

observed in the first heating cycles to melting of crystalline polymer. Such first heating cycle endotherms that disappear in subsequent heating cycles have been observed by others. Various mechanisms have been proposed to explain this phenomenon including liquid-liquid transition, loss of a volatile constituent (e.g., solvent) from the sample, and a change in physical contact between sample and sample pan due to liquid flow.^{18,19} We tentatively ascribe the 56 °C phenomenon in the DSC curve to the polymer glass transition. This assignment is not made with great certainty since T_g is accompanied by a change in slope of the DSC curve whereas the DSC curve for the naphthyl polymer has what appears to be an endotherm at 56 °C. The 56 °C phenomenon is so weak that it may not be possible to distinguish an endotherm from a change in slope.

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Registry No. Ia, 69288-89-7; Ia (homopolymer), 69288-90-0; Ia (SRU), 101672-00-8; SO₂Cl₂, 7791-25-5; 1-naphthol, 90-15-3; tetrahydrothiophene, 110-01-0.

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Thermotropic Liquid Crystalline Aromatic/Cycloaliphatic Polyesters and Fibers

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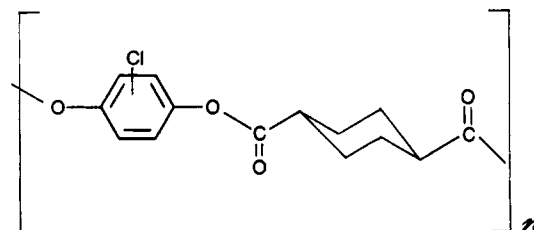
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ABSTRACT: Polyesters prepared from chlorohydroquinone diacetate and hexahydroterephthalic acid (1,4-cyclohexanedicarboxylic acid) were extruded from liquid crystalline melts directly into highly oriented fibers with initial moduli as high as 450 g/denier or 57.5 GPa. Heat-treatment in a relaxed state to near the melting point resulted in a 5- to 6-fold increase in tenacity—up to 20 g/denier (2.5 GPa). These polyesters were characterized by X-ray, NMR, IR, DSC, TGA, and optical microscopic methods. Polyesters based on *cis*- and *trans*-hexahydroterephthalic acid were prepared by both melt and low-temperature solution methods. Solution-prepared *cis* polymer, in which the *cis* configuration was confirmed by high-resolution NMR, was found to form an isotropic melt at 250 °C that converted to a liquid crystalline melt on heating at 310 °C due to *cis*-*trans* isomerization (NMR). The latter indicates the more extended *trans* form is required for melt anisotropy. All melt-prepared polymers were found by NMR to exist in the *trans* configuration and formed anisotropic melts and high-strength fibers on spinning and heat treatment.

Introduction

In the past decade a large number of thermotropic polyesters with mesogenic units either in the main chain or in modifying side groups have been prepared and examined for property-structure relationships.¹⁻¹² Unlike the lyotropic mesomorphic polyamides, polyesters with their reduced hydrogen bonding capability are more apt to form melts below their decomposition temperatures. The melting points can be reduced further by the introduction of limited disorder into the polymer chain with substituents, flexible moieties, bent and crankshaft monomers, and copolymerization.

One polyester system that forms liquid crystalline melts is prepared from 2-chlorohydroquinone and *trans*-hexahydroterephthalic acid.^{1b}



Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate)

The chloro substituent produces a certain amount of dissymmetry and reduction of intermolecular forces by its projection from the main chain and by the introduction of an internal copolymer effect depending on whether the chlorohydroquinone is oriented with all chlorines in the

Table I
Typical GPC Analysis of 2-Chlorohydroquinone Diacetate^a

| compound | wt % |
|------------------------------------|------|
| chlorohydroquinone monoacetate | 0.19 |
| hydroquinone diacetate | 0.15 |
| 2-chlorohydroquinone diacetate | 95.1 |
| 2,5-dichlorohydroquinone diacetate | 3.16 |
| 2,3-dichlorohydroquinone diacetate | 1.22 |

^a Sample was run as a solution in acetone (10% concentrated) on a 6 ft \times 1/8 in. 13% OV-11 on Chromosorb W (HP). Temperature was programmed at 150–200 °C at 2 °C/min. The compounds were identified by mass spectrometry.

same direction, in alternating positions, or in random positions. In addition, the *trans*-hexahydroterephthalic acid may contain the *cis* isomer as an impurity or through isomerization, giving an added copolymer effect. It is remarkable that from these monomers a homopolymer with high crystallinity and exceptional fiber properties can be produced.

Results and Discussion

Polymer and Fiber Processing. Intermediates. 2-Chlorohydroquinone, prepared by the hydrochlorination of benzoquinone in a practical grade, was converted to the diacetoxy derivative for polymerization. The latter was a mixture of related compounds, usually five, which were identified by mass spectrometry as chlorohydroquinone monoacetate, hydroquinone diacetate, chlorohydroquinone diacetate, and 2,5-, 2,3-, and occasionally 2,6-dichlorohydroquinone diacetates. The main ingredient, 2-chlorohydroquinone diacetate (CIPGDA) was present at about 95%. A typical GC analysis is found in Table I.

Several recrystallizations from ethyl alcohol, sublimation, or distillation through a spinning band column did not effectively purify chlorohydroquinone diacetate; however, with the use of an Aldershaw column, chlorohydroquinone diacetate of >99% purity was obtained.¹³ Both the mixture and the pure monomer were used with hexahydroterephthalic acid to prepare polyesters.

Hexahydroterephthalic acid (HT) was available as a 99% *trans* isomer and as *cis*/*trans* mixtures. Separation of the *cis* and *trans* isomers may be accomplished by extraction of the *cis* compound into chloroform by means of a Soxhlet extractor or by stirring the isomeric mixture in hot chloroform and separating the dissolved *cis* isomer by filtration.

It was also possible to convert a *cis*/*trans* isomer mixture to about 98% *trans* by heating at 295 °C (vapor bath temperature) for about 1.5 h under a nitrogen atmosphere and dissolving the small amount of unconverted *cis* isomer with chloroform.¹⁴ Reverse isomerization from *trans* to *cis* can also occur at higher temperatures. When 99% *trans*-hexahydroterephthalic acid was heated for 0.5 h at 305 °C under nitrogen, 25.8% *cis* isomer was obtained; however, heating for 1 h at 283 °C gave only 2.2% of the *cis* form. In work by Stowe,¹⁵ it was found that isomerization of *cis*-hexahydroterephthalic acid (95% *cis*/5% *trans*) is slow but measurable at 188 °C and rapidly increases with increasing temperature up to 280 °C. In this range, *trans*-HT crystallizes from the melt as it is formed. At 301 °C the *trans*-hexahydroterephthalic acid content was 80% vs. 97% at 280 °C. In addition, the melt was now sufficiently hot to keep the *trans* isomer from crystallizing out. From 300 to 312 °C (mp of *trans*-HT), an equilibrium mixture containing 80–85% *trans* isomer was obtained from either *cis*- or *trans*-hexahydroterephthalic acid.¹⁵

Accurate analysis of *cis*/*trans* isomer distribution in a hexahydroterephthalic acid mixture was achieved by gas

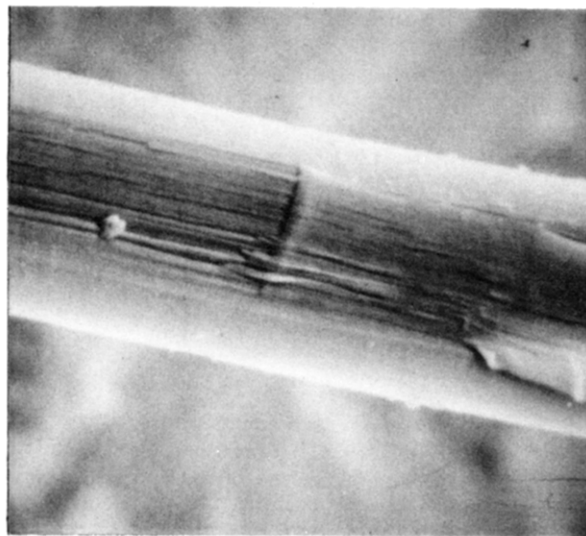


Figure 1. Peeled fiber section of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate).

chromatography after quantitative conversion of the acid to the more volatile silyl ester to allow for a better separation of the two isomers.¹⁶

Differential thermal analysis curves of *trans*-hexahydroterephthalic acid show a small solid–solid endothermic transition at about 140 °C and a large melting endotherm at about 315 °C.¹⁷

Polymerization. Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) and related copolymers were prepared in the melt from molar equivalents of the diacetoxy derivative of diphenols and hexahydroterephthalic acid with and without catalysts under an inert atmosphere. Stirring was employed during the initial atmospheric pressure cycle at 283 °C but not during the vacuum cycle at 305 °C. Polymer synthesis is described in the Experimental Section. During polymerization, a phase transition from isotropic to anisotropic began to occur in about 10 min after the rapid melting of the intermediates to a clear colorless liquid at 283 °C. The clear melt became cloudy and then opalescent with concomitant increase in viscosity. Polyesters with inherent viscosities up to 6 dL/g in dichlorotetrafluoroacetone hydrate were thus obtained.

Melt Spinning of Fibers. For spinning, the polyesters were molded into cylinders which were inserted in a heated melt press–spinning cell. The molten polymer was forced under pressure through a filter pack and spinneret, and the extruded fibers were collected on a bobbin. The quality of spinning and fiber properties were affected by polymer molecular weight, molecular weight distribution, spin temperature, spinneret hole size, and spin stretch (ratio of the velocity at the windup to the velocity in the capillary). However, polymer molecular weight and fiber defects (voids, inclusions, etc.) were dominant factors in determining fiber properties. Inclusions may arise from incompletely melted polymer that may be of higher molecular weight and/or higher crystallinity or even block copolymers. Melt-prepared poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) is highly crystalline compared to the low-temperature solution prepared polymer, which has low crystallinity. Typical crystallinity index numbers (representative of degree of crystallinity) for the melt-prepared polymer were from 70 to 90 (on a scale of 0–100) and crystal size from 130 to 170 Å. With “good”-quality polymer there was no degradation with spin temperatures as high as 345 °C and very few fiber defects.

The fibers were of a highly fibrillar character as shown in electron micrographs of a peeled fiber section (Figure

Table II
Fiber Properties of As-Extruded Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate)

| fiber η_{inh} | SSF ^a | as-extruded fiber ^b | | | | crystallinity | | | |
|--------------------|------------------|--------------------------------|----------|----------------------|------|------------------|------|------|-----|
| | | <i>T</i> | <i>E</i> | <i>M_i</i> | den | CS at 2 θ | | | |
| | | | | | | CI | 18° | 22° | OA |
| 3.1 | 96 | 6.3 | 2.5 | 236 | 3.22 | 75 | 90 Å | 79 Å | 11° |
| 2.6 | 95 | 4.6 | 2.1 | 185 | 3.38 | 69 | 80 Å | 78 Å | 12° |

^aSSF is spin stretch factor. ^bTensile properties are in g/denier.

Table III
Comparison of As-Extruded and Heat-Treated Fiber Properties of Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate)

| | as-extruded | heat-treated ^a |
|--|-------------------------------|--------------------------------|
| <i>T/E/M_i</i> /den | 3.6/2.1%/181/2.7 ^b | 12.2/3.0%/266/3.0 ^b |
| WAXS-CI/CS (18°, 22°, 2 θ)/OA | 69/81 Å, 70 Å/15° | 91/100 Å, 113 Å/13° |
| density | 1.3997 g/cm ³ | 1.4221 g/cm ³ |
| birefringence, $\eta_{ } - \eta_{\perp}$ | 0.146 | 0.149 |
| η_{inh} (TFA/CH ₂ Cl ₂ (60/40)) | 1.9 | 3.5 |

^aHeat-treated from 25 to 290 °C at a heating rate of 0.8 °C/min with nitrogen sweep. ^bTensile properties are in g/denier.

1) and of a fiber-end break (Figure 2). Some fiber properties (filament) of as-extruded poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) are presented in Table II.

Heat Treatment of Fibers. Fibers of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) were strengthened by slow heating in a relaxed state under a nitrogen purge to near the polymer melting point. This resulted in as much as a 5- to 6-fold increase in tenacity up to 20 g/denier (2.5 GPa).¹⁸ Modulus also increased but to a lesser extent. The tenacity and modulus increases were accompanied by substantial increases in molecular weight and crystallinity without loss of molecular orientation. This retention of molecular order through heat treatment eliminates the need for postdrawing. Byproducts from an accompanying 2% weight loss were identified by gas chromatography and mass spectrometry to be water, acetic acid, carbon dioxide, phenol, and monomeric species, most of which would be expected from postpolymerization.

Heat-treating can improve interchain order through increased rotation of chains for a better fit; it also has the potential to heal defects. Increases in crystallinity and molecular weight as a result of heat-treatment are indicated by X-ray, density, and other analyses in Table III. Examples of fibers with improvements in tensile properties

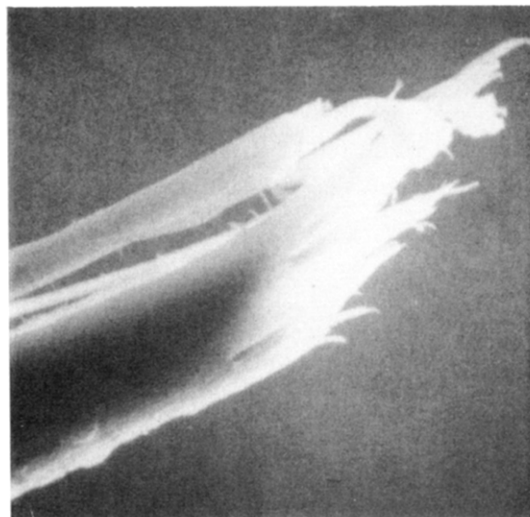


Figure 2. Fiber-end break of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate).

as a result of heat-treatment are shown in Table IV.

Polymer and Fiber Characterization. Crystallinity. Regardless of initial chlorohydroquinone and/or hexahydroterephthalic acid compositions, melt-prepared chloro-1,4-phenylene hexahydroterephthalate polymers are surprisingly highly crystalline. An explanation for this behavior is found in the section on isomerization. From Table V it is apparent that highly oriented as-extruded fibers have less crystallinity and smaller crystals than the polymer, probably as a result of faster cooling and, therefore, reduced crystallization time during spinning. Heat-treated fibers show an increase in crystallinity and crystal size but only moderate to no improvement in crystalline orientation. Heat-treating increases both the length and width of the crystals as seen in Table VI.

Fibers of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) exhibit crystalline polymorphism on heat-treatment. The more desirable α' -crystalline phase results

Table IV
Effect of Heat-Treatment on Tensile Properties of Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) Fiber

| heat-treatment | as-extruded fiber ^a | | | | heat-treated fiber ^a | | | |
|--|--------------------------------|----------|----------------------|-----|---------------------------------|----------|----------------------|-----|
| | <i>T</i> | <i>E</i> | <i>M_i</i> | den | <i>T</i> | <i>E</i> | <i>M_i</i> | den |
| 1 h 170 °C/1 h 230 °C/2 h 260 °C/0.75 h 290 °C | 3.5 | 2.0 | 159 | 3.5 | 17.2 | 2.4 | 320 | 2.4 |
| 0.5 h 170 °C/0.5 h 230 °C/1.5 h 260 °C/0.75 h 290 °C | 5.3 | 2.6 | 182 | 3.9 | 15.8 | 3.1 | 374 | 3.6 |

^aTensile properties are in g/denier.

Table V
Crystallinity in Polymers and Fibers from Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate)

| sample ^a | polymer | | | as-extruded fiber | | | | heat-treated fiber | | | |
|---------------------|---------|---------------|---------------|-------------------|---------------|---------------|-----|--------------------|---------------|---------------|-----|
| | CS | | | CS | | | | CS | | | |
| | CI | 18°2 θ | 22°2 θ | CI | 18°2 θ | 22°2 θ | OA | CI | 18°2 θ | 22°2 θ | OA |
| 1 | 78 | 139 Å | 144 Å | 76 | 87 Å | 89 Å | 11° | 92 | 108 Å | 108 Å | 11° |
| 2 | 59 | 127 Å | 114 Å | 56 | 73 Å | 68 Å | 13° | 88 | 95 Å | 107 Å | 14° |

^a(1) As-extruded fiber *T/E/M_i* = 5.9/2.6%/200 g/denier; heat-treated fiber *T/E/M_i* = 12.2/2.6%/310 g/denier. (2) As-extruded fiber *T/E/M_i* = 3.2/1.6%/277 g/denier; heat-treated fiber *T/E/M_i* = 16.3/3.6%/351 g/denier.

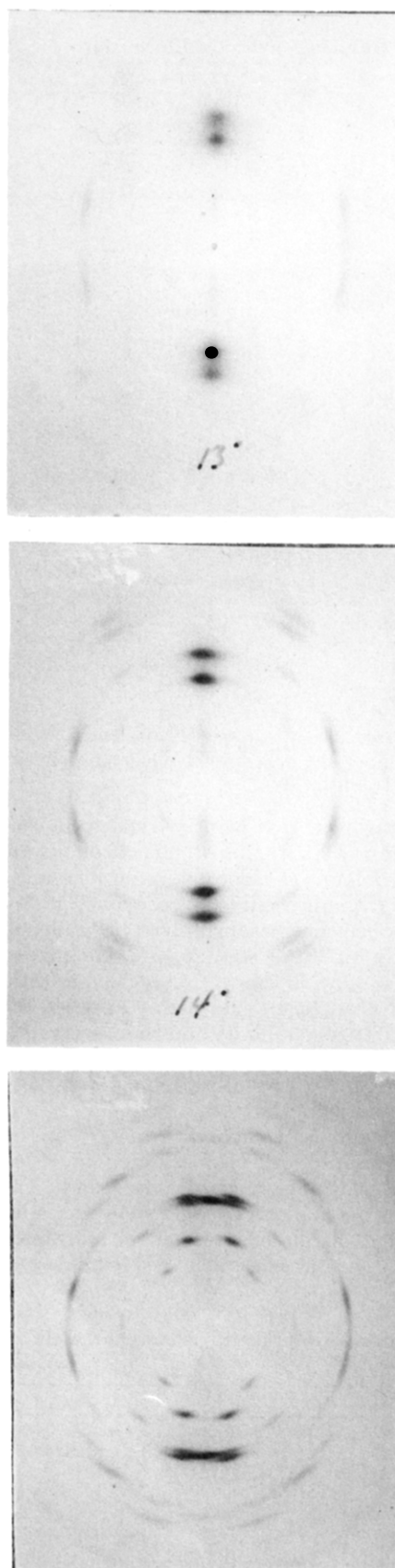


Figure 3. Wide-angle X-ray diffraction patterns of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) fibers: top, as-spun α -phase; middle, annealed high-tenacity α' -phase; bottom, annealed (N_2 sealed tube) low-tenacity β -phase. Direction of fiber axis \leftrightarrow .

from slow heat-treatment under a continuously purged neutral atmosphere at a temperature range below 200 to about 290 °C. This fiber shows an increase in tensile

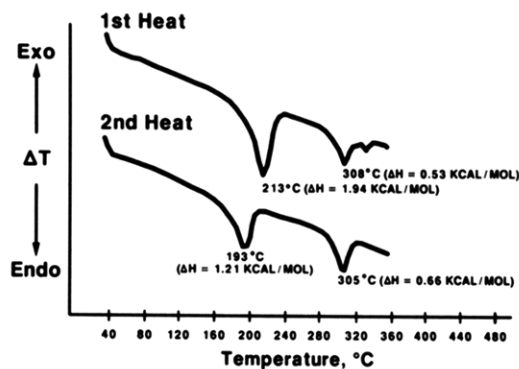


Figure 4. Thermal behavior of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) by DSC.

Table VI
Effect of Heat-Treatment on Crystal Size in
Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate)
Fiber

| fiber | CI | lateral CS, Å | | longitudinal CS, Å | |
|--------------|----|---------------|-------|--------------------|-----|
| | | 18°2θ | 22°2θ | 42°2θ | OA |
| as-extruded | 74 | 84 | 78 | 129 | 12° |
| heat-treated | 93 | 121 | 128 | 163 | 9° |

properties, crystallinity, and molecular weight over the as-extruded one. Heat-treating under a nonpurged atmosphere leads to β -phase formation and fiber with low tenacity and low molecular weight. Wide angle X-ray diffraction patterns for fibers with these crystalline phases are presented in Figure 3. X-ray analysis indicates triclinic packing for the α' -crystalline form (calculated density is 1.429 g/cm³) and hexagonal packing for the β -form (calculated density is 1.434 g/cm³).¹⁹ The experimental fiber densities determined by gradient tube (1.422 for α' , 1.438 for β) were in essential agreement with the unit cell values.

Thermal Behavior. Polymers and fibers of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) are characterized by the presence of two first-order reversible transitions—a major one at about 200 °C which involves a solid–solid transition ($\Delta H \sim 1.2$ –2.5 kcal/mol) and a smaller second one at about 300 °C ($\Delta H \sim 0.5$ kcal/mol) which represents melting of the polymer as depicted in Figure 4. This is consistent with the thermal behavior reported by Kyotani and Kanetsuna for the *trans*-based polymer.¹¹ The melting endotherm is somewhat lower for polymers for 95/5 wt % chlorohydroquinone/dichlorohydroquinone than for polymers from 100% chlorohydroquinone. It increases with polymer molecular weight and has been observed to be as high as 325 °C. Both endotherms are sharpened and increased about 25 °C in heat-treated high strength α' fiber. β -Form heat-treated fibers melted at about the same temperature as α' -fibers but did not display the 200 °C transition. As observed in Figure 5, the transitional enthalpies are higher for heat-treated fiber, indicating that the as-extruded fiber contains a substantial amorphous component.

The 200 °C transition is associated with lateral expansion of the crystal lattice, perhaps a polymer conformational change. Wide angle X-ray diffraction patterns of chloro-1,4-phenylene *trans*-hexahydroterephthalate polymer taken at various temperatures from 25 to 320 °C show an increase in lateral spacing above 210 °C. Wide angle X-rays of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) fiber taken at the same temperatures (Figure 6) present a more graphic picture of what happens

Table VII
Effect of Initial *cis*- to *trans*-Hexahydroterephthalic Acid Ratio on Fiber Properties of Melt-Prepared Poly(chloro-1,4-phenylene hexahydroterephthalate)^a

| HT, % | | as-extruded fiber ^b | | | | | | | | DSC ^c endotherms, °C | | heat-treated fibers ^b | | | |
|------------|--------------|--------------------------------|----------|----------------------|----|----------------------------|---------------|-----|----------------|---------------------------------------|--|----------------------------------|----------|----------------------|----------------|
| <i>cis</i> | <i>trans</i> | <i>T</i> | <i>E</i> | <i>M_i</i> | CI | crystallinity ^c | | OA | η_{inh}^d | | | <i>T</i> | <i>E</i> | <i>M_i</i> | η_{inh}^d |
| | | | | | | CS | | | | | | | | | |
| | | | | | | 18°2 θ | 22°2 θ | | | | | | | | |
| 96 | 4 | 2.9 | 1.5 | 228 | 51 | 70 Å | 58 Å | 10° | 1.45 | 199, 284 | | 9.9 | 2.7 | 295 | 4.1 |
| 62 | 38 | 3.2 | 1.5 | 213 | 63 | 79 Å | 70 Å | 17° | 1.93 | 194, 293 | | 12.6 | 3.7 | 242 | 4.1 |
| 0 | 100 | 4.6 | 2.1 | 185 | 69 | 80 Å | 78 Å | 12° | 2.55 | 196, 293 | | 12.5 | 2.8 | 310 | 3.9 |

^a Polymers were prepared from 100% chlorohydroquinone diacetate and hexahydroterephthalic acid (HT). ^b Tensile properties are in g/denier. ^c CI is the crystallinity index; CS is the crystal size; OA is the orientation angle. ^d Inherent viscosities (dL/g) were determined in dichlorotetrafluoroacetone hydrate. ^e DSC endotherms are for second heat.

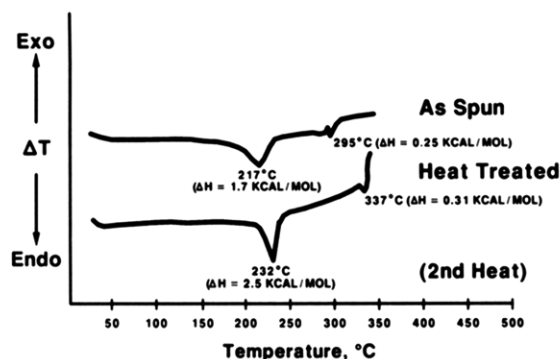


Figure 5. Thermal behavior of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) fiber by DSC.

to the polymer. At 200 °C the previously distinct equatorial diffraction arcs become more diffuse and begin to overlap each other, indicating the presence of much thermal vibration. This molecular motion is also indicated by the DTA 200 °C endotherm. At 225 °C the equatorial arcs become separated and more distinct, indicating a reduction in thermal vibration. Above 300 °C the equatorial arcs again become very diffuse, indicating polymer melting.

Thermal stability measurements by thermal gravimetric analysis for poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) indicate an initial weight loss at about 414 °C and a rapid weight loss at about 460 °C with 96% weight retention at 450 °C. This aromatic/aliphatic polyester is unusually thermally stable—a condition possibly resulting from its highly crystalline nature.

Melt Anisotropy. Melts of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) in a hot-stage polarizing microscope were highly birefringent and of nematic texture similar to anisotropic solutions of extended-chain aromatic polyamides²⁰ and other anisotropic polyester melts.¹ Birefringence extended over a wide temperature range from the onset of melting until degradation occurred, and the melting range varied with the molecular weight of the polymer. Polymer with an inherent viscosity of 0.30 dL/g

(60/40 trifluoroacetic acid/methylene chloride by wt) formed an anisotropic melt at 250 °C and one with an inherent viscosity of 2.60 dL/g, at about 290 °C.

Photomicrographs of films at 240× magnification (Figure 7) obtained by shearing a melt with the edge of a slide in a unidirection and immediately cooling showed an overall birefringence and a regular banded morphology characteristic of a kinked or zigzag chain structure found in liquid crystalline polymers. This ease of orientation is carried over into melt spinning where fibers with orientation angles of 10° to 13° are easily obtained.

Isomerization in Poly(chloro-1,4-phenylene hexahydroterephthalate). Since hexahydroterephthalic acid has the potential to isomerize with heating, it was essential to determine its behavior during polymerization and to study the effect of isomers on polymer and fiber properties.

Fiber Properties. In Table VII a comparison of as-extruded and heat-treated fiber properties of three melt-prepared chloro-1,4-phenylene hexahydroterephthalate polymers with varying initial *cis*-hexahydroterephthalic acid content shows similar tensile properties and crystallinity for all. The 96/4 *cis*/*trans* polymer has somewhat lower tensile properties, but its initial inherent viscosity was lower and the spinning conditions were not identical with those of the other polymers. Thermal behavior by DSC, which varies somewhat with molecular weight, also is similar for the three polymers. All of the fibers could be heat-treated to tenacities of at least 10 g/denier (1.3 GPa).

Proton NMR Analysis. For a study of *cis*/*trans* cyclohexyl isomer content in poly(chloro-1,4-phenylene hexahydroterephthalate), polymers were prepared by melt and by low-temperature solution methods from varied amounts of *cis* and *trans* acid or acid chloride and 100% chlorohydroquinone diacetate. Solutions of these and of *cis*- and *trans*-hexahydroterephthalic acids (as model compounds) in dichlorotetrafluoroacetone deuterate were used to obtain 220-MHz proton NMR spectra. In Table VIII, signals at various values (ppm) are assigned to the cyclohexyl protons in the two acids and five polymers. The three major resonances in the 1.25–2.84 ppm region are due

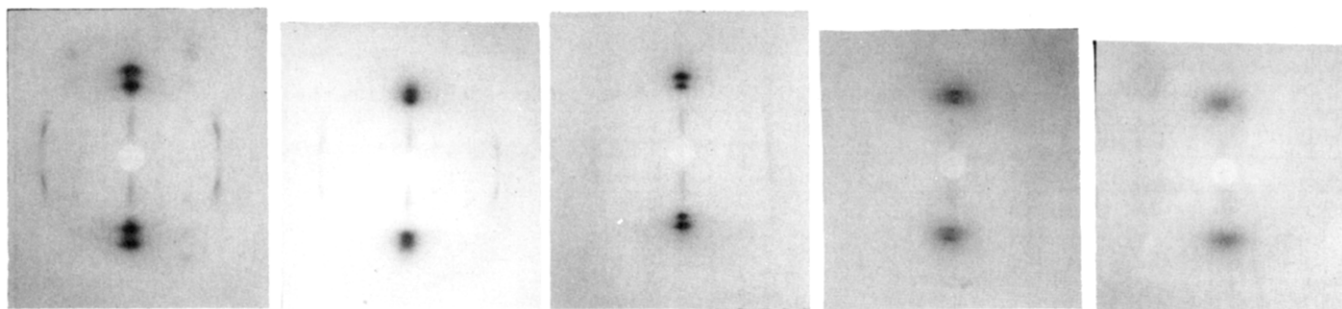


Figure 6. Effect of temperature on the wide-angle X-ray diffraction pattern of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) fiber. From left to right: 150, 200, 225, 300, and 320 °C.

Table VIII
220-MHz ^1H NMR Spectra of Poly(chloro-1,4-phenylene hexahydroterephthalate) from *cis*- and *trans*-Hexahydroterephthalic Acids^a

| | proton chem shifts, ppm from Me_4Si | | |
|---|---|-------------------|------------|
| | $-\text{CH}_2(4)$ | $-\text{CH}_2(4)$ | 1,4-CH-(2) |
| Model Compounds | | | |
| 100% <i>trans</i> -hexahydroterephthalic acid | 1.34 | 1.93 | 2.20 |
| 96% <i>cis</i> -hexahydroterephthalic acid | 1.25 | 1.36 | 2.04 |
| Polymer | | | |
| from 100% <i>cis</i> -HT acid/low temp solution prep. | 1.93 | 2.11 | 2.84 |
| from 100% <i>trans</i> -HT acid/low temp solution prep. | 1.68 | 2.29 | 2.63 |
| from 100% <i>trans</i> -HT/melt-prepared | 1.66 | 2.27 | 2.63 |
| from 96/4% <i>cis/trans</i> -HT/melt-prepared | 1.68 | 2.29 | 2.61 |
| from 62/38% <i>cis/trans</i> -HT/melt-prepared | 1.68 | 2.28 | 2.63 |

^a ^1H NMR spectra were obtained on a Varian HR-220 spectrometer with tetramethylsilane as an internal reference. Acids and polymers were dissolved in dichlorotetrafluoroacetone deuterate (δ 4.43).

to the protons in the cyclohexane rings. Resonances in the aromatic region from 6.93 to 7.16 (not included) are consistent with the three-spin strong coupling pattern expected for trisubstituted aromatic rings. The two isomeric acid monomers have ^1H NMR spectra that are distinct from each other. The same applies to the two polymers prepared by a low-temperature solution method from *cis* and *trans* acids. All of the melt-prepared polymers have spectra identical with each other and with the low-temperature solution-prepared polymer from 100% *trans* acid. For all of the melt-prepared polymers the signals are slightly broadened and shifted downfield relative to the acid monomers.

All *cis*-containing polymers were found to convert to the *trans* form, either during melt polymerization or post-heat-treatment. From comparison with the distinctive spectra found for the cyclohexyl protons of *cis*- and *trans*-hexahydroterephthalic acid monomers, it was concluded that all melt-prepared polymers consist of essentially all-*trans* isomer, regardless of initial *cis*-HT content. The low-temperature prepared *trans*-hexahydroterephthalic acid polymer was identical with the melt-prepared polymers. However, the low-temperature *cis*-HT polymer retained its *cis* form but converted to the *trans* form on heat-treatment at 170/230/260/290 °C for about 5 h (confirmed by ^1H NMR). In addition, identical ^1H NMR spectra indicative of *trans*-HT polymer were obtained for solutions of as-spun and heat-treated fibers of melt-prepared polymer.



Figure 7. Photomicrograph of a unidirectional smear of poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate) at 240 \times magnification.

IR Analysis. These chloro-1,4-phenylene hexahydroterephthalate polymers were examined also by IR and the results were consistent with the ^1H NMR findings.

The spectrum of the low-temperature-prepared *trans*-HT polymer was identical with the melt-prepared polymer from 100% *trans*-HT.

The spectrum of the low-temperature-prepared *cis*-HT polymer differed from that of the *trans*-HT polymer by the absence of bands at 1320 and 970 cm^{-1} , diminished band intensity at 1240 cm^{-1} , and additional band splitting at 1307/1288 and 1180/1160 cm^{-1} .²¹

Polymers prepared by the melt method from 62% *cis*-HT and from 96% *cis*-HT and by the low-temperature method from 100% *trans*-HT exhibited no significant differences by infrared spectroscopy.

Optical Analysis of Melts. The melting behavior of melt- and low-temperature solution-prepared polymers was examined optically with a Leitz hot-stage polarizing microscope. Examination between crossed polarizers with a red retardation plate revealed that all of the melt-prepared chloro-1,4-phenylene hexahydroterephthalate polymers formed anisotropic melts at their flow temperatures of about 300 °C. The melts had nematic textures similar to those previously reported for extended-chain aromatic polyamide solutions²⁰ and for other anisotropic polyester melts.¹ The low temperature solution-prepared polymer from *trans*-HT also formed an anisotropic melt at its flow

Table IX
Poly(chloro-1,4-phenylene hexahydroterephthalate) from Different *Cis/Trans* Ratios of Hexahydroterephthalic Acid^a

| HT | | polymerization method | polymer η_{inh}^b | DSC second heat endotherms, °C | crystallinity ^c CI | optical microscopy | |
|------------|--------------|-----------------------|-------------------------------|--------------------------------|-------------------------------|--------------------|-------------|
| <i>cis</i> | <i>trans</i> | | | | | mp, °C | melt |
| 100 | 0 | low temp soln | 0.16 | | low | ~250 | isotropic |
| 0 | 100 | low temp soln | 0.58 | 272 | low | ~270 | anisotropic |
| 96 | 4 | high temp melt | 1.60 | 185, 297 | 69 | ~300 | anisotropic |
| 62 | 38 | high temp melt | 2.47 | 202, 309 | 85 | ~300 | anisotropic |
| 0 | 100 | high temp melt | 1.97 | 196, 293 | 78 | ~300 | anisotropic |

^a Polymers were prepared from 100% chlorohydroquinone diacetate. ^b Polymer inherent viscosities (dL/g) were determined in dichlorotetrafluoroacetone hydrate. ^c CI = crystallinity index.

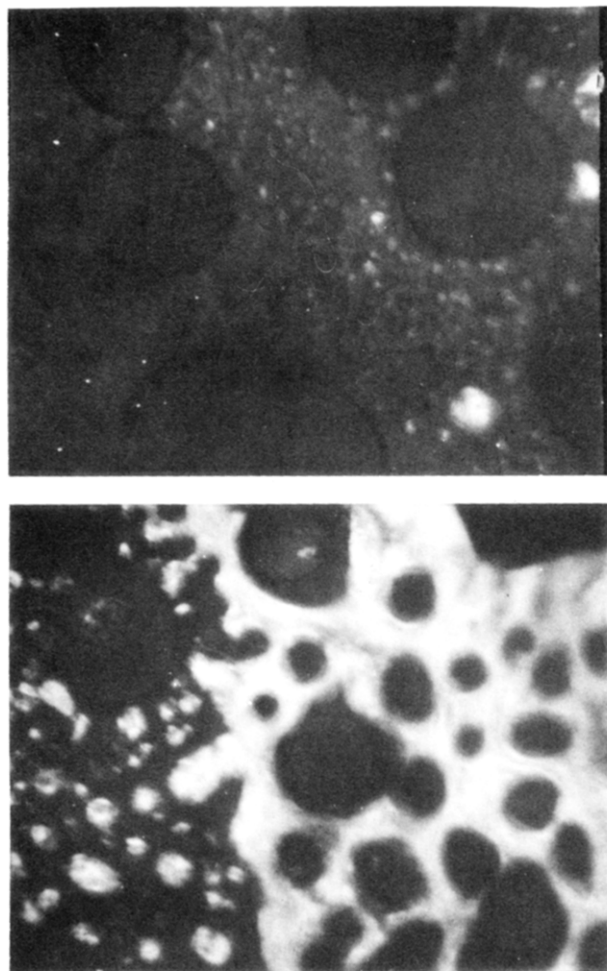


Figure 8. Isotropic to anisotropic conversion of a melt from poly(chloro-1,4-phenylene *cis*-hexahydroterephthalate): top, 20 min at 310 °C; bottom, 40 min at 310 °C (140× magnification).

temperature of about 270 °C. These polymers and related properties are described in Table IX.

The low-temperature solution-prepared polymer from *cis*-HT formed an isotropic melt at its flow temperature of about 250 °C, which was converted to an anisotropic melt upon further heating. When a sample of this polymer was placed on a hot stage of a polarizing microscope at 310 °C, it melted in about 5 min to an isotropic melt. After 20 min the melt became shear birefringent, after 35 min it was about 50% anisotropic, and after 75 min it was about 75% anisotropic. When the melt was heated to 340 °C it became about 100% anisotropic. The melt was cooled slowly to 260 °C, where it solidified. Reheating of the melt to 300 °C resulted in an anisotropic melt at about 290 °C that behaved like the usual "trans" polymer melt. Figure 8 contains photomicrographs at 140× magnification of the above-described melts at 20 min and 40 min of heating at 310 °C, showing the isotropic (dark) to anisotropic (light) conversion. The same "cis" polymer, subjected to heat-treatment at 170/230/260/290 °C for 1/1/2/0.75 h, formed an anisotropic melt at a flow temperature of about 300 °C.

Since the heat-treated "cis" low-temperature solution-prepared polymer and all melt-prepared polymers were found by ¹H NMR to exist in the more highly extended "trans" configuration (Figure 9) it was concluded that isotropic → anisotropic transition observed in the melt was due to *cis* → *trans* isomerization and that the more highly extended "trans" configuration is required for melt anisotropy.

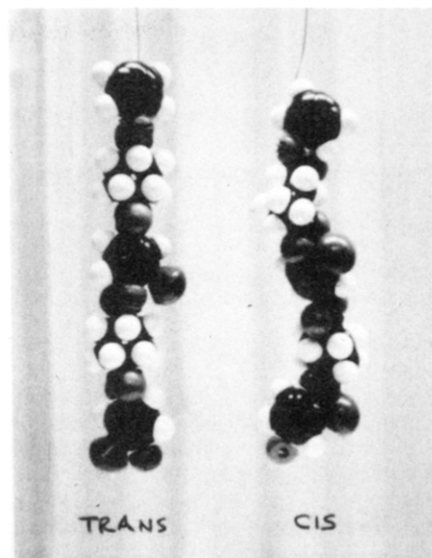


Figure 9. Molecular models of poly(chloro-1,4-phenylene *cis*/*trans*-hexahydroterephthalate).

Summary and Conclusions

High molecular weight thermotropic liquid crystalline polyesters, prepared from chlorohydroquinone or a primarily chlorohydroquinone mixture and hexahydroterephthalic acid by melt polymerization, were melt spun directly into highly oriented fibers (OA ~10°) with initial modulus values as high as 450 g/denier or 57.5 GPa. Slow heat-treating in a relaxed state resulted in a 5- to 6-fold increase in tenacity (up to 20 g/denier or 2.5 GPa). The strengthening response is attributed to postpolymerization and further crystallization without loss of axial orientation. These polyesters formed liquid crystalline melts above a DSC melting point of about 300 °C; they also exhibited a major solid-solid endothermic transition at about 200 °C.

A low-temperature solution-prepared polyester based on chlorohydroquinone and *cis*-hexahydroterephthalic acid formed an isotropic melt at about 250 °C, which was converted to a liquid crystalline melt on heating at 310 °C, due to *cis* → *trans* isomerization (NMR). The latter indicates the more extended *trans* form is required for melt anisotropy. All melt-prepared polymers, regardless of initial *cis*-hexahydroterephthalic acid content, were found by NMR to exist in the *trans* configuration and formed anisotropic melts and high-strength, high-modulus fibers on spinning and heat-treatment.

Experimental Section

Chlorohydroquinone Diacetate. In a 2-L round-bottom flask equipped with a stirrer and condenser with a drying tube were combined 480 mL of acetic anhydride, 10 drops of concentrated H₂SO₄, and 200 g of practical grade chlorohydroquinone. Spontaneous heating occurred to about 80 °C. The mixture was stirred for 0.5–1 h at 70–90 °C, cooled to room temperature, and slowly poured into 500 mL of ice water. It was further stirred until all of the excess acetic anhydride had reacted and the desired product had solidified. The precipitate was filtered, dried, recrystallized 3 times from denatured ethyl alcohol, and sublimed once at reduced pressure, mp 67–69 °C. A typical analysis based on GC and mass spectrometry is found in Table I with chlorohydroquinone diacetate having about 95% purity. Chlorohydroquinone diacetate of >99% purity required distillation with an Aldershaw column.¹³

***trans*-1,4-Cyclohexanedicarboxylic Acid.** Commercial 99% *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-hexahydroterephthalic acid) was purified by extraction with chloroform in a Soxhlet extractor over a period of 48 h. The *cis* isomer was soluble

in the chloroform; the insoluble trans acid was recrystallized from ethyl alcohol, mp 310–312 °C. GC (employing a silyl ester derivative of the acid) indicated 100% *trans*-hexahydroterephthalic acid.

When hexahydroterephthalic acid contained larger amounts of the *cis* isomer, the mixture was converted to the trans acid by heating at 295 °C under a nitrogen atmosphere. A test tube (12 in. × 1.4 in.) was flushed with nitrogen for 10 min and filled with hexahydroterephthalic acid. Nitrogen was conducted through the acid for 2 h by means of a slender tube that had been inserted downward to the bottom of the large test tube. The latter was removed and a Neoprene stopper containing two short tubes was inserted into the large test tube. One tube conducted nitrogen over the surface of the acid and the other tube, to which a Drierite tube was attached, served as a gas outlet. The large test tube was inserted into a fluorene vapor bath (bp 295 °C) and heated for 1.75 h. During this time the sample partially melted and then gradually resolidified. After cooling to room temperature, the diacid was transferred to a round-bottom flask and stirred under reflux with chloroform for about 1 h. The solid remaining after this time was collected by suction filtration and the process was repeated twice more. The solid trans acid was recovered, washed on a Buchner funnel with several small portions of CHCl_3 , and sucked dry. It was recrystallized from denatured ethyl alcohol, mp 311–313 °C. GC analysis (silyl ester derivative) indicated 100% trans acid.

***trans*-1,4-Cyclohexanedicarboxylic Acid Chloride.** *trans*-Hexahydroterephthalic acid (172 g, 1 mol) was combined with 500 mL of thionyl chloride and 3 drops of dimethylformamide and refluxed for 3 h. Excess thionyl chloride was removed under reduced pressure and the residue was recrystallized from spectroscopic grade hexane. The product was further purified by sublimation under reduced pressure. Final yield was 169 g (81%), mp 68–69 °C.

***cis*-1,4-Cyclohexanedicarboxylic Acid Chloride.** *cis*-Hexahydroterephthalic acid (mp 171 °C by DSC) was converted to the acid chloride as above and purified by distillation under reduced pressure.

Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate). The equipment consisted of a 15 in. × 1.25 in. i.d. tube equipped with a 29 × 26 mm ground-glass neck opening and two side arms on opposite sides near the top of the tube with the one being about 0.5 in. lower than the other. The lower arm was used for conducting nitrogen into the tube and the upper arm for removal of acetic acid. The upper arm had attached to it an adapter, condenser, fraction cutter, and flask for collecting the generated acetic acid. A helical stirrer was inserted through a Teflon (Du Pont registered trade mark) TFE-fluorocarbon adapter placed in the neck opening. Prior to use, the tube was flushed with nitrogen that was dried by passing through silica gel. In the tube were combined *trans*-hexahydroterephthalic acid (13.775 g, 0.08 mol) and chlorohydroquinone diacetate (18.291 g, 0.08 mol). The tube with contents was evacuated of air and filled with nitrogen. This procedure was repeated once more and the following heating cycle was used: (i) 1.0 h/283 °C/ N_2 atm (about 30–40 bubbles of nitrogen/min) (the melt was stirred during the entire cycle but at a slower rate for the first 15 min); (ii) 10–15 min/283 °C/vacuum (760 → 0.1 mmHg) (the stirrer was raised prior to applying the vacuum and nitrogen flow was also stopped); (iii) 30 min/305 °C/vacuum (0.1 mmHg) (no stirring was employed).

Upon cooling, the polymer melt solidified and was removed by breaking the glass tube. Polymer inherent viscosity was as high as 5.5 dL/g in dichlorotetrafluoroacetone hydrate. Weight of polymer was about 21 g.

Dilute Solution Viscosity. The inherent viscosity number [$\eta_{\text{inh}} = 2.3 \log (\eta_{\text{rel}})/c$] was determined at 30 °C on solutions containing 0.5 g of polymer per 100 mL of trifluoroacetic acid/ CH_2Cl_2 (60/40 (v/v)) or dichlorotetrafluoroacetone hydrate with a Cannon–Fenske viscometer. Results are reported in deciliters per gram.

X-ray Diffraction. Wide-angle X-ray diffraction patterns were obtained with a Warhus pinhole camera and a Phillips X-ray generating unit having a copper fine-focus diffraction tube and

a nickel β filter. The distance from sample to film was 50 mm. The orientation angle was determined by a densitometer method from the X-ray film. It is reported as the arc length in degrees between the half-maximum intensity points of a principal equatorial diffraction spot. Crystallinity index (CI) was calculated from a ratio of the crystalline and amorphous areas as recorded on an X-ray diffractogram by a Phillips X-ray diffractometer. Apparent crystallite size (CS) was determined from a measurement of the breadth of the peak at $2\theta = 18^\circ$ and 22° , as recorded on the same diffractogram, using the Scherrer equation.

Other Analyses. ^1H NMR spectra were obtained on a Varian HR-220 spectrometer with tetramethylsilane as an internal reference. Acids and polymers were dissolved in dichlorotetrafluoroacetone deuterate (δ 4.43). IR spectra were obtained on a Perkin-Elmer 457 infrared spectrometer.

Gas Chromatography (GC) data for chlorohydroquinone diacetate were obtained from a Perkin-Elmer 900 gas chromatograph interfaced with a Du Pont Model 21-492 double-focusing mass spectrophotometer. For hexahydroterephthalic acid (silyl ester derivatives) a Hewlett-Packard 7620A Gas Chromatograph was used.

The differential thermal analyzer (DTA) and the differential scanning calorimeter (DSC) were Du Pont 900 units, and the thermal gravimetric analyzer was a Du Pont 950. Fiber densities were determined by gradient tube.

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Registry No. *trans*-HT, 619-82-9; *cis*-HT, 619-81-8; (*trans*-HT)-(2-chlorohydroquinone diacetate) (copolymer), 57982-23-7; (*cis*-HT)-(2-chlorohydroquinone diacetate) (copolymer), 101981-88-8; (*trans*-HT)-(2-chlorohydroquinone diacetate) (copolymer), 101981-87-7; (HT)-(chlorohydroquinone monoacetate)-(hydroquinone diacetate)-(2-chlorohydroquinone diacetate)-(2,5-dichlorohydroquinone diacetate)-(2,3-dichlorohydroquinone diacetate) (copolymer), 101981-90-2; poly(chloro-1,4-phenylene hexahydroterephthalate) (SRU), 58071-35-5.

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