Complete Rearrangement of an Organocobalt Polymer: Synthesis of a Thermally Stable Polymer Containing (Cyclobutadiene)cobalt Moieties on the Main Chain

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In spite of the great potential utility of organometallic polymers for electron-conductive, nonlinear optical, and liquid crystalline materials,[1,2] there have been only a few reports dealing with the synthesis of such materials.

Recently, we reported a novel synthetic methodology to obtain air-stable organocobalt polymers having cobaltacyclopentadiene moieties in the main chain by oxidative coupling (i.e., oxidative ring closure) of diynes with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt complex (Scheme 1).[3] The number-average molecular weights ($\bar{M}_n$) of these organocobalt polymers reached 200 000 when a purified cobalt monomer was used.

A thermal rearrangement reaction of derivatives of cobaltacyclopentadiene has been reported to take place to provide the corresponding derivatives of (η^4-cyclobutadiene)cobalt above its melting temperature.[4] The resulting (cyclobutadiene)cobalt compounds are known to be quite stable, since they are isoelectronic with ferrocene.[5] Because polymers containing (cyclobutadiene)cobalt repeating units may serve as novel materials with higher stability, the novel rearrangement of the organocobalt polymer was examined here.

The reaction of the brown-colored organocobalt polymer (**1**, $\bar{M}_n$ = 35100) prepared by the reaction of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt with 4,4′-bis(phenylethynyl)biphenyl[3] was carried out at 110 °C in tetrahydrofuran (THF) for 1 h in a sealed tube without any added reagents, from which a yellow powdery polymer (**2**) was obtained in 79% yield by precipitation with *n*-hexane (Scheme 2). **2** is soluble in organic solvents such as THF, chloroform, and *N*,*N*-dimethylformamide, and its $\bar{M}_n$ was estimated as 33 200 by GPC on the basis of standard polystyrene samples. From the *n*-hexane-soluble fraction in the precipitation process, the eliminated triphenylphosphine was detected.[6] Judging from the similarity in the molecular weights of **1** and **2**, side reactions (such as cleavage of the main chain or a cross-linking reaction) do not take place.

The quantitative conversion of **1** to polymer **2** was supported by the model reaction of **3** under the same conditions. In this case, (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt (**4**) was isolated in 97% yield by column chromatography (Scheme 3).[7] Further, the structure of **2** was confirmed by ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, and IR analyses.[8] In the ^{1}H-NMR spectrum of **2** (Figure 1b), a peak attributable to cyclopentadienyl moieties was observed at 4.66 ppm, while the corresponding peak in **1** appeared at 4.76 ppm (Figure 1a). The integral ratio of the peaks in the aromatic region and that of the cyclopentadienyl group also supported the complete conversion to **2**. In the ^{13}C-NMR spectrum of **2**, the cyclopentadienyl group was detected at 83.29 ppm, which is very close to the corresponding peak in **4** (83.24 ppm). No peak for the starting unit in **1** was observed at 89.70 ppm.[3] As expected, no peak was detected in the ^{31}P-NMR spectrum of **2**.

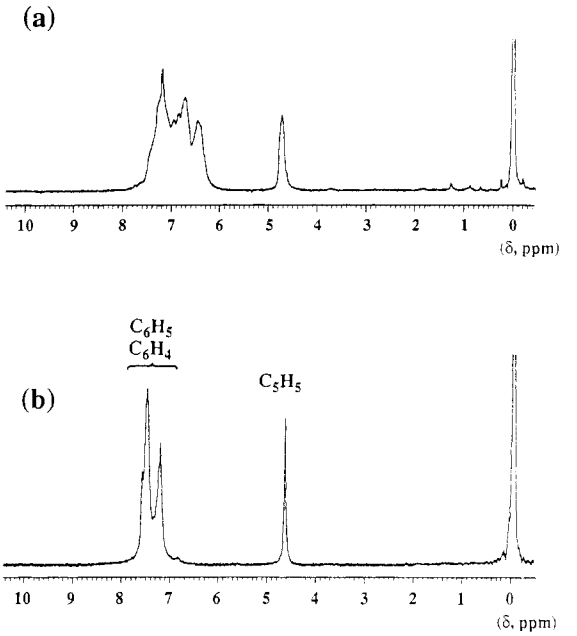
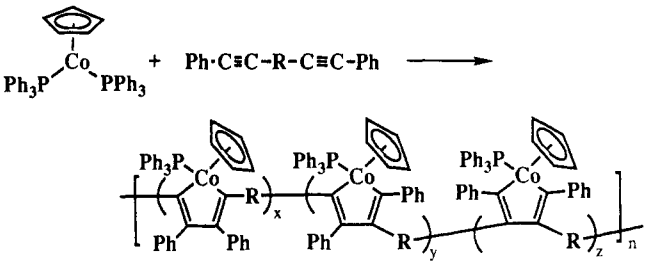
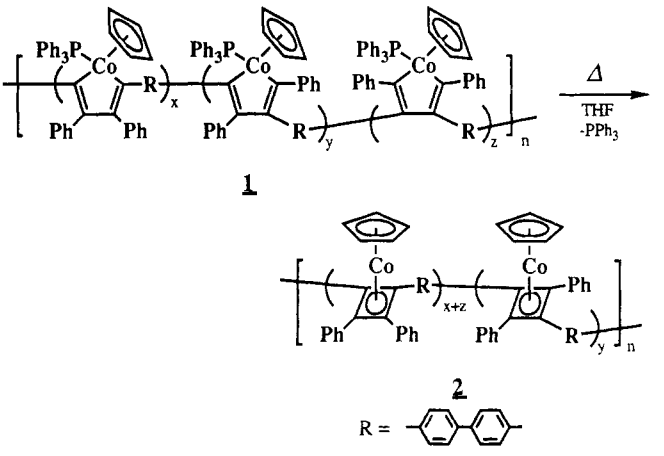


Figure 1. ^{1}H-NMR spectra (90 MHz, in $CDCl_3$) of **1** (a) and **2** (b).

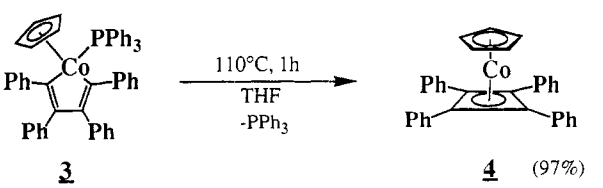
Scheme 1



Scheme 2



Scheme 3



The present reaction could be monitored by the measurement of the ^{1}H-NMR spectra by comparing the integral ratio of the peaks at 4.66 and 4.76 ppm (i.e., the (cyclobutadiene)cobalt and cobaltacyclopentadiene units, respectively). As shown in Table 1, reaction for 50 min was sufficient for complete conversion to **2** at 110 °C.

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Table 1. Conversion of 1 into 2[a]

run	reacn time (min)	conv ratio[b]
1	30	85:15
2	45	90:10
3	50	100:0

[a] Reaction of 1 (0.050 g) was carried out at 110 °C in THF (10 mL) in a sealed tube. [b] (Cyclobutadiene)cobalt unit:cobaltacyclopentadiene unit ratio, determined by ^{1}H-NMR.

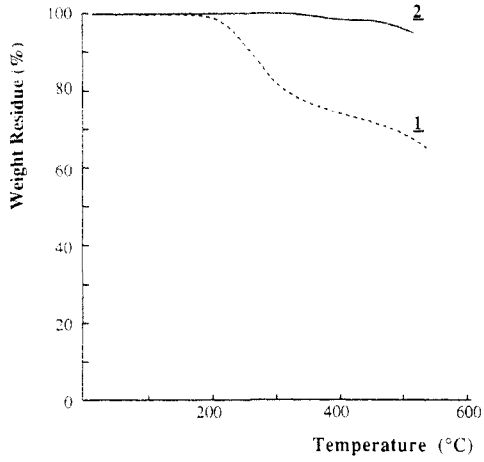

Figure 2. Thermogravimetric analyses (TGA) of 1 and 2 under nitrogen (10 °C/min).

The thermal stability of **2** was estimated by thermogravimetric analysis (TGA) under nitrogen (Figure 2). No weight loss was observed below 400 °C, and the temperature for 5% weight loss (T_{d5}) was 482 °C, which was much higher than that of **1**.[3] From the differential scanning calorimetric analysis (DSC) of **2**, no peaks based on T_g and T_m were observed below the decomposition temperature.

Because the obtained polymer containing (cyclobutadiene)cobalt has good stability, its physical properties are now under investigation.

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References and Notes

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(6) The methanol-soluble fraction also contained triphenylphosphine oxide, presumably by the oxidation.
(7) In the case of the thermal treatment of **3** in the crystalline form, the yield of **4** has been reported as 60% (see ref 4).
(8) **2**: ^{13}C-NMR ($CDCl_3$, δ, ppm) 83.29, 126.14, 128.00, 129.16, 135.73, 136.47, 138.29; IR (KBr) 3055, 3026, 1712, 1599, 1442, 1219, 1180, 1109, 1003, 810, 750, 590, 567 cm^{-1}.