Synthesis of Metal−Carbene Containing Polymers by Polycondensation of a Bifunctional Alkoxycarbene with Diamines

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Received April 20, 1999; Revised Manuscript Received January 21, 2000

ABSTRACT: Organometallic polymers containing Fischer-type aminocarbene moieties in the main chain were prepared for the first time by the polycondensation of a bifunctional alkoxycarbene with diamines. A bifunctional alkoxycarbene with the formula of $(CO)_5W[C(OCH_3)-p\text{-}C_6H_4-C(CH_3)_2-p\text{-}C_6H_4-C(OCH_3)]W(CO)_5$ gave the polymers by the condensation with hexamethylenediamine, 1,3-propanediamine, ethylenediamine, and *p*-xylylenediamine in THF at room temperature. The resulting polymers were stable under aerobic conditions and soluble in common organic solvents. The molecular weights of the polymers were estimated to be 2200−8800 by GPC measurements, and the structures of the polymers were characterized by NMR and IR spectroscopies.

Introduction

The tremendous strides in the organometallic chemistry in the past few decades enabled to generate a variety of organometallic polymers containing metallocene groups, metal−acetylide moieties, metal−arene and metal−metal bonds, and so on.[1] The production of these kinds of polymers has been encouraged by the following two motivations. One is the challenge to supply new materials with unique magnetic, electrical, optical, or redox properties as well as excellent mechanical or thermal properties. The other is the attempt to create new polymer skeletons by the appropriate reactions of highly reactive organometallic polymers.[2]

Among the organometallic compounds, metal−carbene complexes are of great interest due to their unique reactivities toward organic compounds. A wide range of reactions that are attainable only by the use of metal−carbene complexes have been developed.[3] Furthermore, a recent development in polymer chemistry has enabled to achieve various polymerization reactions that are induced by metal−carbene complexes.[4] Therefore, the polymers containing metal−carbene species are expected to serve as new reactive materials that would provide an unexpected polymer architecture by their appropriate polymer reactions. It is unfortunate, however, that there is only one example for the synthesis of a polymer having metal−carbene repeating units as side chains.[5] These backgrounds stimulated us to start a new program to synthesize novel organometallic polymers having metal−carbene moieties. Here we demonstrate a new convenient approach to aminocarbene containing polymers in the main chain.

Results and Discussion

Polymerization. In the present study, we applied a well-established reaction of traditional Fischer-type alkoxycarbenes to a polycondensation, expecting that the satisfactory stability of Fischer-type metal−carbenes[6] will facilitate the access to metal−carbene containing polymers. Our strategy to the target polymers involves the preparation of a bifunctional Fischer-type alkoxycarbene[7] and their condensation with primary diamines (Scheme 1).[8] The bifunctional monomer (**1**) was prepared according to the traditional methodology for the synthesis of alkoxycarbenes.[9] Thus, the appropriate dilithiated arene was treated with tungsten hexacarbonyl, which was followed by the reaction with Me_3OBF_4. Although monomer **1** rapidly decomposes in solution under air, it was stable enough to be treated without any special cautions if **1** was isolated as a solid. It was impossible to isolate a chromium counterpart of **1** due to its instability under the conditions employed.

Polycondensations were performed by mixing **1** and diamines in dry THF at room temperature under nitrogen. After the addition of amines, an immediate color change of the solution took place from dark red to yellow, meaning the rapid aminolysis of the carbene moieties.[10] Isolation of polymers **2** was carried out by evaporating the solvent or reprecipitation into hexane. Table 1 lists the examples of the polycondensation of **1** with primary diamines. In every case, both monomers were completely consumed, which was confirmed by TLC and/or GC analysis. Polymers with relatively high molecular weights were attainable by the polycondensation of **1** with hexamethylenediamine or *p*-xylylenediamine. Because the molecular weight of **1** (MW = 928) was estimated to be 450 by GPC measurement (THF, PSt standard), the absolute molecular weights of the polymers should be higher than ones estimated by GPC. When alkylenediamines were employed, the decrease in number of methylene groups tended to decreasing the molecular weight of the polymers.

Characterization. Figure 1 illustrates the ^{1}H NMR spectra of **2a** and a model compound (**3**) which was synthesized by the reaction of **1** with 2 equiv of butylamine. As shown in Figure 1b, the methoxy signal at 4.77 ppm that was observed in the ^{1}H NMR of **1** is absent, which clearly reveals that the alkoxycarbene moiety underwent quantitative aminolysis. Because of the substantial rotational barrier around the C−N bond of aminocarbenes,[11] the signal attributed to the methylene protons adjacent to nitrogen was separated into 3.2 and 3.9 ppm.[12] Similarly, two peaks due to the N−H protons were observed at 8.4 and 8.8 ppm. An analogous signal pattern was recognized in the ^{1}H NMR of the model compound **3** (Figure 1a). Namely, the signals for the N−H and methylene protons adjacent to nitrogen

10.1021/ma990599r CCC: $19.00
Published on Web 03/01/2000

Scheme 1

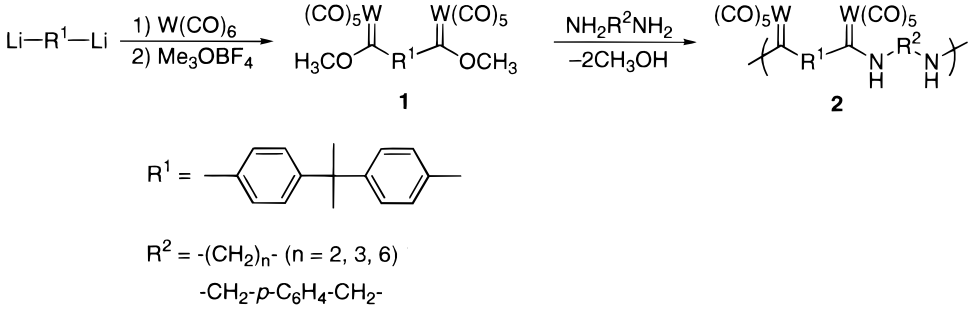

Table 1. Polycondensation of 1 with Diamines[a]

diamine	polymer	M_n[b]	M_w/M_n[b]
$H_2N(CH_2)_6NH_2$	**2a**	8700	2.70
$H_2N(CH_2)_3NH_2$	**2b**	5300	2.29
$H_2N(CH_2)_2NH_2$	**2c**	3900	2.15
$H_2NCH_2-p-C_6H_4-CH_2NH_2$	**2d**	8800	2.90

[a] In THF, RT, 3 h, [carbene] = [diamine] = 0.20 M. [b] By GPC (THF, PSt).

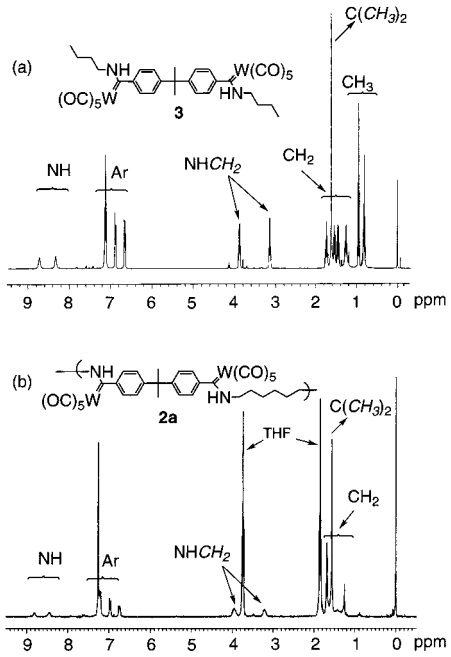

Figure 1. ^{1}H NMR spectra of (a) **3** (in $CDCl_3$) and (b) **2a** (in $CDCl_3$).

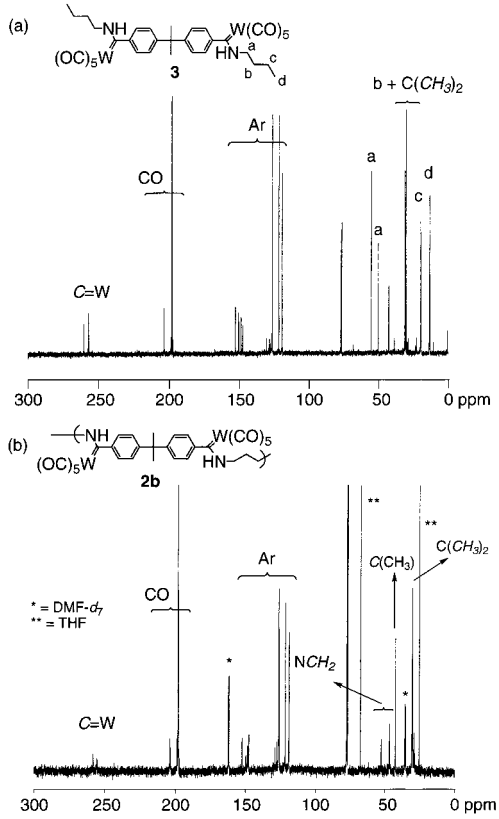

Figure 2. ^{13}C NMR spectra of (a) **3** (in $CDCl_3$) and (b) **2b** (in $CDCl_3$ containing a few drops of DMF-d_7).

were clearly resolved, and the peak positions of these signals are almost identical to those seen in the spectrum of **2a**. In the IR spectrum of **2a**, a sharp absorption peak at 2064 cm^{-1} and a very broad absorption band at around 1900 cm^{-1} with a shoulder (1975 cm^{-1}) were detected, meaning the presence of a metal−carbene moiety.[8b,12] A similar pair of the absorption due to the metal−carbonyl group was also detected in the IR spectrum of **3** (2062, 1973, and 1925 cm^{-1}). All these spectroscopic data readily lead to a conclusion that the main chains of the produced polymers involve the aminocarbene moieties formed by the aminolysis of alkoxycarbene units.

The ^{13}C NMR spectrum provided more detailed information on the structure of the polymer. The ^{13}C NMR spectra of **2b** and **3** are represented in Figure 2. The model compound **3** gave the signals attributed to the carbene carbon ($C_{carbene}$) and carbonyl carbons (CO) around 260 and 200 ppm, respectively. The separation of each signal is due to the presence of both cis and trans configurations with respect to the $C_{carbene}$−N bond.[13] For the same reason, the aromatic carbons gave a complicated spectral pattern as seen in the range between 125 and 155 ppm. In a similar way, doubly resolved signals appeared in each carbon of the butyl group (see the spectral data in the Experimental Section). An almost identical signal pattern was observed in the ^{13}C NMR spectrum of **2b**, as illustrated in Figure 2b. A distinct difference of **3** from **2b** in the spectrum is the more complicated appearance of signal patterns for each carbon. For example, the α-methylene carbon (NCH_2) gave four signals at 46.24, 46.79, 52.42, and 52.68 ppm. Four peaks were also detected for the carbonyl carbons. These indicate that the geometrical structure of one $C_{carbene}$−N bond (cis or trans) influences the magnetical environment of the neighboring carbene unit. Hence, the *β*-methylene carbon of **2b** should exist in three magnetically different environments because the neighboring two $C_{carbene}$−N bonds can take the following geometrical combinations: cis−cis, cis−trans, and trans−trans. This interpretation clearly explains the signal pattern of the

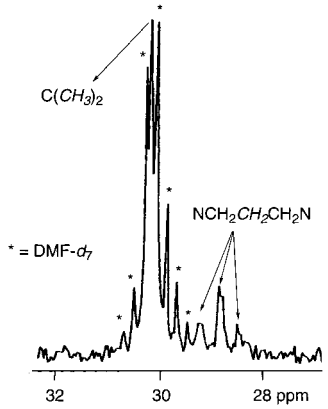

Figure 3. Expanded ^{13}C NMR spectrum of **2b** (in $CDCl_3$ containing a few drops of DMF-d_7).

β-methylene carbon as illustrated in the expanded ^{13}C NMR spectrum (Figure 3).

Polymer Properties. The polymers from **1** were soluble in the majority of solvents including CH_2Cl_2, THF, DMF, and acetone, partly soluble in $CHCl_3$, and insoluble in hexane and ether. Resulting from the moderate reactivity of aminocarbenes,[14] the polymer slowly decomposed in solution at room temperature if air is not excluded from the solution. Rapid degradation of the polymers was observed at elevated temperatures in solution. For example, heating of **2a** ($M_n = 6500$, $M_w/M_n = 2.41$) in DMF at 120 °C for 5 h gave low molecular weight oligomers with M_n and M_w/M_n of 1100 and 2.77, respectively. Emphasis should be placed on the fact that, in the solid state, the polymer was quite stable in air. Both the color and the NMR signals remained unchanged even if the polymers were kept under the aerobic conditions at ambient temperature for more than 1 year. At high temperatures, the polymers readily decomposed even in the solid state. For example, thermogravimetric analysis of **2a** in nitrogen showed that weight loss started at 90 °C. The 10% weight loss temperature of **2a** was at 235 °C, and the weight residue at 700 °C was 36%. DSC analysis of **2a** gave no peak corresponding to the glass transition temperature and melting point. Thanks to the relatively high molecular weight, **2a** exhibited film-forming ability; casting of a THF solution of **2a** gave a free-standing film.

In summary, we have demonstrated the first example for the synthesis of organometallic polymers having aminocarbene moieties in the main chain. The polymers with relatively high molecular weights and well-defined main-chain structures are readily obtained by the polycondensation of bifunctional alkoxycarbenes with diamines under mild conditions. The unique reactivity of aminocarbenes[14] would allow the application of these polymers as a new class of reactive polymers.

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL GSX-270 or EX-400 spectrometer. The ^{13}C NMR data of the produced polymers were obtained in $CDCl_3$ containing a few drops of DMF-d_7 in order to dissolve the polymers completely. NMR solvents were used without purification. All NMR spectra are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. Gas chromatographic analyses were performed by using a Shimadzu model GC-8A chromatograph. Melting points were measured using a Yanaco micro melting point apparatus. TGA and DSC analyses were conducted using a Perkin-Elmer TGA7 thermal analyzer and a Perkin-Elmer Pyris 1 differential scanning calorimeter, respectively. GPC analyses were carried out using two Shodex KF 805L columns (eluent, THF) after calibration with standard polystyrenes. Flash column chromatography was performed on Wakogel C-200 (100−200 mesh) at room temperature. Ether and THF were distilled under nitrogen from sodium benzophenone prior to use. $W(CO)_6$ was purchased from Aldrich and used without purification. Diamines were purified by the usual methods.

Preparation of 2,2-Bis(4-iodophenyl)propane. A mixture of 2,2-diphenylpropane (6.95 g, 35.4 mmol), I_2 (8.07 g, 31.8 mmol), $HIO_4 \cdot 2H_2O$ (2.59 g, 11.2 mmol), water (20 mL), acetic acid (100 mL), and sulfuric acid (3 mL) was stirred at 60 °C for 7 h. The reaction mixture was extracted with ether, and the ether phase was washed with 5% aqueous NaOH (three times) and then 5% aqueous $NaHSO_4$ (three times). The ether phase was dried over Na_2SO_4, filtered, and concentrated. The crude product was recrystallized with ether−hexane to give 2,2-bis(4-iodophenyl)propane as a white solid (11.1 g, 70%). Mp 115−118 °C. ^1H NMR ($CDCl_3$): δ 1.60 (s, 6H), 6.94 (d, 4H, $J = 8.0$ Hz), 7.58 (d, 4H, $J = 8.0$ Hz). ^{13}C NMR ($CDCl_3$): δ 30.3, 42.9, 91.2, 129.0, 137.1, 149.8. IR (KBr): 2967, 1484, 1003, 821 cm^{-1}. Mass spectrum (EI), *m/e* (relative intensity), 448 M^+ (63), 433 (100), 322 (35), 307 (73), 245 (18), 178 (28), 165 (17), 117 (7), 89 (9), 76 (9), 51 (4). Anal. Calcd for $C_{15}H_{14}I_2$: 40.21; H, 3.15. Found: C, 40.08; H, 3.18.

Preparation of 1. Into a suspension of 2,2-bis(4-iodophenyl)propane (4.48 g, 9.99 mmol) in ether (180 mL) was slowly added *t*-BuLi (1.59 N *n*-pentane-solution, 28 mL, 44.5 mmol) at −78 °C. The resulting suspension was stirred at −78 °C for 15 min and then warmed to room temperature over 30 min. $W(CO)_6$ (7.14 g, 20.3 mmol) was added to the solution at room temperature, and the suspension was stirred for an additional 1 h. After ether had been removed under reduced pressure, water (ca. 100 mL) was added, and insoluble materials were removed by Celite filtration. Me_3OBF_4 was added by portions until the solution became acidic. The solution was alkalized by K_2CO_3 and extracted with ether. The ether phase was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by a SiO_2 column chromatography (eluent: hexanes−ether) to give **1** as a red solid (373 mg, 16% yield). Mp 124−128 °C. ^1H NMR ($CDCl_3$): δ 1.73 (s, 6H, CH_3), 4.77 (s, 6H, OCH_3), 7.26 (d, 4H, Ar, $J = 8.1$ Hz), 7.59 (d, 4H, Ar, $J = 8.1$ Hz). ^{13}C NMR ($CDCl_3$): δ 30.5, 43.8, 69.5, 126.2, 127.4, 152.6, 154.2, 197.1, 203.8, 319.8. IR (KBr): 2960 (w), 2067 (s), 1980 (th), 1913 (vs), 1226 (s), 987 (w), 877 (w), 596 (w) cm^{-1}; mass spectrum (FAB), *m/e*, 928 M^+. Anal. Calcd for $C_{29}H_{20}O_{12}W_2$: C, 37.53; H, 2.17. Found: C, 37.75; H, 2.17.

Polymerization. The procedure for the polymerization of **1** with hexamethylenediamine is described as a typical example. Into a suspension of **1** (121 mg, 0.20 mmol) in THF was added a solution of hexamethylenediamine (23 mg, 0.20 mmol) in THF at room temperature, and the resulting solution was kept for stirring for 3 h. THF was removed under reduced pressure to give **2a**. Further purification was carried out by precipitation in hexane. **2a**: ^1H NMR ($CDCl_3$): δ 1.25−1.80 (m, NCH_2CH_2 and CH_3), 3.22 (m, NCH_2), 3.95 (m, NCH_2), 6.73 (m, Ar*H*), 6.97 (m, Ar*H*), 7.24 (m, Ar*H*) 8.44 (br s, NH), 8.81 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 24.28, 25.05, 25.16, 25.40, 27.78 ($NCH_2CH_2CH_2$), 29.58 (CH_3), 41.52 [$C(CH_3)_2$], 49.25, 54.90 (NCH_2), 118.58, 121.10, 125.10, 125.46, 125.98, 147.28, 147.43, 147.52, 148.59, 148.77, 151.64, 151.72 (Ar) 197.51, 197.79, 203.26, 203.56 (CO), 251.76, 252.74, 252.95 ($C_{carbene}$). IR (KBr): 3280 (m), 2920 (m), 2064 (s), 1981 (th), 1815 (vs), 598 cm^{-1} (s). **2b**: ^1H NMR ($CDCl_3$): δ 1.30−1.95 (m, $NCH_2CH_2CH_2$ and $C(CH_3)_2$), 3.42 (m, NCH_2), 3.32 (m, NCH_2), 3.92 (m, NCH_2), 4.13 (m, NCH_2), 6.55−7.35 (m, Ar*H*), 10.30 (br s, NH), 10.42 (br s, NH), 10.73 (br s, NH), 10.80 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 28.50, 28.87, 29.27 (NCH_2CH_2), 30.26 (CH_3), 42.25 [$C(CH_3)_2$], 46.24, 46.79, 52.42, 52.68 (NCH_2), 118.92, 118.99, 121.70, 125.94, 126.30, 147.59, 148.47, 149.53, 152.42 (Ar), 197.88, 198.25, 198.87, 203.55, 203.99 (CO), 255.35, 255.53, 258.20 ($C_{carbene}$). IR (KBr): 3370 (w), 3310 (w), 2965 (m), 2893 (m), 2064 (s), 1958 (th), 1925 (vs), 823 (m), 598 (s), 577 cm^{-1} (s). **2c**: ^1H NMR ($CDCl_3$): δ 4.26 (br s, NCH_2), 4.51 (br s, NCH_2), 6.55−7.59 (m, Ar*H*), 10.75 (br s, NH), 10.87

(br s, NH), 11.08 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 29.88 (CH_3), 41.90 [$C(CH_3)_2$], 47.99, 53.79, 54.25 (NCH_2), 118.61, 121.38, 121.53, 125.50, 125.92, 126.20, 147.58, 148.03, 149.25, 149.52, 151.84, 151.98, 152.11 (Ar), 197.35, 197.40, 197.74, 203.62, 203.28 (CO), 257.60, 257.75, 257.91, 260.16, 260.49 ($C_{carbene}$). IR (KBr): 2980 (m), 2064 (s), 1975 (th), 1918 (vs), 598 (s), 578 cm^{-1} (s). **2d**: ^{1}H NMR ($CDCl_3$): δ 4.40 (s, NCH_2), 5.24 (s, NCH_2), 6.65−7.61 (m, Ar), 10.22 (br s, NH), 10.26 (br s, NH), 10.99 (br s, NH), 11.12 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 30.18 (CH_3), 42.20 [$C(CH_3)_2$], 53.12, 58.80 (NCH_2), 119.32, 121.80, 125.92, 126.10, 127.64, 127.78, 128.09, 128.25, 134.46, 134.90, 135.11, 135.58, 147.55, 147.63, 148.35, 148.58, 149.69, 149.80, 152.24 (Ar), 197.78, 198.23, 203.42, 204.10 (CO), 256.44, 256.20, 257.20 ($C_{carbene}$). IR (KBr): 3370 (w), 3310 (w), 2965 (m), 2893 (m), 2064 (s), 1978 (th), 1920 (vs), 823 (m), 598 (s), 577 cm^{-1} (s).

Synthesis of the Model Compound 3. Into a solution of **1** (160 mg, 0.17 mmol) in dry THF (2 mL) was added butylamine (28.3 mg, 0.39 mmol) at room temperature. The resulting yellow solution was concentrated, and the residue was subjected to a SiO_2 column chromatography (eluent: hexanes−ether) to give **3** as yellow oil in 77% yield. ^{1}H NMR ($CDCl_3$): δ 0.81 (t, CH_3, J = 7.4 Hz), 0.95 (t, 6H, CH_3, J = 7.3 Hz), 1.20−1.32 (m, 4H, CH_2), 1.39−1.80 (m, 10H, CH_2 and $C(CH_3)_2$), 3.13 (q, 2.1H, NCH_2, J = 6.0 Hz), 3.88 (q, 1.9H, NCH_2, J = 6.4 Hz), 6.64−6.72 (m, 2H, Ar), 6.88−6.95 (m, 2H, Ar), 7.08−7.22 (m, 4H, Ar), 8.36 (br s, 1.05H, NH), 8.75 (br s, 0.95H, NH). ^{13}C NMR ($CDCl_3$): δ 13.43, 13.65, 19.61, 19.94, 30.48, 31.17, 31.32, 42.73, 50.37, 55.42, 119.57, 121.92, 126.67, 126.74, 147.81, 148.90, 149.16, 150.55, 150.08, 153.01, 198.14, 198.51, 203.92, 204.03, 257.74, 260.61. IR (neat): 3354 (m), 3289 (m), 2966 (s), 2936 (s), 2062 (s), 1973 (th), 1920 (vs), 1539 (s), 909 (m), 735 cm^{-1} (m). Mass spectrum (FAB), *m*/*e*, 1010 M^+.

Acknowledgment. The authors are grateful to Dr. Tadao Kobatake for obtaining the mass spectra. This work was supported by the Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science, Culture, and Sports of Japan.

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MA990599R