Catalysis of the Copolymerization of Olefins with Carbon Monoxide: Regio- and Stereochemical Control

Giambattista Consiglio*

Abstract: Ligand modification of palladium-based catalytic systems for the strictly alternating copolymerization reaction of olefin with carbon monoxide enables us to influence the stereo- and regiochemistry of the olefin insertion during the growth of the macromolecular chain. An overview of the author's research on the catalyst-based control of the macromolecular architecture and on the factors that are involved in that control is presented.

Keywords: Carbonylation · Cationic palladium(II) complexes · Microstructures · Poly[olefin-*alt*-CO] · Terpolymers

Introduction

Transition metal catalysis in polymerization reactions of various types of monomers has enabled the production of polymeric materials with a controlled microstructure (so-called 'precision polymerization') [1]. A prototype and most important from a commercial standpoint is polymerization catalysis of olefins by complexes of elements of the fourth group [2]; simplified models [3] enable a relatively easy design of possible modifications of the catalytic system to achieve the desired microstructure of the produced polymers [4]. A major drawback of those systems is the very low or lack of compatibility with functionalized substrates. Therefore, a great deal of research has been devoted to tailoring catalyst precursors of the late transition metals, which can be made completely compatible with substrates containing functional groups [5][6]. Among these systems, complexes based on palladium of the type [Pd(L-L')(S$_2$)]X$_2$ (where L-L'{L = or ≠ L'} is a chelate ligand, S is a solvent molecule, and X is an anion with

Correspondence: Prof. Dr. G. Consiglio
Laboratorium für Technische Chemie
Departement Chemie
ETH-Zentrum
Universitätsstrasse 6
CH-8092 Zürich
Tel.: +41 1 632 35 52
Fax: +41 1 632 11 62
E-Mail: consiglio@tech.chem.ethz.ch

low coordination properties) are of particular interest. Indeed, depending on the ligand, these systems are able not only to catalyze the synthesis of poly-1-olefins with peculiar microstructures [7], but also to produce strictly alternating copolymers between 1-olefins and carbon monoxide, the so-called 1,4-polyketones 1 [8] that are sometimes isolated in the isomeric spiroketal form 1' (Scheme 1) [9]. The relative stability of both forms seems to be controlled by entropic reasons [10]. The diphosphine ligands 1,3-bis(diphenylphosphino)propane (dppp) or 1,3-bis(di{2-methoxyphenyl}phosphino) propane (doanpp) gave useful catalysts for the commercial production of Carilon, an alternating olefin-carbon monoxide terpolymer based on ethene (1, R = H) and containing small amounts (5–10%) of propene (1, R = CH$_3$) [11]. Even though it is still unclear as to how the market for this product will evolve, these materials remain of interest because of their potential for chemical transformation, and, therefore as a source of other valuable polymeric materials. As discussed below, poly[1-olefin-*alt*-CO] can be produced with very high enantioselectivity. Therefore, the Baeyer-Villiger oxidation of polyketones is a possible method for obtaining optically active polyhydroxyalkanoates [12], whereas oximation [13] followed by Beckmann rearrangement would give optically active poly-α-amino acids (Scheme 2).

The copolymerization of olefins with carbon monoxide is a typical coordination polymerization as suggested by the *syn*-stereochemistry of the addition to the double bond [14]. The olefin can insert in two directions (primary and secondary, p and s) and with two enantiofaces ((*Re*) and (*Si*)) (Scheme 3) thus leading to six possible diads (Fig. 1). Since the substituted carbon atoms of the main chain are asymmetric, each of the possible diads can, in principle, occur in two enantiomeric forms [15]. It appears that perfect control of the olefin insertion step would enable the synthesis of polymeric materials with very different microstructures and, thus, different properties. The most important results for aliphatic and aromatic olefins will be discussed below.

Copolymers of Aromatic Olefins (Styrene)

The first poly[styrene-*alt*-CO] copolymer was produced using the above-mentioned [Pd(L-L)(S$_2$)]X$_2$ catalyst precursors, modified by 1,10-phenanthroline 2 or 2,2'-bipyridine 3 (Scheme 4) [8]. It is remarkable that the product is an authentic poly[1-oxo-2-phenylpropane-1,3-diyl] with a prevailingly (>90% *u*-diads) syndiotactic microstructure (Scheme 1, R = C$_6$H$_5$) [16]. The triad distribution of the polymeric material is considered to be influenced by one factor
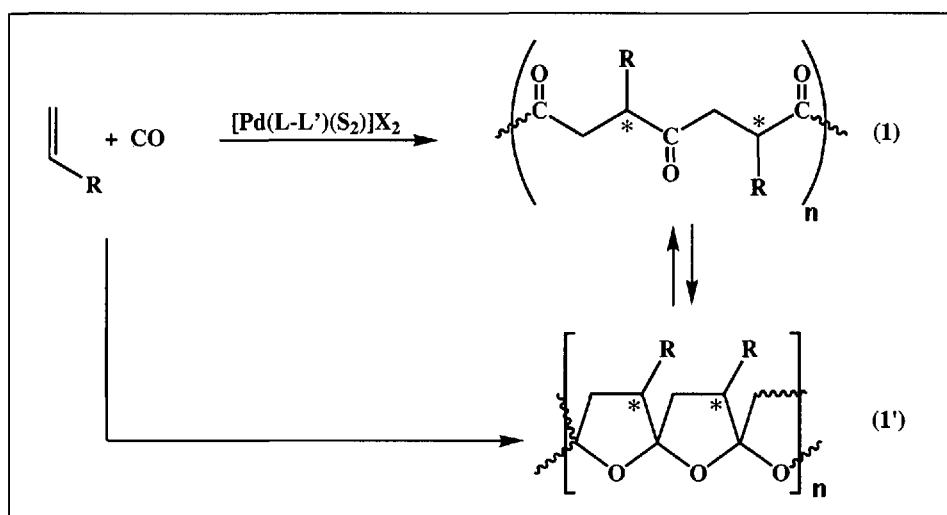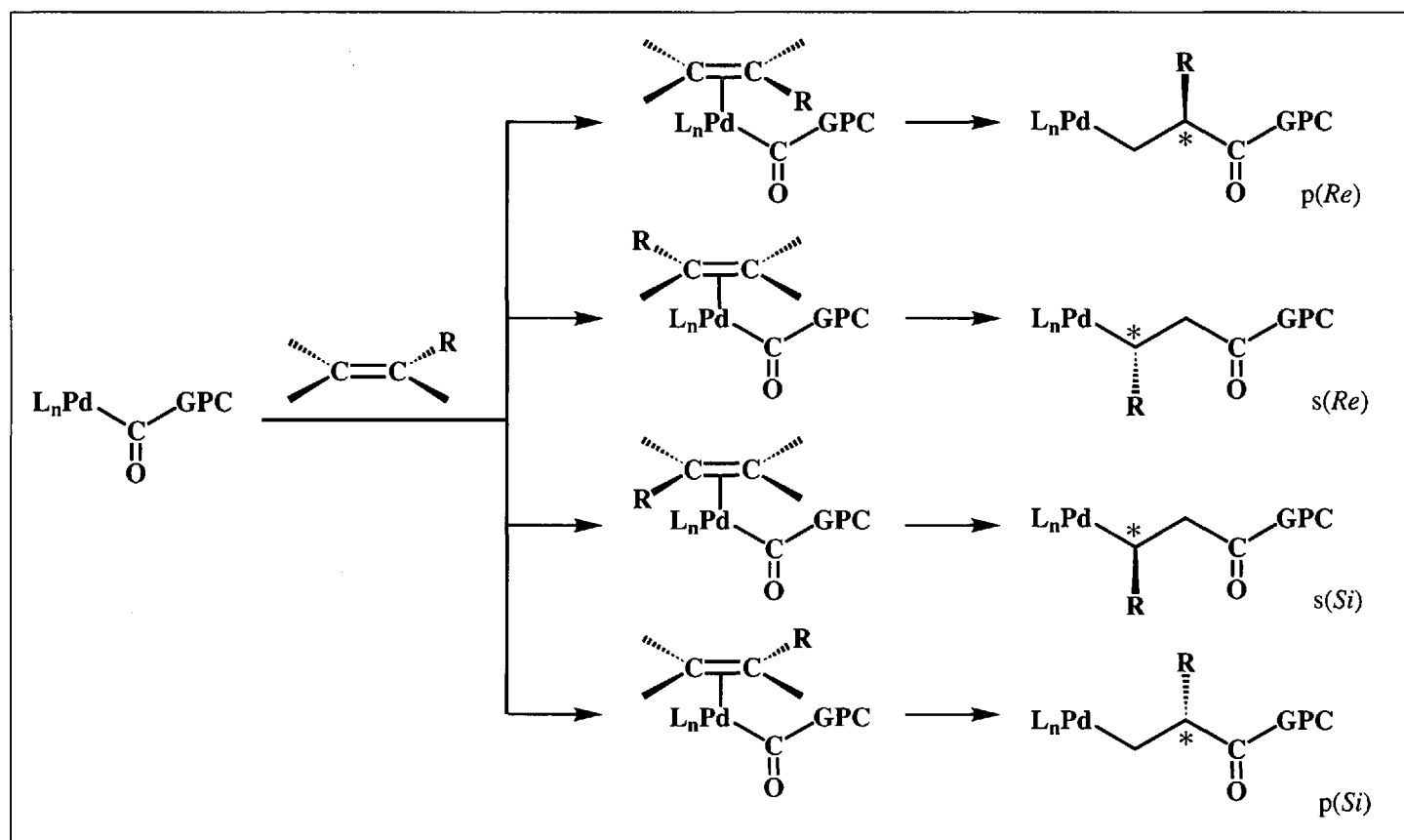
Scheme 1. Isomeric forms for the carbon monoxide-olefin alternating copolymers.
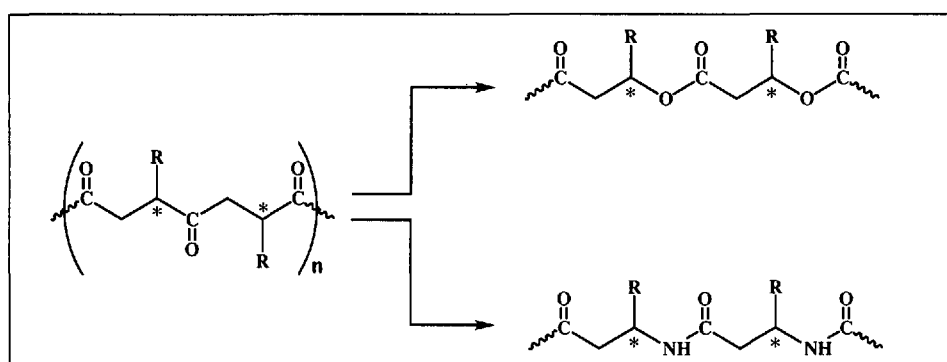
Scheme 2. Possible transformation of optically active carbon monoxide-olefin alternating polymers.

only during the growth, namely by the chain end [17]. Labeling experiments [18] and model NMR studies [19] showed that the growth of the chain takes place by means of secondary insertion of the styrene moiety (Scheme 3, s(*Re*) and s(*Si*)). Secondary insertion of styrene into a metal-to-carbon bond is a common feature of reactions leading to the formation of a carbon–carbon bond and is generally assumed to be driven by stabilization resulting from the so-called benzyl allylic interaction (Scheme 5) [20]. Considering that enantioface discrimination during copolymerization is caused by an asymmetric carbon atom that is not directly bonded to the metal atom due to carbon monoxide insertion, it is surprising that the stereochemical control is so effective. Therefore, it is assumed that the growing chain interacts with the electrophilic metal center causing the metal to become stereogenic [8].

The properties of the syndiotactic poly[1-oxo-2-phenylpropane-1,3-diyl] are not considered to be of interest [21]. Therefore, the synthesis of materials with different microstructure was studied. Probably inspired by the stereochemical relationship between geometry of the catalysts and microstructure of the polymers that had been identified for the polymerization of propene with metallocenes [2],

Scheme 3. Stereo- and regiochemical pathways for olefin insertion during the alternating copolymerization of olefins with carbon monoxide (GPC = growing polymer chain; the descriptors apply for propene).
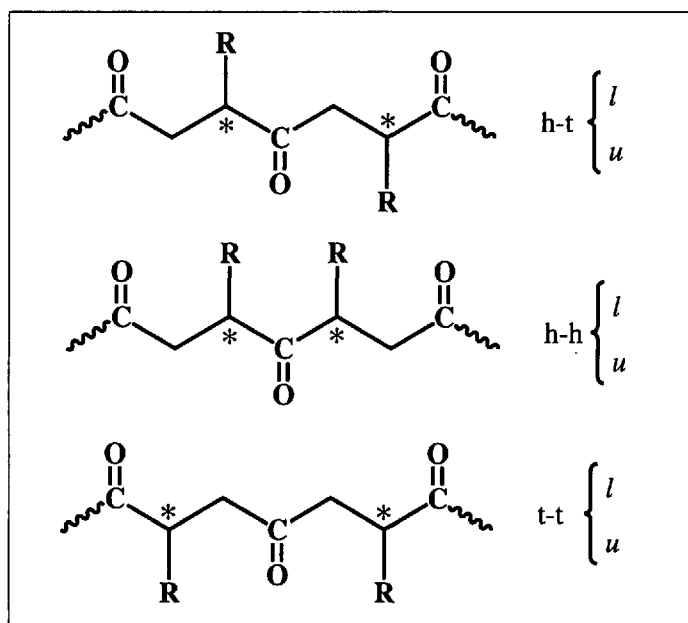
Fig. 1. Possible diads for the carbon monoxide–olefin alternating copolymers.

in the first attempts to produce isotactic copolymers optically active C_2-symmetric dihydrooxazole-based ligands (4 and 5) were used [22][23]. The copolymers were highly isotactic and had a correspondingly high optical activity. In keeping with the type of catalysts used, the stereoregulation is due to the enantiomorphic catalytic site [24]. An additional goal of our study of the isotactic copolymerization was to obtain catalyst systems that are more stable to displacement of the ligand by carbon monoxide. Therefore, the phosphine(dihydrooxazole) hybrid ligands 7 and 10 were used [25]. Because of the phosphorus moiety, these ligands are more suitable for maintaining the catalysts in solution, and thus in the active state. As a result of an investigation of the nature of the substituent(s) on the dihydrooxazole moiety, the intermediate 11 (Fig. 2) was assumed to be responsible for stereoregulation. This assumption is based on the following observations: i) the presence of a substituent in position 4 causes the formation of highly isotactic copolymers, whereas atactic copolymers are formed in its absence [25], ii) equal (two methyl groups) or different (a methyl and a benzyl group) double substitution at that position also results in atactic copolymers [26] and iii) substitution at position 5 (7 vs. 10) is not essential for efficient enantioface discrimination [26]. Remarkably, the pyridine(dihydrooxazole) ligands (6 and 9) still gave prevailingly syndiotactic copolymers, even though the degree of stereoregularity was lower than for the bipyridine ligand [27]. Therefore, a different site for coordination (see 12, Fig. 2) is assumed to be predominantly responsible for the observed stereochemistry.

The optical activity observed in the material, which is due to the presence of some *l*-diads, suggests a preference for the same enantioface as that inserted by the related phosphine(dihydrooxazole) ligand (10 vs. 9). All the catalytic systems shown in Scheme 4 display an essentially complete regioregularity of the inserted styrene, associated with a secondary regiochemistry of the olefin insertion. How can we synthesize regioirregular copolymers, or, in other words how can we change the regiochemistry of the insertion? Considering the current assumptions about the factors influencing the regiochemistry of the olefin insertion into metal-to-carbon bonds (Scheme 3), the possibility of electronic modification of the phosphine moiety of the ligand was discussed. Therefore, we synthesized catalysts modified with the above-mentioned phosphine(dihydrooxazole) ligands bearing substituted diphenylphosphino substituents such as *ortho*-tolyl or *ortho*- and *para*-anisyl. Electronic effects were, however, found to be of minor importance with respect to the steric effects [20]. In particular, with the *ortho*-tolyl ligand, a completely irregular material was obtained, thus suggesting a change in the coordination site and a consequent change in the regiochemistry 13 (Fig. 2) due to the steric requirements of the lig-
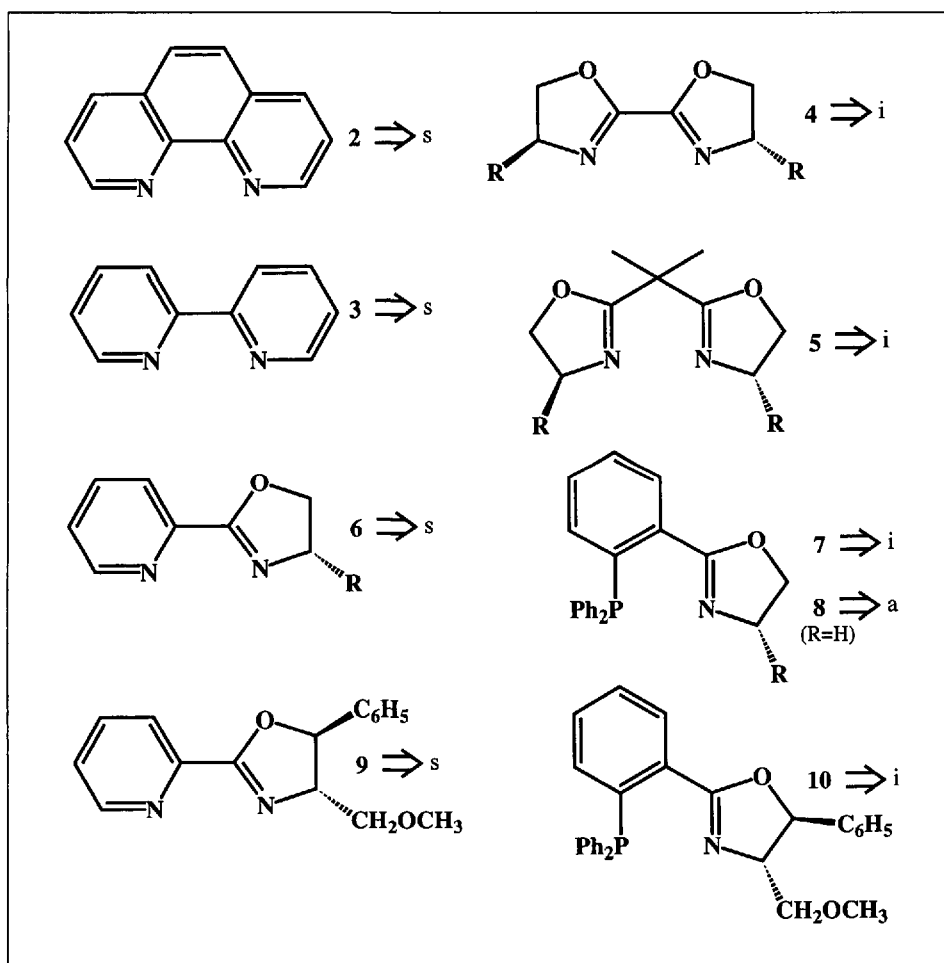
Scheme 4. Ligand used for the alternating copolymerization of styrene with carbon monoxide and prevailing stereochemistry of the produced copolymer (i, s, and a = iso-, syndio- and atactic).
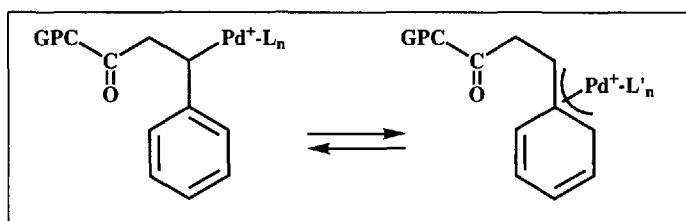
Scheme 5. 'Allyl-type' stabilization of the alkyl-intermediate formed after secondary styrene insertion.

and. Similar models have been proposed for the polymerization of propene catalyzed by zirconocene derivatives [2].

The terpolymerization of ethene and styrene was studied to identify the role of the growing chain as complementary to the enantiomorphic site for the steric control during the copolymerization [28]. The molar ellipticity of the band associated with the n->π* transition of the carbonyl chromophore normalized to the styrene content is very similar both for the terpolymer and the copolymer produced with the same phosphine(dihydrooxazole) ligand, thus showing the very minor effect (if any) of the growing chain. Moreover, ethene had a poisoning effect in the terpolymerization. Despite the inherently lower copolymerization rate of ethene with respect to styrene, ethene is preferred for insertion in the terpolymerization experiments [28]. Considering that the insertion of ethene takes place more rapidly than the insertion of styrene into the palladium-acyl-bond of the model compound [29] [30], the results can be rationalized assuming that the rate of carbon monoxide insertion is higher for benzyl intermediates (Scheme 5) than for primary alkyl intermediates.

Copolymers of Aliphatic Olefins (Propene)

The commercially used catalyst precursors [Pd(P-P')(S₂)]X₂ (i.e. those modified with diphosphine ligands) for the production of Carilon, give completely regio- and stereoirregular materials when used for propene or similar aliphatic olefins. The use of a chiral homologue of dppp, namely of (R,R)-2,4-bis(diphenylphosphino)pentane, resulted in a copolymer with a somewhat better though still incomplete regio- and stereoregularity [31]. Recent studies have surprisingly revealed that the corresponding meso-ligand (R,S)-2,4-bis(diphenylphosphino)pentane performs better than the chiral ligand, not only in terms of stereoregularity [32], but also of activity [33]; in both cases the isotactic structure is prevalent. When the basicity of the diphosphine ligand is increased (e.g. when 1,3-bis(diethylphosphinopropane) is substituted

for 1,3-bis(diphenylphosphinopropane)), the insertion of the olefin is essentially regiospecific and regioregular copolymers are formed [34]. End group analysis suggests that, when basic ligands are used, the growing of the chain takes place by means of primary insertion. Good stereoregularity is also observed for these materials (~83% l-diads). Atropoisomeric diphosphine ligands (e.g. 14) (Fig. 3) with alkyl substituents enabled us to be the first to synthesize a regioregular and stereoregular propene copolymer, formed exclusively in the polyspiroketal structure 1' [9]. The polyketone structure is then formed by dissolving the sample in hexafluoroisopropanol or by heating it. The use of diastereomeric ligands related to 14, namely (allS)(Rₐ)-15 and (allS) (Sₐ)-16 gave a copolymer with good stereoregularity (~95% l-diads) for the latter compound [35], whereas the alternative diastereomer 15 gave a much more active system, which produced the most atactic though still regioregular propene copolymer ever synthesized. In the copolymerization of other olefins such as 1-butene and 4-methyl-1-pentene the stereocontrol of 14 was much less efficient; nevertheless, regioregular copolymers formed. As in the case of styrene copolymerization, C₂-symmetry of the ligand was found to be unnecessary to achieve isotactic copolymerization [35]. Of the chiral ligands tested by us and other groups, those based on ferrocene (e.g. 17) were the most active and were also efficient in the copolymerization of other 1-olefins [36]. A further increase in the activity of the catalyst with respect to the parent ligand was recently achieved by using diaryl-substituted ligating moieties bearing electron withdrawing groups (e.g. the bis(3,5-trifluoromethylphenyl) phosphino group) instead of the diphenylphosphino-group [37].

As mentioned above, the change in the geometry of the ligand (and, as a consequence, of the catalytic complex) from C₂- to Cₛ-symmetry did not result in a change of the microstructure of the copolymers from prevailingly isotactic to syndiotactic, in contrast to metallocene catalysts for the propene polymerization [2]. Attempts were made to change the regioselectivity of the propene insertion from primary to secondary, in the hope of inducing syndiotactic growth, as in the case of the copolymerization of styrene. In particular, catalytic systems modified with ligands 18 and 19 seem to insert propene with an essentially reversed regiochemistry. Nevertheless, both systems produce copolymers with almost com-
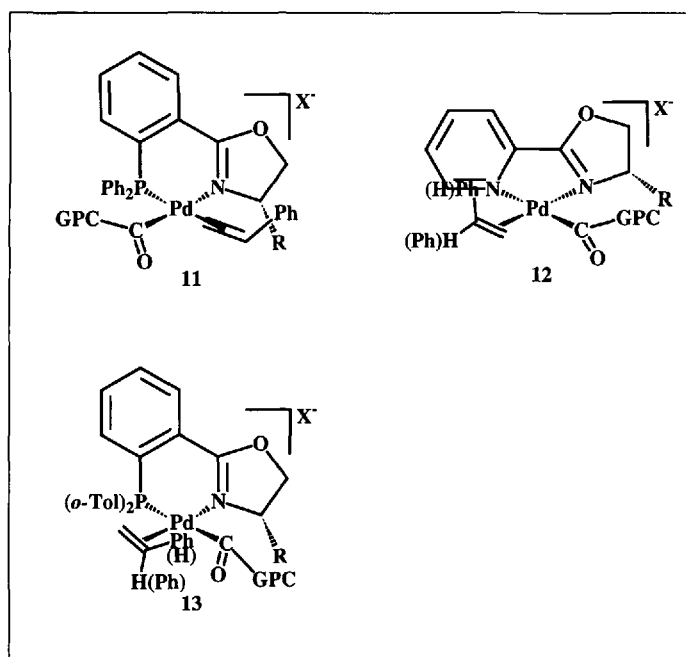

Fig. 2. Regio- and stereochemistry for the coordination of styrene prior to insertion depending on the ligand.
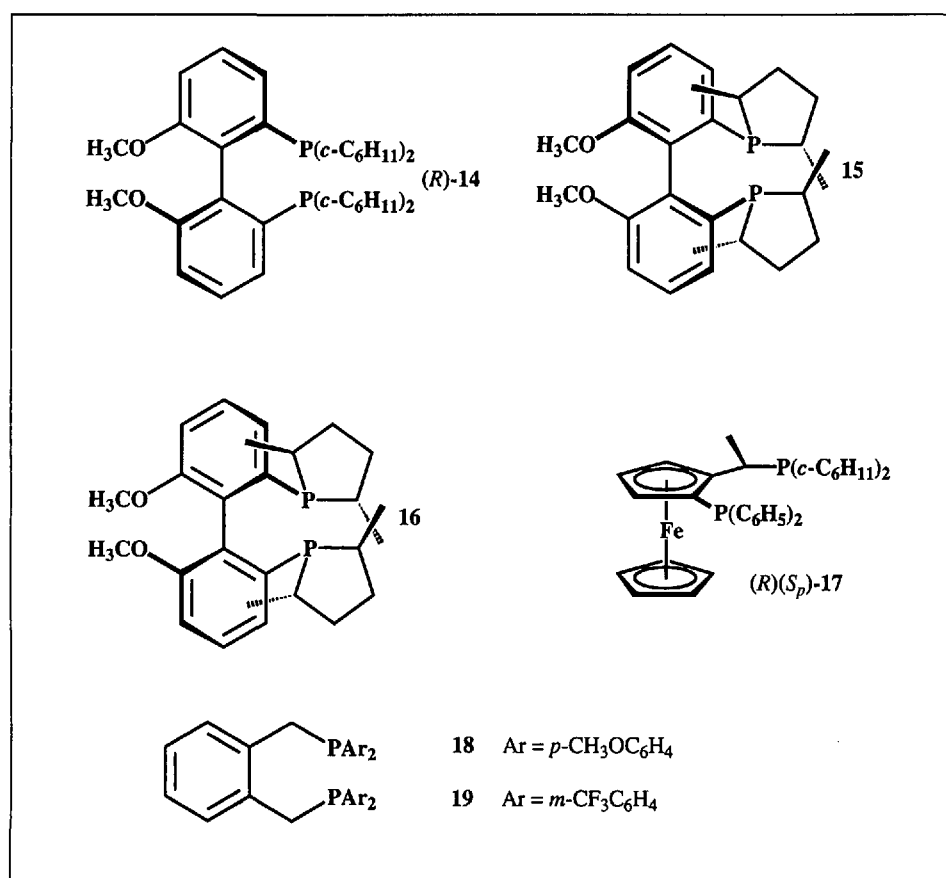
Fig. 3. Some ligands used for the alternating regioregular copolymerization of propene (and other aliphatic 1-olefins) with carbon monoxide.

Conclusions

As discussed above, good control of the regio- and stereochemistry of the carbon monoxide-styrene copolymers was achieved; all the limiting microstructures (iso-, syndio-, and atactic, regioregular and irregular) were accessible. In contrast, the syndiotactic copolymers of aliphatic olefins are still unknown. The known catalysts are not sufficiently active for the copolymerization of internal olefins. Only oligomers could be prepared; competitive isomerization phenomena after the insertion of the olefin substrate were observed. In the copolymerization of cyclopentene, alternating copolymers, in which the enchainment of the olefin comonomer occurs through 1,2- and 1,3-insertion (Fig. 4) are formed with the latter type of insertion being the most usual. The most regioregular copolymers prepared show close to 95% 1,3-enchainment whereas the highest content in 1,2-insertion was about 50% [39]. It is difficult to identify the prevailing stereochemistry of these materials due the lack of resolution in the NMR spectra. However, it appears to be influenced by the coordination ability of the anion of the catalyst precursor as a result of the above-mentioned isomerization. Most importantly, the activity of the catalytic systems must be improved.
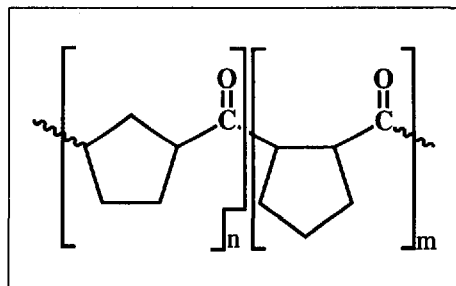

Fig. 4. Structure of the alternating cyclopentene-carbon monoxide copolymer

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The Persistent Radical Effect in Living Radical Polymerization – Borderline Cases and Side-Reactions

Hanns Fischer* and Marc Souaille

Abstract: A theoretical analysis of the basic mechanism of living radical polymerization provides criteria for the rate constants required for optimized processes. It is extended to cover borderline cases and important side reactions as cross-disproportionation, the role of an initial excess of persistent species and of additional initiation.

Keywords: Living radical polymerization · Radical reaction rates · Reaction kinetics

Introduction

Living polymerizations provide polymers which are able to grow whenever additional monomer is supplied [1].

Correspondence: Prof. Dr. H. Fischer,
Physikalisch-Chemisches Institut der Universität
Zürich
Winterthurerstrasse 190
CH–8057 Zürich
Tel.: +41 1 635 44 21
Fax: +41 1 635 68 56
E-Mail: hfischer@pci.unizh.ch

Hence, the chains are extendable, and block-copolymers can be produced. Today, this is mainly achieved by anionic and cationic processes. These suffer little from terminations [2], and, hence, the polymer chains retain reactive ion pair end groups. Initiations are fast compared to the overall polymerization time. Therefore, all chains start to grow essentially instantaneously, and the degree of polymerization increases linearly with monomer conversion and is inversely proportional to the initiator concentration. The width of the chain length distri-

bution grows slower than the degree of polymerization, *i.e.* the polydispersity index decreases with time. Besides living, such polymerizations may also be more correctly called regulated or controlled.

Conventional free radical polymerizations employ slow continuous initiation, and the polymers are formed by termination of the growing chain radicals in coupling or disproportionation reactions. These two features lead to unreactive polymers with essentially time invariant degrees of polymerization and broad molecular weight distributions [2].