# Liquid Crystalline Aromatic Polyesters Derived from 2,5-Thiophene

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ABSTRACT: We have synthesized new liquid crystalline aromatic polyesters composed of 2,5-thiophenedicarboxylic acid and (substituted) hydroquinones as part of a continuing investigation of molecular structural effects on liquid crystallinity. Here we examine the effects of monomer (mesogenic core) nonlinearity on mesophase stability in liquid crystalline polymers. To this end, new polyesters containing 2,5-thiophenedicarboxylic acid are contrasted with corresponding polymers synthesized from terephthalic acid and isophthalic acid. Polyesters containing 2,5-thiophenedicarboxylic acid and substituted hydroquinones form nematic melts; liquid crystallinity is not found in the corresponding isophthalic acid polyesters. The observed melting (softening) temperatures of the polyesters decrease systematically as the core angle—the angle subtended by the exocyclic bonds in the dicarboxylated aromatic rings—changes from 180° (*p*-phenylene) to 148° (2,5-thiophene) to 120° (*m*-phenylene). Thermogravimetric analysis shows that the polyesters containing 2,5-thiophenedicarboxylic acid have thermal stabilities similar to those of polyesters containing terephthalic acid and isophthalic acid. These findings indicate that 2,5-thiophenedicarboxylic acid is a viable monomer for inserting nonlinear "defects" into polyesters while maintaining liquid crystallinity, thereby lowering the melting temperature to give tractable materials.

## Introduction

Thermotropic, main-chain, liquid-crystalline polymers (LCPs) have been intensively studied over the last 2 decades primarily to extend the range of physical properties of high-performance polymers (i.e., to improve thermal stability, processability, mechanical strength, etc.). Most commercially important thermotropic LCPs are a subset of polyesters which retain long-range molecular orientational order in their melts.[1-3] Often they exhibit molecular structural features that are directly related to those of low molar mass liquid crystals (LCs). In the extreme, the primary structure of thermotropic LCPs may simply be a chain of covalently linked, low molar mass, mesogenic cores. (The mesogenic core is the primitive structural unit having the requisite anisotropic excluded-volume interactions and attractive interactions to establish long-range intermolecular order in its melt.) Generally, the mesomorphic behavior exhibited by low molar mass LCs is retained (and frequently stabilized) by polymerizing mesogenic cores into a linear chain or incorporating them as pendant groups—side-chain LCPs.[4] Occasionally, incipient liquid crystallinity may be overtly expressed by polymerizing nonmesogenic cores.[5] Importantly, thermal properties of main-chain LCPs may be molecular-engineered through varying the backbone rigidity (persistence length) by judiciously choosing the linkage groups between cores and/or inserting "defects"—nonlinear or kinked structures—into the core itself. Here we exploit the discovery by Cai and Samulski[6] that the nonlinear 2,5-thiophene moiety may be incorporated into low molar mass mesogenic cores with the retention of liquid crystallinity. Admittedly, their thiophene-based mesogens exhibited very small ranges of thermotropic liquid crystallinity (≤10°). However, we can anticipate from the preceding introductory remarks about LCPs that the range of mesomorphism of the thiophene-based cores will be enhanced when they are incorporated into a linear polymer chain.

Herein we focus on contrasting thermal properties of polyesters having the well-known aromatic diacid monomer units derived from benzene (terephthalic acid and isophthalic acid) with the diacid of thiophene. While both 2,5-thiophenedicarboxylic acid and isophthalic acid introduce nonlinearity into the molecular structure of the polymer and thereby lower melting temperatures, Cai and Samulski showed that the thiophene heterocycle lowers the melting temperature of LCs without destroying liquid crystallinity.[6] That observation prompted us to explore the consequences of inserting thiophene into polyesters. We sought materials with lower melting temperatures which kept the desirable option of mesophase formation and its processing advantages. This study reports the synthesis and properties of several aromatic polyesters consisting of 2,5-thiophenedicarboxylic acid and several substituted hydroquinones. We contrast the melting temperatures and mesophase ranges of thiophene-based nonlinear polyesters with those of phenylene-based polyesters derived from terephthalate and isophthalate monomers.

## Experimental Section

**Synthesis. Purified terephthalic acid and isophthalic acid** were obtained by the hydrolysis of the recrystallized (from $CH_2Cl_2$) dimethyl esters (Aldrich Chemical Co.).

**2,5-Thiophenedicarboxylic acid** (Chem Service) was converted to the diacid chloride with excess thionyl chloride. 2,5-Thiophenedicarbonyl chloride reacted with methanol to form the dimethyl ester, and then the pure 2,5-thiophenedicarboxylic acid was obtained as described above. All the diacids were vacuum dried at 60 °C overnight before the polymerization.

**Hydroquinone and substituted hydroquinones** (Aldrich Chemical Co.) were converted to diacetates by heating the hydroquinones with 10% excess of acetic anhydride and several drops of $H_2SO_4$ at 100 °C for 10 h. The mixture was slowly poured into ice water, and the precipitate was filtered, dried, and recrystallized from 95% ethanol and then from $CH_2Cl_2$. The purities of these hydroquinone diacetates were checked by a constant melting temperature in differential scanning calorimetry (DSC) measurement.

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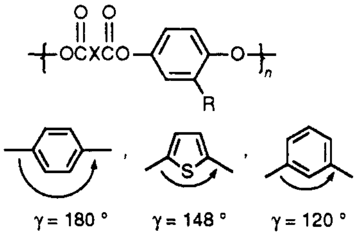
All polyesters were prepared by melt transesterification of the diacetates and the diacids without a catalyst. The reaction apparatus is described in ref 20, and the reaction temperature program was controlled by using vapor baths derived from several high-boiling liquids. The polymerizations were carried out in three stages under argon: (1) 1 h at 282 °C (dimethyl phthalate bath); (2) 1 h at 340 °C (anthracene bath); (3) $^1/_2$ h at 380 °C (anthraquinone bath). This last stage of the polymerization was carried out under vacuum ($P$ = 0.5 mmHg).

**Characterization.** Inherent viscosity values (0.5 g/dL) were determined with an Ubbelohde viscometer at 30 °C for polymer solutions in a mixed solvent $CF_3COOH:CH_2Cl_2$ (3:2). Polarizing microscopy was performed with a Nikon (Microphot-FX) microscope equipped with a Linkam (TMS-90) hot stage. Transition temperatures and enthalpy changes were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter. DSC thermograms were recorded at heating rates of 40 °C/min under a nitrogen flow. The polymer samples were divided into two categories: (A) as-prepared samples and (B) annealed samples, according to their thermal history. The A polymers were taken directly from the reaction tube, and the B polymers were annealed at 250 °C for 20 h immediately before the measurements. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGS-2 at heating rates of 20 °C/min under nitrogen. The softening temperature $T_S$ was measured with a thermomechanical analyzer (TMA; Perkin-Elmer TMA-7) operating at a heating rate of 20 °C/min under a load force of 100 mN.

## Results

In this study, we consider the following three series of polyesters (I) consisting of diacids X and (substituted) hydroquinones:



where X, the central ring, is one of three aromatic diacids: $p$-phenylene (terephthalic acid, TA), $m$-phenylene (isophthalic acid, IA), or 2,5-thiophene (2,5-thiophenedicarboxylic acid, T). The "core angle" $\gamma$ subtending the exocyclic bonds in the diacid X dictates how much the backbone deviates from linearity ($\gamma$ = 180°). The substituent R on the hydroquinone ring may be H, Cl, $CH_3$, or $C_6H_5$. Each member of the matrix of 12 polyesters was synthesized by three-stage melt polymerization in which the temperature of the last stage (380 °C) was selected to maximize the melt mobility in order to achieve high molecular weight polymerization while minimizing thermal degradation. The inherent viscosity numbers of the soluble polyesters in the matrix are given in Table I; the softening temperature, $T_S$, mesophase formation, and decomposition temperatures, $T_D$, are also tabulated. The thermodynamic data of the phase transitions are summarized in Table II. The glass transition temperatures, $T_g$, was measured for the two A and B categories of polymer samples distinguished by their thermal histories: the $T_g$ for the as-prepared samples (virgin) was recorded from the first DSC heating run, and the $T_g$ for the annealed samples was recorded from the second DSC heating run.

**Thermal Behavior. Hydroquinone (HQ) Polyesters.** Poly($p$-phenylene terephthalate) (HQ/TA) and poly($p$-phenylene 2,5-thiophenedicarboxylate) (HQ/T), in which simple hydroquinone is polymerized with TA or T, do not show any transitions below 500 °C as measured by DSC and optical microscopy (see Table I). Poly($p$-phenylene isophthalate) (HQ/IA) exhibits an endothermic peak with an onset temperature at 396 °C in both the virgin and annealed sample. HQ/IA also shows a glass transition at $T_g$ = 158 °C; no corresponding transition was observed for the HQ/TA and HQ/T polymers. In addition to DSC measurements, we used TMA to study the softening temperatures ($T_S$) of these polymers. The softening temperatures of HQ/TA and HQ/T are higher than 500 °C, while HQ/IA exhibits the softening at $T_S$ = 396 °C. The fluidity of the melt of the HQ/IA polymer inferred from TMA and the DSC endothermic transition indicates that the transition at 396 °C corresponds to the melting of HQ/IA.

**Table I**
**Thermal Properties of Polyesters (I)[a]**

| X | R | $\eta_{inh}$, dL/g | $T_s$ ($T_g$), °C | LC? | $T_D$ (5% wt loss) |
|---|---|---|---|---|---|
| TA | H | insol | >500 | | 530 |
| TA | Cl | insol | 348 | yes* | 520 |
| TA | $CH_3$ | insol | 383 | yes* | 514 |
| TA | $C_6H_5$ | 3.7 | 320 | yes | 513 |
| T | H | insol | >500 | | 520 |
| T | Cl | insol | 384 | yes | 529 |
| T | $CH_3$ | insol | 332 | yes | 480 |
| T | $C_6H_5$ | 0.5 | 256 | no | 490 |
| IA | H | insol | 396 | no | 535 |
| IA | Cl | 0.6 | 296 (144) | no | 510 |
| IA | $CH_3$ | 0.5 | 284 (127) | no | 496 |
| IA | $C_6H_5$ | 0.4 | (145) | no | 503 |

[a] $T_s$ is the softening temperature measured by TMA. $T_D$ is the decomposition temperature (5% weight loss) measured by TGA. Asterisks indicate strong stir opalescence.[8]

**Chlorohydroquinone (ClHQ) Polyesters.** Figure 1 shows the DSC heating traces for the ClHQ-based polymers. Poly(chloro-$p$-phenylene terephthalate) (ClHQ/TA) exhibits a reversible transition at 375 °C (Figure 1a). Poly(chloro-$p$-phenylene 2,5-thiophenedicarboxylate) (ClHQ/T) has an endoterm at 410 °C (Figure 1b). Poly(chloro-$p$-phenylene isophthalate) (ClHQ/IA) is a semicrystalline polymer with a glass transition temperature of 146 °C, a crystallization temperature of 240 °C, and a melting temperature of 308 °C (Figure 1c). The glass transition is not observed for the ClHQ/TA and ClHQ/T polymers. From the DSC traces in Figure 1, it appears that ClHQ/T has the highest transition temperature. If we attribute all these reversible endotherms in Figure 1 to a melting transition, then we have to conclude that the linear polymer ClHQ/TA has a lower $T_m$ than the nonlinear polymer ClHQ/T. This apparent contradiction is resolved when these endothermic transitions are examined more closely by TMA and optical microscopy.

Figure 2 shows the TMA data of the same series of polymers. It is clear from the small height change sensed by the TMA penetration probe for ClHQ/TA (around 375 °C) that the corresponding DSC endotherm in Figure 1a corresponds to a solid-state (softening) transition and not, as in the ClHQ/T and ClHQ/IA polymers (Figure 2b,c), to actual melting. In fact, we did not observe the actual melting of ClHQ/TA below 500 °C with polarizing microscopy; i.e., $T_m$ >500 °C for ClHQ/TA. The solid-to-solid transition temperature (~350–375 °C, in Figure 1a) or the softening temperature (~360–380 °C, in Figure 2) of HQ/TA should not be compared with the true melting temperatures of ClHQ/T and ClHQ/IA. For the latter polymers, the TMA data exhibit a complete height change (100% decrease) corresponding to a melting transition. Additionally, the TMA analysis of the ClHQ/IA polymer (Figure 2c) indicates that this polymer has a rubbery region; i.e., the polymer softens gradually above its $T_g$ (144 °C) and melts precipitously at 296 °C.

**Methylhydroquinone (MeHQ) Polyesters.** Figure 3 shows the DSC heating traces for the MeHQ polymers

**Table II**
**Thermodynamic Properties of Polyesters (I)**

| | | as-prepared "virgin" polymer | | | | | annealed polymer | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| X | R | $T_g$, °C | $T_K$,[a] °C | $\Delta H$, kJ·mol$^{-1}$ | $T_m$, °C | $\Delta H$ kJ·mol$^{-1}$ | $T_g$,[b] °C | $T_K$, °C | $\Delta H$, kJ·mol$^{-1}$ | $T_m$, °C | $\Delta H$, kJ·mol$^{-1}$ |
| TA | H | | | | >500 | | | | | >500 | |
| TA | Cl | | 358 | 5.2 | >500 | | | 372 | 9.3 | >500 | |
| TA | $CH_3$ | | 366 | 4.0 | >500 | | | 417 | 3.9 | >500 | |
| TA | $C_6H_5$ | 158 | | | 317 | 5.1 | 158 | | | 353 | 7.4 |
| T | H | | | | >500 | | | | | >500 | |
| T | Cl | | | | 395 | 10.8 | | | | 396 | 9.8 |
| T | $CH_3$ | | | | 335 | 5.2 | | | | 334 | 5.4 |
| T | $C_6H_5$ | 148 | | | 262 | 6.2 | 146 | | | 280 | 9.2 |
| IA | H | 198 | | | 396 | 23.4 | 200 | | | 408 | 24.2 |
| IA | Cl | 146 | 213 | 4.6 | 290 | 5.3 | 173 | | | 326 | 17.8 |
| IA | $CH_3$ | 133 | 168 | 1.5 | 296 | 10.2 | 170 | | | 314 | 14.0 |
| IA | $C_6H_5$ | 150 | | | | | 150 | | | | |

[a] Solid–solid transition. [b] Glass transition measured from a quenched sample in the second heating run.

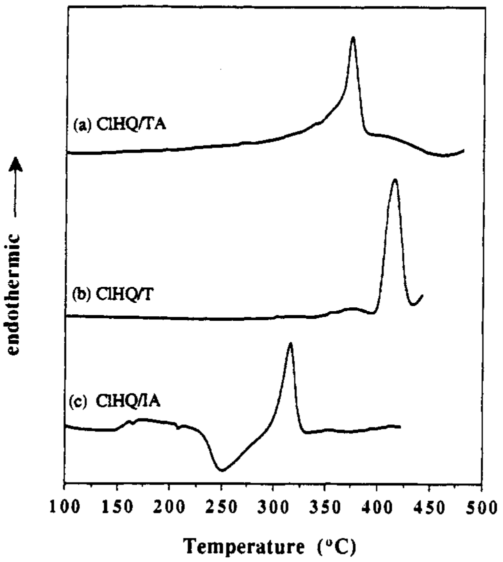


**Figure 1.** DSC traces of polyesters (I) with R = Cl and (a) X = *p*-phenylene (ClHQ/TA), (b) X = 2,5-thiophene (ClHQ/T), and (c) X = *m*-phenylene (ClHQ/IA) (heating rate of 40 °C/min).

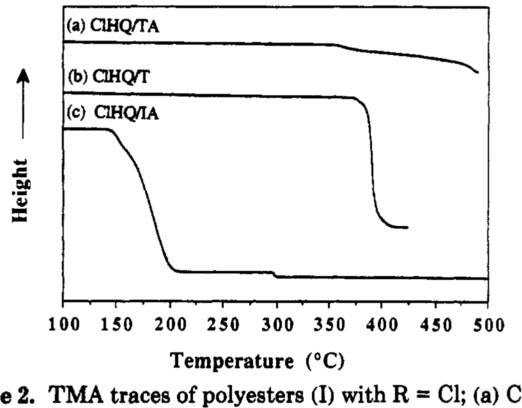


**Figure 2.** TMA traces of polyesters (I) with R = Cl; (a) ClHQ/TA; (b) ClHQ/T; (c) ClHQ/IA (heating rate of 20 °C/min and a load force of 100 mN).

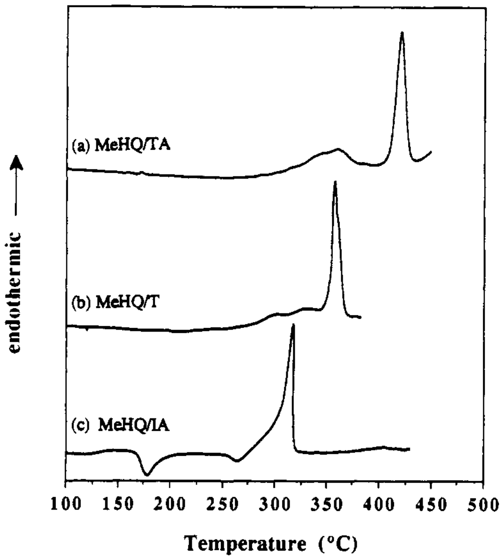


**Figure 3.** DSC traces of polyesters (I) with R = $CH_3$ and (a) X = *p*-phenylene (MeHQ/TA), (b) X = 2,5-thiophene (MeHQ/T), and (c) X = *m*-phenylene (MeHQ/IA) (heating rate of 40 °C/min).

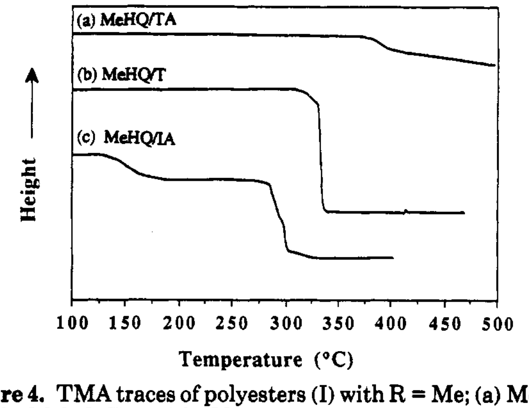


**Figure 4.** TMA traces of polyesters (I) with R = Me; (a) MeHQ/TA; (b) MeHQ/T; (c) MeHQ/IA (heating rate of 20 °C/min and a load force of 100 mN).

(R′ = $CH_3$). Poly(methyl-*p*-phenylene terephthalate) (MeHQ/TA) exhibits a broad transition near 360 °C and a sharp endothermic transition at 400 °C (Figure 3a). In the DSC scan of poly(methyl-*p*-phenylene 2,5-thiophenedicarboxylate) (MeHQ/T), a broad shoulder proceeds the main transition at 350 °C (Figure 3b). Poly(methyl-*p*-phenylene isophthalate) (MeHQ/IA) is a semicrystalline polymer: it exhibits a glass transition at 133 °C and a thermally induced crystallization at ~168 °C, and it finally melts at ~310 °C (Figure 3c). A glass transition was not observed for MeHQ/TA and MeHQ/T. The highest transition temperature $T_X$ of each X-based polyester in this series shifts to lower temperatures as the core angle, $\{\gamma\}$, in the dicarboxylate unit decreases; i.e., as core nonlinearity increases, we find the trend $T_{TA}\{180°\} > T_T\{148°\} > T_{IA}\{120°\}$.

The results of the TMA analysis of the MeHQ polymers are shown in Figure 4. MeHQ/TA softens in the temperature range corresponding to the DSC endothermic transitions (compare Figures 3a and 4a). Optical microscopy confirmed that MeHQ/TA does not flow below 500

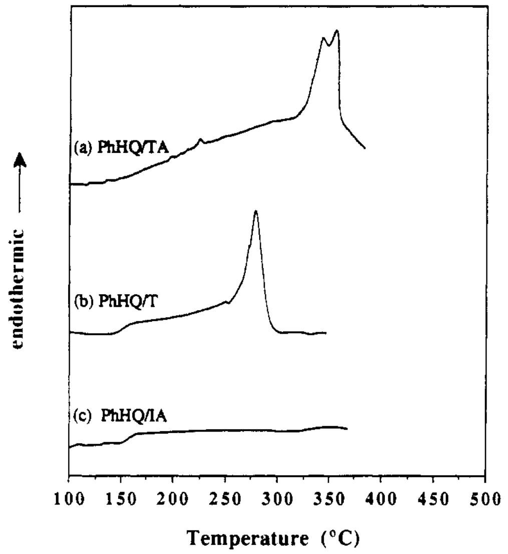


**Figure 5.** DSC traces of polyesters (I) with R = $C_6H_5$ and (a) X = *p*-phenylene (PhHQ/TA), (b) X = 2,5-thiophene (PhHQ/T), and (c) X = *m*-phenylene (PhHQ/IA) (heating rate of 40 °C/min).

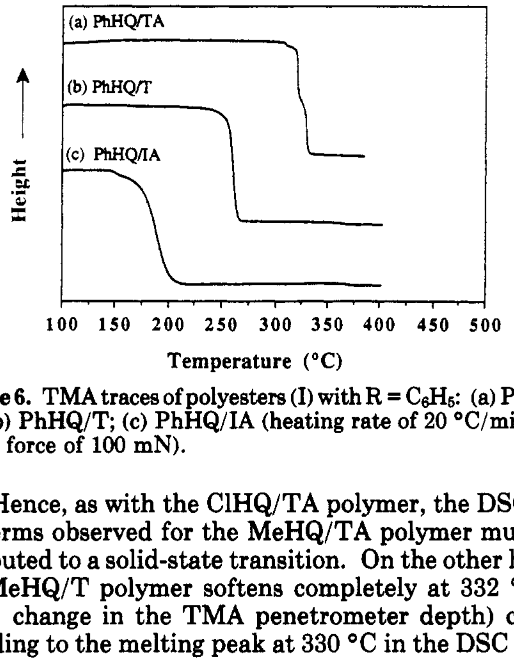


**Figure 6.** TMA traces of polyesters (I) with R = $C_6H_5$: (a) PhHQ/TA; (b) PhHQ/T; (c) PhHQ/IA (heating rate of 20 °C/min and a load force of 100 mN).

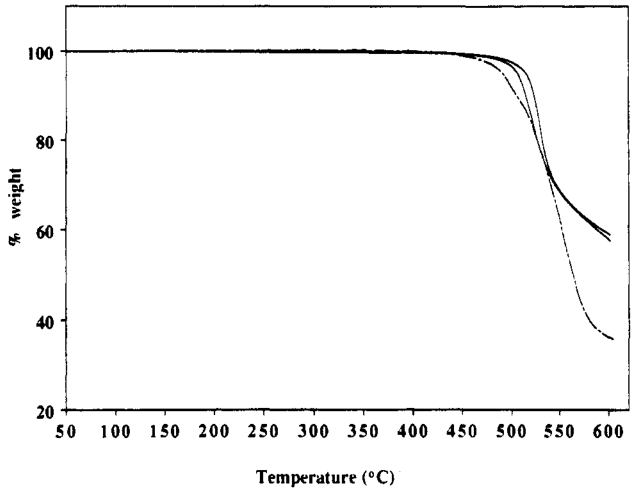


**Figure 7.** TGA traces of polyesters (I) with R = $C_6H_5$ recorded at a heating rate of 20 °C/min in nitrogen: dash line, X = 2,5-thiophene (PhHQ/T); upper solid line, X = *p*-phenylene (PhHQ/TA); lower solid line, X = *m*-phenylene (PhHQ/IA).

°C. Hence, as with the ClHQ/TA polymer, the DSC endotherms observed for the MeHQ/TA polymer must be attributed to a solid-state transition. On the other hand, the MeHQ/T polymer softens completely at 332 °C (a 100% change in the TMA penetrometer depth) corresponding to the melting peak at 330 °C in the DSC trace (Figure 4b). Two regions of softening are indicated for the MeHQ/IA polymer (Figure 4c). The first one (~130 °C) corresponds to the glass transition, and the second one corresponds to the polymer melting.

**Phenylhydroquinone (PhHQ) Polyesters.** The DSC heating traces and TMA data for the PhHQ polymers are shown in Figures 5 and 6, respectively. Poly(phenyl-*p*-phenylene terephthalate) (PhHQ/TA) exhibits complex DSC endotherms around 340 °C (Figure 5a) that correspond to multistage changes in the mechanical properties (Figure 6a; the last transition is simple melting). Poly(phenyl-*p*-phenylene 2,5-thiophenedicarboxylate) (PhHQ/T) with the nonlinear 2,5-thiophene unit exhibits a glass transition at 150 °C, but its TMA curve shows negligible changes in this region; PhHQ/T has a melting transition temperature ~250 °C. Poly(phenyl-*p*-phenylene isophthalate) (PhHQ/IA) is an amorphous polymer showing only a glass transition at $T_g$ = 150 °C (Figure 5c) and a gradual increase in fluidity in the region between 150 and 200 °C (Figures 5c and 6c).

It should be pointed out here that the melting temperatures of ClHQ/TA and MeHQ/TA have been reported to be lower than 400 °C in some earlier literature.[7-9] We therefore studied these polyesters very carefully by DSC, TMA, and optical microscopy and concluded that ClHQ/TA and MeHQ/TA have $T_m$ values higher than 500 °C. As we have demonstrated above, the DSC endotherms observed for ClHQ/TA (400 °C) and MeHQ/TA (370 °C) should be attributed to a reversible solid–solid transition. In contrast with ClHQ/TA and MeHQ/TA, the thiophene polyesters ClHQ/T and MeHQ/T melt below 450 °C. As the chemical (and aromaticity) differences between thiophene and benzene are small,[6] this decrease in melting temperature can be attributed to geometrical effects; i.e., the nonlinear core angle $\gamma$ = 148° in the thiophene unit. In all the polymers studied here, the melting temperature consistently decreases as the core angle decreases from the linear TA ($\gamma$ = 180°), to the intermediate case T ($\gamma$ = 148°), and to the extreme bend IA ($\gamma$ = 120°) in these aromatic diacarboxylates.

**Thermal Stability.** Thermogravimetric analysis (TGA) was carried out for polyesters based on 2,5-thiophenedicarboxylic acid, terephthalic acid, and isophthalic acid in order to compare their thermal stability. All polyesters remain stable up to 450 °C (the 5% weight-loss point, a measure of thermal stability, is found to be higher than this temperature). These results indicate that the thermal stability of polyesters containing 2,5-thiophene is comparable to those of phenylene-based polyesters. Representative TGA traces are shown in Figure 7 for the R = $C_6H_5$ polymers. The PhHQ/T polymer shows a more rapid weight loss with increasing temperature above 550 °C.

**Polarizing Microscopy.** A birefringent fluid melt is the signature of liquid crystallinity, and polarizing microscopy revealed that PhHQ/TA, ClHQ/T, and MeHQ/T polyesters form thermally stable nematic phases with $T_{NI}$ above 500 °C; thermal decomposition in the TA series precluded observation of LC formation in some polymers. All four IA polyesters melt directly into the isotropic liquid phase without forming LC phases. The photomicrograph in Figure 8 showing a typical schlieren texture observed for MeHQ/T is indicative of the nematic texture we observed for all mesogenic polyesters.

## Discussion

Wholly aromatic liquid crystalline polyesters are the most important commercial class of thermotropic LCPs because of their thermal and mechanical properties. Within this class of LCPs, the most widely used monomer

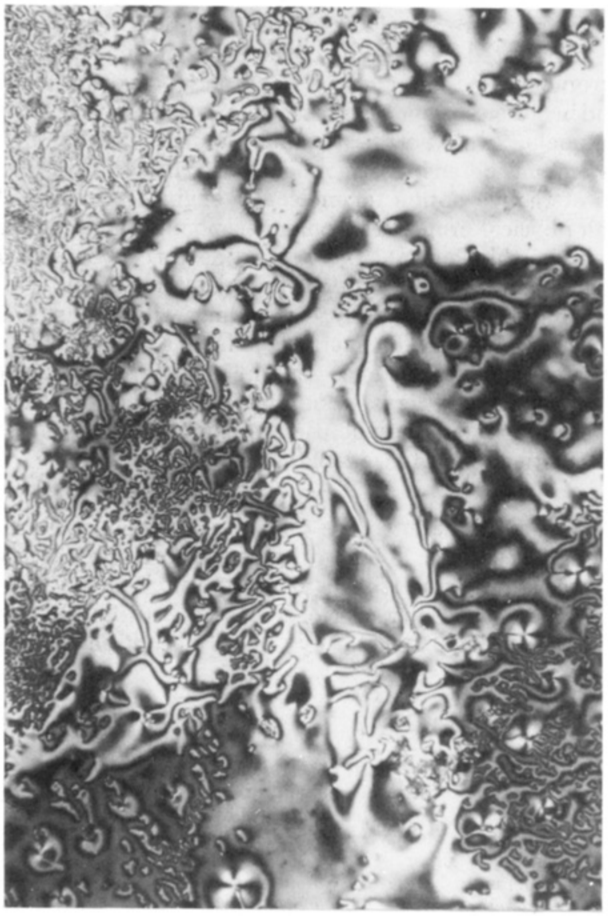


**Figure 8.** Melt of poly(methyl-*p*-phenylene 2,5-thiophenedicarboxylate) at 370 °C showing a schlieren nematic texture (crossed polars, 100×).

constituents are the *p*-phenylene, 4,4′-biphenyl, and 2,6-naphthalene rings.[4,10] In addition to these aromatic monomers, cyclic aliphatic monomers have also been used, e.g., 1,4-*trans*-cyclohexanedicarboxylic acid.[11,12] All of these monomers share a common structural feature: collinear or parallel exocyclic substitution which introduces (local) rigidity and rectilinearity into the polymer chain. The resulting increased persistence length of the chain (locally high aspect ratio) is a prerequisite to the mesophase formation. However, linear aromatic polyesters such as poly(*p*-oxybenzoate) and poly(*p*-phenylene terephthalate) have such high melting temperatures (610 and 600 °C, respectively[13]) that processing such polymers is essentially precluded. Consequently, at an early stage in the development of liquid crystalline polyesters, it became obvious that the high melting temperatures of this class of polymers had to be lowered before they would be used in applications. Several approaches have been used to lower the melting temperatures of aromatic polyesters including: (i) the introduction of bulky substituents into the monomer units to disrupt lateral packing; (ii) copolymerization to lower the symmetry of the polymer primary structure; (iii) the incorporation of flexible linker or spacer chains between rigid mesogenic cores; and (iv) the use of kinked or bent (nonlinear) monomers to lower the persistence length of the polymer in its fluid phases and disrupt lateral interactions in its solid state. All four of these approaches have been successful to some extent. We briefly summarize some representative findings.

**(i) Substitutents**: A variety of substituents have been attached to the *p*-phenylene rings of poly(*p*-phenylene terephthalate), e.g., halides, alkyl, alkoxy, and phenyl groups, to lower the melting temperatures of this polyester. For example, Krigbaum et al.[7] and Jackson et al.[14] reported the synthesis and characterization of polyesters composed of terephthalic acid and substituted hydroquinones. In the case of poly(chloro-*p*-phenylene terephthalate), the melting temperature, while quite variable according to the literature (372,[7] 340,[8] 360,[9] or above 400 °C[14,15]), is clearly lower than that of the parent unsubstituted polymer (~600 °C). Methyl substitution also lowers the melting point: poly(methyl-*p*-phenylene terephthalate) was reported to have a melting temperature of 371[8] or above 400 °C.[14] As anticipated, a large substituent produces a large effect: poly(phenyl-*p*-phenylene terephthalate) has a melting temperature of 340 °C.[14] More relevant to our investigation is the fact that all of these substituted homopolyesters exhibit liquid crystalline phases—anisotropic, birefringent fluid phases above their melting temperatures.

**(ii) Copolymerization**: Alternation of the monomer sense (head-to-head or head-to-tail configuration) lowers the primary structural regularity degrading lateral interactions between chains, thereby lowering polymer melting temperatures. An example of a successful commercial LCP which utilizes this method of producing tractable polyesters is Hoechst Celanese's Vectra, a poly(4-oxybenzoate-*co*-6-oxy-2-naphthalenecarboxylate), with $T_m$ = 250 °C (convenient for processing).[16] Amoco's Xydar, which is composed of terephthalic acid, isophthalic acid, hydroquinone, *p*-hydroxybenzoic acid, and 4,4′-biphenol, is another example; it can be melt-spun between 350 and 400 °C.[17] Numerous other copolyesters and terpolyesters which are thermally tractable have been reported.[18]

**(iii) Flexible spacers**: Roviello and Sirigu first described a regular alternating copolymer having a flexible spacer chain in linear thermotropic LCPs, the nematic poly(oxy-$\alpha,\alpha'$-dimethylbenzalazineoxyalkanoyl).[19] In such aromatic–aliphatic polymers there is a dilution of the aromatic monomer number density which in turn results in lower melting temperatures. However, such LCPs usually have inferior mechanical properties (relative to wholly aromatic polyesters).[20]

**(iv) Nonlinearity**: The influence of monomer linearity on the thermal property of liquid crystalline polyesters was considered in this paper. The classic (extreme) example of this phenomenon may be seen when the terephthalate unit is replaced by the isophthalate unit in homopolyesters. The 120° core angle of the latter unit reduces the chain persistence length and disrupts (local) chain parallelism integral to liquid crystallinity. In contrast to poly(*p*-phenylene terephthalate), poly(*p*-phenylene isophthalate) melts at 396 °C into an ordinary isotropic melt. In order to lower polymer melting temperatures while retaining liquid crystallinity, copolymerization and terpolymerization of various *p*- and *m*-phenylene rings have been explored. However, when the concentration of the nonlinear *m*-phenylene defects is increased beyond a certain critical value, liquid crystallinity in the melt is destroyed. Several results indicate that the critical percentage of meta-substituted phenylene rings compatible with liquid crystallinity is around 60 mol %. For example, the molar percentage of isophthalic acid cannot be increased above 67% in poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) and gives polymers that still retain liquid crystallinity.[21] Similarly, Lenz et al. found that to preserve liquid crystallinity the percentage of *m*-phenylene cannot exceed 60% in poly(chloro-*p*-phenylene-*co*-*m*-phenylene terephthalate)s.[8] These examples indicate that the incorporation of the nonlinear *m*-phenylene defects into polyesters does lower melting temperatures, but, at the same time, this $\gamma$ = 120° defect considerably decreases the mesophase stability.

Herein we pursued further the relationship among chain linearity, melting temperature, and mesophase stability. The motivation for this study was Cai and Samulski's[6] discovery that, contrary to earlier literature reports,[22] molecules based on the nonlinear 2,5-substituted thiophene moiety—bis(*p*-alkoxyphenyl) 2,5-thiophenedicarboxylates—form stable liquid crystal phases. (The bis(*p*-alkoxyphenyl) isophthalates are not liquid crystalline.[6]) While the observed mesophase temperature ranges were generally narrower than those of the corresponding bis(*p*-alkoxyphenyl) terephthalates,[6] the fact that liquid crystallinity was observed at all in a homologous series of low molar mass materials is important because mesophase stability is known to be very sensitive to small structural changes in the mesogen. Their results, in conjunction with the known chemical similarity between thiophene and benzene derivatives, allowed Cai and Samulski to attribute differences in the low molar mass LCs to geometrical differences between the terephthalate and 2,5-thiophenedicarboxylate (and isophthalate) moieties. The key implication of their findings is that the 148° core angle defect of 2,5-substituted thiophene, unlike the 120° core angle defect of isophthaltes, is not a mesophase-debilitating defect. Moreover, we infer that, unlike the isophthalate unit, there is no critical limit on the amount of the 2,5-thiophene unit one may incorporate into polymers as this defect is intrinsically compatible with liquid crystallinity. One may even encounter eutectic-like stabilization of the mesophase (i.e., a wide mesomorphic temperature range) with excellent solid-state properties in those copolymers of TA and T having certain critical ratios of these monomers in the backbone.

The principal findings reported here are conveniently summarized in the set of DSC traces of the methyl- and phenyl-substituted polyesters (see Figures 3 and 5). Above the melting point in both series of polyesters, the phase changes from nematic in the TA and the T polyester to an isotropic, rubbery melt state in the IA polyester. (In PhHQ/T, the combination of the 148° core angle in the thiophene unit and the bulky side chain results in the loss of liquid crystallinity.) This trend of going from a stable nematic phase in linear polyesters to no mesophase in the isophthalate series is in accord with the geometric "rules" advanced by Vorlander 70 years ago for low molar mass LCs: deviations from mesogen core linearity decrease mesophase stability.[23]

## Concluding Remarks

Linear polyesters containing terephthalic acid and substituted hydroquinones (ClHQ/TA and MeHQ/TA) exhibit solid–solid transitions on heating and have melting temperatures greater than 500 °C. The corresponding nonlinear 2,5-thiophene-based polyesters (ClHQ/T and MeHQ/T) melt below 450 °C and exhibit stable nematic phases. Neither of the isophthalic acid based polyesters (ClHQ/IA and MeHQ/IA) are liquid crystalline; the monomer core angle defect in the isophthalate unit is too severe for the extensive chain parallelism in liquid crystals. Thermogravimetric analysis demonstrates that the thermal stability of thiophene-based polyesters is similar to that of the terephthalate and isophthalate polyesters. Hence, our findings indicate that 2,5-thiophenedicarboxylic acid may be readily used to replace linear diacids in polyesters to produce thermally tractable materials without destroying liquid crystallinity. Since the 2,5-thiophene-based polyesters described here exhibit a rather wide mesophase range, we would anticipate that polyesters employing (unsubstituted) hydroquinone and a nonlinear diacid having a core angle between $\gamma = 120°$ and $\gamma = 148°$ might also form liquid crystal phases, e.g., derivatives of furan (where $\gamma \sim 125°$; see ref 24). Recently we have demonstrated the viability of the thiophene moiety in lyotropic LCPs (poly(amide)s[25] and poly(benzoxazole)s[26]) and in nonmesogenic high-performance poly(arylene ether ketone)s.[27] In all of these examples, including the polyesters considered here, thiophene-based materials may be an attractive option for molecular engineering thermal and physical properties from an economic standpoint as well: 2,5-thiophenedicarbonyl chloride can be synthesized from readily available bulk chemicals (adipic acid and thionyl chloride).[28] Generally, our findings with varying the linearity of the comonomers argue for the concept that a critical chain persistence length is a prerequisite for establishing liquid crystalline phases, and a variety of nonlinear monomers may be used in combination to effect this critical persistence length.

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## References and Notes

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**Registry No.** I (X = T, R = H) (polymer), 137768-95-7; I (X = T, R = H) (SRU), 125948-33-6; I (X = T, R = Cl) (polymer), 137768-96-8; I (X = T, R = Cl) (SRU), 125807-03-6; I (X = T, R = $CH_3$) (polymer), 137768-97-9; I (X = T, R = $CH_3$) (SRU), 125807-04-7; I (X = T, R = $C_6H_5$) (polymer), 137768-98-0; I (X = T, R = $C_6H_5$) (SRU), 125807-06-9.