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Electrical Properties of Poly(5,6-dihydroxy-2-cyclohexen-1,4-ylene) Derivatives

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ABSTRACT: A synthesis of *cis*-5,6-dihydroxy-1,3-cyclohexadiene diesters was developed, and both the cis and trans derivatives were polymerized by using radical initiators. The structure of the polymer consisted predominantly (85–90%) of 1,4-cyclohexenylene units with a smaller amount of 1,2-repeat unit. Molecular weight data were consistent with considerable chain transfer taking place during the polymerization of certain ester derivatives. High molecular weight material was obtained from the polymerization of the *cis*-dimethyl carbonate and dipivalate ester derivatives and free-standing films of these materials could be prepared. Pyrolysis of the poly(*cis*-5,6-dihydroxy-2-cyclohexen-1,4-ylene) derivatives resulted in a largely aromatic polymer which contained blocks of *p*-phenylenes containing an average of six phenylene units. Pyrolysis of the trans-substituted polymer gave a material with properties that were inconsistent with a *p*-phenylene polymer. When films prepared from the cis derivatives were heated and then exposed to arsenic pentafluoride, the conductivity of the films was well into the semiconductor range (2 S/cm).

Introduction

There are a considerable number of polymers that are capable of manifesting unique electrical properties after exposure to certain oxidizing or reducing agents (dopants).[1] The common structural feature of nearly all of these polymers is conjugation in the polymer backbone, permitting extensive oxidation or reduction and hence a high concentration of charge carriers. In some cases, conductivities within 2–3 orders of magnitude of the common metallic conductors have been achieved. A number of applications have been proposed based on the utilization of the unusual electrical properties of these materials.

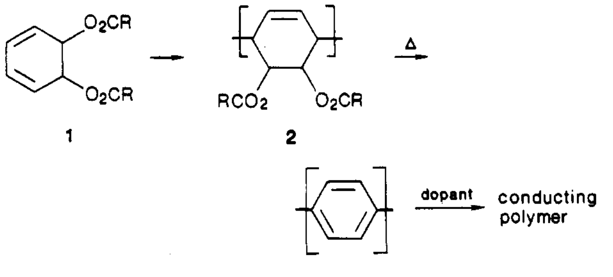
Much of the attractiveness of conducting polymers stems from the potential of these materials to combine ease of processability with high conductivity. However, the rigid-rod structure common to most of the conducting polymers imparts physical properties such as high melting temperatures and insolubility in common casting solvents which severely restrict the ease of processability. Of the commonly studied conducting polymers, poly(*p*-phenylene sulfide) and polyquinoline are exceptional. Poly(*p*-phenylene sulfide)[2] can be melt-processed; however, solution processing is difficult because poly(*p*-phenylene sulfide) is only soluble at high temperatures in certain solvents. Rigid-rod polyquinolines[3] have been processed at room temperature, but the solutions must be formed in acidic solvents or in the polymerization dope (35% di-*m*-cresyl phosphate in *m*-cresol). Another approach to improve the processability of conducting polymers involves the preparation of certain soluble or melt processable precursors or derivatives. For example, several derivatives of polyacetylene have been prepared, including the methyl,[4,5] phenyl,[6] and trimethylsilyl[7] derivatives. All of these materials are more readily processed than the parent polymer; however, in all cases the doped polymers possessed conductivities several orders of magnitude less than that of doped polyacetylene.

Some more unusual solvents capable of forming conducting polymer solutions allow some of the more rigid polymers to be processed. Arsenic trifluoride, for example, has been used as solvent for several of the conducting polymers.[8] The conductivity of films prepared from the removal of solvent from these solutions was often considerably better than the conductivity of films prepared by solid-state doping. Molten iodine has been utilized for the preparation of conducting polymer solutions of polycarbazoles.[9]

Polymer processing properties have been improved by using graft and block copolymers and polymer blends. Composite materials consisting of a conducting polymer and a classical nonconducting polymer have been prepared.[10] Block copolymers of polyacetylene with styrene, isoprene, and methyl methacrylate[11] have been obtained. Improved physical properties over the parent polymer were achieved in all of these materials with sufficient dilution of the polyacetylene portion. However, dilution generally had the effect of reducing or totally removing the conductivity of the material.

The use of precursor polymers has received attention as an indirect means of improving conducting polymer processability. Polyacetylene precursors have been demonstrated to produce polyacetylene following a retro-Diels–Alder reaction.[12] Poly(*p*-phenylene sulfide) may also be considered as a precursor polymer since exposure of the polymer to arsenic pentafluoride causes the formation of dibenzothiophene units.[2]

A soluble poly(*p*-phenylene) precursor was prepared recently by Ballard et al.[13,14] This study demonstrated that aromatization results from the pyrolysis of poly(5,6-dihydroxy-2-cyclohexen-1,4-ylene) (PDC) derivatives (**2**). The purpose of the present study was the reinvestigation of these materials and the determination of the electrical properties of the pyrolysis products. It was anticipated that the use of this methodology (eq 1) would overcome some of the processing limitations imposed by the physical properties of poly(*p*-phenylene).



(1)

Results and Discussion

Monomer Syntheses. Cis and trans derivatives of **1** were the required monomers for this study. The synthesis of the trans diacetate derivative was carried out by a minor modification of the published procedure.[15] A convenient nonenzymic preparation of the cis derivatives was developed (Scheme I). Cis hydroxylation of 1,4-cyclohexadiene gave monoacetate **3** in 77% yield.[16] Hydrolysis of **3** produced the *cis*-diol **4** in 86% yield. Continuous extraction of the aqueous phase resulting from the hydrolysis was necessary in order to obtain a good yield of the diol.

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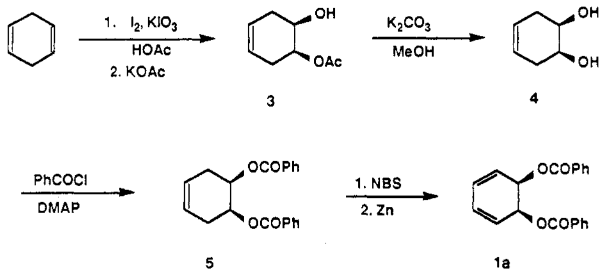
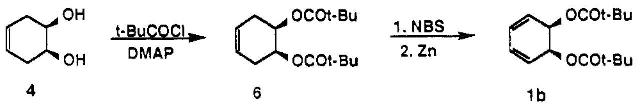
Scheme I



Scheme II



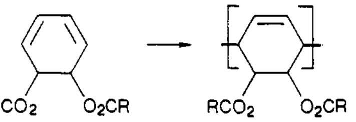
Diol 4 was esterified with benzoyl chloride in the presence of 4-(dimethylamino)pyridine (DMAP) and triethylamine to give diester 5 in 89% yield. Bromination with 2 equiv of *N*-bromosuccinimide (NBS) in the presence of azobis(isobutyronitrile) (AIBN) gave a crude dibromide which was carried on to the next step without purification. Reductive elimination of the dibromide with zinc dust gave *cis*-dibenzoate **1a** in 62% yield. The critical feature in the last step was the use of dry methanol as the solvent for the reaction. When the methanol was wet, a large amount of aromatized material (phenyl benzoate) was obtained, whereas the use of dry methanol gave the desired product almost exclusively.

This synthetic strategy was also used for the preparation of the cis-pivalate ester **1b** (Scheme II). The esterification of diol 4 proceeded in 91% yield to give diester **6**. Treatment of the diester with 2 equiv of NBS followed by reduction with zinc gave pivalate **2b** in 84% yield.

Conversion to Polymer. A number of conditions were explored to optimize the conversion of the cyclohexadiene derivatives 1 to polymer by using various radical initiators. The best conversions were obtained by using standard initiators such as BPO or AIBN at lower temperatures than are normally used. High-temperature conditions resulted in monomer side reactions. For example, *cis*-dibenzoate **1a** was converted nearly completely to phenyl benzoate when the polymerization was carried out by using benzoyl peroxide (BPO) at 90 °C. A number of low-temperature initiators were used; however, a low conversion to polymer was observed in all cases. Use of BPO at 75 °C generally gave the highest conversion to polymer.

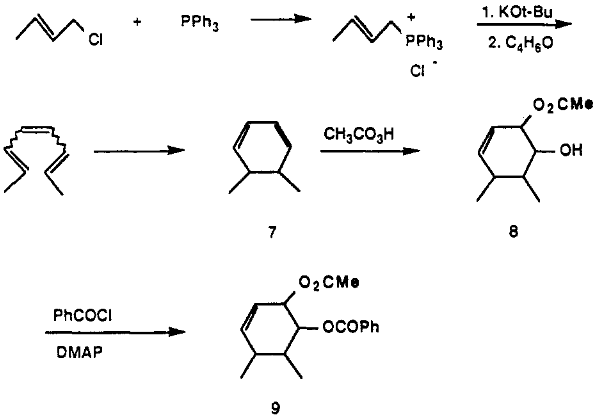
Polymer Properties. Many of the properties of the polymers were dependent on the nature of the substituents (Table I). In all cases the polymers were isolated as white powders which were soluble in a variety of solvents. The *trans*-diacetate **2d** consisted of low molecular weight material as determined by GPC (average degree of polymerization = 15). The *cis*-dibenzoate polymer **2a** also had a low average degree of polymerization even though the weight-average molecular weight was high. Large polydispersity values ($D = M_w/M_n$) of this type are often associated with chain-transfer processes occurring during the course of the polymerization.[17] It was not possible to form free-standing films from solutions of either the *trans*-diacetate **2d** or *cis*-dibenzoate **2a** polymers. The films were brittle and cracked during the solvent evaporation process. However, supported thin films could be formed by spin coating of solutions of either polymer.

Table I
Polymer Properties



derivative	% conversion	M_n (DP)	M_w	M_w/M_n	T_g, °C
cis; R = Ph (**2a**)	84	5 700 (18)	44000	7.7	230
cis; R = *t*-Bu (**2b**)	40	46 000 (165)	68000	1.5	238
cis; R = OMe (**2c**)	35	26 500 (116)	30500	1.2	181
cis; R = OMe (**2c**)	85	18 000 (79)	25500	1.4	169
trans; R = Me (**2d**)	47	3 000 (15)	6300	2.1	190

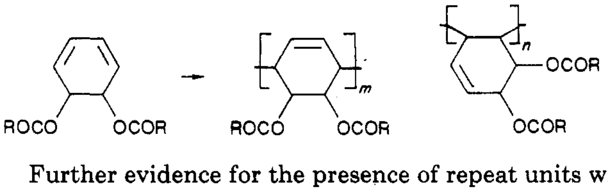
Scheme III



Comparison of polymerization conditions (Table I) for the dicarbonate monomer shows the superiority of the benzoyl peroxide initiator over AIBN for the polymerization. However, the higher temperature polymerization reaction produced lower molecular weight material with a broader dispersity, further evidence of chain transfer during polymerization. Polymerization of the dipivalate ester with BPO gave the highest molecular weight material (**2b**) (average degree of polymerization = 165). Steric hindrance by the bulky pivalate ester groups may help in preventing chain transfer in this case. Free-standing films could be formed from solutions of either the dicarbonate **2c** or dipivalate polymers **2b**.

As expected, the glass transition temperature (T_g) was lower for the polymers which contained the less bulky side chains (**2c**,**d**). The more bulky benzoate and pivalate ester polymers had glass transition temperatures in excess of 230 °C.

Polymer Structure. Both proton and carbon-13 NMR spectra of the polymeric products were consistent with a 1,4-cyclohex-2-enylene structure for the repeat unit. Closer inspection of the proton NMR spectra, however, revealed the presence of a high-field absorbance at $\delta \simeq 2.0$ which could not be accounted for by a 1,4-structure. This absorbance was consistent with the chemical shift expected for the nonallylic proton in the 1,2-structure (eq 2), raising the possibility that the polymer structures consisted of varying ratios (*m* and *n*) of 1,4- to 1,2-units.



(2)

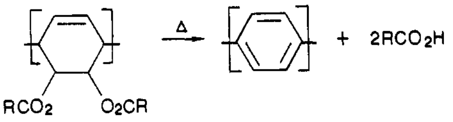
Further evidence for the presence of repeat units with a 1,2-structure was obtained by the preparation of a model compound whose structure was similar to that of the 1,2-repeat unit (Scheme III). *cis*-Dimethylcyclohexadiene 7

Table II
Polymer Structure, Ratio of 1,4- (*m*) to 1,2-Repeat Units (*n*)

polymer	%*m*[a]	%*n*[a]	polymer	%*m*[a]	%*n*[a]
cis; R = Ph (**2a**)	91	9	cis; R = OMe (**2c**)	85	15
cis; R = *t*-Bu (**2b**)	90	10	trans; R = Me (**2d**)	*b*	*b*

[a] From a comparison of the high-field resonance with the resonance of the side chain ester substituent. [b] Value cannot be calculated due to overlapping resonance of the acetate group.

Table III
Isothermal Thermogravimetric Analyses in Nitrogen for PDC Derivatives



polymer	theor wt % remaining	pyrolysis condtn	actual wt % remaining	residual carbonyl absorbance (% of original)
cis; R = Ph (**2a**)	23.7	300 °C (2 h)	23.1	14
cis; R = tBu (**2b**)	27.1	300 °C (6 h)	24.9	9
cis; R = OMe (**2c**)	33.3	300 °C (6 h)	30.1	2
trans; R = Me (**2d**)	38.8	250 °C (4 h)	32.5	10

was prepared in several steps by the Wittig coupling of two allylic reactants followed by an electrocyclic ring closure.[18] Compound **7** was epoxidized with peracetic acid and, during the course of the epoxidation, the epoxide ring was opened. The resulting hydroxy ester **8** was esterified to give **9**. The model compound **9** showed a multiplet between 1.8 and 2.1 ppm in addition to the singlet resonance for the acetate. The close proximity between this resonance and that of the polymer provides further evidence for the proposed structure. Based on the integration of the polymer spectra, an approximate ratio of 1,4- to 1,2-structural units can be calculated (Table II).

Thermal Properties of PDC Derivatives. The thermogravimetric analyses of the *cis*-PDC ester derivatives were consistent, within 4%, with the value expected for the loss of two ester groups and the resulting aromatization (Table III). Moreover, the residues were quite stable for several hours to further weight loss. However, the trans derivative **2d** continued to lose weight after the loss of acetate even at 250 °C. The weight remaining after 4 h at 250 °C was 6% less than the theoretical value and the residue continued to lose weight at an appreciable rate. The thermal behavior of **2d** was significantly different from that of the cis-substituted polymers and suggested that pathways other than aromatization were also occurring.

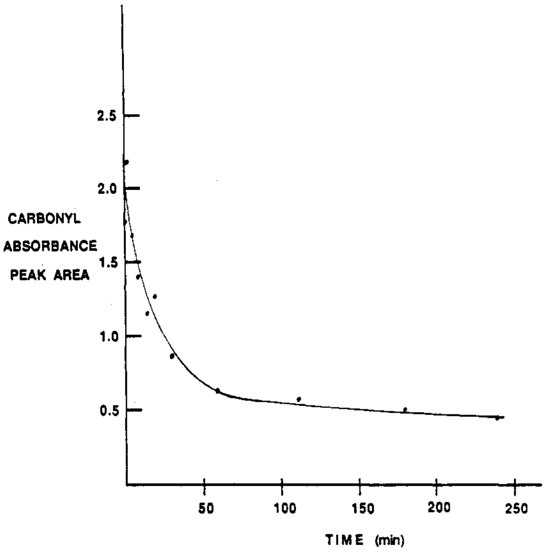
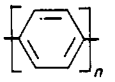


Figure 1. Plot of carbonyl absorbance vs. time for a film of **2a** at 300 °C.

Table IV
IR and UV Characteristics of Poly(*p*-phenylene) Oligomers and Pyrolysis Products of PDC Derivatives



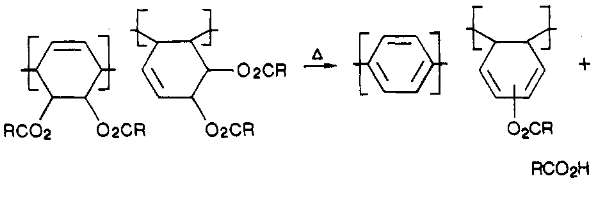
n or polymer source	IR peak, cm^{-1} [b]	UV peak, nm[b]
3	837	280
4	825	300
5	818	310
6	811	318
poly(*p*-phenylene)	805–807	385–395
pyrolyzed **2a**	814	317
pyrolyzed **2b**	815	285
pyrolyzed **2c**	810	320
pyrolyzed **2d**	*a*	<300

[a] No peak observed. [b] These values obtained from ref 19 and 20.

Although the TGA experiments for the cis derivatives gave values close to their theoretical expectations, other evidence was inconsistent with complete aromatization. A film of *cis*-dibenzoate **2a** was pyrolyzed at 300 °C in nitrogen, and the carbonyl absorption was measured at various intervals (Figure 1). Since the benzoic acid byproduct is volatile, complete aromatization would be expected to be accompanied by complete loss of carbonyl absorption. Instead, approximately 15% of the absorption remained after 4 h at 300 °C. Similar results were obtained for the other PDC derivatives (Table III), with the cis-carbonate polymer **2c** showing the least residual carbonyl absorption (2%). In addition, the elemental analyses of the pyrolysis products were inconsistent with complete aromatization. The sum of the carbon and hydrogen percentages was less (by 3–8%) than the expected value for complete aromatization.

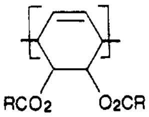
Structure of Pyrolysis Products. Poly(*p*-phenylene) (PPP) oligomers have been characterized by both IR and UV spectroscopy. The IR spectra of PPP oligomers[19] have an absorption between 840 and 800 cm^{-1} which is associated with the carbon–hydrogen bending mode. As the number of phenylene units (*n*) increases, this peak shifts to lower wavenumbers and attains a value of 802 cm^{-1} for the polymer (Table IV). Similarly, the UV absorption spectrum has a long-wavelength absorption maximum which is shifted to longer wavelength, 380–390 nm maximum, with increasing number of phenylene units.[20]

IR and UV absorption data were obtained for films prepared from the PDC derivatives which had been pyrolyzed at 300 °C for 4 h (Table IV). The data for the cis derivatives correspond more closely to oligomers of 5 or 6 units. The *cis*-dibenzoate polymer **2a** and *cis*-dicarbonate **2c** appeared to have the largest number of consecutive phenylene units. The data for the cis deriv-



(3)

Table V
Electrical Conductivity of PDC Derivatives



polymer	σ, S/cm (initial)	σ S/cm (after AsF_5 exposure)
cis-dibenzoate (**2a**)	3.4×10^{-10}	4.0×10^{-6}
cis-dipivalate (**2b**)	5.9×10^{-10}	1.3×10^{-3}
cis-dicarbonate (**2c**)	1.8×10^{-10}	7.2×10^{-7}
trans-diacetate (**2d**)	2.6×10^{-10}	6.7×10^{-6}
pyrolyzed **2a**	1.3×10^{-10}	0.88
pyrolyzed **2b**	1.7×10^{-10}	0.030
pyrolyzed **2c**	4.5×10^{-11}	2.2
pyrolyzed **2d**	8.1×10^{-11}	2.7×10^{-4}
poly(*p*-phenylene)[a]	10^{-10}	50–100

[a] Values from ref 21.

atives indicated that the structure of the pyrolyzed films contained blocks of phenylene units of approximately six units, separated by unaromatized sections, probably having the 1,2-repeat unit structure (eq 3). The structure of the unaromatized unit is unknown; however, the percentage of 1,2-repeat units (10–15%) corresponds closely to the amount of residual carbonyl absorption (10–15%). Furthermore, 1,2-elimination to an aromatic product cannot occur from these structures without double-bond migration.

When higher temperatures were used for pyrolysis, the structure appeared to contain even smaller blocks of phenylene units. For example, when the *cis*-dibenzoate polymer **2a** was heated to 400 °C for 4 h, the UV of the resulting film had an absorption maximum less than 300 nm.

Electrical Properties. Supported films of the PDC ester derivatives were prepared and exposed to arsenic pentafluoride (Table V). In all cases the initial conductivity was less than 10^{-9} S/cm. After exposure to dopant, the conductivities rose by several orders of magnitude, but the materials were still insulating. The only exceptional case was the *cis*-dipivalate polymer **2b**, which showed conductivities into the semiconductor range on exposure to arsenic pentafluoride. A plausible explanation for the increased conductivity in this case was a greater tendency of polymer **2b** to undergo Lewis acid (arsenic pentafluoride) catalyzed aromatization reactions due to the greater steric strain in the polymer repeat unit.

Films prepared from the PDC ester derivatives were pyrolyzed and then exposed to dopant (Table V). All of the polymers had an initial conductivity of less than 10^{-9} S/cm. However, after exposure to arsenic pentafluoride, the conductivity increased by many orders of magnitude in certain cases. The best conductivities were observed for polymers **2a** and **2c** where increases of at least 10 orders of magnitude occurred and the resulting conductivities were well into the semiconductor range. The conductivity of polymer **2b** was 1–2 orders of magnitude lower than that of **2a** or **2c**. The observed conductivities correlated reasonably well with the size of the blocks of the *p*-phenylene units as determined by the UV long-wavelength maxima. Polymer **2d** had a UV maximum at a relatively short wavelength and had a lower conductivity compared to that of the cis derivatives.

The conductive polymers produced in this fashion had limited stability in air. The conductivity was nearly constant for about 1 day; however, the value dropped off rapidly after about 30 h. This behavior contrasts significantly with that of AsF_5–doped poly(*p*-phenylene) which decays only slightly in humid air.[21]

Nearly all of the known conducting polymers have extensive conjugation along the chain. Yet the available evidence for the pyrolyzed PDC derivatives strongly suggests that the material lacks complete conjugation along the chain. Furthermore, the conductivity studies on the PDC derivatives themselves indicate that aromatization during the doping process is unlikely except, perhaps, in the case of the *cis*-dipivalate polymer **2b**. Thus it would appear that reasonable conductivity is possible for systems without extensive conjugation. The question then arises as to the likely mode of conductivity in such cases.

Three transport mechanisms are possible for conducting polymers: transport along a polymer chain (intramolecular), transport between chains (intermolecular), and transport between polymer particles (macroscopic).[1] Current theories for charge transport favor the hopping mechanisms (either intramolecular or macroscopic) as the dominant mode for conducting polymers. The molecular weight of polyacetylene has been shown to have a negligible effect on the conductivity,[22a] suggesting that intramolecular transport does not dominate bulk conductivity. Thus fairly high conductivity levels should be possible for polymers without complete conjugation, as is the case with pyrolyzed PDC derivatives. Acetylene–carbon monoxide copolymers have been synthesized, having an average polyacetylene block of 5 or 6 units[22b] and have been reported to have a relatively high conductivity (σ = 90 S/cm).

Experimental Section

General. All melting points were uncorrected. Infrared spectra were recorded on a Beckman Model 4250 infrared spectrometer or an IBM FT-IR spectrometer. Low-field (60 MHz) proton NMR spectra were run on a Varian Associates Model EM 360 spectrometer. High-field (270 MHz) proton and carbon-13 spectra were performed on an IBM-Bruker WP270-SY spectrometer. NMR spectra were run in a deuteriochloroform solution with tetramethylsilane (proton) or deuteriochloroform (carbon) internal standard unless otherwise stated. Polymer viscosities were measured in dilute chloroform solution by using a Cannon-Ubbelohde microdilution viscometer (size 50). Glass transition temperatures were measured by using a Du Pont 910 differential scanning calorimeter on pressed polymer samples. Molecular weight measurements were done by size exclusion chromatography on a Waters Model 150C liquid/gel permeation chromatograph with refractive index detector (polystyrene standards). Medium-pressure liquid chromatography (MPLC) was performed with an ISCO Model UA-5 absorbance fluorescence monitor equipped with a Type 6 optical unit and a Model 1133 multiplexer–expander using Woelm silica gel, 240–400 mesh. Ultraviolet spectra were run on a Varian Model 635 UV/visible spectrometer. TGA analyses were conducted on a Du Pont Model 951 thermogravimetric analyzer. Electrical measurements were performed using a Keithly Model 616 digital electrometer. Film thickness measurements were determined by Alpha Step.

Materials. THF and ether solvents were distilled from potassium benzophenone. Methanol was distilled from magnesium. All other solvents were distilled from calcium hydride prior to use unless otherwise stated. 1,4-Cyclohexadiene was obtained from Aldrich and used as received. *N*-Bromosuccinimide (NBS), azobis(isobutyronitrile) (AIBN), and benzoyl peroxide (BPO) were purified by standard methods.[23] 5,6-Dimethyl-1,3-cyclohexadiene[18] and *trans*-5,6-diacetoxy-1,3-dicyclohexadiene[15] were synthesized by literature procedures. *cis*-5,6-Bis[(methoxycarbonyl)oxy]-1,3-cyclohexadiene was generously provided by the Imperial Chemical Industries. Arsenic pentafluoride was purchased from Ozark-Mahoning and purified by vacuum transfer at -110 °C. Electrodag 502 was purchased from Acheson Colloids Co.

***cis*-2-Acetoxy-4-cyclohexen-1-ol (3).** Iodine (32 g, 0.12 mol) was added to a mixture of 1,4-cyclohexadiene (20 g, 0.25 mol) and potassium iodate (14 g, 63 mmol) in acetic acid (400 mL). The resulting mixture was heated to 60 °C for 3 h. The mixture was allowed to cool to room temperature and potassium acetate (25 g, 0.26 mol) was added. The resulting mixture was then heated to reflux for 3 h and cooled to room temperature, and the volatile materials were removed by rotoevaporation. The residue was taken up in ether (300 mL) and washed with aqueous saturated sodium sulfite solution (50 mL). The ethereal solution was dried (magnesium sulfate), concentrated, and distilled to give 30 g (77%) of **3**: bp 87–96 °C (1.4 mm) [lit.[16] 83–92 °C (1.4 mm)]; IR (neat) 3470, 2940, 1740, 1660, 1250 cm^{-1}; ^{1}H NMR (60 MHz) δ 5.57 (m, 2 H), 5.03 (m, 1 H), 4.03 (m, 1 H), 2.57 (br s, 1 H), 2.33 (m, 4 H), 2.08 (s, 3 H).

***cis*-4-Cyclohexene-1,2-diol (4).** Potassium carbonate (51 g, 0.37 mol) was added to a solution of *cis*-2-acetoxy-4-cyclohexen-1-ol (29 g, 0.19 mol) in methanol (200 mL) at 0 °C. The resulting mixture was stirred 1 h at 0 °C and then 16 h at room temperature. The volatile materials were removed by rotoevaporation. The residue was taken up in water (100 mL), neutralized with sulfuric acid, and saturated with sodium chloride. The aqueous phase was continuously extracted with ether for 4 days. The ether phase was dried (sodium sulfate) and concentrated to give 18 g (86%) of **4**: mp 83–84 °C (ether/hexane) (lit.[16] 80–82 °C); ^{1}H NMR (60 MHz) δ 2.29 (m, 4 H), 2.88 (br s, 2 H), 4.02 (t, 2 H, J = 5 Hz), 5.65 (t, 2 H, J = 2 Hz).

***cis*-4,5-Bis(benzoyloxy)cyclohexene (5).** Benzoyl chloride (18 mL, 0.16 mol) followed by 4-(dimethylamino)pyridine (1.8 g, 15 mmol) was added to a solution of *cis*-4-cyclohexene-1,2-diol (8.6 g, 75 mmol), triethylamine (26 mL, 0.19 mol), and dichloromethane (100 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and at room temperature for 16 h. Water (5 mL) was added and the mixture was stirred rapidly for 5 min. The mixture was then diluted with dichloromethane (200 mL) and washed with 10% hydrochloric acid solution (2 × 50 mL), water (50 mL), 5% sodium hydroxide solution (50 mL), water (50 mL), and saturated sodium chloride solution (50 mL). The organic phase was then dried (magnesium sulfate), concentrated, flash chromatographed (silica gel, 40% ether/hexane), recrystallized (ethanol/water), and dried to give 22 g (89%) of **5**: mp 80–80.5 °C; IR (CHCl$_3$) 2880, 1730, 1385, 1190, 1020 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.4–2.8 (m, 4 H), 5.62 (t, 2 H, J = 6 Hz), 5.78 (t, 2 H, J = 1 Hz), 7.45–7.70 (m, 6 H), 8.0–8.2 (m, 4 H). Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.42; H, 5.67.

***cis*-5,6-Bis(benzoyloxy)-1,3-cyclohexadiene (1a).** A mixture of **5** (1.0 g, 3.1 mmol) and *N*-bromosuccinimide (1.1 g, 6.4 mmol) in carbon tetrachloride (50 mL) was degassed with argon and then heated to reflux. AIBN (10 mg, 0.06 mmol) was added and the heating was continued for 4 h. At the end of the heating all of the solid material was floating on the surface. The mixture was allowed to cool to room temperature and filtered through Celite. The solid precipitate was washed with carbon tetrachloride (20 mL). The combined carbon tetrachloride phase was concentrated to give crude dibromide. The crude dibromide was dissolved in methanol (10 mL) and cooled in an ice bath. Zinc dust (1.0 g, 16 mmol) was added and the resulting mixture was stirred 1 h at 0 °C and then 4 h at room temperature. The mixture was filtered through Celite and concentrated. The residue was dissolved in dichloromethane (50 mL) and washed with aqueous 10% hydrochloric acid solution (25 mL), water (25 mL), aqueous 5% sodium hydroxide solution (25 mL), water (25 mL), and aqueous saturated sodium chloride solution (25 mL). The dichloromethane solution was dried (magnesium sulfate), concentrated, and purified by flash chromatography (40% ether/hexane) to give 0.62 g (62%) of **1a**: mp 91–92 °C (ethanol/water); IR (CCl$_4$) 1735, 1520, 1245 cm^{-1}; ^{1}H NMR (270 MHz) δ 5.89 (br s, 2 H), 6.05–6.15 (m, 2 H), 6.15–6.3 (m, 2 H), 7.25–7.6 (m, 6 H), 7.85–8.05 (m, 4 H); ^{13}C NMR (68 MHz) δ 67.90, 125.52, 126.42, 128.33, 129.76, 132.98, 165.86. Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.04. Found: C, 74.80; H, 5.08.

***cis*-4,5-Bis(pivaloyloxy)cyclohexene (6).** Pivaloyl chloride (13 g, 0.11 mol) followed by DMAP (1.3 g, 11 mmol) was added to a solution of **4** (4.0 g, 35 mmol) and triethylamine (17 mL, 0.12 mol) in dichloromethane (100 mL) at 0 °C. The resulting solution was stirred 30 min at 0 °C and 16 h at room temperature. Water (5 mL) was added and the resulting mixture stirred 5 min at room temperature. The mixture was diluted with ether (200 mL) and washed with aqueous 10% hydrochloric acid solution (2 × 50 mL), water (50 mL), aqueous 5% sodium hydroxide solution (2 × 50 mL), water (50 mL), and aqueous sodium chloride solution (50 mL). The organic phase was dried (magnesium sulfate), concentrated, and distilled to give 9.2 g (93%) of **6**: bp 105–108 °C (1.0 mm); IR (neat) 3050, 2990, 1740, 1660, 1290, 1150 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.22 (s, 18 H), 2.38 (m, 4 H), 5.18 (m, 2 H), 5.63 (m, 2 H); ^{13}C NMR (68 MHz) δ 26.9, 28.4, 38.6, 68.6, 123.3, 177.4. Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.98; H, 9.16.

***cis*-5,6-Bis(pivaloyloxy)-1,3-cyclohexadiene (1b).** A mixture of **6** (9.2 g, 33 mmol) and NBS (12 g, 68 mmol) in carbon tetrachloride (100 mL) was heated to reflux and AIBN (53 mg, 0.33 mmol) was added. The mixture was heated at reflux for 5 h after which the solid material was observed to float on the surface. The mixture was allowed to cool to room temperature and filtered through Celite. The solution was concentrated to give crude dibromide. To a solution of crude dibromide in methanol (50 mL) at 0 °C was added zinc dust (8.5 g, 0.13 mol). The resulting mixture was stirred 1 h at 0 °C and 3 h at room temperature. The mixture was filtered through Celite and washed with dichloromethane (20 mL). The volatile materials were removed by rotoevaporation and the residue was taken up in ether (200 mL). The ethereal phase was washed with aqueous 10% hydrochloric acid solution (2 × 50 mL), water (50 mL), aqueous 5% sodium hydroxide solution (50 mL), water (50 mL), and aqueous sodium chloride solution (50 mL), then dried (magnesium sulfate), and concentrated to give 7.7 g (84%) of **1b**. The material was further purified by MPLC (4% ethyl acetate/hexane) and bulb-to-bulb distillation: bp 95 °C (0.01 mm); IR (neat) 3080, 3000, 1750, 1490, 1290, 1150 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.20 (s, 18 H), 5.49 (m, 2 H), 5.88 (m, 2 H), 6.07 (m, 2 H); ^{13}C NMR (68 MHz) δ 27.0, 38.8, 67.2, 125.7, 125.9, 175.5. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 67.95; H, 8.59.

Poly(*cis*-5,6-bis(benzoyloxy)-2-cyclohexen-1,4-ylene) (2a). A mixture of **1a** (1.0 g, 3.1 mmol), benzoyl peroxide (15 mg, 0.060 mmol), and benzene (0.2 mL) was degassed and then heated to 75 °C in a sealed tube for 48 h. The contents of the tube were dissolved in chloroform (2 mL) and added dropwise to rapidly stirred hexane (20 mL). The solid product was filtered and dried to give 0.84 g (84%) of polymer **2a** [η] = 0.1 dL/g; IR (film) 1740, 1270, 1110 cm^{-1}; ^{1}H NMR (270 MHz) δ 2.3–3.5 (m, 2 H), 5.1–6.4 (m, 4 H), 6.4–8.6 (m, 10 H); ^{13}C NMR (68 MHz) δ 70, 127, 129, 132, 166. Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 74.79; H, 5.06.

Poly(*cis*-5,6-bis(pivaloyloxy)-2-cyclohexen-1,4-ylene) (2b). A solution of **1b** (1.0 g, 3.6 mmol) and BPO (8.6 mg, 0.040 mmol) was degassed by three freeze–thaw cycles and sealed in vacuo in a polymerization tube. The tube was then heated to 75 °C for 48 h. The tube was allowed to cool to room temperature and the solid contents were dissolved in dichloromethane (2 mL). The dichloromethane phase was added dropwise to rapidly stirred methanol (400 mL). The resulting solid was filtered and dried to give 0.40 g (40%) of a white powder: [η] = 0.4 dL/g; IR (film) 2973, 1734, 1480, 1281, 1157 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.9–1.7 (m, 18 H), 2.5–3.2 (m, 2 H), 4.8–6.2 (m, 4 H); ^{13}C NMR (68 MHz) δ 28, 39, 69, 128, 178. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 66.74; H, 8.35.

Poly(*cis*-5,6-bis[(methoxycarbonyl)oxy]-2-cyclohexen-1,4-ylene) (2c). A mixture of *cis*-5,6-bis[(methoxycarbonyl)oxy]-1,3-cyclohexadiene (1.0 g, 4.4 mmol) and BPO (11 mg, 0.040 mmol) was degassed with argon and then sealed in vacuo in a polymerization tube. The tube was heated to 75 °C for 48 h. The tube was allowed to cool to room temperature and then the contents were dissolved in chloroform (10 mL). The chloroform solution was added dropwise to rapidly stirred hexane (300 mL). The resulting solid was filtered and dried to give 0.85 g (85%)

of a white powder: [η] = 0.4 dL/g; IR (film) 1750, 1440, 1270 cm^{-1}; ^1H NMR (270 MHz) δ 2.4–3.1 (m, 2 H), 3.4–4.1 (m, 6 H), 4.8–6.2 (m, 4 H); ^{13}C NMR (68 MHz) δ 36, 55, 73, 127, 155. Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 51.83; H, 5.35.

Poly(*trans*-5,6-diacetoxy-2-cyclohexen-1,4-ylene) (2d). A solution of 5,6-diacetoxy-1,3-cyclohexadiene (**1d**) (1.4 g, 7.0 mmol) and BPO (17 mg, 0.073 mmol) was degassed by three freeze–thaw cycles and sealed in vacuo in a polymerization tube. The tube was heated in a bath at 75 °C for 48 h. The tube was allowed to cool to room temperature and the contents were dissolved in chloroform (4 mL). The solution was filtered and then added dropwise to a rapidly stirred volume of hexane (250 mL). The resulting solid was filtered and dried to give 0.65 g (47%) of a white powder: [η] = 0.1 dL/g; IR (film) 1744 cm^{-1}; ^1H NMR (270 MHz) δ 1.8–2.4 (m, 6 H), 2.4–3.1 (m, 2 H), 4.5–6.0 (m, 4 H). Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.20; H, 6.17. Found: C, 60.36; H, 5.94.

3-Acetoxy-4-(benzoyloxy)-5,6-dimethylcyclohexene (9). A 35% peracetic acid solution (0.92 g, 4.3 mmol) was added to a mixture of 5,6-dimethyl-1,3-cyclohexadiene (0.46 g, 4.3 mmol) and sodium acetate (0.49 g, 6.0 mmol) in dichloromethane (5 mL) at −20 °C. The resulting mixture was stirred 1 h at −20 °C and 1 h at room temperature. The mixture was diluted with ether (50 mL) and washed with 5% aqueous sodium hydroxide solution (20 mL), water (20 mL), and saturated aqueous sodium chloride solution (20 mL). The organic phase was dried (magnesium sulfate) and concentrated to give crude hydroxy ester **8**. To a solution of crude hydroxy ester (0.54 g, 2.9 mmol), triethylamine (0.59 g, 5.9 mmol), and benzoyl chloride (0.50 g, 3.5 mmol) in dichloromethane (10 mL) was added DMAP (72 mg, 0.59 mmol). The resulting solution was stirred 16 h at room temperature. The mixture was diluted with ether (50 mL) and washed with 10% aqueous hydrochloric acid solution (50 mL), water (50 mL), 5% aqueous sodium hydroxide solution (50 mL), water (50 mL), and saturated aqueous sodium chloride solution (50 mL). The organic phase was dried (magnesium sulfate) and concentrated. The crude material was purified by MPLC (4% ethyl acetate/hexane) and bulb-to-bulb distillation to give 20 mg (2.0%) of **9**: bp 80 °C (0.1 mm); IR (CCl_4) 2940, 1725, 1710, 1430, 1240, 1085 cm^{-1}; ^1H NMR (270 MHz) δ 0.99 (d, J = 7.2 Hz, 3 H), 1.08 (d, J = 7.2 Hz, 3 H), 1.8–2.1 (m, 1 H), 1.97 (s, 3 H), 2.2–2.4 (m, 1 H), 5.31 (m, 1 H), 5.50 (m, 2 H), 5.82 (m, 1 H), 7.41 (m, 3 H), 8.01 (m, 2 H); MS, *m/e* 166 (M − $PhCO_2H$), 106 (M − $PhCO_2H$ − CH_3CO_2H), 91 (C_7H_7). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.53; H, 7.08.

Infrared and Ultraviolet Studies on Pyrolyzed Films of *cis*-Dibenzoate Polymer 2a (Representative Case). A solution was prepared by dissolution of **2a** (0.24 g) in 1,2-dichloroethane (1.5 g). The solution was filtered through a 0.2-μm millipore filter and then spin coated on both 1-in. silicon wafers and 0.5-in. quartz wafers at 3000 rpm for 90 s. The wafers were baked at 100 °C for 10 min. The films coated on silicon wafers were pyrolyzed on a hotplate (preheated to 300 °C) and periodically monitored by infrared analysis. The films on quartz wafers were baked at a given temperature in an oven with nitrogen flow and monitored periodically by ultraviolet analysis.

Representative Conductivity Experiment. A solution of *cis*-dibenzoate polymer **2a** (0.49 g) and 1,2-dichloroethane (3.0 g) was filtered through a 0.5-μm filter. The solution was spin coated on 18-mm Corning No. 1 square glass covers at 2300 rpm for 90 s. The films were then baked at 100 °C for 10 min. An average film thickness was measured at 0.86 μm (average of four measurements at different film locations). The film was then heated for 4 h at 300 °C in an oven in a nitrogen stream. The film thickness was then measured to be 0.19 μm (average of four locations). The film with glass support was then mounted to a four-probe device using Electrodag to maintain electrical and mechanical contact. The average distance between the center probes was measured to be 0.32 cm (average of 10 measurements). The sample was placed in a chamber which was evacuated for 16 h. An initial resistance was measured followed by the introduction of 500 Torr of purified arsenic pentafluoride. Periodic electrical measurements were performed over 151 h. Conductivities were calculated from the resistance (R) (eq 5)

$$\sigma = \frac{l}{twR} \tag{5}$$

where l = length between center probes (0.32 cm), t = film thickness (1.9×10^{-5} cm), w = sample width (1.8 cm), and R = sample resistance.

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Registry No. **1a**, 86504-06-5; **1b**, 86504-08-7; **2a**, 86504-13-4; **2b**, 86504-19-0; **2c**, 86504-18-9; **2d**, 86504-22-5; **3**, 65173-63-9; **4**, 65173-64-0; **5**, 108592-06-9; **6**, 108592-07-0; **7**, 5715-27-5; **8**, 108592-09-2; **9**, 108592-08-1; AsF_5, 7784-36-3; PhCOCl, 98-88-4; *t*-BuCOCl, 3282-30-2; 1,4-cyclohexadiene, 628-41-1; peracetic acid, 79-21-0.

References and Notes

(1) For a review of conducting polymers, see: Frommer, J. E.; Chance, R. R. In *Encyclopedia of Polymer Science and Engineering*; Grayson, M., Kroschwitz, J., Eds.; Wiley: New York, in press.

(2) Shacklett, L. W.; Elsenbaumer, R. L.; Chance, R. R.; Eckhardt, H.; Frommer, J. E.; Baughman, R. H. *J. Chem. Phys.* **1981**, *75*, 1919.

(3) Tunney, S. E. Ph.D. Dissertation, Colorado State University, 1986. Tunney, S. E.; Suenaga, J.; Stille, J. K. *Macromolecules* **1983**, *16*, 1398.

(4) Wnek, G. E.; Chien, J. C. W.; Karasz, F. E.; Lillya, C. P. *Polymer* **1979**, *20*, 1141.

(5) Wesslig, R. A.; Zimmermann, R. G. U.S. Patent 3 401 152, 1968; *Chem. Abstr.* **1968**, *69*, 87735q.

(6) Chiang, A. C.; Waters, P. F.; Aldridge, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1807. Masuda, T.; Yamamoto, K.; Higashimura, T. *Polymer* **1982**, *23*, 1663.

(7) Voronkov, M. G.; Pukhnarevich, V. B.; Sushchinskaya, S. P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 53.

(8) Frommer, J. E. *Acc. Chem. Res.* **1986**, *19*, 2.

(9) Jenekhe, S.; Wellinghoff, S.; Reed, J. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 175.

(10) Bocchi, V.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1986**, 148, and references cited therein. Roncali, J.; Garnier, F. J. *J. Chem. Soc., Chem. Commun.* **1986**, 783, and references cited therein.

(11) Armes, S. P.; Vincent, B.; White, J. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1525, and references cited therein.

(12) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595. Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395.

(13) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1983**, 954. Ballard, D. G. H.; Courtis, A.; Shirley, I. M. *Eur. Pat. Appl.* EP 76605 A1, 1983.

(14) During the course of these studies a patent appeared concerning the conductivity of polyphenylene powder prepared from PDC derivatives: Ballard, D. G. H.; Moran, K. T.; Shirley, I. Eur. Pat. Appl. EP 122079 A2, 1984.

(15) Platt, K. L.; Oesch, F. *Synthesis* **1977**, 449.

(16) Krow, G. R.; Carmosin, R.; Mancuso, A. *Org. Prep. Proced.* **1977**, *9*, 9285.

(17) Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981; p 281.

(18) Jacobson, B. M.; Arvanitis, G. M.; Eliasen, C. A.; Mitelman, R. *J. Org. Chem.* **1985**, *50*, 194.

(19) Kovacic, P.; Oziomek, J. *J. Org. Chem.* **1964**, *29*, 100.

(20) Kovacic, P.; Hsu, L. C. *J. Polym. Sci. A-1* **1966**, *4*, 5.

(21) Shacklette, L. W.; Chance, R. R.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *Synth. Met.* **1979**, *1*, 307.

(22) (a) Schen, M. A.; Karasz, F. E.; Chien, J. C. W. *Makromol. Chem., Rapid Commun.* **1984**, *1*, 217. (b) Chien, J. C. W.; Warakomski, J. M.; Karasz, F. E.; Schen, M. A. *Macromolecules* **1985**, *18*, 2380.

(23) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1980.