Organometallics **2001,** *20,* 2697−2703

Enantioselective Alternating Copolymerization of α-Olefins with Carbon Monoxide Using a Cationic Palladium−Chiral Diphosphine Complex

Jian-Chao Yuan and Shi-Jie Lu*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

Received January 22, 2001

Enantioselective alternating copolymerization of carbon monoxide with propylene, 1-heptene, 1-octene, and styrene was carried out using a palladium catalyst modified by 1,4−3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (DDPPI). The chiral diphosphine was proved to be effective for enantioselective copolymerization. The pure poly(1,4-ketone)s were obtained by dissolving the copolymers containing spiroketal and 1,4-ketone units in 1,1,1,3,3,3-hexafluoro-2-propanol and reprecipitating with methanol. Optical rotation, elemental analysis, and ^{1}H NMR, ^{13}C NMR, and IR spectra showed that our copolymers were optically active, isotactic, alternating poly(1,4-ketone) structures. An oxidant and a weakly or noncoordinating anion were important in the copolymerization.

Introduction

Alternating copolymerization of olefins with carbon monoxide (CO) catalyzed by cationic palladium−ligand complexes is of great interest due to the potential use of the resulting polymer as a new material.[1] Initial methods employing either free radical or transition metal-containing initiators under extremely high pressures and temperatures yielded copolymers whose CO content varied markedly with the partial pressure of CO.[2] It was later discovered[3] that several neutral Pd−phosphine complexes copolymerize propylene with CO under milder conditions to yield perfectly alternating copolymers despite reaction conditions where $P_{\mathrm{olefin}} > P_{\mathrm{CO}}$. Highly reactive polymerization catalysts have been reported that consist of a cationic Pd^{2+} species with a noncoordinating anion[4] and either bipyridine-type or diphosphine ligands.[5]

Insertions of CO into a transition metal−carbon σ-bond[6] and olefin into an acyl−palladium bond[7] are the key steps in the homogeneous catalytic processes. Utilizing CO and olefins, a wide range of studies have been devoted to this subject.[8] When α-olefins are used for this copolymerization, the regio- and enantioselectivity of the olefin insertion arise and the related control becomes a key issue for obtaining stereoregular polyketones. In the head-to-tail copolymer, a chirotopic center exists per monomer unit. If the same enantioface of each α-olefin is selected by the catalyst, the resulting copolymer is isotactic, where all the chirotopic carbons in a polymer backbone possess the same absolute configuration. Thus, asymmetric copolymerization using chiral catalysts is now attracting much attention. Most of the successful reports on this subject deal with C_2 symmetrical ligands.[9] For example, Consiglio[9a] used complexes of C_2 symmetric diphosphine BICHEP for the asymmetric copolymerization of propylene with CO; Sen[9b] used C_2 symmetric diphosphine DUPHOS for the asymmetric copolymerization of α-olefins with CO; enantioselective copolymerization of (4-*tert*-butylphenyl)ethene with CO has been reported by Brookhart[9c] using a Pd(II)-chiral bisoxazoline complex as a catalyst. Recently, ligands of C_1 symmetry have already been successfully applied to the enantioselective copolymerization of α-olefins with CO.[10] For example, Consiglio[10abc] used phosphine−oxazoline bidentate ligands for the asymmetric copolymerization of styrene with CO. Phosphine−phosphinite bidentate ligands have been disclosed by Keim[10d] and Nozaki.[10e]

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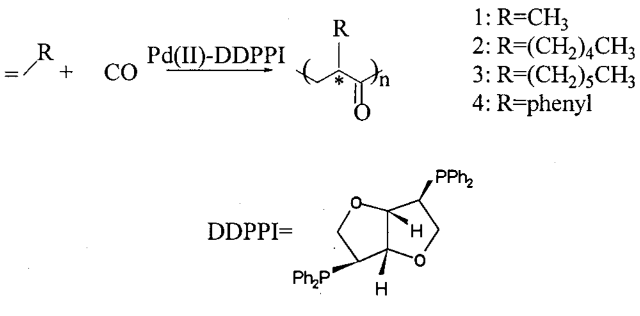
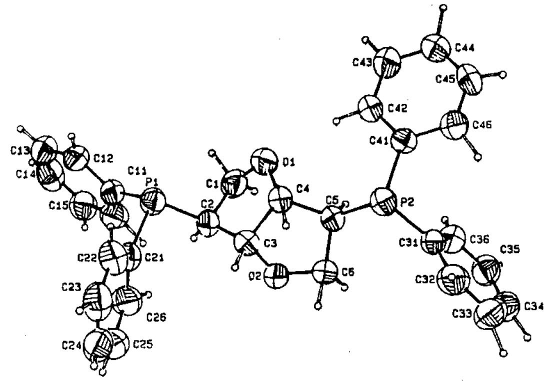
10.1021/om010046g CCC: $20.00
Publication on Web 05/30/2001

Scheme 1



Scheme 2



Recently, we have reported enantioselective copolymerization of styrene with CO using the $PdCl_2-CuCl_2$ chiral diphosphine catalytic system.[11a] Here, we report enantioselective alternating copolymerization of CO with propylene (P), 1-heptene (H), 1-octene (O), and styrene (ST) using the chiral catalyst $[Pd(DDPPI)(CH_3CN)_2](BF_4)_2$ (DDPPI:[11b]1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol) (Scheme 1).

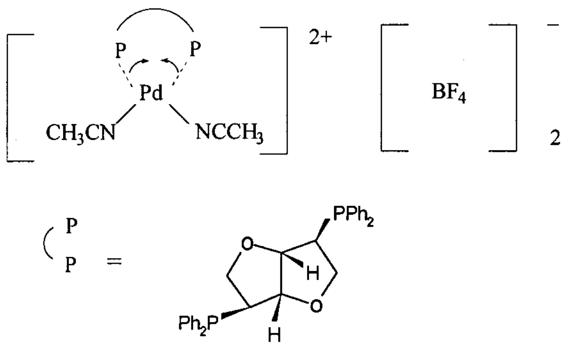
Results and Discussion

Characterization of the Catalyst $[(DDPPI)Pd(CH_3CN)_2](BF_4)_2$. The molecular structure of DDPPI was determined by X-ray diffraction analysis (Scheme 2).[11] The crystal data are as follows: $F(000) = 1016$, orthorhombic space group $P2_12_12_1$, $a = 9.460(8)$ Å, $b = 14.822(5)$ Å, $c = 18.424(6)$ Å, $V = 2.583(2)$ Å^3, $Z = 4$. DDPPI has four chiral carbon centers, two of them, connected to phosphorus atoms, are in *S* form. The bond distance P_1-P_2 is 6.24 Å. These features lead to a nonchelating or weakly chelating character and are responsible for highly chiral induction of the copolymerizaton reactions.

The catalyst $[(DDPPI)Pd(CH_3CN)_2](BF_4)_2$ was prepared by codissolving a 1:1 molar ratio of $[Pd(CH_3CN)_2](BF_4)_2$ and DDPPI in dry CH_3CN. It could be isolated from CH_3CN solution in high yield, and its elemental analysis was consistent with the structure shown.

We have characterized the catalyst precursor $[Pd(CH_3CN)_2](BF_4)_2$ and catalyst $[(DDPPI)Pd(CH_3CN)_2](BF_4)_2$ using ^{1}H NMR. The signals at ~2.60 ppm clearly indicate that CH_3CN is coordinated to the palladium center.

Scheme 3



We have also characterized the catalyst using ^{31}P NMR. The ^{31}P NMR spectrum shows a weak resonance at +31.0 ppm, which indicates that the P atoms coordinate to the palladium center (the P atoms of free DDPPI show one signal at −14.27 ppm).

According to the weakly chelating or nonchelating structure of DDPPI, the P atoms should coordinate to the palladium center with one strong coordination and one weak coordination; also possibly, one DDPPI molecule coordinates two palladium centers. The copolymerization of CO and olefins always requires *cis*-arrangement of vacant sites, so we suggest that the P atoms coordinate to the palladium center with one strong coordination and one weak coordination, and the strong coordination and weak coordination can be exchanged during catalysis (Scheme 3).

Spiroketal and 1,4-Ketone Structures of α-Olefin−CO Copolymers. In the presence of alcohol, the following mechanism for the formation of the polyketone of olefins with CO has been proposed by Sen.[2] (i) Initiation takes place through insertion of an olefin unit into a metal hydride or into a metal−carbalkoxy bond. (ii) Propagation consists of insertions of carbon monoxide units into a metal−alkyl bond and of olefin units into a metal−acyl bond. (iii) Termination takes place through alcoholysis of a metal−acyl bond, through β-hydrogen elimination from, or through protonolysis of, a metal−alkyl species.

But, Consiglio[12] proposed a different mechanism involving Pd−carbene species to explain the formation of polymers with spiroketal repeating units in the presence of alcohol.

In our copolymers of propylene, 1-heptene, 1-octene, and styrene with CO, the resonances (in $CDCl_3$) at 113.2 ppm (propylene−CO copolymer), 113.0 ppm (1-heptene−CO copolymer), 113.7 ppm (1-octene−CO copolymer), and 113.7 ppm (styrene−CO copolymer) of the ^{13}C NMR spectra of the copolymers indicated the presence of the spiroketal groups (C−O−C) in the copolymers (Table 1).[13] By contrast, in the ^{13}C NMR spectra of same samples dissolved in the mixture of $CDCl_3/(CF_3)_2CHOH$ (1:1, v/v) only the signals attributable to carbonyl groups (propylene−CO copolymer 215.2 ppm; 1-heptene−CO copolymer 214.1 ppm; 1-octene−CO copolymer 214.7 ppm; styrene−CO copolymer 213.2 ppm) in addition to those corresponding to the α-olefin carbon atoms can be detected.

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Table 1. Absorptions of IR (KBr) and ^{13}C NMR in the Carbonyl Region of Pure Ketone and Ketone/Spiroketal Copolymers of α-Olefins with CO

copolymer	structure	^{13}C NMR(ppm)	IR (cm^{-1})
propylene−CO	pure ketone	215.2(CO)	1703(CO)
	spiroketal/ketone	213.1(CO),113.2(COC)	1703(CO),1020−1273(COC), 839(COC)
1-heptene−CO	pure ketone	214.1(CO)	1708(CO)
	spiroketal/ketone	210.2(CO),113.0(COC)	1710(CO),1063−1241(COC),836(COC)
1-octene−CO	pure ketone	214.7(CO)	1706(CO)
	spiroketal/ketone	205.4(CO),113.7(COC)	1700(CO),1119−1157(COC),842(COC)
styrene−CO	pure ketone	213.2(CO)	1714(CO)
	spiroketal/ketone	209.5(CO),113.7(COC)	1715(CO),1026−1181(COC),842(COC)

Consistently, the IR spectra of the untreated samples in the KBr pill show medium bands in the region of the carbonyl stretching (propylene−CO copolymer 1703 cm^{-1}, 1-heptene−CO copolymer 1710 cm^{-1}, 1-octene−CO copolymer 1700 cm^{-1}, styrene−CO copolymer 1715 cm^{-1}); in addition there are some medium bands in the region 1300−1000 cm^{-1} and one band for each copolymer at 839 cm^{-1} (propylene−CO copolymer), 836 cm^{-1} (1-heptene−CO copolymer), 842 cm^{-1} (1-octene−CO copolymer), and 842 cm^{-1} (styrene−CO copolymer). When the copolymers were dissolved in hexafluoro-2-propanol and reprecipitated with methanol, the very strong bands at 1703, 1708, 1706, and 1714 cm^{-1}, respectively, appear, whereas the bands at low wavenumbers disappear (Table 1).

To explain the formation of our copolymers with spiroketal units, we thought that the relation of spiroketal and ketone units may be sought in the stage of the product because the poly(spiroketal) and poly(1,4-ketone) interchange can occur in the absence of a metal catalyst.[12,1b,9b] So, we thought that the two-step mechanism for chain growth involving the alternate insertions of carbon monoxide into Pd−alkyl bonds and olefins into Pd−acyl bonds is adapted to these copolymerization processes of α-olefins with CO, but the spiroketal units can be interchanged with the 1,4-ketone units.

Alternating Copolymerization of α-Olefins with Carbon Monoxide. The cationic palladium(II)−DDPPI system catalyzed the alternating copolymerization of carbon monoxide with α-olefins, such as propylene, 1-heptene, 1-octene, and styrene. The formed propylene−CO, 1-heptene−CO, 1-octene−CO, and styrene−CO copolymers were alternating, exclusively head-to-tail, and highly isotactic structure (Scheme 1) in the polymer backbones. The structures of the polymers were characterized mainly by IR and NMR spectroscopy and were supported by the results of elemental analysis.

The strong absorption of IR radiation by the carbonyl group in the backbone of these copolymers (reprecipitated from $(CF_3)_2CHOH$) appearing at 1700−1720 cm^{-1} confirms that α-olefins (propylene, 1-heptene, 1-octene, and styrene) and carbon monoxide do copolymerize in the presence of $[Pd(DDPPI)(CH_3CN)_2][BF_4]_2$ catalyst.

The perfect alternating copolymerization of the α-olefins and carbon monoxide can also be confirmed by the resonances in the carbonyl region for the polymer backbones (Figure 1). The ^{13}C NMR spectra ($CDCl_3$/$(CF_3)_2CHOH$) of P−CO, H−CO, O−CO, and ST−CO copolymers exhibited resonances at 215.2, 214.1, 214.7, and 213.2 ppm, respectively, due to the head-to-tail C═O carbons of the ketone repeating units in the polymer backbones. The signals attributable to head-to-head and tail-to-tail enchainment (∼220 and ∼210 ppm, <1%) have very small intensity.[14] The perfect alternating copolymerization of α-olefins and CO can also be supported by the results of elemental analysis (in Experimental Section).

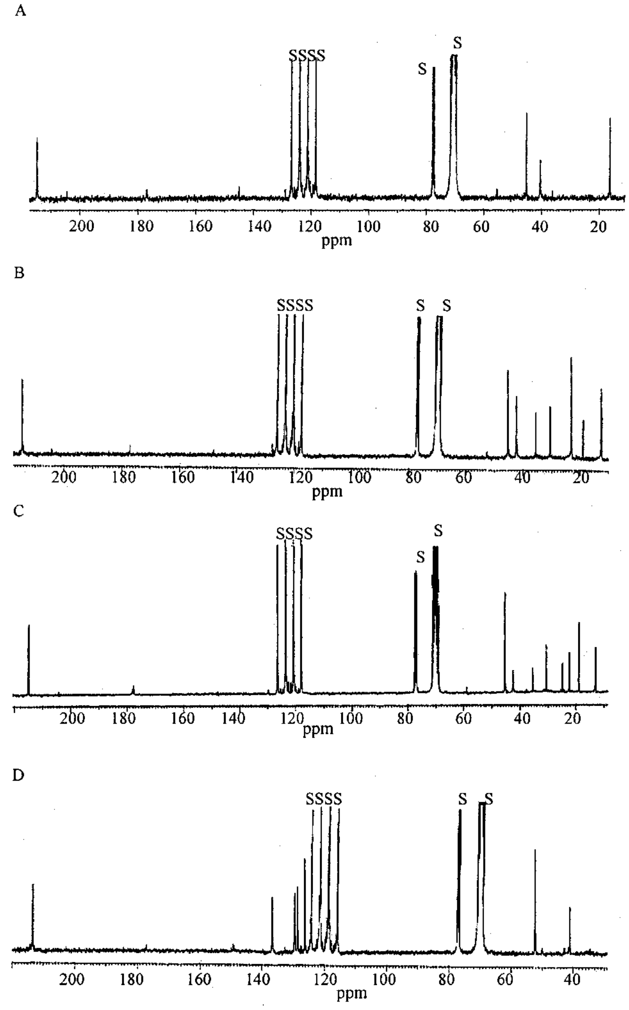

Figure 1. ^{13}C NMR spectra ({1:1 (v/v) $CDCl_3$/$(CF_3)_2$-CHOH}, 400 MHz): (A) Spectrum of alternating isotactic P−CO copolymer. (B) Spectrum of alternating isotactic H−CO copolymer. (C) Spectrum of alternating isotactic O−CO copolymer. (D) Spectrum of alternating isotactic ST−CO copolymer. (S = solvent.)

Regio- and Stereoselectivity of the Copolymerization of α-Olefins with Carbon Monoxide. The nature of chiral phosphine ligands plays an important role in enantioselective copolymerization reactions of olefins with carbon monoxide. The results in Table 2 show that DDPPI is a highly effective chiral ligand for the enantioselective copolymerization of carbon mon-

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Table 2. Enantioselective Copolymerization of α-Olefins with CO Catalyzed by $[(DDPPI)Pd(CH_3CN)_2](BF_4)_2$

copolymer	M_n	M_w	M_w/M_n	productivity ($g \cdot g^{-1}$ $Pd \cdot h^{-1}$)	$[\alpha]^{20}_{589}$ (CH_2Cl_2) (5 mg/mL)
propylene−CO	1.43×10^4	3.89×10^4	2.72	24.53	52°
1-heptene−CO	4.02×10^3	6.25×10^3	1.55	13.76	63°
1-octene−CO	7.31×10^3	1.73×10^4	2.37	16.12	61°
styrene−CO	6.23×10^3	1.07×10^4	1.72	20.05	359°

oxide with propylene, 1-heptene, 1-octene, and styrene. The molecular structure of DDPPI shows that this diphosphine is a bicycle compound with high rigidity and it contains four chiral carbon atoms whose configurations are all *S*. High optical activity and good yields were obtained under our reaction conditions.

The P−CO, H−CO, O−CO, and ST−CO copolymers synthesized appear to be isotactic since optically active materials were obtained when enantiomerically pure DDPPI was used. Note that syndiotactic α-olefin−CO copolymers should only exhibit vanishingly small optical activity.

The pure poly(1,4-ketone)s can be obtained by treating α-olefin−CO polymers containing spiroketal units with acidic solvents such as 1,1,1,3,3,3-hexafluro-2-propanol. The pure copolymers showed a singlet signal at δ 210−220 ppm in the ^{13}C NMR spectra due to an exclusive head-to-tail structure.[15] Single dominant resonances for the CH_2 (δ 40−45 ppm) and CH (δ 42−52 ppm) groups in the polymer backbone confirm the presence of high stereoregularity in the polymers (Figure 1). Similarly, the high regio- and stereoregularity of the copolymers are easily recognized also in the ^1H NMR spectra (Figure 2). The coupling constants for the diastereotopic methylene protons (signals at δ 2.40−2.80 and δ 2.85−3.20 ppm) can be easily evaluated despite some overlapping of the signals at lower field with that of the methine proton.[9b,16] The values of those constants (15−17 and 3.1 Hz; 15−17 and 9.2 Hz) suggest a conformational homogeneity for the copolymers in solution, in keeping with the high optical rotation.[9b,16] It is very clear from the ^1H NMR and ^{13}C NMR spectra that the degrees[9b,9c,16] of regioregularity and stereoregularity in the optically active, isotactic P−CO, H−CO, O−CO, and ST−CO copolymers were all >90%.

The solution of the propylene−CO copolymer in $CDCl_3/(CF_3)_2CHOH$ showed that the ^1H NMR (Figure 2A, and Chart 1, **1**) resonance at δ 1.12 ppm was clearly due to the methyl group in the repeating unit, $-CH(CH_3)CH_2CO-$. The coupling constants indicated that the H atom absorbing at 2.78 ppm (d, $J = 15.7$ Hz) was not coupled with the methyl group and, therefore, was one of the CH_2 hydrogens and that the CH hydrogen resonated at δ 3.05−3.20 ppm, overlapping with the absorption of the second H atom of the CH_2 group in which the two H atoms are diastereotopic and therefore nonequivalent. The ^{13}C NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum (Figure 1A) exhibited resonances at δ 215.2, 45.4, 40.5, and 16.2 ppm due to the C=O, CH_2, CH, and CH_3 groups of the $-CH(CH_3)CH_2CO-$ units in the copolymer, respectively. These NMR parameters are in accord with those reported by Consiglio.[16]

The ^1H NMR ($CDCl_3/(CF_3)_2CHOH$) of the 1-heptene−CO copolymer (Figure 2B, and Chart 1, **2**) showed resonances at δ 2.80−3.10 (m, 2H), 2.65 (d, $J = 16.2$ Hz, 1H), 1.65 (m, 1H), 1.35 (br, 7H), and 0.95 (t, br, 3H) ppm, respectively, due to the two overlapping protons from both the backbone CH_2 and CH groups, the other diastereotopic proton of the backbone CH_2, one diastereotopic proton of the side chain CH_2 adjacent to the methine group, the rest of the methylene protons in the side chain, and the CH_3 protons in the $-CH((CH_2)_4CH_3)CH_2CO-$ repeating units of the polymer. The ^{13}C NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum of 1-heptene−CO copolymer (Figure 1B) exhibited resonances at δ 214.1, 45.0, 42.4, 35.5, 30.7, 23.0, 19.2, and 13.5 ppm due to, respectively, the C=O, CH, and CH_2 groups in the backbone, the four methylene groups in the side chain, and CH_3 groups.

Similarly, the attributions of the signals of the ^1H NMR spectrum ($CDCl_3/(CF_3)_2CHOH$) of the 1-octene−CO copolymer are shown in Figure 2C and Chart 1, **3**. The ^{13}C NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum of the

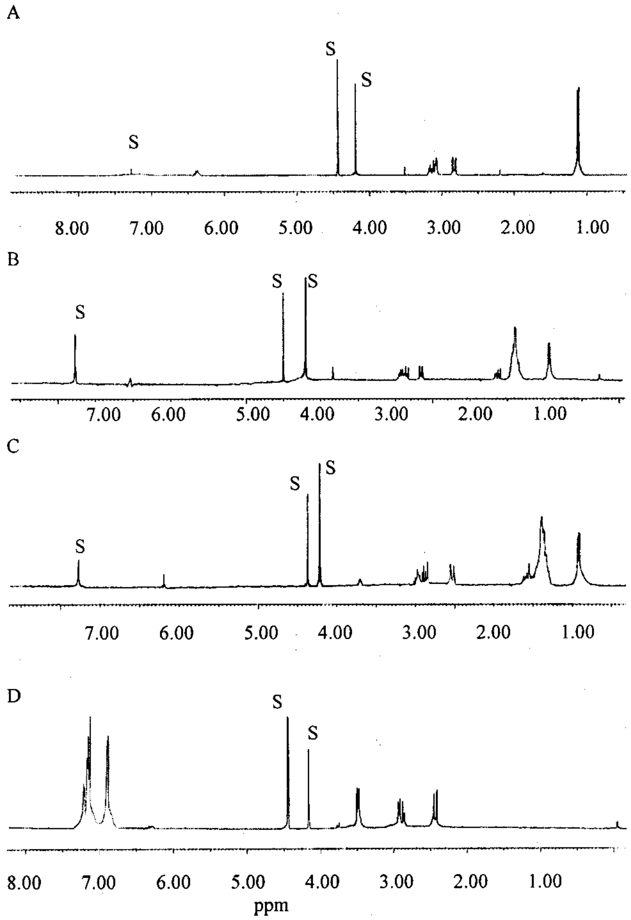

Figure 2. ^1H NMR spectra ({1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}, 400 MHz): (A) Spectrum of alternating isotactic P−CO copolymer. (B) Spectrum of alternating isotactic H−CO copolymer. (C) Spectrum of alternating isotactic O−CO copolymer. (D) Spectrum of alternating isotactic ST−CO copolymer. (S = solvent.)

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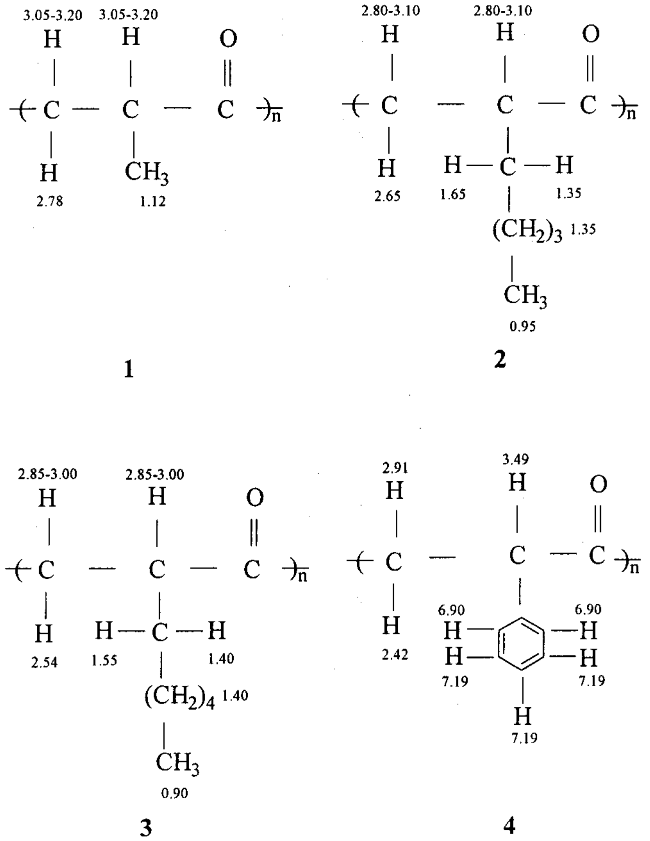
Chart 1



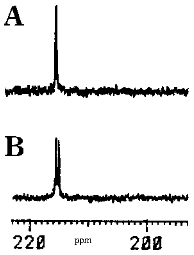
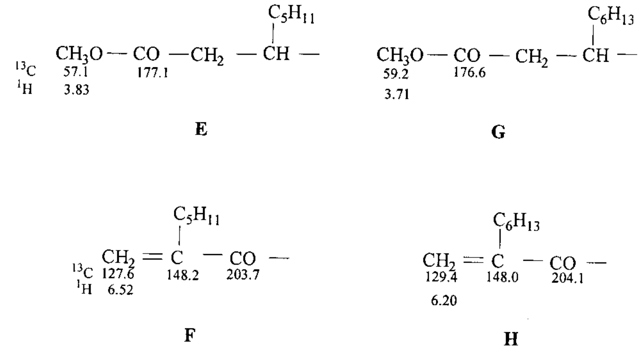


Figure 3. ^{13}C NMR spectrum ({1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}, 400 MHz) of ST−CO poly(1,4-ketone) in the presence of europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (molar ratio of Eu(III) and ST−CO repeating units: 1:5): (A) optically active, (B) racemic.

Chart 2



1-octene−CO copolymer (Figure 1C) exhibited resonances at δ 214.7, 44.8, and 42.0 ppm due to the C=O, CH, and CH_2 groups in the backbone and resonances at 35.3, 30.3, 25.4, 22.5, 18.8, and 12.8 ppm attributable to the five methylene groups in the side chain and the CH_3 group, respectively.

The attributions of signals of the ^{1}H NMR spectrum ($CDCl_3/(CF_3)_2CHOH$) of the styrene−CO copolymer are shown in Figure 2D and Chart 1, **4**. The ^{13}C NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum of the styrene−CO copolymer (Figure 1D) exhibited absorptions at δ 213.2, 52.0, and 41.2 ppm due to the C=O and backbone CH and CH_2 groups and absorbances at δ 137.5, 128.9, 128.3, and 126.1 ppm attributable to the phenyl group. The above parameters are consistent with those reported by Consiglio.[10a]

In the ^{13}C NMR spectrum of the styrene−CO copolymer prepared using chiral diphosphine (DDPPI), weak resonances indicative of chain end groups $CH_3OCOCH_2CH(Ph)-$ [δ 173.3 (*C*O), 50.1 ($\mathit{C}H_3OCOCH_2CH(Ph)-$), 42.5 ($CH_3OCOCH_2\mathit{C}H(Ph)-$), 34.4 ($CH_3OCO\mathit{C}H_2CH(Ph)-$) ppm] and $PhCH{=}CHCO-$ [δ 202.4 (*C*O), 148.5 ($Ph\mathit{C}H{=}CHCO-$), 132.1 (*ipso*), 127.5 ($PhCH{=}\mathit{C}HCO-$) ppm] are detected. A secondary regioselectivity for the insertion of styrene into the growing chain and the predominant termination by a β-hydrogen elimination from the last inserted styrene unit can be inferred from two chain end groups. The above results are in accord with those reported by Consiglio,[10c] who has spectroscopically identified the intermediates showing that the high regioselectivity was due to a secondary 2,1-insertion of styrene.

In contrast to the copolymerization of styrene and carbon monoxide, major primary insertion of propylene into a Pd−COOR bond is inferred from the identification of the end groups $CH_3OCOCH_2CH(CH_3)-$ [δ 177.0 (CO), 55.6 ($\mathit{C}H_3OCOCH_2CH(CH_3)-$), 36.2 ($CH_3OCO\mathit{C}H_2CH(CH_3)-$) ppm] and $CH_2{=}C(CH_3)CO-$ [δ 204.3 (CO), 144.9 ($CH_2{=}\mathit{C}(CH_3)CO-$), 128.2 ($\mathit{C}H_2{=}C(CH_3)CO-$)] of the propylene−CO copolymer obtained using DDPPI as the ligand in the presence of 2,6-dimethylbenzoquinone. This is consistent with the results reported by Nozaki.[17]

Very interestingly, the end groups of E, F of 1-heptene−CO and G, H of 1-octene−CO copolymers (Chart 2) were clearly detected. Therefore, primary insertions of 1-heptene and 1-octene into the Pd−COOR bonds were inferred. But, the concentrations of the unsaturated terminal groups (F and H) are smaller than that of the ester end groups (E and G). The ester groups may be the initial end groups of α-olefin 1,2-insertion into Pd−COOR bonds and partial terminal groups by methanolysis of the last α-olefin units (2,1-insertion). So, secondary insertions of 1-heptene and 1-octene into the Pd−COOR bonds may be in existence.

In the presence of europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate], the ^{13}C NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum of optically active ST−CO poly(1,4-ketone) exhibited only a dominant singlet (Figure 3) for the carbonyl resonance. However, the singlet turned doublet when the racemic poly(1,4-ketone) was employed.[7] So the degree of enantioselectivity in the optically active ST−CO poly(1,4-ketone) was greater than 90%.

Roles of the Anion and the Oxidant. The copolymerization catalysts generally show a higher activity in the presence of added oxidants such as quinones and

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weakly coordinating or noncoordinating anions such as BF_4^-. In our experiments, absence of 2,6-dimethylbenzoquinone and BF_4^- (if BF_4^- was used instead of other anions such as Cl^-, CH_3COO^-) would result in very low yield of the polymer.

Our catalyst complex, $[(DDPPI)\ Pd(CH_3CN)_2][BF_4]_2$, also required a weakly coordinating or noncoordinating anionic ligand (BF_4^-) apart from the requirement of neutral diphosphine ligand (DDPPI). The higher reactivity of the catalyst formed with such an anion is thought to stem, at least partly, from the easier access of the substrate molecules to the coordination sites at the metal center. A less strongly coordinating anion (BF_4^-), because of its easier dissociation from the ion-pair, may generate a more electrophilic palladium center. The lower electron density at the palladium center may cause a lower binding energy with the monomers because of less back-donation from metal to ligand. The intermediate palladium species, which are involved in the catalytic cycle, would therefore be less stable, with the result that carbon monoxide occupying vacant coordination sites at the palladium center can be displaced by the α-olefin and vice versa.[18]

A chain of the polymer can be started either from a palladium hydride or from a palladium methoxy in a protic solvent. But for a diphosphine system, the palladium hydride can “drop out” of the catalytic cycle.[19] The most obvious way for it to do so is by decomposition to Pd^0 (eqs 1, 2). These reactions reduce the rate at which palladium hydride can reenter the catalytic cycle. Oxidants function by oxidizing some or all of these “dead-ends” to Pd^{2+}, which can then immediately reenter the cycle, as in eq 3.

$$L_2PdH^+ \rightarrow L_2Pd^0 \tag{1}$$

$$L_2Pd^0 + L_2Pd^{2+} \rightarrow [L_2Pd]_2^{\ 2+} \tag{2}$$

$$[L_2Pd]_2^{\ 2+} + 2H^+ + OC_8H_8O \rightarrow 2L_2Pd^{2+} + HOC_8H_8OH \tag{3}$$

The Pd^0 can be oxidized to Pd(II) in the presence of 2,6-dimethylbenzoquinone; the possible mechanism is reported by Milani.[20]

Conclusions

The compound $[(DDPPI)Pd(CH_3CN)_2](BF_4)_2$ has been found to be an effective catalyst for the copolymerization of carbon monoxide with α-olefins such as propylene, 1-heptene, 1-octene, and styrene. The formed copolymers were a mixture of spiroketal and 1,4-ketone structures. The pure poly(1,4-ketone)s were obtained by dissolving the copolymers containing spiroketal and 1,4-ketone units in 1,1,1,3,3,3-hexafluoro-2-propanol and reprecipitating with methanol. The pure poly(1,4-ketone)s were highly optically active, alternating, and isotactic copolymers determined mainly by IR and NMR and supported by the results of optical rotation and elemental analysis.

Secondary insertion of styrene into the palladium−acyl bond and primary insertion of propylene, 1-heptene, and 1-octene into the palladium−acyl bond are inferred from the study of the end groups of our copolymers. We also studied the roles of the anion, BF_4^-, and the oxidant, 2,6-dimethylbenzoquinone. The copolymerization rate can be increased in the presence of BF_4^- and 2,6-dimethylbenzoquinone.

Experimental Section

General Considerations. Carbon monoxide (>99%) and propylene (c.p. grade) were used as received without further purification. 1-Heptene, 1-octene, and styrene were distilled from calcium hydride under dry nitrogen. 2,6-Dimethylbenzoquinone and $NOBF_4$ were purchased from Aldrich. The solvents were purified according to standard methods. DDPPI was prepared in our laboratory.[11] The molar mass was measured by Water gel permeation chromatography (GPC), and polystyrene was used as the standard, using tetrahydrofuran (THF) as the eluent. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer. The chemical shifts of ^{13}C NMR resonances were referenced to internal tetramethylsilane (TMS). IR spectra were recorded on a Bruker IFS 120HR spectrophotometer using KBr pellets. Optical rotation measurements of chiral polymers were performed on a JASCOJ-20C (Japan) polarimeter using a sodium lamp. Elemental analysis of the polymers was carried out by a VARIO EL (Germany) elemental analyzer. Differential scanning calorimeter was performed with a Perkin-Elmer DSC7 at a 10 °C/min heating rate.

Preparation of $[Pd(CH_3CN)_4](BF_4)_2$. The catalyst precursor $[Pd(CH_3CN)_4](BF_4)_2$ was prepared according to a published approach.[21] Under argon, Pd sponge (0.53 g, 5.0 mmol) and $NOBF_4$ (1.17 g, 10 mmol) were added to 25 mL of dried CH_3CN and stirred under a slow flow of argon at room temperature for 24 h. The yellow solution was filtered into anhydrous ether. The resulting pale yellow precipitate was washed with anhydrous ether and dried under vacuum with a yield of 92%. Anal. Calcd for $PdC_8H_{12}N_4B_2F_8$: C, 21.7; H, 2.8; N, 12.3. Found: C, 21.6; H, 2.9; N, 12.2. IR: 2338 cm^{-1} (−CN), 1000−1100 cm^{-1} (BF_4^-), 762 cm^{-1} (BF_4^-). ^1H NMR (CD_3NO_2): 2.65 ppm (CH_3-CN).

Preparation of the Catalyst $[Pd(DDPPI)(CH_3CN)_2](BF_4)_2$. A mixture of $[Pd(CH_3CN)_4](BF_4)_2$ (0.444 g, 1 mmol) and DDPPI (0.482 g, 1 mmol) was codissolved in 100 mL of dry CH_3CN, and the resultant solution was allowed to magnetically stir under a slow flow of nitrogen at room temperature for 5 h. After the solution was concentrated under vacuum, a solid precipitate was obtained by addition of diethyl ether. The product (0.89 g) was washed with anhydrous ether and dried under vacuum. ^1H NMR [1:3 (v/v) C_6H_6/CH_3NO_2]: 2.62 ppm (s, 6H of CH_3CN), 3.05 ppm (d, 4H of ligand), 4.22 ppm (m, 4H of ligand), 7.25−7.60 ppm (m, 20H of ligand). ^{31}P NMR [1:3 (v/v) C_6H_6/CH_3NO_2]: 31.0 ppm. Anal. Calcd for $PdC_{34}H_{34}N_2B_2F_8O_2P_2$: C, 48.3; H, 4.0; N, 3.3. Found: C, 48.6; H, 4.2; N, 3.2.

Preparation of Optically Active, Isotactic, Alternating Propylene−CO Copolymer. A solution containing 0.05 mmol of $[Pd(DDPPI)(CH_3CN)_2](BF_4)_2$ and 0.08 mmol of 2,6-dimethylbenzoquinone in 6 mL of a 3:1 (v/v) methylethyl ketone/CH_3OH mixture was placed in a stainless steel reactor (volume 100 mL) under nitrogen, and then the reactor was charged with 10 g of propylene and 9 MPa of CO. The reaction mixture was magnetically stirred at 45 °C for 32 h. After depressurization, the mixture was precipitated by the addition

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of methanol and dried under vacuum at ambient temperature for 24 h, and then 3.9 g of the copolymer was obtained. ^{1}H NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 3.05−3.20(m, 2H, CH*H* and C*H*), 2.78(d, $J = 15.7$ Hz, 1H, CH*H*), 1.12(d, $J = 6.7$ Hz, 3H, C*H₃*). ^{13}C NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 215.2, 45.4, 40.5, 16.2, and small absorbances at 204.3, 177.0, 144.9, 128.2, 55.6, 36.2. IR (KBr, cm^{-1}) [the sample was reprecipitated from $(CF_3)_2CHOH$]: 1703 (C═O). Anal. Calcd for C_3H_6−CO: C, 68.6; H, 8.6. Found: C, 68.9; H, 8.4. Molecular weight: $M_n = 1.43 \times 10^4$ versus polystyrene, $M_w/M_n = 2.72$. Optical rotation: $[\alpha]^{20}_{589}$ +52° (CH_2Cl_2, 5.0 mg/mL). $T_m = 203$ °C, $T_g = 35$ °C.

Preparation of Optically Active, Isotactic, Alternating 1-Heptene−CO Copolymer. The reaction was performed following a procedure analogous to the one employed for propylene, but 1-heptene (10 mL) was used instead of propylene. The reaction mixture was magnetically stirred at 45 °C for 48 h. After depressurization, the mixture was precipitated by the addition of methanol and dried under vacuum at ambient temperature for 24 h, and then 3.5 g of the copolymer was obtained. ^{1}H NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 2.80−3.10(m, 2H, backbone CH*H* and C*H*), 2.65(d, $J = 16.2$ Hz, 1H, backbone CH*H*), 1.65(m, 1H, side chain $CHHC_4H_9$), 1.35(m, 7H, side chain $CHH(CH_2)_3CH_3$), 0.95(t, br, 3H, CH_3), and small resonances of end groups at 6.52, 3.83. ^{13}C NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 214.1, 45.0, 42.4, 35.5, 30.7, 23.0, 19.2, 13.5, and small absorbances at 203.7, 177.1, 148.2, 127.6, 57.1. IR (KBr, cm^{-1}) [reprecipitated from $(CF_3)_2CHOH$]: 1708 (C═O). Anal. Calcd for C_7H_{14}−CO: C, 76.1; H, 11.2. Found: C, 76.3; H, 11.4. Molecular weight: $M_n = 4.02 \times 10^3$ versus polystyrene, $M_w/M_n = 1.55$. Optical rotation: $[\alpha]^{20}_{589}$ +63° (CH_2Cl_2, 5.0 mg/mL). $T_m = 194$ °C, $T_g = 11$ °C.

Preparation of Optically Active, Isotactic, Alternating 1-Octene−CO Copolymer. The reaction was performed following a procedure analogous to the one employed for propylene, but 1-octene (10 mL) was used instead of propylene. The reaction mixture was magnetically stirred at 45 °C for 48 h. After depressurization, the mixture was precipitated by the addition of methanol and dried under vacuum at ambient temperature for 24 h, and then 4.1 g of the copolymer was obtained. ^{1}H NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 2.85−3.00(m, 2H, backbone CH*H* and C*H*), 2.54(d, $J = 16.4$ Hz, 1H, backbone CH*H*), 1.55(m, br, 1H, side chain $CHHC_5H_{11}$), 1.40-(m, 9H, side chain $CHH(CH_2)_4CH_3$), 0.90(t, br, 3H, CH_3), and small resonances of end groups at 6.20, 3.71. ^{13}C NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 214.7, 44.8.0, 42.0, 35.3, 30.3, 25.4, 22.5, 18.8, 12.8, and small resonances of end groups at 204.1, 176.6, 148.0, 129.4, 59.2. IR (KBr, cm^{-1}) [reprecipitated from $(CF_3)_2CHOH$]: 1706 (C═O). Anal. Calcd for C_8H_{16}−CO: C, 77.1; H, 11.4. Found: C, 77.5; H, 11.3. Molecular weight: $M_n = 7.31 \times 10^3$ versus polystyrene, $M_w/M_n = 2.37$. Optical rotation: $[\alpha]^{20}_{589}$ +61° (CH_2Cl_2, 5.0 mg/mL). $T_m = 204$ °C, $T_g = 3$ °C.

Preparation of Optically Active, Isotactic, Alternating Styrene−CO Copolymer. The reaction was performed following a procedure analogous to the one employed for propylene, except styrene (10 mL) was used instead of propylene. The reaction mixture was magnetically stirred at 45 °C for 24 h. After depressurization, the mixture was precipitated by the addition of methanol and dried under vacuum at ambient temperature for 24 h, and then 3.1 g of the copolymer was obtained. ^{1}H NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 7.19-(m, 3H, phenyl), 6.90(d, $J = 7.3$ Hz, 2H, phenyl), 3.49(dd, $J = 9.2$ Hz, 3.1 Hz, 1H, backbone C*H*), 2.91(dd, $J = 16.2$ Hz, 9.2 Hz, 1H, backbone CH*H*), 2.42(dd, $J = 16.2$ Hz, 3.1 Hz, 1H, backbone CH*H*). ^{13}C NMR (ppm) {1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$}: 213.2, 137.5, 128.9, 128.3, 126.1, 52.0, 41.2, and small resonances of end groups at 202.4, 177.3, 148.2, 132.1, 127.5, 50.1, 42.5, 34.4. IR (KBr, cm^{-1}) [reprecipitated from $(CF_3)_2CHOH$]: 1714 (C═O). Anal. Calcd for C_8H_8−CO: C, 81.8; H, 6.1. Found: C, 82.1; H, 6.5. Molecular weight: $M_n = 6.23 \times 10^3$ versus polystyrene, $M_w/M_n = 1.72$. Optical rotation: $[\alpha]^{20}_{589}$ +359° (CH_2Cl_2, 5.0 mg/mL). $T_m = 305$ °C, $T_g = 127$ °C.

Acknowledgment. The authors would like to thank the National Natural Science Foundation of the People's Republic of China for financial support (No. 29673052).

OM010046G