Thermotropic Polyesters (Part 3): Synthesis, Characterization and Thermal Transition of Random Copolyesters Containing Terephthalate and Isophthalate Units

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ABSTRACT

Thermotropic copolyesters containing an isophthalate unit and mesogenic 4,4'-bis (ω-hydroxyalkyloxy) biphenyls with different numbers of methylene units have been synthesized by melt polymerization. The effect of monomer structure and copolymer composition on liquid crystallinity has been studied on the prepared copolymers from isophthaloyl chloride, terephthaloyl chloride, and mesogenic 4,4'-bis (ω-hydroxyalkyloxy) biphenyl (n=4,6) and it is compared with that of the analogous homopolymers. Our finding shows that high contents of terephthalic acid depend on spacer type have deleterious effects on liquid crystallinity. All of the obtained compounds were characterized by conventional spectroscopic methods.

Key Words:
thermotropic copolyesters; optical texture; DSC; terephthalate; isophthalate.

INTRODUCTION

Main chain thermotropic liquid crystalline polymers have been intensively studied during the past two decades [1]. In the last decade several synthetic strategies for improving the solubility and lowering the melting transitions of thermotropic liquid crystalline polymers (TLCP) have been developed and are commonly employed in TLCP design [2]. In order to improve the solubility and to modulate the thermal properties of such stiff polymers, several structural
modifications have been performed, such as the insertion of flexible spacers [3,4]; the addition of bulky or non-symmetrical substituents [5]; the inclusion of non-linear or bent monomers [6-8]; and copolymerization of different monomers [9-11]. The non-linear (bent) monomers such as resorcinol, isophthalic acid, and \( m \)-hydroxybenzoic acid are generally used for the preparation of thermotropic copolyesters in order to decrease their crystal-to-nematic transitions, \( T_m \), to a convenient level [12]. In general, the incorporation of each of these monomers is limited to a certain critical amount beyond which the liquid crystallinity of thermotropic copolyester is destroyed. The critical amount for a non-linear monomer in thermotropic copolyester is determined not only by its chemical structure but also by the chemical structures of other mesogenic monomers.

Fischer et al. [13] originally reported the meso-phase behaviour of polyesters and polyurethanes containing 4,4'-bis (6-hydroxyhexyloxy) biphenyl (BHBB). They claimed that the polyesters of BHBB and isophthalic acid (IA), as well as BHBB and terephthalic acid (TA), formed liquid crystalline mesophase of the smectic type. However, Khan et al. [14, 15] corroborated that the IA polyester did form a biphasic nematic-smectic A phase, but TA polyester crystallized directly on cooling the melt, without forming a mesophase. The IA polyester has a monotropic liquid crystal phase as the mesophase is only observed on cooling.

In our previous paper, liquid crystalline polyesters containing isophthalate unit and mesogenic diols 4,4'-bis (\( \omega \)-hydroxyalkyloxy) biphenyl were prepared [8]. The presence of non-linear moiety (IA unit) substituted with different spacer lengths led to a reduced rigidity of polymers and increased solubility in common organic solvents. In this work, in order to study the effect of terephthaloyl moieties on liquid crystallinity of a semiflexible copolyester, we prepared copolyesters containing 4,4'-bis (6-hydroxyhexyloxy) biphenyl (BHBB) and 4,4'-bis (6-hydroxybutyloxy) biphenyl (BHBB) with isophthalate and terephthalate units with different molar percentages. These mesogenic diols were selected for this study because the mesophase behaviour of the IA homopolymers is well characterized in our previous work [8].

**EXPERIMENTAL**

**Materials**
The purification or drying of compounds and solvents have been performed according to the common procedure. Isophthaloyl chloride, terephthaloyl chloride purchased from Merck.

**Methods**
Spectroscopic characterization utilized the following instrumentation: Melting points were recorded with an electrothermal apparatus. FTIR Spectra were recorded on a Brucker spectrometer. \(^1\)H NMR Spectra were taken on a 400 MHz Brucker versus, TMS in CDCl\(_3\). The inherent viscosities of the samples were determined by an Ubbelhode viscosimeter at 25 C in chloroform. A differential scanning calorimeter STA 625 was used to determine phase transition temperatures at the heating and cooling rates of 10 C/min. An optical Zeiss polarizing microscope equipped with long working distance objectives was also used to observe phase transitions. The samples were heated and cooled with a THMSE 600 hot stage and associated temperature controller. Very small powdered fragments of polymers were placed on the glass slide and heated to about 20 C above the isotropization temperature. The melt was quite viscous and did not form a thin layer spontaneously. Hence, it was sheared between the glass plates in the isotropic state [8]. All of polymers were stable in this condition and textural features appeared to be generally reproducible on several heat-cool cycles with the same specimen.

**Synthetic Procedures**

*Polyesters of 4,4'-bis (\( \omega \)-hydroxyalkyloxy) Biphenyl and Isophthaloyl Chloride, PI\(_n\) (n=4, 6)*
The exact synthetic procedure and characterization of the monomers and IA homopolymers were presented in earlier work [8].

*Polyesters of 4,4'-bis (\( \omega \)-hydroxyalkyloxy) Biphenyl and Terephthaloyl Chloride, PT\(_n\) (n=4, 6)*
A similar procedure to the previous polymerization was used. Monomer (BHBB or BHBB) (0.01 mol) and terephthaloyl chloride (2.1g, 0.01 mol) were placed in a polymerization flask equipped with a magnetic stirrer, a gas inlet /outlet, and a vacuum inlet. The polymer-
ization flask was evacuated and then filled with nitrogen. This cycle was repeated four times. A slow stream of nitrogen was then maintained in the flask to carry off the hydrogen chloride produced during the polymerization. The flask was heated in an oil bath to 200°C. When it became too viscous to be stirred, vacuum was applied and the temperature was maintained for 3-4 h. The flask was cooled to room temperature under vacuum, and the product was mechanically crashed extracted with acetone, and dried at 50°C. Dissolving in chloroform, filtering, and reprecipitating with acetone purified the polymers.

For copolymer PI4-co-PT4 (Z=50%): FTIR (KBr): 3422 (OH), 2950 and 2870 (CH$_2$), 1718 (C=O), 1470 (aromatics), 1271 and 1101 (C-O-C) cm$^{-1}$; 1H NMR (CDCl$_3$): δ 10 (S, -OH, carboxylic-acid), 8.69 (S, 1H aromatic , between the - C=O ), 8.21 (d, 2H aromatic, ortho to O), 8.09 (S, 4H aromatic, phenyl), 7.51 (t, 1H aromatic, meta to each -C=O), 7.43 (d, 2H aromatic, ortho to O), 6.93 (d, 2H aromatic, meta to O), 4.43 (t, CH$_2$, α to -O-C=O), 4.05 (t, CH$_2$, α to -OAr), 3.72 (t, -OH ), 3.62 (t, CH$_2$, α to -OH), 1.98 (b, CH$_2$, β to -O-C=O and -OAr), 1.26 (m, CH$_2$, β and γ to -OH).

Random copolymers with 75:25, 50:50 and 25:75 ratio of isophthaloyl chloride: terephthaloyl chloride (PT4): FTIR (KBr): 3520 (OH), 2956 and 2860 (CH$_2$), 1730 (C=O), 1470 (aromatics), 1258 and 1160 (C-O-C) cm$^{-1}$; 1H NMR (CDCl$_3$): δ 10 (s, -OH, carboxylic acid), 8.08 s, 4H aromatic, phenyl), 7.44 (d, 2H aromatic, ortho to O), 6.93 (d, 2H aromatic, meta to O), 4.42 (t, CH$_2$, α to -O-C=O), 3.88 (b, -OH), 3.62(t, CH$_2$, α to terminal -OAr), 1.99 (b, CH$_2$, β to -O-C=O and -OAr), 1.26 (m, CH$_2$, β and α to -OH).

Polyester of BHBB with terephthaloyl chloride (PT6): FTIR (KBr): 3520 (OH), 2958 and 2860 (CH$_2$), 1729 (C=O), 1470 (aromatics), 1260 and 1160 (C-O-C) cm$^{-1}$; 1H NMR (CDCl$_3$): δ 10 (s, -OH, carboxylic acid), 8.09 s, 4H aromatic, phenyl), 7.44 (d, 2H aromatic, ortho to O), 6.92 (d, 2H aromatic, meta to O), 4.36 (t, CH$_2$, α to -O-C=O) 3.96 (t, CH$_2$, α to -OAr), 3.89 (t, -OH), 3.55 (t, CH$_2$, α to -OH), 1.81 (b, CH$_2$, β to -O-C=O and -OH and γ to -O-C=O ) , 1.54-1.55 (b, the rest CH$_2$ protons).

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Polyester**

The mesogenic monomers 4,4′-bis (4-hydroxybutyl-oxy) biphenyl (BHBB) and 4,4′-bis (6-hydroxyhexyl-oxy) biphenyl (BHHB) were synthesized by the standard method [8,16]. The synthetic route for the synthesis of the monomers and IA homopolymers are shown in Schemes I and II.

The homopolymers of PT$_4$ and PT$_6$ [15] as well as PI$_4$ [8] and PI$_6$ [8, 15] were prepared by melt polycondensation of respective synthesized monomers with terephthaloyl chloride. The reaction scheme for the synthesis of the TA homopolymers is shown in Scheme III. The polyesters were characterized by FTIR and $^1$H NMR [15].

A similar polymerization procedure to the polyesters was used for the synthesis of all copolyesters. The chemical structure of copolymers is shown in Scheme IV.
The 1H NMR Spectra of PI₆-co-PT₆ (Z=50%) are shown in Figure 1. The observation of very small peak at 10 ppm in 1H NMR spectra of polyesters shows that the terminal -COCl group in polyesters hydrolyze to -COOH group during the purification process [8]. The number-average molecular weight (Mₐ) was estimated from end group analysis by 1H NMR. The intensity of the C-H proton peak of methylene unit in position to terminal -OH group was used for the Mₐ estimation. This peak was seen at 3.55 ppm for PI₆-co-PT₆ (Z =
Composition of copolymers was also obtained from $^1$H NMR spectrum. For example, the intensity of the peaks at 8.21 ppm and 8.09 ppm of PI$_6$-co-PT$_6$ (Z = 50%) copolymer due to the aromatic protons of the isophthaloyl and terephthaloyl units respectively, were definitely used for this purpose (Figure 1).

The molecular weights, average degree of polymerization (DP) and copolymer composition are listed in Table 1. These amounts show that the prepared copolymers have usually the lower molecular weight in comparison with IA homopolymers. As shown in the

### Table 1. Copolymerization of 4,4'-bis (ω-hydroxyalkyloxy) biphenyls ($n=4$ or 6) with isophthaloyl chloride and terephthaloyl chloride.

<table>
<thead>
<tr>
<th>Polyesters</th>
<th>Composition (P:Z)</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\eta$ (dL/g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI$_4$-co-PT$_4$</td>
<td>100:0 $^{(d)}$</td>
<td>10000</td>
<td>0.13</td>
<td>90</td>
</tr>
<tr>
<td>PI$_4$-co-PT$_4$</td>
<td>75:25</td>
<td>19000</td>
<td>0.19</td>
<td>75</td>
</tr>
<tr>
<td>PI$_4$-co-PT$_4$</td>
<td>50:50</td>
<td>11000</td>
<td>0.15</td>
<td>70</td>
</tr>
<tr>
<td>PI$_4$-co-PT$_4$</td>
<td>0:100</td>
<td>9000</td>
<td>0.08</td>
<td>80</td>
</tr>
<tr>
<td>PI$_6$-co-PT$_6$</td>
<td>100:0 $^{(d)}$</td>
<td>19500</td>
<td>0.19</td>
<td>96</td>
</tr>
<tr>
<td>PI$_6$-co-PT$_6$</td>
<td>75:25</td>
<td>18500</td>
<td>0.18</td>
<td>90</td>
</tr>
<tr>
<td>PI$_6$-co-PT$_6$</td>
<td>50:50</td>
<td>5500</td>
<td>0.07</td>
<td>92</td>
</tr>
<tr>
<td>PI$_8$-co-PT$_8$</td>
<td>25:75</td>
<td>5000</td>
<td>0.06</td>
<td>88</td>
</tr>
</tbody>
</table>

(a) Obtained by $^1$H NMR; (b) Estimated from end group analysis by $^1$HNMR; (c) Concentration of 0.25 g/dL of CHCl$_3$ at 25°C; (d) Ref. [8].

50% in Figure 1. Composition of copolymers was also obtained from $^1$H NMR spectrum. For example, the intensity of the peaks at 8.21 ppm and 8.09 ppm of PI$_6$-co-PT$_6$ (Z = 50%) copolymer due to the aromatic protons of the isophthaloyl and terephthaloyl units respectively, were definitely used for this purpose (Figure 1).

**Scheme III.** Synthesis of polyesters of 4,4'-bis (ω-hydroxyalkyloxy) biphenyl and isophthaloyl chloride.

**Scheme IV.** Chemical structure of copolyesters.
Table 1 increasing the terephthaloyl unit in copolymer composition leads to a molecular weight decreasing. The monomer ratio in the feed was almost as the ratio of the two monomeric units in all copolymers, because the monomer reactivity ratios are close together.

Thermal Transition of PIₙ-co- PTₙ Polyesters

In order to study the monomer structural effects on liquid crystallinity, we examined thermal properties and mesomorphic behaviour in PIₙ-co-PTₙ (n=4, 6) copolymers. It was found that PT₆ prepared from TA and BHHB melts directly to the isotropic liquid phase [15]. The polyesters of PIₙ may be modified by the introduction of a rigid terephthaloyl unit in the suitable proportion. Therefore, we investigated how much of the linear terephthalate unit can be tolerated in liquid crystalline polyesters. First, we consider the PI₄-co-PT₄ (P + Z = 100) copolyesters containing two repeat units, where P is the molar percentage of biphenylene isophthalate and Z is the molar percentage of biphenylene terephthalate units. The phase transition temperatures of copolyesters PI₄-co-PT₄ are given in Table 2.

Figure 2 shows a phase diagram of copolyesters PI₄-co-PT₄ in which the transition temperatures are plotted against the molar percentage of Z, the biphenylene terephthalate repeat units.

Copolyesters PT₄ (Z = 100%) exhibit a melting temperature of 191°C. As Z decreases, the melting temperature of this polyester decreases rapidly. Similarly, the copolymer PI₄-co-PT₄ (Z = 75%) has a melting temperature form only isotropic melts at 160°C. However, the copolyester PI₄-co-PT₄ with Z ranging from 25 to 0% exhibits a smectic A mesophase. For example, the copolymer PI₄-co-PT₄ (Z = 25%) has a Tₘ of 122°C and a mesophase range of 13.5°C. This copolymer exhibits a smectic A phase.

Encouraged by our finding that PI₄-co-PT₄ copolyesters with a low percentage of the biphenylene terephthalate unit exhibit liquid crystallinity, we pursued the possibility of incorporating the longer methylene spacer into these copolyesters to alternate monomer sense and

### Table 2. Phase transition temperatures of the PI₄-co-PT₄ copolymers determined by DSC at scan rate 10°C/min on the first cooling and second heating and microscopy observation.

<table>
<thead>
<tr>
<th>PI₄-co-PT₄ (P:Z)</th>
<th>Cooling (°C)</th>
<th>Heating (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti-SA</td>
<td>Ti-K*(a)</td>
</tr>
<tr>
<td>0: 100</td>
<td>169*</td>
<td>-</td>
</tr>
<tr>
<td>50: 50</td>
<td>119*</td>
<td>-</td>
</tr>
<tr>
<td>75: 25</td>
<td>116.5</td>
<td>103</td>
</tr>
<tr>
<td>100:0(b)</td>
<td>121.9</td>
<td>113.3</td>
</tr>
</tbody>
</table>

(a) Without mesophase forming; (b) Ref. [8].

### Table 3. Phase transition temperatures of the PI₆-co-PT₆ copolymers determined by microscopy observation and DSC at scan rate of 10°C/min on the first cooling and second heating.

<table>
<thead>
<tr>
<th>PI₆-co-PT₆ (P:Z)</th>
<th>Cooling (°C)</th>
<th>Heating (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti-SA</td>
<td>Ti-K*(a)</td>
</tr>
<tr>
<td>0: 100</td>
<td>126*</td>
<td>-</td>
</tr>
<tr>
<td>25: 75</td>
<td>117*</td>
<td>-</td>
</tr>
<tr>
<td>50: 50</td>
<td>116</td>
<td>103</td>
</tr>
<tr>
<td>75: 25</td>
<td>110</td>
<td>73</td>
</tr>
<tr>
<td>100:0(b)</td>
<td>115.6</td>
<td>68</td>
</tr>
</tbody>
</table>

(a) Without mesophase forming; (b) Ref. [8].
Figure 3 shows that the polyester PI₆-co-PT₆ (Z = 100 %) melts at 152 °C. The Tₘ of the polyester PI₆-co-PT₆ (Z = 75 %) is fairly constant at about 148 °C. Additionally, Tₘ decreases steeply when Z decreases from 50% to 0%. Optical microscopy shows that polyesters PI₆-co-PT₆ form a smectic A phase with a 13 and 37 °C range, when Z = 50% and 25%, respectively (Figure 4a). As shown in Figure 4b, the crystallization of copolymers leads to a spherulitic texture.

CONCLUSION

The synthesis and characterization of new thermotropic copolyesters based on IA and 4,4'-bis (ω-hydroxyalkyloxy) biphenyls with different numbers of methylene units have been reported. The structural modifications have been resulted reducing melting point and extending (LC) range accompanied by LC properties. Also, we have been synthesized and characterized copolyesters formed by condensation of the 4,4'-bis (ω-hydroxyalkyloxy) biphenyl smectic monomers with isophthaloyl chloride and terephthaloyl chloride. The presence of non-linear moiety (IA unit) substituted with different length spacers led to a reduced rigidity of polymers. The copolyesters with a low percentage of the p-biphenylene terephthalate unit exhibit liquid crystallinity, while the copolymers with molar percentages of terephthalate unit melt directly to the isotropic liquid phase. These results show the importance of the copolymerization method to modulate the thermal properties of such polyesters.

REFERENCES