Polymer Bulletin 30, 179–186 (1993)

Polymer Bulletin

Synthesis of novel organometallic polymers having metallacyclopentadiene moieties in the main chain by the reaction of diynes with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt complex

Ikuyoshi Tomita, Akinori Nishio, Tadashi Igarashi, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Summary

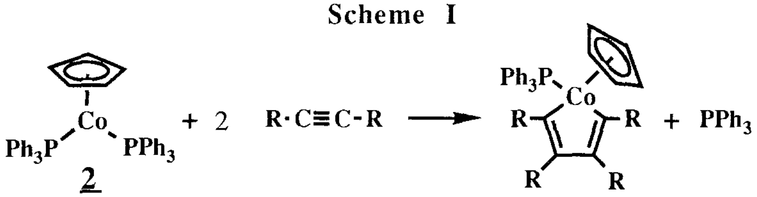
Polymerization reactions of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt complex (**2**) and diyne monomers (**3a**-**3c**) were examined to obtain novel organometallic polymers bearing metallacyclopentadiene moieties in the main chain. When the polymerization reaction of **2** with 4,4'-bis(phenylethynyl)biphenyl (**3a**) was carried out in toluene at 50°C for 3days, an organometallic polymer having cobaltacyclopentadiene in the main chain was obtained quantitatively. The structure of the resulting polymer was confirmed by ^{1}H-, ^{13}C-NMR, IR, and UV spectra. The number-average molecular weight of the obtained polymer was evaluated as 9,600 (GPC, on the basis of polystyrene).

Introduction

Organometallic polymers consisting of carbon-metal bonds connected with π-delocalized organic building blocks are of great interest, since they may be expected to have potential functions such as the electron-conductive, non-linear optical, and liquid crystalline materials [1,2]. However, there are a few examples [2] dealing with the synthetic methodology to produce such materials, mainly due to the instability of the organometallic moieties.

Some organometallic compounds having metallacyclopentadiene structures such as cobaltacyclopentadienes are known to be stable under air [3]. Accordingly, if polymers consisting of cobaltacyclopentadiene moieties were produced, they might be expected to have sufficient stability to be utilized for novel materials demonstrating the novel characteristics described above.

Scheme I

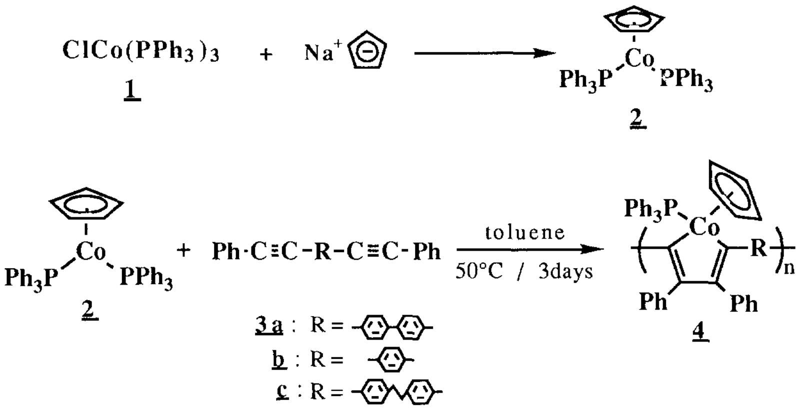


---

*Corresponding author

Yamazaki *et al.* have reported that the reaction of substituted acetylenes and **2** gives the corresponding cobaltacyclopentadienes which are stable under air (Scheme I) [3]. By the direct application of this reaction to the polymer synthesis using bifunctional diyne monomers, the corresponding polymers containing cobaltacyclopentadiene moieties will be produced. Herein, we describe the first example to obtain organometallic polymers consisting of metallacyclopentadiene moieties in the main chains by the reactions of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt complex (**2**) and diyne monomers (**3a**-**3c**) (Scheme II).

Scheme II

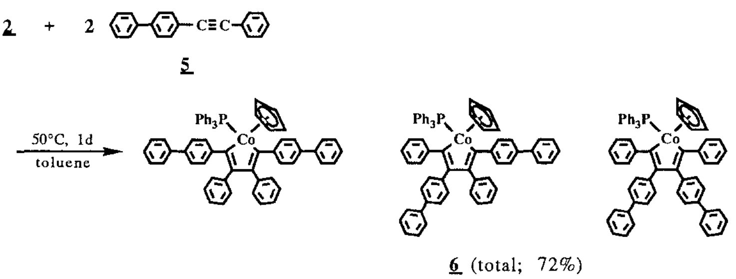


Results and Discussion

The reaction of **2** prepared *in situ* from a little excess amount of $CoCl(PPh_3)_3$ (**1**) and sodium cyclopentadienylide with 4,4'-bis(phenylethynyl)biphenyl (**3a**) was carried out in toluene at 50°C for 3 days under nitrogen [4]. After the reaction, the reaction mixture was poured into excess *n*-hexane to precipitate a brown powdery polymer (**4a**) in 94% yield. **4a** was soluble in organic solvents such as chloroform, benzene, and tetrahydrofuran (THF). The number-average molecular weight (M_n) of **4a** was estimated as 9,600 by GPC on the basis of standard polystyrene samples. As expected, the molecular weight of **4a** never decreased even after the exposure of the isolated polymer under air for several days, indicating that **4a** was stable under air.

The structure of the obtained polymer was confirmed by ^1H-, ^{13}C-NMR, IR, and UV spectra. The ^1H-NMR spectrum of **4a** was estimated in comparison with that of the model compound (**6**) prepared from 2-(4-biphenyl)phenylacetylene (**5**) (Scheme III) [5]. In the ^1H-NMR spectrum of **6**, protons of biphenyl, phenyl groups adjacent to cobaltacyclopentadiene as well as those of triphenylphosphine were observed at 6.52-7.52ppm, and protons of cyclopentadienyl group were also observed at 4.76ppm (Figure 1). Similarly to the case of **6**, ^{1}H-NMR spectrum of **4a** showed the corresponding peaks around the same area. The integral ratio of these two peaks was appeared to be 37:5 which is close to the calculated value (33:5). If the present polymerization reaction accompanies a cyclotrimerization reaction of acetylene moieties as the side reaction to form the branched structure in the polymer chain, the relative intensity of the peak of cyclopentadienyl group for the phenyl groups should be decreased. Therefore, the good agreement of the integral ratio may support the formation of linear structure in the present reaction. At least, it can be noted that a gelation never took place within the examined reaction condition.

Scheme III



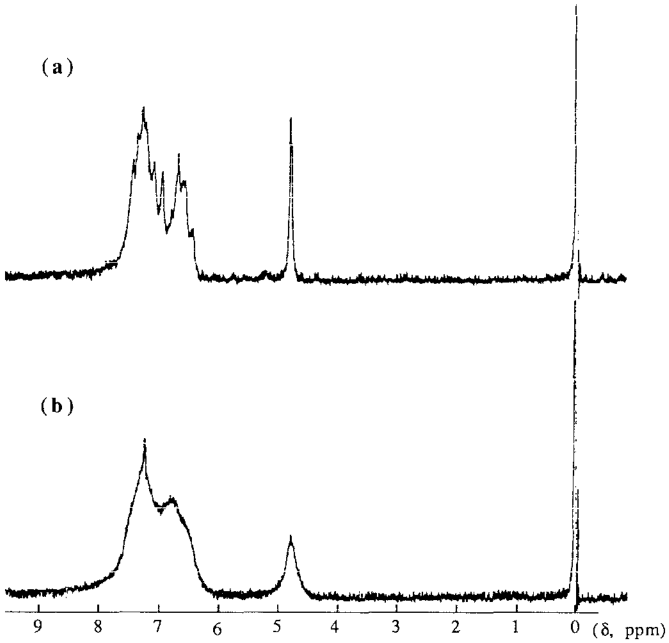


Figure 1 ^{1}H-NMR spectra of (a) a model compound (6) and (b) an organometallic polymer (4a).

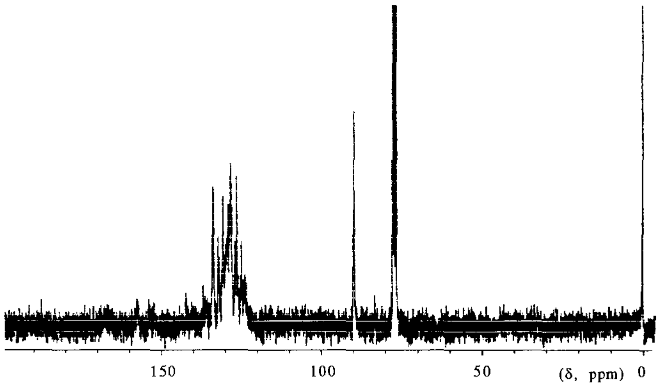


Figure 2 ^{13}C-NMR spectrum of 4a.

In the ^{13}C-NMR spectrum, a single peak at 89.7ppm attributable to the cyclopentadienyl group, and complex peaks at 122.6-137.3ppm to all the other carbons were observed (Figure 2).

It is said that a larger substituent on the starting acetylene favors the 2,5- rather than 3,4-position in the metallacycle [6]. However, **3a** seems to have two substituents having similar steric effect (phenyl vs. biphenyl). Therefore, at the present time, we believe that the structure of the polymer (**4a**) is composed of 2,5-, 2,4-, and 3,4-linked backbone.

Although the IR spectrum of **4a** showed no significant peaks to support the structure, a small peak at 2,213cm^{-1} for the $C\equiv C$ vibration of the monomer structure was detected. Therefore, the polymer structure includes the unreacted acetylene moieties at the end of the polymer chain. Judging from UV spectra of **4a** and **6**, polymer (**4a**) was found to have its $\pi-\pi^*$ transition absorption at longer wavelength (Figure 3). This result may indicate a somewhat higher conjugation of **4a** in comparison with **6**, in spite of the highly substituted cobaltacyclopentadiene rings.

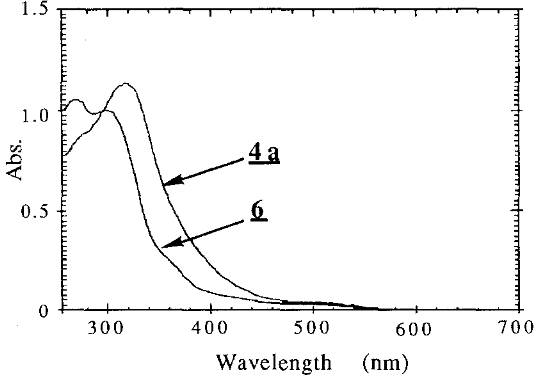


Figure 3 UV spectra of 4a and 6.

When the dependence of the molecular weight of the resulting polymer on the reaction time was evaluated by GPC, the molecular weight of the polymer was gradually increased as is usual for the step-growth polymerization (Figure 4).

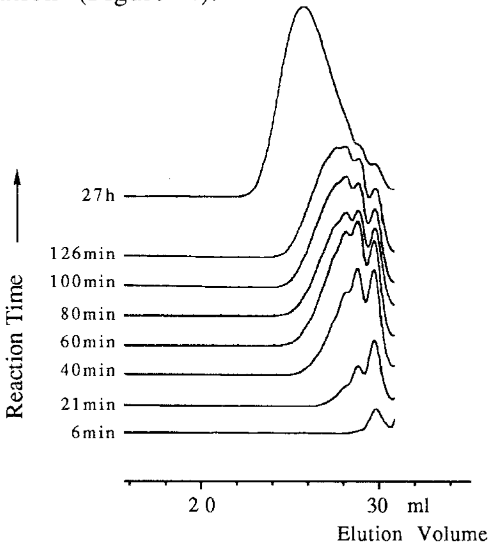


Figure 4 GPC traces of the polymerization reaction between 2 and 3a after designated reaction times.

Table I Polymerization between 2 and Diyne Monomers (3a-c).

run	R		Yield$^{a)}$ (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)$^{b)}$
1		(3a)	94	9600 (2.4)
2		(3b)	87	5100 (2.1)
3		(3c)	78	4200 (2.6)

a) Isolated yield, based on diyne.
b) Estimated by GPC (THF), polystyrene standard.

The results of polymerization reactions of three different diyne monomers (**3a**-**3c**) are summarized in Table I. Monomers having two acetylene moieties connected with π-system (**3a** and **3b**) gave the corresponding polymers (**4a** and **4b**, respectively) which may have organometallic conjugated backbone. The UV spectrum of the polymer (**4c**) did not show a specific red shift in comparison with those of **4a** and **4b**, as expected from the monomer structure (Figure 5).

Thermogravimetric analysis of **4a** was carried out under nitrogen (Figure 6). At 197°C, a weight loss started [7] and about 40wt% of the residue remained after the heating at 1000°C. When the pyrolysis was continued at 1000°C for 3hours, the weight loss was completed to give the residue in 9wt%. This result might indicate that some inorganic components remained after the pyrolysis. From the differential scanning calorimetric analysis of **4a**, no peaks were observed below 180°C. Therefore, **4a** has no Tg below the decomposition temperature.

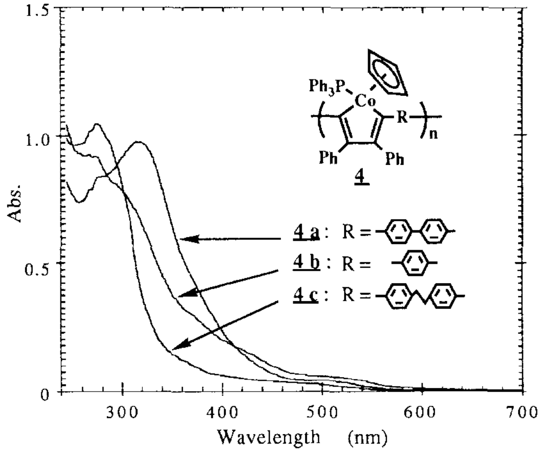


Figure 5 **UV spectra of organometallic polymers (4a-4c).**

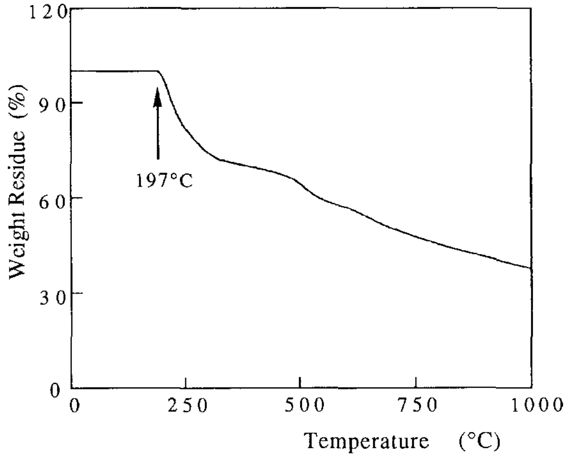


Figure 6 **Thermogravimetric analysis of 4a under air.**

Since the cobaltacyclopentadienes are known to have the reactivity towards small molecules having unsaturated compounds such as isocyanate, carbon disulfide, nitrile, and acetylene [8], the polymer obtained here may serve as a novel type of reactive polymer which can be replaced the backbone structure of the polymers [9]. The interesting physical properties and the reactivity of the organometallic polymers will be reported in near future.

Experimental Section

Materials and Instruments **1** was prepared as previously described and was recrystallized from ethanol [10]. Sodium cyclopentadienylide (2.0M in THF) was obtained from Aldrich Chemical Co. Toluene was dried over sodium and was distilled before use. All the other reagents were used as recieved.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a JEOL EX-60 or on a JEOL EX-90 instrument (60MHz or 90MHz, respectively, tetramethylsilane as an internal standard). ^{13}C-NMR spectrum was recorded in $CDCl_3$ on a JEOL EX-270 instrument (67.8MHz, tetramethylsilane as an internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. UV spectra were obtained on Shimadzu UV-2100 spectrophotometer in chloroform (0.020mg/ml). Gel permeation chromatographic analysis was carried out on a Tosoh CCPD (TSK gel G2500, G4000, and G5000, THF as an eluent) on the basis of standard polystyrene samples. TGA measurement was carried out on Seiko TG/DTA 220 instrument at a heating rate of 10°C/min. under nitrogen. DSC analysis was performed on Seiko DSC 220C at a heating rate of 5°C/min.

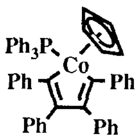
Synthesis of Diyne Monomers (3a-3c). To a mixture of 4,4'-diiodobiphenyl (4.06g, 10mmol), $PdCl_2$ (0.019g, 0.11mmol), CuI (0.010g, 0.05mmol), triphenylphosphine (0.112g, 0.43mmol), and diethylamine (60ml), phenylacetylene (3ml, 27mmol) was added which was stirred at 50°C for 12 hours. After the removal of the solvent, chloroform was added and was washed with water for 3 times. The chloroform layer was dried over $MgSO_4$ and was concentrated. Recrystallization from chloroform gave pure **3a** as a white crystal. Yield; 1.66g (4.6mmol, 46%); mp 246-247°C; ^{1}H-NMR (δ, ppm) 7.18-7.80 (m, C_6H_5, C_6H_4); IR (KBr) 3052, 2216, 1591, 1499, 918, 752, 690cm^{-1}. Similarly, **3b** and **3c** were obtained from phenylacetylene and the corresponding diiodide. **3b**; Yield; 92% (orange crystal); mp; 176-177°C (benzene) ; ^{1}H-NMR (δ, ppm) 7.06-7.74 (m, C_6H_5, C_6H_4); IR (KBr) 3054, 2206, 1595, 1514, 910, 845, 828, 752, 687cm^{-1}. **3c**; Yield; 42% (white crystal); mp 185-186°C (acetone) ; ^{1}H-NMR (δ, ppm) 2.93 (s, $-CH_2-$, 4H), 6.97-7.65 (m, C_6H_5, C_6H_4, 18H); IR (KBr) 3030, 2920, 2853, 2218, 1593, 1510, 1439, 833, 756, 693cm^{-1}.

Synthesis of Organometallic Polymers (4a-4c). To a 80ml toluene solution of **1** (14.10g, 16.0mmol), sodium cyclopentadienylide (2.0M in THF, 8.8ml, 17.6mmol) was added under nitrogen. After the reaction for 30 minutes, aqueous ammonium chloride (10%, 12ml) was added which was stirred for 5 minutes. To the resulting solution of **2**, **3a** (3.55g, 10.0mmol) was added and was heated at 50°C for 3 days. The obtained polymer solution was poured into *n*-hexane to give brown powdery polymer (**4a**). The obtained **4a** was further purified by the reprecipitation with acetone, and then with ethyl acetate. **4a**; Yield 6.96g (94%); ^{1}H-, ^{13}C-NMR, and UV spectra are shown in Figures 1, 2, and 3, respectively; IR (KBr) 3052, 3021, 1595, 1480, 1433, 1238, 1088, 1001, 810, 745, 696cm^{-1}. Anal. Calcd for $C_{51}H_{38}PCo$: C, 82.69; H, 5.17, Ash (Co), 7.96. Found: C, 83.95, H, 5.63, Ash, 10.52.

Similarly, **4b** and **4c** was obtained by the reaction of **2** with **3b** and **3c**, respectively. **4b**; Yield 87%; ^{1}H-NMR (δ, ppm) 4.70 (br, C_5H_5, 5H), 5.64-7.84 (m, C_6H_5, 29H); IR (KBr) 3054, 1591, 1481, 1435, 1190, 1119, 810, 750, 696cm^{-1}. **4c**; Yield 78%; ^{1}H-NMR (δ, ppm) 2.63 (m, $-CH_2-$, 4H), 4.79 (br, s, C_5H_5, 5H), 6.08-7.97 (m, C_6H_5, C_6H_4, 33H); IR (KBr) 3028, 2926, 1591, 1511, 1435, 754, 695cm^{-1}.

References and Notes

1. M. H. Chisholm, *Angew. Chem. Int. Ed. Engl.*, **30**, 673 (1991).
2. S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 3 (1984).
3. H. Yamazaki, Y. Wakatsuki, *J. Organomet. Chem.*, **139**, 157 (1977).
4. The molecular weight of the resulting polymer was somewhat effected when the amount of **1** used for polymerization was varied and was found to be reached to its maximum when a little excess amount (1.6eq.) of **1** was used. This might be based on the purity of monomer (**2**) prepared from **1** and sodium cyclopentadienylide.
5. For the preparation of the model complex (**6**), **5** and **2** were reacted under the same condition for the present polymerization reaction. In this case, **6** was isolated in 72% yield. Although, it is proper to consider that the isolated **6** consists of three isomeric mixtures, as shown in Scheme III, it was rather difficult to get information of the composition ratio due to the similar physical properties of three isomers.
6. Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, *J. Amer. Chem. Soc.*, **105**, 1907 (1983).
7. In ref. (3), the melting point (decomposition) of a model compound (**7**) has been reported to be 193-194°C, which is very close to 197°C. Therefore, the decomposition of **4a** might be started from the decomposition of the organometallic moieties in the main chain.



7

8. (a) P. Hong, H. Yamazaki, *Synthesis*, 50 (1977). (b) Y. Wakatsuki, T. Kuramitsu, H. Yamazaki, *Tetrahedron Lett.*, 4549 (1974).
9. A few examples of this kind of reactive polymers have been reported: (a) Y. Chujo, I. Tomita, Y. Hashiguchi, T. Saegusa, *Macromolecules*, **24**, 3010 (1991). (b) *Idem*, *Polym. Bull.*, **25**, 1 (1991).
10. M. Aresta, M. Rossi, A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).

Accepted December 25, 1992 S