



Regio- and stereoselective alternating copolymerization of α -olefins with carbon monoxide using a cationic palladium-chiral diphosphine catalyst

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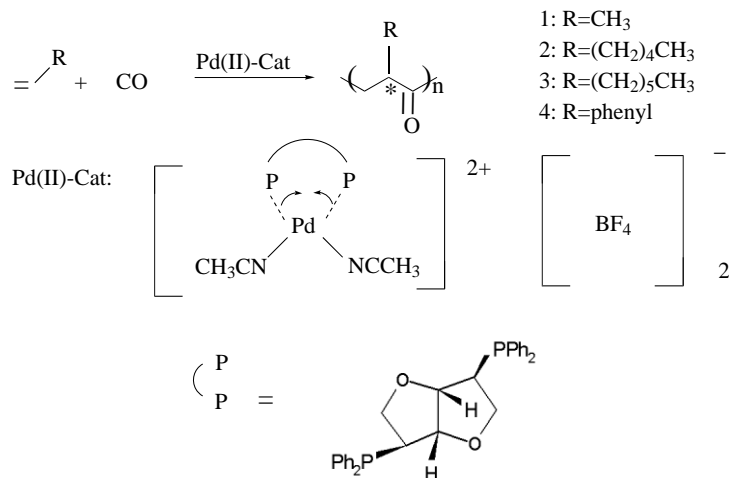
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Abstract—Enantioselective alternating copolymerization of carbon monoxide with propylene, 1-heptene, 1-octene, and styrene was carried out using a palladium catalyst modified by 1,4-3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (DDPPI). The pure poly(1,4-ketone)s were obtained by dissolving the copolymers containing spiroketal and 1,4-ketone units in 1,1,1,3,3,3-hexafluoro-2-propanol and reprecipitating with methanol. Optical rotation, elemental analysis and ^1H , ^{13}C NMR and IR spectra showed that our copolymers were optically active and isotactic with an alternating poly(1,4-ketone) structure. © 2001 Elsevier Science Ltd. All rights reserved.

Alternating copolymerization of α -olefins with carbon monoxide (CO) catalyzed by cationic palladium-ligand complexes is of great interest due to the potential use of the resulting polymer as a new material.^{1–6} Most of the successful enantioselective copolymerizations of α -olefins with CO on this subject deal with C_2 symmetrical bidentate ligands.^{7,8} Recently, ligands of C_1 symmetry have been successfully applied to the enantioselective copolymerization of α -olefins with CO.^{9–12}

More recently, we have reported the enantioselective copolymerization of styrene with CO using the $\text{PdCl}_2\text{-CuCl}_2$ -chiral phosphine catalytic system.¹³ Here, we report the first enantioselective alternating copolymerization of CO with propylene (P), 1-heptene (H), 1-octene (O) and styrene (ST) using the chiral palladium catalyst $[(\text{DDPPI})\text{Pd}(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ (DDPPI: 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol) (Scheme 1).¹⁴



Scheme 1.

Keywords: palladium catalyst; chiral ligand; enantioselective alternating copolymerization; isotactic copolymer; optical activity.

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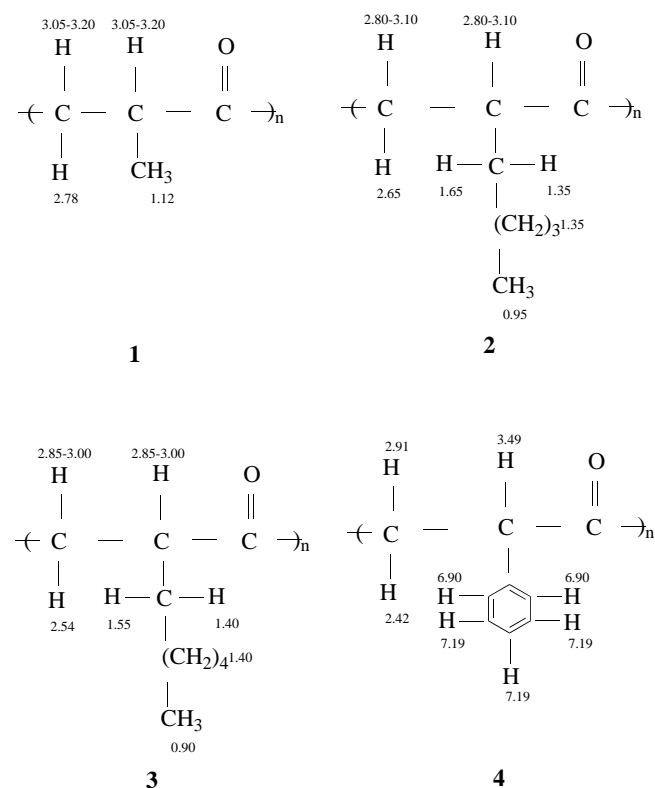
The nature of the chiral phosphine ligands plays an important role in enantioselective copolymerization reactions of olefins with carbon monoxide. The results in Table 1 show that DDPPI is an effective chiral ligand for the enantioselective copolymerization of carbon monoxide with propylene, 1-heptene, 1-octene, and styrene. The molecular structure of DDPPI¹⁴ (Scheme 1) shows that this diphosphine is a bicyclic compound with high rigidity and that it contains four chiral carbon atoms whose configurations are all *S*. High optical activity and good yields were obtained under our reaction conditions.

The P-CO, H-CO, O-CO, and ST-CO copolymers synthesized appear to be isotactic since optically active materials were obtained when enantiomerically pure DDPPI was used. Note that syndiotactic α -olefin-CO copolymers should only exhibit vanishingly small optical activity.

The pure poly(1,4-ketones) can be obtained by treating the α -olefin-CO containing spiroketal units with acidic solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol. The pure copolymers showed a single carbonyl absorption at 210–220 ppm in their ¹³C NMR spectra due to the exclusive head-to-tail structure.¹⁵ Single dominant resonances for the CH₂ (40–45 ppm) and CH (42–52 ppm) groups in the polymer backbone support the presence of high stereoregularity in the polymers (Fig. 1). Similarly, the high regio- and stereoregularity of the copolymers is easily recognized in their ¹H NMR spectra (Fig. 2). The coupling constants for the diastereotopic methylene protons (signals at 2.40–2.80 ppm and 2.85–3.20 ppm) can be evaluated easily in spite of some overlapping of the signals at lower field with that of the methine proton.^{7,16} The values of these constants (15–17 and 3.1 Hz; 15–17 and 9.2 Hz) suggest a conformational homogeneity for the copolymers in solution, in keeping with the high optical rotation.^{7,16} It is very clear from the ¹H NMR and ¹³C NMR spectra that the degrees^{7,8,16} of regioregularity and stereoregularity in the optically active, isotactic P-CO, H-CO, O-CO, and ST-CO copolymers were all >90%.

The high tacticity of the polymers was also supported by their ¹H NMR spectra. The solution of the propylene-CO copolymer in CDCl₃/(CF₃)₂CHOH showed that the ¹H NMR (Fig. 2A and structure 1) resonance at 1.12 ppm (d, *J*=6.7 Hz, 3H, CH₃) was clearly due to the methyl group in the repeating unit, -CH(CH₃)CH₂CO-. The coupling constants indicated that the H atom absorbing at 2.78 ppm (d, *J*=15.7 Hz, 1H, CHH) was not coupled with the H atoms of the methyl group, and therefore, was one of the hydrogen atoms of the CH₂ group. The H atom of the CH group resonating at 3.05–3.20 (m, 2H, CHH and CH) ppm overlapped with the absorption of the second H atom of the CH₂ group (the two H atoms of the CH₂ group are diastereotopic and therefore nonequivalent). The ¹³C NMR (CDCl₃/(CF₃)₂CHOH) spectrum (Fig. 1A) exhibited resonances at 215.2, 45.4, 40.5, and 16.2 ppm due to the C=O, CH₂, CH, and CH₃ groups of the

-CH(CH₃)CH₂CO- units in the copolymer, respectively. These NMR parameters are in accord with those reported by Consiglio and co-workers.¹⁶



The ¹H NMR (CDCl₃/(CF₃)₂CHOH) (Fig. 2B and structure 2) spectrum of the 1-heptene-CO copolymer shows resonances at 2.80–3.10 (m, 2H, backbone CHH and CH), 2.65 (d, *J*=16.2 Hz, 1H, backbone CHH), 1.65 (m, 1H, side-chain CHH(C₄H₉)), 1.35 (m, 7H, side-chain CHH(CH₂)₃CH₃), 0.95 (t, br, 3H, CH₃) ppm, respectively, due to the two overlapping protons from both the backbone CH₂ and CH groups, the other diastereotopic proton of the backbone CH₂, the one diastereotopic proton of the side-chain CH₂ adjacent to the methine group, the rest of the methylene protons in the side-chain and the CH₃ protons in the -CH(CH₂)₄CH₃CH₂CO- repeating units of the polymer. The ¹³C NMR (CDCl₃/(CF₃)₂CHOH) spectrum of 1-heptene-CO copolymer (Fig. 1B) exhibited resonances at 214.1, 45.0, 42.4, 35.5, 30.7, 23.0, 19.2, and 13.5 ppm due to, respectively, the C=O, CH, and CH₂ groups in the backbone, the four methylene groups in the side-chain, and the CH₃ groups.

Similarly, the ¹H NMR (CDCl₃/(CF₃)₂CHOH) (Fig. 2C and structure 3) spectrum of the 1-octene-CO copolymer exhibits absorbances at 2.85–3.00 (m, 2H, backbone CHH and CH) and 2.54 (d, *J*=16.4 Hz, 1H, backbone CHH) ppm due to the two overlapping protons from both the backbone CH₂ and CH groups, the other diastereotopic proton of the backbone CH₂. Resonances at 1.55 (m, br, 1H, side-chain CHH(C₅H₁₁)), 1.40 (m, 9H, side-chain CHH(CH₂)₄CH₃), 0.90 (t, br,

Table 1. Enantioselective copolymerization of α -olefins with CO catalyzed by $[(\text{DDPPI})\text{Pd}(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ ^a

Copolymer	Propylene-CO	1-Heptene-CO	1-Octene-CO	Styrene-CO
M_n^b	1.43×10^4	4.02×10^3	7.31×10^3	6.23×10^3
M_w^b	3.89×10^4	6.25×10^3	1.73×10^4	1.07×10^3
M_w/M_n^b	2.72	1.55	2.37	1.72
Productivity ($\text{g g}^{-1}\text{Pd h}^{-1}$)	24.53	13.76	16.12	20.05
$[\alpha]_{589}^{20}$ (5 mg/mL) ^c	52°	63°	61°	359°
Tg (°) ^d	35	11	3	127
Tm (°) ^d	203	194	204	305
Anal. calcd (found)	C, 68.6 (68.9)H,8.6(8.4)	C, 76.1 (76.3)H,11.2(11.4)	C, 77.1 (77.5)H,11.4(11.3)	C, 81.8 (82.1)H,(6.1(6.5)
IR(C=O)(cm^{-1}) ^e	1703	1708	1706	1714

^a Reaction conditions: α -olefins (10 ml); $[\text{Pd}(\text{DDPPI})(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$ (0.05 mmol); 2,6-dimethylbenzoquinone (0.08 mmol); solvent [3:1 (v/v) methylethylketone / CH_3OH] (6 mL); CO 9 MPa; temperature 45°C; time: 32 h (propylene-CO), 48 h (1-heptene-CO), 48 h (1-octene-CO), 24 h (styrene-CO).

^b Molecular weight and its distribution were measured by GPC relative to polystyrene standard.

^c CH_2Cl_2 was used as the solvent.

^d Tg and Tm were measured by DSC.

^e The samples were reprecipitated from $(\text{CF}_3)_2\text{CHOH}$ by addition of methanol.

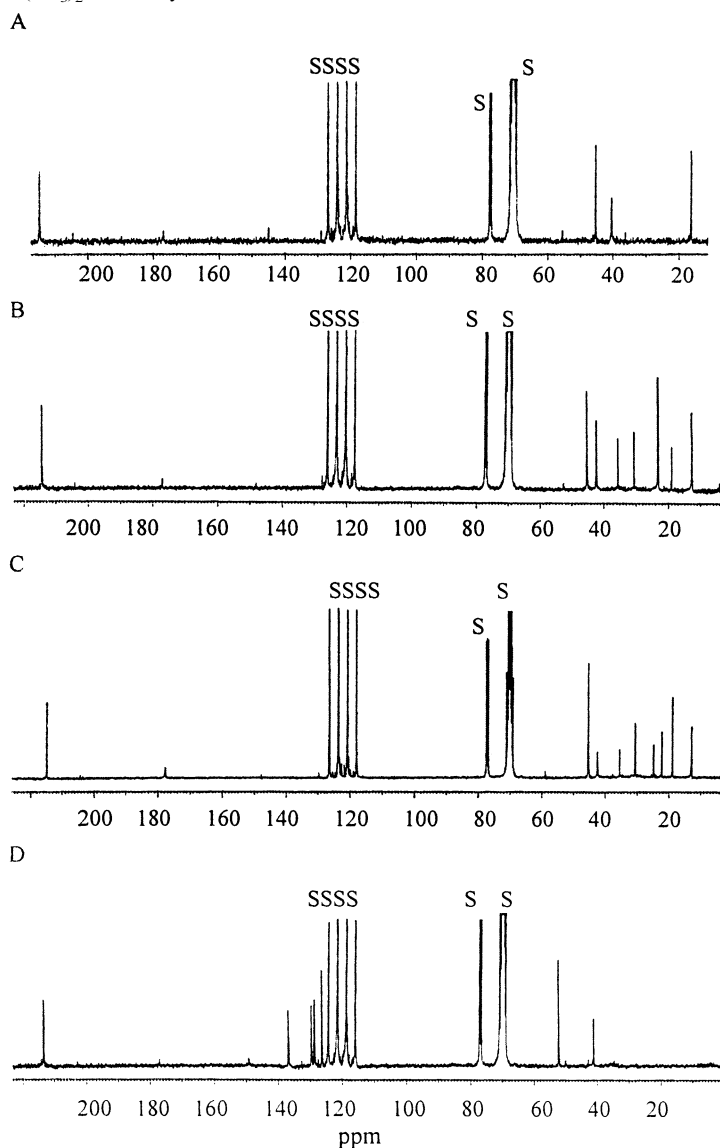


Figure 1. ^{13}C NMR spectra ($\{1:1 \text{ (v/v) } \text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}\}$, 400 MHz). (A) Spectrum of alternating isotactic P-CO copolymer; (B) spectrum of alternating isotactic H-CO copolymer; (C) spectrum of alternating isotactic O-CO copolymer; (D) spectrum of alternating isotactic ST-CO copolymer. (S=solvent).

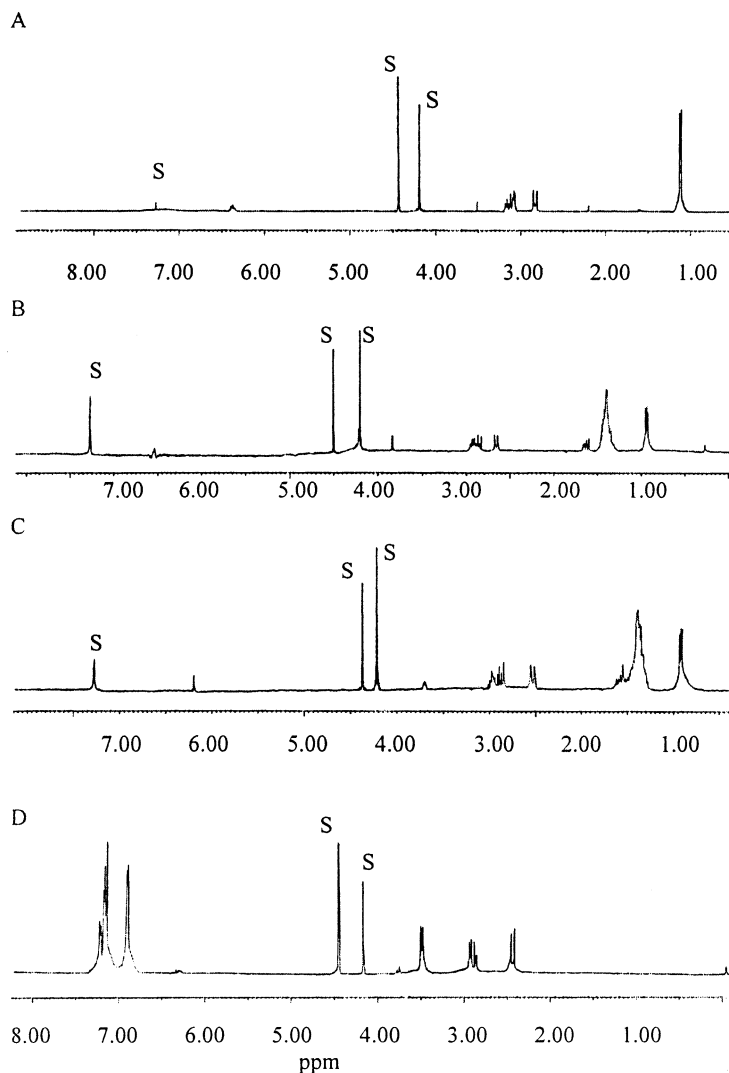


Figure 2. ^1H NMR spectra ($\{1:1 \text{ (v/v) } \text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}\}$, 400 MHz). (A) Spectrum of alternating isotactic P-CO copolymer; (B) spectrum of alternating isotactic H-CO copolymer; (C) spectrum of alternating isotactic O-CO copolymer; (D) spectrum of alternating isotactic ST-CO copolymer. (S=solvent).

3H, CH_3) ppm were due to the diastereotopic proton of the side-chain CH_2 adjacent to the methine group, the rest of the methylene protons in the side-chain, and the CH_3 protons in the $-\text{CH}((\text{CH}_2)_3\text{CH}_3)\text{CH}_2\text{CO}-$ repeat units of the polymer. The ^{13}C NMR ($\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$) spectrum of 1-octene-CO copolymer (Fig. 1C) exhibited resonances at 214.7, 44.8, and 42.0 ppm due to the $\text{C}=\text{O}$, CH, and CH_2 groups in the backbone, resonances at 35.3, 30.3, 25.4, 22.5, 18.8, and 12.8 ppm attributable to the five methylene groups and CH_3 group in the side-chain, respectively.

The solution of the styrene-CO copolymer in a 1:1 (v/v) $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$ mixture showed ^1H NMR (Fig. 2D and structure 4) absorptions at 7.19 (m, 3H, phenyl) and 6.90 (d, $J=7.3$ Hz, 2H, phenyl) ppm due to the phenyl group. The resonances at 3.49 (dd, $J=9.2$ Hz, 3.1 Hz, 1H, backbone CH), 2.91 (dd, $J=16.2$ Hz, 9.2 Hz, 1H, backbone CHH), 2.42 (dd, $J=16.2$ Hz, 3.1

Hz, 1H, backbone CHH) ppm were due to the backbone CH and CH_2 groups, respectively. The ^{13}C NMR ($\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$) spectrum of the styrene-CO copolymer (Fig. 1D) exhibits absorptions at 213.2, 52.0, and 41.2 ppm due to the $\text{C}=\text{O}$, and backbone CH and CH_2 groups. The absorptions at 137.5, 128.9, 128.3, and 126.1 ppm were attributable to the phenyl group. The above parameters are consistent with those reported by Consiglio.⁹

In the presence of europium tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorate], the ^{13}C NMR ($\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$) spectrum of optically active ST-CO poly(1,4-ketone) exhibited only a dominant singlet for the carbonyl resonance (Fig. 3). However, the singlet appeared as a doublet when the racemic poly(1,4-ketone) was employed.⁷ Hence, the degree of enantioselectivity in the optically active ST-CO poly(1,4-ketone) was greater than 90%.

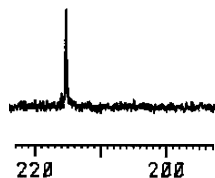


Figure 3. ^{13}C NMR spectrum ($\{1:1 \text{ (v/v) CDCl}_3/(\text{CF}_3)_2\text{CHOH}\}$, 400 MHz) of optically active ST-CO poly(1,4-ketone) in the presence of europium tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorate] molar ratio of Eu(III) and ST-CO repeating units is 1:5.

Acknowledgements

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