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Alternating copolymerization of carbon monoxide and α-olefins

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Summary

Pd^{++} catalysts with bis(diphenylphosphino)alkane ligand and methanol as coinitiator were found to be very active for the alternating copolymerization of carbon monoxide with propylene, butene-1 and hexene-1. The catalysts with bis(diphenylphosphino) propane and butane have the highest polymerization activities but only modest regiospecificity. The chiral (-)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane-Pd catalyst has good activity as well as regioselectivity to produce semi-crystalline CO/propylene alternating copolymer.

Introduction

The alternating copolymerization of carbon monoxide and ethylene has been described both in the scientific[1-4] and patent[5-10] literature. Even though there have been claims of alternating copolymerization of CO with propylene, the actual examples in the patents are those of ethylene, propylene, CO terpolymerization. There has been no scientific report on copolymerization of CO and propylene or other α-olefins. We have disclosed a very active catalyst for ethylene/CO copolymerization involving methanol as a coinitiator: $[Ph_2P(CH_2)_3PPh_2]Pd^{+2}/MeOH$.[4] This type of catalyst is used to copolymerize α-olefins and CO in this work. The copolymerization behavior and the structure of the alternating propylene/CO copolymers are described below.

Experimental

The catalysts synthesized are $[Ph_2P(CH_2)_nPPh_2Pd(CH_3CN)_2(BF_4)_2$, which are designated as bisphosphine(*n*)Pd. They were all obtained by reacting $[Pd(CH_3CN)_4](BF_4)_2$ with equimolar quantity of bisphosphine ligand from Aldrich. A 300 mL Paar reactor was dried,

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purged with argon, catalyst solution was cannulated in to it, then monomers added through high pressure hoses. The mixture was heated to the polymerization temperature (T_p). At the end of a copolymerization the unreacted monomers were vented, and the product was purified by dissolution in 1,2-dichlorethane and precipitation with methanol. Molecular weights were determined by Waters GPC using $CHCl_3$ as a solvent. ^{13}C-NMR spectra were recorded on a Varian XL-200 spectrometer using $CDCl_3$ as solvent.

Results and Discussion

All the copolymers of CO/C_3(propylene), CO/C_4(butene-1), and CO/C_6(hexene-1) have alternating structures according to analysis. Found (calculated): ACP, C, 68.41(68.6), H, 8.44(8.6); C_4/CO-ACP, C, 67.6(71.4), H, 9.0(9.5); C_6/CO-ACP, C, 75.0(75.0), H, 10.3(10.4). Their ^{13}C-NMR and IR spectra are consistent with the alternating structures.

The catalyst activity (*A*) of bisphorphine(3)Pd was low at T_p = 30°C and much higher at 50 and 70°C. But the MW and T_g of the C_3/CO-ACP both decrease with the increase of T_p. (Table I, runs no. 1 to 3). *A* is also strongly dependent on the ligand structure; the *A* value is highest for $n = 3$ and 4 and decreases greatly when the alkylene spacer is either shorter or longer.

The ^{13}C NMR of the carbonyl region contains three peaks at 207-209, 211-213 and 314-216 ppm assignable to T-T, H-T, and H-H sequences (T = tail, H = head); the corresponding calculated chemical shifts are 209, 212 and 215 ppm using $\delta = 210.9$ ppm $+ \Sigma Z$ (Z is the side chain methyl substituent effect). The % of H-T in C_3/CO-ACP produced by bisphosphine(3)Pd catalyst (run no. 1,2,3,5, Table I) ranges from 57 to 62 % for low regioselectivity. The % of H-T is very high for bisphosphine(5)Pd catalyst, but it has very low catalyst activities.

The catalyst with an optically active ligand (-)DIOP(=(-)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) is highly regiospecific. It has an *A* value (run no. 11, Table I) which is about 24 times greater than that of bisphosphine(5)Pd catalyst and is still about as highly regioselective. The catalyst with the best balance of *A* and regioselectivity is the bisphosphine(4)Pd catalyst (run no. 6, Table I).

The carbonyl NMR contains fine structures obviously due to stereoisomerism of the C_3/CO-ACP. This is better seen with the methylene and methine ^{13}C resonances. Samples of C_3/CO-ACP are being epimerized to obtain estimates of stereoselectivity in the copolymerizations.

Table I Alternating copolymerization of CO and α-olefins

Run no.	Catalyst[a] (n)	Olefin	T_p (°C)	A^f x10^{-4}	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	T_g (°C)	T_m (°C)	ΔH_f J/g	% H-T
1	(3)	C_3^b	30	1.7	27,400	2.6	18.4	144	5	57
2	(3)	C_3^b	50	9.8	2,700	4.5	-7.4	158	7	59
3	(3)	C_3^b	70	9.6	600	6.2	-14.3	-		62
4	(2)	C_3^c	50	0.21						
5	(3)	C_3^c	50	5.2			-10.7			58
6	(4)	C_3^c	50	4.8			-8.1			79
7	(5)	C_3^c	50	0.07			20.5^g	142^g	24.8^g	85
8	(6)	C_3^c	50	0.01						
9	(3)	C_4^d	30	1.8	20,000	1.6	3.0			
10	(3)	C_6^e	30	1.7	25,000	1.4	0			
11	(-)DIOP	C_3	50	1.7	600	6.8	8.9^g	129^g	31.6^g	79

[a] $[Ph_2P(CH_2)_nPPh_2]Pd[BF_4]_2$; [b] $p_{C_3H_6}$ = 80 psig; [c] $p_{C_3H_6}$ = 50 psig; [d] $p_{C_4H_8}$ = 20 psig; [e] 60 mL hexene; [f] A in g ACP (mol Pd • h)$^{-1}$; [g] CH_3OH insoluble fraction.

The $(Ph_3P)_2Pd(CH_3CN)_2$ catalyst has *A* of only 5.1×10^2 g polymer (mol Pd • h)$^{-1}$ in propylene CO copolymerization. Furthermore, the products are oligomers and NMR showed non-alternating structure, i.e. two or more propylene in a sequence between carbonyls. The PPh_3 ligands probably occupy trans coordinations. As a result cis insertion of olefin to the Pd-R bond is unfavorable for polymerization. Furthermore, any dissociation of the Ph_3P ligand during a chain growth would cause loss of regioselectivity. Ligands like bisphosphine with trimethylene, tetramethylene, or (-)DIOP spacers are chelated and occupy the cis coordinations leaving Pd-R and Pd-olefin cis to one another, favorable for regio-selective propagation.

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