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Metal-catalyzed synthesis of stereoregular polyketones, polyesters, and polycarbonates †

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Stereocontrol of the stereogenic centers in the main chain during the synthesis of polyketones, polyesters, and polycarbonates has been reviewed. The examples described may be classified in the following ways. Retention of the configuration which exists in the monomer: as described in the ring opening polymerization of (*S*,*S*)-lactide and (*R*)-β-butyrolactone to give poly[(*S*)-lactic acid] (PSLA) and poly[(*R*)-3-hydroxybutyrate] (PRHB), respectively. Enantiomer selection either by the catalyst or by the chain-end: presented examples are the synthesis of heterotactic and isotactic PLAs from racemic lactide and the preparation of syndiotactic and isotactic PHBs from a racemic mixture of β-butyrolactone. Selection of enantiotopic sites of a *meso* monomer by the catalyst or by the chain-end: syndiotactic and heterotactic PLAs from *meso*-lactide and isotactic poly(epoxide-*alt*-CO_2) from *meso*-epoxide are the examples described here. Creation of a new stereogenic center upon polymerization starting from prochiral monomers. The catalyst or the chain-end selects one of the two enantiofaces of an α-olefin in the olefin/CO alternating copolymerization to give either isotactic or syndiotactic polyketones. Thus, a variety of stereoregular polymers are now available owing to the remarkable achievements of precise design and synthesis of single-site catalysts.

Introduction

In order to obtain stereoregular polymers, coordination polymerization using well-defined metal complexes has played a leading role in the last two decades. Because a complex endowed with a single-active site can be designed at the molecular level, the precise modification of catalysts provides us with a variety of stereoregular polymers. For example, not only isotactic and syndiotactic, but also hemiisotactic and stereoblock isotactic–atactic polypropylenes are now available. Also, tacticity control has been successfully developed for polymerization of other vinyl-monomers, such as styrene and methyl (meth)-acrylate. Excellent review articles on the stereocontrol of vinyl-monomer polymerization have been published.[1–5]

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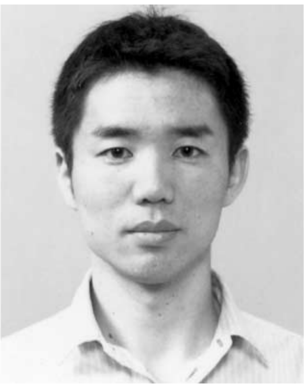
Tamejiro Hiyama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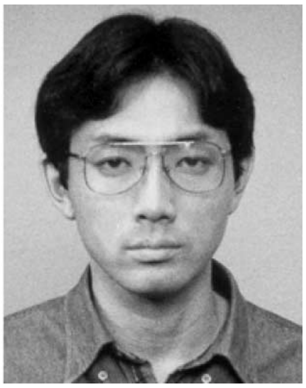
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Polymers bearing functional groups show unique physical properties depending on the nature of the functional groups. Among the common functional groups, carbon–oxygen double bonds are most widely employed. This review describes stereocontrol in metal-complex catalyzed polymerization to produce polymers including carbonyl groups in the main chain; those are polyketones, polyesters, and polycarbonates. We limit the subject to the polymers whose main chain consists of substituted methylene or ethylene and –C(=O)–, –C(=O)O– or –OC(=O)O– (see Fig. 1). Unlike simple homopolymers of vinyl monomers, the polymers discussed here are chiral in several cases. Accordingly, stereocontrol producing a single enantiomer is described in addition to the conventional tacticity control. Carbonyl groups in the main chain are expected to influence the polymer conformation influenced by the C=O dipole moment. We briefly summarize the relation between the stereoregularity of the polymer and its structure, especially in crystals. Formation of stereocomplexes is also mentioned.

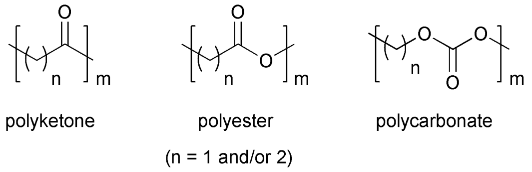


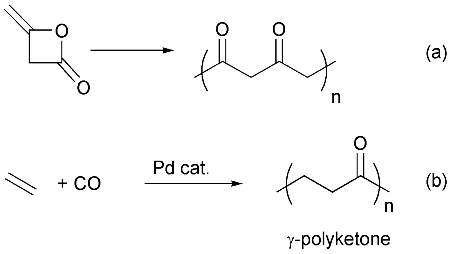
Fig. 1 Polyketone, polyester, and polycarbonate consists of $–CH_2–$ or $–CH_2CH_2–$ and –C(=O)–, –C(=O)O– or –OC(=O)O–.

Thus, this review is separated into three major sections: (1) polyketones, (2) polyesters, and (3) polycarbonates. Each section includes general information about the synthesis of the polymers, the origin of any stereoregularity, recent examples of selective synthesis, and examples of structural studies on the polymers. When two stereogenic centers are connected by a symmetrical bridging group, *e.g.* methylene, ethylene or carbonyl, the diad is called *meso* (*m*) or *racemo* (*r*) for the same or the opposite relative configurations, respectively. When two stereogenic centers are connected with an unsymmetrical bridging group, *e.g.* $–CH_2–CHR–$ ($R \neq H$), the diad is named *like* (*l*) or *unlike* (*u*) for the same or the opposite relative configurations, respectively.

1. Polyketones

1.1 Synthesis of polyketones

Although β-polyketones (1,3-polyketones, polyketide) are attractive as a substitute for polyacetylene, only a few reports concerning its synthesis are available. Shown in Scheme 1 (a) is the polymerization of ketene or diketene.[6,7] It was reported that the polyketones mainly form polyenol structures. γ-Polyketones (1,4-polyketones) in which the two carbonyl groups are connected with an ethylene group can be synthesized by the palladium catalyzed alternating copolymerization of olefins with carbon monoxide (Scheme 1 (b)). The olefin/CO copolymerization will be the first major topic of this review.



Scheme 1 Synthesis of β-polyketone (1,3-polyketone, polyketide) and γ-polyketone (1,4-polyketone).

1.2 Origin of stereochemistry

β-Polyketone formally has two regular patterns: isotactic and syndiotactic although easy epimerization of the α-carbon of the β-diketone moiety due to enolization precludes the polymer from stereochemical studies. For γ-polyketone, isotactic and syndiotactic polymers exist (Fig. 2 (a) and (b)). In addition, control of the absolute configuration of the asymmetric carbon atoms becomes a problematic issue. Because the mono-substituted ethylene group has a directionality along the polymer backbone, the isotactic regioregular polyketone is chiral by virtue of its main-chain stereochemistry; in contrast, its syndiotactic counterpart is achiral. Here we do not discuss stereochemistry for the di-substituted ethylene in the main chain because the alternating copolymerization with carbon monoxide hardly proceeds with internal olefins.

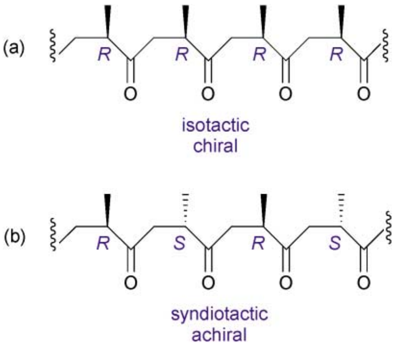


Fig. 2 Stereoregularities in γ-polyketones.

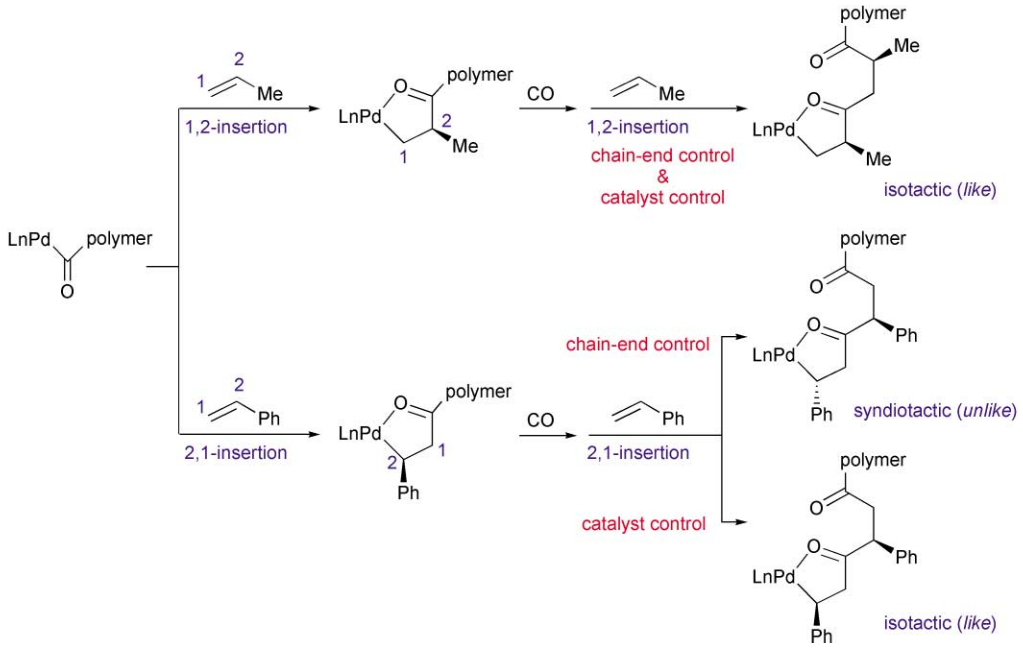
1.3 Alternating copolymerization of aliphatic 1-alkenes with carbon monoxide: general aspects

Copolymerization of ethene with carbon monoxide using transition metal catalysts provides a γ-polyketone, poly(1-oxo-trimethylene), which possesses engineering plastic properties, high crystallinity, excellent mechanical properties, and chemical resistance.[8–11] Here we discuss the alternating copolymerization of mono-substituted ethenes with carbon monoxide. The alkenes are classified into aliphatic 1-alkenes and vinylarenes. The major difference between the two classes of olefins is the direction of olefin insertion: propene inserts to an acyl–palladium bond so that palladium binds the terminal carbon (1,2-insertion) while palladium is attached to the α-position of the phenyl group (2,1-insertion) in the case of styrene. When an achiral catalyst is employed for the copolymerization, under chain-end control in other words, the propene/CO alternating copolymer is either atactic or rich in the isotactic (*like* diad) form, while styrene/CO alternating copolymer is rich in the syndiotactic (*unlike* diad) form. Unlike an achiral catalyst, a chiral catalyst is able to select one of the two enantiofaces of alkenes so that an isotactic alternating copolymer is produced both from popene and styrene (catalyst control, see Scheme 2).

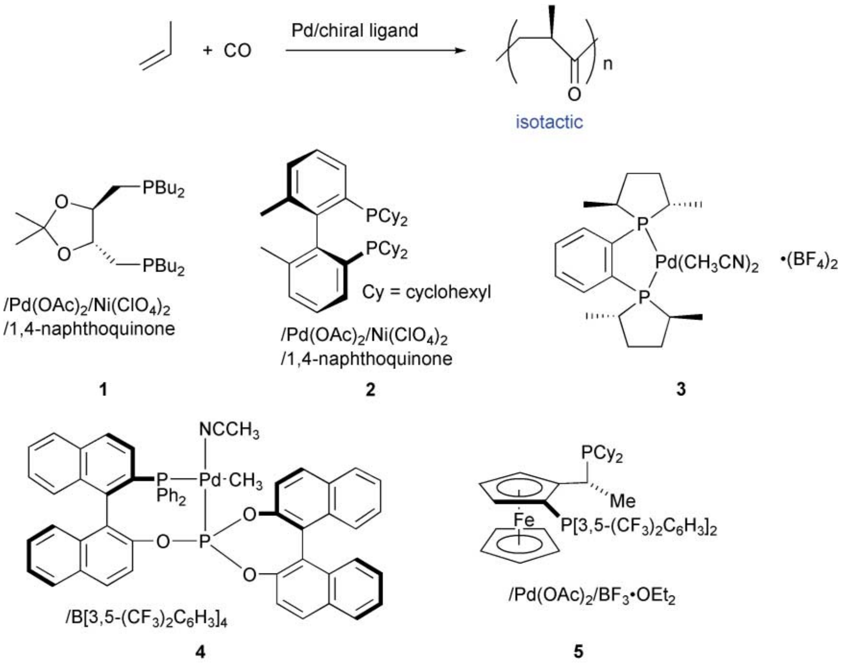
1.4 Alternating copolymerization of aliphatic 1-alkenes with carbon monoxide

The first example of the alternating copolymerization of propene with carbon monoxide was reported in a patent from Shell in 1985.[12] The regioselectivity of propene was not controlled and three kinds of regioisomers existed in the polyketone. The catalyst $[Pd(L^{\wedge}L')(S)_2][X]_2$ where $L^{\wedge}L'$($L = $ or $\neq L'$) is a chelate diphosphine ligand, S is a solvent molecule and X is an anion with low coordination capability was employed. Consiglio raised the head-to-tail selectivity to >99% using a bis(trialkylphosphine), dippp [1,3-bis(diisopropylphosphino)propane], as a ligand.[13]

Isotactic polyketone. Several chiral ligands have been developed for the synthesis of isotactic polyketone. Because the



Scheme 2 Difference between aliphatic 1-alkenes and vinylarenes in the palladium catalyzed alternating copolymerization of olefins with carbon monoxide.



Scheme 3 Asymmetric alternating copolymerization of propene with CO to give isotactic polyketone.

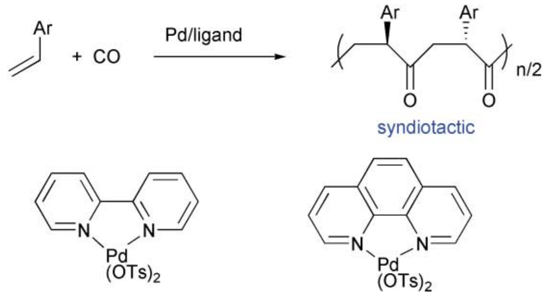
catalyst selects one of the two enantiofaces, it is possible to produce one of the two enantiomers of the isotactic polyketone when a single enantiomer of chiral catalyst is employed. In 1990, Wong patented the synthesis of a propene/CO alternating copolymer which showed a specific rotation of $[\alpha]^{25}_{\mathrm{D}}$ +10.4 (in HFIP ($((CF_3)_2CHOH)$)) using (−)-4,5-bis(dibutylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (**1**) (Scheme 3).[14] In 1992, a successful example of asymmetric copolymerization was reported by Consiglio, using the chiral bisphosphine complex **2**.[15–17] The sereoregularity for head-to-tail structure was 100% and for *like*-diad was 93%. High enantioselectivity was suggested by optical rotation and CD ($[\alpha]^{20}_{\mathrm{D}}$ +26 (in HFIP) and $\varepsilon = -1.39$ (in HFIP)). Summarized in Scheme 3 are the representative catalysts reported for the asymmetric alternating copolymerization of propene with CO to date.[18–20] The ligands are classified as (i) symmetrical bisphosphines, (ii) unsymmetrical bisphosphines, and (iii) phosphine-phosphites. Currently, a modified Josiphos system **5** shows the highest catalytic activity with almost complete regio- and stereo-selectivity. Thus, under 7.5 MPa of CO pressure at 50 °C, 1797 g of copolymer was given from 1 g of Pd per hour and the molecular weight was 14.0×10^3. The selectivity was 97.5% of *like*-diad, $[\alpha]_{\mathrm{D}} = -34.6$ (in HFIP) and $\varepsilon = +1.26$ (in HFIP).[20]

Assignment of tacticity is usually carried out by ^{13}C NMR. Isotactic polyketone exhibits a peak at 218.0 ppm due to its carbonyl carbon. In order to determine the degree of enantioselectivity, several methods were examined. Sen employed chiral NMR shift reagents to measure the ^{13}C NMR.[18] Consiglio[21] and Nozaki[19] demonstrated that the absolute configuration of the chirotopic carbons atom are controlled with at least 98% ee (*R*) and 95% ee (*S*) when the polyketone is produced by **2** and **4**, respectively.

Syndiotactic polyketone. So far, no reports have appeared descibing the syndiospecific copolymerization of aliphatic 1-alkenes with CO.

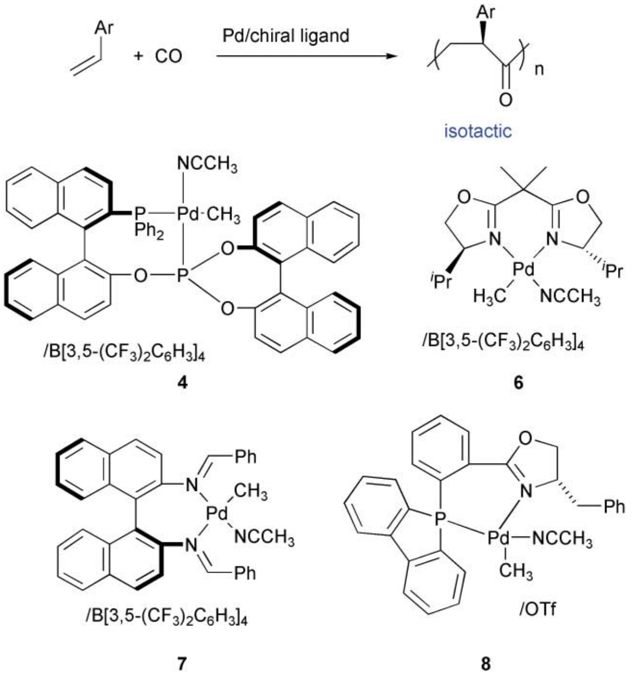
1.5 Alternating copolymerization of vinylarenes with carbon monoxide

Syndiotactic polyketone. Drent[22] and Consiglio[23] obtained perfectly alternating copolymers from styrene and carbon monoxide in a regioregular head-to-tail manner using bidentate nitrogen ligands, such as 2,2′-bipyridine or 1,10-phenanthroline (Scheme 4). The tacticity was prevailingly syndiotactic, with a triad ratio *uu* : *ul* : *lu* : *ll* = 0.8 : 0.1 : 0.1 : 0.[24] When 5-nitro-1,10-phenanthroline was substituted as the ligand for 1,10-phenanthroline an increase in the concentration of the *uu*-triad to ≈90% was observed.[25] The stereochemical composition is usually analyzed by ^{13}C NMR in the region of the *ipso*-carbon atom.[26] The methylene carbon peak of the main chain is also characteristic.[27,28]



Scheme 4 Alternating copolymerization of vinylarene with CO to give syndiotactic polyketone.

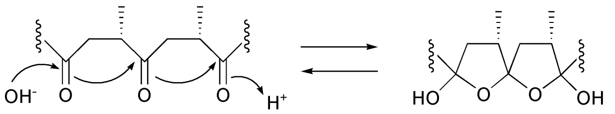
Isotactic polyketone. Catalyst control is essential to produce an isotactic polyketone from styrene or its derivatives because syndiotactic polyketone would be given if the chain-end control is dominant. Brookhart first reported the asymmetric alternating copolymerization of 4-*tert*-butyl-styrene (TBS) with carbon monoxide using a chiral bisoxazoline ligand **6** to give completely isotactic copolymer (Scheme 5).[28] Since one enantioface is discriminated against by the other using a chiral catalyst, it is probable that the copolymer is also of high enantiopurity. The representative examples of the isospecific copolymerization catalysts are summarized in Scheme 5. Except for **4**,[19,29] bidentate sp^2-nitrogen ligands are mostly used for the reaction rather than bisphosphines. In order to estimate the enantioselectivity, optical rotation or circular dichroism is employed for poly(styrene-*alt*-CO). Also, as a model study, Consiglio revealed that styrene insertion into an acyl palladium complex derived from **8**, [Pd(C(=O)Me)(MeCN)(P^N)](OTf), was completely regioselective for 2,1-insertion and was enantioselective to produce [Pd(CHPhCH$_2$C(=O)Me)(P^N)](OTf) as a single species.[30]



Scheme 5 Asymmetric alternating copolymerization of vinylarene with CO to give isotactic polyketone.

1.6 Conformational studies on the polyketones

Sen reported the observation of reversible interchange between polyketone and polyspiroketal (Scheme 6).[18] In the solid state, isomerization of the ketone unit to the spiroketal unit in the isotactic 1-heptene/CO copolymer was observed. The ratio of spiroketal/ketone in the copolymer increased after standing as a solid at ambient temperature for 11 days. The spiroketal form of this copolymer was stable in CDCl$_3$ and the spiroketal/ketone ratio did not change significantly in solution over 7 days. In contrast, the spiroketal structure is stable only in the solid state for propene/CO and 1-butene/CO copolymers and pure polyketones were detected when they were dissolved in CDCl$_3$. Spiroketal formation is unique for highly isotactic copolymers generated from propene or other higher aliphatic 1-alkenes.



Scheme 6 For highly isotactic poly(propene-*alt*-CO), an equilibrium between polyketone and polyspiroketal exists. The polyketone form is preferred in HFIP ((CF$_3$)$_2$CHOH).

Due to their isotactic nature, the formation of a helical conformation would be anticipated for the optically active polyketones. However, by optical rotation[18] or CD,[31,32] no evidence has yet been obtained indicating the presence of a stable helical conformation in solution. Meanwhile, an extended conformation was estimated for isotactic poly(propene-*alt*-CO) by static light scattering measurements, which might correspond to a helical structure.[31] In one of the possible helical conformations, a carbonyl oxygen of a polyketone comes close to the neighboring carbonyl carbon. It should be noted that the higher population of spiroketal structure in solution was reported for the fluorinated polyketones. This might be attributed to the preferable helical conformation for fluorinated polyketones compared to other polyketones.[33,34]

In a solid amorphous state, a helical structure is suggested below T_g for optically active methylstyrene/1-decene/CO terpolymer.[35] At certain temperatures above T_g, the molar ellipticity of a film drastically decreases while the molar ellipticity in solution does not. Recently, Nozaki and Kato reported that a side chain liquid crystalline polyketone forms a chiral nematic phase. A helical conformation of the main chain may be responsible.[36]

In crystalline states, the conformation of the polyketone has been well investigated. The crystal structure of poly(ethene-*alt*-CO) in well-oriented fibers (α-structure) was determined by wide-angle X-ray scattering methods.[37] The cross-sectional area of the unit cell perpendicular to the fiber axis amounts to 0.352 nm^2, which is even smaller than the polyethylene unit cell (0.362 nm^2). The very dense packing is a result of the arrangement of the dipoles in the crystal lattice, giving rise to strong lateral forces between the polymer chains. In an imperfectly alternating copolymer, the β-crystal was formed,[37] while the α-crystal was formed in a perfectly alternating copolymer.[38] Both crystalline structures have two polymer chains in an all-*trans* conformation along the *c*-axis, but the chain packing is different. The α-structure has denser packing than the β-structure (ρ_C = 1.30 g cm^{-3}). Klop showed that the α-form was dominant in the perfectly alternating copolymer at room temperature and the phase

Table 1 Melting points of isotactic polyketones and their stereocomplexes

Copolymer	mp (T_m)/°C
(+)- or (−)-propene–CO	171
(±)-propene–CO complex	239
(+)- or (−)-1-butene–CO	137
(±)-1-butene–CO complex	265
(+)- or (−)-allylbenzene–CO	62
(±)-allylbenzene–CO complex	169
(+)-propene–CO/(−)-1-butene–CO	230

transition from α to β was observed at 110–125 °C.[39] Crystallization from the melt on slow cooling to room temperature gives the α-phase,[39] while rapid cooling affords the β-phase.[40]

Only one example has been reported for the crystal structure of the alternating propene–CO copolymer. High molecular weight propene–CO copolymer with random regio- and stereoregularity exhibits elastomeric behavior.[41] A 3_1 helical structure was proposed by an X-ray investigation of an elastic film of the copolymer at 650% elongation.[42]

For syndiotactic poly(styrene-*alt*-CO), a nearly *trans*-planar conformation with *tc* glide plane symmetry is suggested.[43] As shown in Fig. 3 (a), the side-chain phenyls are oriented in the same direction of the planar main chain but they are not exactly stacking. For isotactic poly(styrene-*alt*-CO), a *s*(2/1) helical conformation was confirmed by powder X-ray diffraction for optically pure styrene/CO polyketone (Fig. 3 (b)).[44,45] The observed chain conformation has a repeat period almost identical to that observed in syndiotactic polyketone in spite of the different symmetry connecting the monomeric units, *s*(2/1) instead of *tc*.

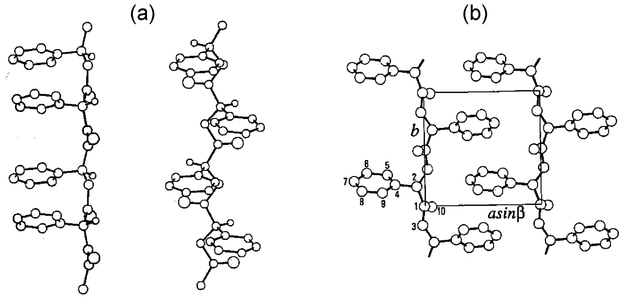


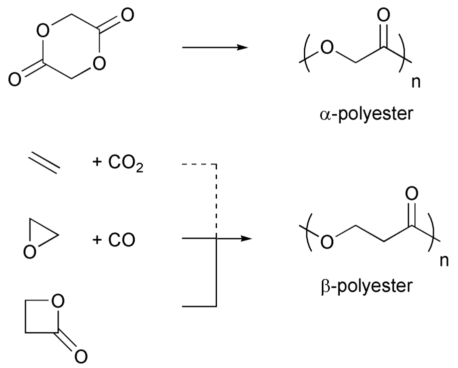
Fig. 3 From the left, the chain conformation of syndiotactic poly(styrene-*alt*-CO), the same polymer from another view point, and two chains of isotactic poly(styrene-*alt*-CO). Transferred from (a) ref. 43 and (b) ref. 44 with permission from (a) Elsevier and (b) American Chemical Society.

It has been known that blending two polymers with the same chemical composition but a different stereochemical sequence gives a polymer–polymer stereocomplex.[46–48] A stereocomplex was suggested to be formed from racemic mixtures of enantiomeric polyketones (Table 1).[49] Optically pure (+)- and (−)-poly(1-alkene-*alt*-CO) were prepared from propene, 1-butene, and allylbenzene using Pd–(*S*)-Me-DUPHOS and its enantiomer. For all the three kinds of polyketones, the higher T_m was observed for a 1 : 1 mixture of (+)- and (−)- poly(1-alkene-*alt*-CO) when compared with optically pure (+)- or (−)- poly(1-alkene-*alt*-CO). Furthermore, chiral recognition and the stereocomplexation between two different polyketones, such as (+)-propene/CO and (−)-1-butene/CO, were confirmed.

2. Polyesters

2.1 Synthesis of polyesters

α-Polyester (polyester of α-hydroxycarboxylic acid) is easily prepared *via* ring-opening polymerization of a cyclic dimer (see Scheme 7). Ring-opening polymerization of lactide to produce poly(lactic acid) (PLA) is one of the hottest topics in stereocontrolled polymerization.[50,51] Formally, alternating copolymerization of olefins with carbon dioxide would give a polyester of β-hydroxycarboxylic acid but no reports have ever appeared on this subject. Alternatively, the polyesters can be prepared by the alternating copolymerization of epoxide with carbon monoxide, although the molecular weight is still not satisfactorily high.[52] Practically, the polyester is made by the ring-opening polymerization of β-propiolactones.[51,53]



Scheme 7 Synthesis of α-polyester (polymer of α-hydroxycarboxylic acid) and of β-polyester (polymer of β-hydroxycarboxylic acid).

2.2 Origin of stereochemistry

Poly(lactic acid) (PLA), the methyl-substituted α-polyester, has been synthesized in three types of stereoregularity; isotactic, syndiotactic and heterotactic as shown in Fig. 4 (a), (b) and (c). Depending on the substitution pattern, two regioisomers exist for β-polyester; the difference being methyl-substitution either at the α-position (Fig. 4 (d) and (e)) or at the β-position (Fig. 4 (f) and (g)) of a carbonyl. Each of the regioisomers has isotactic and syndiotactic structures. In this manuscript, we will discuss the ring-opening polymerization of β-butyrolactone affording (f) or (g). Much less work has been reported for (d) and (e).

2.3 Ring-opening polymerization of lactide

Synthesis of PLAs has been studied intensively due to their biocompatible and biodegradable properties and their potential applications in medical and agricultural fields.[54,55] Ring-opening polymerization of lactide, a cyclic diester of lactic acid, provides PLA. A variety of metal alkoxides has been used as initiators and catalysts. Nucleophilic addition of alkoxide to the ester carbon of lactide induces the cleavage of the acyl–oxygen bond with retention of the configuration at the stereogenic centers. There are two diastereomers for cyclic lactide; *meso*-lactide and *rac*-lactide depending on the relative configuration of the α-carbon atoms. As stereoregular polymers, syndiotactic and heterotactic PLAs have been successfully prepared from *meso*-lactide. Starting from enantiomerically pure (*S*,*S*)-lactide, ring-opening polymerization takes place without epimerization at the asymmetric centers to give optically pure poly[(*S*)-lactic acid] (PSLA). Enantiomer-selective polymerization is reported for the racemic mixture of (*S*,*S*)- and (*R*,*R*)-lactide so that one enantiomer is polymerized while the other enantiomer remains untouched. Alternating incorporation of the two enantiomers provides heterotactic PLA.

Syndiotactic poly(lactic acid). In order to synthesize syndiotactic PLA from *meso*-lactide, polymerization should take place through stereoselective ring-opening; continuous acyl–oxygen bond cleavage at one enantiontopic site, either **A** or **B** in Scheme 8. The first synthesis of syndiotactic PLA was reported by Coates in 1999.[56] Using enantiopure chiral aluminium complex (*R*)-**9** (R = ^{i}Pr), polymerization of *meso*-lactide yielded syndiotactic PLA with an enantioselectivity of 96% by

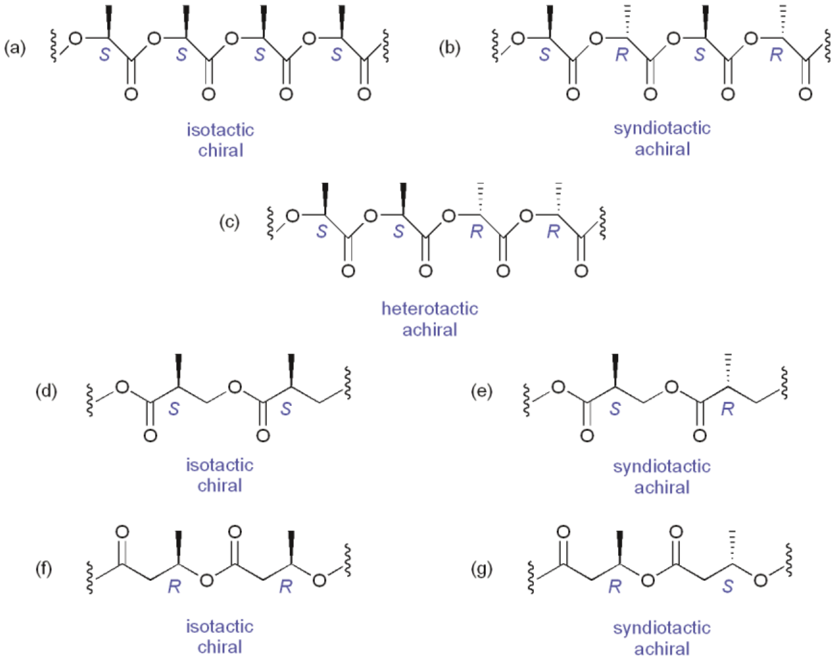
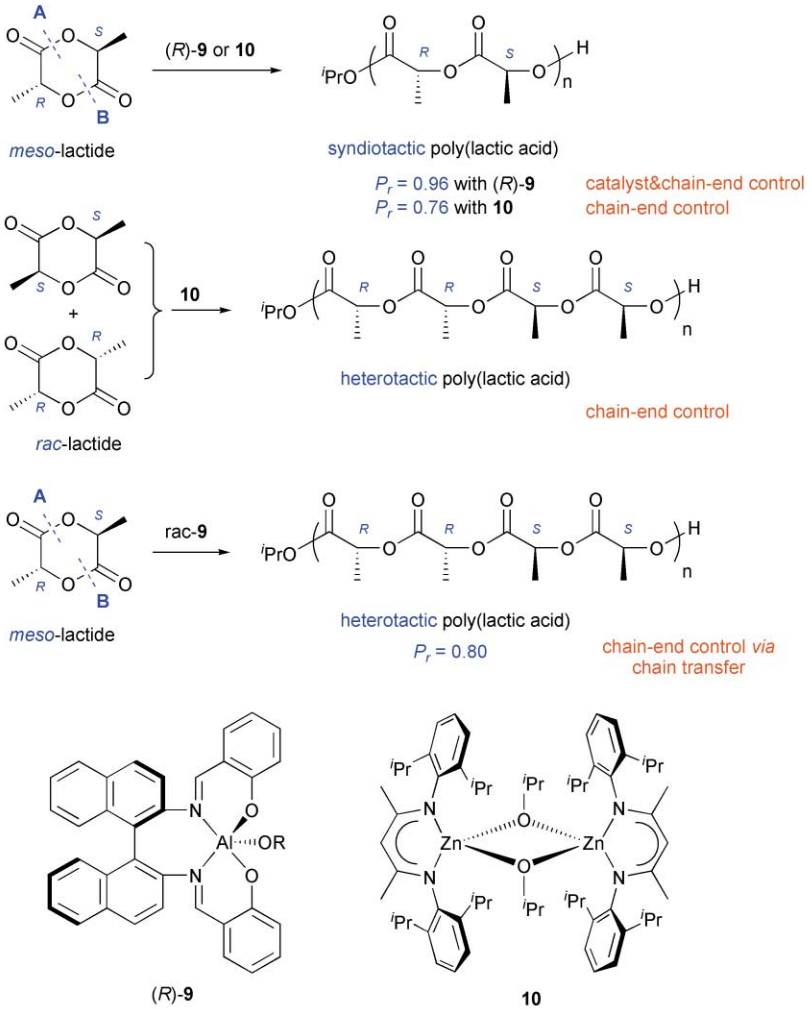


Fig. 4 Stereoregularities in α- and β-polyesters.



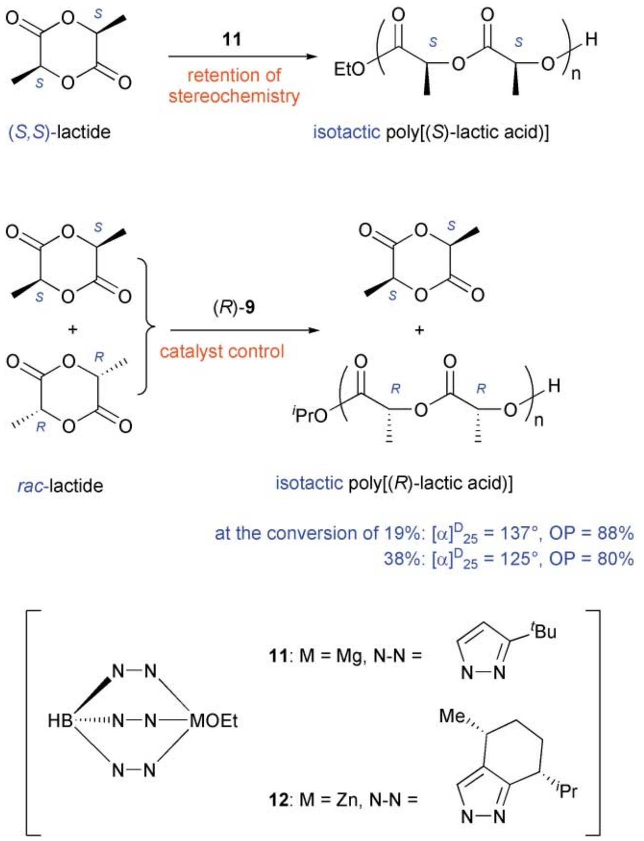
Scheme 8 Ring-opening polymerizations of *meso*-lactide to give syndiotactic or heterotactic PLA and of *rac*-lactide to give heterotactic PLA.

enantiomorphic site-control mechanism (catalyst-control, Scheme 8). The catalyst selected one of the two enantiotopic acyl–oxygen bonds at the initiation. In fact, stoichiometric reaction of (*R*)-**9** with *meso*-lactide underwent bond cleavage at site **A** with 97% selectivity.[57] This high stereoregularity caused the resulting polymer to be crystalline with a T_g value of 51 °C and a T_m value of 149 °C. Coates also reported that the achiral zinc(II) alkoxide **10**, which is ligated by a bulky β-diketiminate, gave syndiotactic PLA from *meso*-lactide through a chain-end control mechanism although the P_r value (the probability of racemic linkages between monomer units) of 76% is lower than in the case of complex (*R*)-**9** (Scheme 8).[58]

Heterotactic poly(lactic acid). In 1995, Kasperczyk synthesized predominantly heterotactic (disyndiotactic) PLA from *rac*-lactide by using lithium *tert*-butoxide.[59,60] More recently, Coates reported the synthesis of heterotactic PLA from *rac*-lactide by using Zn alkoxide **10** (Scheme 8).[58,61] The probability (P_r) of (*R*,*R*)-lactide (or (*S*,*S*)-) incorporated after (*S*,*S*)-lactide (or (*R*,*R*)-) was estimated to be 94% on the basis of ^{1}H NMR. This high stereocontrol was achieved *via* the chain-end control mechanism derived from the bulky β-diketiminate ligand. They also reported that a chiral but racemic catalyst *rac*-**9** (R = ^{i}Pr) produced heterotactic poly(lactic acid) from *meso*-lactide where the probability (P_r) of acyl–oxygen cleavage at one enantiotopic site following the cleavage at the opposite site is 80%.[57] Chain-transfer between the two enantiomers of **9** is proposed for the reaction with *rac*-**9** in order to explain the different selectivity between (*R*)-**9** and *rac*-**9**. Despite the high stereoregularity, heterotactic PLA is an amorphous polymer with T_g <45 °C.

Isotactic poly(lactic acid). The most simple way to produce isotactic, optically pure PLA is the polymerization of optically pure (*S*,*S*)-lactide (or (*R*,*R*)-lactide) using a catalyst such as aluminium tris(alkoxide)[62,63] or tin bis(carboxylate).[64] Chisholm reported that magnesium ethoxide with tris-pyrazolylborate ligand **11** showed high activity for the polymerization of (*S*,*S*)-lactide to give isotactic poly[(*S*)-lactic acid] (PSLA). The polymerization proceeded by a living mechanism and the molecular weight distribution remained under 1.2 up to the [monomer]/[**11**] ratio of 1000 : 1.[65,66]

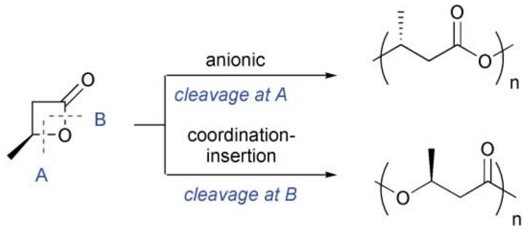
In order to produce isotactic PLA from abundant *rac*-lactide, Spassky and co-workers found that the enantiomerically pure, chiral aluminium complex (*R*)-**9** (R = Me) gave optically active isotactic poly[(*R*)-lactic acid] (PRLA) through the highly selective kinetic resolution of *rac*-lactide.[67] At moderate conversion of 38%, the optical purity of the obtained isotactic PRLA was high, exceeding 80%. The polymerization proceeded in a living fashion. Chisholm and co-workers also investigated the enantiomer-selective polymerization of *rac*-lactide using a chiral zinc complex **12** bearing an optically active tris(tetrahydroindazolyl)borate ligand, resulting in moderate enantioselectivity (Scheme 9).[66]



Scheme 9 Ring-opening polymerizations of (*S*,*S*)-lactide or *rac*-lactide to give isotactic PLA.

2.4 Ring-opening polymerization of β-lactones

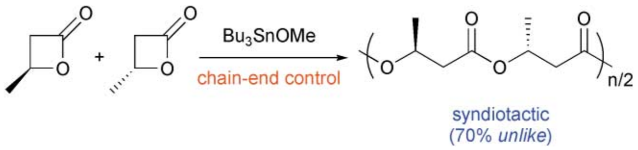
Poly(3-hydroxybutyrate) (PHB) is a naturally occurring polyester produced by a wide variety of bacteria. Natural PHB consists of a repeating unit of *R* configuration at the β-position of the ester carbon, which plays a key role in its biocompatibility, biodegradability and high crystallinity. PHBs can be synthesized by the ring-opening polymerization of β-butyrolactone. This synthetic method tailors PHBs with a diversity of stereochemical sequences (*e.g*. atactic and syndiotactic PHBs), which enables the investigation of the effects of stereochemical and morphological parameters on the mechanical and biological properties. Metal alkoxides are widely used as initiators and catalysts, and some of them provide polyesters with controlled molecular weights and stereochemical sequences. It is well known that there are two mechanisms for the polymerization catalyzed by metal alkoxides (Scheme 10). In the anionic polymerization, the alkyl–oxygen bond of β-butyrolactone gets detached, resulting in the inversion of the configuration at the β-carbon of the monomer. On the other hand, in the coordination–insertion mechanism, ring-opening takes place *via* bond cleavage at the acyl–oxygen bond with retention of the asymmetric center configuration.



Scheme 10 Ring-opening polymerization of β-lactone.

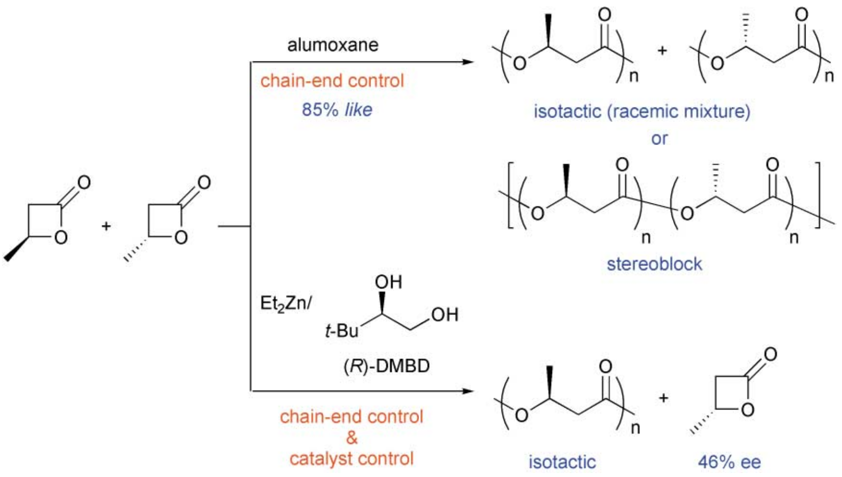
Recently, Coates revealed that zinc complex **10** (Scheme 8) was an unprecedentedly active catalyst for the polymerization of racemic β-butyrolactone under mild conditions to give atactic poly(3-hydroxybutyrate).[68] The reaction proceeded *via* a coordination–insertion mechanism, in a living fashion, and the monomeric zinc species was suggested to be the active species.

The first demonstration of the syndiospecific ring-opening polymerization of racemic β-butyrolactone was reported by Gross in 1993 (Scheme 11).[69] The stereochemistry is controlled by the chain-end. The polymerization was carried out by using tributyltin methoxide (Bu$_3$SnOMe) to give PHB enriched in syndiotactic diads (*unlike*/*like* = 0.7/0.3). Other alkyltin methoxides (Bu$_2$Sn(OMe)$_2$, BuSn(OMe)$_3$) and alkyltin oxides ((Bu$_3$Sn)$_2$O, (Ph$_3$Sn)$_2$O) also catalyze the syndiospecific polymerization.[70–73]



Scheme 11 Ring-opening polymerization of racemic β-lactone to produce syndiotactic β-polyester.

One of the simple ways to produce isotactic PHB is the polymerization of optically pure β-butyrolactone without racemization of the asymmetric centers, like the synthesis of isotactic PLA from optically pure lactide as mentioned above. Many catalysts, complex **10** for example, have been reported for

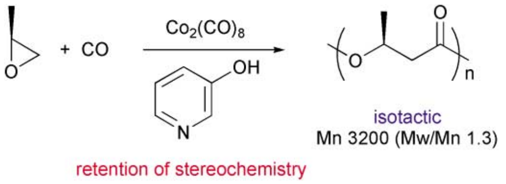


Scheme 12 Ring-opening polymerization of racemic β-lactone to give isotactic and/or stereoblock β-polyester.

the polymerization of enantiopure β-butyrolactone.[68] Ring-opening polymerization of racemic β-butyrolactone to produce isotactic PHB has also been investigated.[74–77] Holden showed that an oligomeric alumoxane obtained by the reaction of Et_3Al with H_2O catalyzed the polymerization to produce PHB with an isotactic (*like*) diad content of 85%.[75] This synthetic PHB is similar to optically active bacterial poly[(*R*)-3-hydroxybutyrate] (PRHB) in melting point, enthalpy of fusion and X-ray crystal structure. Although such high isotacticity indicates the long –*RRRRR*– and –*SSSSS*– sequences of the polymer, it is unknown whether the single chain of the polymer contains only *S* or *R* monomer units or alternating long –*RRRRR*– and –*SSSSS*– sequences (stereoblock) (see Scheme 12). In 1989, Spassky *et al.* reported the asymmetric polymerization of racemic β-butyrolactone using Et_2Zn/(*R*)-DMBD (DMBD = 3,3-dimethylbutane-1,2-diol) catalyst to give optically active PHB.[78] The 46% enantiomeric excess of the unreacted monomer confirmed that the *R* enantiomer of β-butyrolactone was preferentially incorporated in the polymer, leading to the high *like* diad proportion.

2.5 Alternating copolymerization of epoxide with carbon monoxide

There have been a limited number of reports on the ring-opening copolymerization of epoxides with carbon monoxide, although it has been known for a long time.[79] Drent and co-workers patented a mixture of $Co_2(CO)_8$ and 3-hydroxypyridine as a catalyst for the carbonylation of epoxide resulting in the formation of β-lactones.[80] Later, Alper[81] and Rieger[52] independently used the same catalyst system to find that polyester, not the lactone, was the major product. The polymers are regio-regular and isotactic when using enantiomerically pure propene oxide (Scheme 13). Osakada examined the effect of additives and reported that polyesters with higher regularity were obtained with bidentate amines or a cocatalyst $Ru_3(CO)_{12}$.[82]



Scheme 13 Alternating copolymerization of epoxide with carbon monoxide to give β-polyester.

2.6 Conformational studies of poly(lactic acid) and poly(3-hydroxybutyrate)

Poly(lactic acid). The biodegradability of aliphatic polyester has a great dependence on its morphology such as crystallinity, packing mode and arrangement of molecular chains. Accordingly, many studies have been carried out on the solid-state conformation of PSLA to find three crystal modifications (α-, β- and γ-forms) with different helix conformations and cell symmetries. The single crystal of the most stable α-form of PSLA was first proposed to be an orthorhombic unit-cell with two chains of 10_3 helical conformation by De Santis and Kovacs in 1968.[83] Other researchers also investigated the crystal structure of the α-form of PSLA and reported essentially similar unit-cell parameters.[84–86] Hoogsteen proposed that the interchain contact between methyl groups in the α-form of the crystal lead to a distortion of the pure 10_3 helical conformation (see Fig. 5).[84] Recently, Puiggali *et al.* reported on their theoretical studies suggesting that such a distortion resulted from the near-hexagonal packing of helices with antiparallel arrangements.[87] The β-form, first observed by Eling in 1982,[88] was recently reported to form a frustrated packing of 3_1 helices in a trigonal unit cell.[89] In spite of the fact that the 3_1 helix chain of PSLA was calculated to be more stable than the 10_3 one,[90] the β-form was easily converted into the α-form by annealing. This

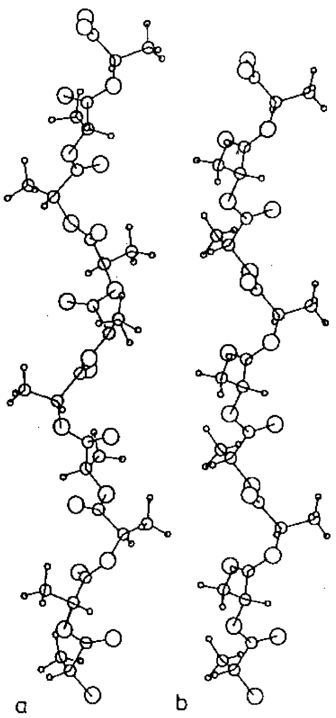


Fig. 5 The chain conformation of (a) 10_3 helix and (b) 3_1 helix of PSLA reported by Hoogsteen *et al.* Transferred from ref. 84 with permission from the American Chemical Society.

was explained by the more dense packing of the α-form than the β-form. Finally, the third modification, γ-form, was obtained by epitaxial crystallization of PSLA on hexamethylbenzene.[91] Cartier reported that two antiparallel helices are packed in an orthorhombic unit-cell which differs from the α-form.

A stereocomplex formation was first reported for an equimolar mixture of PSLA and PRLA by Ikada in 1987 based on wide angle X-ray diffraction.[92] Blending an equimolar amount of PSLA with PRLA of identical M_w makes the single crystal hexagonal as reported by Cartier.[93] In contrast to the β-form of PSLA where more stable 3_1 helices cannot be packed densely, left- and right-handed 3_1 helices in the stereocomplex are able to pack densely *via* van der Waals forces.[94] This special stabilization causes the 50 °C higher melting point of the stereocomplex crystal than that of the PSLA crystal.[92]

As mentioned above,[67] the chiral aluminium complex (*R*)-**9** (R = Me) gave optically active isotactic PRLA at low conversion through the highly selective kinetic resolution of *rac*-lactide. Although the reaction proceeds more slowly, the remaining (*S*,*S*)-lactide was also incorporated in the polymer chain at higher conversion, to give a stereoblock polymer of PRLA and PSLA. This stereoblock polymer (conversion 97.5%) shows a higher melting point (187 °C) than that of PSLA due to the stereocomplexation between the block of (*S*)- and (*R*)-units.

Poly(3-hydroxybutyrate). Isotactic and syndiotactic PHBs show high crystallity. An X-ray diffraction pattern of stretched and annealed isotactic PRHB films indicate that two antiparallel 2-fold helixes are packed in orthorhombic unit cell.[95] Conformational analysis based on the intramolecular energy calculation shows that the helix has a left-handed conformation.[96] Based on X-ray diffraction patterns, the crystalline form of racemic PHB was suggested to compose of two kinds of crystallites, each consists of either PRHB or PSHB helical chains. Thus, unlike PLA, the racemic isotactic PHB do not form a stereocomplex. The crystal structure of syndiotactic PHB was also investigated using X-ray diffraction techniques and molecular modeling.[97] The unit cell of the crystal of PHB with 69% syndiotactic diads was reported to be orthorhombic. A pseudo-2-fold helical conformation, more extended than that of isotactic PHB, was proposed and there is no energy preference for a right-handed or left-handed helical conformation.

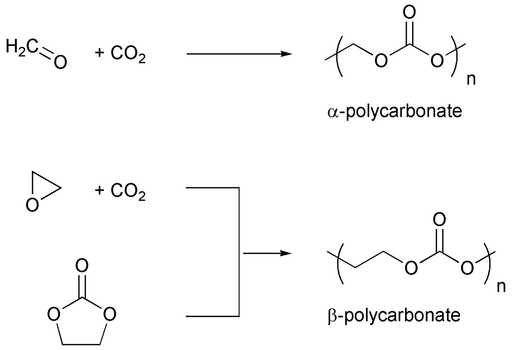
3. Polycarbonates

3.1 Synthesis of polycarbonates

Although copolymerization of formaldehyde with carbon dioxide provides α-polycarbonates, stereochemistry is not the topic for this type of polycarbonate due to the lack of substituents. The polycarbonate of 1,2-diol can be prepared *via* the alternating copolymerization of epoxide with carbon dioxide. Alternatively, the polycarbonate is available by the ring-opening polymerization of a cyclic carbonate (Scheme 14). Here in this section, the epoxide/CO_2 alternating copolymerization will be mainly discussed.

3.2 Origin of stereochemistry

For polycarbonates, the same pattern of symmetry exists as for polyketones because the –O(C=O)O– is symmetrical as was so for >C(=O). Accordingly, a mono-substituted ethylene bridge causes chirality in the main chain (Fig. 6 (a) and (b)). For symmetrically di-substituted polycarbonates, four patterns of stereoregularity are summarized as Fig. 6 (c)–(f). By alternating the copolymerization of *meso*-epoxide with carbon dioxide, the stereoselective synthesis of the compound shown in Fig. 6(c) has been reported.



Scheme 14 Synthesis of α-polycarbonate (alternating copolymer of formaldehyde and carbon dioxide) and of β- polycarbonate (alternating copolymer of epoxide and carbon dioxide).

3.3 Alternating copolymerization of epoxide and carbon dioxide

The utilization of carbon dioxide as a feedstock for organic compounds has received worldwide interest. One of the most promising processes for CO_2 utilization is the alternating copolymerization of epoxide and carbon dioxide to yield aliphatic polycarbonate.[98–101] 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 Et_2Zn/water mixture as a catalyst.[102] Since this report, intensive studies have been devoted to the copolymerization-catalyst development but the activity remained rather low until the 1990's (*ca.* 50 g polymer per 1 g zinc). Over the last decade, significant advances in catalytic activity have been achieved for the copolymerization of cyclohexene oxide and carbon dioxide. Darensbourg developed a series of Zn phenoxide catalysts; dimeric zinc complex **13** which produced 790 gram of polymer per gram of zinc (Scheme 15).[103–107] Coates reported well-defined zinc complexes **14** which produce the copolymer at an extremely high rate (TON = 830 g polymer per 1 g zinc, TOF = 4980 g polymer per 1 g zinc per h) under relatively mild conditions (50 °C, 7 atm).[108–110] High catalytic activity was also achieved using **15** and **16** with fluorinated ligand in supercritical CO_2 both as a reactant and as a solvent.[111–115]

An accepted reaction mechanism for the copolymerization of epoxide and carbon dioxide is (i) CO_2 insertion into a Zn–alkoxide bond to form zinc carbonate, and (ii) the ring-opening of epoxide by the back-side attack of the resulting carbonate anion.[116] Thus, if the ring-opening copolymerization of *meso*-epoxide with CO_2 takes place *via* configuration inversion at one of the two chirotopic centers selectively, optically active aliphatic polycarbonate consisting of either (*R*,*R*)- or (*S*,*S*)-*trans*-1,2-diol unit should be produced.[117] In 1999, Nozaki and co-workers reported the first example of asymmetric alternating copolymerization of *meso*-epoxide with CO_2.[118] Optically active poly[cyclohexene oxide-*alt*-CO_2] was obtained using an equimolar mixture of Et_2Zn and (*S*)-diphenyl(pyrrolidin-2-yl)methanol (**17**) as a chiral catalyst (Scheme 16). Because polycarbonates can be hydrolyzed into *trans*-1,2-diol and CO_2 by alkali-treatment, the degree of asymmetric induction, 70% ee, could be evaluated unambiguously. In 2000, Coates reported asymmetric alternating copolymerization using a well-defined Zn-imine oxazoline ligand complex **18** which showed higher activity and controlled molecular weight compared to **17**.[119] More recently, Nozaki reported the improved enantioselectivity of 80% by using dimeric zinc complex **19** in which one of the two zinc atoms is attached to an ethoxy group while the other is attached to an ethyl group.[120] The copolymer obtained with **19** has an EtOCOO– end group, indicating that the initiation reaction occurred by the insertion of CO_2 into the Zn–OEt bond. In spite of its high stereoregularity, the copolymer of 80% ee shows a glass transition temperature at 117 °C, the value being

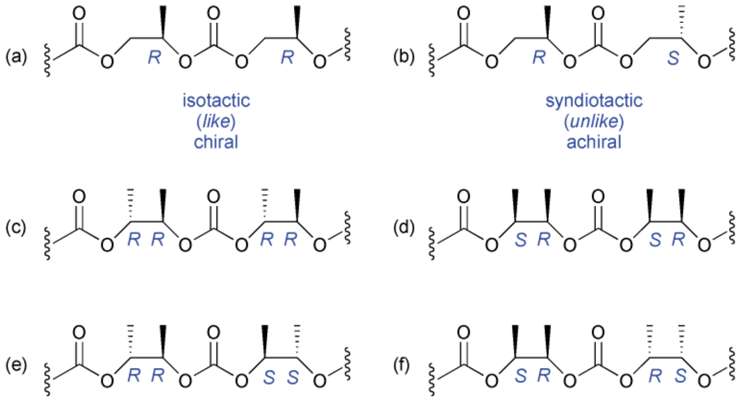
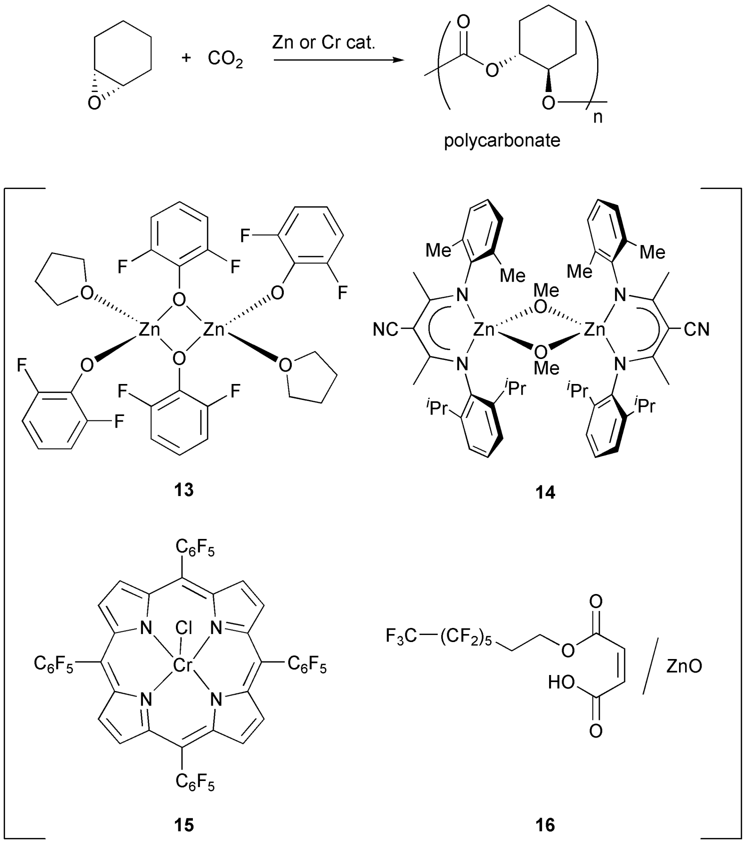
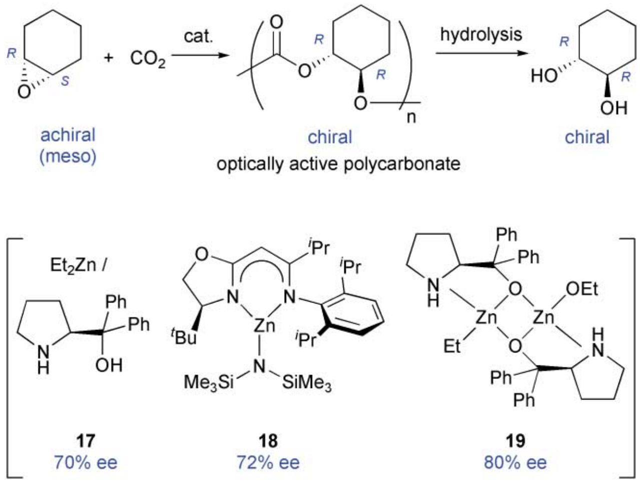


Fig. 6 Stereoregularities in β-polycarbonates.



Scheme 15 Alternating copolymerization of cyclohexene oxide with carbon dioxide.



Scheme 16 Asymmetric alternating copolymerization of cyclohexene oxide and carbon dioxide.

very close to the ones previously reported for copolymers with lower stereoregularity.

Outlook

In this article, stereocontrol of the stereogenic centers in the main chain during the synthesis of polyketones, polyesters, and polycarbonates has been reviewed. The examples described in this article may be classified in the following four patterns. (1) Retention of the configuration which exists in the monomer: as described in the ring opening polymerization of (*S*,*S*)-lactide and (*R*)-β-butyrolactone to give poly[(*S*)-lactic acid] (PSLA) and poly[(*R*)-3-hydroxybutyrate] (PRHB), respectively. (2) Enantiomer selection either by the catalyst or by the chain-end: presented examples are, (2-i) the synthesis of heterotactic and isotactic PLAs from racemic lactide; and (2-ii) the preparation of syndiotactic and isotactic PHBs from a racemic mixture of β-butyrolactone. (3) Selection of enantiotopic sites of a *meso* monomer by the catalyst or by the chain-end: (3-i) syndiotactic and heterotactic PLAs from *meso*-lactide; and (3-ii) isotactic poly(epoxide-*alt*-CO$_2$) from *meso*-epoxide are the examples described here. (4) Creation of a new stereogenic center upon polymerization starting from prochiral monomers. The catalyst or the chain-end selected one of the two enantiofaces of an α-olefin in the olefin/CO alternating copolymerization to give either isotactic or syndiotactic polyketones. Thus, a variety of stereoregular polymers are now available owing to the remarkable achievements of precise design and synthesis of single-site catalysts.

The stereoregular polymers show high crystallinity and the crystal structures significantly depend on the regularity of the main-chain tacticity. For syndiotactic and isotactic poly-(styrene-*alt*-CO), nearly *trans*-planar conformations with *tc* glide plane symmetry and with *s*(2/1) helical conformation was suggested, respectively. Helical structures were revealed for isotactic PLA, isotactic PHB, and syndiotactic PHB. Stereocomplex formation is another subject of morphological interest when multiple stereoregular polymers are mixed together. Formation of stereocomplexes were reported for γ-polyketones and PLAs. Among the polymers discussed in this article, structures of stereoregular aliphatic polycarbonates are unknown.

Needless to say, the potential utility of polymers depend on the functional groups included in the polymers; ketones, esters, or carbonates. 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 enable the production of polymers of different stereoregularity, even if the polymerization employs the same monomer(s). The different stereoregularity caused large differences in physical properties as observed in some of the polymers.

Unlike the polymerization of vinyl monomers, not only tacticity but also chirality becomes a critical issue in some of the polymers discussed in this review article. 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 view point of chirality: when we consider that our product plastics are used in the environment, we cannot avoid thinking about how they affect nature. Because mother nature is chiral, enantiomeric polymers should be considered as being different products from each other, as is so in pharmacology.

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