Notes

Rearrangement of the Main Chain of the Organocobalt Polymers. 3. Synthesis of Novel Poly(thiophene-diyl-*alt*-biphenyl-4,4′-diyl)s by the Reaction with Sulfur

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Introduction

While many reactive polymers provide various functional materials through polymer reactions, very few of them can undertake the modification of the main chain structure. To construct novel main chain reactive polymers, we have recently synthesized air-stable organocobalt polymers having cobaltacyclopentadiene moieties in the main chain (**1**) by the reaction of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt with diynes bearing functional groups, in which the structural design of the organocobalt polymers can be attained simply by the molecular design of the diyne structures.[1]

As expected from the versatile reactivity of the repeating cobaltacyclopentadiene units,[2] the organocobalt polymers (**1**) revealed unique reactivities. For instance, the thermally stable polymers containing (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt repeating units were obtained by the rearrangement of the main chain.[3] The reaction of **1** with isocyanates or with nitriles led successfully to the polymers bearing six-membered heterocyclic units (i.e., 2-pyridone or pyridine moieties, respectively).[4] By means of these types of polymer reactions, a new polymer synthetic method based on the main chain-reactive polymers will be established.[5]

Because of the practical and potential applications of poly(thiophene) and its analogues, it might be of importance to develop new synthetic methods for these polymers. Herein, we wish to describe the reaction of the organocobalt polymers (**1**) with elemental sulfur to explore the reactivity of the organocobalt polymers and to establish a new synthetic method for thiophene-containing polymers (Scheme 1).

Experimental Section

Materials. Organocobalt polymers (**1**) were obtained as previously described.[1b] Elemental sulfur was purified by recrystallization from carbon disulfide. Toluene was dried over sodium and distilled under nitrogen. Other reagents were used as received.

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Synthesis of Thiophene-Containing Polymers (2a−d) (Typical Procedure for 2a). To a test tube were added **1a** (M_n = 14 300, M_w/M_n = 1.4, 0.222 g, 0.200 mmol unit), sulfur (0.32 g, 10 mmol, 50 equiv excess), and toluene (15 mL) under nitrogen, and the mixture was kept stirring at 80 °C for 24 h. To the reaction mixture was added an ethanol (30 mL) solution of $NaBH_4$ (0.76 g, 20 mmol) with stirring overnight in order to remove the remaining sulfur. The crude products were dissolved in chloroform and washed with water. After filtration and concentration, the resulting solution (ca. 2 mL) was precipitated with 100 mL of methanol. The resulting yellowish green powder was collected by filtration, washed with methanol, and then dried in vacuo to give 0.135 g of **2a**. Polymers **2b−d** were prepared under similar conditions.

2a: green powder; ^{1}H NMR (δ, ppm) 0.88 (−CH_3, br, 6H), 1.20−1.50 (−CH_2−, 36H), 1.75 (−CH_2−, br, 4H), 3.80−4.00 (−OCH_2−, 4H), 4.62 (C_5H_5, br, 5H × 0.14), 6.60−7.60 (−C_6H_4−, −C_6H_4O−, 16H); ^{13}C NMR (δ, ppm) 14.11 (−CH_3), 22.69, 26.09, 29.25, 29.34, 29.47, 29.63, 31.90 (−CH_2−), 67.82, 67.93 (−OCH_2−, −C_4−), 83.02 (C_5H_5), 113.96, 114.29, 114.53, 126.09, 126.58, 128.63, 129.38, 130.35, 131.35, 131.88, 157.85, 158.46 (−C_6H_4O−, −C_6H_5, SC_4); IR (KBr, cm^{-1}) 3030, 2924, 2853, 1609, 1508, 1285, 1246, 1175, 1026, 824, 721. Anal. Calcd for 0.86($C_{52}H_{66}SO_2$) + 0.14($C_{57}H_{71}CoO_2$): C, 82.44; H, 8.76; S, 3.66. Found: C, 82.31; H, 8.91; S, 3.59.

2b (from **1b** (0.233 g, 0.200 mmol) and sulfur (0.32 g, 10 mmol)): yield 72% (0.118 g, 0.143 mmol unit); brown powder; ^{1}H NMR (δ, ppm) 0.87 (−CH_3, br, 6H), 1.20−1.50 (−CH_2−, br, 36H), 1.74 (−CH_2−, br, 4H), 4.20−4.40 (−CO_2CH_2−, br, 4H), 4.66 (−C_5H_5, br, 5H × 0.14), 6.90−8.10 (−C_6H_4−, −C_6H_4-CO_2−, br, 16H); ^{13}C NMR (δ, ppm) 14.09 (−CH_3), 22.65, 26.01, 28.68, 29.31, 29.49, 29.60, 30.29, 31.88 (−CH_2−), 65.19 (−OCH_2−), 83.49 (−C_5H_5), 125.48, 126.52, 126.87, 128.90, 129.34, 129.47, 129.67, 130.79, 131.43 (−C_6H_4−, SC_4), 166.43 (CO); IR (KBr, cm^{-1}) 3029, 2963, 2922, 2853, 1719, 1605, 1464, 1262, 1098, 1020, 801, 700. Anal. Calcd for 0.86($C_{54}H_{66}SO_4$) + 0.14($C_{59}H_{71}CoO_4$): C, 79.75; H, 8.16; S, 3.40. Found: C, 79.84; H, 8.05; S, 3.32.

2c (from **1c** (0.140 g, 0.200 mmol) and sulfur (0.32 g, 10 mmol)): yield 85% (0.063 g, 0.170 mmol unit); yellowish green powder; ^{1}H NMR (δ, ppm) 0.60−1.70 (−CH_2−, −CH_3, 14H), 2.30−2.80 (−CH_2−, 4H), 4.64 (−C_5H_5, s, 5H × 0.23), 7.30−7.80 (−C_6H_4−, 8H); ^{13}C NMR (δ, ppm) 13.58, 13.67, 13.83, 14.00 (−CH_3), 22.38, 22.47, 22.98, 23.14, 27.17, 27.44, 28.26, 32.40, 32.80, 33.24, 34.13 (−CH_2−), 81.19, 81.43 (C_5H_5), 126.10, 126.23, 126.49, 126.58, 126.96, 128.02, 129.67, 130.51, 131.99, 134.21, 136.99, 137.15, 138.05, 139.16, 139.27 (−C_6H_5, SC_4); IR (KBr, cm^{-1}) 3027, 2963, 2859, 2361, 1605, 1539, 1262, 1098, 1024, 804, 727. Anal. Calcd for 0.77($C_{24}H_{26}S$) + 0.23($C_{29}H_{31}$-Co): C, 82.32; H, 7.46; S, 7.12. Found: C, 82.10; H, 7.66; S, 7.07.

2d (from **1d** (0.159 g, 0.200 mmol) and sulfur (0.32 g, 10 mmol), the reaction was carried out for 3 days): yield 90% (0.140 g, 0.180 mmol unit); brown powder; ^{1}H NMR (δ, ppm) 0.60−3.00 (−CH_2−, −CH_3, 34H), 7.50−8.15 (−C_6H_4−, br, 4H); ^{13}C NMR (δ, ppm) 14.02 (−CH_3), 22.54, 29.01, 31.70 (−CH_2−), 125.45, 128.0,4, 129.49, 129.70, 133.53 (−C_6H_4−, SC_4), 187.56, 196.57 (CO); IR (KBr, cm^{-1}) 3059, 2924, 2853, 1725, 1671, 1603, 1570, 1520, 1462, 1261, 1107, 1015, 802, 721. Anal. Calcd for $C_{28}H_{38}SO_2$: C, 76.67; H, 8.73; S, 7.31. Found: C, 76.63; H, 8.77; S, 7.55.

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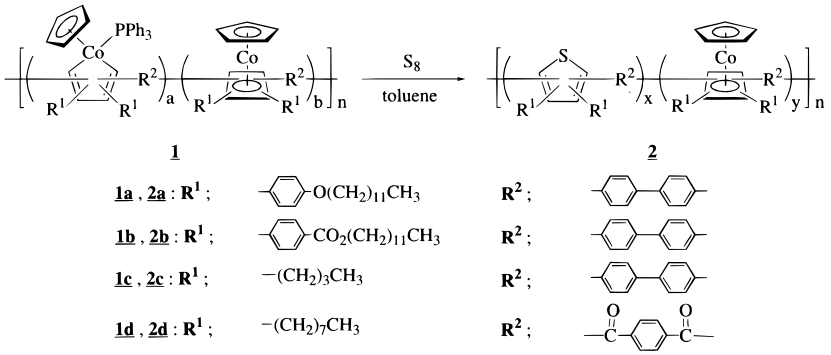
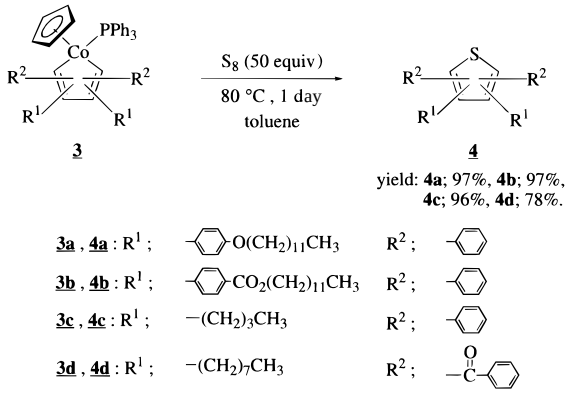
Scheme 1



Scheme 2



Results and Discussion

Reactions. Yamazaki et al. have reported that the reaction of the cobaltacyclopentadienes with sulfur gives the substituted thiophenes in moderate to good yields.[2i] However, if any side reactions take place, all of the undesired units should be incorporated into the produced polymers by the reaction of the polymers (**1**). To examine all of the detectable side products and to find out the effects of the characters of the substituents in the cobaltacyclopentadiene derivatives on the conversion into the thiophenes, the model reactions were carried out by using **3a**−**d** with an excess of sulfur in toluene at 80 °C. As a result, the corresponding thiophene derivatives (**4a**−**d**) could be isolated in almost quantitative yields by HPLC (Scheme 2). The reaction rate seems to be affected by the character of the substituents in **3**, because the complete conversion was observed within 1 day in the cases of **3a**−**c**, while it required 3 days for **3d**. It is notable that any side products could not be detected in these reaction systems irrespective of the substituents.

On the basis of the model experiments, the organocobalt polymers (**1a**−**d**) were subjected to the reaction with sulfur at 80 °C (Table 1). The reaction proceeded homogeneously, and the powdery polymers (**2a**−**d**) were isolated by precipitation with methanol in 72−90% yields.[6] The organocobalt polymers (**1a**−**d**) consisted of 79−100% of the cobaltacyclopentadiene moieties. The good agreement of the thiophene contents in the resulting polymers (**2a**−**d**) (77−100%, determined by ^{1}H NMR, ^{13}C NMR, IR, and elemental analyses, vide infra) did support that the cobaltacyclopentadiene moieties in **1** were converted quantitatively to the thiophene moieties.[7] Similar to the model experiment of **3d**, the reaction of **1d** required a longer period. However, the resulting polymer (**2d**) was found not to be contaminated by the CpCbCo unit because we could prepare **1d** containing 100% of the cobaltacyclopentadiene unit.

Table 1. Reaction of Organocobalt Polymers (1) with Sulfur[a]

1				2			
reactant	ratio of a[b]	M_n(M_w/M_n)[c]		product	yield (%)[d]	ratio of x[b]	M_n(M_w/M_n)[c]
1a	82	14 100 (1.4)		**2a**	88	86	14 300 (1.4)
1b	82	9 000 (1.3)		**2b**	72	86	12 100 (1.5)
1c	79	10 700 (1.6)		**2c**	85	77	11 400 (1.5)
1d[e]	100	4 700 (1.7)		**2d**	90	100	4 900 (1.9)

[a] The reaction was carried out in toluene at 80 °C for 24 h under N_2. [b] Determined by ^{1}H NMR and ^{13}C NMR spectra. [c] Estimated by GPC (THF, PSt standard). [d] Isolated yields by the precipitation with MeOH. [e] The reaction was carried out for 3 days.

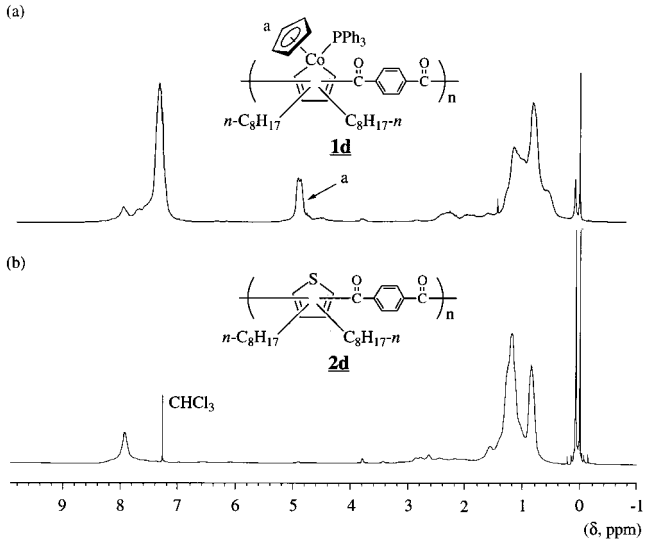


Figure 1. ^{1}H NMR spectra of **1d** (a) and **2d** (b).

In the ^{1}H NMR spectrum of the starting **1d** (Figure 1a), peaks attributable to the cyclopentadienyl group (Cp) (4.4−5.2 ppm) and those of aromatic protons both in skeletal phenylene and in ligated triphenylphosphine (7.0−8.4 ppm) were observed. In the case of **2d** (Figure 1b), no peak attributable to the Cp was observed and the intensity of those of the aromatic protons decreased because of the disappearance of triphenylphosphine. The integral ratio of the phenylene and the lateral alkyl groups of **2d** was also in good agreement with that of the expected structure. It is also confirmed by the ^{13}C NMR spectrum that **2d** was not contaminated by the CpCbCo unit.[8] Accordingly, it was supported that the cobaltacyclopentadiene moieties in **1d** were selectively converted into the thiophene moieties. In the IR spectrum of **2d**, the peaks attributable to the C═O

Table 2. Electrochemical, UV−Vis Absorption, and Thermal Degradation Data for Poly(thiophene-diyl-*alt*-biphenyl-4,4'-diyl)s (2a−d)

polymer	E_{pa}/V vs SCE[a]	$\Delta E_{pa1,2}$/V vs SCE[a]	λ_{max}/nm[b]	Td_{10}/°C[c]	weight loss at 500 °C/%
2a	1.10, 1.32	220	328	425	46
2b	1.40, 1.61	210	337	388	47
2c	1.15, 1.46	310	282	257	30
2d	*d*	*d*	270	338	50

[a] Precast film immersed in 0.1 M Bu_4NBF_4/CH_3CN. [b] In $CHCl_3$. [c] 10% weight loss. [d] Not detected.

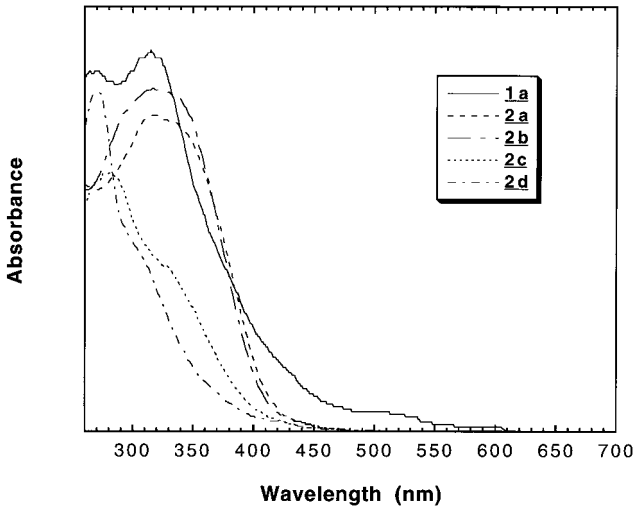


Figure 2. UV−vis spectra of **1a** and **2a**−**d** in $CHCl_3$.

stretching in the polymer backbone were observed at 1671 cm^{-1}, indicating that the C=O moieties in the polymer backbone were intact throughout the reaction. The C=C stretching of the thiophene ring was also observed at 1520 and 1107 cm^{-1}.

From our previous work,[1b] the regioselectivities in the main chain linkages at the cobaltacyclopentadiene moieties of **1a**−**d** were estimated as 2,5-:2,4-:3,4- = 25:50:25, 25:50:25, and 60:40:0 for **1a**, **1b**, and **1c**, respectively, and as 2,5-:2,4- and 3,4- = 89:11 for **1d**. Although we could not observe directly the regioregularities of **2a**−**d**, they must be the same as those of **1a**−**d**, because the reaction with sulfur should not bring about any isomerizations.

The molecular weights of the polymers (**2a**−**d**) were estimated by GPC using polystylene calibration curves. Compared to those of **1a**−**d**, no change or a slight increase of the molecular weights was observed, which might be, however, due to the factors originated from the GPC method and/or due to the loss of lower molecular weight fractions during the precipitation, because the absolute molecular weights of the polymers should decrease by 20−30% by the displacement of Cp-(PPh_3)Co with S moieties.

Physical Properties of the Polymers (Table 2). UV−vis spectra of the organocobalt polymer (**1a**) and the obtained thiophene-containing polymers (**2a**−**d**) are shown in Figure 2. The λ_{max} of the lowest energy $\pi-\pi^*$ absorption peaks of **1a** and **2a**−**d** were observed at 316, 328, 337, 282, and 270 nm, respectively. Compared with the UV−vis spectrum of **2d**, the lowest energy $\pi-\pi^*$ absorption of **2a** and **2b** shifted to a longer wavelength by ca. 60 nm, which might indicate the conjugation of repeating units along the polymer backbone.[9] Although **1a** shows an absorbance in the range of 400−600 nm, probably due to the metal to ligand electron transfer, the corresponding absorption was absent in the UV−vis spectra of the thiophene-containing polymers (**2a**−**d**) because of the complete conversions.

The cyclic voltamogram (CV) of the thiophene-containing polymers (**2a**−**d**) was masured by using precast films of **2** on the Pt working electrode immersed in 0.1 M Bu_4NBF_4/acetonitrile at a scaning rate of 50 mV s^{-1}. In the range 0−1.8 V (vs SCE), **2a**, **2b**, and **2c** revealed two oxidation peaks, while a partial or no reduction process was observed. In the case of **2d**, however, no peak was observed within the examined range, which might be due to the higher oxidation potential caused by breaking off of the main chain π-conjugation and by introducing the electron-withdrawing carbonyl groups. The separations of the oxidation peaks by ca. 200−300 mV were predicted from the electrochemistry of the well-defined thiophene oligomers, which has been explained by the two stepwise one-electron oxidation process.[10] Judging from the first and second oxidation potentials of **2a**−**c** in the film state, the differences in the oxidation potentials are probably effected simply by the electronic properties of the substituent.[11] The rather high oxidation potentials of **2a**−**c** in comparison with those of the reported poly(3-substituted thiophene)s might be due to the sterically more hindered thiophene units and the irregularity in the main chain linage. Although the CpCbCo unit may undertake oxidation at ca. 0.8 V,[12] the corresponding oxidation wave was not observed in **2a**−**c** from these CV traces.

The thermal properties of the thiophene-containing polymers (**2**) were estimated by thermogravimetric analyses (TGA). The 10% weight loss (Td_{10}) of **2a** was observed at 425 °C, while the starting organocobalt polymer (**1a**) had Td_{10} at 228 °C.[13] The polymer (**2b**) showed a degradation profile similar to that of **2a**, while **2c** and **2d** lost their weights at a lower temperature than **2a** (Td_{10}'s of **2c** and **2d** were observed at 257 and 338 °C, respectively). The degradations of **2a**−**d** below 500 °C might be originated from the decompositions of the lateral alkyl moieties because their weight losses observed at 500 °C are approximately equal to the weights of their soft segments. From the differential scanning calorimetric (DSC) analyses of **2a** and **2b**, no peak based on the glass transition or melting was observed below the decomposition temperatures.

Summary

The reaction of the organocobalt polymers (**1a**−**d**) with sulfur yielded novel thiophene-containing polymers (**2a**−**d**) with various substituents in excellent efficiency. By the structural analyses, the polymers (**2**) were found to contain 77−100% of the thiophene moieties, which was in accordance with the cobaltacyclopentadiene contents in **1**. Poly(thiophene-diyl-*alt*-biphenyl-4,4′-diyl)s (**2a**−**c**) were supposed to have a partially π-conjugated main chain judging from their UV−vis spectra and CVs. From TG analyses, the polymers **2a** and **2b** with higher aromatic contents revealed higher thermal stabilities undergoing no significant weight loss below 400 °C.

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Supporting Information Available: Text giving synthetic details and spectral data of the model compounds (**4a**−**d**) (3 pages). Ordering information is given on any current masthead page.

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(5) A few examples of the main chain-reactive polymers have been reported. See: (a) Chujo, Y.; Tomita, I.; Saegusa, T. *Makromol. Chem., Macromol. Symp.* **1993**, *70/71*, 47. (b) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5365.

(6) The reaction of poly((η^5-cyclopentadienyl)(triphenylphosphine)-diphenylcobaltacyclopentadienediyl-*alt*-biphenyl-4,4′-diyl), prepared from 4,4′-bis(phenylethynyl)biphenyl and CpCo(PPh$_3$)$_2$, with sulfur was carried out in toluene at 80 °C for 24 h to give an insoluble black solid. The low solubility of the product made it difficult to characterize the structure and the properties. Accordingly, the organocobalt polymers bearing soft segments (**1a**−**d**) were used for the present study.

(7) The remaining units in both **1** and **2** (ca. 23−0%) were identified as the CpCbCo unit by their ^{1}H and ^{13}C NMR spectra.

(8) The ^{13}C NMR spectrum of **2d** did not indicate any peaks attributable to the Cp in the cobaltacyclopentadiene or the CpCbCo moieties in the range 80−90 ppm. The peaks for the Cp of the cobaltacyclopentadiene derivatives and those of the CpCbCo derivatives are observable in the range of 80−90 ppm. See ref 1b.

(9) The λ_{max} of the lowest energy $\pi-\pi^*$ absorption peaks of the model compounds (**4a** and **4b**) were observed at 275 and 286 nm, respectively, by which the existence of the conjugation through the polymer main chain might be supported. The polymer (**2c**) indicated a substantial blue shift in comparison with **2a** or **2b**, which might contradict with the fact that **2c** has a higher 2,5-regioselectivity and longer main chain length in comparison with **2a** or **2b**. The reason for the substantial blue shift of the λ_{max} of **2c** might be simply due to the difference in the structure of the repeating unit. However, a shoulder at about 330 nm could be found from the UV−vis spectrum of **2c**, which might indicate that at least a few parts of **2c** maintained a longer π-conjugation through the polymer main chain.

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(12) The oxidation of (η^5-cyclopentadienyl)(η^4-cyclobuta-1,2,3,4-tetraphenyl)cobalt was observed at 0.8 V under the same conditions (i.e., in 0.1 M Bu_4NBF_4/acetonitrile at a scaning rate of 50 mV s^{-1}).

(13) The organocobalt polymers (**1**) showed two-step decompositons on TG below 500 °C. The first decomposition was ascribed to the rearrangement of the cobaltacyclopentadiene unit to the CpCbCo unit by which the elimination of triphenylphosphine occurred. See ref 1b.

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