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Synthesis and properties of conjugated copolymers having a tricarbonyl(arene)chromium and thiophene units in the main chain

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Summary

Palladium-catalyzed polymerization of η^6-(1,4-diethynylbenzene)tricarbonyl chromium (**1**) with 3-alkyl-2,5-dibromothiophene (**2a-c**) was carried out to give the corresponding alternating conjugated copolymers (**5a-c**) in good yields. The structures of the polymers were supported by ^{1}H NMR and IR spectra. The polymers obtained were soluble in common solvents such as THF, CH_2Cl_2, $CHCl_3$ and toluene. The molecular weights of the polymers were determined by GPC. Their thermal, optical and electrical properties were investigated in detail.

Introduction

Due to the unique optical, electrochemical, and non-linear optical properties of novel π-conjugated polymers, their synthesis has received extensive attention [1]. π-Conjugated polymers containing transition metal complexes are of increasing interest [2], because they not only provide enormous opportunity to tune the physical properties of the resulting materials easily by exchange of a ligand coordinated to the metal center, but can also be converted to various kinds of functional organic polymers by polymer reactions. Therefore, a number of polymers having organometallic units in the main chain or in the side chain have been prepared so far. Among those, the polymers containing transition metals π-coordinated to the phenylene units in the polymer backbones (e.g., cyclopentadienyliron [3], cyclopentadienylruthenium [3e,4], tricarbonylmolybdenum [5], and tricarbonylchromium [6]) have been synthesized, and exhibit interesting properties.

On the other hand, a tricarbonylchromium unit is a very attractive functional group because it is able to change the reactivity of an aromatic group from nucleophilicity to electrophilicity [7]. Namely, a tricarbonylchromium-coordinated phenylene unit has a potential to act as a strong acceptor. However, little work has been carried out on the synthesis of polymers having a tricarbonylchromium unit [6], and no alternating donor-acceptor conjugated copolymer has yet been reported. In addition, most of the tricarbonyl(arene)chromium, (η^6-arene)$Cr(CO)_3$, containing polymers prepared so far are insoluble in common organic solvents. The present research is focused on the synthesis and properties of soluble donor-acceptor conjugated copolymers having a tricarbonyl(arene)chromium unit as an acceptor and a thiophene unit as a donor in the main chain.

Experimental

General

1H and 13C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. Samples were analyzed in CDCl3, and the chemical shift values were expressed relative to Me4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in THF at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in THF at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using chloroform as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 ^{o}C/min). Cyclic voltammetry was carried out on a BAS-CV50W. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 236 source measure unit.

Materials

1,4-Dioxane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. HNPr$^{i}_{2}$ was distilled from KOH. 1,4-Dichlorobenzene, trimethylsilylacetylene, NaOH, Cr(CO)$_6$, PdCl$_2$(PPh$_3$)$_2$, triphenylphosphine (PPh$_3$), CuI, 3-alkylthiophene, NBS, ethynylbenzene were obtained commercially, and used without further purification. Pd(PPh$_3$)$_4$ [8], η^6-(1,4-dichlorobenzene)tricarbonylchromium (**4**) [9], η^6-(1,4-diethynylbenzene)tricarbonylchromium (**1**) [10], and 3-alkyl-2,5-dibromothiophenes (**2a-c**) [11] were prepared as described in the literature.

Polymerization

A typical procedure is as follows [12]. A 50-mL Pyrex flask was charged with **1** (52 mg, 0.20 mmol), **2c** (82 mg, 0.20 mmol), PdCl$_2$(PPh$_3$)$_2$ (14 mg, 2.0x10^{-2} mmol), PPh$_3$ (11 mg, 4.0x10^{-2} mmol), CuI (6.0 mg, 3.0x10^{-2} mmol), THF (2.0 mL), HNPr$^{i}_{2}$ (2.0 mL) and a stirring bar under a flow of nitrogen. The reaction was carried out at 60 ^{o}C for 24 h with stirring under a nitrogen atmosphere, and then ethynylbenzene (10 mg, 0.10 mmol) was added. The mixture was stirred for further 2 h. After filtration of the precipitated ammonium salt, the filtrate was concentrated and dried in vacuo. The residue was dissolved in CHCl$_3$ and poured into a large amount of MeOH to obtain the corresponding polymer (**5c**) in 81% yield (85 mg, 0.16 mmol) as an orange powder.

5a. Yield: 65 mg, 80%. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.82 (br, 3H), 1.20-1.47 (m, 8H), 2.61 (br, 2H), 5.47 (br, 2.7H), 7.00 (s, 1H), 7.25 (br, 1.6H), 7.44 (br, 2.3H); IR (film): 2202, 1970, 1899 cm^{-1}.

5b. Yield: 80 mg, 83%. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.87 (br, 3H), 1.20-1.62 (m, 14H), 2.69 (br, 2H), 5.55 (m, 2.6H), 7.08 (s, 1H), 7.25 (br, 1.6H), 7.48 (br, 2.4H); IR (film): 2206, 1972, 1908 cm^{-1}.

5c. Yield: 85 mg, 81%. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.87 (br, 3H), 1.24-1.58 (m, 20H), 2.69 (br, 2H), 5.55 (br, 2.6H), 7.07 (s, 1H), 7.28 (br, 1.7H), 7.48 (br, 2.5H); IR (film): 2202, 1970, 1910 cm^{-1}.

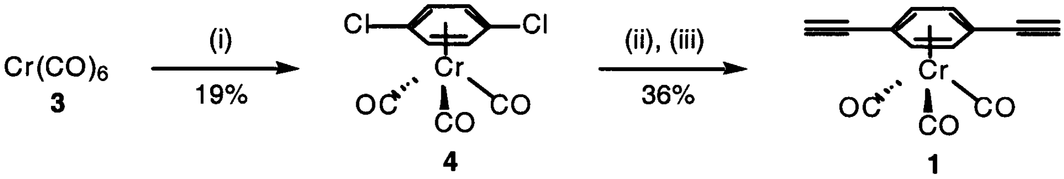
*Synthesis of the model compound (**6**) [13]*

A 50-mL Pyrex flask was charged with η^6-(ethynylbenzene)tricarbonylchromium [14] (95 mg, 0.40 mmol), 2,5-diiodothiophene (67 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 2.0×10^{-2} mmol), CuI (5.7 mg, 3.0×10^{-2} mmol), THF (3.0 mL), $HNPr^i_2$ (3.0 mL), and a stirring bar under a flow of nitrogen. The reaction mixture was stirred at reflux temperature for 6 h. After filtration of the precipitated ammonium salt, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, hexane-Et_2O v/v = 1/1) to provide 55 mg (50%) of **6** as an orange solid. ^1H NMR ($CDCl_3$, 270 MHz): δ 5.32 (m, 6H), 5.52 (d, J = 5.7 Hz, 4H), 7.18 (s, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 82.6, 89.4, 90.8, 91.3, 91.5, 95.1, 124.4, 133.6, 232.3; IR (KBr): 2210, 1967, 1890 cm^{-1}.

Results and Discussion

We initially examined the palladium-catalyzed polymerization of η^6-(1,4-diethynylbenzene)tricarbonylchromium (**1**) with 3-alkyl-2,5-dibromothiophene (**2a-c**). The synthesis of **1** is shown in Scheme 1. The procedure for the synthesis of **5** is as follows (Scheme 2), and the results are summarized in Table 1. Treatment of **1** with **2** in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ (5 mol % to an acetylene unit), PPh_3, and CuI in 1:1 THF:$HNPr^i_2$ for 24 h under a nitrogen atmosphere gave a dark-red solution. Ethynylbenzene was added to the solution for end-capping. The polymers obtained were soluble in common solvents such as THF, CH_2Cl_2, $CHCl_3$, and toluene. The molecular weight measurements were performed by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards. For example, the polymer (**5c**) (R = n-dodecyl) had the number-average molecular weight (M_n) of 5200, which corresponds to a degree of polymerization of 10, with M_w/M_n of 3.6 (Table 1, run 3).

Scheme 1



Scheme 2

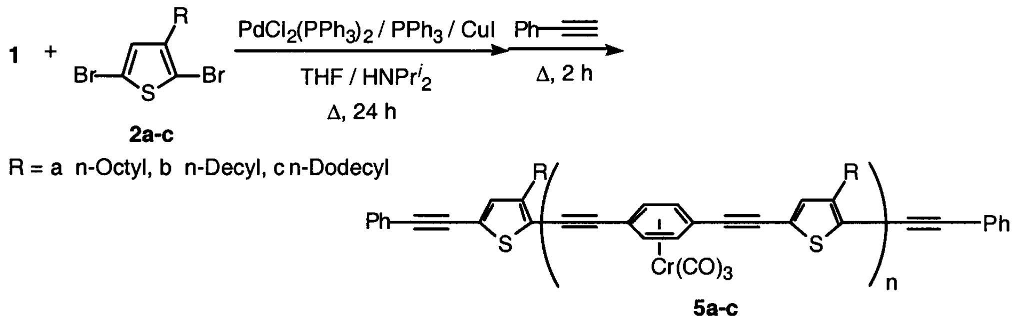


Table 1 . Polycondensation of **1** with **2a-c**^{a} and optical properties of the polymers **5a-c**

polym.	yield (%)^{b}	$M_w{}^{c}$	$M_n{}^{c}$	$M_w/M_n{}^{c}$	UV λ_{max} (nm)^{d}	PL λ_{max} (nm)^{d,e}
5a	80	4200	13500	3.2	386	450
5b	83	6900	24400	3.5	382	450
5c	81	5200	18700	3.6	375	450

a A mixture of **1** (0.20 mmol), **2** (0.20 mmol), PdCl2(PPh3)2 (0.020 mmol), CuI (0.030 mmol), PPh3 (0.040 mmol), THF (2.0 mL) and HNPri2 (2.0 mL) in a 50-mL Pyrex flask was heated at 60 oC for 24 h under a nitrogen atmosphere. Ethynylbenzene was added for end-capping. b Isolated yields after reprecipitation into MeOH. c GPC (CHCl3), polystyrene standards. d Absorption and emission spectra were recorded in dilute THF solutions. e Excited at 370 nm.

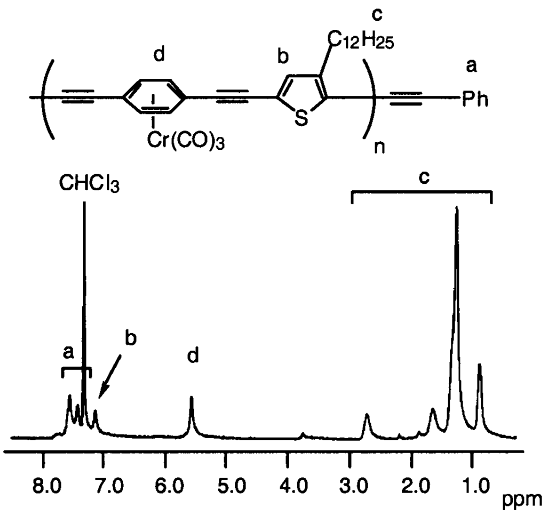


Figure 1. ^{1}H NMR spectrum of the polymer (**5c**) in $CDCl_3$.

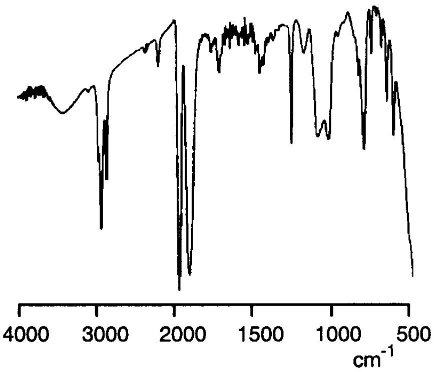


Figure 2. IR spectrum of the polymer (**5c**) in the film state.

These polymers were characterized by ^{1}H NMR and IR spectra. In the ^{1}H NMR spectrum of **5c** in CDCl$_3$ (Figure 1), the peak corresponding to terminal alkyne protons at 3.0 ppm of **1** disappeared. The peak at 5.5 ppm is attributed to the protons of the phenylene unit coordinated to chromium. The peak at 7.0 ppm is attributed to the proton connected to thiophene. End-capped phenyl protons appeared at 7.2-7.4 ppm and were overlapped with aromatic protons of the phenylene unit by thermal- or photo-dissociation of tricarbonylchromium moieties. **5c** was found to consist of 65% chromium coordinated phenylene and 35% phenylene moieties. According to the ^{31}P NMR spectrum of the polymer (**5c**), no peak derived from triphenylphosphine-coordinated chromium complexes appeared. The ^{13}C NMR spectra of the polymers were not clearly obtained due to their relatively low solubility. IR spectrum of **5c** in the film state exhibited a weak absorption peak at 2202 cm^{-1} and strong absorption peaks at 1970 and 1910 cm^{-1} due to stretching vibrations of a carbon-carbon triple bond and metal carbonyls, respectively (Figure 2).

The polymers (**5a-c**) were very stable under air in the solid state. The thermal stability of the polymer (**5c**) was investigated by thermogravimetric analysis (TGA), the results of which are shown in Figure 3. **5c** sustained a 10% weight loss at a temperature of 340 ^{o}C in air at a heating rate of 10 ^{o}C/min, and the weight loss was completed above 500 ^{o}C. The decomposition of the polymer (**5c**) involved two steps. Completion of the first step may be assigned to thermal dissociation and oxidation of tricarbonylchromium moieties, and the second step can be attributed to the decomposition of the polymer backbone.

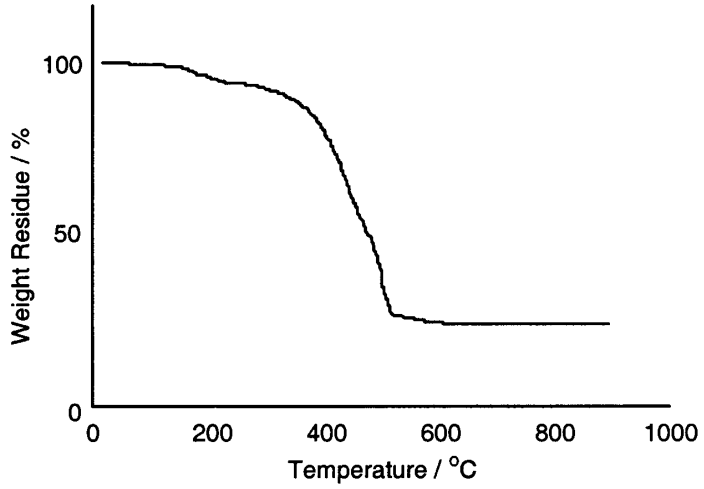
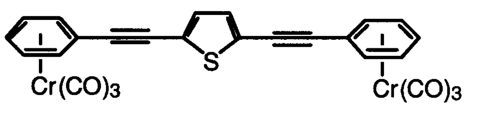
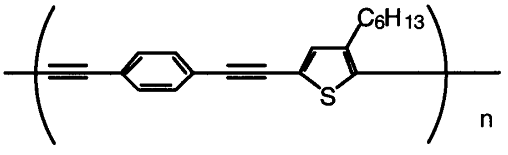


Figure 3. Thermogravimetric analysis (TGA) of the polymer (**5c**) under air (10 ^{o}C/min).



Model compound **6**



Polymer **7**

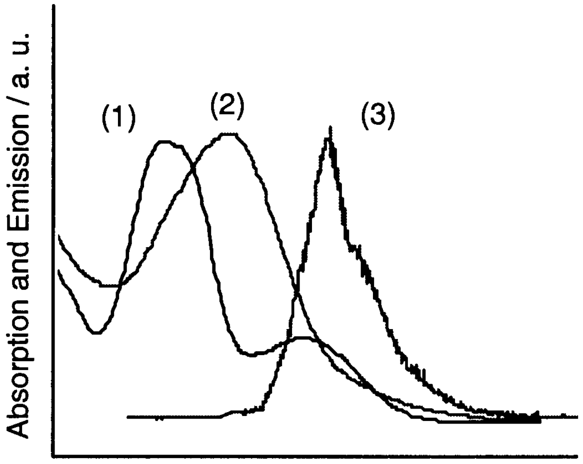


Figure 4. (1) UV-visible spectrum of **6**, (2) UV-visible spectrum of **5c** in THF solution, and (3) fluorescence emission spectrum of **5c** in THF on the excitation at 370 nm.

We investigated the optical properties of the polymer obtained. The results are listed in Table 1. Figure 4 shows the UV-vis absorption spectra of the polymer (5c) and the model compound (6) [13], and the fluorescence spectrum of the THF solution of 5c at room temperature. One broad absorption band of 5c was observed at 375 nm (Figure 4-(2)), whereas the model compound (6) showed an absorption maximum at 328 nm (Figure 4-(1)). The 375 nm band was red-shifted about 50 nm compared with that of 6. This finding clearly indicates the highly extended π--delocalization length. On the other hand, the polymer (7) showed an absorption maximum at 418 nm [15]. This result suggests that the coplanarity of each monomer in 5 is poorer due to steric hindrance caused by the tricarbonylchromium unit in the polymer chain. In the fluorescence spectra, a weak emission λmax of 5a-c was observed in a visible green region with an excitation wavelength at 370 nm. The absorption and fluorescence spectra of 5a-c in the solid state were very similar to those in solution.

Electrochemical activity of the polymer (5c) was investigated using cyclic voltammetry at room temperature in a conventional three-electrode cell in CH3CN solution containing 0.1 M Et4NBF4 at 300 mVs-1 (Pt electrode vs. Ag/Ag+). The result is that the solution of 5c gave a single-broad irreversible oxidation peak at about 1.5 V. On the other hand, the electrical conductivity of the cast film of 5c was 8.1x10-6 S cm-1 at 25 ^{o}C, which showed a semiconductive nature in the undoped state.

In conclusion, the palladium-catalyzed polycondensation of η6-(1,4-diethynylbenzene)tricarbonylchromium (1) with 3-alkyl-2,5-dibromothiophene (2a-c) gave the corresponding alternating conjugated copolymers (5a-c) having a tricarbonyl(arene)chromium unit as an acceptor and a thiophene unit as a donor in the main chain in good yields. The polymers obtained were stable under air and soluble in common solvents. The polymers showed an extension of π-delocalization according to the UV-vis absorption spectrum in comparison with that of the model compound (6). The polymers showed a semiconductive nature in the undoped state. Further studies on the synthesis of novel π-conjugated polymers having a tricarbonyl(arene)chromium unit as an acceptor are now underway.

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