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Synthesis of Conjugated Polymers Using a (η^6-Arene)$Cr(CO)_3$ Monomer

Michael E. Wright

Department of Chemistry and Biochemistry, Utah State University,
Logan, Utah 84322-0300.
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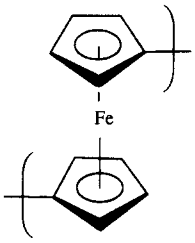
ABSTRACT: The palladium-catalyzed polycondensation of $\{\eta^6\text{-}1,4\text{-}C_6H_4Cl_2\}Cr(CO)_3$ with 1,4-bis[(trimethylstannyl)ethynyl]benzene or 4,4'-bis[(trimethylstannyl)ethynyl]biphenyl produces a new series of conjugated polymers (**8**). Thermogravimetric analysis (TGA) of the polymers under argon shows an initial weight loss due to carbon monoxide explosion (~10–12%) and thereafter displays excellent thermal stability. Infrared spectroscopy, combustion analysis data, and differential scanning calorimetry support that carbon monoxide loss is occurring at the chromium metal centers. TGA of the polymers under air shows a break point of 381 °C and rapid weight loss to give CrO_3. The monomeric model compound $1,4\text{-}[\{\eta^6\text{-}C_6H_5C{\equiv}C\}\text{-}Cr(CO)_3]_2C_6H_4$ (**9**) was prepared from the palladium-catalyzed reaction of $\{\eta^6\text{-}C_6H_5Cl\}Cr(CO)_3$ and 1,4-bis-[(trimethylstannyl)ethynyl]benzene.

Introduction

In recent years organometallic polymers have attracted considerable attention and have led to several reviews in the area.[1] Polymers containing transition metals can be basically divided into the two general areas of coordination and pendant type. In coordination-type polymers, the integrity of the polymer backbone depends on the coordination of the ligands to the metal center (e.g., **1**). Pendant-type polymers possess organic polymer backbones and some covalently attached ligand suitable for complexation to a transition metal. Common pendant ligands include mono(**2**) and bidentate phosphines,[2] η^5-cyclopentadienyl rings (**3**),[3] and η^6-arenes (**4**).[4,5]



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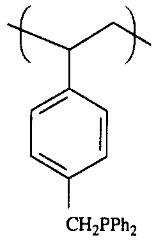

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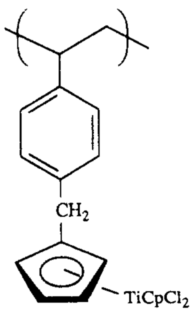

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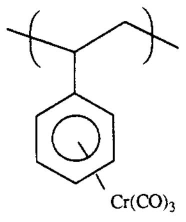

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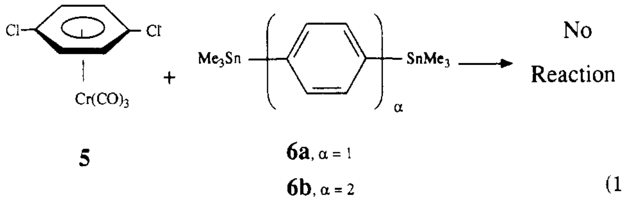
The introduction of ligand and/or transition metal has been accomplished by a variety of polymer modification and copolymerization techniques. Both methods have specific advantages and disadvantages which depend upon the type of ligand, the transition-metal complex being attached, and the macroscopic properties desired in the final polymer.[6]

An area of organometallic polymer chemistry which has received little attention is the preparation of conjugated organic polymers having transition-metal complexes coordinated to the polymer backbone.[7] It is the subject of this paper to present a very efficient and controlled means of preparing conjugated polymers via the palladium-catalyzed polycondensation of group 6 arene complexes with organostannane compounds.

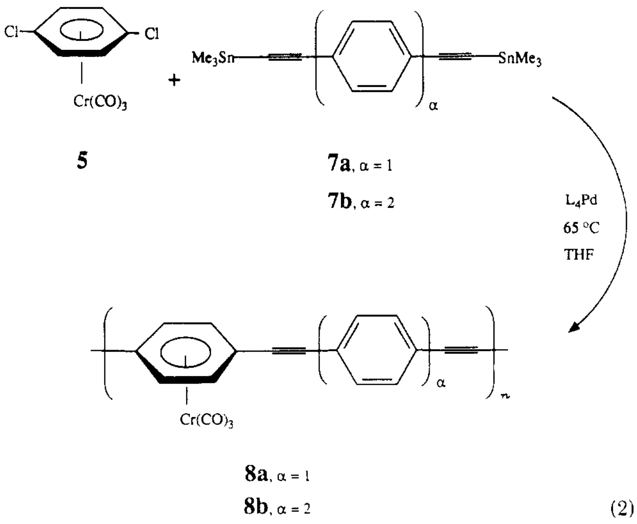
Results and Discussion

Recently in our laboratory we developed a synthetic route to complexes of the general type $\{\eta^6\text{-}1,3\text{-}$ and $\eta^6\text{-}1,4\text{-}$dihaloarene$\}Cr(CO)_3$ (**5**).[8] Results from our laboratory and that of Scott[9] demonstrated that the related complex (η^6-chlorobenzene)$Cr(CO)_3$ participates in the palladium-catalyzed cross-coupling reaction with organostannane reagents. In contrast, reaction of **5** with **6** under a variety of conditions failed to give cross-coupling products (eq 1). At elevated temperatures, decomposition of **5** was the predominate reaction path.



(1)

Treatment of **5** with **7** using 2 mol % $(Ph_3P)_4Pd(0)$ as the catalyst affords polymers **8a** and **8b** in excellent yield (>92%) (eq 2). The polymers are isolated as deep red solids, exhibiting very low solubility in all organic solvents.



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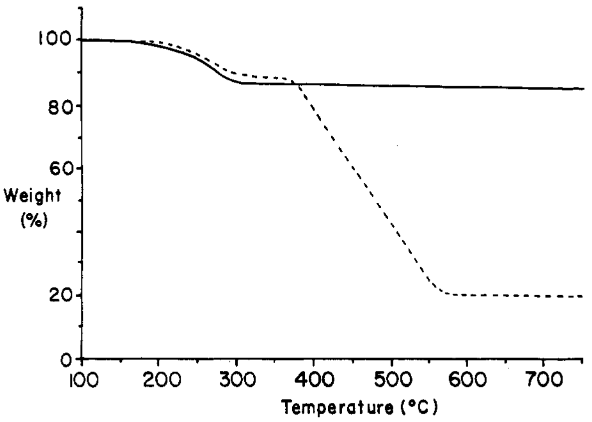
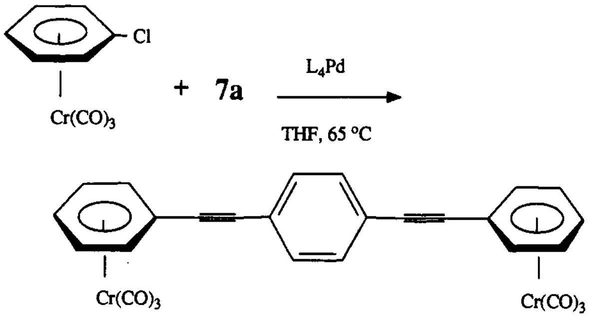


Figure 1. Thermogravimetric analysis of polymer **8b** under atmospheres of argon (—) and air (- - -). Heating rate used was 10 °C/min.

The red shift for the charge-transfer band is consistent with the $Cr(CO)_3$ unit interacting with the extended π-system of the polymer.[10]

Polymer **8b** was prepared with imbalanced stoichiometry (**5**/**7b**, 0.95/1.00) and subjected to combustion analysis. As anticipated, the chlorine content was zero weight percent. This indicates that the end groups are indeed trimethylstannane moieties and that no chlorotrimethylstannane is contaminating the polymer. The weight percent of tin in the polymer indicates a DP of ~18, corresponding to a number-average molecular weight of ~7800. The chromium content is lower than expected by ~1.6%, which could be due to a limited amount of **7b** undergoing a homocoupling type of reaction. A similar side reaction has been noted for organoalane partners in nickel-catalyzed cross-coupling reactions.[11]

We have prepared the model compound **9** via the palladium-catalyzed reaction of 2 mol equiv of (η^6-chlorobenzene)$Cr(CO)_3$ with **7a** (eq 3). Compound **9** exhibits infrared data similar to that of polymer **8** and also shows a red shift for the charge-transfer band.



(3)

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Thermal Analysis of Polymers 8 and Complex 9. Polymers **8a** and **8b** and complex **9** were subjected to thermogravimetric analysis (TGA) under an atmosphere of argon (Figures 1 and 2). The thermolysis of polymer **8b** was also carried out under an atmosphere of air (Figure 1). The polymers show an initial weight loss of ~10–12% and then excellent stability thereafter if under argon. A breakpoint of 381 °C is observed for polymer **8b** for the TGA done in air. Analysis of a sample of **8b** after heating to 200 °C under nitrogen and then cooling displays infrared bands at 1975 and 1932 cm^{-1}. The weight loss and change in the infrared spectrum are consistent with carbon monoxide loss followed by some form of cross-linking (e.g., coordination to a nearby alkyne unit, eq 4).[12] A similar change in the infrared spectrum for the polymers can be obtained by irradiating (medium-pressure Hg lamp) the samples.

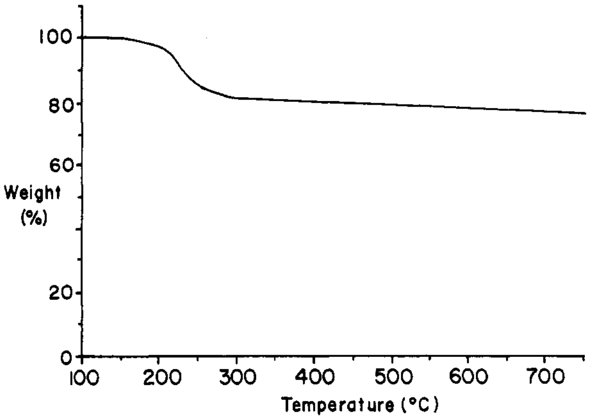
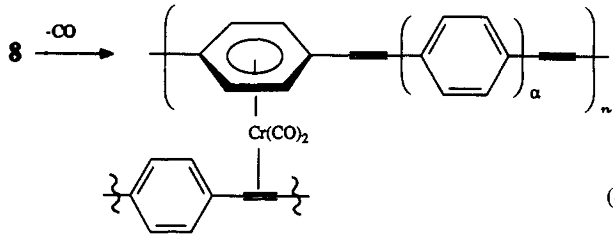


Figure 2. Thermogravimetric analysis of complex **9** under an atmosphere of argon. Heating rate used was 10 °C/min.

Table I
Elemental Analysis Data for Polymers 8 and Complex 9

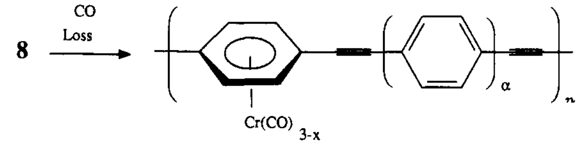
compd	% calcd C	H	Cr	Sn	% found C	H	Cr	Sn
8a[a]	65.1	2.5			65.8	3.0		
8a (TGA)					66.6	1.2		
8b[b]	71.3	3.1	11.8	3.0	70.1	3.6	10.3	2.9
8b, x = 1	73.2	3.3						
8b, x = 2	75.4	3.5						
8b, x = 3	78.0	3.8						
8b (TGA)					73.0	1.3		
9	61.0	2.6			61.4	2.7		
9 (TGA)					59.6	1.1		

[a] Percentages for **8a** are based upon a DP of 10 and random end groups. TGA after the compound indicates that the sample has been through a complete TGA run and cool down under an argon atmosphere. [b] Analyses were performed with the polymer prepared from imbalanced stoichiometry; see the text.



(4)

Combustion analysis of the polymer samples after the TGA runs lends further insight into the chemistry taking place. In Table I we have presented combustion analysis data for the compounds used in the study and that anticipated after carbon monoxide loss (eq 5).



(5)

A consistent trend in the combustion data for the TGA residues is a lower total hydrogen content. This suggests that the phenyl rings are undergoing a common type of cross-linking reaction seen in other thermally stable polymers.[13] Complex **9** behaves analogously, showing considerable hydrogen depletion. The combustion analysis data also reveal an increase in percent carbon for both polymers; however, in both cases the percent increase does not match that calculated for complete carbon monoxide loss but rather shows an estimated ~50% loss (Table I).

At 600 °C ligands coordinated to the chromium center must be in rapid equilibrium due to the low thermody-

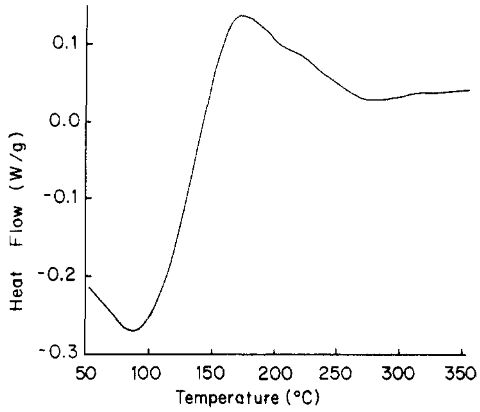


Figure 3. Differential scanning calorimetry plot for polymer **8a** under an argon atmosphere. Heating rate used was 10 °C/min.

namic strength of the bonds. Thus, the high-performance polymer becomes a ligand matrix, trapping the chromium metal centers and carbon monoxide through many rapid and facile exchange reactions.

Differential scanning calorimeter analysis of **8a** under argon shows the initial weight loss (i.e., CO explosion) to be concomitant with an exothermic process (Figure 3). These data are consistent with carbon monoxide ejection since a $+\Delta S$ term would be expected to dominate the thermodynamics of the cross-linking process.[14]

Concluding Remarks. Through the palladium-catalyzed polycondensation of (η^6-1,4-dichlorobenzene)$Cr(CO)_3$ and bis(trimethylstannyl)acetylenic monomers we have prepared a new series of pendant-type organometallic polymers. The consequence of having a thermally stable and conjugated polymer backbone provides an intriguing environment to study the chemistry of $Cr(CO)_3$ complexes, some of which we have presented. Continuing studies examining the scope of the polycondensation methodology and the synthesis of other conjugated polymers containing Group 6 metals are under way.

Experimental Section

General Procedures. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[15] Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ vs Me_4Si in ^1H NMR and by assigning the $CDCl_3$ resonance at 77.00 ppm in ^{13}C spectra. $(PPh_3)_4Pd$,[16] $(PPh_3)_2PdCl_2$,[17] 1,4-bis[(trimethylstannyl)ethynyl]benzene,[18] (η^6-chlorobenzene)$Cr(CO)_3$,[19] 1,4-bis(trimethylstannyl)benzene,[20] and 4,4′-bis(trimethylstannyl)biphenyl[21] were prepared by literature methods. (Trimethylsilyl)acetylene, chlorotrimethylstannane, copper(I) iodide (98%), 4,4′-dibromobiphenyl, and 1,4-dibromobenzene were purchased from Aldrich Chemical Co. and used as received. Chromium hexacarbonyl was purchased from Pressure Chemical Co. Palladium dichloride was purchased from Alfa. Polymer analyses were performed on a Du Pont 9900 thermal analysis data station. Elemental analyses were performed at Atlantic Microlab Inc. (C,H) or Galbraith Laboratory Inc. (Cr, Sn).

4,4′-Diethynylbiphenyl. A flask was charged with 4,4′-dibromobiphenyl (5.74 g, 18.4 mmol), (trimethylsilyl)acetylene (5.00 g, 52 mmol), triethylamine (100 mL), copper(I) iodide (0.20 g), and $(PPh_3)_2PdCl_2$ (130 mg, 1 mol %), in that order. The mixture was heated to 60 °C for 12 h, coded, and then diluted with ether (250 mL). The mixture was diluted with water and the layers were separated. The organic layer was washed with water (3 × 100 mL) and then treated with methanolic potassium hydroxide (100 mL, saturated with KOH) for 3 h. The mixture was diluted with H_2O (100 mL), the layers were separated, and then the organic layer was washed (2 × 100 mL H_2O; then brine) and dried over K_2CO_3. The solvents were removed and the product was sublimed at reduced pressure to afford a white solid (75%, 2.80 g, mp 160–162 °C, lit.[22] mp 163–164 °C).

4,4′-Bis[(trimethylstannyl)ethynyl]biphenyl (7b). A THF solution (50 mL) maintained at −78 °C containing **7b** (1.35 g, 6.7 mmol) was treated with *n*-BuLi (2.5 M in hexanes, 2.70 mL) and allowed to stir for 30 min. A THF (10 mL) solution containing chlorotrimethylstannane (3.07 g, 15.4 mmol) was cannulated into the reaction mixture and the cooling bath removed. The mixture was allowed to react with stirring for 18 h. The mixture was diluted with ether (250 mL) and washed several times with H_2O (3 × 250 mL) and finally brine. The ether layer was dried over K_2CO_3 and the solvent removed under reduced pressure. The product was recrystallized from pentane (−78 °C) to afford white crystals (2.86 g, 81%, mp 156–158 °C). ^1H NMR ($CDCl_3$) δ 7.52 (s, 4 H), 0.37 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 139.8, 132.4, 126.7 (CH's), 122.8 (ipso C), 108.7, 94.6 (C≡). Anal. Calcd for $C_{22}H_{26}Sn_2$: C, 50.06; H, 4.97. Found: C, 50.18; H, 5.01.

1,4-Bis[{η^6-$C_6H_5Cr(CO)_3$}ethynyl]benzene (9). A THF (10 mL) solution containing {η^6-C_6H_5Cl}$Cr(CO)_3$ (0.59 g, 2.4 mmol), **7a** (0.54 g, 1.2 mmol), and $(PPh_3)_4Pd$ (55 mg, 2 mol %) was maintained at 50 °C for 18 h. The mixture was diluted with dichloromethane (50 mL), washed with water (3 × 50 mL), and then dried over K_2CO_3. The mixture was filtered, concentrated (~10 mL), and then placed at −78 °C. The orange crystalline product was collected, washed with cold ether, and dried under reduced pressure (0.42 g, 65%). ^1H NMR ($CDCl_3$) δ 7.49 (s, 4 H), 5.50 (d, J = 7 Hz, 4 H), 5.38 (t, J = 7 Hz, 4 H), 5.30 (t, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 131.9, 94.8, 91.4, 90.7 (CH's); IR (CH_2Cl_2) ν_{CO} 1975, 1903 cm^{-1}. Anal. Calcd for $C_{28}H_{14}Cr_2O_6$: C, 61.0; H, 2.6. Found: C, 60.4; H, 2.7.

Polymer Syntheses. A reaction flask was charged with THF (5 mL), (η^6-1,4-dichlorobenzene)$Cr(CO)_3$ (100 mg, 0.35 mmol), **7b** (186 mg, 0.35 mmol), and $(PPh_3)_4Pd$ (8 mg, 2 mol %), in that order. The mixture was placed in an oil bath at 65 °C and allowed to react for 18 h with stirring. The mixture was diluted with ether (10 mL) and the polymer product collected on a glass frit. The rubberlike product was minced and washed with hot chloroform (3 × 25 mL) and then hot THF (3 × 25 mL) and dried under reduced pressure at 65 °C for 24 h (0.135 g, 93%).

Thermal Analysis of Polymers. Samples (10–12 mg) of the polymers were palced in quartz TGA sample holders and positioned inside the TGA chamber. The sample chamber was purged with the appropriate gas (argon or compressed air, 50 mL/min) for 15 min. The samples were equilibrated at 50 °C and then heated at a ramp rate of 10 °C/min to final temperature of 750 °C. The samples were allowed to cool to ambient temperature under an atmosphere of argon.

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Registry No. (5)(7a) (copolymer), 116628-66-1; (5)(7b) (copolymer), 120120-23-2; **7a**, 72621-00-2; **8a**, 120120-24-3; **8b**, 120120-25-4; **9**, 120120-21-0; (η^6-chlorobenzene)$Cr(Co)_3$, 12082-03-0; 4,4′-diethynylbiphenyl, 38215-38-2; 4,4′-dibromobiphenyl, 92-86-4; (trimethylsilyl)acetylene, 1066-54-2; chlorotrimethylstannane, 1066-45-1.

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Influence of Molecular Weight on the Thermotropic Mesophases of Poly[6-[4-(4-methoxy-β-methylstyryl)phenoxy]hexyl methacrylate]

Virgil Percec,* Dimitris Tomazos, and Coleen Pugh

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106-2699. Received November 14, 1988;
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ABSTRACT: Poly[6-[4-(4-methoxy-β-methylstyryl)phenoxy]hexyl methacrylate] (4-6-PMA) with different molecular weights and molecular weight distributions was synthesized by group transfer and radical polymerization of the corresponding monomer. The phase behavior of liquid crystalline 4-6-PMA with varying molecular weights was compared to that of its monomeric and dimeric model compounds. The number and nature (i.e., virtual, monotropic, or enantiotropic) of phase transitions were determined by a combination of thermodynamic and kinetic factors. Since the rate of formation of highly ordered phases (crystalline and smectic) decreases with increasing polymer molecular weight, the number and nature of the liquid crystalline phases exhibited by 4-6-PMA vary with increasing molecular weight according to the following trend: monotropic nematic, enantiotropic nematic and enantiotropic smectic, enantiotropic nematic and monotropic smectic, enantiotropic nematic. Phase transition temperatures increase up to a degree of polymerization of about 10–12 and are thereafter essentially molecular weight independent. The rate by which the number of transitions decreases also decreases with increasing polymer molecular weight. However, the enthalpy change associated with the nematic–isotropic transition is molecular weight independent.

Introduction

Why should there be a new investigation concerning the influence of polymer molecular weight on the phase behavior of side-chain liquid crystalline polymers when there are already several such experiments available in the literature?[1-7] The simple reason is that even a recent review article's[8] attempt to discuss this relationship could not answer a number of straightforward questions and, at the same time, raised a series of additional questions.

So far, there is general agreement that an increase of the polymer molecular weight increases mesomorphic–mesomorphic and mesomorphic–isotropic phase transition temperatures up to a certain degree of polymerization, above which they become molecular weight independent.[1-8] However, there is disagreement concerning the exact degree of polymerization above which phase transitions are molecular weight independent. While most of the authors claim that the required degree of polymerization is about 10–12,[3-5,7] results from two research groups consider that it is as high as a few hundred.[1,2,6] Most of the authors claim that the type of mesophase exhibited by a certain polymer is molecular weight independent;[1-5,7] however, a recent publication demonstrates that it too is molecular weight dependent.[6] The dependence of phase transitions on molecular weight led to the conception of the "polymer effect", which assumes that the polymer backbone enhances the tendency of side groups to form mesophases, enlarges the thermal stability of the mesophase, transforms monotropic mesophases into enantiotropic ones, and gives rise to higher ordered mesophases.

The most contradictory issue concerns the influence of molecular weight on the enthalpy changes of mesomorphic phase transitions. Most publications do not report data on this dependence. While one publication reports that this enthalpy change is strongly molecular weight dependent up to degrees of polymerization as high as 400,[1]

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