Alternating Copolymerization of Various Alkenes with Carbon Monoxide Using a Cationic Pd(II) Complex of (*R,S*)-BINAPHOS as an Initiator

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ABSTRACT: Using a cationic Pd(II) complex of unsymmetrical chiral bidentate phosphine-phosphite, (*R,S*)-BINAPHOS (= (*R*)-2-diphenylphosphino-1,1'-binaphthalen-2'-yl (*S*)-1,1'-binaphthalen-2,2'-diyl phosphite), asymmetric alternating copolymerization have been performed with (1) higher 1-alkene and CO and (2) styrene or its derivatives and CO. The polymerization proceeded in a completely alternating manner with 1-alkenes and some *para*-substituted styrenes. Almost complete head-to-tail and isotactic selectivities have been revealed by ¹³C NMR spectrometry. While the copolymerization of aliphatic 1-alkene with CO proceeded in a living fashion, the existence of a significant chain-transfer has been suggested in the copolymerization of styrene with CO. Effect of a functional group in a monomer and an alternating copolymerization of an alkene with CO are also mentioned briefly.

KEY WORDS Asymmetric / Alternating Copolymerization / Alkenes / Carbon Monoxide / Palladium / Chiral / Phosphine-phosphite /

Since the discovery of completely alternating copolymerization of ethene with carbon monoxide catalyzed by a transition metal complex in early 1950's, Pd(II) became the most promising catalyst among the several transition metals examined. The research was then more focused on the ligands and counter anions. Higher catalytic activity and higher molecular weight have been attained by the use of a *cis*-bidentate phosphine ligand and a non-coordinating counter anion.^{1–7} When such a 1-alkene as propene or styrene is used in place of ethene, three more factors arise to be controlled in order to obtain a stereoregular alternating copolymer (Chart 1). These are, (1) Regioselectivity: Depending on the regioselectivity of alkene incorporation into a polymer chain, there are three different kinds of possible units, namely, head-to-tail, head-to-head, and tail-to-tail. If a chain grows uniformly in either 1,2- or 2,1-insertion, the resulting polymer should consist of solely head-to-tail units. (2) Tacticity selectivity: A uniform head-to-tail copolymer possesses asymmetric carbons in the main chain. In a syndiotactic copolymer, the absolute configuration of the asymmetric carbons is in the order of an alternating manner, *RSRS*---, while the same absolute configuration order either *RRRR*--- or *SSSS*--- can be observed in an isotactic copolymer. (3) Enantioselectivity: An isotactic copolymer is chiral; there exist two enantiomers, *RRRR*--- and *SSSS*---.

Chart 1

In order to obtain a completely alternating isotactic copolymer in an enantiomerically pure form, asymmetric copolymerization using a chiral catalyst is now attracting much attention.⁸ In contrast that most of successful reports on this subject deal with *C*₂ symmetrical bidentate ligands,^{9–16} we recently have reported that a cationic Pd(II) complex of unsymmetrical chiral bidentate phosphine-phosphite, (*R,S*)-BINAPHOS (= (*R*)-2-diphenylphosphino-1,1'-binaphthalen-2'-yl (*S*)-1,1'-binaphthalen-2,2'-diyl phosphite),^{17,18} serves as an efficient initiator for the asymmetric copolymerization of propene with carbon monoxide.¹⁹ A highly isotactic polyketone was obtained with high enantioselectivity.

Figure 1

Isolation of various intermediate palladium complexes and theoretical studies provided a possible mechanism for the alternating copolymerization.²⁰ The unique unsymmetrical character of this bidentate ligand makes the two coordination sites of Pd(II) available for the copolymerization non-equivalent, resulting in several characteristic features of this system as summarized in Scheme 1.

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Scheme 1

Some additional chiral and achiral phosphine-phosphite ligands shown in Chart 2 were synthesized and applied to the copolymerization.²¹ A slight change around the phosphine site strongly affects the stereo regularity of the polyketone. An opposite enantioface of propene was selected by (*R,S*)-(*c*-Pen)₂-BINAPHOS with as high isotacticity as by the parent (*R,S*)-BINAPHOS. Use of achiral phosphine-phosphites described below resulted in either no reaction or formation of stereo irregular polyketone. Therefore, we concluded that not only the electronic bias of (*R,S*)-BINAPHOS but also its steric demand is essential to produce completely isotactic copolymer from propene and CO in highly enantioselective fashion.

Scheme 2

When 1,4-pentadiene or 1,5-hexadiene were used as a substrate, a cyclocopolymerization took place, affording copolymers containing a cyclopentanone or cyclohexanone moiety, respectively, in a main chain (Scheme 2).^{22,23}

On the basis of studies described above, here we present our further studies on this subject: (1) copolymerization of higher 1-alkenes and functionalized 1-alkenes with CO, (2) copolymerization of styrene and its derivatives with CO, and (3) copolymerization of an allene with CO.

EXPERIMENTAL

Asymmetric Alternating Copolymerization of Olefins with CO Catalyzed by [Pd(CH₃)(CH₃CN){(*R,S*)-BINAPHOS}][B{3,5-(CF₃)₂-C₆H₃}₄] (I).

A solution of **1**²⁰ in CH₂Cl₂ (2.0 mL) was degassed by three cycles of freeze-thaw. After treating with CO (1 atm), an olefin (5.0 mmol) was added and the mixture was stirred under CO (20 atm) in a 50-mL autoclave at 25 °C. The pressure was then released and 0.2 mL of CH₃OH was added. The mixture was treated with CO (20 atm) again, in order to cleave the Pd-C bond by carbomethoxylation. After 1 h, the reaction mixture was poured into CH₃OH (100 mL) under air to precipitate the poly(olefin-*alt*-CO). Values of *M*_n and *M*_w/*M*_n were estimated from a SEC profile based on a standard polystyrene calibration. The results are summarized in Tables 1 and 2.

Alternating Copolymerization of Phenylallene with CO Catalyzed by **1**.

Phenylallene (434 mg, 3.73 mmol) was treated with CO under the reaction conditions as mentioned above. A small amount (14.9 mg, 3% yield, 1490 g of polymer/mol of Pd) of the corresponding alternating copolymer was obtained (*M*_n = 19 500, *M*_w/*M*_n = 1.4).

Alternating Copolymerization of Phenylallene with CO Catalyzed by RhH(CO)₂{(*R,S*)-BINAPHOS}.

A solution of Rh(CO)₂(acac) (2.6 mg, 0.010 mmol) and (*R,S*)-BINAPHOS (8.4 mg, 0.011 mmol) in toluene (2 mL) was degassed by three freeze-thaw cycles and then treated with H₂/CO (10 atm/10 atm) for 2 h in a 50 mL-autoclave to form RhH(CO)₂{(*R,S*)-BINAPHOS}.¹⁸ Excess H₂ was removed by bubbling CO through the solution for a minute. To this solution, was added phenylallene (0.60 mL, 5.3 mmol), and CO (20 atm) was charged. After stirring at 25 °C for 20 h, the mixture was poured into CH₃OH (100 mL) under air to precipitate an alternating copolymer (544 mg, 71% yield, 54 400 g of polymer/mol of Rh. *M*_n = 35 000, *M*_w/*M*_n = 1.3). When RhH(CO)₄ was used as an initiator, the polymer (*M*_n = 8 700, *M*_w/*M*_n = 1.0) was obtained in 2% yield.

RESULTS AND DISCUSSION

Alternating Copolymerization of Higher 1-Alkenes and Functionalized 1-Alkenes with CO

In addition to ethene and propene,²⁰ 1-alkenes with a longer alkyl chain were examined. The results are summarized in Table 1. Completely alternating copolymerization proceeded with such 1-alkenes as 1-hexene (run 4) dodecene (run 5) and 1-eicocene (run 6) with a reaction rate comparable to that of 1-propene (run 3).

Almost complete head-to-tail and isotactic selectivities have been revealed from their ^{13}C NMR charts. In CDCl_3 , the poly(1-hexene-*alt*-CO) partially cyclized to give a polyspiroketal, but the addition of $(\text{CF}_3)_2\text{CHOH}$ to this solution afforded back pure polyketone.¹² Molar optical rotation $[\Phi]_D$ of a copolymer increased with a longer alkyl chain. Completely alternating copolymerization underwent with an olefin having a large substituent, *t*-Bu group, attached to the C=C double bond, although the reaction rate was much slower (run 7).

Existence of a trimethylsilyl group affected the reactivity of the C=C double bond. Vinylsilane and allylsilane were both inert against the copolymerization (runs 8 and 9). When a trimethylsilyl group is separated from the C=C group by at least two methylene groups, electronic effect of silicon becomes negligible (runs 10 and 11). A trialkoxysilyl group which potentially enables the attachment of the polymer to silica gel by -O-Si-O- bond could be incorporated in the substrate (run 12). Although Sen reported an alternating copolymerization of ω -alkenol or ω -alkenoic acid and CO using a bisphosphine-Pd(II) complex as an initiator,¹⁴ no reaction took place in our attempted copolymerization with 3-buten-1-ol, 2-propen-1-ol, or 10-undecenoic acid. No polymeric product was obtained from 3,3,3-trifluoropropene, allylamine, 3-butenyl phenyl sulfide, allyl benzyl ether, methyl acrylate, vinyl acetate, or acrylonitrile, either.

Table 1. Asymmetric Alternating Copolymerization of Various Alkenes with Carbon Monoxide.^a

run	R	time (h)	g of polymer/ mol of Pd	M_n (M_w/M_n) ^b	$[\Phi]_D^c$
1 ^d	H	24	53 200	nd ^f	nd ^f
2 ^e	Me	24	12 600	43 000 (1.1)	-43.99
3	Me	24 ⁱ	23 300	20 000 (1.7)	-43.91
4	Bu	24 ⁱ	44 100	15 000 (1.8)	-45.95
5	<i>n</i> -C ₁₀ H ₁₉	24 ⁱ	59 600	14 000 (2.0)	-63.49
6	<i>n</i> -C ₁₈ H ₃₇	24 ⁱ	40 900	16 000 (1.8)	-73.22
7 ^f	<i>t</i> -Bu	120	2 500	6 900 (1.3)	-40.02
8	SiMe ₃	96	— ^k	—	—
9	CH ₂ SiMe ₃	14	— ^k	—	—
10 ^g	CH ₂ CH ₂ SiMe ₃	24	8 900	nd ^f	nd ^f
11	(CH ₂) ₆ SiMe ₃	24	38 900	11 000 (1.6)	-89.51
12 ^h	(CH ₂) ₆ Si(OMe) ₃	18	13 400	35 000 (1.5)	nd ^f

^a A CH_2Cl_2 (2.0 mL) solution of olefin (5.0 mmol) was treated with CO (20 atm) at 25 °C in a 50-mL autoclave in the presence of the initiator (0.010 mmol), unless otherwise stated. ^b Molecular weight was estimated by SEC (THF eluent) using polystyrene as a standard. ^c $c = 0.49\text{--}0.51$ in CHCl_3 at 26.8 °C. ^d Ethene (5 atm, 10.4 mmol) and the initiator (0.013 mmol) were used in CH_2Cl_2 (5.0 mL). ^e Propene (3 atm, 6.24 mmol) and the initiator (0.012 mmol) were used in CH_2Cl_2 (5.0 mL). ^f 3,3-Dimethyl-1-butene (3.47 mmol) was used. ^g 4-Trimethylsilyl-1-butene (3.50 mmol) was used. ^h The olefin (2.28 mmol) was used. ⁱ At 40 °C. ^j Not determined due to a low solubility of a obtained polymer in solvents. Formation of the polyketone was confirmed by IR. ^k No polymeric material was obtained. ^l An inorganic polymer was gradually formed.

Alternating Copolymerization of Styrene and Its Derivatives with CO

Alternating copolymerization of styrene and its derivatives have been successfully reported using Pd(II)-diimine^{10,15,16}

or Pd(II)-phosphine-imine complexes.^{24,25} On the other hand, it has been reported that the use of Pd(II)-bisphosphine complex as an initiator results in much less molecular weights.^{26,27} Thus, it is noteworthy that a completely alternating copolymer of 4-*tert*-butyl-styrene-CO was obtained with $M_n = 3\,900$ using (*R,S*)-BINAPHOS.²⁰ Here in this study, we examined a series of *para*-substituted styrenes. Copolymers were obtained with styrene (run 1), *para*-alkyl-substituted styrenes (runs 2–6), and *para*-chlorostyrene (run 7). On the other hand, however, styrene with an electron withdrawing group such as -NO₂ (run 8) or -CF₃ (run 9) resulted in no reaction. Styrene with an electron donating -OMe group gave a homopolymer; no copolymer was obtained (run 10). The homopolymer showed an atactic structure with a large M_w/M_n value suggesting that it was produced by a radical polymerization.

Table 2. Asymmetric Alternating Copolymerization of Various Styrene Derivatives with Carbon Monoxide.^a

run	X	time	g/mol of		$[\Phi]_D^c$
			Pd	M_n (M_w/M_n) ^b	
1	H	24	5 940	3 900 (1.8)	-451.54
2	Me	24	7 440	4 200 (1.8)	-318.35
3	<i>t</i> -Bu	3	2 870	4 900 (1.3)	-373.64
4	<i>t</i> -Bu	6	2 010	4 500 (1.4)	-418.24
5	<i>t</i> -Bu	12	3 450	3 200 (1.8)	-432.02
6	<i>t</i> -Bu	24	5 580	3 900 (1.5)	-446.75
7	Cl	24	2 050	3 100 (1.5)	-403.56 ^f
8	NO ₂	24	— ^d	—	—
9	CF ₃	24	— ^d	—	—
10	OMe	24	— ^e	—	—

^a A CH_2Cl_2 (2.0 mL) solution of styrene or its substituted analog (5.0 mmol) was treated with CO (20 atm) at 25 °C in a 50-mL autoclave in the presence of the initiator (0.010 mmol), unless otherwise stated. ^b Molecular weight was estimated by SEC (THF eluent) using polystyrene as a standard. ^c Measured at $c = 0.30\text{--}0.50$ in CHCl_3 at 25–27 °C, unless otherwise stated. ^d No polymeric material was obtained. ^e An atactic homopolymer was obtained. ^f Measured at $c = 0.045$ due to a low solubility of the polymer.

The copolymerization of propene with CO proceeded in a living fashion when the reaction was catalyzed by Pd(II)-(*R,S*)-BINAPHOS. In contrast, the existence of a significant chain-transfer has been suggested in the copolymerization of styrene derivatives with CO. As shown in Table 2, runs 3–6, longer reaction times resulted in higher yields but the molecular weight of the copolymers was essentially unchanged after 3 h. For Pd(II)-bisphosphine complexes, a β -hydride elimination from alkylpalladium species is suggested to take place very easily to terminate the polymerization when a styrene derivative is used as a substrate.^{26,27} Thus, it is probable that a β -hydride elimination is a chain-termination step, and the resulting Pd-H species re-initiates another alternating copolymerization (equation 3). Similar molar optical rotations of the copolymers in runs 3–6 suggest that an enantioselectivity for the olefin incorporation is unchanged by the chain transfer reaction.

Alternating Copolymerization of an Allene with CO

Alternating copolymerization of allenes with CO has been reported by Sen²⁸ and by Osakada–Yamamoto,²⁹ using a Pd(II) and Rh(I) complex, respectively. Prompted by their success, we applied our ligand system to the copolymerization of phenylallene with CO. Only a small amount (3% yield) of an alternating copolymer was obtained when cationic palladium **1** was used as an initiator. In sharp contrast, completely alternating copolymerization took place using $\text{RhH}(\text{CO})_2\{(\text{R},\text{S})\text{-BINAPHOS}\}$.^{17,18} The stereochemistry of an exo C=C bond was Z, the same manner as was reported by Osakada and Yamamoto. Much lower catalytic activity was observed with $\text{RhH}(\text{CO})_4$. With this substrate, an olefin insertion to an acyl–metal bond provides an allylmatal species. Thus, the higher catalytic activity of Rh than Pd may be attributed to an easier CO insertion to an allyl–Rh bond than to an allyl–Pd.

CONCLUDING REMARKS

Completely alternating, highly isotactic, and highly enantioselective copolymerizations of α -olefins with CO has been achieved using a unique initiator system, Pd(II)–(*R,S*)-BINAPHOS. Not only propene and styrene, several terminal olefins were applicable to the asymmetric alternating copolymerization. Thus, a variety of γ -polyketones have been synthesized in an enantioselective manner. Due to an easy availability of the monomers, the products may have potential applications as new materials which might match polyolefin compounds.

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