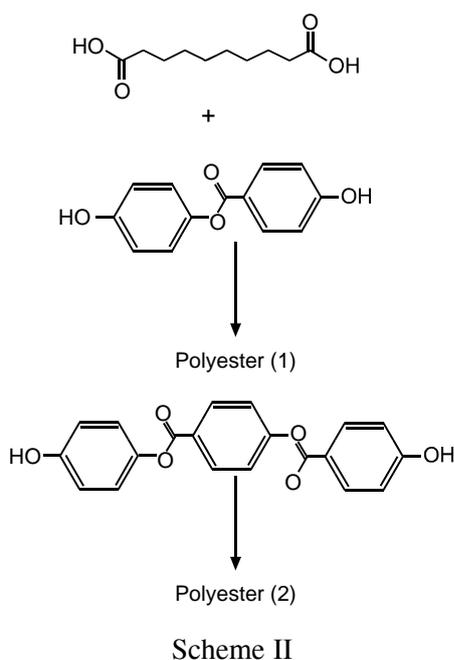
extent possible in 50 mL of methanol near its boiling point. The solution was filtered while hot to remove a substantial amount of insoluble material. About 100 mL of water was added to the methanol solution to precipitate the monomer (1). The white solid was twice redissolved in methanol and reprecipitated. The product was collected and dried for 2 h at 100°C and then was left overnight at 25°C under vacuum. The reaction yield was 40-45%.

#### Monomer (2)

The above procedure was repeated using 0.55 g (5 mmol) of hydroquinone, 1.38 g (10 mmol) *p*-hydroxybenzoic acid, 7 mg *p*-toluenesulphonic acid and 4 mL *o*-dichlorobenzene. The reaction was carried out for 2 h. After cooling the solid was extracted with 50 mL of hot methanol, collected on a filter and washed with hot methanol and dried sufficiently in vacuo at 25°C and 80°C. The reaction yield was 85-90%.

#### Polymer Preparation

The synthesized monomers were individually incorporated into a polycondensation reaction at high temperature with sebacoyl chloride with a non-equimolar ratio of starting materials (acid chloride excess) as described below (Scheme II):



#### Polymer (1)

0.47 g (2 mmol) of monomer (1), 0.717 g (3 mmol) of sebacoyl chloride, 10 mL of diphenyloxide and a few

drops of pyridine were placed in a 3-necked round-bottomed flask equipped with a magnetic stirring bar, a condenser, a thermometer and a N<sub>2</sub> inlet. The flask was flushed with N<sub>2</sub> for 15 min, and was stirred and heated in an oil bath up to 190°C under slow N<sub>2</sub> flow. The reaction mixture became homogeneous after several minutes and the evolution of HCl was observed. The reaction continued until the evolution of HCl was no longer detectable by moistened litmus paper (about 4h). The hot reaction mixture was poured cautiously into 100 mL of toluene and cooled. The oily residue that separated was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed 3 times with distilled water. The solution was filtered and concentrated through evaporating. The concentrated solution was precipitated by the use of a mixture of methanol/ water. The reaction yield was found to be 65-75%.

#### Polymer (2)

The above procedure was repeated using 0.7g (2 mmol) of monomer (2), 0.717 g (3 mmol) sebacoyl chloride, 10 mL of diphenyl oxide and a few drops of pyridine. The reaction yield was 65-75%.

#### Characterization

The monomers and polymers were characterized by FTIR (Perkin-Elmer FTIR Spectrometer), and <sup>1</sup>HNMR Spectrometer operating at 500 MHz and 80 MHz (TMS as internal standard), at room temperature. Chemical shifts were measured in DMSO-d<sub>4</sub>. Mass spectra were obtained on a mass spectrometer (Shimadzu LH800 model). Thermal studies were performed with a DSC (TA Instrument 2010 model) at a scanning rate of 10°C/min. In order to enhance the thermal contact between the samples and the heat source and omit the thermal history effects, the samples in the form of a powder were firstly melted to take up the shape of the aluminium sample pan, then cooled at 10°C/min and after that heated again with a rate of 10°C/min. Optical microscopy studies were performed with a Leitz DMR polarizing microscope equipped with hot stage. The magnification used was 100. The variations of the depolarizing transmittance of the polyester with temperature were obtained through the measurements of the exposure time using a Leica MPS 60 automatic exposure time measuring unit attached to the microscope. Reciprocal of this time was projected to be proportional to the intensity of light transmitted through the sample.

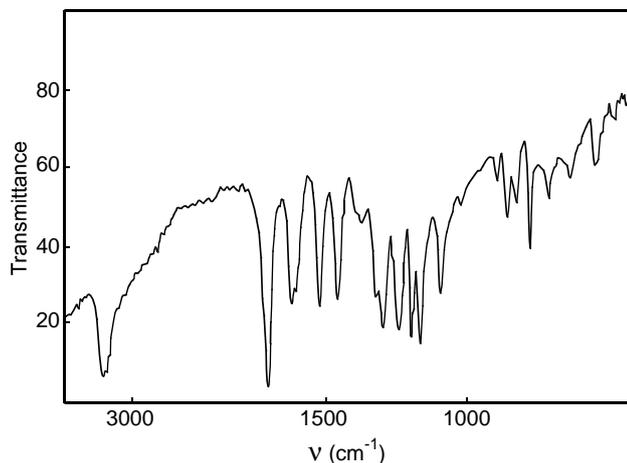


Figure 1. Infrared spectrum of monomer (1).

## RESULTS AND DISCUSSION

### Monomers

Infrared spectra of monomers (1), (2) (Figures 1 and 2, respectively) show strong absorption at 1680-1700  $\text{cm}^{-1}$  which is characteristic for carbonyl stretching, and at 3300-3400  $\text{cm}^{-1}$  which is characteristic of phenolic hydroxyl group.

$^1\text{H}$  NMR Spectra of monomers (1) and (2) are shown in Figures 3 and 4, respectively.  $^1\text{H}$  NMR was used to verify the structure of monomers and to confirm the presence of phenolic end groups. The spectrum of monomer (1) has signals at about 10.59 ppm (singlet, 1H), 9.5 ppm (singlet, 1H), 7.95 ppm (doublet, 2H), 6.85 ppm (multiple, 6H).

The spectrum of monomer (2) has signals at about 10.41 ppm (singlet, 2H), 7.95 ppm (doublet, 4H), 7.29 ppm (singlet, 4H), 6.95 ppm (doublet, 4H).

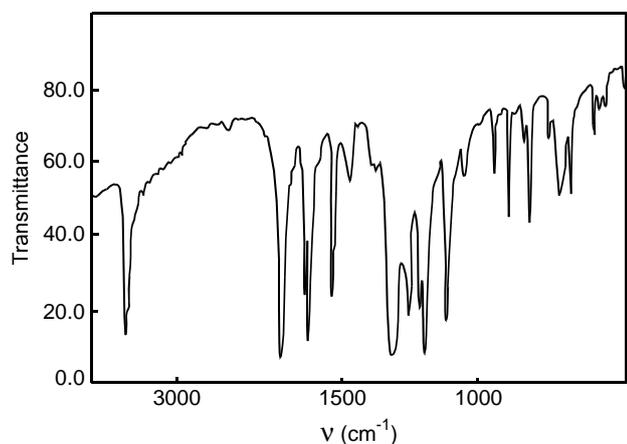


Figure 2. Infrared spectrum of monomer (2).

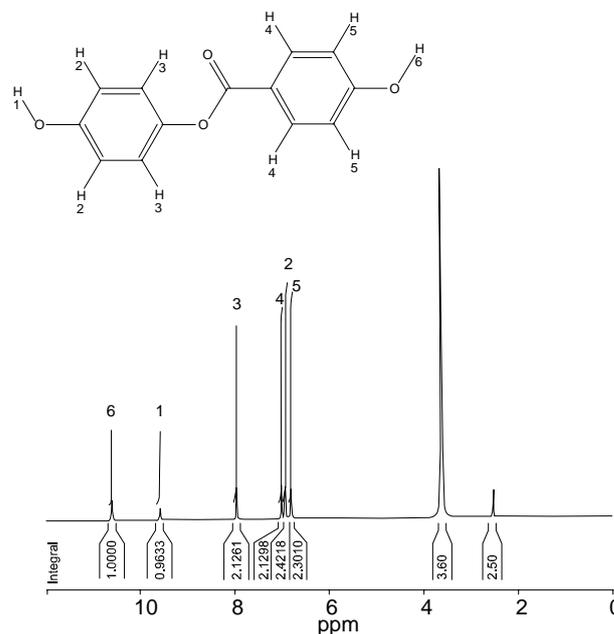


Figure 3.  $^1\text{H}$  NMR Spectrum of monomer (1).

Table 1 indicates the mass spectra data of monomers (1) and (2). The mass spectrum of monomer (1) exhibits a main peak at 230  $m/e$  ( $\text{C}_{13}\text{H}_{10}\text{O}_4$ ) and that of monomer (2) shows molecular ion peak at 350  $m/e$  ( $\text{C}_{20}\text{H}_{14}\text{O}_6$ ).

Table 1. Mass spectrum data of monomers (1) and (2).

Monomer (1) ( $m/e$ )	Monomer (2) ( $m/e$ )
38	38
56	
64	64
70	
72	92
81	
93	121
97	
113	241
120	
138	350
149	
167	
230	

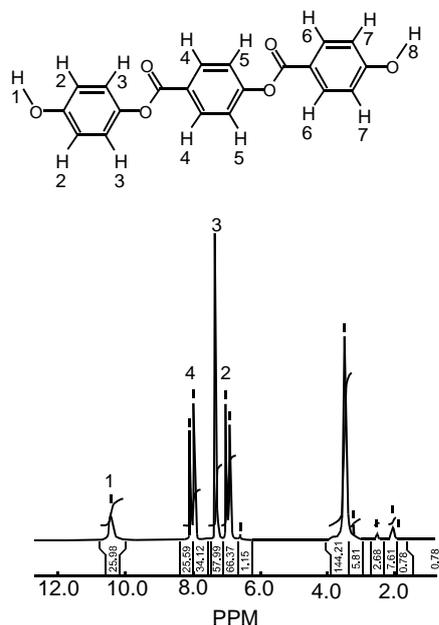


Figure 4.  $^1\text{H}$  NMR Spectrum of monomer (2).

### Polymers

Infrared spectra of polymers (1) and (2), are presented in Figures 5 and 6, respectively. These spectra show strong absorptions at  $1730\text{--}1750\text{ cm}^{-1}$  which are characteristic for carbonyl, at  $3430\text{--}3450\text{ cm}^{-1}$  characteristic of acidic hydroxyl group, and at  $2910\text{ cm}^{-1}$  characteristic of aliphatic CH.

To establish that the polymers had carboxyl functionality at their chain end, they were analyzed by  $^1\text{H}$  NMR spectroscopy.

$^1\text{H}$  NMR Spectra of polymers (1) and (2) (Figures 7 and 8, respectively) show acidic protons at about 12 ppm. The spectrum of polymer (1) has signals at about 12.0095 ppm and 7.23–8.19 ppm assignable to aromatic protons and at about 1.15–2.64 ppm assignable to aliphatic protons. The spectrum of polymer (2) has signals at about 11.96 ppm, 7.03–8.2 ppm and 1.3–2.6 ppm which are assignable to acidic proton, aromatic protons and aliphatic protons, respectively.

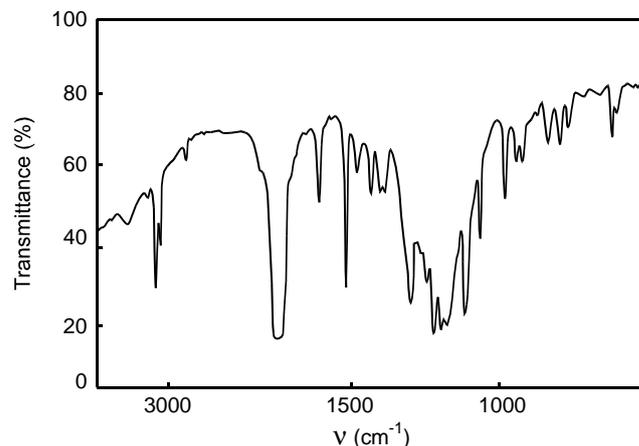


Figure 5. FTIR Spectrum of polymer (1).

The solubility of the synthesized polymers is shown in Table 2. These compounds exhibited virtually no solubility in common solvents such as acetone but displayed fairly high solubility in DMSO.

The thermal behaviour of the prepared polymers was investigated using hot stage polarized light microscopy, and differential scanning calorimetry. The DSC trace of polymer (1) exhibited two endothermic peaks in  $194^\circ\text{C}$  and  $235^\circ\text{C}$  as shown in Figure 9. The additional endothermic peak could be correlated to the transition from the liquid crystalline phase to the isotropic melt.

The microscopic observations under polarized light confirm that polymer (1) melts to a mesomorphic phase (Figure 10).

The DSC trace of polymer (2) showed three endothermic peaks in the  $196.6^\circ\text{C}$ ,  $213.39^\circ\text{C}$ , and  $260.13^\circ\text{C}$ , as illustrated in Figure 11. The additional endothermic peaks could be related to the mesophase transitions.

The microscopic observation under polarized light confirmed that polymer (2) melts to a mesophase (Figure 12).

Among the several hundreds of liquid crystalline

Table 2. The solubility of the polyesters and the monomers in different solvents.

Solvent	Polyester (1)	Polyester (2)	Monomer (1)	Monomer (2)
DMF*	Slightly soluble	Insoluble	Soluble	Soluble
THF**	Insoluble	Insoluble	Soluble	Soluble
DMSO***	Soluble	Soluble	Soluble	Soluble

(\*) *N,N*-Dimethylformamide (Merck); (\*\*) Tetrahydrofuran (Merck); (\*\*\*) Dimethylsulphoxide (Merck).

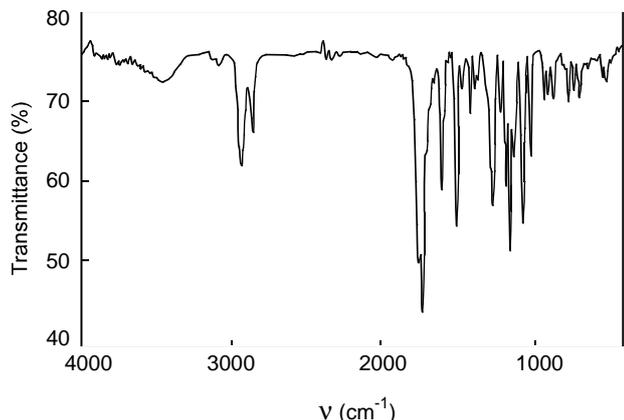


Figure 6. FTIR Spectrum of polymer (2).

polymers reported in different papers and patents, thermotropic segmented - chain polyester comprises a very important category [4-5].

As it previously mentioned to synthesize the polyesters, at first we prepared the mesogenic monomers. The procedures described above for monomer preparation showed that diphenols can be readily synthesized in substantial quantities by direct esterification. Monomer (1) in spite of low yield of the reaction (42%) had a defined chemical structure and was well separated during the purification steps. But monomer (2) has a by-product, which can be formed in the reaction described here that shows no distinguishable characteristics through melting point, IR spectra and <sup>1</sup>H NMR spectrum with monomer (2). But this by-product that we can call it monomer (3) is detectable by mass spec-

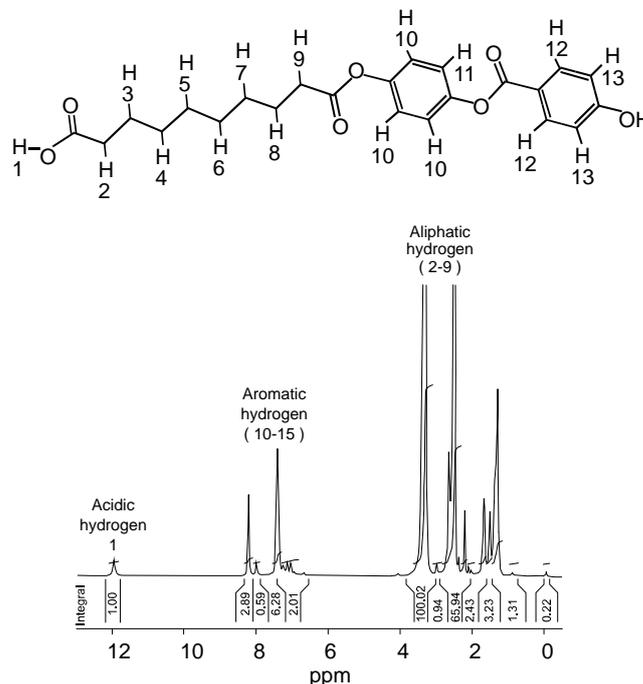


Figure 8. <sup>1</sup>H NMR Spectrum of polymer (2).

troscopy. The mass spectrum of monomer (2) exhibited a peak at 241 m/e, which can be assignable to the following structure:

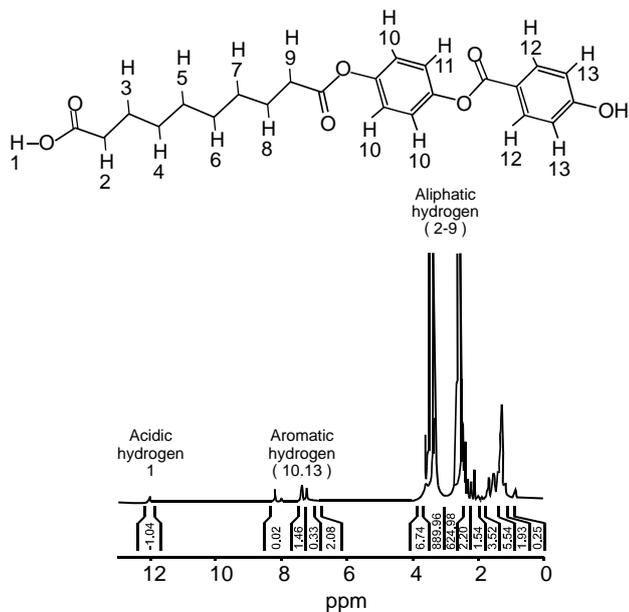
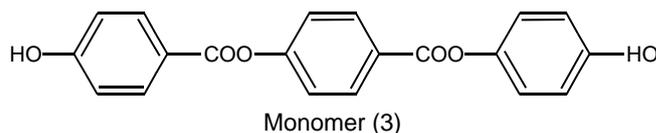


Figure 7. <sup>1</sup>H NMR Spectrum of polymer (1).

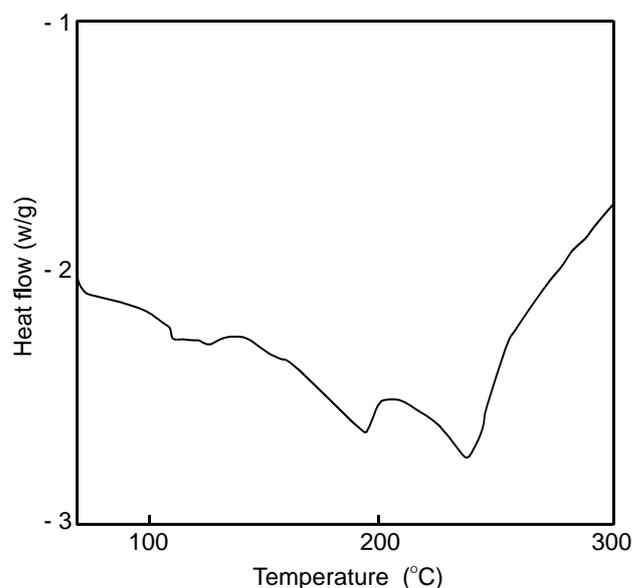
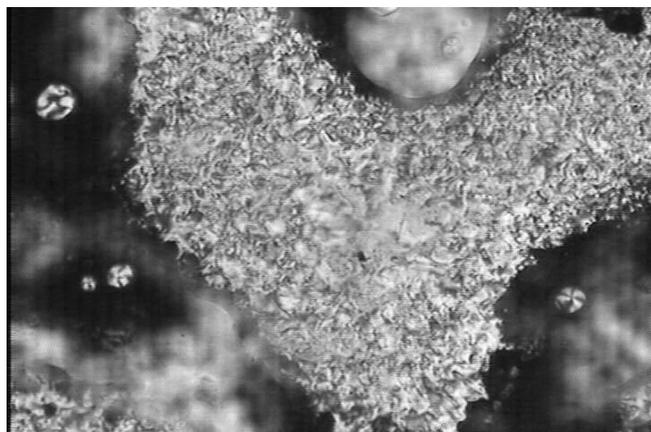


Figure 9. DSC Thermograph of polymer (1).



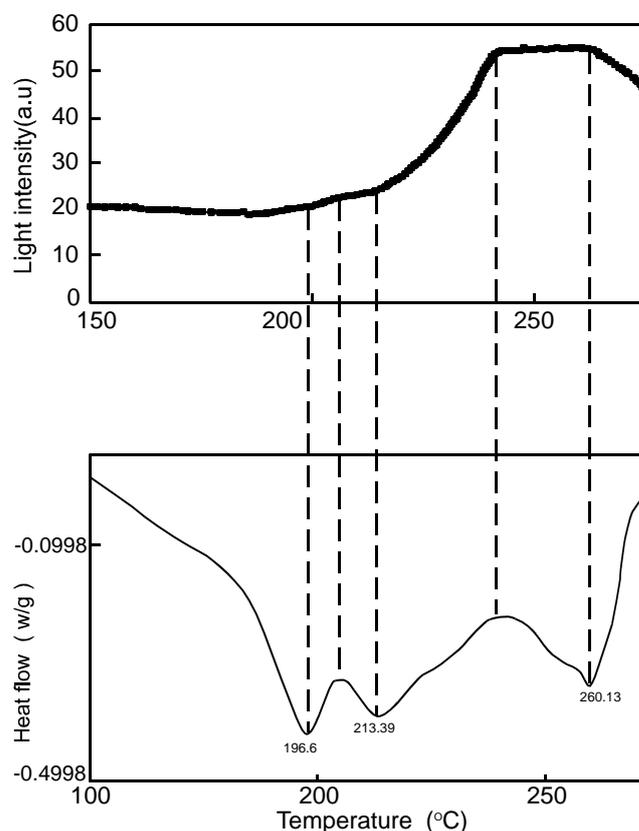
**Figure 10.** Cross-polarized microphotograph of polyester (2) taken at 210°C (magnification 100×).

The polymerization was designed to be carried out in a mild condition, to minimize the side reactions, e.g. transesterification and to prevent the destruction of ester bonds between aromatic rings. To reach this object, the reactions were performed in the presence of a high boiling point solvent, diphenyloxide, and a high reactive monomer, sebacoyl chloride. On the other hand, since we wanted to obtain the linear polyesters with low molecular weight and COOH-end groups, the polymerizations were carried out in a non-equivalence condition of proportion of starting materials. The ratio of the starting materials is an extremely important factor, and it determines the limiting size of the molecule, which can be formed under the given condition. The mean molecular weight of the polycondensation product of a bimonomer reaction, MW can be obtained by the following equation [19]:

$$MW = 100/q * (M_a + M_b + 2Z) + M_a$$

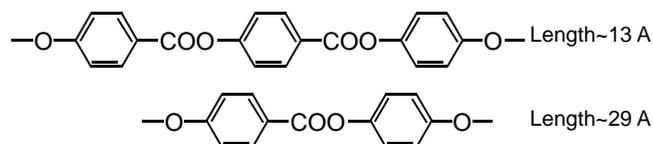
Where,  $M_a$ , the molecular weight of the monomer taken in q moles percent excess,  $M_b$ , the molecular weight of second component and Z, the molecular weight of product split out (HCl). The ratio of the mesogenic monomers to sebacoyl chloride was selected 2:3, and the calculated and measured molecular weights are listed in Table 3. The molecular weight of the synthesized polyesters was measured by the method of end-group analysis [19].

There is a general agreement in the synthesized polyesters that the transition temperatures of these polymers depend on their molecular weights. Another important parameter that affects the transition tempera-



**Figure 11.** DSC Heating curve (below) and depolarizing transmittance curve (above) of polyester (2), heating rate 10°C/min.

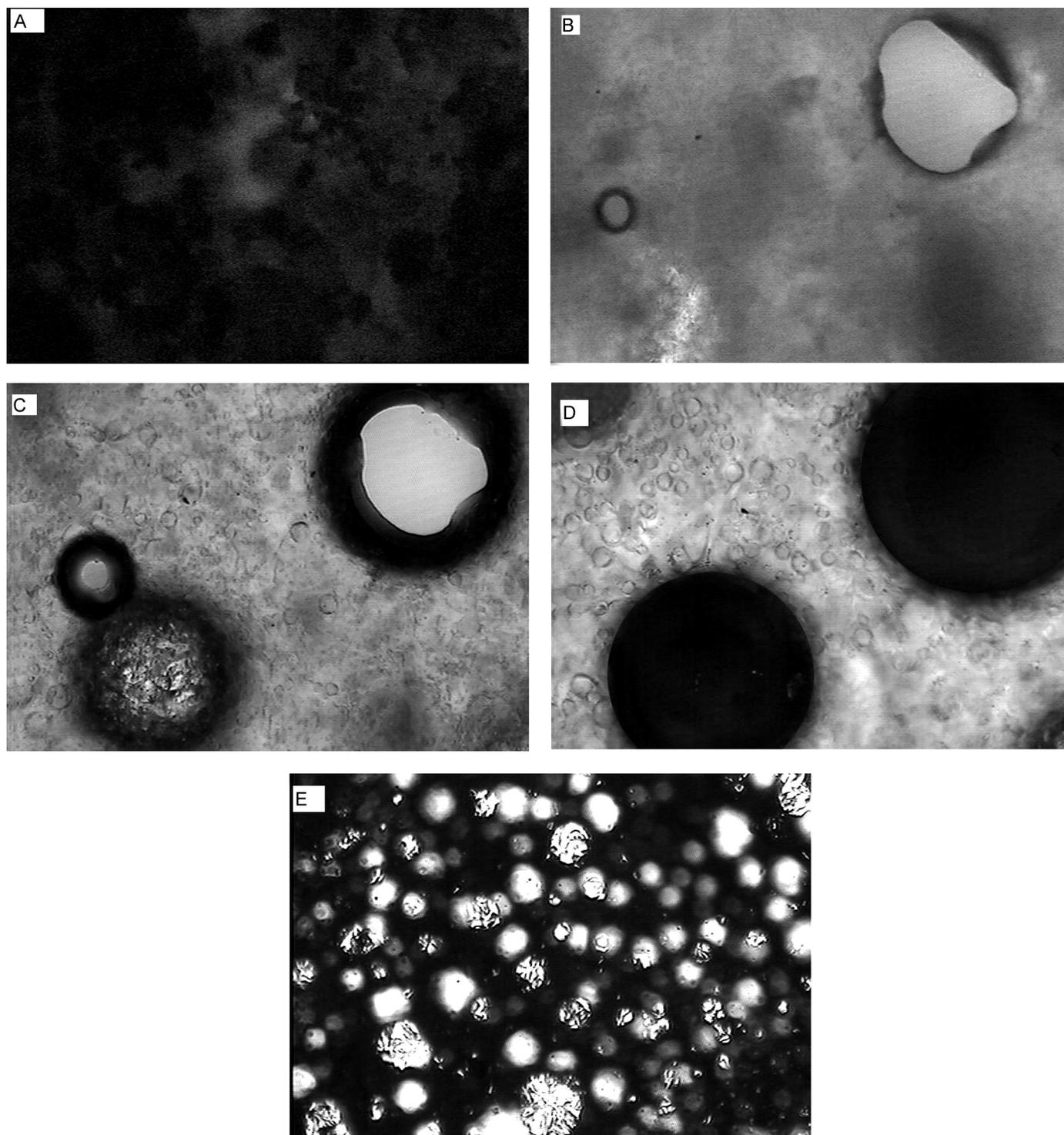
tures of the segmented-chain liquid crystalline polyesters is the length of the rigid segment. To highlight the effect and impact of this parameter we attempted to change the size of the rigid segment while keeping the number of methylene units constant. The interested rigid segments were;



In polyester (1), prepared by dyad aromatic

**Table 3.** The calculated and measured molecular weight of the polyesters.

Polyester	$M_{theory}$	$M_{measured}$
(1)	1270	1395
(2)	1510	1640



**Figure 12.** Cross-polarized microphotograph of polyester (2) taken at different temperatures: (A) 170°C; (B) 196°C; (C) 210°C; (D) 223°C; and (E) 260°C (magnification 100×).

monomer there were two transition temperatures at 194 °C and 235 °C. While for polyester (2) which was prepared by triad aromatic monomer, three transition temperatures have been observed at 196.6 °C, 213.39 °C,

and 260.13 °C.

Polyesters (1) and (2) have drastically different mesomorphic behaviour. The isotropization temperature for polyester (2) ( $T_I = 260.13$  °C) is much higher

than for the polyester (1) ( $T_1 = 235^\circ\text{C}$ ). But apparently the first transitions for the both polymers occurred approximately at the same temperature (i.e.,  $194^\circ\text{C}$  for polyester (1) and  $196.6^\circ\text{C}$  for polyester (2)). To clarify and identify the transitions of these polymers, we carried out further, careful optical microscopic studies. We found that the polyester (1) melts and forms a phase similar to a  $\text{fan}$  or  $\text{focal-conic}$  texture of smectic A phase at  $194^\circ\text{C}$  and further transforms to the isotropic state at  $230^\circ\text{C}$ . These correspond with the two transition phenomena observed in the DSC peaks. The larger enthalpy change in the second transition with respect to the first one can confirm the optical microscopic observations and suggests that the polyester (1) has a texture resembling smectic in the melting state. This result is a new finding that according to the best of our knowledge has not been reported before for the synthesized polymer with the specified molecular weight. So this meso-phase behaviour can be attributed to the lower molecular weight of our polyester and the existence of flexible segments predominantly at the end of polymer chains.

Furthermore, microscopic optical observations have been made for polyester (2). As can be seen in Figure 12, the polymer starts to melt to form the nematic phase at  $213^\circ\text{C}$ . This behaviour has also been reported by some other authors [16, 20-21]. In order to identify the transitions of this polyester, we measured the depolarizing transmittance of it during heating process. Figure 15 illustrates the temperature dependence of the depolarizing transmittance of the polyester (2). Heating and cooling rates of  $10^\circ\text{C}/\text{min}$  were used in this study. Although there is a transition with a large enthalpy change at  $196^\circ\text{C}$ , we could not observe any considerable change occurring in either the depolarizing transmittance or optical texture corresponding to this temperature. This transition in the DSC tracing can be attributed to a partial melting or a concealed phase transition in the solid state (crystal to crystal).

In conclusion it is quite evident that the molecular weight and the length of rigid segment are relevant parameters that must be taken into full account. The liquid crystalline properties of our polyesters are related to the above-mentioned parameters and it is possible to reach thermotropic polyesters with controllable transition temperatures.

## CONCLUSION

A segmented-chain liquid crystalline thermoset polyester was designed in which low cost monomers were used and a simple process was employed to synthesize the polymers. It was shown that the transition temperatures of these polyesters is controllable through adjusting the molecular weight, and changing the length of rigid segments. The polymerization reactions were carried out in a non-equivalence condition in the viewpoint of controlling the MW and molecules end groups. The mesomorphic states of the synthesized polymers were detected by DSC and polarized light microscopy, which showed the first transitions at  $194^\circ\text{C}$  for polyester (1) and at  $213^\circ\text{C}$  for polyester (2). By increasing the rigid segment length the temperature of transition to the mesophase of the synthesized polymers showed a raise of about  $19^\circ\text{C}$ .

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