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Synthesis and characterization of novel aromatic polyesters derived from thiophenes

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Novel aromatic polyesters have been synthesized by solution condensation reactions between hydroquinone and 3,4-disubstituted 2,5-thiophenedicarbonyl chlorides. The introduction of phenyl substituents in these poly(*p*-phenylene 3,4-disubstituted 2,5-thiophendicarboxylate)s did not enhance the fusibility nor the solubility of the resulting material when compared to the unsubstituted parent polyester. The presence of ethyl groups led to the formation of an insoluble semicrystalline aromatic polyester with a melting transition at 304°C. Poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicarboxylate) was found to be soluble in chloroform and exhibited a melting transition at 242°C. All these polyesters are stable up to 350–400°C. However, in contrast to the unsubstituted parent polymer, all these aromatic polyesters did not show any evidence of liquid crystallinity in the melt. On the basis of theoretical calculations, this behaviour can be related to the ca. 143° core angle of 3,4-disubstituted thiophenes.

(Keywords: aromatic polyesters; substituted thiophenes; characterization)

INTRODUCTION

Main-chain thermotropic liquid-crystalline polymers have been intensively studied during the past two decades[1,2]. These studies have resulted in a good knowledge of their structure–property relationships. This class of materials can be described as long rigid rods usually derived from *para*-substituted cylic units. However, 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 comonomer units (spacers), the addition of flexible side chains onto the stiff backbone and the inclusion of non-linear or kinked defects[1,2]. In this respect, Samulski *et al.*[3] have recently reported an interesting study on the influence of the 'core angle' (the valence angle between exocylic bonds) of non-linear moieties upon the formation of liquid-crystalline phases in aromatic polyesters. They have shown that the incorporation of non-linear units such as thiophene (core angle of about 148°) can allow the formation of liquid-crystalline phases in aromatic polyesters, whereas the presence of 1,3-phenylene moieties (core angle of 120°) inhibits the formation of mesophases.

In relation to these results, it could be interesting to incorporate substituted thiophene units in these aromatic polyesters since the presence of non-linear moieties substituted with flexible side chains should lead to a further decrease of the transition temperatures and, possibly, to the formation of soluble high-molecular-weight polymers. The addition of flexible chains is particularly promising since it has been shown that the transition temperature as well as the structure of the mesophases are strongly dependent upon the side-chain length[4–8]. For this purpose, we report the synthesis and characterization of novel aromatic polyesters derived from substituted thiophenes. Theoretical calculations on model compounds were also carried out in order to obtain more information about the conformational structure of these polymers. All these studies should lead to a better knowledge of the structure–property relationships in this class of materials.

EXPERIMENTAL

Synthesis

3,4-Hexadione, 2,3-hexadione and benzyl were obtained from Aldrich Co. Hydroquinone (Aldrich) was purified by sublimation. Dimethylthiodiacetate was prepared from thiodiglycolic acid (Aldrich) and 2,2-dimethoxypropane (Aldrich) in the presence of *p*-toluenesulfonic acid[9,10].

3,4-Diethyl-2-carbomethoxy-5-thiophenecarboxylic acid (**1**). In a dry three-necked, 500 ml flask fitted with a condenser, magnetic stirrer and nitrogen inlet, 17.3 g (150 mmol) of t-butoxypotassium was added to 100 ml of t-butanol, previously distilled over $CaSO_4$. This solution was cooled at 0°C and a mixture of 17.0 g (149 mmol) of 3,4-hexadione and 17.8 g (100 mmol) of dimethylthiodiacetate was then rapidly added. The brown solution was stirred for 45 min. After this time, the solution was acidified with 25 ml of 5 N HCl, giving a viscous yellow solution. The excess solvent was distilled off and the resultant solution dissolved in a mixture of 40 ml of water and 10 ml of diethyl ether The organic

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product was recovered from extractions using diethyl ether. The organic fractions were combined and the desired product was extracted using 2 N NH_4OH solutions. The residual diethyl ether in this aqueous solution was distilled off and the product was then precipitated by the addition of a 2 N HCl solution. This solution was stirred for 1 h and a pale yellow powder was obtained. This solid was recovered and dried under reduced pressure at 90°C (yield = 10%). ^1H n.m.r. (CDl$_3$, ppm): 1.17 (3H, t, $J = 3.4$ Hz); 1.28 (3H, t, $J = 7.5$ Hz); 2.59 (2H, q, $J = 7.5$ Hz); 2.99 (2H, q, $J = 7.4$ Hz); 3.90 (3 H, s).

3,4-Diethyl-2,5-thiophenedicarboxylic acid (**2**). In a 50 ml flask, 2.46 g (10.2 mmol) of the crude compound **1** was refluxed for 5 h in 20 ml of an aqueous solution of KOH (5% v/v). The solution was cooled at 0°C and then acidified by the addition of concentrated HCl. A solid precipitated and was recrystallized in acetic acid (yield = 29%, m.p. = 98–100°C). ^1H n.m.r. ((CD$_3$)$_2$CO, ppm): 1.15 (6H, t, $J = 7.5$ Hz); 2.99 (4H, q, $J = 7.5$ Hz). ^{13}C n.m.r. ((CD$_3$)$_2$CO, ppm): 15.31; 21,23; 126.68; 152.57; 163.09. I.r. (neat, NaCl, cm^{-1}): 3260–3240; 2990; 2955; 1670; 1540; 1480; 1290; 1245; 1170; 1090; 1055; 932; 890; 779; 765; 734.

3,4-Diethyl-2,5-thiophenedicarbonyl chloride (**3**). In a 25 ml flask, in the presence of 9.79 g (82.3 mmol) of thionyl chloride, 0.664 g (2.91 mmol) of **2** was added with 0.5 ml of dimethylformamide (DMF). This mixture was refluxed for 5 h, HCl produced in the course of this reaction being trapped in water. After this treatment, the excess of thionyl chloride was distilled off under reduced pressure at room temperature. The desired liquid was finally purified by distillation under reduced pressure (yield = 19%, b.p. = 94°C/0.3 mmHg). ^1H n.m.r. (CDCl$_3$, ppm): 1.16 (6H, t, $J = 7.5$ Hz); 2.91 (4H, q, $J = 7.5$ Hz). ^{13}C n.m.r. (CDCl$_3$, ppm): 13.85; 21.36; 138.70; 149.25; 158.53. I.r. (neat, NaCl, cm^{-1}): 2980; 2940; 2880; 1755; 1508; 1470; 1458; 1435; 1415; 1373; 1337; 1312; 1252; 1200; 1165; 1103; 1065; 1049; 1028; 991; 914; 868; 772; 747; 715; 682; 635.

3-Methyl-4-propyl-2-carbomethoxy-5-thiophenecarboxylic acid (**4**). This product was synthesized from 17.1 g (150 mmol) of 2,3-hexadione and 16.8 g (94 mmol) of dimethylthiodiacetate following the same procedure as that described for 1. A viscous liquid was obtained with a yield of 41%. ^1H n.m.r. (CDCl$_3$, ppm): 0.99 (3H, t, $J = 7.3$ Hz); 1.55 (2H, s); 2.51 (3H, s, $J = 7.2$ Hz); 2.96 (2H, t, $J = 7.9$ Hz); 3.90 (3H, s).

3-Methyl-4-propyl-2,5-thiophenedicarboxylic acid (**5**). This compound was synthesized by hydrolysis of **4** following the same procedure as that described above for **1** (yield = 84%). This solid undergoes a decarboxylation reaction at 185°C. ^1H n.m.r. ((CD$_3$)$_2$CO, ppm): 0.95 (3H, t, $J = 7.3$ Hz); 1.54 (2H, m); 2.49 (3H, s); 2.97 (2H, t, $J = 7.9$ Hz). ^{13}C n.m.r. ((CD$_3$)$_2$CO, ppm): 13.74; 14.29; 23.24; 30.96; 131.37; 131.56; 146.46; 151.52; 153.28; 163.52. I.r. (KBr, cm^{-1}): 3520–3200; 2980; 2860; 2790; 1680; 1575; 1460; 1400; 1280; 1258; 1169; 1090; 1035; 905; 768.

3-Methyl-4-propyl-2,5-thiophenedicarbonyl chloride (**6**). Following a similar procedure to that described for the preparation of **3** a liquid was obtained with a yield of 19% (b.p. = 160°C/25 mmHg). ^1H n.m.r. (CDCl$_3$, ppm): 0.99 (3H, t, $J = 7.3$ Hz); 1.52 (2H, m); 2.47 (3H, s); 2.89 (2H, t, $J = 7.9$ Hz). ^{13}C n.m.r. (CDCl$_3$, ppm): 13.79; 14.39; 22.42; 30.03; 138.46; 138.81; 149.17; 154.21; 158.62; 158.96. I.r. (neat, NaCl, cm^{-1}): 2950; 2920; 2860; 1745; 1505; 1450; 1412; 1370; 1320; 1270; 1223; 1198; 1162; 1100; 1040; 1010; 951; 869; 820; 747; 717; 700.

3,4-Diphenyl-2-carbomethoxy-5-thiophenecarboxylic acid (**7**). Following the procedure described for the synthesis of **1**, the desired solid was obtained from 63.1 g (300 mmol) of benzyl and 35.6 g (200 mmol) of dimethylthiodiacetate with a yield of 43%. ^1H n.m.r. (CDCl$_3$, ppm): 3.75 (3H, s); 7.03–7.96 (10H, m).

3,4-Diphenyl-2,5-thiophenedicarboxylic acid (**8**). From the hydrolysis of **7** following a procedure similar to that previously described for **1**, a white powder was recovered with a yield of 66%. ^1H n.m.r. ((CD$_3$)$_2$CO, ppm); 7.06–7.09 (8H, m); 7.14–7.17 (2H, m). ^{13}C n.m.r. ((CD$_3$)$_2$CO, ppm): 127.98; 128.04; 128.26; 128.81; 129.76; 131.01; 162.83. I.r. (KBr, cm^{-1}) 3340–3120; 1670; 1530; 1488; 1463; 1442; 1420; 1390; 1348; 1290; 1265; 1214; 1153; 1138; 1068; 1027; 916; 848; 768; 740; 682; 661; 627; 603; 497.

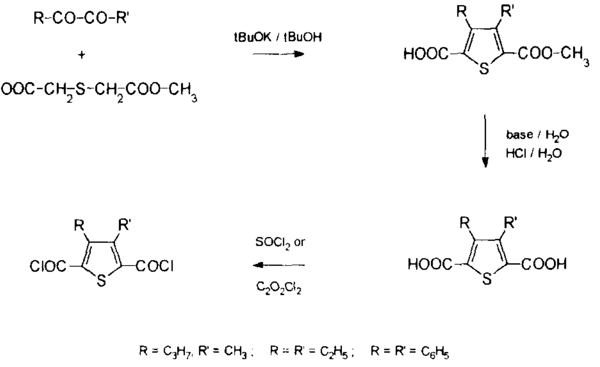
3,4-Diphenyl-2,5-thiophenedicarbonyl chloride (**9**). This was prepared following similar procedures to those reported above using oxalyl chloride (Aldrich) as chlorinating agent. After purification by distillation under reduced pressure ($T_b = 175\%/10$ mmHg), the desired product was obtained with a yield of 23%. ^1H n.m.r. ((CD$_3$)$_2$CO, ppm): 6.97 (4H, m); 7.00 (4H, m); 7.25 (2H, m). ^{13}C n.m.r. ((CD$_3$)$_2$CO, ppm): 127.98; 128.04; 128.26; 128.81; 129.76; 131.01; 162.83. I.r. (KBr, cm^{-1}): 3060; 3030; 1760; 1510; 1440; 1415; 1346; 1256; 1156; 1120; 1070; 1020; 932; 898; 860; 749; 710; 689; 646; 602; 580; 470.

Polymerization

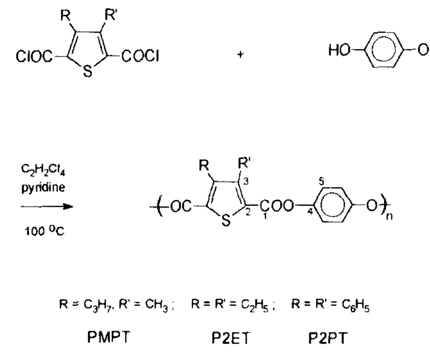
All polymerization reactions were carried out following a procedure similar to that described by Ballauf[4]. As an example, poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicarboxylate) (PMPT) was prepared as follows: In a three-necked, 50 ml flask equipped with a condenser, a magnetic stirrer and a nitrogen inlet, 1.012 g (3.82 mmol) of **6** and 420 mg (3.82 mmol) of freshly purified hydroquinone were added to 12 ml of tetrachloroethane. The mixture was stirred for a few minutes, and 2.5 ml (31 mmol) of pyridine was then added. The solution was heated at 100°C for 3 h. After cooling at room temperature, the solution was poured into 120 ml of tetrachloroethane and then precipitated in 2000 ml of methanol. The fine white powder is filtered, washed with methanol and dried under reduced pressure for several days; 1.254 g of the white polymer is obtained for a yield of 92%.

Characterization

*FT*i.r. measurements were recorded on a Bio-Rad FTS-25 spectrophotometer. Solution and solid-state n.m.r. measurements were performed with a Varian VXR-300 spectrometer. Deuterated chloroform or



Scheme 1



Scheme 2

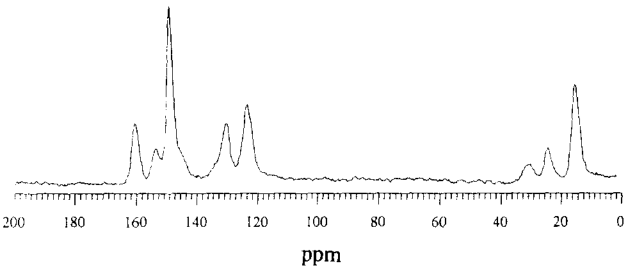


Figure 1 Solid-state ^{13}C n.m.r. spectrum of poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicarboxylate) (PMPT)

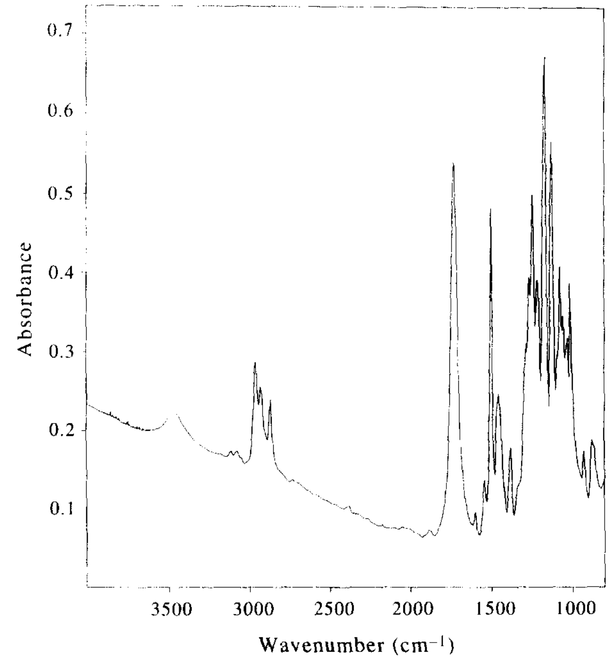


Figure 2 *FT*i.r. spectrum of poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicaboxylate) (PMPT)

acetone was used as solvent and reference. Size exclusion chromatography (s.e.c.) measurements were carried out with a Waters apparatus using a series of three Ultrastyragel columns with upper porosity limits of 10, 50 and 100 nm. The calibration curve was obtained by running monodisperse polystyrene standards in chloroform. Thermal characterization of the polymers was obtained with a differential scanning calorimeter (TA Instrument, DSC 2910) at a heating rate of 10°C min^{-1} under a nitrogen flow. Modulated dynamic scanning calorimetric measurements were carried out with an amplitude of 1°C and a period of 60 s for an oscillation. Thermogravimetric measurements (t.g.a.) were performed with Shimadzu TA-50 apparatus under an argon atmosphere at a heating rate of 10°C min^{-1}. The decomposition temperature is determined as the temperature where a 5% weight loss is observed[3]. Polarized optical microscopy was carried out with a Walter A. Carveth microscope equipped with a thermal controller (Reichert Austria).

THEORETICAL CALCULATIONS

The starting geometry was obtained from the program MODEL, which enables us to draw the structure, optimize roughly the geometry using the MM2 force field, and finally generate the corresponding Cartesian coordinates[11]. A more precise geometry optimization was then obtained using the AM1 Hamiltonian from the AMPAC package (SEMI-CHEM 1993), version 4.5[12,13].

RESULTS AND DISCUSSION

In order to obtain high-molecular-weight polyesters derived from thiophenes, it was first very important to find a synthetic method that could yield well defined derivatives of 2,5-thiophenedicaboxylic acids (or 2,5-thiophenedicarbonyl chlorides). The procedure developed by Hinsberg[14] is the method of choice since it can give in one-step reaction tetra-substituted thiophenes, which can be easily converted into 3,4-disubstituted 2,5-thiophenedicarboxylic acids (see *Scheme 1*). These compounds have been converted into diacid chlorides (*Scheme 1*) and then polymerized with hydroquinone to give the desired polyesters following the procedure described in *Scheme 2*.

Following this polymerization procedure, all polyesters have been obtained in good yields (ca. 90%). Poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicarboxylate) (PMPT) has been found to be soluble in chloroform, whereas poly(*p*-phenylene 3,4-diethyl-2,5-thiophenedicaboxylate) (P2ET) and poly(*p*-phenylene 3,4-diphenyl-2,5-thiophenedicarboxylate) (P2PT) are not soluble in common organic solvents. Size exclusion chromatography (s.e.c.) measurements have thus been performed on PMPT in chloroform. These measurements give a number-average molecular weight of 7600 with a polydispersity of 3.4 for this polymer, indicating that polymers with moderate degrees of polymerization (ca. 25) can be obtained with this type of polymerization reaction.

Table 1 The ^{13}C n.m.r. chemical shifts and assignments for PMPT, P2ET and P2PT

	Chemical shift (ppm)		
	PMPT	P2ET	P2PT
C_1	160.0	160.2	166.2
C_2	153.2	154.9	160.9
C_4	148.2	148.4	147.3
C_3	130.0	130.0	128.7
C_5	122.8	122.8	120.8
$C_{RR'}$	30.0	21.4	125.0–140.0
	23.0	15.0	
	14.0		

Table 2 Infra-red absorption positions and assignments[a] for PMPT, P2ET and P2PT

	Wavenumber (cm^{-1})		
	PMPT	P2ET	P2PT
ν(CH arom.)	3100–3000	3100–3040	3080–3000
ν(CH aliph.)	2960	2980	
	2930	2940	
	2870	2875	
$\nu(C = O)$	1730	1750	1720
$\nu(C = C$ thio.)	1500	1500	1500
$\nu(C = C$ phen.)	1600	1600	1600
	1450	1455	1440
$\gamma(= CH$ phen.)	750	748	752

[a] ν = stretching, γ = out-of-plane bending

Table 3 Summary of the thermal properties PMPT, P2ET and P2PT

	T_g (°C)	T_c (°C)	ΔH_c ($J g^{-1}$)	T_m (°C)	ΔH_m ($J g^{-1}$)	T_d[a] (°C)
PMPT	122[b]	187	22.8	242	33.1	360
P2ET	140	241	5.4	304	33.2	345
P2PT				> 395		395

[a] Measured by t.g.a.
[b] Glass transition measured by modulated d.s.c.

In order to characterize well all these aromatic polyesters, solid-state ^{13}C n.m.r. and *FT*i.r. measurements have been performed. As an example, the solid-state ^{13}C n.m.r. and *FT*i.r. spectra of PMPT are shown in *Figures 1* and *2*, respectively. Moreover, the spectroscopic data of all polymers can be found in *Tables 1* and *2*. All materials exhibit n.m.r. and *FT*i.r. spectra in perfect agreement with their expected structure. Particularly, the sharp absorption peak at 1730 cm^{-1} in *Figure 2* is a clear indication of the ester-forming reaction. The absorption band around 3500 cm^{-1} can be attributed to polymer end-groups (acid or hydroxyl) but also to water and/or methanol trapped within the polymer. Similar features have also been observed with P2PT and P2ET.

The thermal transitions were then characterized by dynamic scanning calorimetry and modulated dynamic scanning calorimetry (m.d.s.c.). The latter technique allows the identification of 'reversible' thermal transitions (such as glass transition or melting) and 'non-reversible' thermal transitions (such as cold crystallization phenomenon). The 'non-reversibility' of a thermal transition is related to strong kinetic effects. As shown in the first curve (combining reversible and non-reversible phenomena) of *Figure 3*, PMPT exhibits an exothermic peak at 187°C and an endothermic peak at 242°C. Modulated d.s.c. indicates that the first peak is irreversible in the timescale of the experiment and can be related to the cold crystallization of PMPT. On the other hand, the endothermic melting transition is reversible. The glass transition (at 122°C) can be clearly observed in the curve of reversible phenomena. Similar thermal transitions were obtained with P2ET, while P2PT did not exhibit any transition before decomposition (see *Table 3*). As expected, the presence of flexible side chains strongly decreased the temperature of the thermal transitions (the related unsubstituted polyester does not show any transition below 500°C (ref. 3)) while good thermal stability is maintained up to 350–400°C.

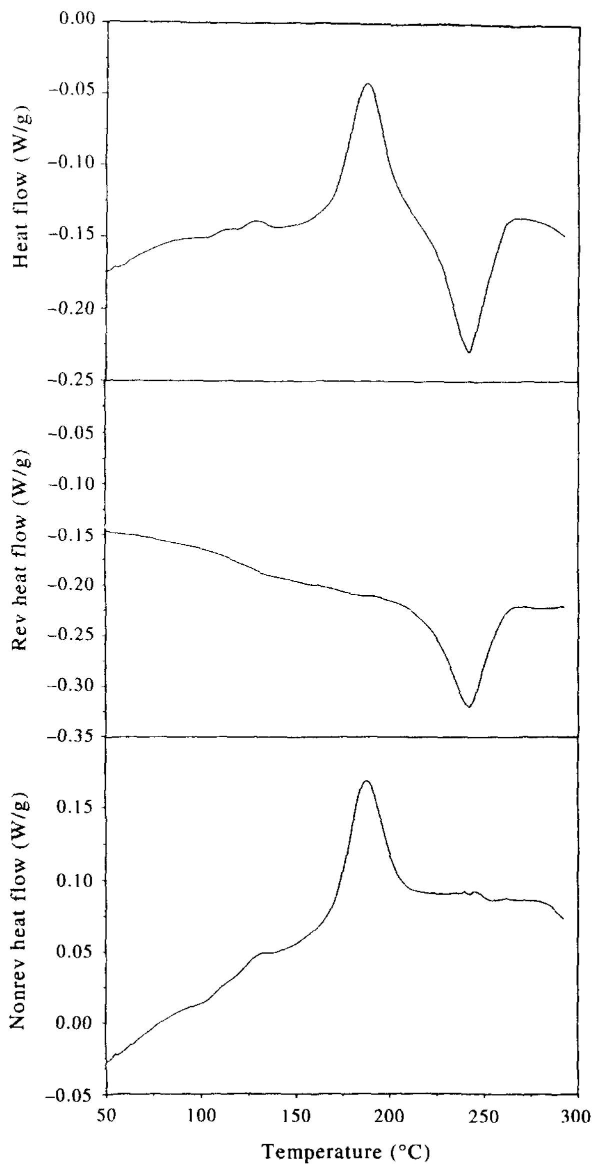


Figure 3 Modulated d.s.c. thermograms of poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicarboxylate) (PMPT). First curve, total heat flow; second curve, reversible heat flow; and third curve, non-reversible heat flow

To obtain an understanding of the endothermic phenomena observed in PMPT and P2ET, polarized optical microscopy measurements have been performed.

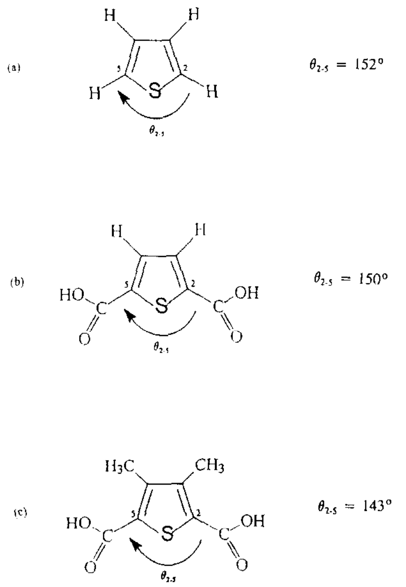


Figure 4 Core angle in several thiophene model compounds

Table 4 Angles around the sulfur atom determined by AMPAC calculations for three model compounds

Molecule	Angle $H(C_1)-C_2-S$ (deg)	Angle C_5-S-C_2 (deg)
Thiophene	122.8	93.8
2,5-Thiophenedicarboxylic acid	122.3	94.3
3,4-Dimethyl-2,5-thiophene-dicarboxylic acid	118.8	94.7

Unfortunately, these studies did not reveal any liquid-crystalline phase in PMPT and P2ET. These results indicate that aromatic polyesters derived from substituted thiophene units melt directly into the isotropic liquid phase without forming liquid-crystalline phases. It is important to note that mesophases were observed by Samulski *et al.*[3] in similar polyesters with small substituents on the hydroquinone unit. It can therefore be considered that the addition of substituents onto the thiophene moieties do not allow the formation of mesophases.

This feature could be related to a stronger deviation from a colinear conformational structure. Indeed, as reported by Samulski *et al.*[3], the thiophene unit exhibits a core angle (the angle subtending the exocyclic bonds in the 2,5-thiophene diacid) of about 148° but it is not clear that a similar angle can be kept in the 3,4-dialkyl-2,5-thiophenedicarboxylic acids. In order to obtain more information about this aspect, theoretical calculations (AMPAC) were performed on model compounds. More details on the success of this semiempirical calculation applied to similar aromatic systems to predict the ground-state structural characteristics can be found in recent publications[15-18]. *Table 4* shows the calculated angles (AMPAC) around the sulfur atom for these substituted thiophene rings, which allows us to obtain from simple geometric means the core angles shown in *Figure 4*. A core angle of 152° is calculated for thiophene. This value is slightly smaller (ca. 150°) in 2,5-thiophenedicarboxylic acid and is in good agreement with that reported by Samulski *et al.*[3]. However, the presence of two methyl groups at the 3- and 4-positions leads to a strong modification of the core angle from 150° to 143°. Although the absolute value of this angle must be taken with caution, it clearly indicates that 3,4-dialkyl-2,5-thiophenedicarboxylic acids induces a more important deviation than the unsubstituted 2,5-thiophenedicarboxylic acid. Consequently, it may explain why no liquid-crystalline phase was observed in PMPT and P2ET. It is important to note, again, that Samulski *et al.*[3] had already reported that *m*-phenylene units with a core angle of 120° inhibit the formation of mesophases. However, it can be assumed that the introduction of substituted dithiophene units (in *anti* conformation) should lead to a more linear backbone and therefore stabilize the formation of liquid-crystalline phases. Polyesters derived from bithiophenes are being prepared as well as other polyesters with an even number of thiophene units. It is believed that the introduction of tetrathiophenes or sexithiophenes can lead to the development of electroactive and photoactive liquid-crystalline polymers.

CONCLUSIONS

Novel aromatic polyesters derived from 3,4-disubstituted-2,5-thiophenedicarbonyl chlorides and hydroquinone have been prepared. The introduction of phenyl substituents on the thiophene moiety did not lead to a substantial decrease of the thermal transitions when compared to the unsubstituted polyester ($T_m > 345°C$). The presence of more flexible side chains such as ethyl groups has given a semicrystalline polymer that melts at 308°C. However, this polymer is insoluble in common organic solvents. An asymmetric substitution pattern (e.g. poly(*p*-phenylene 3-methyl-4-propyl-2,5-thiophenedicarboxylate)) has led to a soluble aromatic polyester with a melting temperature at 242°C. All these materials are stable up to 350–400°C. However, in contrast to the unsubstituted polyester, no birefringence was observed in the melt. On the basis of theoretical calculations, this absence of liquid crystallinity can be explained by the presence of non-linear units with a core angle of about 143°.

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