Enantioselective Alternating Copolymerization of Propylene with Carbon Monoxide Using Cationic Palladium-Chiral Diphosphine Catalyst

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Abstract: Enantioselective alternating copolymerization of carbon monoxide with propylene was carried out using palladium catalyst modified by 1,4-3,6-dianhydro-2,5-dideoxy-2,5-bis (diphenylphosphino)-L-iditol (DDPPI). The chiral diphosphine was proved to be effective at enantioselective copolymerization. Optical rotation, elemental analysis, ^{1}H, ^{13}C-NMR and IR spectra showed that the copolymer was optically active, isotactic, alternating poly(1,4-ketone) structure.

Keywords: Palladium catalyst, chiral ligand, enantioselective alternating copolymerization, isotactic copolymer, optical activity.

Alternating copolymerization of α-olefins with carbon monoxide (CO) catalyzed by cationic palladium-chiral ligand complexes is of great interest due to the potential use of the resulting polymer as a new material[1]. Recently, enantioselective alternating copolymerization of CO with styrene has been reported by us using $PdCl_2$-$CuCl_2$-chiral phosphine catalyst[2]. Here, we first report enantioselective alternating copolymerization of CO with propylene (P) using $[(DDPPI)Pd(CH_3CN)_4](BF_4)_2$ as the catalyst (DDPPI: 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis (diphenyl phosphino) -*L*-iditol) **(Scheme 1)**. This copolymerization was carried out in mild conditions (45°C, 9 MPa; Sen's report[3], 50°C, 10 MPa). Compared with our previous reported catalyst[2], the reactivity of this catalyst was 24.53 $g \cdot g^{-1} Pd \cdot h^{-1}$, higher than that of previous reported catalyst (7.37 $g \cdot g^{-1} Pd \cdot h^{-1}$).

The nature of the chiral phosphine ligand 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. The molecular structure of DDPPI[2] (**Scheme 1**) shows that this diphosphine is a bicycle compound with high rigidity and it contains four chiral carbon atoms whose configurations are all S. High optical activity and good yield were obtained in our reaction conditions.

The P-CO copolymer synthesized appears to be isotactic since optically active material was obtained when enantiomerically pure DDPPI was used. Note that syndiotactic α-olefin-CO copolymers should only exhibited vanishingly small optical activity.

Scheme 1

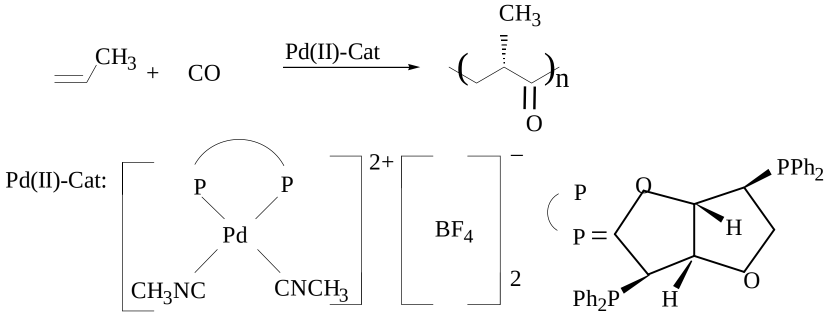


Table 1 Enantioselective copolymerization of propylene with CO catalyzed by $[(DDPPI)Pd(CH_3CN)_2](BF_4)_2$[a]

Copolymer	Propylene-CO
M_n[b]	1.43×10^4
M_w[b]	3.89×10^4
M_w/M_n[b]	2.72
Productivity($g\cdot g^{-1}Pd\cdot h^{-1}$)	24.53
$[\alpha]^{20}_{589}$ (3.5×10^{-4}mol/L)[c]	52
Tg(℃)[d]	35
Tm(℃)[d]	203
Anal. Calcd (Found)	C,68.6(68.9) H,8.6(8.4)
IR(C=O)(cm^{-1})[e]	1703

[a] Reaction conditions: propylene 10 g; $[Pd(DDPPI)(CH_3CN)_2](BF_4)_2$ 0.05 mmol; 2,6-dimethylbenzoquinone 0.08 mmol; solvent [3:1(v/v) methylethylketone /CH_3OH] 6 mL; CO 9 MPa; temperature 45℃; time 32 h.

[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.

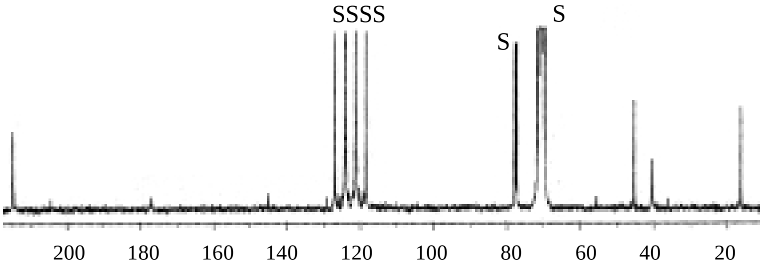
[e] The samples were reprecipitated from $(CF_3)_2CHOH$ by addition of methanol.

In our propylene copolymer, the signal at 113.2 ppm in ^{13}C-NMR spectrum ($CDCl_3$) indicated the presence of the spiroketal group (C-O-C) in the copolymer[3]. In contrast with the ^{13}C-NMR spectrum of the same sample dissolved in the mixture of $CDCl_3$/$(CF_3)_2CHOH$ (1:1, v/v) only the signal of carbonyl group (215.2 ppm) was detected, no signal of C-O-C could be observed.

Consistently, the IR spectrum of the untreated sample in the KBr pill shows medium band in the region of the carbonyl stretching (1703 cm^{-1}); in addition there are some medium bands in the region 1300-1000 cm^{-1} and one band at 839 cm^{-1}. When the copolymer was dissolved in hexafluoro-2-propanol and reprecipitated with methanol, the very strong band at 1703 cm^{-1} appeared whereas the bands at low wavenumbers disappeared.

The pure poly(1,4-ketone) can be obtained by treating propylene-CO containing spiroketal units with acidic solvents such as 1,1,1,3,3,3-hexafluro-2-propanol[4]. The pure copolymers showed a single carbonyl signal at 215.2 ppm in the ^{13}C-NMR spectrum due to an exclusive head-to-tail structure[5]. Single dominant signals for the CH_2 (40.5 ppm) and CH (45.4 ppm) groups in the ^{13}C-NMR spectrum of the polymer backbone support the presence of highly stereoregularity in the polymer (**Figure 1**). It is very clear from the resonances of carbonyl region and the backbone CH and CH_2 that the degree of regioregularity and stereoregularity in the optically active, isotactic P-CO copolymer was > 90% (The degree of regioregularity and stereoregularity of our copolymer may be higher than 90%, but the resolution in the NMR spectrum does not allow us to make that claim with accuracy).[4]

Figure 1 ^{13}C-NMR spectrum of alternating isotactic P-CO copolymer



in 1:1 (v/v) $CDCl_3$/ $(CF_3)_2CHOH$, 400MHz, S=solvent

The high tacticity of the polymer was also supported by its ^1H-NMR spectrum. The solution of the propylene-CO copolymer in $CDCl_3$ / $(CF_3)_2CHOH$ showed that the signal at 1.12 ppm (d, J = 6.7Hz, 3H, CH_3) in ^1H-NMR was asigned as the methyl group in the repeating unit, $-CH(CH_3)CH_2CO-$. The coupling constants indicated that the H atom absorbing at δ 2.78 ppm (d, J = 15.7Hz, 1H, $CH\underline{H}$) was not coupled with the hydrogen atoms of methyl group, but coupled with another H atom of the CH_2 group, therefore, the signal at δ 2.78 ppm was attributable to one H atom of CH_2 group. Another H atom of the CH_2 group resonated at 3.05-3.20 ppm, overlapping with the signal of H atom of the CH group (m, 2H, $CH\underline{H}$ and $C\underline{H}$; the two H atoms of the CH_2 group are diastereomers). The ^{13}C-NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum (**Figure 1**) exhibited resonances at 215.2, 45.4, 40.5, and 16.2 ppm due to the C = O, CH_2, CH, and CH_3 groups of the $–CH(CH_3)CH_2CO-$ units in the copolymer, respectively. These NMR parameters are in accord with those reported by Consiglio[6].

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