Stereo- and Enantioselective Alternating Copolymerization of α-Olefins with Carbon Monoxide. Synthesis of Chiral Polymers

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ABSTRACT: Palladium(II) compounds of the type $[PdL_2(MeCN)_2](BF_4)_2$ (L_2 = chiral bidentate ligand) have been used as catalysts for the synthesis of chiral alternating α-olefin–carbon monoxide copolymers. For the synthesis of the chiral propylene–carbon monoxide copolymer and the ethylene–propylene–carbon monoxide terpolymer, chiral bidentate phosphines were employed as the ligand. The alternating styrene–carbon monoxide copolymers made thus far have been highly syndiotactic and since isotactic segments in the polymer backbone were required for chirality, a new ligand system was needed. When 2-pyridinecarboxaldehydeimine derivatives were used as the bidentate ligand, the ratio of isotactic to syndiotactic segments in the styrene–carbon monoxide copolymers was found to increase with increasing steric size of the substituent on the imine nitrogen, and when the enantiomerically pure 2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine was employed, chiral alternating styrene–carbon monoxide copolymers were obtained. Finally, it appears that the optical rotations of the chiral copolymers were primarily due to the presence of stereogenic tertiary carbon centers in the polymer backbone with only minimal contribution from polymer conformation.

Chiral polymers have been used as chromatographic supports for the separation of enantiomers[1] and as reagents and catalysts for asymmetric synthesis.[2] More recently the chirality has been used to impose structural asymmetry required in piezoelectric, ferroelectric, and nonlinear optical materials.[3] In nature, chiral polymers are derived from the readily available pools of chiral monomers such as amino acids and sugars. Most man-made chiral polymers are also derived from chiral monomers.[4] Given the limited availability of most enantiomerically enriched monomers, it is far more attractive to design synthetic strategies involving the enantioselective polymerization of prochiral monomers. However, reports of such procedures where the polymer chirality arises from asymmetric backbone configurations rather than restricted conformational states (e.g., helicity) are exceedingly rare.[5]

We and others have reported on the palladium(II) catalyzed alternating copolymerization of α-olefins with carbon monoxide.[6] An important difference between an alternating α-olefin–carbon monoxide copolymer and a poly(α-olefin) is that the former contains truly stereogenic centers in the polymer backbone. It is therefore not appropriate to use the terms "meso" and "racemic" in descriptions of polymer stereoregularity. Using the *R,S* convention instead, the dyads can be described as *RR* or *SS* and *RS* or *SR*. Similarly, the four possible triads are *RRR* or *SSS*, *RSR* or *SRS*, *RSS* or *SRR*, and *RRS* or *SSR*. As is evident from Figure 1, at the high molecular weight limit, a *syndiotactic* alternating α-olefin–carbon monoxide copolymer chain will always show vanishingly small optical activity since the absolute configuration of the stereogenic centers in the backbone *alternates* (i.e., ...*RSRSRS*...). On the other hand, the stereogenic centers in the individual chains of an *isotactic* alternating α-olefin–carbon monoxide copolymer sample have the *same* absolute configurations (i.e., ...*RRRRRR*... or ...*SSSSSS*...) and, thus, the synthesis of optically active isotactic alternating α-olefin–carbon monoxide copolymers should be possible. Indeed, any alternating α-olefin–CO copolymer having tertiary carbons with a ratio of configurations $R/S \neq 1$ must be chiral. Herein we report the synthesis of chiral alternating propylene–CO copolymer (P–CO copolymer), ethylene–propylene–CO terpolymer (E–P–CO terpolymer), and styrene–CO copolymer (S–CO copolymer). These constitute a new class of chiral polymers, and except for brief preliminary reports on chiral P–CO copolymers,[7] we are unaware of any previous synthesis of chiral α-olefin–CO copolymers.

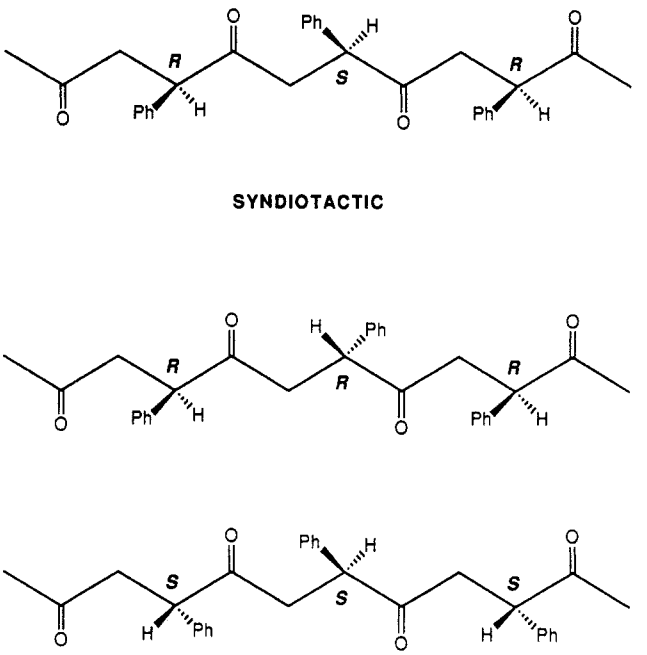

Figure 1. The syndiotactic and isotactic structures for the alternating copolymers of α-olefins with carbon monoxide.

Results and Discussion

Propylene–CO Copolymer and Ethylene–Propylene–CO Terpolymer. The alternating copolymerization of propylene with CO catalyzed by $[PdL_2(MeCN)_2](BF_4)_2$ [L_2: (*S,S*)-(+)-DIOP, (*R,R*)-(−)-DIOP, (*S,S*)-(−)-BDPP, (*R,R*)-(+)-BDPP, (*S*)-(−)-BINAP, and (*R*)-(+)-BINAP] led

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Table 1. Structures and Properties of the Alternating Propylene-Carbon Monoxide Copolymers Synthesized Using Chiral Chelating Phosphine Ligands

ligand	productivity[a] (g polymer/g-Pd)	M_n (GPC)[b] (M_w/M_n)	regioselectivity (%)[c] H-H	H-T	T-T	$[\Phi]_D^{20}$ [d]
(2*R*,3*R*)-(−)-DIOP	500	5.2×10^3 (1.7)	11	78	11	−5°
(2*S*,3*S*)-(+)-DIOP						+4°
(2*R*,4*R*)-(+)-BDPP	630	1.9×10^4 (1.4)	12	76	12	−20°
(2*S*,4*S*)-(−)-BDPP						+20°
(*R*)-(+)-BINAP	300	3.1×10^3 (3.7)	17	66	17	+25°
(*S*)-(−)-BINAP						−24°

[a] Productivities were for reactions at 45 °C for 2 days using 500 psi of CO and 35 g of propylene. [b] Molecular weights and their distributions were measured by GPC relative to polystyrene standards. [c] Percentages of head-to-head (H-H), head-to-tail (H-T), and tail-to-tail (T-T) arrangements in the polymer backbone were obtained from the intensities of the ^{13}C NMR carbonyl resonances of the P-CO copolymer. [d] CH_2Cl_2 was used as the solvent, [Φ]: molar optical rotation.

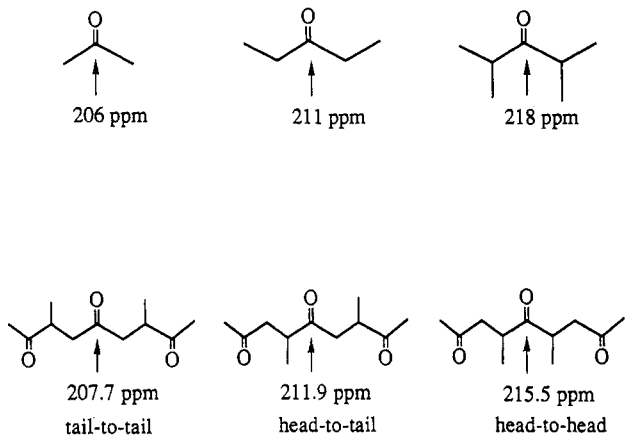
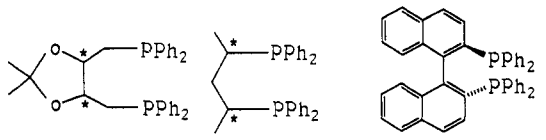


Figure 2. A comparison of the ^{13}C NMR resonances for the carbonyl groups in model compounds and in the repeating units of the alternating propylene–CO copolymer.

to the formation of chiral P–CO copolymers, and the results are shown in Table 1.

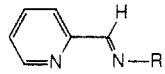


All the P–CO copolymers were alternating, and the IR, ^1H, and ^{13}C NMR spectra were very similar to those of the P–CO copolymer reported previously.[6b,8,9] The $^{13}C\{^1H\}$ NMR spectra had absorptions at 215.5, 211.9, and 207.7 ppm due to the carbonyl groups flanked by head-to-head, head-to-tail, and tail-to-tail propylene units based on the ^{13}C NMR resonances of the carbonyl groups of model compounds as shown in Figure 2. The degrees of regioselectivity were calculated from the intensities of the carbonyl ^{13}C NMR resonances and are shown in Table 1. It was indeed unusual that the catalysts were able to induce configurational asymmetry in the backbone without imposing strict regioselectivity. Of the chiral chelating phosphines used, DIOP was least effective in inducing backbone chirality. This was presumably due to the greater distance of the chiral center of DIOP from the coordinating phosphorus atoms.

Chiral E–P–CO terpolymers[8] were obtained when a mixture of ethylene and propylene were used instead of propylene alone. The terpolymerization of ethylene, propylene, and carbon monoxide catalyzed by [Pd(BDPP)-$(MeCN)_2](BF_4)_2$ at 70 °C in nitromethane/methanol mixture led to the formation of E–P–CO terpolymer containing alternating E–CO and alternating P–CO units with ratio of E–CO units/P–CO units = 7:3. The ^1H NMR ($CDCl_3$) spectrum of the polymer exhibited absorptions at 2.71 (s), 3.1–2.5 (br), and 1.10 (d, J = 6.5 Hz) ppm due to the $-CH_2CH_2-$ groups of the E–CO units and $-CH_2CH-$ and $-CH_3$ groups of the P–CO units, respectively. The ratio of E–CO units/P–CO units was calculated from the ^1H NMR spectrum. The $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum of the terpolymer showed absorbances at 211.86, 207.79, 45.46, 40.78, 35.93, 34.65, and 16.58 ppm. The resonances at 211.86 and 207.79 ppm were due to the carbonyls in head-to-tail, $-CH_2C(O)CH(CH_3)-$, and tail-to-tail, $-CH_2C(O)CH_2-$, arrangements. The presence of head-to-head propylene units in the backbone was statistically unlikely, and this was confirmed by the absence of a carbonyl resonance at 215.5 ppm. The resonances at 45.46, 40.78, and 16.58 ppm were ascribed to the $-CH_2CH(CH_3)-$ groups of the P–CO units. The absorptions at 35.93 and 34.65 ppm were attributable to methylene groups of the E–CO units in $-CH_2C(O)CH_2-$ and $-CH(CH_3)C(O)CH_2-$ arrangements, respectively. The formed E–P–CO terpolymer was soluble in chloroform and methylene chloride and had a molecular weight (versus polystyrene standards) of 1.6×10^4 with polydispersity of 2.2. The E–P–CO terpolymer had a molar optical rotation of +19° (20 °C, CH_2Cl_2) based on the P–CO units when (*S*,*S*)-(−)-BDPP was the ligand, which changed to −20° (20 °C, CH_2Cl_2) when (*R*,*R*)-(+)-BDPP was used.

Styrene–CO Copolymers. Thus far, the reported synthesis of alternating S–CO copolymers involves the use of 1,10-phenanthroline or 2,2′-dipyridyl derivatives of palladium(II) as catalysts[10] and invariably leads to the synthesis of highly syndiotactic copolymers.[11] Since isotactic segments in the polymer backbone are required for chirality, it was first necessary to determine the factors that govern tacticity in the alternating S–CO copolymers. We started with the working hypothesis that π-stacking due to the interaction of the styrene phenyl group with the π-system of the planar ligand played a part in the formation of syndiotactic S–CO copolymers. Accordingly, we examined the role of substituents capable of sterically disrupting π-stacking. Using [Pd(1,10-phenanthroline)-$(MeCN)_2](BF_4)_2$ as catalyst and either 4-methylstyrene or 3-methylstyrene as substrate resulted in the formation of highly *syndiotactic* alternating structures. On the other hand, an *atactic* copolymer was obtained when 2-methylstyrene was a monomer. The structure and properties of syndiotactic 4-methylstyrene–CO copolymer have been previously reported.[10a] The structure of 3-methylstyrene–CO copolymer was found to be similarly alternating, exclusively head-to-tail, and highly tactic. The ^1H NMR ($CDCl_3$) spectrum of the polymer showed absorptions at 6.80–6.89 (2H, m), 6.53 (1H, d, J = 6.9 Hz), and 6.40 (1H, s) ppm due to the protons on the phenyl groups, resonances at 4.07 (1H, t), 3.01 (1H, dd), 2.64 (1H, dd) ppm due to the $-CH_2CH-$ groups, and a methyl absorbance at 2.03 (3H, s) ppm. The coupling among the three protons of

Table 2. Molecular Weights and Their Distributions (in Parentheses) for Alternating Copolymers of Styrenes with Carbon Monoxide Prepared Using A as the Ligand[a]

A: 

	R		
copolymer	$-(CH_2)_3CH_3$	$-CH(CH_3)C_2H_5$	$-CH(CH_3)C_6H_5$
4-methylstyrene–CO	2.2×10^4 (1.4)	9.0×10^3 (1.2)	1.4×10^4 (1.2)
styrene–CO	insoluble in $CHCl_3$	partially soluble in $CHCl_3$	5.6×10^3 (1.3)

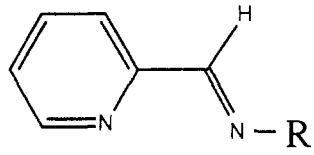
[a] Molecular weights and their distributions were measured by GPC relative to polystyrene standards.

the $-CH_2CH-$ groups was indicative of the presence of a stereoregular structure. It is known, for example, that base-catalyzed epimerization of syndiotactic S–CO copolymers results in broadening of the three resonances.[10a,11] The $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum of 3-methylstyrene–CO copolymer had single dominant resonances at 206.51, 137.99, 136.63, 128.57, 128.28, 127.75, 125.64, 53.23, 43.20, and 21.18 ppm and further supported the tactic structure. The polymer was soluble in common organic solvents such as chloroform and methylene chloride and had a molecular weight of 4.1×10^4 (M_p, versus polystyrene standards) with polydispersity of 1.9. In contrast, the 2-methylstyrene–CO copolymer formed was an alterating *atactic* copolymer with strictly a head-to-tail structure. The polymer showed broad ^1H NMR ($CDCl_3$) absorptions at 6.20–7.05 (4H, m), 4.35 (1H), 3.01 (1H), 2.48 (1H), 2.17 (3H) ppm due to its atacticity. The $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum also exhibited broad resonances centered at 206.74, 136.29, 135.55, 130.72, 127.16, 126.83, 126.27, 49.42, 42.49, and 19.64 ppm. ^{13}C NMR resonances of the carbonyl groups of the *syndiotactic* alternating 4-methylstyrene–CO copolymer and the *atactic* alternating 2-methylstyrene–CO copolymer are compared in Figure 3. The presence of a *single* set of resonances was consistent with a head-to-tail structure in both polymers (cf., the P–CO and E–P–CO copolymers discussed above); however, the multiple resonances seen in the latter spectrum was consistent with its atactic structure. The molecular weight (M_p, versus polystyrene standards) and molecular weight distribution of 2-methylstyrene–CO copolymer were found to be 5.8×10^3 and 1.3, respectively. It is clear from the above that the presence of a substituent close to the olefinic functionality had a dramatic effect in reducing the stereoselectivity in the copolymerization of styrene and carbon monoxide.

The presence of substituents on the ligand periphery of either 1,10-phenanthroline or 2,2′-dipyridyl derivative of palladium(II) also resulted in a decrease in the syndiotacticity of the S–CO copolymer derived therefrom. Thus, the degree of tacticity of 4-methylstyrene–CO copolymer decreased when 3,4,7,8-tetramethyl-1,10-phenanthroline or 4,4′-dimethyl-2,2′-bipyridine was used as the ligand. This was manifested by the presence of additional minor resonances in the carbonyl region of the ^{13}C NMR spectrum (Figure 3). Note that the methyl substituents on the ligands are away from the catalyst center and cannot *directly* interfere with the stereoselectivity in the olefin insertion step *except* through disruption of π-stacking. The copolymerization reaction was completely suppressed when 2,9-dimethyl-1,10-phenanthroline was used as the ligand. Presumably, in this instance, the methyl groups directly interfered with the chain growth sequence.

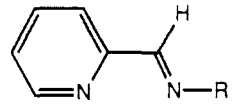
While the experiments described above do not unequivocally establish the existence of π-stacking, they do demonstrate that it is possible to lower the syndiotacticity in S–CO copolymers through substituent steric effects. Therefore, we sought a new ligand system where the effect of the substituent can be studied more systematically and easily. The 2-pyridinecarboxaldehydeimine derivatives, **A**, appear to be such a class of ligands. They were readily synthesized following a modified literature method.[12] For example, refluxing a 1:1 molar mixture of 2-pyridinecarboxaldehyde and a primary amine in methanol followed by vacuum distillation generally gave **A** in >95% yield.

Table 3. Percentages of Triads in the Styrene–Carbon Monoxide Copolymer Synthesized Using Ligand A with Different R Groups[a]



	R		
triad	$-(CH_2)_3CH_3$ (%)	$-CH(CH_3)CH_2CH_3$ (%)	$-CH(CH_3)C_6H_5$ (%)
RSR/SRS	80	70	56
RSS/SRR	10	13	20
RRS/SSR	10	13	20
RRR/SSS	0	4	4

[a] All reactions were run at 60 °C for 40 h using 6.8×10^{-2} mmol of $[Pd(A)(MeCN)_2](BF_4)_2$, 4.0 mL of styrene, and 1000 psi of CO.



A

The compounds, $[Pd(A)(MeCN)_2](BF_4)_2$ (R = $(CH_2)_3CH_3$, **1**; $CH(CH_3)CH_2CH_3$, **2**; $CH(CH_3)Ph$, **3**), formed in situ by codissolving a 1:1 (molar ratio) mixture of $[Pd(MeCN)_4](BF_4)_2$ and **A** in nitromethane/methanol, catalyzed the alternating copolymerization of styrene derivatives and carbon monoxide. The molecular weights and molecular weight distributions of the formed copolymers are summarized in Table 2. The parent styrene–CO copolymers were alternating, head-to-tail, and primarily syndiotactic. The NMR spectra of the polymers were very similar to those of the S–CO copolymer prepared using $[Pd(1,10\text{-phenanthroline})(MeCN)_2](BF_4)_2$ as the catalyst except for the degree of tacticity. The solubility of the styrene–CO copolymers were dependent on the catalyst employed and was attributable to the differences in degree of stereoregularity and resultant crystallinity of the polymer samples. The $^{13}C\{^1H\}$ NMR spectra of the ipso carbons of the styrene–CO copolymers synthesized using **2** and **3** as catalysts exhibited a resonance due to isotactic *RRR/SSS* triads in addition to those corresponding to *RSS/SRR*, *RRS/SSR*, and *RSR/SRS* triads observed with highly syndiotactic S–CO copolymers such as that made using **1** as catalyst (Figure 4).[13] The distributions of triads in the alternating styrene–CO copolymers are shown in Table 3. It is clear that the decrease in syndiotacticity and increase in isotacticity of the S–CO copolymers paralleled the increase in size of the substituent, *R*, on the 2-pyridinecarboxaldehydeimine ligand. Further increase in bulkiness, however, led to inactive catalysts. For an example, no polymer was formed when 2-pyridinecarboxaldehyde-*N*-*tert*-butylimine or 6-methyl-2-pyridinecarboxaldehyde-*N*-*n*-butylimine was used as the ligand.

The 4-methylstyrene–CO copolymers were also alternating, head-to-tail, and primarily syndiotactic.

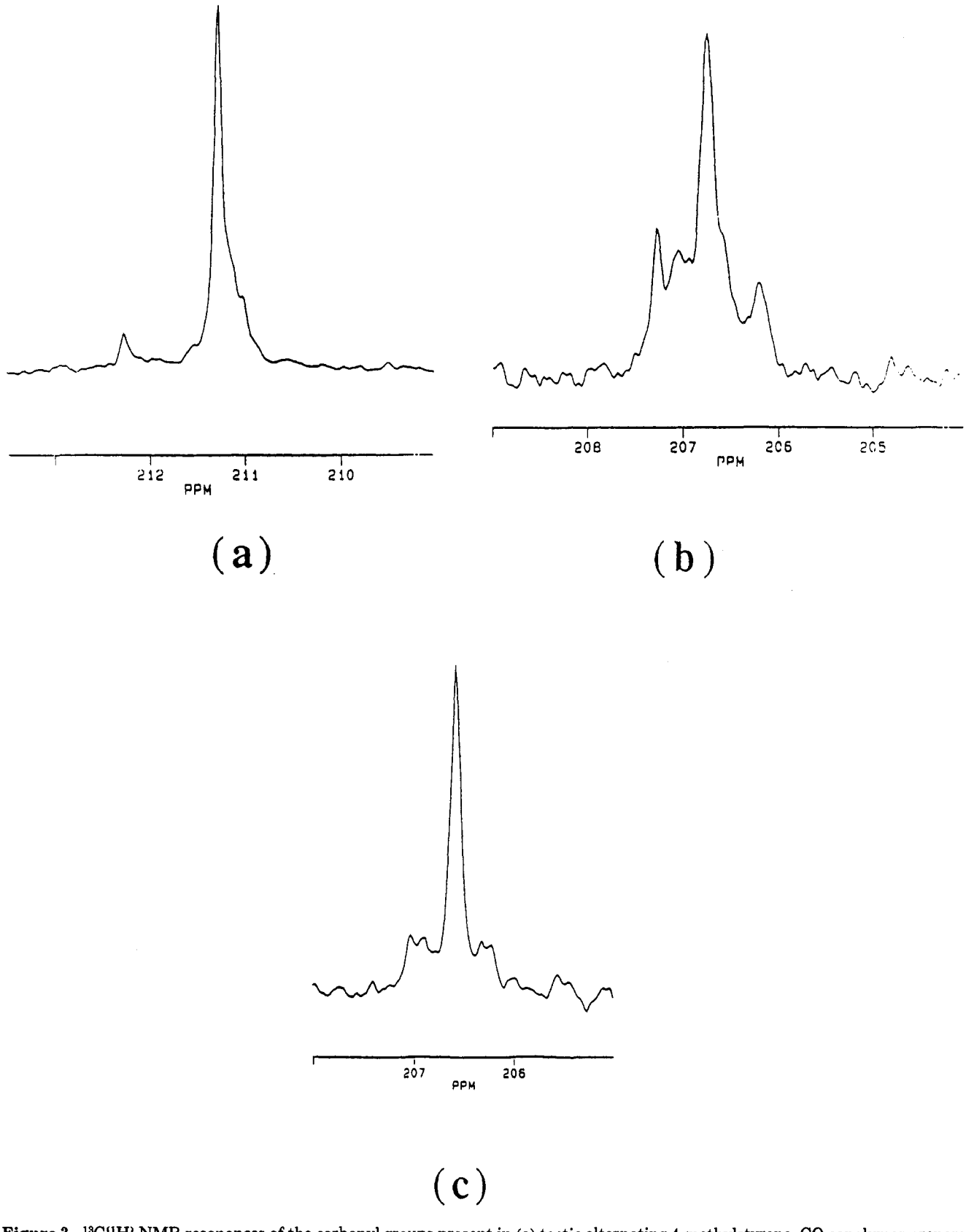
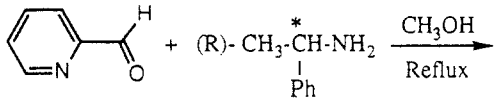


Figure 3. $^{13}C\{^1H\}$ NMR resonances of the carbonyl groups present in (a) tactic alternating 4-methylstyrene–CO copolymer prepared using 1,10-phenanthroline as ligand (NMR solvent: $(CF_3)_2CHOH$)), (b) atactic alternating 2-methylstyrene–CO copolymer prepared using 1,10-phenanthroline as ligand (NMR solvent: $CDCl_3$), and (c) alternating 4-methylstyrene–CO copolymer prepared using 4,4′-dimethyl-2,2′-bipyridine as ligand (NMR solvent: $CDCl_3$).

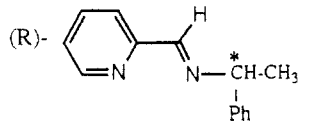
The NMR spectra of the copolymers were very similar to those of the copolymers prepared previously except for the degree of tacticity. The copolymers were soluble in common organic solvents, such as chloroform and methylene chloride, due to the presence of the methyl substituent.

As stated previously, a purely syndiotactic olefin–CO copolymer cannot be chiral; an isotactic structure is required for chirality. The fact that use of 2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine ligand resulted in the formation of S–CO copolymers with low syndioselectivity made the enantiomers of the ligand logical

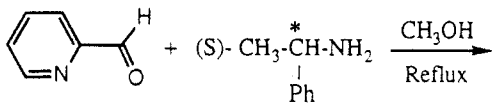
choices for enantioselective copolymerization of styrenes with carbon monoxide. The *R* and *S* enantiomers of 2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine were prepared through condensation reaction between 2-pyridinecarboxaldehyde and optically pure α-methylbenzylamines in accordance with the following equations.



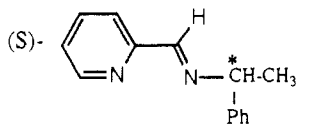
$[\alpha]_D^{23} = +38°$(neat)



$[\alpha]_D^{20} = -29°$(neat)



$[\alpha]_D^{23} = -39°$(neat)



$[\alpha]_D^{20} = +30°$(neat)

It should be mentioned that the configurations of the chiral $-CH(CH_3)Ph$ group remained unchanged during the reactions, and the specific optical rotations of the resultant products were independent of the reaction time. The alternating styrene–CO copolymer and 4-methylstyrene–CO copolymer synthesized using (*R*)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylamine as ligand had molar optical rotation of +22° (20 °C, CH_2Cl_2, *c* 13 mg/mL) and +19° (20 °C, CH_2Cl_2, *c* 19 mg/mL), respectively. On the other hand, use of the (*S*)-ligand changed the numbers to −21° (20 °C, CH_2Cl_2, *c* 13 mg/mL) and −20° (20 °C, CH_2Cl_2, *c* 19 mg/mL), respectively. The optical activity of the copolymers was not due to catalyst contamination. The polymers were purified by reprecipitation in $CHCl_3/Et_2O$/pentane, and NMR spectra indicated that the copolymers were pure and free of any ligand. In addition, epimerization of the chiral polymers in the presence of a base caused gradual decrease in their optical activity. For example, we observed almost complete loss of optical activity for the styrene–CO copolymer with starting molar optical rotation of +21° by heating a solution of the polymer (*c* 5 mg/mL) in CH_2Cl_2 at 45 °C in the presence of sodium 2-chlorophenolate (*c* 4.1 mg/mL).

The distribution of triads in the alternating styrene–CO copolymer formed by using either the *R* or the *S* enantiomer of 2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine was identical to that in the copolymer obtained using the racemic ligand (Table 3). Therefore, based on the triad distribution, the *maximum* possible ratio between the *R* and *S* centers in a given styrene–CO copolymer can be calculated to be 68:32 [$^2/_3$(56 + 20 + 20) + 1 (4): $^1/_3$(56 + 20 + 20) + 1 (0)], assuming 100% enantioselectivity (*R* or *S*) in the formation of the triads.

Relationship between Optical Activity and Polymer Conformation. The optical rotations of the chiral P–CO, E–P–CO, and S–CO copolymers that we have synthesized appear to be primarily due to the presence of stereogenic tertiary carbon centers in the polymer backbone with only minimal contribution from polymer conformation. Thus, the molar optical rotation of the copolymers showed only slight temperature dependence (see Figure 5). Polymers whose chirality arise from restricted conformational states (e.g., helicity) tend to exhibit a fairly large decrease in optical rotation with increasing temperature.[14] The temperature dependence of the molar optical rotation, $\Delta[\Phi]_D/\Delta T$, for the (+)-P–CO copolymer and the (−)-S–CO copolymer were −0.14°/°C and +0.05°/°C, respectively, and may be compared

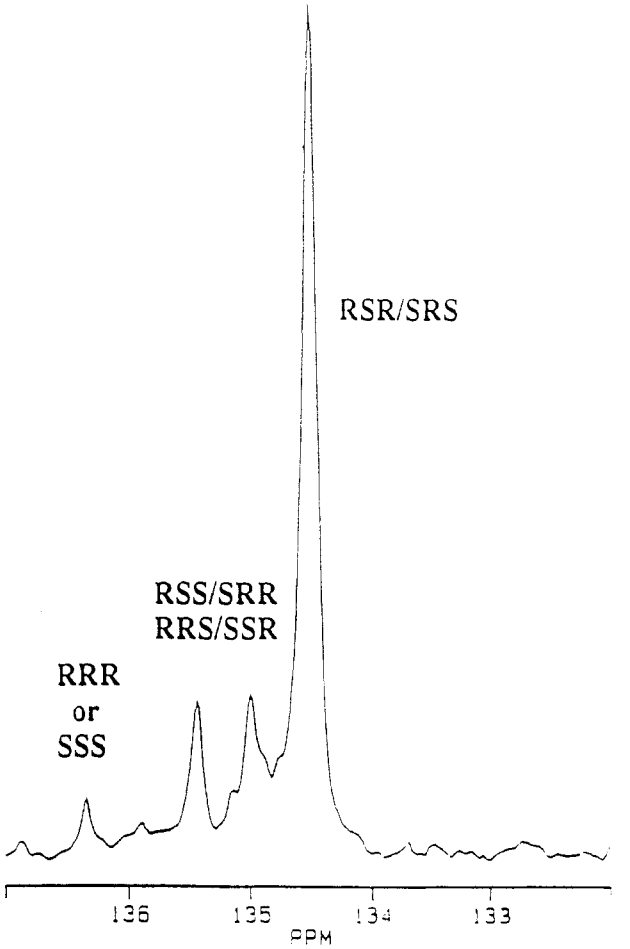


Figure 4. $^{13}C\{^1H\}$ NMR resonances for the ipso carbons of the primarily syndiotactic alternating styrene–CO copolymer prepared using 2-pyridinecarboxaldehyde-*N*-isobutylimine ligand.

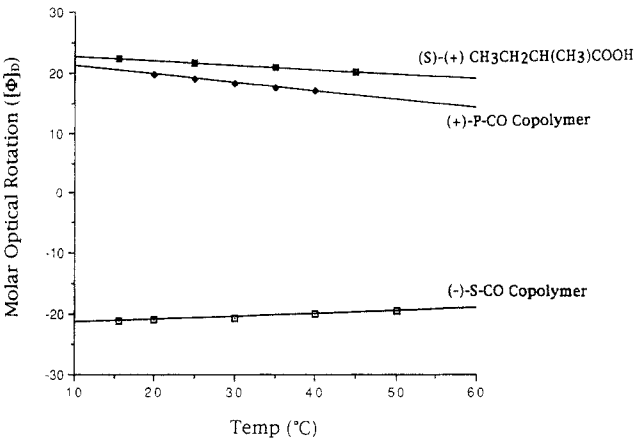


Figure 5. Dependence of molar optical rotation ($[\Phi]_D$) on temperature. CH_2Cl_2 was the solvent for the alternating propylene–CO and styrene–CO copolymers, and CH_3OH was the solvent for 2-methylbutyric acid.

with those of S-(+)-2-methylbutyric acid and S-(+)-2-phenylbutyric acid, −0.07°/°C and −0.41°/°C, respectively. It should be noted, however, that values of $\Delta[\Phi]_D/\Delta T$ similar to those observed for (+)-P–CO and the (−)-S–CO copolymer have been used as evidence for the presence of solution helical conformations for polyolefins.[15] By employing the same chiral catalyst, $[Pd(BDPP)(MeCN)_2](BF_4)_2$, the P–CO copolymer and E–P–CO terpolymer formed had almost identical molar optical rotations *based on* the P–CO units. This also strongly suggests that the observed optical rotations of the copolymers resulted from the catalyst-controlled enantioselectivity in the formation of P–CO units and was independent of the polymer conformation since the latter is expected to be different for the two polymers.

Experimental Section

a. Materials. C.P. grade chemicals were used as received unless otherwise stated. (*S,S*)-(+)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(*S,S*)-(+)-DIOP], (*R,R*)-(−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(*R,R*)-(−)-DIOP], (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-(+)-BINAP], (*S*)-(−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*S*)-(−)-BINAP], (*R*)-(+)-α-methylbenzylamine, and (*S*)-(−)-α-methylbenzylamine were purchased from Aldrich. (*S,S*)-(−)-2,4-Bis(diphenylphosphino)-pentane [(*S,S*)-(−)-BDPP] and (*R,R*)-(+)-2,4-bis(diphenylphosphino)pentane [(*R,R*)-(+)-BDPP] were obtained from Strem Chemicals. $[Pd(MeCN)_4](BF_4)_2$ was prepared according to the literature method.[16] Nitromethane was dried over CaH_2 and vacuum-transferred. Methanol was treated with sodium methoxide and distilled.

b. General Methods. All catalyst solutions were prepared in a dry nitrogen-filled glovebox. Copolymerization of propylene and carbon monoxide was performed under nitrogen atmosphere due to the sensitivity of the catalysts to air. However, all reactions of styrene derivatives with carbon monoxide were set up in air. ^1H and ^{13}C NMR spectra were recorded on an AM300 FT-NMR spectrometer. A delay time of 2 s was used between pulses. This was deemed sufficient since the relative intensities of the ^{13}C NMR resonances of the ipso carbons of the styrene–CO copolymer did not change when the delay time was increased to 5 s. The chemical shifts were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency. Molecular weights and molecular weight distributions of polymers were measured on a Water Associates liquid/gel permeation chromatograph using Microstyragel columns and a differential refractometer. Methylene chloride was used as the solvent, and polystyrene standards were used to calibrate the instrument. Optical rotation measurements of chiral polymers were performed on a Perkin-Elmer 241 polarimeter using a sodium lamp. C, H analyses were performed by Galbraith Laboratories and were found to be satisfactory for all the polymers described.

c. Preparation of 2-Pyridinecarboxaldehydeimine Derivatives. 2-Pyridinecarboxaldehydeimines were prepared according to a modified literature procedure.[12] Typically, a solution containing a 1:1 (molar ratio) mixture of 2-pyridinecarboxaldehyde (or 6-methyl-2-pyridinecarboxaldehyde) and a primary amine in methanol was stirred at 60 °C for 8–12 h. At the end of the reaction, the product was isolated by vacuum distillation in >95% yield.

2-Pyridinecarboxaldehyde-*N*-*n*-butylamine: ^1H NMR ($CDCl_3$, ppm) 8.63 (1H, m), 8.38 (1H, s), 7.99 (1H, m), 7.70 (1H, m), 7.27 (1H, m), 3.67 (2H, t, J = 7.2 Hz), 1.71 (2H, quintet, J = 7.2 Hz), 1.40 (2H, sextet, J = 7.2 Hz), 0.95 (3H, t, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 161.26, 154.35, 149.00, 136.06, 124.16, 120.77, 60.85, 32.41, 20.05, 13.50; density (25 °C) 0.951 gm/mL.

2-Pyridinecarboxaldehyde-*N*-isobutylimine: ^1H NMR ($CDCl_3$, ppm) 8.64 (1H, m), 8.38 (1H, s), 8.01 (1H, m), 7.70 (1H, m), 7.27 (1H, m), 3.31 (1H, sextet, J = 6.4 Hz), 1.64 (2H, m), 1.27 (3H, d, J = 6.4 Hz), 0.86 (3H, t, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 159.35, 154.42, 148.97, 136.05, 124.11, 120.95, 67.66, 30.15, 21.79, 10.63; density (25 °C) 0.945 gm/mL.

2-Pyridinecarboxaldehyde-*N*-*tert*-butylimine: ^1H NMR ($CDCl_3$, ppm) 8.62 (1H, m), 8.38 (1H, s), 8.03 (1H, m), 7.68 (1H, m), 7.24 (1H, m), 1.32 (9H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 155.75, 154.99, 148.66, 135.83, 123.80, 120.34, 57.19, 29.05; density (25 °C) 0.937 gm/mL.

2-Pyridinecarboxaldehyde-*N*-α-methylbenzylimine: ^1H NMR ($CDCl_3$, ppm): 8.55 (1H, m), 8.47 (1H, s), 8.05 (1H, m), 7.56 (1H, m), 7.42 (2H, d, J = 7.2 Hz), 7.30 (2H, t, J = 7.2 Hz), 7.20 (1H, t, J = 7.2 Hz), 7.13 (1H, m), 4.59 (1H, q, J = 6.6 Hz), 1.58 (3H, d, J = 6.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 159.90, 154.17, 148.74, 144.06, 135.90, 127.98, 126.50, 126.19, 124.15, 120.85, 69.04, 24.16; density (25 °C) 1.07 gm/mL.

6-Methyl-2-pyridinecarboxaldehyde-*N*-*n*-butylimine: ^1H NMR ($CDCl_3$, ppm) 8.35 (1H, s), 7.80 (1H, d, J = 7.7 Hz), 7.58 (1H, t, J = 7.7 Hz), 7.12 (1H, d, J = 7.7 Hz), 3.66 (2H, t, J = 7.2 Hz), 2.57 (3H, s), 1.70 (2H, quintet, J = 7.2 Hz), 1.39 (2H, sextet, J = 7.2 Hz), 0.94 (3H, t, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 161.44, 157.47, 153.69, 136.11, 123.60, 117.68, 60.75, 32.30, 23.81, 19.93, 13.38; density (25 °C) 0.937 gm/mL.

d. Preparation of (*R*)-(−)-2-Pyridinecarboxaldehyde-*N*-α-methylbenzylimine and (*S*)-(+)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine. The optically pure (*R*)-(−)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine and (*S*)-(+)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine were synthesized following the same procedure described above using the corresponding chiral (*R*)-(+)-α-methylbenzylamine and (*S*)-(−)-α-methylbenzylamine. The NMR spectra of (*R*)-(−)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine and (*S*)-(+)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine were identical to those of the racemic mixture. The specific optical rotations were found to be −29° (20 °C, neat) for the *R*-enantiomer and +30° (20 °C, neat) for the *S*-enantiomer.

e. Copolymerization of Propylene and Carbon Monoxide. In a typical reaction, a solution containing 2.3×10^{-2} mmol of $[Pd(MeCN)_4](BF_4)_2$ and 2.3×10^{-2} mmol of (*S,S*)-(−)-BDPP in 3 mL of a 1:1 (v/v) CH_3NO_2/CH_3OH mixture was placed in a Parr bomb under nitrogen and charged with 35 g of propylene and 600 psi of CO. After stirring at 45 °C for 2 days, the resultant polymer solution was added to CH_2Cl_2 and run through a short stem silica gel column to remove the catalyst. An optically active P–CO copolymer (yield: 1.5 g; molar optical rotation: +20° (20 °C, CH_2Cl_2) was obtained after complete removal of the solvent. Following an analogous procedure and using (*R,R*)-(+)-BDPP, (*R*)-(+)-BINAP, (*S*)-(−)-BINAP, (*R,R*)-(−)-DIOP, and (*S,S*)-(+)-DIOP, P–CO copolymers with different optical activities were synthesized. The structures of the P–CO copolymers were determined by NMR spectroscopy and were found to be very similar to the P–CO copolymer prepared using $[Pd(Ph_2P(CH_2)_3PPh_2)(MeCN)_2](BF_4)_2$ as the catalyst except for the degree of regioselectivity and enantioselectivity. Properties of the chiral P–CO copolymers are given in Table 1.

f. Terpolymerization of Ethylene, Propylene, and Carbon Monoxide. A solution containing 2.3×10^{-2} mmol of $[Pd(MeCN)_4](BF_4)_2$ and 2.3×10^{-2} mmol of (*R,R*)-(+)-BDPP in 3 mL of a 1:1 (v/v) CH_3NO_2/CH_3OH mixture was placed in a Parr bomb under nitrogen and charged with 45 g of propylene and 400 psi of ethylene and 400 psi of CO. The reaction mixture was stirred at 70 °C for 23 h. At the end of this period, CH_2Cl_2 was added to dissolve the formed solid terpolymer. Addition of the solution to a CH_3OH/Et_2O/pentane mixture yielded 1.53 g of E–P–CO terpolymer as a precipitate. The terpolymer was washed with CH_3OH/Et_2O and Et_2O and dried in vacuo.

E–P–CO terpolymer: ^1H NMR ($CDCl_3$, ppm) 2.71 (s), 3.1–2.5 (br), 1.10 (d, J = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 211.86, 207.79, 45.46, 40.78, 35.93, 34.65, 16.58; M_n (GPC) = 1.6×10^4; polydispersity = 2.2.

The E–P–CO terpolymer contained 30% (molar ratio) of P–CO units based on the ^1H NMR spectrum. It was soluble in common organic solvents such as chloroform and methylene chloride. The molar optical rotation ($[\Phi]_D^{20}$) of the polymer was found to be −20° (CH_2Cl_2) assuming that only the P–CO units made a contribution to the optical activity of the terpolymer. The above reaction was repeated using (*S,S*)-(−)-BDPP instead of (*R,R*)-(+)-BDPP, the E–P–CO terpolymer thus prepared had a $[\Phi]_D^{20}$ of +19° (CH_2Cl_2).

g. Copolymerization of Styrene and Carbon Monoxide. To a catalyst solution containing 6.8×10^{-2} mmol of $[Pd(MeCN)_4](BF_4)_2$, 6.8×10^{-2} mmol of 2-pyridinecarboxaldehyde-*N*-*n*-butylimine, and 9.3×10^{-2} mmol of 1,4-benzoquinone in 6 mL of a 2:1 (v/v) CH_3NO_2/CH_3OH mixture was added 4.0 mL (35 mmol) of styrene. The resultant solution was placed in a Parr bomb and charged with 1000 psi of CO. After stirring at 60 °C for 40 h, the unreacted CO was released. The formed copolymer was isolated by addition of diethyl ether/pentane into the reaction mixture followed by filtration. The polymer product (0.5 g) was washed with methanol/Et_2O mixture and vacuum dried. The above reaction was repeated using 2-pyridinecarboxaldehyde-*N*-isobutylimine, (±)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine, (*R*)-(−)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine, and (*S*)-(+)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine as ligands. The styrene–CO copolymer was insoluble in common organic solvents, such as chloroform and methylene chloride when 2-pyridinecarboxaldehyde-*N*-*n*-butylimine was used as the ligand, partially soluble when 2-pyridinecarboxaldehyde-*N*-isobutylimine was used, and completely soluble when (±)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine was employed.

The NMR spectra of the copolymers formed were very similar to those of the syndiotactic S–CO copolymer reported in the literature except for the degree of tacticity.[10a,11] The quantitative results on the distribution of triads are summarized in Table 3. The S–CO copolymers formed using chiral (*R*)-(−)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine and (*S*)-(+)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine were further purified by reprecipitation in $CHCl_3/Et_2O$/pentane and were found to be optically active with molar optical rotation of +22° (20 °C, CH_2Cl_2, 13 mg/mL) and −21° (20 °C, CH_2Cl_2, 13 mg/mL), respectively.

No polymer was obtained when a bulky ligand such as 2-pyridinecarboxaldehyde-*N*-*tert*-butylimine or 6-methyl-2-pyridinecarboxaldehyde-*N*-*n*-butylimine was employed.

h. Copolymerization of 4-Methylstyrene and Carbon Monoxide Using 4,4′-Dimethyl-2,2′-bipyridine and 3,4,7,8-Tetramethyl-1,10-phenanthroline as Ligands. To a solution containing 6.8×10^{-2} mmol of $[Pd(MeCN)_4](BF_4)_2$, 6.8×10^{-2} mmol of 4,4′-dimethyl-2,2′-bipyridine, and 9.3×10^{-2} mmol of 1,4-benzoquinone in 6 mL of a 2:1 (v/v) CH_3NO_2/CH_3OH mixture was added 4.0 mL (35 mmol) of 4-methylstyrene. The mixture was placed in a 125-mL Parr bomb and charged with 1000 psi of CO. After stirring at 60 °C for 20 h, the precipitated polymer (2.1 g) was filtered, washed with acetone, and dried under vacuum. The above reaction was repeated using 3,4,7,8-tetramethyl-1,10-phenanthroline instead of 4,4′-dimethyl-2,2′-bipyridine. The resultant 4-methylstyrene–CO copolymers were soluble in chloroform and had identical structures based on NMR spectra as the alternating tactic 4-methylstyrene–CO copolymer synthesized previously using 1,10-phenanthroline as ligand except for the degree of tacticity.[10a]

Using 2-Pyridinecarboxaldehydeimine Derivatives as Ligands. The reactions were performed following a procedure analogous to the one employed for 4,4′-dimethyl-2,2′-bipyridine. The copolymerization reactions were run at 60 °C for 2 days, and the copolymers were obtained by the addition of Et_2O/pentane to the reaction mixture followed by filtration and washing with CH_3OH/Et_2O/pentane. Final yields as a function of the ligand used were as follows: 2-pyridinecarboxaldehyde-*N*-*n*-butylimine, 0.6 g; 2-pyridinecarboxaldehyde-*N*-isobutylimine, 0.3 g; (±)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine, 0.3 g. The 4-methylstyrene–CO copolymers were soluble in chloroform and methylene chloride and had identical structures based on NMR spectra as the alternating tactic 4-methylstyrene–CO copolymer formed using 1,10-phenanthroline as ligand except for the degree of tacticity.[10a] The copolymers prepared employing (*R*)-(−)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine and (*S*)-(+)-2-pyridinecarboxaldehyde-*N*-α-methylbenzylimine as ligands were optically active and exhibited corresponding molar optical rotations of +19° (20 °C, CH_2Cl_2, *c* 19 mg/mL) and −20° (20 °C, CH_2Cl_2, *c* 19 mg/mL).

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