

Asymmetric catalytic synthesis of polyketones and polycarbonates*

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Abstract: Two examples are presented for the synthesis of optically active polymers with main-chain chirality from achiral monomers using chiral metal-complexes as catalysts. Asymmetric alternating copolymerization of α -olefins with carbon monoxide provided optically active polyketones when catalyzed by an (*R,S*)-BINAPHOS–Pd complex. From propene and CO, highly isotactic polyketone with high enantioselectivity (>97 % like diad and >95 % ee). Spectroscopic and theoretical studies revealed that the olefin insertion is the key step for the enantiofacial selection and that this step takes place at *cis* to the phosphine part of (*R,S*)-BINAPHOS. The catalyst is applicable not only to propene/CO but also to styrene/CO, which enabled the first asymmetric terpolymerization of propene/styrene/CO. The catalyst tolerates functional groups such as fluorocarbons and a nitrile group so that they can be incorporated in the side chain. Optically active polycarbonate was also synthesized by the alternating copolymerization of cyclohexene oxide with carbon dioxide via the desymmetrization of the *meso*-epoxide. Dinuclei zinc species prepared from diethylzinc, ethanol, and α,α' -diphenylprolinol, was revealed to be the real active species.

INTRODUCTION

C₁ resources such as carbon monoxide, carbon dioxide, methane, and methanol have been considered to be attractive raw materials for the chemical industry, as alternative to unrecoverable fossil resources, especially petroleum. Use of CO in combination with transition-metal catalysts has recently made great advances in the manufacturing of industrial chemicals [1]. Since early 1990s, we have been engaged in the development of fine-chemical processes, especially asymmetric catalysis, utilizing CO. In 1993, we reported a striking improvement in the enantioselectivity of asymmetric hydroformylation using a rhodium complex of a chiral phosphine-phosphite (*R,S*)-BINAPHOS, an unsymmetrical bidentate ligand [2]. Several classes of alkenes, such as arylalkenes, conjugated dienes, and hetero-atom functionalized alkenes, were converted into their corresponding chiral aldehydes mostly over 90 % ee. Even after one decade since its first discovery, the catalyst still keeps the highest regio- and enantioselectivities among other examples [3]. The unique feature of the ligand is its two nonequivalent phosphorus atoms, which enabled the exclusive apical-equatorial coordination to the trigonal bipyramidal rhodium center producing a single active species. With this unique ligand in hand, we examined another type of asymmetric carbonylation of olefins, the alternating copolymerization of α -olefins with CO. Optically active polyketones with main-chain chirality could be thus produced from achiral monomers. As another example of asymmetric polymerization of achiral monomers, here we present the asymmetric al-

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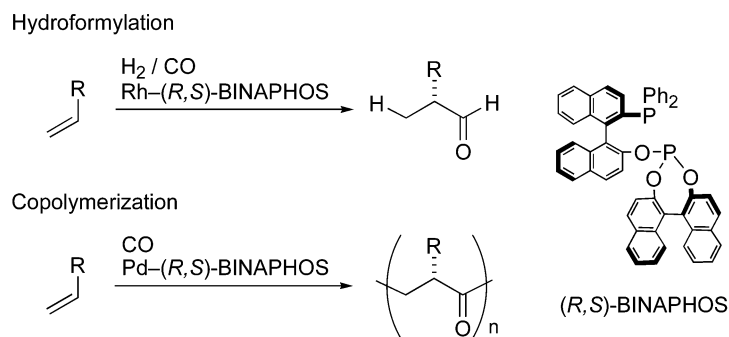


Fig. 1 Highly selective asymmetric carbonylation of olefins.

ternating copolymerization of *meso*-epoxide with carbon dioxide to afford optically active aliphatic polycarbonates.

ASYMMETRIC SYNTHESIS OF POLYKETONES

Selectivities to be controlled in the alternating copolymerization of olefins with carbon monoxide

The copolymerization of ethene with CO using transition-metal catalysts provides the perfectly alternating copolymer, poly(1-oxo-trimethylene) [4]. When a 1-alkene such as propene or styrene is used in place of ethene, three more factors must be controlled for obtaining stereoregular alternating copolymers (Fig. 2). (1) Regioselectivity: depending on the insertion direction of α -olefin, there are three kinds of possible unit structures, namely, head-to-tail, head-to-head, and tail-to-tail. When all the monomers insert with the same regioselectivity, the resulting polymer consists of a head-to-tail structure. (2) Tacticity: the head-to-tail copolymer possesses asymmetric centers in the main-chain. Two kinds of tacticity are drawn in Fig. 2; the syndiotactic copolymer consists of the alternating order of the absolute configuration, *RSRS*—, while isotactic copolymer contains the same absolute configuration order either *RRRR*— or *SSSS*—. (3) Enantioselectivity: Two enantiomers exist for the isotactic copolymer, *RRRR*— and *SSSS*—. We examined the catalytic asymmetric synthesis of the isotactic copolymer.

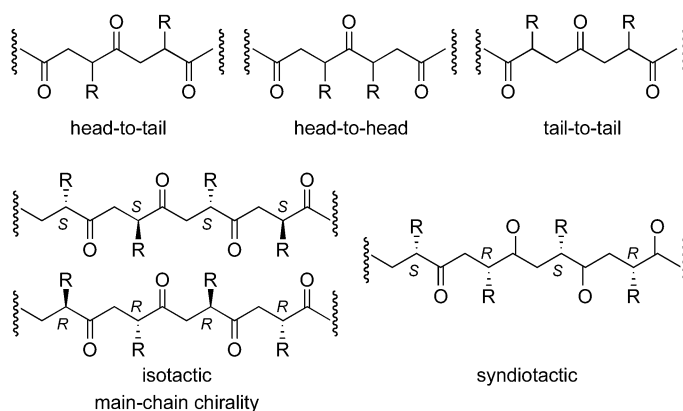
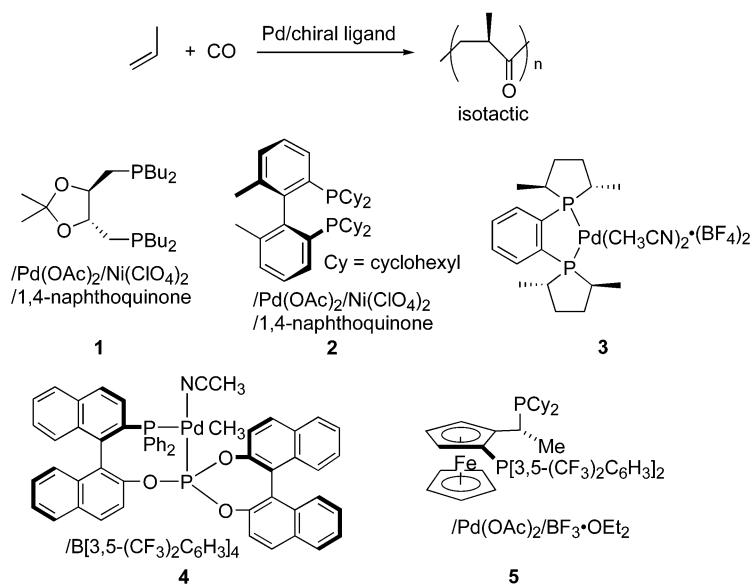


Fig. 2 Selectivities to be controlled in the alternating α -olefins/CO copolymerization.

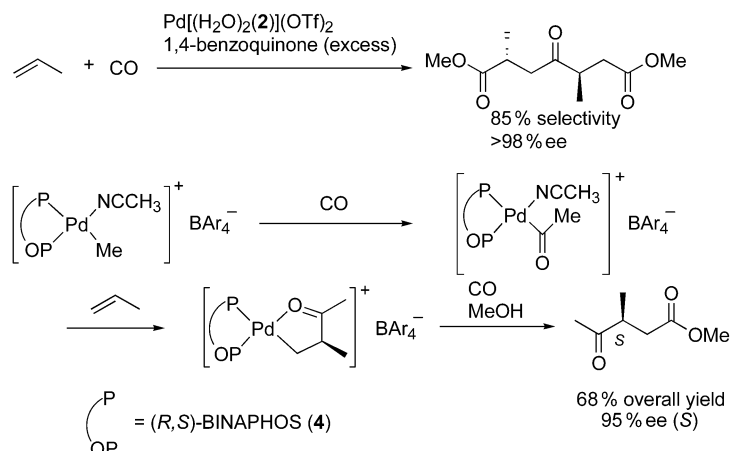
Asymmetric alternating copolymerization of propene with carbon monoxide

The first example of the alternating copolymerization of propene with carbon monoxide was reported in the patent from Shell in 1985 using L_2PdX_2 (L_2 = bidentate phosphine such as dppp, X = a weakly or noncoordinating anion) as a catalyst [4]. Consiglio improved the head-to-tail selectivity to >99 % using a bis(trialkylphosphine), dipp [1,3-bis(diisopropylphosphino)propane], in place of dppp [5]. Chiral ligand was first employed for copolymerization of propene with carbon monoxide by Wong in 1990 [6]. The polymer which showed a specific rotation of $[\alpha]_D^{25} +10.4$ (in HFIP) was obtained using a chiral bisphosphine ligand, (–)-4,5-bis(dibutylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (**1**) (Scheme 1). In 1992, the first successful example of asymmetric copolymerization was reported by Consiglio, using chiral bis(dialkylmonoarylphosphine) with axial asymmetry, BICHEP (**2**), as a ligand [7]. With the ligand, a stereoregularity of the polyketone is 100 % of head-to-tail structure and 93 % of *like*-diad, exhibiting a high degree of $[\alpha]_D^{20} +26$ (in HFIP) and $\epsilon = +1.56$ (in HFIP). In 1995, Sen reported that completely head-to-tail and isotactic copolymer was obtained by the use of chiral bis(dialkylmonoarylphosphine), (*S,S*)-Me-DUPHOS (**3**) [8]. Also, in 1995, we achieved the synthesis of the polyketone using chiral phosphine-phosphite ligand, (*R,S*)-BINAPHOS (**4**), the polymer showing the highest molecular weight of $M_n = 65\,300$ and molar rotation of $[\Phi]_D^{24} -40$ ($c\ 0.51$ in HFIP) [9]. The polyketone obtained by $[Pd\{(R,S)\text{-BINAPHOS}\}(Me)(CH_3CN)][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ system was perfectly isotactic polymer. Very recently, another example of unsymmetrical bidentate ligand **5** was reported to be an efficient catalyst for the asymmetric propene/CO copolymerization [10].



Scheme 1 Asymmetric alternating copolymerization of propene with CO.

Sen reported that the degree of the enantioselectivity of absolute configuration of asymmetric carbon was found to be >90 % by the ^{13}C NMR observation of carbonyl carbon in the presence of chiral NMR shift reagent [8]. Consiglio showed that a head-to-tail dimer, *anti*-dimethyl 4-oxodimethylheptanedioate, was obtained in 85 % selectivity over other diastereomers with >98 % ee using **2**, when the shorter oligomers were produced by adding a large amount of an oxidant (Scheme 2, above) [11]. Nozaki demonstrated that the absolute configuration of the polyketone produced by Pd-(*R,S*)-BINAPHOS system is *S*, by the preparation of a model compound, methyl (*S*)-3-methyl-4-oxo-pentanoate, obtained in the initiation reaction of polymerization (Scheme 2, below)

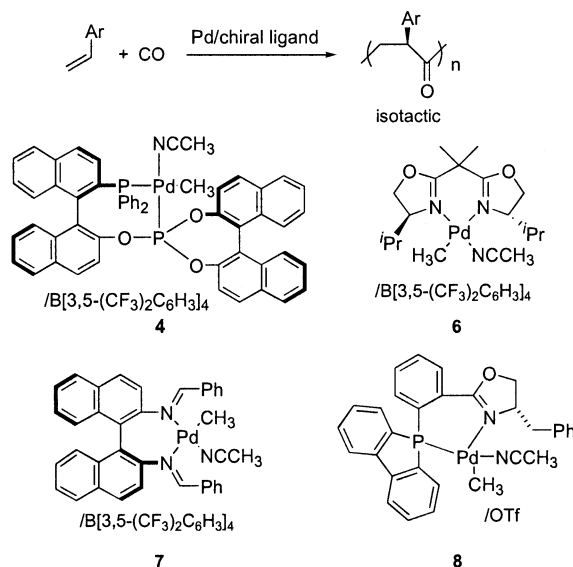


Scheme 2 Model studies to determine the enantioselectivity of the copolymerization.

[9]. The degree of enantiomeric excess of the model compound is 95 %, which indicates that the absolute configuration of asymmetric carbon in the polymer main-chain is perfectly controlled to be *S*. Also (*S*)-polyketone showed the positive optical rotation in HFIP and negative in CHCl_3 .

Asymmetric alternating copolymerization of vinylarene with carbon monoxide

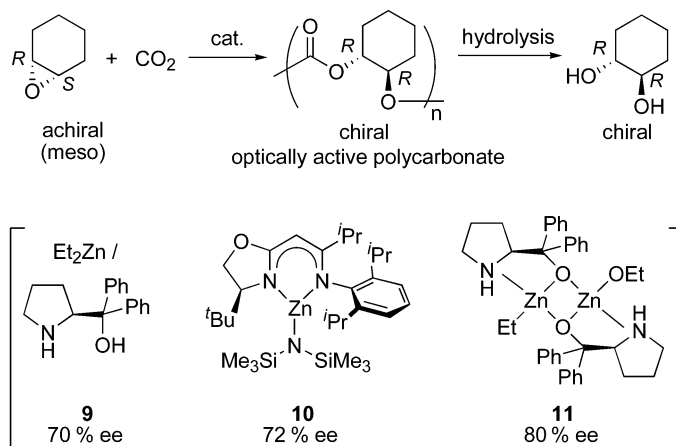
Aryl-substituted alkenes, such as styrene and its analogs, show different polymerization behavior from the aliphatic 1-alkenes described above. Perfectly alternating copolymer with over 90 % syndiotactic diad is given from styrene and CO when a bidentate nitrogen ligand, such as 2,2'-bipyridine or 1,10-phenanthroline is employed. Brookhart first reported the asymmetric alternating copolymerization of 4-*tert*-Bu-styrene with carbon monoxide using a chiral bisoxazoline ligand **6** to give completely isotactic copolymer (Scheme 3) [12]. Except for **4** [9], bidentate sp^2 -nitrogen ligands are mostly used for the reaction rather than bisphosphines.



Scheme 3 Asymmetric alternating copolymerization of vinylarene with CO.

ASYMMETRIC SYNTHESIS OF POLYCARBONATES

The utilization of carbon dioxide as a feedstock for organic compounds receives worldwide interest. One of the most promising processes for CO₂ utilization is the alternating copolymerization of epoxide and carbon dioxide to yield aliphatic polycarbonate [13]. In 1969, Inoue first reported the synthesis of high-molecular-weight poly(propylene carbonate) by the alternating copolymerization of propene oxide and carbon dioxide using Et₂Zn/water mixture as a catalyst [14]. An accepted reaction mechanism for the copolymerization of epoxide and carbon dioxide is (i) CO₂ insertion into Zn–alkoxide bond to form zinc carbonate, and (ii) the ring-opening of epoxide by the back-side attack of the resulting carbonate anion [15]. Thus, if the ring-opening copolymerization of *meso*-epoxide with CO₂ takes place via the configuration inversion at one of the two chirotopic centers selectively, optically active aliphatic polycarbonate consists of either (*R,R*)- or (*S,S*)-*trans*-1,2-diol unit should be produced [16]. In 1999, we reported the first example of the asymmetric alternating copolymerization of *meso*-epoxide with CO₂ [17]. Optically active poly[cyclohexene oxide-*alt*-CO₂] was obtained by using an equimolar mixture of Et₂Zn and (*S*)-diphenyl(pyrrolidin-2-yl)methanol (**9**) as a chiral catalyst (Scheme 4). Because polycarbonate can be hydrolyzed into *trans*-1,2-diol and CO₂ by alkali-treatment, the degree of asymmetric induction, 70 % ee, could be evaluated unambiguously. In 2000, Coates reported the asymmetric alternating copolymerization using a well-defined Zn–imine oxazoline ligand complex **10**, which showed higher activity and controlled molecular weight compared to **9** [18]. More recently, we reported the improved enantioselectivity of 80 % by using dimeric zinc complex **11** in which one of the two zinc atoms is attached to an ethoxy group while the other is to an ethyl group [19]. The copolymer obtained with **11** has EtOCOO- end group, indicating that the initiation reaction occurred by the insertion of CO₂ into the Zn–OEt bond. In spite of its high stereoregularity, the copolymer of 80 % ee shows glass-transition temperature at 117 °C, the value being very close to the ones previously reported for the copolymers with lower stereoregularity.



Scheme 4 Asymmetric alternating copolymerization of cyclohexene oxide with CO₂.

CONCLUSION

Needless to say, the potential utility of polymers depend on the functional groups included in the polymers. At the same time, the solid-state arrangement of the polymer chains also significantly affects their properties. As was evidenced in this review article, single-site metal complexes enabled to produce polymers of different stereoregularity, even if the polymerization employ the same monomer(s). The different stereoregularity may induce difference in physical property.

Asymmetric synthesis of chiral polymers from achiral monomers is now achieved for several polymers. The content of each enantiomer is essential to control the stereocomplex formation. In addition, here we propose another viewpoint of chirality: when we consider that our product plastics are used in our environment, we cannot avoid thinking about how it affects the nature. Because Mother Nature is chiral, enantiomeric polymers should be considered as different a product from each other, as is so in pharmacology.

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