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Rhodium-Catalyzed Copolymerization of Norbornadienes and Norbornenes with Carbon Monoxide

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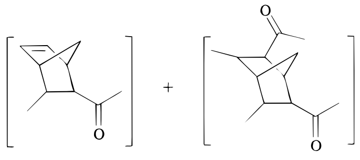
ABSTRACT: Alternate copolymerization of norbornadienes and norbornenes with carbon monoxide is catalyzed by a rhodium complex under water gas shift reaction conditions selectively to give corresponding polyketones in high yields. The structures of copolymers have been characterized by spectral analyses as well as chemical reactions. On the basis of the structures of isolated co-oligomers, a copolymerization mechanism is proposed.

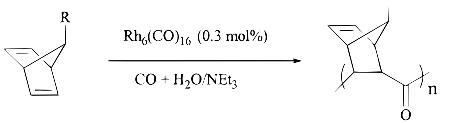
Introduction

Copolymerization of olefins and carbon monoxide is a topic of current academic and industrial interest. During the 1950s to 1970s, the copolymerization of olefins with carbon monoxide initiated by free radicals or induced by γ-rays under high pressure and high temperature was reported.[1] In recent years, use of transition-metal catalysts has been receiving much attention because the copolymerization catalyzed by transition-metal complexes occurs under a lower pressure and at a temperature as low as 25 °C, and the resultant polymers have a strictly alternating structure and significantly higher molecular weight.[2] Among transition metals, mono- and dicationic palladium complexes have predominantly been investigated and developed as an excellent catalyst for the perfectly alternating copolymerization of olefins with carbon monoxide.[3] The palladium catalytic system has also been extended to the copolymerization of dienes such as 1,4-pentadiene, 1,5-hexadiene, and 1,3-cyclopentadiene with carbon monoxide giving saturated poly(cyclic ketone)s.[4] Some reports described the copolymerization of norbornadiene with carbon monoxide in the presence of palladium complexes,[3a,5] but the resulting copolymers were characterized to be a mixture of structures **I** and **II** (Chart 1) except the alternating copolymers formed from 2,3-substituted norbornadiene derivatives.[6] Other than palladium complexes, few effective catalysts are known for the copolymerization of olefins with carbon monoxide, although the copolymerization of ethylene[7] and arylallenes[8] with carbon monoxide catalyzed by rhodium complexes has been reported. In the course of our study on carbonylation of alkynes under water gas shift reaction conditions,[9] we have found that norbornadienes can smoothly be copolymerized with carbon monoxide by the catalysis of rhodium complexes to produce alternating polyketones, in which one of the two carbon−carbon double bonds of norbornadiene remains intact (eq 1), and have already communicated a preliminary result.[10] In this paper, we wish to report the scope of the copolymerization of norbornadienes with carbon monoxide and the complete characterization of the copolymers, as well as the copolymerization of norbornene and its derivatives with carbon monoxide which occurs under the same reaction conditions. Also we focus on the initiation and termination of the copolymerization and discuss a possible copolymerization mechanism based on the structure of oligomeric products.

Chart 1



I **II**



1 **2** (1)

Experimental Section

IR spectra were determined with a Perkin-Elmer system 2000 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on either JEOL EX-270 (270 MHz) or JEOL JNM-LA600 (600 MHz) system in $CDCl_3$ with tetramethylsilane as an internal standard. Chemical shifts are given in ppm. High-resolution solid-state ^{13}C NMR (CPMAS) spectra were measured on a JEOL JNMGSX-270 with DOTY DSI-698 5 mm MAS probe. Thermogravimetric analysis (TGA) was carried out by using a Shimadzu thermal analysis system, TGA-50. Molecular weight measurements were performed by a Shimadzu LC-6AD liquid chromatograph using columns of Shimadzu GPC-805, −804 and −8025 with polystyrene standards. Mass spectra were measured on a JEOL MS−H600 (ionization mode: FAB; Xe gas) or a JEOL MS-DX300 (ionization mode: EI; 70 eV). Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer at the Material Analysis Center, ISIR, Osaka University.

Materials. Benzene was distilled before use. $Rh_6(CO)_{16}$ was prepared by the method previously reported.[11] 7-Phenylnorbona-2,5-diene (**1c**) was prepared as described in the literature.[12] 2,3-Substituted norbornadiene derivatives **1g**, **1h**, and **1i** were prepared by a Diels−Alder reaction between cyclopentadiene and the corresponding alkynes.[13] All other chemicals available commercially were used without further purification.

General Procedure for the Copolymerization of Norbornadienes and Norbornenes with Carbon Monoxide. In a stainless autoclave (100 mL), a mixture of norbornadiene derivative **1** (5 mmol), $Rh_6(CO)_{16}$ (0.015 mmol, 15 mg), triethylamine (2 mL), and water (1 mL) in benzene (15 mL) was stirred at 55 °C for 24 h under 100 atm of carbon monoxide. After venting the gases from the autoclave at room temperature, the reaction solution was poured into a large amount of

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methanol (ca. 200 mL). Precipitates formed were collected by filtration, washed several times with methanol, and dried in a vacuum at 50 °C overnight to give polyketone **2**. The reaction of norbornene derivatives was performed under the same conditions. In some cases, hexane was used instead of methanol for reprecipitation of polymers.

2a: isolated yield, 92%; GPC (polystyrene standard), M_w 24 500, $M_\mathrm{w}/M_\mathrm{n}$ 1.38; IR (KBr) 3059, 2975, 2935, 2873, 1715 (C═O), 1630, 1474, 1390, 1364, 1258, 1237, 1195, 1105, 1025, 898, 737, 710 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.20 (br, 2H, CH═CH), 4.10−3.60 (br, 1H, Bu^{t}OCH), 3.60−2.40 (br, 4H, 4CH), 1.17 (s, 9H, 3CH_3). ^{13}C NMR (150 MHz, NNE-EXMOD, $CDCl_3$) δ 207.2 (br, 1C, C═O), 135.5 (br, 2C, CH═CH), 83.0 (s, 1C, Bu^{t}O*C*H), 73.7 (s, 1C, C), 59.0−49.0 (br, 4C, 4CH), 28.0 (s, 3C, 3CH_3); ^{13}C NMR (68 MHz, solid) δ 207.6 (br, *C*═O), 135.6 (br, *C*H═*C*H), 84.8 (s, Bu^{t}O*C*H), 74.0 (s, *C*(CH_3)$_3$), 51.8 (s, 4*C*H), 28.9 (s, C(*C*H_3)$_3$). Anal. Calcd for $[C_{12}H_{16}O_2]_n$: C, 74.96; H, 8.39. Found: C, 74.60; H, 8.71. Thermogravimetric analysis (TGA) revealed that **2a** appeared to degrade by a two-step process with a mass loss of 72% at the first degradation step. This mass loss rate is correspondent to the value (C_5H_5-O^{t}Bu/$C_{12}H_{16}O_2$ = 0.719) which is calculated for the case where all of the *tert*-butoxycyclopentadiene moieties (C_5H_5O^{t}Bu)$_n$ of **2a** are liberated by a retro Diels−Alder reaction.[6]

2b: isolated yield, 95%; insoluble in organic solvents; IR (KBr) 3060, 2972, 2925, 2875, 1708 (C═O), 1632, 1458, 1364, 1232, 1121, 1023, 906, 805, 709 cm^{-1}; ^{13}C NMR (68 MHz, solid) δ 209.1 (*C*═O), 139.9 (*C*H═*C*H), 57.4, 47.6, 37.2, 12.9. Anal. Calcd for $[C_8H_8O]_n$: C, 79.97; H, 6.71. Found: C, 79.57; H, 6.35.

2c: isolated yield, 85%; GPC (polystyrene standard), M_w 9000, $M_\mathrm{w}/M_\mathrm{n}$ 1.38; IR (KBr) 3060, 3027, 2972, 2891, 1713 (C═O), 1602, 1497, 1448, 1367, 1156, 1121, 1031, 816, 730, 699 (phenyl) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (br, 5H, phenyl), 6.05 (br, 2H, C*H*═C*H*), 3.74−2.00 (br, 4H, 4CH), 1.58 (br, 1H, C*H*Ph); ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.3 (br, *C*═O), 135.4 (br, *C*H═*C*H), 140.1, 128.5, 127.6, 126.8 (phenyl carbons), 57.5−51.6 (br, 4*C*H), 14.8 (s, *C*HPh). Anal. Calcd for $[C_{14}H_{12}O]_n$: C, 85.68; H, 6.16. Found: C, 85.35; H, 6.41.

2d: isolated yield, 90%; GPC (polystyrene standard), M_w 25 500, $M_\mathrm{w}/M_\mathrm{n}$ 1.60; IR (KBr) 3022, 2986, 2915, 2856, 1710 (C═O), 1461, 1446, 1371, 1254, 1126, 1094, 1012, 915, 756, 707 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60−6.90 (br, 4H), 4.60−2.50 (br, 4H, 4CH), 2.10−1.20 (br, 6H, 2CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.0 (br, *C*═O), 147.9, 126.1, 120.5, 115.8, 60.0, 48.3, 20.8. Anal. Calcd for $[C_{15}H_{14}O]_n$: C, 85.68; H, 6.71. Found: C, 85.70; H, 6.55.

2e: isolated yield, 75%; GPC (polystyrene standard), M_w 4300, $M_\mathrm{w}/M_\mathrm{n}$ 1.29; IR (KBr) 2991, 2956, 1760 (OC═O), 1715 (C═O), 1633, 1485, 1434, 1372, 1198, 1165, 1094, 1016, 959, 899, 822 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (br, 2H), 4.10−2.70 (br, 4H), 2.25 (br, 6H, 2C*H*$_3$), 1.75 (br, 2H, C*H*$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.2 (br, *C*═O), 169.1, 141.7, 120.3, 54.3, 45.8, 20.8 (*C*H_2). Anal. Calcd for $[C_{15}H_{14}O]_n$: C, 67.13; H, 4.93. Found: C, 66.90; H, 4.93.

2f: isolated yield, 81%; GPC (polystyrene standard), M_w 2600, $M_\mathrm{w}/M_\mathrm{n}$ 1.24; IR (KBr) 3050, 3027, 1774 (weak), 1704 (C═O), 1626, 1462, 1352, 1281, 1188, 1156, 1124, 977, 904, 852, 755, 666 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80−6.80 (br, 4H), 5.80−5.20 (br, 2H), 3.50−2.50 (br, 1.50H), 2.05 (br, 0.5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.2 (*C*═O), 144.4, 126.8, 119.3, 80.8, 55.3, 31.9 (weak). Anal. Calcd for $[C_{11}H_8O_2]_n$: C, 76.73; H, 4.68. Found: C, 76.96; H, 4.53.

2g: isolated yield, 73%; GPC (polystyrene standard), M_w 2600, $M_\mathrm{w}/M_\mathrm{n}$ 1.25; IR (KBr) 2957, 1759 (weak), 1703 (C═O), 1618, 1361, 1291, 1188, 1144, 1067, 903, 841, 729 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.50−4.50 (br, 2H), 3.20−2.00 (br, 1.80H), 1.87 (br, 0.2H). Anal. Calcd for $[C_9H_4O_2F_6]_n$: C, 41.88; H, 1.56. C, 40.64; H, 1.89.

2h: isolated yield, 81%; GPC (polystyrene standard), M_w 2500, $M_\mathrm{w}/M_\mathrm{n}$ 1.20; IR (KBr) 2995, 2985, 2954, 1774 (weak), 1730 (ester), 1708 (C═O), 1624, 1455, 1267, 1154, 1095, 1022, 780, 756 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 (br, 4H, 2OC*H*$_2$CH$_3$), 3.80−2.80 (br, 4H), 2.40−1.50 (br, 2H), 1.25 (br, 6H, 2OC*H*$_2$CH$_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.5 (*C*═O), 164.0 (O*C*═O), 145.5 (*C*═*C*), 61.2 (O*C*H$_2$CH$_3$), 56.0−44.0 (m, *C*H and *C*H$_2$), 29.0 (weak). Anal. Calcd for $[C_{14}H_{16}O_5]_n$: C, 63.63; H, 6.10. Found: C, 63.31; H, 6.24.

2i: isolated yield, 93%; GPC (polystyrene standard), M_w 2300, $M_\mathrm{w}/M_\mathrm{n}$ 1.17; IR (KBr) 2998, 2955, 1775 (weak), 1732 (ester), 1705 (C═O), 1622, 1435, 1338, 1270, 1195, 1154, 1118, 1095, 1021, 781, 757 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (br, 6H, 2OC*H*$_3$), 3.75−2.75 (br, 4H), 2.40−1.50 (br, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.7 (*C*═O), 164.4 (O*C*═O), 146.4 (*C*═*C*), 52.2 (O*C*H$_3$), 55.0−43.0 (m, *C*H and *C*H$_2$), 29.5 (weak). Anal. Calcd for $[C_{12}H_{12}O_5]_n$: C, 61.02; H, 5.12. Found: C, 60.70; H, 4.99.

2j: isolated yield, 87%; GPC (polystyrene standard), M_w 2300, $M_\mathrm{w}/M_\mathrm{n}$ 1.29; IR (KBr) 2955, 2891, 1732 (ester), 1715 (C═O), 1435, 1352, 1206, 1101, 1057, 932 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.65 (br, 6H, 2OC*H*$_3$), 3.40−1.20 (8H, 6C*H* and C*H*$_2$). Anal. Calcd for $[C_{12}H_{14}O_5]_n$: C, 60.50; H, 5.92. Found: C, 60.21; H, 6.15.

2k: isolated yield, 75%; GPC (polystyrene standard), M_w 2600, $M_\mathrm{w}/M_\mathrm{n}$ 1.24; IR (KBr) 2956, 2883, 1790 (weak), 1732 (ester), 1715 (C═O), 1634, 1435, 1301, 1266, 1209, 1139, 1049, 967, 783 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (br, 6H, 2OC*H*$_3$), 2.90−1.20 (8H, 6C*H* and C*H*$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.5 (*C*═O), 162.0 (O*C*═O), 142.0 (*C*═*C*), 52.3 (O*C*H$_3$), 48.0−25.0 (m, *C*H and *C*H$_2$). Anal. Calcd for $[C_{14}H_{14}O_5]_n$: C, 64.12; H, 5.38. Found: C, 63.82; H, 5.62.

2l: isolated yield, 80%; GPC (polystyrene standard), M_w 2100, $M_\mathrm{w}/M_\mathrm{n}$ 1.21; IR (KBr) 2962, 2882, 1763 (weak), 1704 (C═O), 1451, 1424, 1361, 1297, 1180, 1117, 939, 866, 802 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.00−1.00 (5C*H* and 2C*H*$_2$), 2.15 (C*H*$_3$). Anal. Calcd for $[C_{10}H_{12}O_2]_n$: C, 73.15; H, 7.37. Found: C, 72.91; H, 7.32.

2m: isolated yield, 67%; GPC (polystyrene standard), M_w 3000, $M_\mathrm{w}/M_\mathrm{n}$ 1.29; IR (KBr) 3058, 2962, 2881, 1770 (weak), 1704 (C═O), 1682 (C═O) 1597, 1580, 1448, 1360, 1296, 1222, 1181, 1004, 943, 886, 739, 695 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00−7.00 (br, 5H, C_6*H*$_5$), 3.50−1.00 (9H, 5C*H* and 2C*H*$_2$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.9 (*C*═O), 200.9 (C═O), 136.4, 133.4, 129.0, 58.7, 54.0, 49.2, 45.0−35.0, 33.9. Anal. Calcd for $[C_{15}H_{14}O_2]_n$: C, 79.62; H, 6.24. Found: C, 79.54; H, 6.52.

2n: isolated yield, 91%; IR (KBr) 2954, 2872, 1791, 1722, 1713 (C═O), 1476, 1455, 1355, 1299, 1240, 1171, 1141, 1037, 1008, 976, 951, 876, 799 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70−2.10 (2H), 1.90−0.90 (8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.0 (several peaks, *C*═O), 176.8 (several peaks, lactone, O*C*═O), 142.5 and 119.0 (several peaks, *C*═*C*), 57.0−36.6 and 14.4 (*C*H), 39.6−26.7 and 22.5 (*C*H$_2$). Mass (ionization mode, FAB): *m*/*z* 121, 177, 215, 229, 243, 244, 321 (366 − 45), 337, 366, 367, 443 (488 − 45), 489, 565 (610 − 45), 610, 687 (732 − 45), 732. Anal. Calcd for $[C_8H_{10}O]_n$: C, 78.65; H, 8.25. Found: C, 78.41; H, 8.54.

2n′: isolated yield, 42%; IR (KBr) 2958, 2874, 1786, 1723, 1453, 1305, 1228, 1173, 1140, 1039, 1008, 948, 916, 869, 733 cm^{-1}; ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.4 (O*C*═O), 142.3 and 141.8 (C═*C*O), 120.6 and 120.4 (*C*═CO), 48.9 and 48.7 (*C*H), 45.1 and 44.0.9 (*C*H), 42.8 (*C*H), 40.6 and 40.5 (*C*H), 40.2 and 39.7 (*C*H$_2$), 39.9 and 39.4 (*C*H), 36.6 and 36.3 (*C*H), 35.4 and 35.3 (*C*H$_2$), 34.1 and 34.0 (*C*H$_2$), 29.2 and 29.1 (*C*H$_2$), 28.2 and 28.0 (*C*H$_2$), 27.8 (*C*H$_2$), 27.3 and 27.2 (*C*H$_2$). Mass (ionization mode, EI 70 eV): *m*/*z* 244. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.52; H, 8.44.

Reaction of 2a with Bromine. A solution of Br_2 (0.10 g, 1.25 mmol) in THF (1 mL) was added dropwise to a solution of **2a** (0.10 g, 0.52 mmol; M_w 15 700, $M_\mathrm{w}/M_\mathrm{n}$ 1.34) in THF (5 mL). After being stirred at room temperature for 10 h, the orange reaction solution was evaporated and was then dissolved in 1 mL of THF. The solution was poured into 20 mL of methanol. Precipitates formed were collected by filtration, washed several times with methanol, and dried in a vacuum at 50 °C overnight to give poly(dibromoketone) **3a** (0.154 g, 84% yield).

3a: GPC (polystyrene standard), M_w 23 660, $M_\mathrm{w}/M_\mathrm{n}$ 1.47; IR (KBr) 2976, 2870, 1715 (C═O), 1474, 1393, 1366, 1265, 1191, 1103, 1042, 942, 900, 741, 710 cm^{-1}; ^{1}H NMR (600 MHz,

C_4D_8O) δ 4.32 (br, 2H, BrCH−CHBr), 4.15−2.00(br, 5H, Bu^{t}OCH and 4CH), 0.94 (s, 9H, 3CH_3); ^{13}C NMR (150 MHz, C_4D_8O) δ 207.5 (br, C═O), 137.4 and 132.1 (dbr, BrHC−CHBr), 83.9 and 82.8 (ds, Bu^{t}OCH), 73.7 (s, C), 59.0−49.0 (br, 4CH), 28.4 and 27.8 (ds, 3CH_3). Anal. Calcd for $[C_{12}H_{16}O_2Br_2]_n$: C, 40.94; H, 4.58; Br, 45.39. Found: C, 40.81; H, 4.30; Br, 45.24.

Reaction of 2a with $LiAlH_4$. To a solution of **2a** (0.30 g, 1.55 mmol; M_w 24 500, M_w/M_n 1.38) in THF (20 mL) at 0 °C was added $LiAlH_4$ (15 mL, 1.0 *M* solution in THF) slowly under argon. The mixture was then stirred at 65 °C for 24 h, and the resulting solution was treated with a solution of HCl in H_2O/MeOH. Precipitates formed were collected by filtration and washed several times with water and then methanol to give off-white powders. The powders were again dissolved in 1 mL of THF and the suspension was filtrated with a 0.2 μm filter. The THF solution was poured into 30 mL of methanol. Precipitates were collected by filtration, washed several times with methanol, and dried in a vacuum overnight to give poly(alcohol) **4a** (0.273 g, 90% yield).

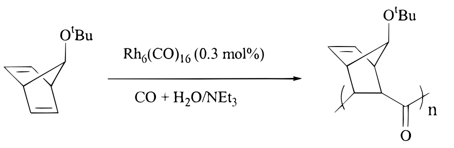
4a: GPC (polystyrene standard), M_w 31 200, M_w/M_n 1.48; IR (KBr) 3395 (OH), 3058, 2975, 2933, 2873, 1473, 1390, 1363, 1256, 1237, 1196, 1097, 1024, 901, 740 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.08 (br, 2H, CH═CH), 4.15−2.00 (br, 7H), 1.10 (s, 9H, 3CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.0 (br, HC═CH), 83.8 (br, Bu^{t}OCH), 79.7 (br, CHOH), 52.0−40.0 (br, 4CH), 28.5 (s, 3CH_3). Anal. Calcd for $[C_{12}H_{18}O_2]_n$: C, 74.19; H, 9.33. Found: C, 73.91; H, 9.10.

Reaction of 4a with PhCOCl. To a solution of **4a** (0.20 g, 1.0 mmol; M_w 31 200, M_w/M_n 1.48) in THF (10 mL) were added PhCOCl (5 mL) and then dimethylanilline (5 mL) under argon. After the mixture was stirred at room temperature for 12 h, water was added at 0 °C. The product was extracted with three 5 mL portions of ethyl ether and was precipitated by methanol. Precipitates were collected by filtration, washed several times with methanol, and dried in a vacuum overnight to give poly(ester) **5a** (0.231 g, 78% yield).

5a: GPC (polystyrene standard), M_w 55 200, M_w/M_n 1.43; IR (KBr) 3057, 2975, 2873, 1722 (OC═O), 1620, 1471, 1455, 1392, 1363, 1277, 1196, 1099, 1027, 901, 712 cm^{-1}; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.20 (br, 5H), 6.10 (br, 2H, CH═CH), 4.15−2.00 (br, 5H, Bu^{t}OCH and 4CH), 1.10 (s, 9H, 3CH_3). Anal. Calcd for $[C_{19}H_{22}O_3]_n$: C, 76.48; H, 7.43. Found: C, 76.29; H, 7.68.

Results and Discussion

In the presence of a catalytic amount of $Rh_6(CO)_{16}$, 7-*tert*-butoxynorborna-2,5-diene (**1a**) smoothly reacted with carbon monoxide in benzene under water gas shift reaction (WGSR) conditions to give corresponding copolymer **2a** in 92% yield (eq 2). Copolymer **2a** is soluble in a variety of organic solvents such as acetone, chloroform, benzene, and THF, and the GPC analysis (polystyrene standards) indicated **2a** to be a polymer with a molecular weight of 24 500 and a molecular weight distribution of M_w/M_n = 1.38. IR, ^{1}H NMR, and ^{13}C NMR spectra as well as thermogravimetric analysis supported the structure of **2a** (see ref 10 and Experimental Section).

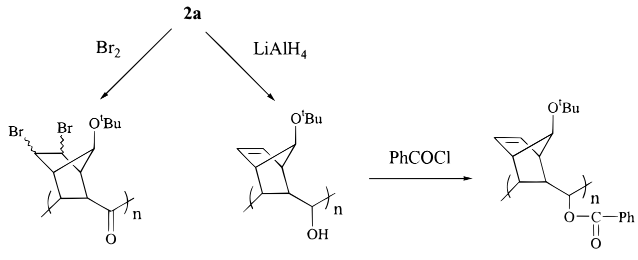


(2)

1a **2a** (92% yield)

Because **2a** has one C═O group and one C═C bond in the repeating unit, it may be easily modified chemically. Thus, we examined the chemical reactivity of **2a** to confirm the polymer structure of **2a**, and simultaneously to convert it into functionalized polymers. As shown in Scheme 1, treatment of **2a** with an excess of bromine at room temperature gave poly(dibromoketone) **3a** in 84% yield. The reaction of **2a** with $LiAlH_4$ in THF proceeded at 65 °C selectively to give poly(alcohol) **4a** in 90% yield. The IR, ^{1}H NMR, and ^{13}C NMR spectra as well as elemental analyses of **3a** and **4a** supported their structures (see Experimental Section). In addition, when poly(alcohol) **4a** was treated with PhCOCl in *N*,*N*-dimethylaniline/THF, poly(ester) **5a** was obtained in 78% yield. The ^{1}H NMR spectrum of **5a** revealed that one of the two C═C bonds in the norbornadiene skeleton remained intact since a ratio of 2:5 for two olefinic protons to five aromatic protons was recorded. The formation of polymers **3a**, **4a**, and **5a** from **2a** is consistent with the regular structure of **2a**.

Scheme 1

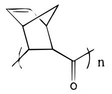
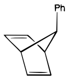
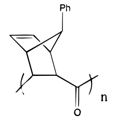
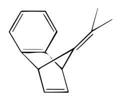
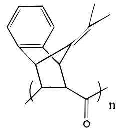
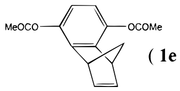
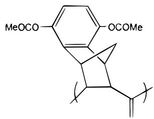
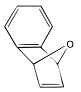
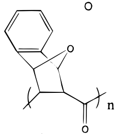
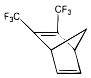
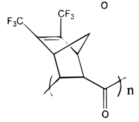
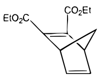
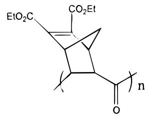
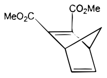
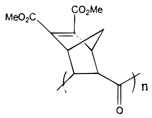
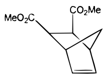
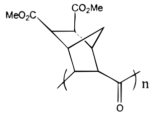
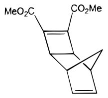
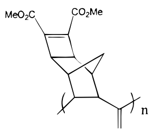
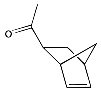
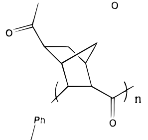
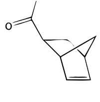
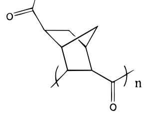


3a (84% yield) **4a** (90% yield) **5a** (78% yield)

Besides 7-*tert*-butoxynorborna-2,5-diene (**1a**), norbornadiene itself (**1b**) and other derivatives **1c**−**i** were also copolymerized with carbon monoxide under the same reaction conditions. Results obtained from the copolymerization of norbornadienes **1b**−**i** with carbon monoxide are summarized in Table 1. The reaction of norbornadiene **1b** gave copolymer **2b** which is almost insoluble in organic solvents. This is possibly due to cross-linking of the polymer like partial structure II in Chart 1. However, the high-resolution solid-state ^{13}C NMR (CPMAS) spectrum and the elemental analysis of the polymer suggested **2b** to have a similar structure as **2a**. 7-Phenylnorborna-2,5-diene (**1c**), which was prepared by treatment[11] of 7-*tert*-butoxynorborna-2,5-diene with PhMgBr, also reacted with carbon monoxide to give copolymer **2c** in a good yield with a molecular weight of M_w 9000 (M_w/M_n 1.38). Interestingly, 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (**1d**), having a norbornadiene skeleton, was copolymerized with carbon monoxide to give copolymer **2d** with a high molecular weight (M_w = 25 500) in a high yield. In contrast to **1d**, the reactions of **1e** and **1f** which have a similar skeleton to **1d** gave the corresponding copolymer in a good yield but with a lower molecular weight (Table 1, entries 4 and 5). Similarly, 2,3-substituted norbornadienes **1g**, **1h**, and **1i** reacted with carbon monoxide smoothly to give copolymers **2g**, **2h**, and **2i** in good yields, but also with low molecular weights (entries 6−8). These experimental results suggest that the chain growth of copolymers seems to be affected strongly by the substituents on the norbornadiene skeleton in the present reaction system.

Under the same reaction conditions, we examined the reaction of norbornenes and found that norbornenes **1j**−**m** were also copolymerized with carbon monoxide. The results (entries 9−12) are added to Table 1. All the reactions proceeded smoothly to give the corresponding copolymers in good yields but with lower molecular weights. In these reactions, the starting materials disappeared completely after 24 h although the forma-

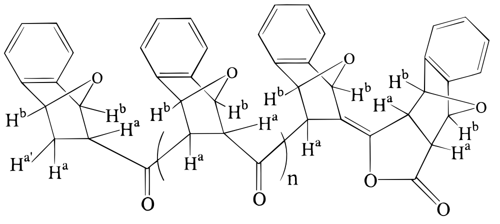
Table 1. Copolymerization of Norbornadienes and Norbornenes with Carbon Monoxide Catalyzed by a Rhodium Carbonyl Complex[a]

Entry	Monomer **1**	Copolymer **2**	Isolated yield of **2** (%)	Molecular weight of **2** M_w (M_w/M_n)
1	 (**1b**)	 (**2b**)	>95	*insoluble*
2	 (**1c**)	 (**2c**)	85	9,000 (1.38)
3	 (**1d**)	 (**2d**)	90	25,500 (1.60)
4	 (**1e**)	 (**2e**)	75	4,300 (1.29)
5	 (**1f**)	 (**2f**)	81	2,600 (1.24)
6	 (**1g**)	 (**2g**)	73	2,600 (1.25)
7	 (**1h**)	 (**2h**)	81	2,500 (1.20)
8	 (**1i**)	 (**2i**)	93	2,300 (1.17)
9	 (**1j**)	 (**2j**)	87	2,300 (1.29)
10	 (**1k**)	 (**2k**)	75	2,600 (1.24)
11	 (**1l**)	 (**2l**)	80	2,100 (1.21)
12	 (**1m**)	 (**2m**)	67	3,000 (1.29)

[a] Reaction conditions: monomer **1**, 5 mmol; $Rh_6(CO)_{16}$, 15 mg (0.015 mmol, 0.3 mol %); benzene, 15 mL; triethylamine, 2 mL; water, 1 mL; reaction temperature 55 °C; CO pressure, 100 atm; reaction time, 24 h.

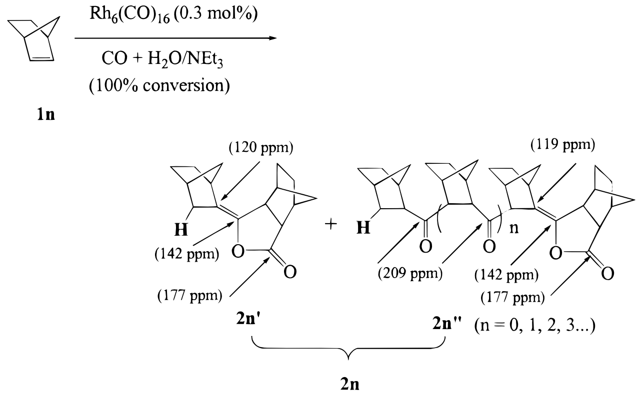
tion of some co-oligomers were observed. The IR spectra of **2f** and **2g** with lower molecular weights showed a strong absorption due to ν_{CO}, as well as a weak but significant absorption at 1774 and 1759 cm^{-1}, respectively, which might be caused by a cyclic ester group, suggesting the existence of a cyclic ester terminus in these copolymers.[14] Information about initiation and termination may provide an important insight into the copolymerization mechanism. Taking a close mechanistic relationship between oligomerization and polymerization into consideration, we focused on the process of co-oligomerization to envisage the mechanism of the copolymerization. Thus, we carefully characterized oligomeric products by spectral analyses. Because of the lower molecular weight of **2f**, the ^1H NMR spectrum of **2f** showed a distinct signal at 2.05 ppm which can be

Chart 2. Possible Structure of Copolymer 2f



2f

Scheme 2. Co-oligomers and Codimer of Norbornene with Carbon Monoxide and Their ^{13}C NMR Data



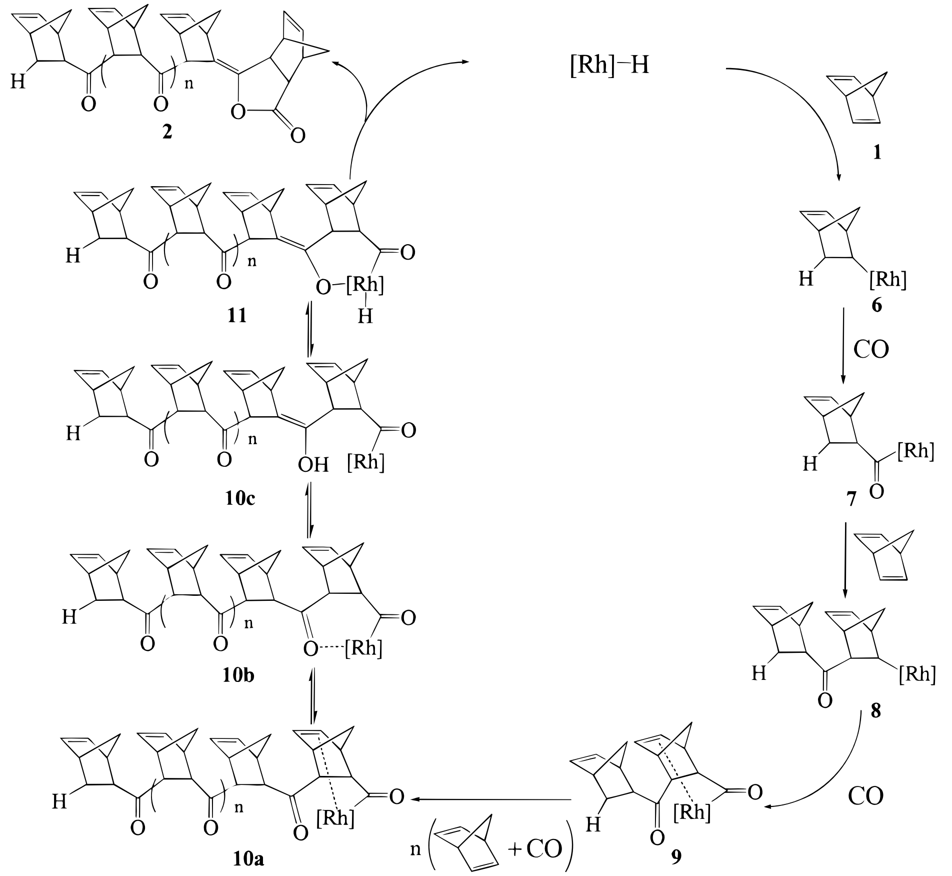
assigned to the terminal protons of norbornene skeleton. Together on the basis of its IR spectral data, the structure of copolymer **2f** could be presumed as shown in Chart 2, that is, a polyketone structure with two different terminal groups. In fact, the ^{1}H NMR spectrum of **2f** demonstrated that the intensity of the protons at 5.50 ppm (H^b of the polyketone) is equal to the sum of the intensities for the protons at 3.30 ppm (H^a of the polyketone) and at 2.05 ppm (H$^{a'}$ of the terminal group). The ^{1}H NMR spectrum of **2g** exhibited a similar result.

When the reaction of norbornene **1n** was performed under the same reaction conditions as that for norbornadiene, no high molecular weight copolymers were detected neverthless the complete conversion of **1n**. As illustrated in Scheme 2, only co-oligomers **2n** were formed. These co-oligomers were recorded on mass spectroscopy as a series of peaks, which consist of *m/z* 244 [2 × (**1n** + CO)] (relative intensity, 100%), 366 [3 × (**1n** + CO)] (relative intensity, 38%), 488 [4 × (**1n** + CO)] (relative intensity, 24%), 610 [5 × (**1n** + CO)] (relative intensity, 20%), and 732 [6 × (**1n** + CO)] (relative intensity, 13%). The peaks for 7- and 8-mers have a very low intensity (ca. 8%). The highest intensity was observed for the codimer of $m/z = 244$. The IR spectrum of the co-oligomers exhibited strong bands at 1791 and 1722 cm^{-1} and at 1713 cm^{-1}, in which the former two bands are attributed to γ-lactone and the latter to a ketonic carbonyl group.[14] The assignment is supported by the ^{13}C NMR spectra which exhibited signals at 209, 177, 142, and 119 ppm by a quaternary carbon observation measurement. The signals at 209 and 177 ppm are attributable to the carbonyl group and cyclic ester group of terminal lactone, respectively. The signals at 142 and 119 ppm may be assigned to the two sp^2 carbons of the terminal γ-unsaturated lactone.

To know the structures of co-oligomers, we isolated codimer **2n′**, which has an *m/z* of 244 from a mixture of co-oligomers **2n** by a preparative silica gel plate chromotography. The structure of **2n′** was inferred from the IR and ^{1}H and ^{13}C NMR spectra as well as the comparison with the spectral data previously reported[14] as shown in Scheme 2. In IR spectrum of **2n′**, two sharp bands at 1786 and 1723 cm^{-1} may be attributable to γ-lactone with an exocyclic double bond. In the spectrum, the absorption at 1713 cm^{-1} due to a ketonic carbonyl group was not observed. The ^{13}C NMR of **2n′** exhibited each pair of signals due to *E* and *Z* isomers in a ratio of ca. 1:2. In contrast to that of **2n**, the signal at 209 ppm disappeared completely, and a signal at 177 ppm due to a cyclic ester group was recorded as well as signals at 142 and 120 ppm due to the two sp^2 carbons of the exocyclic double bond. On the basis of these data, we have concluded **2n′** to be a codimer between each two molecules of norbornene and carbon monoxide, which has a γ-lactone skeleton with an exocyclic double bond.

The formation of **2n** suggests that a [Rh]−H species might initiate the present copolymerization of norbornene with carbon monoxide. Although a chain transfer process triggered by H_2 could be also taken into considerations, Sen and co-workers had proposed [Rh]−H as a catalytic species for the co-oligomerization of ethylene with carbon monoxide catalyzed by rhodium phosphine complexes under the water gas shift reaction conditions.[8d] In most cases of the carbonylations of alkynes or alkenes under the water gas shift reaction conditions, the [Rh]−H species is often postulated to be an active one which undergoes insertion of a carbon−carbon double or triple bond.[9,15] In the present reaction system, we have confirmed that the copolymerization does not occur in the absence of water and amine. This fact similarly suggests that the copolymerization is initiated by a [Rh]−H species generated from the reaction of rhodium carbonyl with water and amine. On the other hand, the co-oligomerization of norbornene **1n** with carbon monoxide mentioned above gave co-oligomer **2n″** and co-dimer **2n′**, the structures of which suggest that the reaction might be initiated by addition of [Rh]−H to **1n** and terminated by elimination of [Rh]−H to give a γ-lactone skeleton. Here, on the basis of our experimental results as well as those obtained previously,[9] we propose a reaction mechanism which may reasonably interpret the present copolymerization. As shown in Scheme 3, a [Rh]−H species is likely to act as an active initiator, and alternate insertion of a double bond of **1** and carbon monoxide (CO) into the [Rh]−H species would form acylrhodium intermediate **7**.[8d] The rhodium acyl species can be propagated by successive and alternate insertions of **1** and CO to give corresponding copolymer **2**. When the reaction of 7-*tert*-butoxynorborna-2,5-diene **1a** was stopped after 6 h, a copolymer with a molecular weight of 4200 was obtained. In an IR spectrum of the copolymer, weak but distinct absorptions were observed at 1780 and 1722 cm^{-1}, suggesting the existence of a terminal γ-lactone group.[14] Furthermore, a weak signal at 1.90 ppm due to the terminal proton was also recorded in the ^{1}H NMR spectrum, indicating the initiation by the Rh−H species in the copolymerization of norbornadienes. On the basis of these observations, the present copolymerization of norbornadienes with CO might be also initiated by [Rh]−H and terminated to form a γ-lactone group as similarly observed for the co-oligomerization of norbornene (see Scheme 2). Under the same reaction conditions, other rhodium complexes such as $Rh_4(CO)_{12}$, $RhCl_3{\cdot}3H_2O$, and $[Rh(nbd)Cl]_2$ also catalyzed the copo-

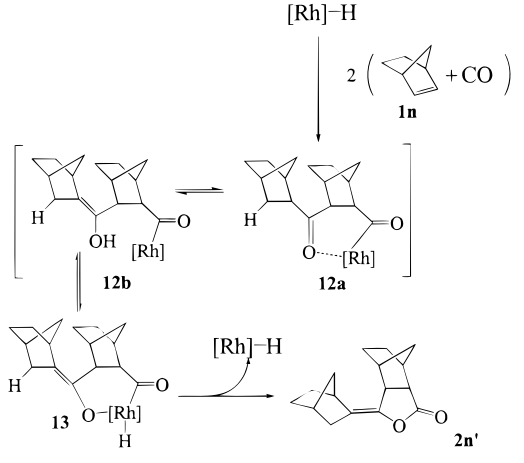
Scheme 3. Proposed Mechanism for the Copolymerization of Norbornadiene with Carbon Monoxide



lymerization of 7-*tert*-butoxy-2,5-norbornadiene with carbon monoxide. $RhCl_3 \cdot 3H_2O$ as a mononuclear complex would be converted to a rhodium carbonyl cluster under the reaction conditions. It is possible that some mononuclear [Rh]−H species and also some cluster species would exist in the reaction system at the same time. At present although it is not clear that which one is the real catalytic species, mononuclear or cluster, [Rh] could be considered to be a cluster complex based on the experimental results we have reported previously and other references under the reaction conditions.

In general, the propagation of polymerization essentially depends on many factors. In the propagation of the present system, electronic and steric effects of monomers could be considered to affect the chain growth of copolymers. The fact that norbornadienes gave copolymers with a higher polymerization degree than norbornenes leads us to postulate different intermediates **9** (Scheme 3) and **12a** (Scheme 4) at the propagation steps for the polymerization of diene **1** and monoene **1n**, respectively. Intermediate **9** would involve an intramolecular interaction of the growing polymer chain with [Rh], while coordination of the keto group to [Rh] may form intermediate **12a**.[16] If the termination step is assumed to pass through intermediates **11** (Scheme 3) and **13** (Scheme 4), the stability of intermediates **9** and **12a** would control the propagation step. In the case of norbornene, the lower stability of intermediate **12a** may cause easy transformation to [Rh]−enolate **12b** and then to **13**. Codimer **2n′** is the product derived directly from **13** by a reductive elimination of **2n′** regenerating [Rh]−H. On the other hand, in the case of norbornadiene the interaction between the double bond and the rhodium is probably may prevent the interaction between the rhodium and the keto group, resulting in successive insertions of norbornadiene and CO to form intermediate **10a** with a higher polymerization degree. Finally, the copolymerization may be terminated via **10b 10c** and then [Rh]−enolate **11**, giving copolymer **2**.

Scheme 4. Possible Formation Route of Codimer 2n′



In summary, the alternating copolymerizations of norbornadienes with CO are effectively catalyzed by a rhodium complex under water gas shift reaction conditions to produce unsaturated poly(ketone)s, which are transformed to new functional polymers by chemical reactions. The similar carbonylations of norbornenes also give oligomeric poly(ketone)s whose structures are characterized by spectral methods to provide useful mechanistic information on the present copolymerization.

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