Rearrangement of the Main Chain of an Organocobalt Polymer: Synthesis of Novel 2-Pyridone-Containing Polymers by the Reaction with Isocyanates

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ABSTRACT: Novel polymers having pyridone moieties as well as aromatic systems in the main chain were synthesized by the reaction of an organometallic polymer having cobaltacyclopentadiene moieties in the main chain (**1**) with various isocyanates (**2**). When dark brown **1** and 5 equiv of *n*-butyl isocyanate (**2a**) were heated in tetrahydrofuran at 120 °C for 6 h in a sealed tube, a greenish polymer (**3a**) was obtained in 99% yield by precipitation with methanol. From the spectroscopic measurements, the resulting polymer was found to contain *N*-*n*-butyl-2-pyridone and (η^4-cyclobutadiene)cobalt moieties (68% and 32%, respectively). By changing the feed ratio of **2a/1**, the composition of 2-pyridone and cyclobutadienecobalt moieties could be controlled. Using various isocyanates (**2a**−**2d**), 2-pyridone-containing polymers with various substituents were obtained. The cross-linking reaction could be also possible by using diisocyanate (**2f**).

Introduction

Reactive polymers such as poly(*p*-(chloromethyl)-styrene) and poly(glycidyl methacrylate) are important polymeric precursors that can produce various kinds of functional polymers by the so-called polymer reactions. In general, such polymers contain reactive moieties on the side chain, by which various functional groups can be introduced into the side chain of the polymer. The backbones of the polymers, however, could not be modified by using such systems. In other words, these reactive polymers have inert backbones against polymer reactions. Recently, materials with novel and specified functions such as electron conductivity have been claimed, whose functions are largely dependent on the structure of the backbone of polymers. For these reasons, polymers bearing reactive groups in the main chain may become of great importance as synthetic precursors for novel functional materials. However, only a few types of such reactive polymers have been reported.[1]

Recently, we have reported a novel synthetic methodology to obtain air-stable organocobalt polymers having cobaltacyclopentadiene moieties in the main chain by the oxidative coupling (i.e., the oxidative ring closure) of diynes with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt (Scheme 1).[2] The number average molecular weights ($\bar{M}_n$) of these organocobalt polymers have reached 2.0×10^5 by using a purified cobalt monomer.

Because of the potential reactivities of cobaltiocyclopentadienes (i.e., the repeating polymer units), organocobalt polymers may serve as novel reactive polymers that can provide various functional materials. By the thermal rearrangement reaction of these organocobalt polymers, polymers containing a cobalt sandwich complex on their main chains were obtained that were quite thermally stable.[3] Ligand displacement of the organocobalt polymers has been also examined, by which the side chain of the polymers could be successfully modified by the facile polymer reactions (Scheme 2).[4]

Cobaltacyclopentadienes have been reported to be converted to derivatives of 2-pyridone, pyridine, and 1-alkoxyphosphole oxides by reactions with isocyanates,[5] nitriles,[6] and trialkyl phosphites,[7] respectively. When these reactions are applied to the organocobalt polymers, organic polymers containing various structures in the main chain might be obtained along with the rearrangement of the main chain. Thus, as a first example, a novel polymer reaction was examined here with various isocyanates (Scheme 3).

Results and Discussion

The reaction of an organocobalt polymer (**1**), which was prepared by the reaction of (η^5-cyclopentadienyl)-bis(triphenylphosphine)cobalt with 4,4′-bis(phenylethynyl)biphenyl, with 5 molar equiv of *n*-butyl isocyanate (**2a**) was carried out at 120 °C in tetrahydrofuran (THF) for 6 h in a sealed tube. After the reaction, the reaction mixture was poured into excess MeOH to precipitate a green powdery polymer (**3a**) in 99% yield.

For the structural elucidation, a model reaction was carried out under similar reaction conditions (Scheme 4). By the reaction of **4** with **2a** (8.7 equiv) at 120 °C in THF, a derivative of 2-pyridone (**5a**) was isolated by chromatography in 77% yield.[8] Though the complete isolation was unsuccessful, a derivative of (cyclobutadiene)cobalt (**6**) was also detected in the reaction mixture. The formation of **6** may be explained by the unimolecular rearrangement of **4**. In fact, **6** was obtained almost quantitatively by the reaction above 110 °C in the absence of **2a**.[3]

The structure of **3a** was confirmed by IR and ^{31}P- and ^{1}H-NMR spectra in comparison with those of the model compound (**5a**). In the IR spectra of **3a** as well as **5a**, the peak attributable to the C=O stretching in the amide moieties was observed around 1630 cm^{-1}. While a single peak at 50.9 ppm attributable to Co−PPh_3 was observed in the ^{31}P-NMR of **1**, no peak was observed in that of **3a**, indicating the complete conversion of cobaltacyclopentadiene moieties in **1**.[9] In the ^{1}H-NMR spectrum of **3a** (Figure 1b), peaks attributable to the *n*-butyl group (0.55−2.02 and 3.82 ppm) and those of aromatic protons in phenyl groups as well as the biphenyl groups in the main chain (6.03−7.96 ppm) were observed, similar to the case of **5a** (Figure 1a). In the ^{1}H-NMR spectrum of **3a**, a peak for the cyclopen-

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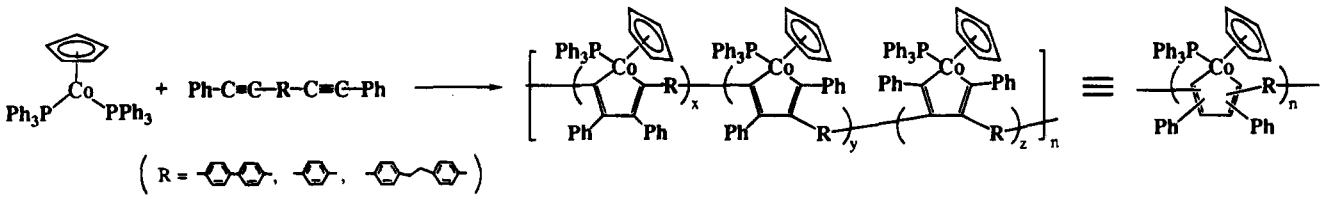
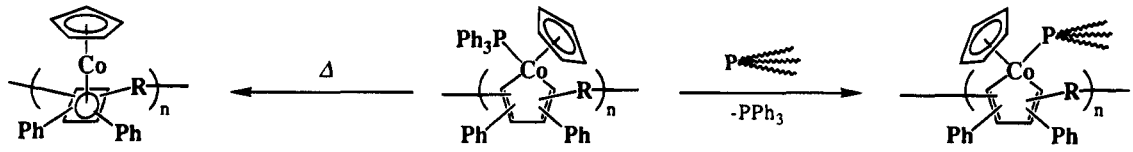
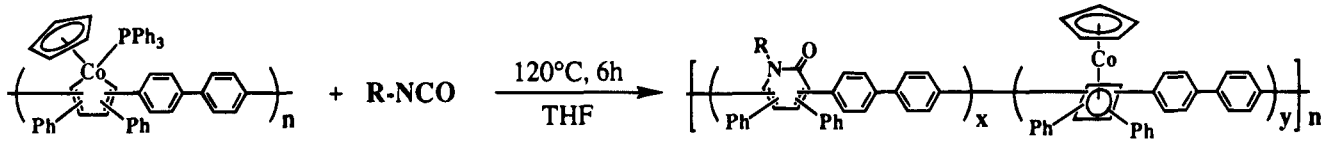
Scheme 1



Scheme 2

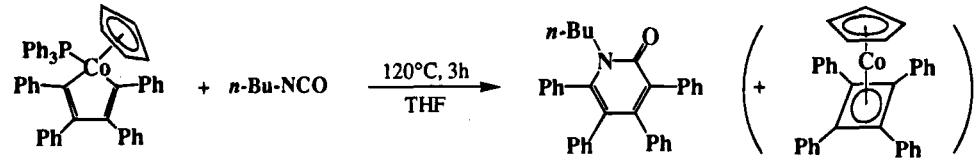


Scheme 3



1 **2** **a**: R= *n*-Bu-
b: R= Et-
c: R= n-$C_{18}H_{37}$-
d: R= Ph-
e: R= PhCO-
f: OCN-$(CH_2)_6$-NCO **3**

Scheme 4



4 **2a** **5a** **6**

tadienyl group was observed at 4.61 ppm, while the cyclopentadienyl group in the starting polymer (**1**) appeared at 4.76 ppm. The cyclopentadienyl group must be attached to (cyclobutadiene)cobalt moieties judging from its chemical shift, the model experiment, and the result obtained by the ^{31}P-NMR measurement. From the integral ratio of protons at the cyclopentadienyl ring and the methylenes adjacent to the nitrogen atom, **3a** was found to consist of 68% 2-pyridone and 32% (cyclobutadiene)cobalt moieties.

On the basis of the proposed reaction mechanism for the various types of reactions starting from cobaltacyclopentadienes,[5-7] the present polymer reaction can be considered to proceed, as shown in Scheme 5. That is, the triphenylphosphine in the cobalt atom dissociates at the initial stage to produce the coordinatively unsaturated species, to which the isocyanate may add as a ligand. From the resulting complex, the insertion of C=N moieties of isocyanates toward the carbon–cobalt bond takes place, followed by the reductive elimination of (cyclopentadienyl)cobalt (CpCo) species. Without the coordination of isocyanates, the coordinatively unsaturated cobaltacyclopentadiene may undergo a rearrangement to form (cyclobutadiene)cobalt moieties.

As expected from the above mechanism, the content of 2-pyridone and (cyclobutadiene)cobalt could be controlled when the reactions of **1** with **2a** were carried out by changing the feed ratio of **2a/1** (Table 1). All the cobaltacyclopentadiene rings in **1** were converted to (cyclobutadiene)cobalt moieties when the reaction was carried out without **2a** under similar reaction conditions, as reported previously.[3] Similar to this result, no starting units were detected in all the polymers after the reaction. In the case of stoichiometric conditions, the 2-pyridone content in the polymer was 23% (run 1). In the present reaction system, each eliminated CpCo moiety may require two ligands (i.e., **2a** and/or triphenylphosphine). This might reduce the formation of the pyridone ring under the stoichiometric conditions. By use of an excess amount of **2a**, the content of the pyridone moieties increased (runs 2 and 3).[10] When the reaction was carried out at a higher reaction temperature (i.e., at 150 °C, run 5), some part of the resulting polymer became insoluble in organic solvents. The THF-soluble part was found to have almost the same composition as that prepared at 120 °C.[11]

Reactions of various isocyanates (**2a–2f**) with **1** were carried out by using an excess amount of isocyanates (Table 2). Increasing the length of alkyl groups in the isocyanates gradually decreased the content of the 2-pyridone moieties. However, the resulting polymer appeared in higher molecular weight regions in GPC probably due to the larger size of the alkyl substituents. With an aromatic isocyanate (**2d**), the polymer consist-

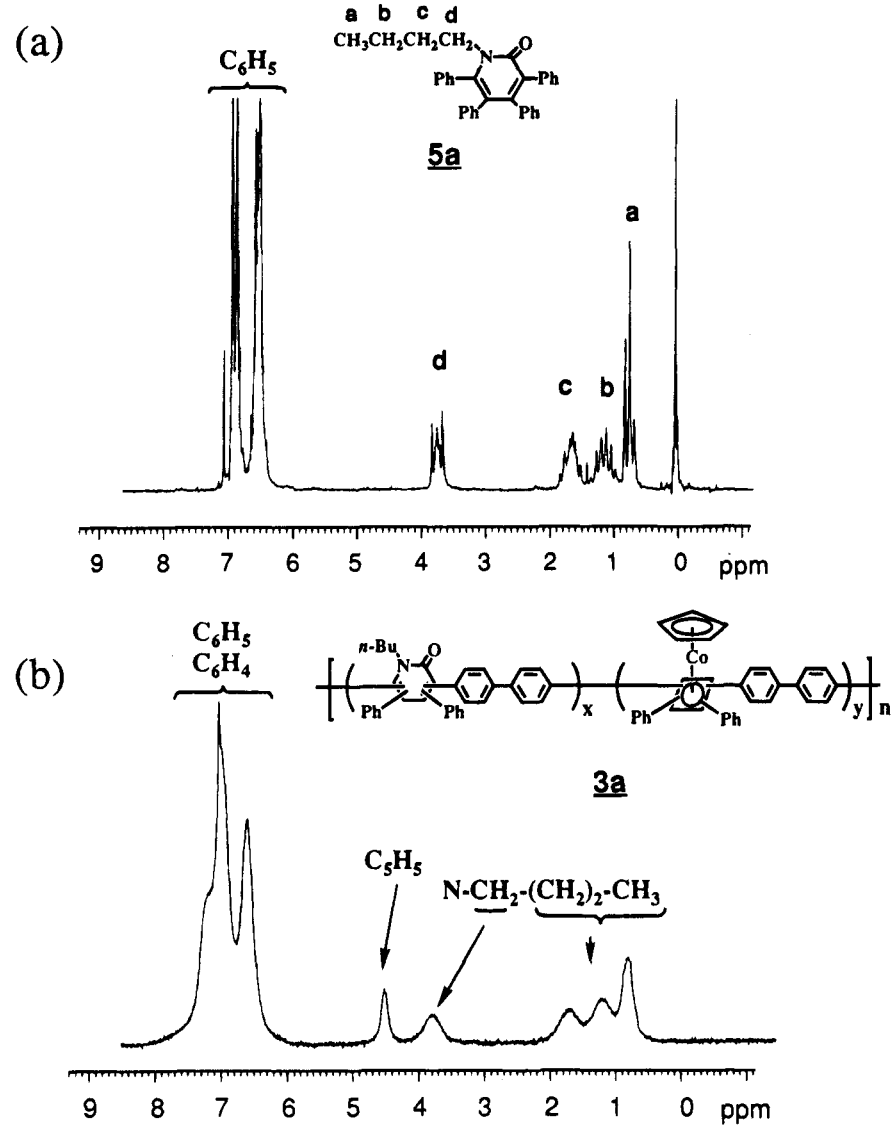


Figure 1. ^{1}H-NMR spectra ($CDCl_3$, 90 MHz) of **5a** (a) and **3a** (b).

Table 1. Reactions of 1 with 2a under Various Conditions[a]

run	[**2a**]/[Co] ratio	reacn temp (°C)	x:y[b]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]
1	1	120	23:77	16 000 (2.6)
2	5	120	68:32	13 000 (2.6)
3	10	120	73:27	12 900 (2.4)
4	5	150	65:35	9 190 (2.5)[d]

[a] Reactions were carried out in THF for 6 h using **1** ($\bar{M}_n$ = 15 000, $\bar{M}_w/\bar{M}_n$ = 2.0). [b] Determined by ^{1}H-NMR after precipitation with MeOH. [c] Estimated by GPC (THF, PSt, Std). [d] The product became partially insoluble in THF.

ing of only aromatic systems (**3d**) could be also prepared. On the other hand, an isocyanate having an electron-withdrawing group such as benzoyl isocyanate (**2e**) did not react with **1** under the same conditions. In this case, 33% of the starting units were detected in the recovered product, indicating that **2e** may interact with the coordinatively unsaturated cobalt atom to reduce the possibility for the unimolecular rearrangement. Though the reaction efficiency based on isocyanates was rather low, a cross-linked polymer could be obtained by the reaction with hexamethylene diisocyanate (**2f**, run 4).

The properties of the pyridone-containing polymer (**3a**, in Table 2, run 1) were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). From the TGA measurement of **5a**, the

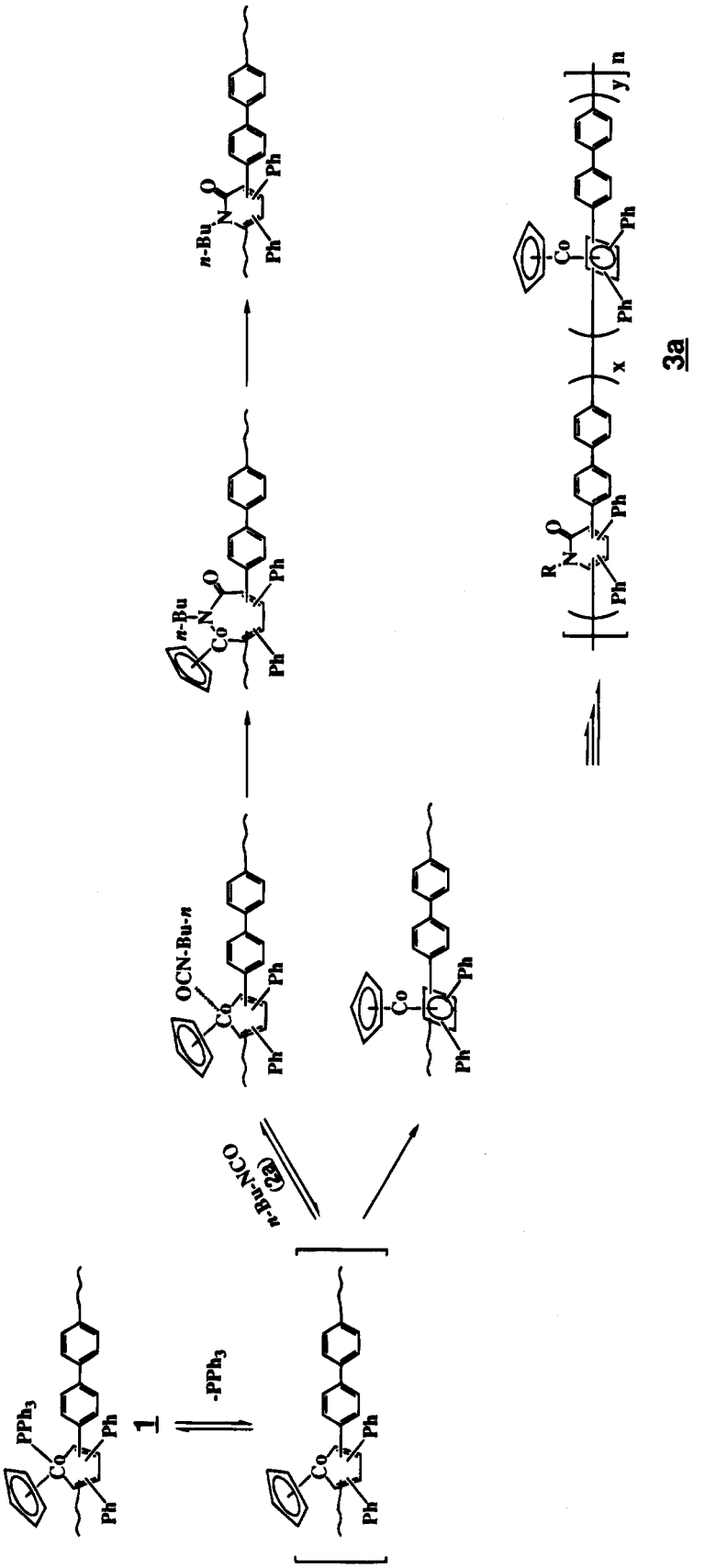
Table 2. Reactions of an Organocobalt Polymer (1) with Various Isocyanates (2a–2f)[a]

run	isocyanate	[**2**]/[Co] ratio	yield (%)[b]	2-pyridone unit:(cyclobutadiene) (x:y)[c]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[d]
1	Et-NCO (**2b**)	5	96	73:27	9 200 (2.8)
2	n-BuNCO (**2a**)	5	99	68:32	13 000 (2.6)
3	n-$C_{18}H_{37}$NCO (**2c**)	9	60[e]	55:45	26 800 (1.8)
4	PhNCO (**2d**)	5	90	65:35	9 200 (2.3)
5	PhCONCO (**2e**)	5	nd[f]	0:67[g]	nd[f]
6	$OCN(CH_2)_6NCO$ (**2f**)	6	nd[f]	gelation	

[a] In all cases, reactions were carried out in THF at 120 °C for 6 h by using **1** ($\bar{M}_n$ = 15 000, $\bar{M}_w/\bar{M}_n$ = 2.0). [b] MeOH-insoluble part. [c] Determined by ^{1}H-NMR. [d] Estimated by GPC (THF, PSt, Std). [e] Et_2O-insoluble part. [f] Not determined. [g] The product contained 33% of the unreacted cobaltacyclopentadiene unit.

10% weight loss (Td_{10}) was observed at 431 °C, while the starting organocobalt polymer and a polymer containing (cyclobutadiene)cobalt had Td_{10} at 257 °C and above 500 °C, respectively (Figure 2). As the (cyclobutadiene)cobalt unit in **5a** may have a high thermal stability, the degradation of **5a** may originate from the decomposition of 2-pyridone moieties. From the DSC analysis of **5a**, no peaks based on glass transition and melting were observed below the decomposition temperature.

Scheme 5



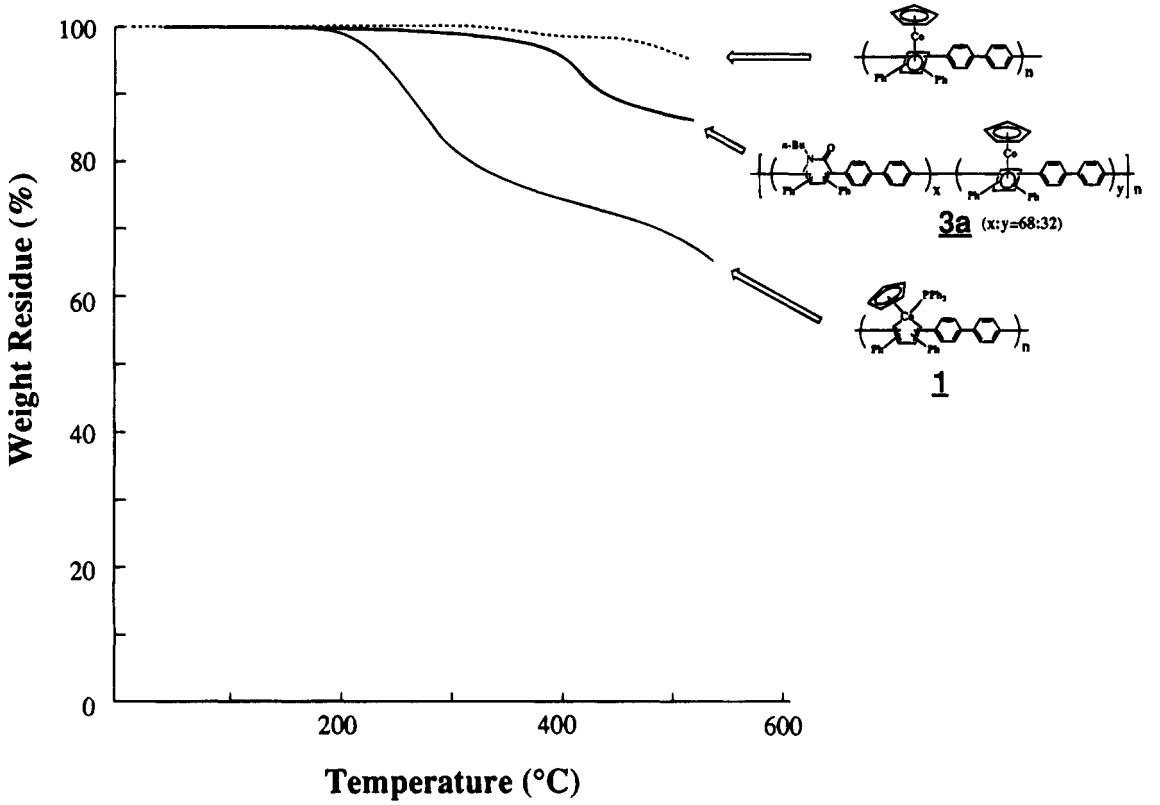


Figure 2. Thermogravimetric analyses (TGA) of a prepolymer (**1**), a polymer containing (cyclobutadiene)cobalt units, and a pyridone-containing polymer (**3a**) under nitrogen (10 °C/min).

Physical functions of the obtained polymers and other types of polymer reactions of organocobalt polymers are now in progress.

Experimental Section

Materials and Instruments. **1** was prepared as previously described by using the isolated crystals of the (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt complex with 4,4′-bis(phenylethynyl)biphenyl and was isolated by precipitation with *n*-hexane.[2] All isocyanates (**2a**–**2f**) were distilled before use. THF was dried over sodium and was distilled under nitrogen. All the other reagents were used as received.

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a JEOL EX-90 instrument (90 and 22.5 MHz for ^{1}H- and ^{13}C-NMR, respectively, tetramethylsilane as an internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh CCPD (TSK gel G4000, THF as an eluent) on the basis of standard polystyrene samples. TGA measurements were carried out on a Seiko TG/DTA 220 instrument at a heating rate of 10 °C/min under nitrogen. DSC analysis was performed on a Seiko DSC 220C at a heating rate of 5 °C/min.

Synthesis of 2-Pyridone-Containing Polymer (3a, in Table 1, Run 2). To a test tube were added **1** (0.101 g, containing 0.136 mmol unit of Co), **2a** (0.069 g, 0.70 mmol), and THF (5 mL) under nitrogen. The tube was degassed and sealed. After the reaction at 120 °C for 6 h, the tube was opened and the reaction mixture was poured into an excess amount of methanol. **3a** was obtained as a greenish powder in 99% yield (0.0608 g). Similarly, all the polymers in Table 1 were prepared by changing the feed ratio of **2a/1** as indicated in the Table. The ^{1}H-NMR spectrum is shown in Figure 1b. IR (KBr): 3028, 2961, 2868, 1635, 1491, 1440, 1365, 1296, 1261, 1180, 1107, 1066, 1026, 1005, 804, 748, 696, 567, 540 cm^{-1}.

3b (from **1** (0.054 g, 0.073 mmol unit) and **2b** (0.026 g, 0.37 mmol)): yield 96% (0.030 g); ^{1}H-NMR (δ, ppm) 1.00–1.50 (m, N–C–CH_3), 3.70–4.40 (br, N–CH_2–C), 4.40–4.80 (br, C_5H_5), 6.40–8.00 (m, C_6H_5, C_6H_4); IR (KBr) 3055, 3028, 2962, 1635, 1599, 1496, 1440, 1259, 1091, 1070, 1024, 1005, 808, 750, 698, 590, 570 cm^{-1}.

3c (from **1** (0.052 g, 0.070 mmol unit) and **2c** (0.18 g, 0.62 mmol)): yield 60% (0.024 g); ^{1}H-NMR (δ, ppm) 0.80–2.00 (m, N–C–$(CH_2)_{16}$–CH_3), 3.60–4.10 (br, N–CH_2–), 4.68 (br, C_5H_5), 6.60–7.90 (m, C_6H_5, C_6H_4); IR (KBr) 3057, 3030, 2916, 2851, 1639, 1575, 1496, 1467, 1442, 1296, 1238, 1180, 1070, 1005, 831, 810, 752, 721, 698, 590, 569 cm^{-1}.

3d (from **1** (0.0513 g, 0.069 mmol unit) and **2d** (0.042 g, 0.36 mmol)): yield 90% (0.029 g); ^{1}H-NMR (δ, ppm) 4.67 (br, C_5H_5), 6.10–8.62 (m, C_6H_5, C_6H_4); IR (KBr) 3055, 3028, 1636, 1180, 1111, 835, 754, 700 cm^{-1}.

3f (from **1** (0.053 g, 0.071 mmol unit) and **2f** (0.037 g, 0.22 mmol)): yield 0.054 g (after Soxhlet extraction with THF for 12 h); IR (KBr) 2930, 2856, 1689, 1631, 1518, 1464, 1369, 1209, 1066, 835, 700 cm^{-1}.

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References and Notes

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(8) **5a**: mp 204–206 °C (lit.[6] mp 206–207 °C); ^{13}C-NMR (δ, ppm) 13.4, 20.2, 30.8, 47.2, 121.4, 125.5, 125.7, 126.2, 126.4, 126.9, 127.3, 127.9, 129.9, 130.0, 130.1, 131.1, 131.8, 134.9, 136.6, 137.5, 138.2, 146.2, 161.7 ppm; IR (KBr) 3055, 3026, 2959, 2932, 2860, 1630, 1518, 1487, 1442, 1365, 1180, 1151, 1090, 1028, 746, 698, 607 cm^{-1}.
(9) Judging from the signal-to-noise ratio under the measurement conditions, the content of the remaining triphenylphosphine might be less than 2% of the total units in the polymer.
(10) Although the complete conversion to pure poly(2-pyridone) was unsuccessful, the content of 2-pyridone units increased to 83% in the presence of a further excess of **2a** (~100 equiv).
(11) From the IR spectrum of the THF-insoluble parts obtained by the reaction at 150 °C, the structure of the less soluble parts was also found to be almost identical to that of the soluble parts.

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