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Review

Stereoselective alternating copolymerization of carbon monoxide with alkenes☆

Kyoko Nozaki *, Tamejiro Hiyama

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

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Abstract

Stereoselective alternating copolymerization of carbon monoxide with various alkenes is reviewed. Using Pd(II) complexes of chiral ligands, completely alternating, isotactic, and enantioselective copolymerizations have been achieved from aliphatic 1-alkenes and from vinylarenes. Alternating copolymerization of carbon monoxide with other olefins are also described, such as functionalized ones, dienes, and allenes. Polymer conformation is mentioned briefly both in solid phase and in solution. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Stereoselective; Asymmetric; Alternating copolymerization; Carbon monoxide; Alkene

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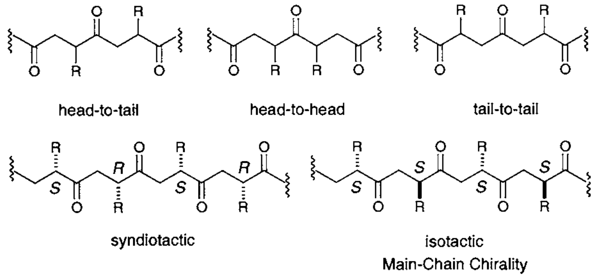
1. Introduction

Completely alternating copolymerization of carbon monoxide with ethene was achieved in the early 1950's by a group from Shell, using a transition metal catalyst [1]. In the early days, several metals were examined such as, Ni(II), Pd(II), and Rh(I) [2]. Among them, Pd(II) became the most promising candidate and 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 *cis*-bidentate phosphine ligand and non-coordinating counter anion. The achievements are summarized in the excellent review articles by Drent [3], and Sen [4].



When 1-alkenes such as propene or styrene are used in place of ethene, three more factors need to be controlled in order to obtain a stereoregular alternating copolymer. Those are, (1) regioselectivity: depending on the regioselectivity of the alkene incorporation into the polymer chain, there are three different kinds of possible units, namely head-to-tail, head-to-head, and tail-to-tail. If the chain grows in the same regioselectivity, either 1,2- or 2,1-insertion, the polymer should consist of solely head-to-tail units. (2) Tacticity selectivity: the 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) Enan-

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☆ This paper is dedicated to Professor Jiro Tsuji and Professor Richard F. Heck.

* Corresponding author. Fax: +81-75-753-5555.

E-mail address: nozaki@npco5.kuic.kyoto-u.ac.jp (K. Nozaki)

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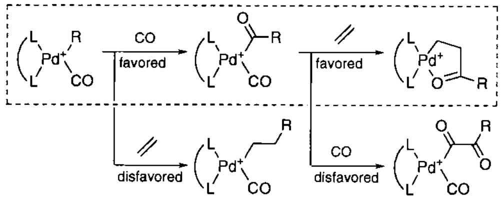


Scheme 1.

tioselectivity: isotactic copolymer is chiral and there exist two enantiomers, *RRRR*– and *SSSS*–.

This review aims to summarize the efforts devoted to obtain a head-to-tail isotactic copolymer in an asymmetric manner from a 1-alkene and carbon monoxide. Studies on the reaction mechanism of the copolymerization are first summarized and then success of controlling the regioselectivity is described and that of enantioselective copolymerization using chiral ligands will follow. The description for the regio- and enantioselective copolymerization is made up of three parts on the basis of alkenes, those are, propene, styrene, and others.

2. Mechanism of copolymerization of alkenes with CO

The mechanism for the copolymerization of ethene with CO has been studied intensively from both experimental and theoretical view points. The completely alternating nature has been the main subject of these studies. The copolymer forms via alternating migratory insertion of carbonyl alkylpalladium and alkene acylpalladium complexes but not of carbonyl acyl- or alkene alkyl-. In his early publications, Sen has demonstrated that double carbonylation is thermodynamically very unfavorable in Pd-phosphines [5]. Recently, Brookhart measured the activation energy for ethene and CO insertion to alkylpalladium modified with phenanthroline, and concluded that the CO insertion is kinetically favored over ethene insertion [6]. The achievements were further investigated theoretically by Morokuma [7], and Ziegler [8], using model ligands (*Z*)-$H_2NCH{=}CHNH_2$ and (*Z*)-$H_2PCH{=}CHPH_2$, respectively. The results essentially matched to those of the experimental ones (Scheme 1).

3. Asymmetric alternating copolymerization of carbon monoxide with propene or higher aliphatic 1-alkenes

The first example of alternating copolymerization of propene with CO is found in the patent from Shell in 1985 using L_2PdX_2 in which L_2 represents a bidentate phosphine and X stands for a weakly or non-coordinating anion [9]. The copolymer was completely alternating but the regiochemistry was not controlled in this example. Consiglio first raised the head-to-tail selectivity up to almost complete using a bis(trialkylphosphine), dippp [1,3-(diisopropylphosphino)propane] in place of dppp [10]. With this achiral ligand, the isotacticity of the copolymer triad was ca. 65%.

In 1992, Consiglio reported the first successful example of asymmetric copolymerization of propene with CO by use of a chiral electron rich bisphosphine ligand, BICHEP [11] as a ligand for Pd(II) [12]. The obtained copolymer was isotactic (ca. 72%) and this isotacticity was even improved to almost complete by their report in 1994 [13]. Similarly, completely isotactic alternating copolymerization of propene–CO was reported, by Sen in 1994 using chiral bis(dialkylmonoarylphosphine) Me-DUPHOS [14], and by Takaya and Nozaki in 1995 using chiral phosphine-phosphite (*R*,*S*)-BINAPHOS [15]. Shown in Fig. 1 is the ^{13}C-NMR chart of the copolymer obtained with [Pd(Me)(MeCN){(*R*,*S*)-BI-

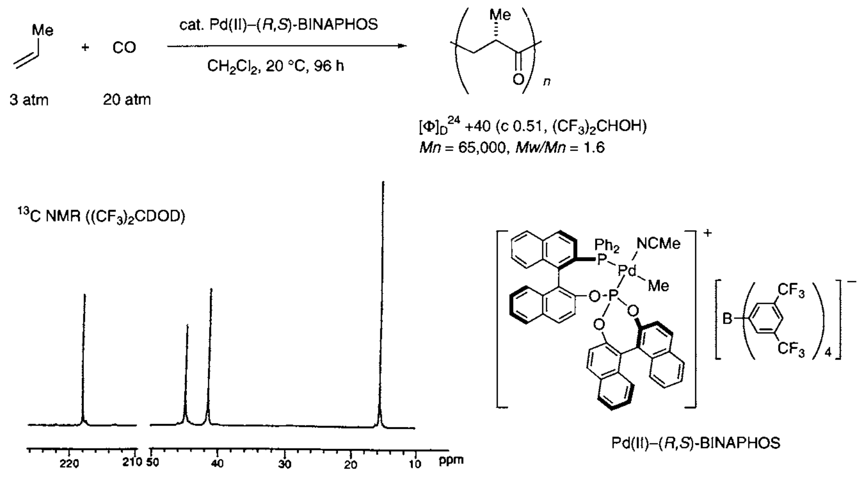
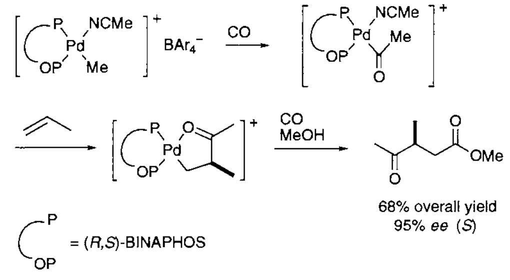
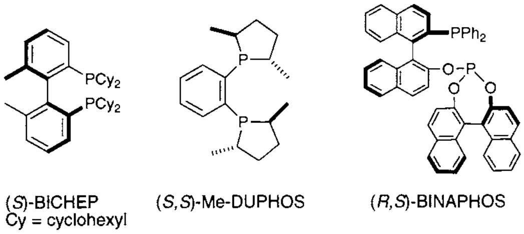


Fig. 1.



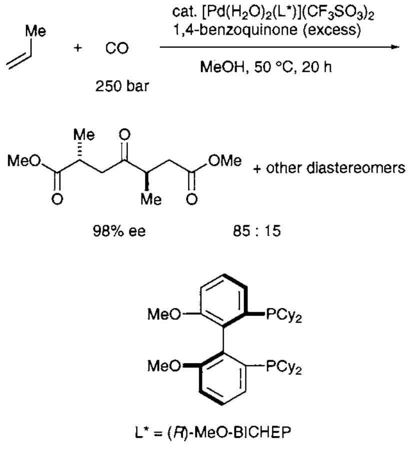
Scheme 2.

NAPHOS}]·[B{3,5-$(CF_3)_2C_6H_3$}$_4$]. No peaks are detected for those of syndiotactic or atactic structure.



Absolute configuration of the asymmetric carbon in the copolymer main chain was first determined by Consiglio comparing the CD spectrum of the polyketone with that of (*S*)-3-methylpentan-2-one [13]. A model study by Nozaki and Hiyama confirmed the relation that the copolymer with *S*-absolute configuration in the main chain shows plus optical rotation in $(CF_3)_2CHOH$ and minus in $CHCl_3$ [15,16]. In the latter study, a model compound, methyl (*S*)-4-oxo-pentanoate was prepared as shown in Scheme 2. The study also revealed that the enantioselectivity for the propene insertion was at least 95% ee.

In contrast, under the condition employed by Consiglio, copolymerization starts by the propene insertion to the palladium–carbon bond of Pd(COOMe). Addition of a large amount of an oxidant resulted in shortening the copolymer chain, and with this manner, dimers were prepared in order to estimate the %ee of the asymmetric carbons in the polymer main chain [17]. Using MeO-BICHEP as the chiral ligand, a head-to-tail and *anti*-diastereomer was obtained in 85% selectivity over other diastereomers with >98% ee (Scheme 3).



Scheme 3.

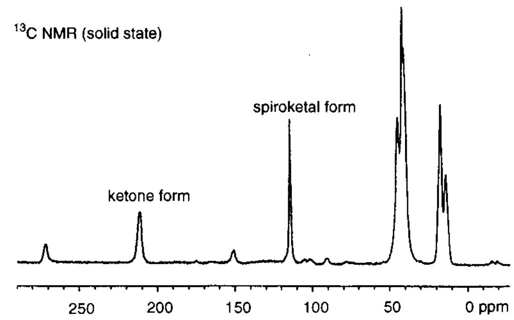


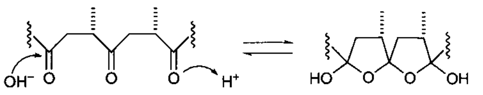
Fig. 2.

The copolymer has a γ-polyketone structure in a solution of chloroform or $(CF_3)_2CHOH$. On the other hand, however, it partially forms polyspiroketal structure in a solid state. For example, when the polymer of Fig. 1 was precipitated from $CHCl_3$ by the addition of methanol, the polymer was observed as a mixture of polyketone and spiroketal by solid state NMR (Fig. 2). This interconversion easily takes place in the presence of proton [18] (Scheme 4).

A higher aliphatic 1-alkene reacts with a slightly lower reactivity. Both the head-to-tail and isotactic selectivities are as high as those observed for propene. The product copolymers from higher 1-alkenes tend to prefer the polyspiroketal form more extensively than the copolymer from propene. For example, poly(1-hexene-*alt*-CO) was detected as a mixture of polyketone and polyspiroketal, even in a $CDCl_3$ solution (Fig. 3).

4. Asymmetric alternating copolymerization with styrene

Aryl-substituted alkenes, such as styrene and its analogs, show different behaviors from the aliphatic 1-alkenes described above. Drent [19] and Consiglio [20] obtained completely alternating copolymer from styrene and CO in a completely head-to-tail manner using such an achiral bidentate nitrogen ligand as 2,2′-



Scheme 4.

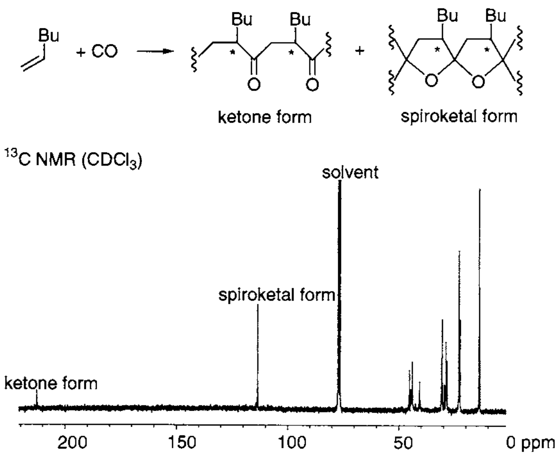
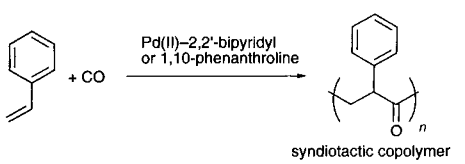
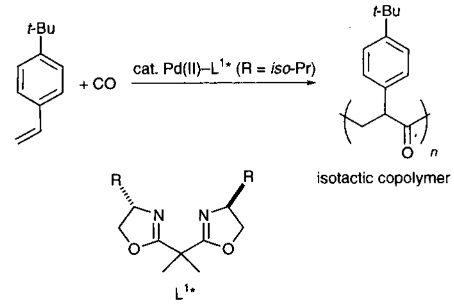


Fig. 3.

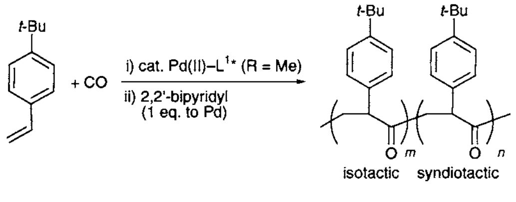


Scheme 5.

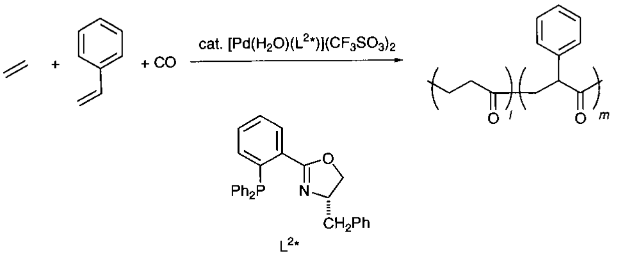
bipyridyl or 1,10-phenanthroline (Scheme 5). The fact that the copolymer was >90% syndiotactic suggests that the enantioface of the incoming styrene is distinguished by the chiral carbon of the last-incorporated styrene, in other words, chain-end control. The chain propagation was nicely observed by Brookhart [21]. It is noteworthy that only low molecular weight oligoketone can be obtained with phosphine ligands. Drent attributed this fact to the higher electron density on the Pd center with phosphine ligands than with nitrogen ligands, because the styrene/CO copolymer has a higher tendency than the propene/CO to terminate by β-hydride-elimination [3].



Scheme 6.



Scheme 7.



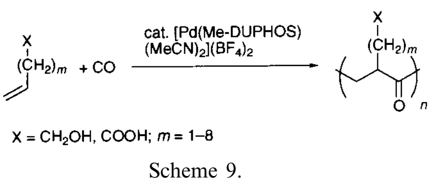
Scheme 8.

The first example of the asymmetric copolymerization was given by Brookhart using a chiral bisoxazoline ligand [22a] (Scheme 6). In this reaction, the enantioface was selected by the chiral ligand instead of the chain-end, and as a result, the polymer was completely isotactic. Since one enantioface was discriminated against the other by the chiral catalyst, it is probable that the copolymer also has high enantiopurity. As an interesting extension of this work, a stereoblock polyketone was synthesized by an alternating copolymerization of 4-*tert*-butyl-styrene with carbon monoxide using a combination of achiral and chiral ligands (Scheme 7) [22b]. The copolymerization was started with a chiral bisoxazoline ligand affording isotactic polyketone. Addition of 2,2′-bipyridyl into the reaction mixture resulted in the elongation of the polyketone in a syndiotactic manner. The efficient displacement of the bisoxazoline by 2,2′-bipyridyl enabled the stereoblock copolymer formation.

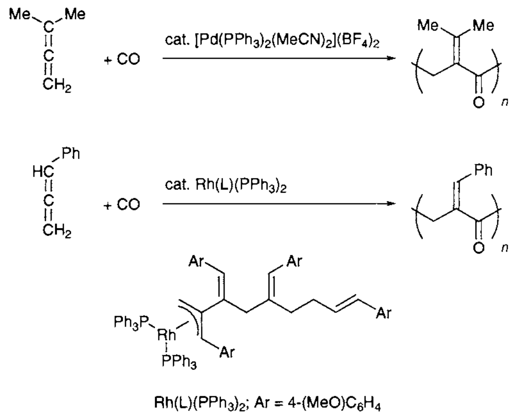
With (*R*,*S*)-BINAPHOS [16] or a chiral phosphine-imine ligand [23], successful results are also reported. These unsymmetrical bidentate ligands seem to have overcome the electronic problem of bisphosphine type ligands. Using the Pd-phosphine-imine complex, terpolymerization of styrene, ethene, and CO has been most recently achieved [24] (Scheme 8).

5. Asymmetric alternating copolymerization with other alkenes

The existence of functional groups might lower the catalytic activity by blocking a coordination site on the metal center. Interestingly, however, Sen reported that the alternating copolymerization proceeds with alkenes



Scheme 9.

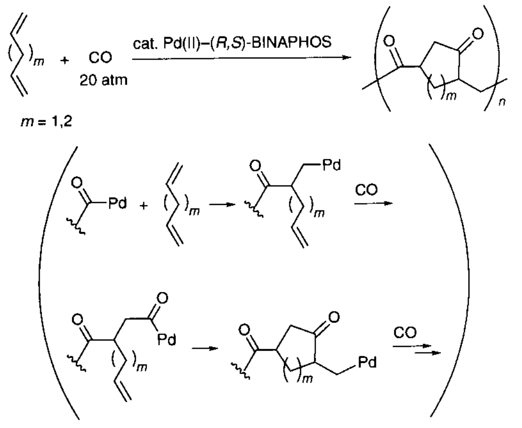


Scheme 10.

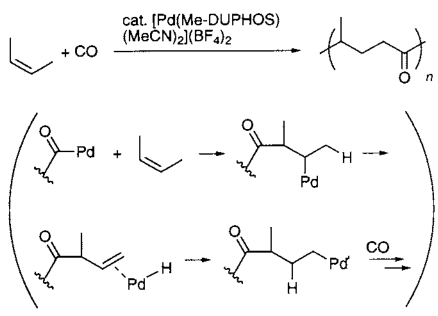
having hydroxyl and carboxylic groups [25]. The –OH groups of these substrates give rise to complex structures of the polymer by nucleophilic additions to the carbonyl group in the main chain (Scheme 9).

Recently, employment of allene as a substrate for the copolymerization has been reported. Sen used a Pd(II) complex with Me-DUPHOS for the copolymerization of 3-methyl-1,2-butadiene with CO [26]. The less substituted double bond was incorporated into the main chain. Meanwhile, Osakada and Yamamoto reported the copolymerization with arylallene [27]. It is noteworthy that an Rh-catalyst was successfully applied to this particular system (Scheme 10).

When an α,ω-diene is used as the alkene moiety, cyclocopolymerization proceeds if the two C–C double bonds are separated with an adequate distance as shown in Scheme 11. A probable cyclization process is drawn below the Scheme. Thus cyclocopolymerization has been reported for 1,5-hexadiene [28] and 1,4-pentadiene [29]. In both examples, complete cyclization has been achieved but the *cis*/*trans* relative configuration between the two substituents on the cycloalkanone was not controlled.



Scheme 11.



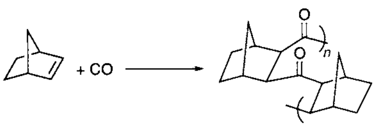
Scheme 12.

Internal alkenes are much less reactive in comparison with terminal ones. For (*Z*)-2-butene, only an oligomer with number of repeating units (ca. 7) was obtained using Pd–Me-DUPHOS as a catalyst [18]. It should be noted that, with this substrate, three carbons of the alkene, instead of just two, are incorporated into the main chain of the oligomer (Scheme 12). Thus, an isomerization via β-hydride elimination and olefin re-insertion is suggested to have taken place during the cooligomerization process.

When the internal alkenes are activated with molecular strain, such an isomerization process is not required. Thus, norbornene, norbornadiene, and their analogs are known to copolymerize with carbon monoxide [30]. In the polymer main chain, the two acyl groups are attached to a norbornane group at its *exo*-positions in most of the repeating units [31] (Scheme 13).

6. Conclusions

Thus, in this manuscript, several types of selectivities have been discussed concerning to the alternating copolymerization of various alkenes with carbon monoxide. It is of much interest to see how the choice of anions and ligands affects the activity and selectivity of the palladium catalyzed reactions. Amongst all, the completely alternating, highly isotactic, and highly enantioselective copolymerization of 1-alkenes with CO presents a new direction of stereoregular polymer synthesis, in the view that the concept of asymmetric synthesis of small molecules could be applied to polymer synthesis. From commercial view points, the products may have potential utility due to the easy availability of the monomers, which may match to



Scheme 13.

polyolefin compounds. High stereoregularity may be expected to induce additional utilities of the polyketones.

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