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Functional Derivatives of Poly(phenylacetylenes)

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ABSTRACT: Methyl *p*-ethynylbenzoate was polymerized at room temperature in toluene using WCl_6/Ph_4Sn as catalyst, giving high molecular weight poly(methyl *p*-ethynylbenzoate) with a predominantly trans structure. Lithium trimethoxyaluminum hydride reduction and subsequent oxidation with dimethyl sulfoxide/oxalyl chloride gave poly(*p*-ethynylbenzyl alcohol) and poly(*p*-ethynylbenzaldehyde), respectively. Yields for the above reactions were 90%, 97%, and 89%, respectively. Insoluble cis polymers of *p*-ethynylbenzaldehyde and *p*-ethynylbenzyl alcohol were also produced in lower yields by direct polymerization of the monomers using higher catalyst concentrations.

Introduction

Polyacetylenes[3a] are a unique class of polymers in that the polymer chain contains conjugated double bonds. Such extended conjugation reduces the gap between the bonding and antibonding molecular orbitals. In polyacetylene, this gap is approximately 1.4 eV, producing interesting semiconducting properties in the parent hydrocarbon and simple derivatives.

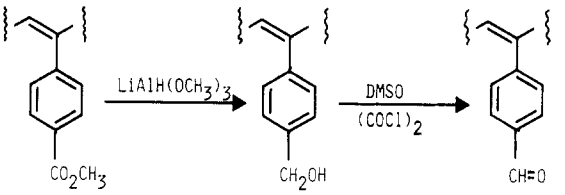
Polyacetylene can be produced in two forms, cis and trans, having conductivities of about 10^{-10} and 10^{-6} $(\Omega\ cm)^{-1}$, respectively. The trans polymer is photoconducting.[3b] The conductivities can be raised to about 10^3 by doping with such materials as iodine and AsF_5.[3c]

Phenylacetylene can be polymerized with a variety of catalysts, most commonly tungsten and molybdenum compounds, yielding polymers of fairly high molecular weight.[4] When tungsten compounds are used, the polymer chain contains predominantly trans double bonds, which allow the overlap needed for extended conjugation. These polymers are red. On the other hand, molybdenum compounds give a high cis content, resulting in yellow polymers with minimal conjugation due to steric hindrance. Furthermore, the red trans polymers are amorphous and soluble in a variety of solvents, whereas the yellow cis polymers are crystalline and insoluble.[4] These crystalline polymers have been assigned a cis–cisoidal microstructure, while the cis–transoidal form, obtained under certain conditions of Ziegler–Natta catalysis, is amorphous and soluble.[5a] Furlani et al. have produced a soluble, yellow, stereoregular polymer which is presumably the cis–transoid form by using a Rh(I) catalyst.[5c] Under certain conditions, cyclohexadiene structures are also present.[5a,b]

Although the unique structure of these compounds, together with the favorable solubility properties of the transoid polymers, should make them good candidates for further study, the number of functional derivatives reported has been limited to *p*-methoxy, *p*-methyl, *p*-chloro,[6] fluoro- and trifluoromethyl,[7] nitro,[8] and alkyl and chloro on the chain.[9] A few sulfur- and nitrogen-containing derivatives form the basis of a Japanese patent.[10]

In contrast to semiconducting parent polyacetylenes, poly(phenylacetylenes) are insulators. The latter have been shown, however, to have other interesting properties attributable to the conjugated polymer chain. For example, photoconductivity which is especially sensitive to long wavelength light has been demonstrated.[11]

Scheme I
Conversion of Poly(methyl *p*-ethynylbenzoate) to Poly(*p*-ethynylbenzyl alcohol) and Poly(*p*-ethynylbenzaldehyde)



1 2 3

In this paper, we describe the preparation of poly(methyl *p*-ethynylbenzoate) 1 (Scheme I); poly(*p*-ethynylbenzyl alcohol), 2; and poly(*p*-ethynylbenzaldehyde), 3. These derivatives give new properties to the polymers and provide reactivity that should allow further modification of the polymer side chains.

Results and Discussion

Our primary interest was in the formyl derivative, 3. However, numerous initial attempts to polymerize *p*-ethynylbenzaldehyde and its dimethyl acetal using the conditions of Higashimura et al.[4] failed. Similar attempts to polymerize *p*-ethynylbenzyl alcohol also failed. Finally, it was found that methyl *p*-ethynylbenzoate would polymerize if a higher concentration of catalyst was used, giving the brick-red polymer characteristic of the trans structure. Later experiments using carefully purified monomer showed that polymerization would occur at room temperature using catalyst amounts similar to those of Higashimura et al., giving 90% yield.

When even higher concentrations of catayst were used, the aldehyde and alcohol also polymerized but gave insoluble yellow polymers (presumably cis–cisoid). Their insolubility made them unsuitable for our purposes. Thus, it was necessary to convert the methyl ester into the al-

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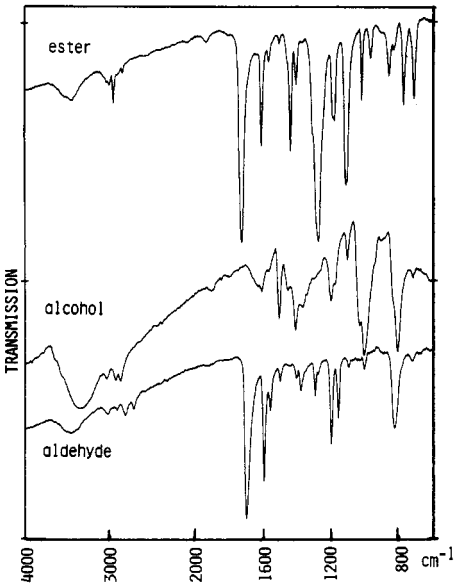

Figure 1. Infrared spectra of poly(methyl *p*-ethynylbenzoate) (top), poly(*p*-ethynylbenzyl alcohol) (middle), and poly(*p*-ethynylbenzaldehyde) (bottom).

dehyde via the alcohol. This was done by using the route shown in Scheme I.

Reduction of an ester to the alcohol is usually done using lithium aluminum hydride. However, use of this reagent gave precipitation during the reaction, leading to incomplete reduction. This was presumably due to intermolecular bridging through the aluminum.[12] When lithium trimethoxyaluminum hydride was used instead, such precipitation did not occur, since only one reactive site remained on the aluminum. Complete reduction occurred, as shown by the total disappearance of the carbonyl band at 1724 cm^{-1} in the infrared spectrum (see Figure 1). The yield was 97%.

The workup of the reaction was critical to the solubility of the product. Thus, evaporation of solutions resulted in very insoluble polymer which was almost black. Such insolubility was presumably due to strong hydrogen bonding when the polymer came out of solution at high concentration and not to crystallization, since the black solid showed no X-ray scatter pattern.[13] On the other hand, merely filtering the suspension obtained after extracting out the aluminum salts with 10% sulfuric acid and washing with sodium bicarbonate and water gave the familiar brick-red amorphous product which retained good solubility for the oxidation step. Similar, although less severe, solubility behavior was encountered with the polyaldehyde.

Oxidation of the alcohol to the aldehyde was successfully accomplished using dimethyl sulfoxide and oxalyl chloride as described by Swern et al.[14] The yield was 89%, and the conversion was judged to be at least 95%, based on the size of the residual C–O stretch band at 1012 cm^{-1} (see Figure 1). Since the infrared spectra were measured as KBr pellets, the size of the OH stretch peak at ca. 3300 cm^{-1} cannot be used as a measure of residual hydroxyl, as all samples give at least a small peak there.

The molecular weight distribution of the polymerized ester, obtained by using gel permeation chromatography, is given in Figure 2. The distribution is skewed due to the exclusion limit of the columns (ca. 10^6). Average molecular weights could not be calculated due to this skewing and due to the fact that the columns were calibrated with polystyrenes, which would have a different monomer molecular weight and different conformation in

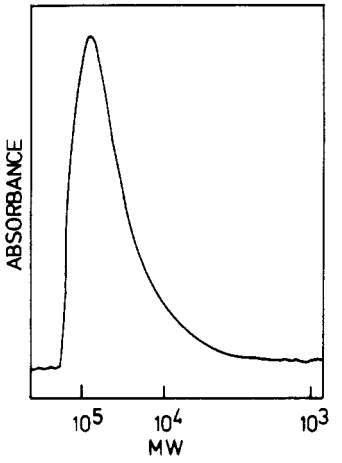

Figure 2. Molecular weight distribution of poly(methyl *p*-ethynylbenzoate).

solution. Nevertheless, it can be seen that these polymers were of high molecular weight. The aldehyde gave a similar distribution, shifted to somewhat lower molecular weight, due to incomplete solubility in the eluent (chloroform) during sample preparation. The alcohol was insufficiently soluble in $CHCl_3$ but presumably would not differ from the others.

Carbon-13 NMR analysis of the poly(methyl *p*-ethynylbenzoate) and similarly prepared poly(phenylacetylene) showed no evidence of cyclohexadiene structures (no peaks in the 50–70 ppm range except methoxyl). Such structures are related to termination end groups and to thermal cyclization of internal hexatriene units.[5a,b] Their absence may be related to the much higher yields in the present work or the use of tetraphenyltin as a cocatalyst.

The peaks at 870 and 910 cm^{-1}, which were used previously to distinguish between cis and trans double bonds, respectively, in poly(phenylacetylenes),[4b] were not present in the infrared spectra of these derivatives. Thus, infrared spectroscopy could not be used to characterize the geometry about the double bonds. Percec and Rinaldi[5a] have assigned ^{13}C NMR resonances at 126.6 and 131.7 ppm to the β carbons of the trans and cis structures, respectively (all other resonances overlapped for the two structures). The spectrum of our polymeric ester showed resonances at 127 and 131.5 ppm. These peaks overlap with the C2–C6 ring carbons (128–129 ppm), but a crude estimate of their relative intensities gives a trans content of 70–90%, the remainder being cis. We have no basis for assigning the conformational structure (cisoid versus transoid) about the chain single bonds. The colors of the polymers are also consistent with their assigned structures.

Experimental Section

General. Infrared spectra were taken on a Hitachi 270-30 spectrophotometer. NMR spectra were obtained on a Varian EM-390, and in looking for cyclohexadiene structures, a JOEL GX-400 was used. Gel permeation chromatography was done on a Japan Analytical Instrument Company LC-08 using Jaigel 2H + 3H columns calibrated with polystyrene standards, eluting with chloroform and monitoring UV absorption at 254 nm. Molecular weights shown in Figure 2 are for polystyrene, and may differ somewhat for our polymer.

Methyl *p*-ethynylbenzoate was prepared in three steps from *p*-bromobenzoic acid in 59% overall yield according to the method of Havens and Hergenrother.[15] *p*-Ethynylbenzyl alcohol was prepared by the lithium aluminum hydride reduction of the ester. *P*-Ethynylbenzaldehyde was made in two steps from *p*-bromobenzaldehyde in 45% overall yield by the method of Austin et al.[16] All transfers in the reactions (not workups) that follow were done in inert atmospheres by using syringes. All monomers were

recrystallized as described in the literature and sublimed in vacuo.

***trans*-Poly(methyl *p*-ethynylbenzoate).** A modification of the procedure for polymerization of phenylacetylene was used.[4b] Thus, a mixture of 0.320 g of tetraphenyltin and 0.300 g of tungsten hexachloride was dissolved in 10 mL of toluene after the air had been replaced with nitrogen. This mixture was stirred for 10 min at 25 °C and then added to a stirred solution of 2.5 g of sublimed methyl *p*-ethynylbenzoate in 20 mL of toluene under nitrogen via syringe. When the addition was approximately 50% complete, a rapid polymerization began and the solution warmed up. The mixture was stirred for 15 min, poured into 250 mL of methanol, and stirred for an additional 10 min. The precipitated polymer was filtered, rinsed with methanol, and air dried to give 2.40 g of brick-red polymer. The polymer was reprecipitated by dissolving in ca. 50 mL of tetrahydrofuran and pouring into 250 mL of methanol to give 2.26 g (90.4%) of product. IR (KBr): 3000, 2952, 1724 (C=O), 1608, 1438, 1278 (C—O), 1180, 1114 (C—O), 1020, 772, and 710 cm^{-1}. ^1H NMR ($CDCl_3$): 3.9 (OCH_3) and 5.2–8.3 ppm (arom. and vinyl). ^{13}C NMR ($CDCl_3$): 51 (OCH_3), 124–148 (arom. and vinyl), and 166 ppm (C=O). More specific assignments in the hydrocarbon region, based on those of Percec and Rinaldi,[5a] are 127 ($C\beta_{trans}$), 128–129 (C2–C6 ring), 131.5 ($C\beta_{cis}$), 139 (C1 $ring_{cis\ and\ trans}$), 142.5 ($C\alpha_{cis\ and\ trans}$), and 145.5 ppm (unassigned).

***trans*-Poly(*p*-ethynylbenzyl alcohol).** Lithium trimethoxyaluminum hydride was prepared by adding 3.4 mL (2.7 g, 84 mmol) of methanol to 94 mL of 0.30 M (28 mmol) $LiAlH_4$ in THF at 0 °C under nitrogen.[12] To this solution was added dropwise a solution of 1.50 g (9.4 mmol of repeat units) of poly(methyl *p*-ethynylbenzoate) in 60 mL of dry THF as the mixture was allowed to warm to ambient temperature. The mixture was then refluxed with stirring for 2.5 h. Water (ca. 5 mL) was added (hydrogen evolution due to 50% excess of reducing agent), and the mixture was filtered, giving a colorless filtrate. The solid was air dried, finely divided, and stirred for 30 min in 75 mL of 10% sulfuric acid. The solid was filtered and washed with water, 5% $NaHCO_3$, and water to give 1.20 g (97%) of polymer. The color for several batches ranged from brick red to chocolate, whereas evaporation of solutions led to almost black polymer. IR(KBr): 3320 (vbr, OH), 2930, 2872, 1610 (br), 1508, 1410, 1208, 1110, 1012 (C—O), and 816 cm^{-1}. ^1H NMR (CD_3OD): 5.5–8.0 (arom, vinyl), 4.9 (OH), and 4.2–4.9 ppm (CH_2).

***trans*-Poly(*p*-ethynylbenzaldehyde).** A solution of 2.41 g (31.0 mmol) of dimethyl sulfoxide in 8.0 mL of methylene chloride was added slowly to a solution of 2.03 g (16.0 mmol) of oxalyl chloride in 40 mL of CH_2Cl_2 at −60 °C under nitrogen. After 5 min, a solution of 1.06 g (8.03 mmol of repeat units) of poly(*p*-ethynylbenzyl alcohol) dissolved in 16 mL of DMSO (excessive DMSO complicates isolation of the product) and diluted with 16 mL of CH_2Cl_2 was added, and the mixture was stirred for 2.0 h at −60 °C. Triethylamine (11.2 mL) was added, and the mixture was stirred for 0.5 h while warming to 25 °C. Methanol (450 mL) was added, and the mixture was filtered after 10 min. The solid was washed with water and methanol and air dried to give 0.93 g (89%) of brick-red product. IR (KBr): 3432 (small resid. OH), 2928, 2832, 2736 (ald. C—H), 1704 (C=O), 1604, 1566, 1390, 1306, 1210, 1168, 1102, 1054, 1016, and 834 cm^{-1}. ^1H NMR (pyridine-d_5): 6–8.5 (arom. and vinyl) and 9.8 ppm (aldehyde). UV–Vis was similar to that of poly(phenylacetylene) obtained by WCl_6 catalysis in benzene,[17] including a long-wavelength tail extending from 350 nm (ϵ 3610) to beyond 600 nm (ϵ 200).

Polymerization of *p*-Ethynylbenzyl Alcohol. Toluene (1.5 mL) was added to a mixture of 0.042 g of tetraphenyltin and 0.042 g of tungsten hexachloride under nitrogen. The mixture was stirred for 10 min at 25 °C and added to a stirred solution of 0.160 g (1.21 mmol) of *p*-ethynylbenzyl alcohol in 1.5 mL of toluene under nitrogen. The solution was stirred for 40 min at 25 °C and, when no evidence of polymerization was seen, it was heated to 65 °C for 18 h, during which time most of the toluene was absorbed by the rubber septum. The solid product was suspended in methanol and filtered to give 0.050 g (38%) of buff-colored, insoluble polymer. IR (KBr): 3436 (br, OH), 3024, 2924, 2856, 1682 (st., C=C), 1610, 1510, 1414, 1358, 1270, 1088, 1016, 960, and 816 cm^{-1}.

Polymerization of *p*-Ethynylbenzaldehyde. Toluene (2.5 mL) was added to a mixture of 0.210 g of tetraphenyltin and 0.198 g of tungsten hexachloride under nitrogen. After stirring at 25 °C for 10 min, the mixture was added to a solution of 0.130 g (1.00 mmol) of *p*-ethynylbenzaldehyde and 0.10 mL of acetophenone (GC internal standard) in 2.5 mL of toluene. After the mixture stirred for 90 min, GC analysis showed that the monomer was almost gone, so the mixture was poured into ca. 30 mL of methanol, stirred for 10 min, and filtered to give 0.050 g (38%) of a buff-colored product. IR (KBr): 3020, 1700, 1604, 1504, 1415, 1305, 1212, 1170, 1015, 970, and 822 cm^{-1}.

Registry No. *trans*-Poly(methyl *p*-ethynylbenzoate), 115859-42-2; poly(*p*-ethynylbenzaldehyde), 115859-44-4; poly(*p*-ethynylbenzyl alcohol), 115859-43-3.

References and Notes

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