Macromolecules

Volume 20, Number 6 June 1987

Synthesis of Conductive Polymers Containing Poly(*p*-phenylene methide) Units

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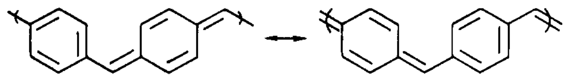
ABSTRACT: We have synthesized the title polymer via a Wittig reaction between 1,4-cyclohexanedione and the bis(triphenylphosphonium) salt of α,α'-dichloro-*p*-xylene. In the course of this reaction considerable dehydrogenation has occurred, and the resulting polymer, I, contains poly(phenylene methide) units. The ^1H and ^{13}C NMR spectra of I suggest ring equivalence. Doping of I with AsF_5 leads to a saturation conductivity of 3×10^{-3} S/cm. AsF_3 accelerates the doping by AsF_5. The role of AsF_3 is ascribed to its solvent effect and the resulting changes in morphology. Preliminary ESCA studies suggest that considerable charge delocalization occurs in the doped polymer. The conductivity of the three-ring model compound was found to increase from 10^{-12} to 4.6×10^{-7} S/cm after doping with AsF_5.

Introduction

The search for electrically conducting organic polymers has expanded enormously since the preparation of polyacetylene film[1] and the subsequent discovery[2] that its electrical conductivity, on doping with various oxidants, can be varied over a range of 11 orders of magnitude to a maximum value of 560 S/cm. The intervening years have seen the synthesis of other conducting organic polymers such as poly(phenylacetylene),[3] poly(methylacetylene),[4] poly(2,5-thiophenediyl),[5] poly(propargyl halides),[6] poly((trifluoromethyl)acetylene),[7] polypyrrole,[8] poly(phenylene sulfide),[9] poly(*p*-phenylene),[10] and poly(phenylenevinylene).[11] A number of reviews have also appeared.[12]

We now report the synthesis of a polymer, I, that contains poly(1,4-xylylidene-2′,5′-cyclohexadien-1′,4′-ylidene) units by the Wittig reaction[13] of *p*-xylenebis(triphenylphosphonium chloride) with 1,4-cyclohexanedione. We have previously reported the synthesis of the model compound, 1,4-cyclohexadienylbis(benzylidene) by the same route.[14]

The poly(*p*-phenylene methide) unit in polymer I represents a new class of conjugated polymers in which benzenoid rings alternate with quinonoid rings. We believe that this molecular system should be characterized by a high degree of electron delocalization because it can be described in terms of two equivalent resonance forms each of which contains relatively high-energy quinonoid rings:



The structural features that impart conductivity to an organic polymer have not yet been definitely established, although most investigators have accepted the basic requirement of an extended conjugated chain.[15] Theoretical calculations[16] on various structures, including poly(arene methides), have been published in an attempt to understand the conduction mechanism and to catalyze further research. At least two recent articles,[17,18] however, show that interruptions in chain conjugation do not destroy conductivity. The question of structure–conductivity relationship thus remains open.

We now report the synthesis and characterization of polymer I, containing poly(*p*-phenylene methide) (PPM) units, as part of our program to explore the relationship between molecular structure and electrical conductivity.

Experimental Section

Materials. Materials whose commercial sources are not given were purchased from Aldrich Chemical Co. Only those materials that were purified are listed. α,α'-Dichloro-*p*-xylene and 1,4-cyclohexanedione were recrystallized from CCl_4. *N,N*-Dimethylformamide (DMF) (Gold Label 99+%), *p*-xylene (99+% reagent), *p*-dioxane (99%), tetrahydrofuran (THF) (99%), and ethanol (Florida Distillers) were dried over 4A molecular sieves. Dichlorodicyano-*p*-benzoquinone (DDQ) was dried in a vacuum dessicator over Drierite and transferred under N_2. Aluminum chloride (anhydrous powder) was sublimed under reduced pressure before use and transferred under N_2. Potassium bromide (99+% infrared grade) was kept in an oven to ensure dryness. Benzyl chloride was fractionally distilled under reduced pressure, and a middle fraction was used under N_2.

Instrumentation. IR spectra were recorded on a Perkin-Elmer 710B spectrophotometer using pressed KBr pellets. UV spectra were recorded on an IBM Model 9420 UV–visible spectrometer or on a Cary 14 spectrophotometer using solutions of ca. 10^{-4} M. ^1H and ^{13}C NMR spectra were recorded on an FT NMR Joel FX 90Q spectrometer; more routine ^1H NMR spectra were recorded on a Varian EM360A spectrometer. Chemical shifts are reported

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relative to Me_4Si. ESR spectra were recorded on a Varian E-109 instrument. Mass spectra were measured on powdered samples with a Nicolet FTICR mass spectrometer. Galbraith Laboratories provided the molecular weight of hydrogenated I by vapor-phase osmometry. Hydrogenations were performed in a Parr apparatus (Parr Instrument Co., Model 3911). ESCA spectra were recorded on a McPherson ESCA 36 photoelectron spectrometer. Samples were excited with Al(K) X-rays ($h\omega$ = 1486.6 eV). The C(1s) photoelectrons are therefore estimated to have an escape depth of ca. 20 Å. Samples were pressed into 0.5-in. disks at 16 000 lb/cm^2 prior to doping. Doped samples were transferred from the doping chamber to the spectrometer under N_2 atmosphere. Invariably, however, a significant O(1s) spectrum was present. The base pressure in the spectrometer sample chamber was maintained at 10^{-7} Torr with a Sargent-Welch Turbo molecular pump and a CTI Cryotoer-Cryogenic pump. The As(3d) signal remained constant as a function of pumping time; therefore, we concluded that XPS data were obtained on physically stable samples. Manipulations requiring controlled atmospheres were carried out in a D. L. Herring Corp. Model DRI Lab HE-43 glovebox equipped with a Vacuum Atmospheres Co. Dri-Train HE-493.

Elemental Analyses. Samples were analyzed by Galbraith Laboratories, Inc., Knoxville, TN, and/or by M-H-W Laboratories, Phoenix, AZ.

Synthesis of Polymer I. To 62.4 g (0.089 mol) of *p*-xylenebis(triphenylphosphonium chloride) (XTPPC) dissolved in dry DMF was added 15.0 g (0.18 mol) of phenyllithium through a double-tipped needle. The originally insoluble XTPPC dissolved on adding the PhLi. A solution of 10.0 g (0.089 mol) of 1,4-cyclohexanedione in DMF was added slowly, after which the temperature of the mixture was raised under N_2 to 145 °C over 5 days. After the mixture was cooled, a lemon-green solid was filtered off, washed with methanol, and dried under vacuum. The solid product (20% conversion), mp 265–267 °C, is slightly soluble in CS_2 and was purified by extracting it with CS_2 in a Soxhlet apparatus. Anal. Calcd for $C_{14}H_{14}$ (Ia): C, 92.25; H, 7.72. Anal. Calcd for $C_{14}H_{10}$ (I): C, 94.34; H, 5.66. Anal. Calcd for $C_{14}H_{12}$: C, 93.28; H, 6.72. Found: C, 93.17; H, 6.71. IR (KBr pellet) 3080, 3050, 1600, 1515, 1450, 810, 745, 685 cm^{-1}; ^{13}C NMR (CS_2) δ 126.561, 126.886, 127.591, 128.67; ^1H NMR (CS_2) δ 6.99 (s, 1 H), 7.39 (m, 4 H); UV (CS_2) λ_{max} 234.7, 355.6, 378.4 nm. The ESR spectrum neat and in CS_2 solvent showed no indication of unpaired electrons.

Hydrogenation of Polymer I. Hydrogenation was carried out in a Parr apparatus using Pd/C as catalyst. Approximately 0.5 g PPM was mixed with a few milligrams of Pd/C in dry dioxane and the mixture left under H_2 at ca. 3 atm for 3 days at room temperature. Approximately 1 molar equiv of H_2 was absorbed. The originally insoluble PPM was converted into a white, dioxane-soluble solid. It was purified by dissolving in $CHCl_3$ and reprecipitating with methanol to afford a quantitative yield: mp 72–80 °C; IR (KBr pellet) 3100, 3050, 2920, 2850, 1600, 1510, 1450, 1120, 1070, 800, 720, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (s), 6.8 (s), 2.7. Anal. Calcd for $C_{14}H_{12}$: C, 93.28; H, 6.72. Anal. Calcd for $C_{14}H_{14}$: C, 92.25; H, 7.72. Found: C, 91.06; H, 8.45. The molecular weight was determined by Galbraith Laboratories to be 172 by vapor-phase osmometry.

Dehydrogenation of Polymer I. Approximately 0.2 g of PPM was heated in a test tube to the melting point under N_2. At that point, a few milligrams of tris(triphenylphosphine)rhodium(I) chloride was added. The color changed instantly from green to black. The insoluble, black residue was washed with CS_2 to remove starting material and catalyst: IR (KBr pellet) 1700, 1640, 1590, 1490, 1410, 1240, 1180, 1120, 1060, 1010, 940, 890, 800, 740, 680 cm^{-1}. No melting point was observed up to 390 °C. Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 80.4; H, 5.17.

Model Compound. We prepared this compound by the method reported earlier[14] in order to have a sample for comparison. The ^1H NMR spectrum showed only two resonances at δ 6.4 (s, 1 H) and 7.2 (m, 7 H).

p Type Doping and Conductivity Measurements. Doping of polymer samples with AsF_5 was carried out and the conductivity monitored by using the standard two-probe or four-probe technique on pressed pellets mounted on Pt wires using Electrodag 502 cement[22] (Table I).

Table I
Conductivity of I vs. Time of Doping with AsF_5

time, h	conduct., S/cm	time, h	conduct., S/cm
0 (no dopant)	10^{-12}	4	5.6×10^{-6}
0.005	7.0×10^{-5}	17	1.4×10^{-4}
0.5	8.0×10^{-5}	24	2.8×10^{-4}
0.7	2.0×10^{-6}	48	1.6×10^{-3}
1.8	1.8×10^{-6}	72	3.0×10^{-3}
3.3	2.6×10^{-6}		

That doping actually occurred was shown by the infrared spectrum which showed intense absorption throughout the range from 4000 to 1000 cm^{-1}. The band due to AsF_6^- at 695 cm^{-1} was the only outstanding absorption.

After standing for 2 months under ambient conditions, an AsF_5-doped pellet of I was found to have a conductivity in air of 10^{-5} S/cm.

Doping with iodine was carried out by using the same type of circuitry. In this case, however, no enhancement was observed at atmospheric pressure. The experiment was repeated[21] under an argon pressure of 2 atm for 63 h to give a conductivity of 1.2 × 10^{-4} S/cm after vacuum drying. The conductivity of the same sample before doping was 5.2×10^{-9} S/cm.

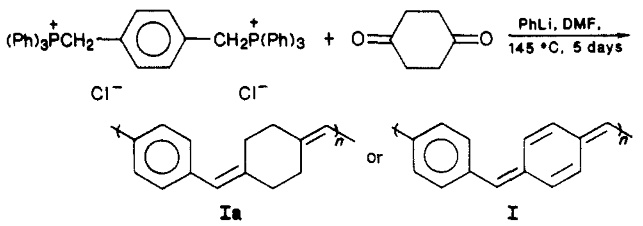
The model compound exhibited a conductivity of ca. 10^{-12} S/cm before doping and a final value of 4.6×10^{-7} S/cm after doping with AsF_5.

Mass Spectroscopy of Polymer I. Up to a temperature of 320–325 °C, the highest significant mass observed in the spectrum was at *m/z* 283, which corresponds to a three-ring unit. Masses at *m/z* 979 and 1944—corresponding to $(C_{14}H_{10})_{5.5}$ and $(C_{14}H_{10})_{11}$, respectively—were also observed, but these were less intense. At temperatures above 130–140 °C, *m/z* 282 and 283 were the major masses. Spectra taken at very short delay time—60 μs—show mainly *m/z* 282, while *m/z* 283 forms later by ion–molecule reactions. An ion at *m/z* 178, corresponding to one two-ring repeating unit of the polymer, was also present.

Mass spectroscopy of the model compound showed *m/z* 180 and 181 as the first ions. At 50 eV, *m/z* 179 was the most abundant peak with no heating of the probe required. At 2-μs reaction time, *m/z* 282 and 283 were observed as ion–molecule reaction products. The 50-eV spectra at 60 μs gave major peaks at *m/z* 178, 179, and 180, and smaller peaks at *m/z* 165 and 152. The molecular ion peak at *m/z* 256 was not observed.

Discussion of Results

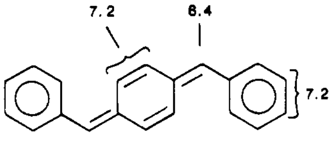
Synthesis of Polymer I. We have prepared I by the Wittig reaction



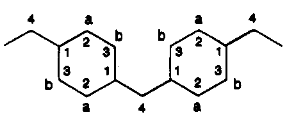
We had expected to obtain the usual Wittig product Ia but obtained a product, polymer I, which has undergone considerable dehydrogenation. This product (20% conversion, mp 265–267 °C) is a lemon-green, flaky solid, soluble in CS_2. Dehydrogenation could not occur as a result of air oxidation because the reaction was carried out under a nitrogen atmosphere. We suggest that dehydrogenation occurs thermally to produce the insoluble polymer I, which contains considerable aromaticity.

Characterization. The elemental analysis of our polymer I leads to the empirical formula C_7H_6. This formula corresponds to one saturated CH_2CH_2 group per two ring units. Spectral data, however, are precisely consistent with a completely unsaturated polymer. The ^{13}C NMR spectrum showed only four resonances, and the ^1H NMR spectrum showed only two at δ 6.99 (1 H) and

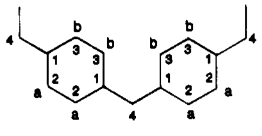
7.39 (4 H). The spectra suggest that the rings in I are conjugated and equivalent. In the formulas below, letters refer to the different ring protons and numbers refer to the different carbon atoms. From these formulas we can see that ^{13}C NMR cannot be used to distinguish between cis and trans isomers.



model compound



all trans



all cis

We note that the ^{1}H NMR spectrum of our previously reported[14] model compound also shows two different protons.

The UV absorption of I at 378.4 nm is also consistent with considerable electron delocalization when compared with 295, 305, and 320 nm for the model compound.[14]

Mass spectral analysis using a solid probe gives maximum values at m/z 979 and 1944. These values correspond to species of $\overline{\mathrm{DP}}$ 5.5 and 11, respectively. The maximum value at m/z 1944 represents only the maximum molecular weight of volatile molecules. We assume that higher molecular weight molecules are also present.

Our polymer has a narrow melting point range (265–267 °C). We attribute the relatively narrow range to a narrow molecular weight distribution resulting from precipitation of the product from the reaction mixture as it reaches a molecular weight that renders it insoluble.

Hydrogenation of I should produce polybenzyl. In our hands, I yielded a gray-white solid upon hydrogenation over Pd/C in dioxane. This solid was soluble in $CHCl_3$, and its ^{1}H NMR spectrum shows two singlets in the aromatic region at δ 7.2–6.8 and one singlet at δ 2.7. This aromatic/aliphatic ratio was 2:1. The infrared spectrum shows aliphatic CH_2 stretch bands at 2850 and 2920 cm^{-1}. Authentic polybenzyl[19] shows two ^{1}H NMR resonances. The appearance of two singlets instead of one in the aromatic region of our hydrogenated I may be explained by the presence of phenyl end groups—toluene, diphenylmethane, and other species—produced by hydrogenolysis. A molecular weight determination of this hydrogenated product gave a value of 172 by vapor-phase osmometry. This value is less than one repeat unit ($C_{14}H_{12}$) and affords evidence of extensive hydrogenolysis during reaction with hydrogen.

Recent calculations on polymer I predict an energy gap of 1.17 eV.[16] This value corresponds to a λ_{max} of 1060 nm. We observed no such absorption maximum in the spectrum of I, possibly because of low solubility. Our λ_{max} of 378.4 nm corresponds to an energy gap of 3.3 eV. This discrepancy between calculated and observed energy gap raises the question whether this polymer is fully conjugated or whether it contains some insulating CH_2 groups in the backbone. To answer this question, we subjected I to further dehydrogenation by heating it with tris(triphenylphosphine)rhodium(I) chloride. The green solid immediately turned black, was insoluble in CS_2, the best solvent for polymer I, and did not melt up to 400 °C. The most prominent bands in the infrared spectrum are weak and occur in the range 1300–1000 cm^{-1}. This spectrum also shows the loss of strong bands in the range 1000–690 cm^{-1}. The latter corresponds to the C–H out-of-plane bending bands diagnostic of aromatic substitution pattern and suggest either that the substitution pattern has changed as the result of cross-linking or that dehydrogenation has introduced a greater degree of rigidity into the polymer. At any rate, the conductivity of this polymer was not significantly different from that of the original polymer I.

Doping. Although we observed no effect of doping polymer I with I_2 at atmospheric pressure, we observed a conductivity of 1.2×10^{-5} S/cm after doping with iodine under pressure.[21] This represents a conductivity increase of 4 orders of magnitude. We attribute the increase in conductivity at higher pressure to the greater concentration of I_2 and/or to possible changes in morphology.

Polymer I doped with AsF_5 exhibits a conductivity of 3×10^{-3} S/cm after a few days of exposure. As doping proceeds the lemon-green colored polymer changes to a brassy color, then to a bronze-like metallic luster, and finally to black at the point of saturation. Doping occurs at the surface as can be seen by breaking the pellet. Conductivity vs. time measurements showed a rapid increase in conductivity during the first 2 min, followed by a drop in the conductivity, and finally by a continuous increase to the level of saturation (Table I). We attribute this unusual behavior to the formation of AsF_3 during doping.[22]

$$3AsF_5 + 2e^{-1} \rightarrow AsF_3 + 2AsF_6^-$$

AsF_3 plays a dual role. First, as a plasticizer, it changes the morphology of the polymer, probably decreasing T_g. As a result, the conductivity declines when AsF_3 becomes available. Second, as a plasticizer, AsF_3 helps the AsF_5 penetrate further into the polymer, and the conductivity again rises.

The IR spectrum of doped I supports this doping mechanism by exhibiting intense absorption throughout and by the appearance of a strong, broad band at 695 cm^{-1}, which corresponds to AsF_6^-. Our spectrometer did not allow us to detect the band at 395 cm^{-1}.

We note that the model compound undergoes a conductivity enhancement of 5.5 orders of magnitude on doping with AsF_5. We note further that a 2-month-old sample of AsF_5-doped I had a conductivity of 10^{-5} S/cm. This suggests that this material is relatively stable. We are pursuing the investigation of this stability further.

Electron spectroscopy for chemical analysis (ESCA) has been employed to characterize $FeCl_3$-doped polyacetylene,[23] AsF_5-doped polyacetylene,[24] and iodine-doped polyacetylene.[25,26] We have monitored the C(1s), As(3d), and valence band spectra of AsF_5-doped I as a function of dopant concentration. Figure 1 contains the C(1s) photoelectronic spectra as a function of AsF_5 doping time for polymer I. Spectrum a is the C(1s) spectrum of undoped I and consists of only a single line with no secondary features. Such a spectrum is typical of material with only one class of carbon.

Upon doping with AsF_5 (spectrum b), we observed additional higher binding energy features: a distinct line at 290 eV and a shoulder to the main photoline at ca. 288 eV. These features have been reported to be the result of single particle or collective excitations generated in conjunction with the removal of an electron from the C(1s) level of $(C_2H_2)_x$ when the polymer is doped with AsF_5 to the highly electronically conducting state.[25] We suggest that a similar mechanism is likely in the doping of I with AsF_5 and that any charge transferred to the polymer is delocalized.

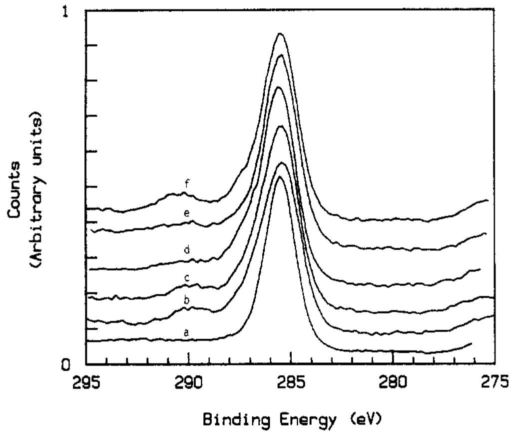


Figure 1. C(1s) ESCA spectra of doped polymer I: (a) before AsF$_5$ vapor was introduced; (b) after 1-min exposure (400 mmHg); (c) after 3-min exposure; (d) after 1-h exposure; (e) after 3-h exposure; (f) after 6-h exposure.

The results of our ESCA study of polymer I will be reported in a future publication.

Acknowledgment. We thank David King and Dr. William E. Swartz, Jr., of this department for the ESCA spectra and for their interpretation of these results. We thank Dr. Michael J. Barber of the USF Biochemistry Department for ESR spectra. We thank Dr. John R. Eyler of the Chemistry Department, University of Florida, for mass spectral data and their interpretation and Dr. Rebecca O'Malley of this department for helpful discussions about mass spectra. We also thank the Research Corporation and the University of South Florida Division of Sponsored Research for their support of this work.

Registry No. I (copolymer), 93454-68-3; I (SRU), 93473-55-3; Ia (SRU), 107890-81-3; XTPPC, 1519-47-7; AsF$_3$, 7784-35-2; AsF$_5$, 7784-36-3; 1,4-cyclohexanedione, 637-88-7.

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