

Palladium(II)-Catalyzed Isospecific Alternating Copolymerization of Aliphatic α -Olefins with Carbon Monoxide and Isospecific Alternating Isomerization Cooligomerization of a 1,2-Disubstituted Olefin with Carbon Monoxide. Synthesis of Novel, Optically Active, Isotactic 1,4- and 1,5-Polyketones

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Abstract: The compound [Pd(Me-DUPHOS)(MeCN)₂](BF₄)₂, **1** [Me-DUPHOS = 1,2-bis(2,5-dimethylphospholano)benzene], has been found to be an effective catalyst for the highly enantioselective, alternating copolymerization of aliphatic α -olefins with carbon monoxide to form optically active, isotactic polymers. The α -olefin–carbon monoxide copolymers, as synthesized in CH₃NO₂/CH₃OH, had a mixture of 1,4-ketone and spiroketal repeating units in the backbone. The interchange between 1,4-keto and spiroketal units was observed even in the absence of any added metal catalyst. The temperature dependence of the molar optical rotation of the isotactic pure poly(1,4-ketone)s indicated that the chirality of the copolymers was due to the presence of stereogenic tertiary carbons in the polymer backbone rather than due to polymer conformation. The degree of enantioselectivity in the formation of chiral, isotactic propylene–carbon monoxide copolymer was found to be >90% (as determined by NMR spectroscopy using a chiral NMR shift reagent). The isotactic α -olefin–carbon monoxide copolymers serve as excellent starting materials for the synthesis of other classes of chiral polymers. For example, the complete reduction of the propylene–carbon monoxide copolymer resulted in the formation of a novel, optically active poly(1,4-alcohol). Finally, **1** was also found to be a catalyst for the novel alternating isomerization cooligomerization of 2-butene with carbon monoxide to form optically active, isotactic poly(1,5-ketone).

Most synthetic chiral polymers are derived from chiral monomers.¹ Given the limited availability of 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.^{1,2}

We and others have reported on the palladium(II)-catalyzed alternating copolymerization of α -olefins with carbon monoxide to form poly(1,4-ketone)s³ (Figure 1). These α -olefin–carbon monoxide copolymers, unlike poly(α -olefin)s, have truly ste-

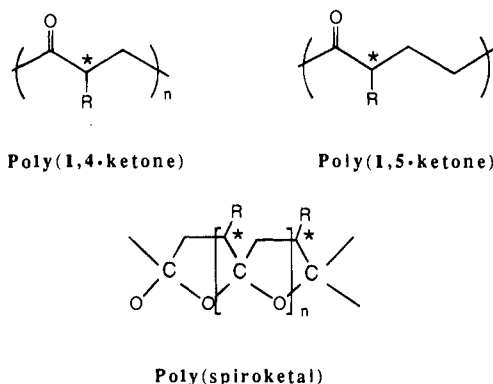


Figure 1. Three kinds of repeating units that are present in alternating olefin–carbon monoxide cooligomers/copolymers.

reogenic centers in the polymer backbone. Using the *R,S* convention, 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 2, 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. Furthermore, given the

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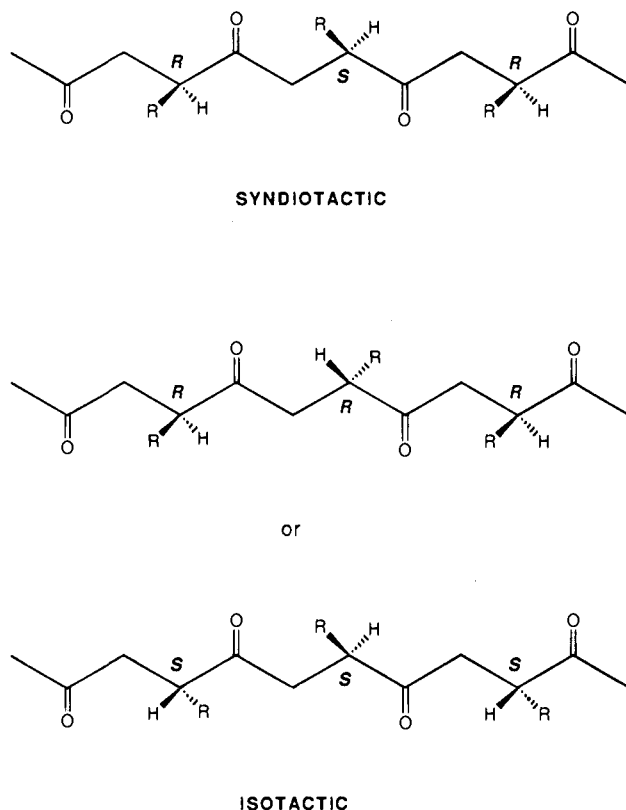


Figure 2. Syndiotactic and isotactic structures for the alternating copolymers of α -olefins with carbon monoxide.

ease with which the carbonyl group can be chemically modified, such polymers should be excellent starting materials for other classes of chiral polymers. Brookhart has recently reported the isospecific copolymerization of styrene with carbon monoxide using a chelating bisamine ligand-based catalyst system.^{3e} On the other hand, the optimal catalysts for the copolymerization of aliphatic α -olefins with carbon monoxide are based on chelating bisphosphines.^{3a-d,g-m} In the few instances the synthesis of chiral aliphatic α -olefin-carbon monoxide copolymers has been reported, the enantioselectivity has been either low or not determined (for example, the possible presence of heterochiral chains has not been eliminated).^{3b-di} In this paper, we describe for the first time the synthesis of optically active, isotactic aliphatic α -olefin-carbon monoxide copolymers with very high enantioselectivity (>90% by NMR spectroscopy).

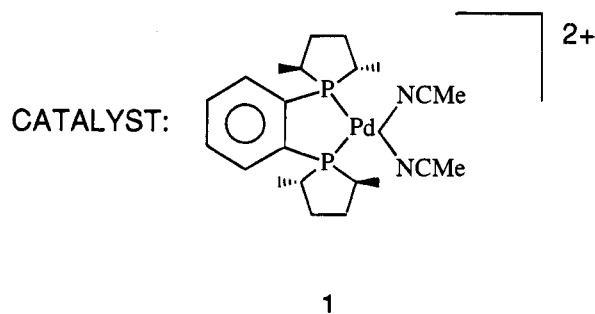
In a recent paper,⁴ Consiglio proposed an unusual chain growth mechanism involving cationic Pd-carbene species in order to account for the formation of polymers with spiroketal repeating units (Figure 1) under certain conditions.^{3g,4} This mechanism differs from the usually accepted two-step mechanism for chain growth involving the alternate insertions of carbon monoxide into Pd-alkyl bonds and olefin into Pd-acyl bonds.^{3a} In this paper we show that while spiroketal repeating units may be present in stereoregular alternating copolymers of α -olefins with carbon monoxide, the poly(1,4-ketone)-poly(spiroketal) interchange can occur *in the absence of a metal catalyst*, and therefore it is unnecessary to invoke a special chain growth mechanism for the formation of poly(spiroketal).

Finally, we report the unprecedented alternating isomerization cooligomerization of an acyclic *internal* olefin, such as 2-butene, with carbon monoxide. Very interestingly, the product was a poly(1,5-ketone) rather than the poly(1,4-ketone) that is invariably observed with α -olefins (Figure 1). Furthermore, the

cooligomer synthesized was isotactic and optically active. The synthesis of an atactic polymer with *both* 1,4- and 1,5-keto groups in the backbone starting from cyclopentene and carbon monoxide has been reported previously.⁵

Results and Discussion

Catalyst. The catalyst used for the alternating copolymerization of olefins with carbon monoxide was [Pd(Me-DUPHOS)-(MeCN)₂](BF₄)₂, **1**. It was usually prepared *in situ* by codissolving a 1:1 molar ratio of [Pd(MeCN)₄](BF₄)₂ and a Me-DUPHOS⁶ enantiomer in a nitromethane/methanol mixture. The compound **1** could be isolated from a nitromethane solution in high yield (96%). Its ³¹P{¹H}-NMR spectrum in CD₃NO₂ exhibited a single resonance at 83.66 ppm, and its elemental analysis was consistent with the structure shown. The copolymerization reactions using **1** were carried out at 30–70 °C.



Alternating Copolymerization of α -Olefins with Carbon Monoxide. Compound **1** catalyzed the alternating copolymerization of carbon monoxide with α -olefins, such as propylene, 1-butene, 1-heptene, and allylbenzene. The formed propylene-carbon monoxide (P-CO), 1-butene-carbon monoxide (B-CO), 1-heptene-carbon monoxide (H-CO), and allylbenzene-carbon monoxide⁷ (A-CO) copolymers were alternating, exclusively head-to-tail, and highly isotactic and had a mixture of 1,4-ketone and spiroketal structures (Figure 1) in the polymer backbone. The structures of the polymers were characterized mainly by IR and NMR spectroscopy and were supported by elemental analysis results (see next section for more details).

The solid state ¹³C-NMR spectra (Figure 3) of the P-CO and B-CO copolymers exhibited resonances at 114.3 and 113.8 ppm, respectively, due to the ketal carbons of the spiroketal repeating units in the polymer backbones. The weak resonances at 211.4 ppm for the P-CO copolymer and at 211.9 ppm for the B-CO copolymer indicated the presence of keto groups in both polymers in addition to the spiroketal repeating units. The IR spectra (KBr) of the P-CO and the B-CO copolymers showed strong C-O-C bands at 832 and 810 cm⁻¹, respectively. A moderate carbonyl absorbance at 1710 cm⁻¹ was also observed for both polymers. Similarly, the IR spectra of the H-CO and A-CO copolymers exhibited corresponding moderate absorptions at 1709 and 1706 cm⁻¹ and very strong bands at 825 and 816 cm⁻¹, respectively, due to the keto and spiroketal structures present in the polymer backbone. A CDCl₃ solution of the H-CO copolymer showed ¹³C{¹H}-NMR resonances at 212.86, 45.27, 44.70, 31.84, 31.35, 26.58, 22.43, and 14.01 ppm due to the -CH(*n*-C₅H₁₁)CH₂CO- units and absorbances at 113.61, 44.12, 40.75, 32.48, 29.00, 28.20, 22.65, and 14.10 ppm

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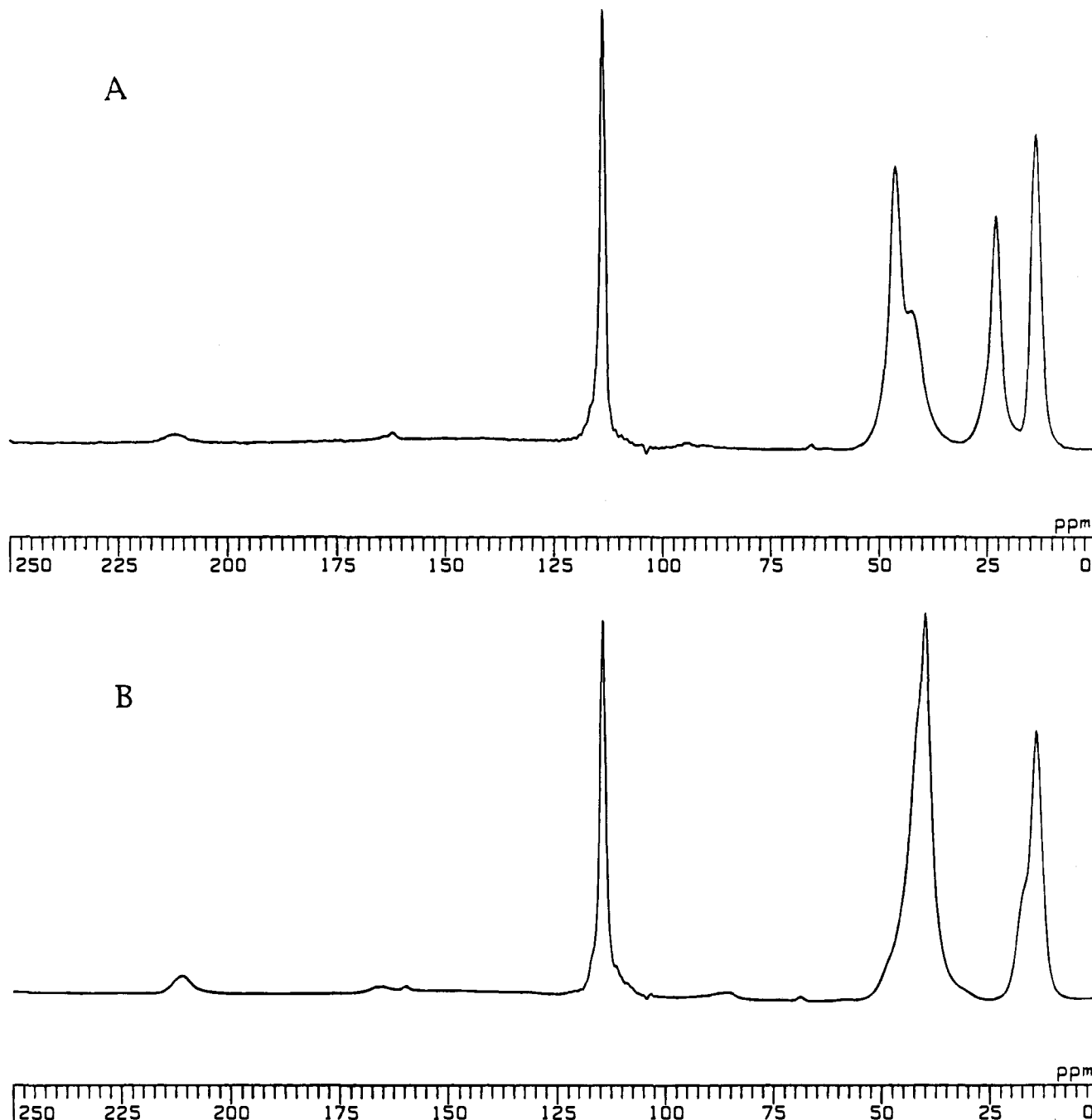


Figure 3. Solid state ^{13}C -NMR spectra of (A) isotactic alternating 1-butene-CO copolymer and (B) isotactic alternating propylene-CO copolymer, both showing the predominance of spiroketal units in the backbone.

due to the spiroketal repeating units in the polymer. The solid state ^{13}C -NMR spectrum of the A-CO copolymer exhibited resonance absorptions at 210.86 (weak) and 113.78 (strong) ppm attributable to the keto and spiroketal units in the main chain of the polymer.

As previously reported, α -olefin-CO copolymers with spiroketal units can be converted to pure poly(1,4-ketone)s upon treatment with acidic solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol.^{3g,4} Thus, P-CO, B-CO, H-CO, and A-CO copolymers with only 1,4-keto groups were obtained after reprecipitation from the polymer solutions in either $(\text{CF}_3)_2\text{CHOH}$ or a $(\text{CF}_3)_2\text{CHOH}/\text{CHCl}_3$ mixture into methanol. Unlike the poly(spiroketal/1,4-ketone) copolymers, the resultant polymers had no C-O-C IR absorptions in the $810\text{--}830\text{ cm}^{-1}$ range while the carbonyl stretching band at $\sim 1710\text{ cm}^{-1}$ was dramatically intensified. Additionally, no spiroketal ^{13}C -NMR resonances were detected at $\sim 113\text{ ppm}$.

Interchange between 1,4-Ketone and Spiroketal Repeating Units in the Isotactic, Alternating α -Olefin-CO Copolymers.

Under certain conditions, we have observed the facile interchange between 1,4-ketone and spiroketal repeating units in the α -olefin-CO copolymers *even in the absence of any added metal catalyst*. For instance, the B-CO copolymer as formed contained mainly spiroketal units. Dissolution of the copolymer in CDCl_3 caused its complete conversion to poly(1,4-ketone), and its $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum exhibited a carbonyl resonance at 212.7 ppm but no ketal absorbance at $\sim 113\text{ ppm}$ (Figure 4). The polymer solution was then concentrated, and the polymer was precipitated out by the addition of methanol. The resultant precipitate was then washed with methanol and dried under vacuum at ambient temperature. The solid state ^{13}C -NMR spectrum of this material showed a resonance at 113.78 ppm, clearly indicating the reisoimerization of 1,4-keto groups to

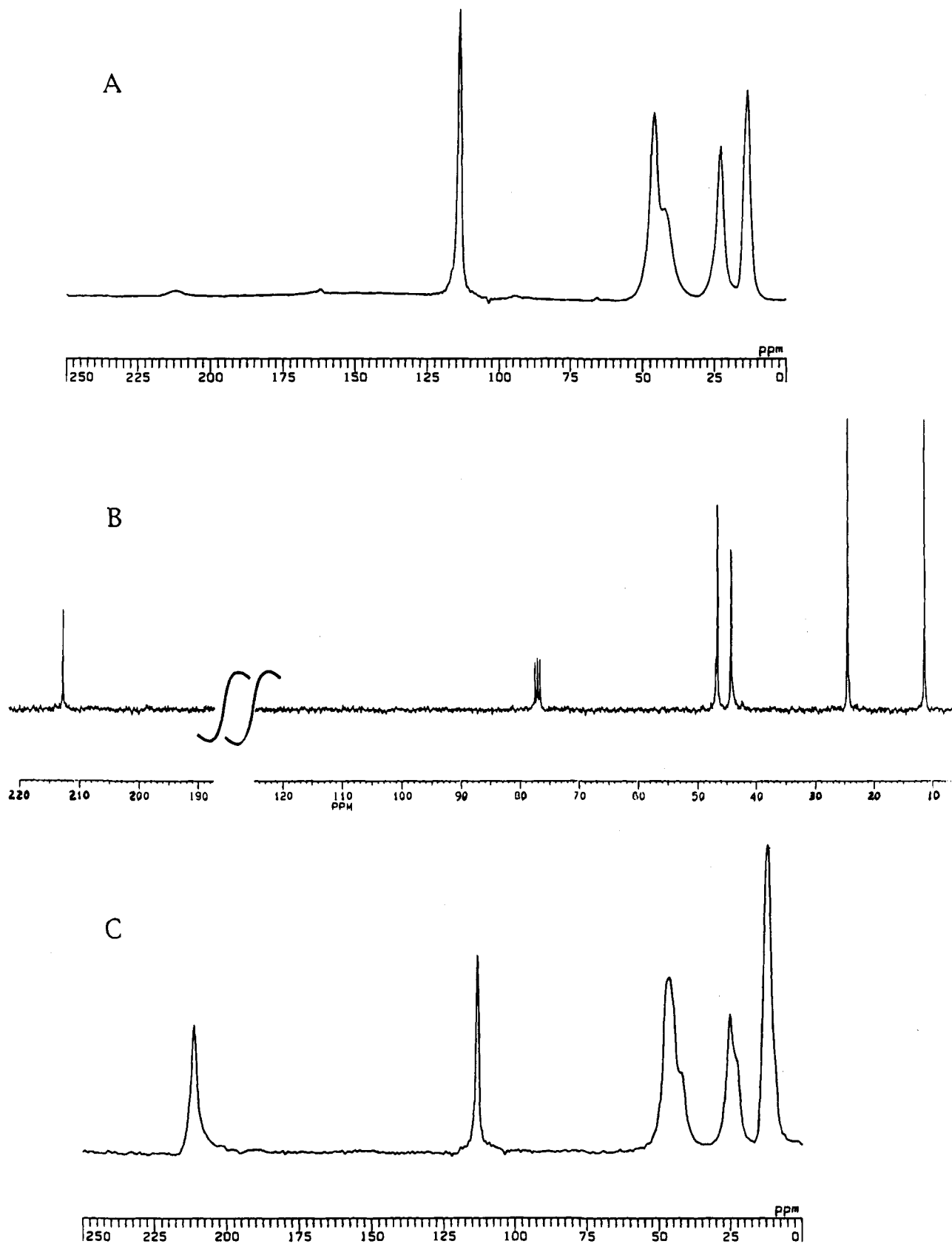


Figure 4. Interchange between the backbone 1,4-keto and the spiroketal units in the isotactic alternating 1-butene-CO copolymer: (A) solid state ^{13}C -NMR spectrum of the polymer as synthesized; (B) $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the polymer in CDCl_3 ; (C) solid state ^{13}C -NMR spectrum of the polymer reprecipitated from CDCl_3 by the addition of CH_3OH .

spiroketal units. In another experiment, a sample of solid H-CO copolymer which was mainly poly(1,4-ketone) containing a small amount of spiroketal units was monitored periodically by running a $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of a portion of it in

CDCl_3 . Over a period of 11 d at ambient temperature, the percentage of spiroketal units in the copolymer sample was found to increase significantly (Figure 5). It should be noted that, unlike the B-CO copolymer, the H-CO poly(spiroketal/

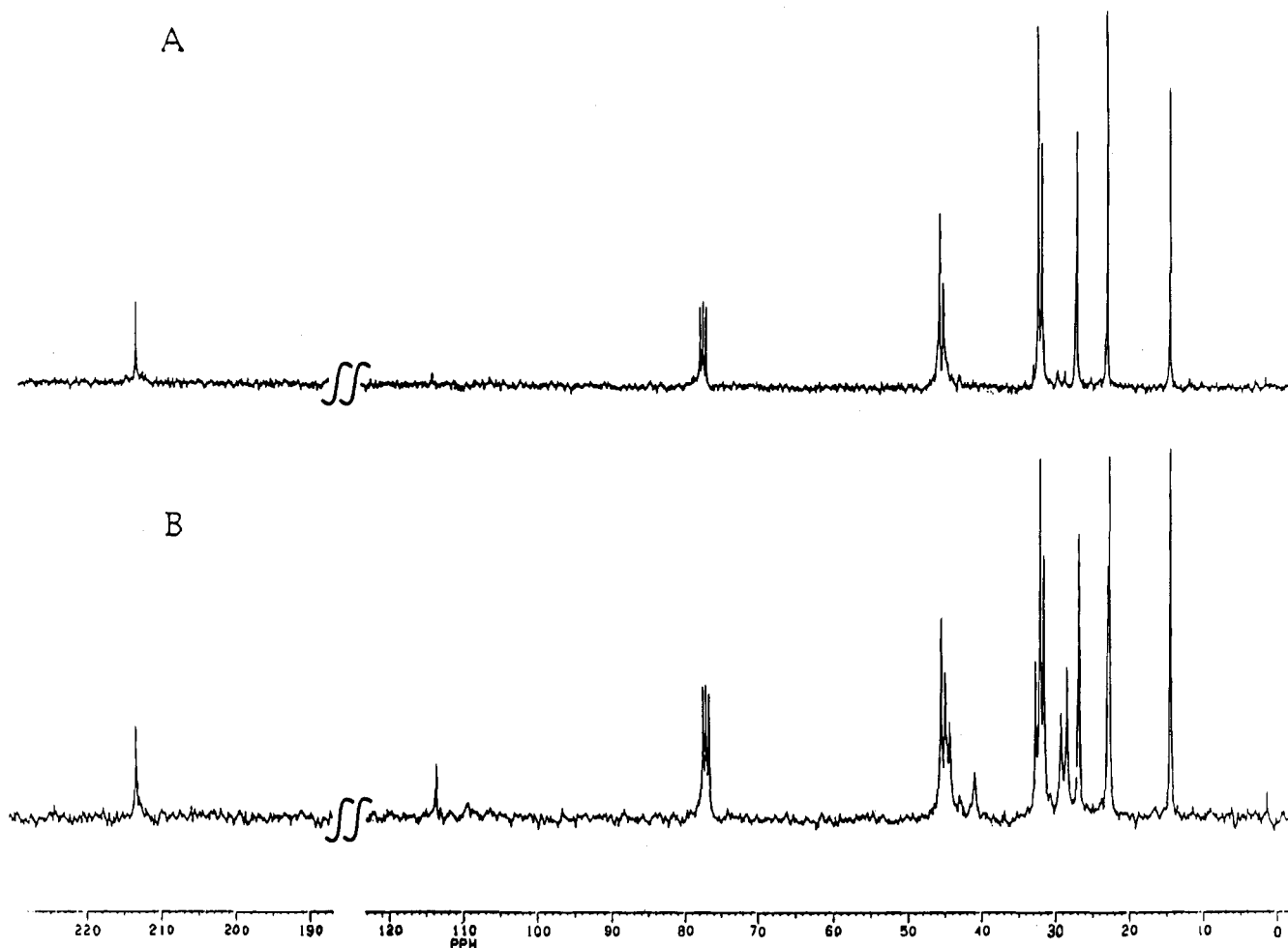


Figure 5. Isomerization of the backbone 1,4-keto to the spiroketal units in the isotactic alternating 1-heptene-CO copolymer: (A) $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) spectrum of the starting polymer; (B) $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) spectrum of the polymer after standing as a solid at ambient temperature for 11 d.

1,4-ketone) copolymer was stable in CDCl_3 and the ratio of spiroketal versus keto units did not change significantly over 7 d in solution as monitored by ^{13}C -NMR spectroscopy. Furthermore, the pure A-CO poly(1,4-ketone) copolymer, formed by precipitation from a $(\text{CF}_3)_2\text{CHOH}/\text{CHCl}_3$ mixture, was found to *reisomerize* in pure chloroform solution to the poly(spiroketal) structure. At high concentrations, the isomerization reaction caused eventual precipitation of a polymer with predominantly spiroketal repeating units due to the lower solubility of this material. The solid state $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the precipitated poly(spiroketal/1,4-ketone) showed resonances at 210.86 (weak), 141.44, 128.91 (br), 113.78 (strong), 46.97, 41.25, and 36.01 ppm, and the polymer was essentially identical to the A-CO poly(spiroketal/1,4-ketone) copolymer initially synthesized in a $\text{CH}_3\text{NO}_2/\text{CH}_3\text{OH}$ mixture. At a lower concentration (4 mg/mL), the keto/spiroketal isomerization proceeded homogeneously and no precipitate was observed. Thus, the rate of the isomerization could also be followed by periodic measurement of the molar optical rotation of the polymer in solution. Figure 6 shows the change in molar optical rotation versus time starting with pure A-CO poly(1,4-ketone) copolymer in chloroform solution at ambient temperature. The value decreased from $+165^\circ$ to $+9^\circ$ in 36 d. The initial very slow isomerization appears to indicate that the formation of first spiroketal repeating units from the 1,4-keto structure was the rate-determining step in the reaction.

In general, it appears that in the alternating α -olefin-CO copolymers the spiroketal structure was more stable in the solid

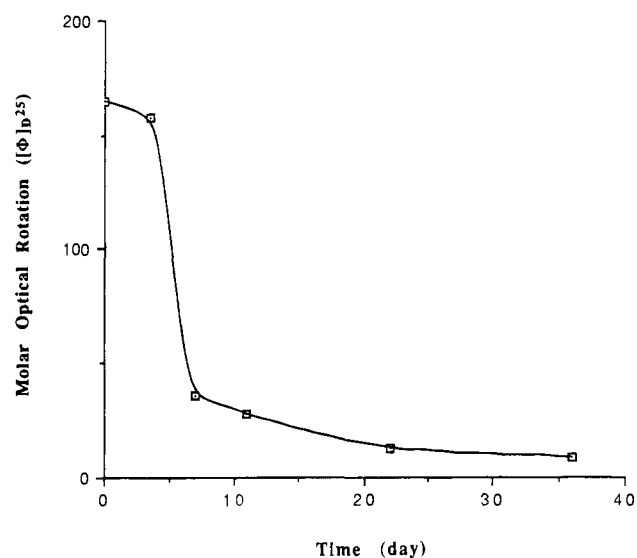
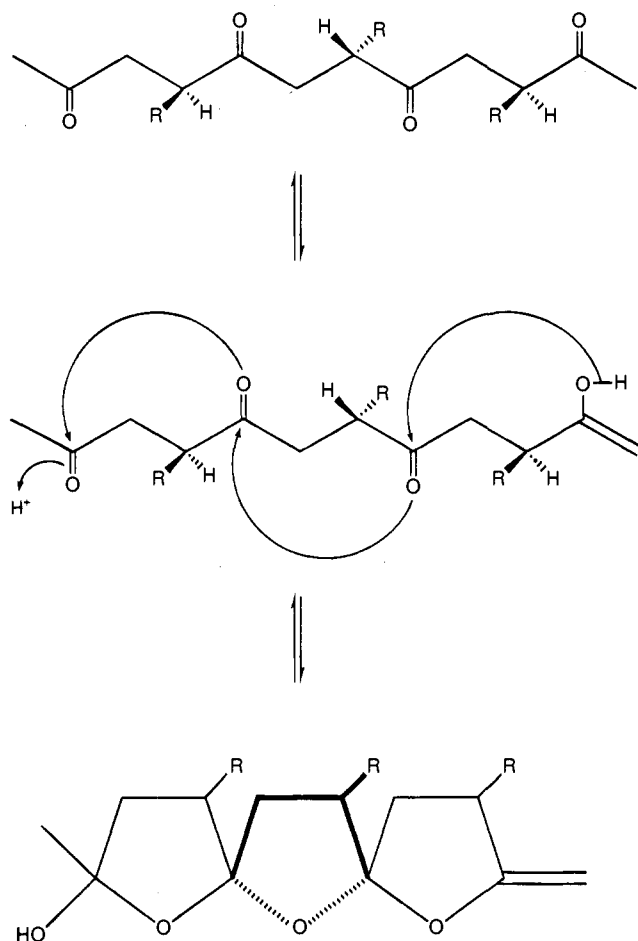


Figure 6. Change in molar optical rotation ($[\Phi]_{\text{D}}^{25}$) versus time for the isotactic allylbenzene-CO poly(1,4-ketone) copolymer in chloroform solution ($c = 4.09$ mg/mL) at ambient temperature.

state than in solution. Furthermore, the stability of the spiroketal structure in organic solvents like chloroform increased dramatically with an increase in the size of the alkyl substituent. Thus, the spiroketal structure was only detected in the solid state for the P-CO and B-CO copolymers but was observed and found to be stable in both the solid state and in chloroform solution

Scheme 1. A Possible Mechanism for the Interchange between the Backbone 1,4-Keto and the Spiroketal Units in the Isotactic Alternating α -Olefin-CO Copolymers



for the H-CO and A-CO copolymers. Indeed, for the last copolymer, the spiroketal structure was thermodynamically favored over the 1,4-ketone structure in solution. *It should be noted that the polymer samples used for the 1,4-ketone/spiroketal interchange studies were virtually free of any catalyst residues.* For example, elemental analysis revealed that the A-CO copolymer had 0.031% Pd.

Scheme 1 depicts one possible mechanism for the interchange between 1,4-ketone and spiroketal repeating units in an α -olefin-CO copolymer. It appears that a more regio/stereoregular disposition of the carbonyl groups favors the tandem cyclization to the spiroketal structure since this repeating unit has only been observed for α -olefin-CO copolymers with high regio- and stereoregularity.^{3b,4}

Finally, the α -olefin-CO copolymers with spiroketal repeating units show very different physical properties and chemical reactivities compared to the corresponding pure poly(1,4-ketone)s. For instance, the B-CO and H-CO poly(spiroketal/1,4-ketone) copolymers were insoluble in acetone while the pure poly(1,4-ketone) isomers were completely soluble. The P-CO copolymer containing mostly spiroketal units was insoluble in most common organic solvents, such as chloroform and methylene chloride, and was completely inert toward strong reducing agents such as LiAlH_4 . The material was recovered unchanged after a suspension of the copolymer in dry tetrahydrofuran (THF) containing excess LiAlH_4 was stirred at 70 °C for 3 d. In contrast, the pure P-CO poly(1,4-ketone) was soluble in chloroform and methylene chloride, and complete reduction of the carbonyl groups by LiAlH_4 occurred in THF in less than 12 h at 63 °C.⁸

Tacticity in Poly(1,4-ketone)s Formed from α -Olefins and Carbon Monoxide. As described above, α -olefin-CO copolymers with spiroketal units can be converted to pure poly(1,4-ketone)s upon treatment with acidic solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol. The pure poly(1,4-ketone)s thus formed showed a single carbonyl absorption at 214–218 ppm in the ^{13}C -NMR ($(\text{CF}_3)_2\text{CHOH}/\text{CDCl}_3$) spectra due to an exclusive head-to-tail structure (Figure 7).^{3b-d,k,4,9} Single dominant resonances for the CH_2 (~43–45 ppm) and CH (~41–48 ppm) groups in the polymer backbone support the presence of high stereoregularity in the polymers (Figure 7).

The high tacticity of the polymers was also supported by their ^1H -NMR spectra which exhibited proton couplings among the adjacent CH and CH_2 groups in the polymer backbone; only broad absorptions were observed for the corresponding atactic α -olefin-CO copolymers. For example, a solution of the P-CO copolymer in $(\text{CF}_3)_2\text{CHOH}$ showed ^1H -NMR resonances at 3.19–3.11 (2H, m), 2.80 (1H, d, $J = 15.2$ Hz), and 1.20 (3H, d, $J = 6.5$ Hz) ppm. While the resonance at 1.20 ppm was clearly due to the methyl group in the repeating unit, $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}-$, the coupling constants indicated that the H atom absorbing at 2.80 ppm was not coupled with the CH_3 group and, therefore, was not the methine CH group in the polymer backbone. Indeed, ^1H -NMR homodecoupling experiments showed that the H atom at 2.80 ppm was one of the CH_2 hydrogens and that the CH hydrogen resonated at 3.11–3.19 ppm, overlapping with the absorption of the second H atom of the CH_2 group. Thus, no change was observed for the absorption at 2.80 ppm upon irradiation of the methyl group at 1.20 ppm. On the other hand, both the resonances at 2.80 and 1.20 ppm turned into singlets when the absorbances at 3.11–3.19 ppm were irradiated. Note that the two H atoms of the CH_2 group are diastereotopic and therefore nonequivalent. The ^1H -coupled ^{13}C -NMR spectrum of the polymer exhibited absorptions at 217.49 (s), 44.31 (t, $J = 127$ Hz), 40.93 (d, $J = 130$ Hz), and 15.17 (q, $J = 127$ Hz) ppm due to the $\text{C}=\text{O}$, CH_2 , CH , and CH_3 groups of the $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}-$ units in the copolymer. The above NMR parameters are in accord with those reported recently by Consiglio.^{3c,d}

Similarly, the B-CO poly(1,4-ketone) copolymer showed ^1H -NMR (CDCl_3) absorbances at 2.98 (1H, dd, $J = 17.6, 10.3$ Hz), 2.88 (1H, m, br), 2.66 (1H, d, $J = 17.6$ Hz), 1.57 (1H, m), 1.36 (1H, m), and 0.86 (3H, t, $J = 7.3$ Hz) ppm. The resonances at 2.98 and 2.66 ppm were attributable to the two diastereotopic methylene protons adjacent to the carbonyl in the polymer main chain, and the resonance at 2.88 ppm was due to the backbone methine protons. It should be noted that the coupling constants between the two backbone methylene protons and the adjacent methine proton were substantially different, with one being fairly large (10.3 Hz) and the other being too small to be detected. The absorptions at 1.57 and 1.37 ppm were clearly due to the other CH_2 group next to the methyl which resonated at 0.86 ppm. The ^1H -coupled ^{13}C -NMR {2:1 (v/v) $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$ } spectrum of the polymer exhibited absorbances at 216.79 (s), 47.40 (d, $J = 132$ Hz), 43.79 (t, $J = 127$ Hz), 24.44

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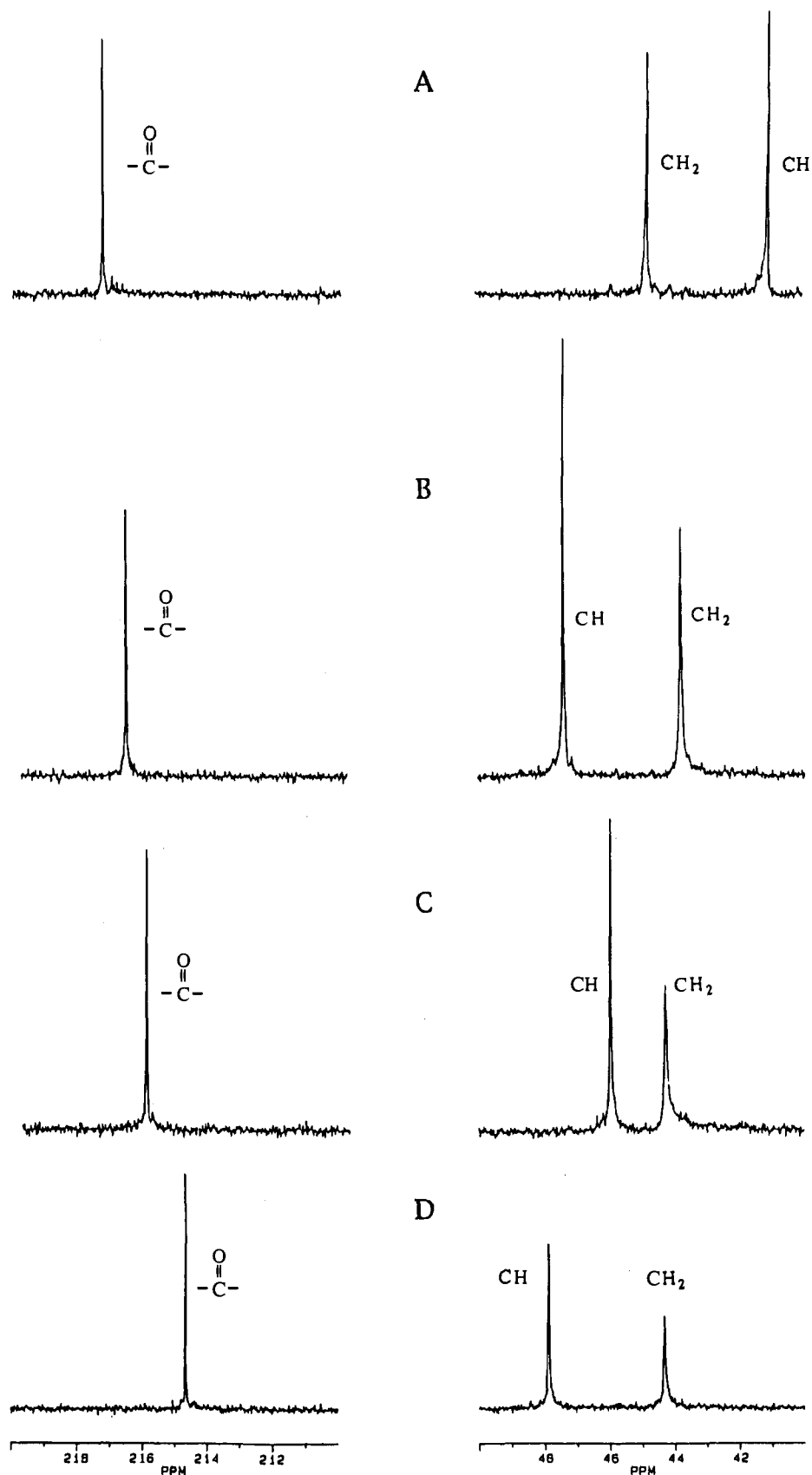


Figure 7. $^{13}\text{C}\{^1\text{H}\}$ -NMR ($\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$) resonances for the backbone carbonyl, methylene, and methine groups of the isotactic poly(1,4-ketone) copolymers: (A) propylene-CO; (B) 1-butene-CO; (C) 1-heptene-CO; (D) allylbenzene-CO.

(t, $J = 129$ Hz), and 10.58 (q, $J = 126$ Hz) due to the C=O, CH, CH₂ (next to the carbonyl), CH₂ (next to the methyl), and CH₃ groups of the $-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CO}-$ repeating units of the polymer.

The ^1H -NMR (CDCl_3) spectrum of the H-CO poly(1,4-ketone) copolymer showed resonances at 2.92 (2H, m, br), 2.68 (1H, d, $J = 16.5$ Hz), 1.49 (1H, br), 1.25 (7H, br), and 0.88 (3H, t, br) ppm due to, respectively, the two overlapping protons

Table 1. Molecular Weights and Molar Optical Rotations of Chiral, Isotactic, Alternating α -Olefin-CO Pure Poly(1,4-ketone)s^a

isotactic α -olefin-CO copolymer	ligand, Me-DUPHOS	molecular weight (M_p) ^b (M_w/M_n)	$[\Phi]^{25}_D$, (CHCl ₃) (c, mg/mL)	$[\Phi]^{25}_D$ ((CF ₃) ₂ CHOH) (c, mg/mL)
propylene-CO	(-)-(R,R)	3.6×10^4 (2.4)	+49° (3.22)	-21° (18.1)
	(+)-(S,S)			+22° (18.1)
1-butene-CO	(-)-(R,R)	3.8×10^4 (2.8)	+65° (3.26)	-7° (7.27)
	(+)-(S,S)			+7° (7.27)
1-heptene-CO	(-)-(R,R)	8.7×10^3 (2.2)	+90° (3.20)	-91° (3.20)
	(+)-(S,S)			+165° (4.09)
allylbenzene-CO	(-)-(R,R)	7.1×10^3 (2.0)	+165° (4.09)	

^a The pure α -olefin-CO poly(1,4-ketone)s were prepared by reprecipitation of the poly(spiroketal/1,4-ketone) copolymers in either (CF₃)₂CHOH/CH₃OH or (CF₃)₂CHOH-CHCl₃/CH₃OH. ^b Molecular weights and molecular weight distributions were measured by GPC relative to polystyrene standards.

from both the backbone CH₂ and CH groups, the other diastereotopic proton of the backbone CH₂, the one diastereotopic proton of the side chain CH₂ adjacent to the methine group, the rest of the methylene protons in the side chain, and the CH₃ protons in the -CH₂CH((CH₂)₄CH₃)CO- repeating units of the polymer. The ¹H-coupled ¹³C-NMR {2:1 (v/v) CDCl₃/(CF₃)₂CHOH} spectrum exhibited absorptions at 216.22 (s), 45.93 (d, *J* = 131 Hz), 44.25 (t, *J* = 128 Hz), 31.77 (t, *J* = 127 Hz), 31.29 (t, *J* = 127 Hz), 26.68 (t, *J* = 126 Hz), 22.36 (t, *J* = 125 Hz), and 13.62 (q, *J* = 124 Hz) due to, respectively, the C=O, CH, and CH₂ groups in the backbone, the four methylene units in the side chain, and CH₃ groups.

The solution NMR spectra of pure A-CO poly(1,4-ketone) copolymer were obtained using a mixture of CDCl₃/(CF₃)₂CHOH as the solvent due to the keto/spiroketal structural isomerization of the polymer in pure CDCl₃. The use of 1,1,1,3,3,3-hexafluoro-2-propanol completely inhibited the isomerization reaction and therefore enabled us to closely examine the degree of regio- and stereoregularity of the polymer. The solution of pure A-CO poly(1,4-ketone) copolymer, (-CH₂-CH(CH₂Ph)CO-)_n, in a 1:1 (v/v) (CF₃)₂CHOH/CDCl₃ mixture showed ¹H-NMR absorbances at 7.14 (3H, m), and 6.95 (2H, d, *J* = 7.0 Hz) ppm due to the phenyl groups, resonances at 2.99 (1H, m), 2.66 (1H, dd, *J* = 13.8, 6.2 Hz), and 2.33 (1H, dd, *J* = 13.8, 7.9 Hz) ppm due to the backbone CH and CH₂ groups, and an absorption at 2.51 (2H, m) due to the benzylic protons. The ¹H-coupled ¹³C-NMR spectrum of the polymer exhibited resonances at 214.65 (s), 47.87 (d, *J* = 132 Hz), and 44.31 (t, *J* = 127 Hz) ppm due to the C=O, and backbone CH and CH₂ groups, resonances at 138.10 (s), 129.10 (d, *J* = 160 Hz), 128.95 (d, *J* = 160 Hz), and 127.11 (d, *J* = 167 Hz) ppm attributable to the phenyl groups, and absorption at 37.22 (t, *J* = 130 Hz) due to the benzylic carbons.

The high tacticity of the polymers also led to high crystallinity and reduced solubility in organic solvents. For example, the tactic P-CO poly(1,4-ketone) was found to be insoluble in THF although its atactic analog was soluble.

Optical Activity of the Chiral, Isotactic, Alternating α -Olefin-CO Copolymers. The P-CO, B-CO, H-CO, and A-CO copolymers synthesized appear to be isotactic since optically active materials were obtained when enantiomerically pure **1** was used as the catalyst. Note that syndiotactic α -olefin-CO copolymers should only exhibit vanishingly small optical activity (Figure 2). The molecular weights and molar optical rotations (the latter measured in both CHCl₃ and (CF₃)₂CHOH) of the optically active, isotactic poly(1,4-ketone)s are given in Table 1. The values of molar optical rotation ($[\Phi]_D$) of the chiral copolymers were significantly affected by the solvent used, and even the sign of $[\Phi]_D$ for the P-CO and B-CO copolymers changed upon a change of solvent. Furthermore, the molar optical rotation of the P-CO copolymer in (CF₃)₂CHOH was dependent on the concentration, with $[\Phi]_D$

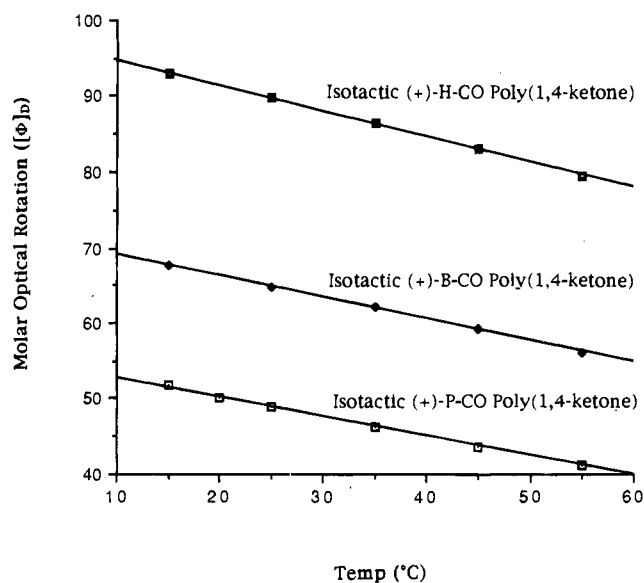


Figure 8. Dependence of molar optical rotation ($[\Phi]_D$) on temperature in CHCl₃ for the isotactic alternating 1-heptene-CO (H-CO), 1-butene-CO (B-CO), and propylene-CO (P-CO) pure poly(1,4-ketone)s.

increasing from 16° to 22° when the solution concentration was increased from 1.78 to 18.1 mg/mL. The reason for the dramatic solvent effect on optical rotation remains unclear. The possibility¹⁰ that the presence of strong hydrogen bonds between the carbonyl oxygens in the polymer backbone and the (CF₃)₂CHOH may disrupt certain polymer conformational states that may otherwise contribute to the molar rotation in a less interacting solvent such as CHCl₃ appears unlikely. For example, a similar effect was also observed for the optically active, atactic, alternating P-CO copolymer possessing a mixture of head-to-head, head-to-tail, and tail-to-tail arrangements in the polymer backbone. It was shown earlier that the optical rotation exhibited by the latter polymer in CHCl₃ was primarily due to the presence of stereogenic tertiary carbon centers in the polymer backbone and not due to restricted conformational states^{3b} (also see below).

The molar optical rotations summarized in Table 1 and Figure 8 are the values for pure poly(1,4-ketone)s, and the presence of spiroketal units in the polymers will change the numbers. For example, both H-CO and A-CO copolymer samples containing spiroketal units were found to have lower $[\Phi]_D$ values compared to the corresponding pure poly(1,4-ketone) isomers (cf. Figure 6). In CHCl₃, the molar optical rotation of the poly(1,4-ketone)s showed only a slight temperature dependence (Figure 8) as was observed for the chiral, atactic P-CO and

(10) (a) Overberger, C. G.; Kaye, H. *J. Am. Chem. Soc.* **1967**, *89*, 5649. (b) Pino, P.; Ciardelli, F.; Zandomeneghi, M. *Annu. Rev. Phys. Chem.* **1970**, *21*, 561.

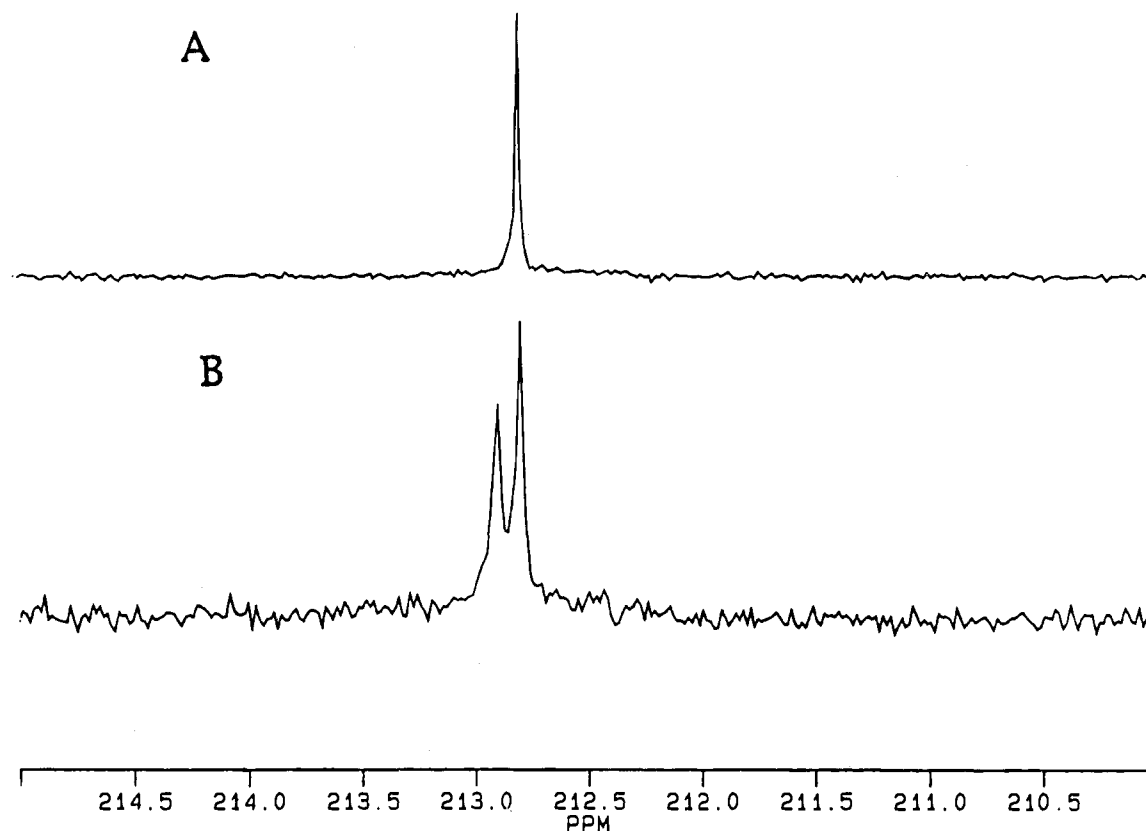


Figure 9. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) resonances of the carbonyl group of P-CO poly(1,4-ketone) in the presence of tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) (molar ratio of the Eu(III) reagent versus the P-CO repeating units, 1:5): (A) optically active, propylene-CO poly(1,4-ketone) sample [$[\Phi]_D^{25} = +49^\circ$ ($c = 3.22 \text{ mg/mL}$, CHCl_3)]; (B) racemic propylene-CO poly(1,4-ketone) sample.

styrene-CO copolymers.^{3b} The $\Delta[\Phi]_D/\Delta T$ values were $-0.26^\circ/\text{C}$ for the P-CO copolymer, $-0.29^\circ/\text{C}$ for the B-CO copolymer, and $-0.34^\circ/\text{C}$ for the H-CO copolymer. These values are comparable to those for model small molecules such as (*S*)-(+)-2-methylbutyric acid ($-0.07^\circ/\text{C}$) and (*S*)-(+)-2-phenylbutyric acid ($-0.41^\circ/\text{C}$). On the other hand, polymers whose chirality arises from restricted conformational states (e.g., helicity) tend to exhibit a fairly large decrease in optical rotation with increasing temperature since more random conformational states become accessible at higher temperatures.¹¹ It is, therefore, reasonable to conclude that the optical rotations of the isotactic P-CO, B-CO, and H-CO copolymers that we have synthesized are due to the presence of stereogenic tertiary carbon centers in the polymer backbone with only a minimal contribution from polymer conformation.

Degree of Enantioselectivity (% ee) in the Isospecific Alternating Copolymerization of α -Olefins with Carbon Monoxide. The determination of % ee in enantioselective polymerization reactions constitutes a very difficult problem.^{1a} The most direct procedure for the analysis of enantiomeric purity of the repeating units in a chiral polymer is to degrade the polymer down to the repeating units and then determine the ratio of the *R* and *S* isomers present. Such a procedure is hard to carry out as it requires very efficient degradation of the polymer backbone, as well as the protection of the stereogenic centers in the polymer from being racemized during the degradation process. Thus, we employed an optically active NMR shift reagent to resolve the two enantiomeric repeating units and to determine the degree of enantioselectivity (ee =

[number of *R* repeating units - number of *S* repeating units]/total number of repeating units) in the isotactic α -olefin-CO poly(1,4-ketone)s.¹² In the presence of tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III), the $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) spectrum of the optically active, isotactic P-CO poly(1,4-ketone), prepared using (-)-(*R,R*)-Me-DUPHOS as the ligand, exhibited only dominant singlets. However, all four singlets turned into "doublets" when the corresponding racemic P-CO poly(1,4-ketone) was employed. This is illustrated in Figure 9 for the carbonyl resonance which, as expected, showed the largest separation between the two peaks. *It is very clear from the above study that the degree of enantioselectivity in the optically active, isotactic P-CO copolymer was >90% (the % ee may actually be much higher, but the resolution in our NMR spectra does not allow us to make that claim) and the possible presence of heterochiral chains (i.e., chains with ...RRRRRRRRSSSSS...) can be excluded.*

The high degree of isotacticity and enantioselectivity in the optically active, isotactic poly(1,4-ketone)s was further supported by the structures of the poly(1,4-alcohol)s derivatized from the polyketones. For example, the isotactic P-CO polyketone copolymer was completely hydrogenated by LiAlH_4 in dry THF to the polyalcohol ($-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{OH})-$)_{*n*}. The resultant polymer showed two strong bands at 3405 and 1017 cm^{-1} in its IR spectrum due to O-H and C-O stretches. The absence of any absorption at $\sim 1710 \text{ cm}^{-1}$ clearly indicated that the carbonyl groups of the P-CO copolymer were quantitatively reduced to the alcohol functionality. The ^1H -NMR spectrum of the polyalcohol exhibited absorbances at 4.87 (1H, s), 3.58–3.68 (1H, br), 1.62–1.75 (2H, br), 1.15–1.35 (1H, m, br), and 0.94 (3H, m) due to OH, CH (adjacent to OH), CH_2 , CH

(11) For specific examples, see: (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (b) Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 8850. (c) Green, M. M.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452. (d) Reference 10b.

(12) Review on use of chiral NMR shift reagents: Sullivan, G. R. *Top. Stereochem.* **1978**, *10*, 287.

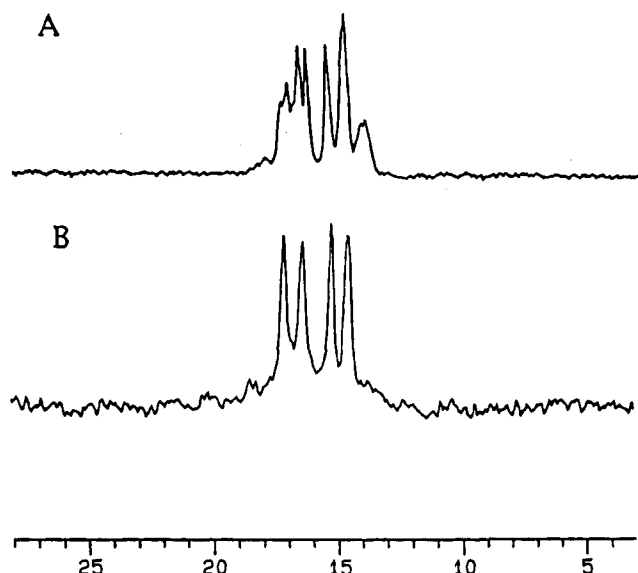
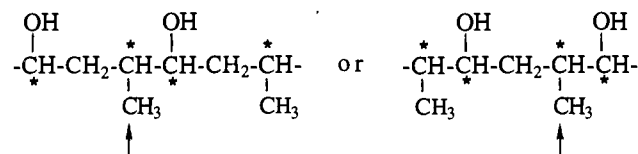


Figure 10. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (CD_3OD) of the methyl group of (A) the achiral polyalcohol $(-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{OH})-)_n$ prepared by the reduction of the atactic, exclusively head-to-tail, alternating propylene-CO poly(1,4-ketone) and (B) the chiral polyalcohol prepared by the reduction of the optically active, isotactic, alternating propylene-CO poly(1,4-ketone).

(adjacent to CH_3), and CH_3 groups, respectively. The $^{13}\text{C}\{^1\text{H}\}$ -NMR absorptions of the polymer due to the CH (adjacent to OH), CH (adjacent to CH_3) and CH_2 , and CH_3 groups were observed at 72.18–75.15 (m), 36.82–39.36 (m), and 17.13, 16.37, 15.20, and 14.53 ppm. It seems that the ^{13}C -NMR chemical shift of the methyl group (arrow labeled) was sensitive to the configuration of the stereogenic tertiary carbon attached to it and the configurations of the three adjacent stereogenic tertiary carbons bearing hydroxyl or methyl groups (see below).

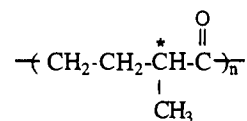


The four nearly equally intense methyl resonances at 17.13, 16.37, 15.20, and 14.53 ppm (Figure 10) can be explained by assuming (a) that virtually all the asymmetric tertiary carbons attached to methyl groups had the same configuration as a result of very high enantioselectivity in the formation of the parent isotactic P-CO poly(1,4-ketone) (see above) and the complete retention of their configuration during reduction and (b) that the two asymmetric tertiary carbons bearing hydroxyl groups adopted random configurations (either *R* or *S*) as a result of a nonenantioselective attack on the carbonyl groups of the P-CO copolymer by LiAlH_4 . The retention of configuration of the tertiary carbons attached to the methyl groups was indicated by the optical activity of the polyalcohol. For example, the poly(1,4-alcohol) synthesized from the isotactic P-CO poly(1,4-ketone) ($[\Phi]^{25}_{\text{D}} = +49^\circ$, CHCl_3) had a molar optical rotation $[\Phi]^{25}_{\text{D}} = +12.8^\circ$ in CH_3OH .

The above assumption was further supported by the observation of eight ^{13}C -NMR resonances (at 17.07, 16.78, 16.31, 16.00, 15.18, 14.42, 13.79, and 13.64 ppm) for the methyl group in the repeating units of the poly(1,4-alcohol) prepared by the reduction of an atactic, achiral, exclusively head-to-tail, alternating P-CO poly(1,4-ketone) (Figure 10). Eight corresponds to eight pairs of tetraads ($R_1R_2R_3R_4/S_1S_2S_3S_4$, $R_1R_2R_3S_4/S_1S_2S_3R_4$,

$R_1R_2S_3R_4/S_1S_2R_3S_4$, $R_1S_2R_3R_4/S_1R_2S_3S_4$, $S_1R_2R_3R_4/R_1S_2S_3S_4$, $R_1R_2S_3S_4/S_1S_2R_3R_4$, $R_1S_2S_3R_4/S_1R_2R_3S_4$, and $R_1S_2R_3S_4/S_1R_2S_3R_4$) for four different stereogenic tertiary carbons, with each randomly adopting either the *R* or the *S* configuration.

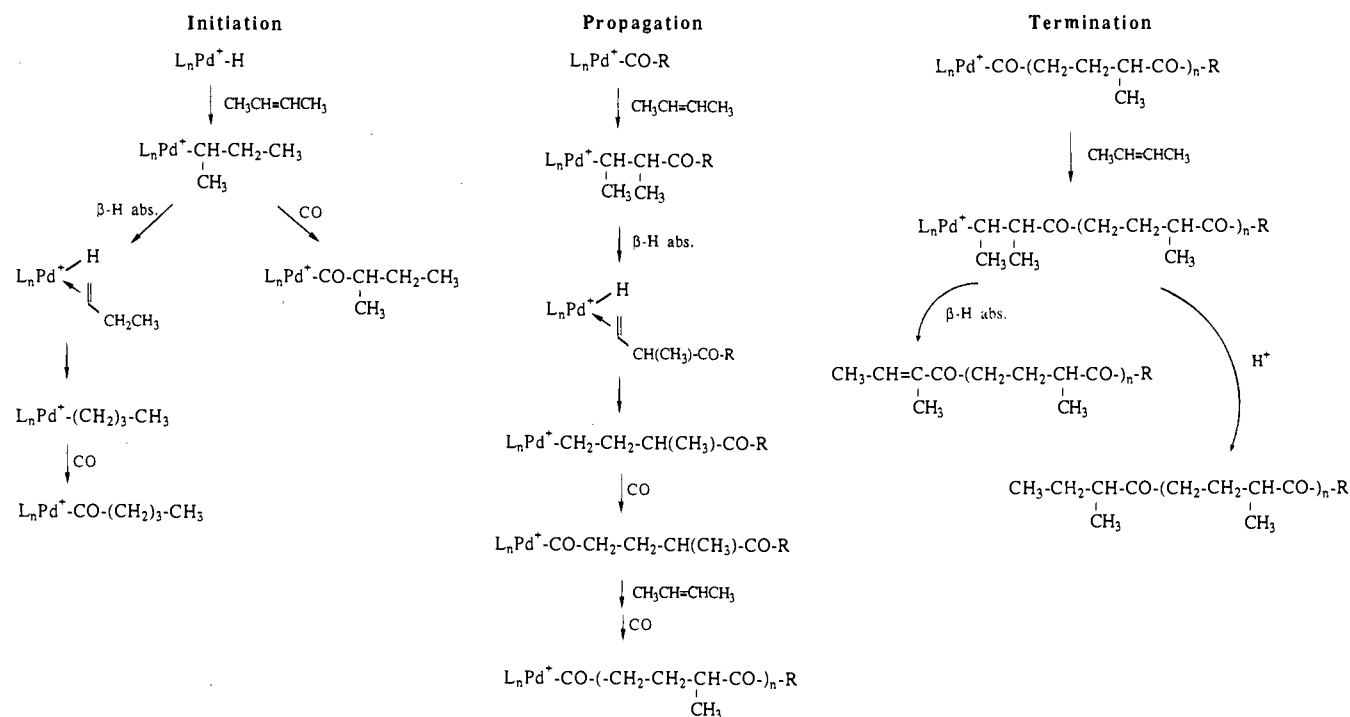
Isospecific Alternating Isomerization Cooligomerization of an Acyclic 1,2-Disubstituted Olefin with Carbon Monoxide. *cis*-2-Butene was allowed to cooligomerize with CO in the presence of 1 with (–)-(*R,R*)-Me-DUPHOS ligand as the catalyst. The structure of the resultant alternating cooligomer was characterized by IR and NMR spectroscopies and is shown below.



The IR spectrum of the oligomer exhibited a strong band at 1705 cm^{-1} due to the carbonyl groups in the polymer chain. Single dominant resonances at 213.73, 45.63, 38.57, 26.91, and 16.75 ppm in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum indicated both the presence of an exclusively head-to-tail arrangement and the presence of high stereoregularity in the oligomer backbone. The proton-coupled ^{13}C -NMR spectrum of the cooligomer showed absorptions at 213.73 (s), 45.63 (d, $J = 129\text{ Hz}$), 38.57 (t, $J = 125\text{ Hz}$), 26.91 (t, $J = 130\text{ Hz}$), and 16.75 (q, $J = 127\text{ Hz}$) ppm clearly due to the C=O, CH, CH_2 (adjacent to carbonyl), CH_2 (adjacent to CH), and CH_3 groups, respectively. The ^1H -NMR resonances of the cooligomer at 2.58 (1H, m), 2.48 (2H, t, br), and 1.05 (3H, d, $J = 6.7\text{ Hz}$) ppm were due to the corresponding CH, CH_2 (adjacent to carbonyl), and CH_3 groups, and those at 1.86 (1H, m) and 1.56 (1H, m) ppm were attributable to the two diastereotopic protons of the CH_2 groups adjacent to the CH groups. The cooligomer appears to be isotactic and was found to be optically active with molar optical rotation $[\Phi]^{25}_{\text{D}} = -22.2^\circ$ (2-propanol, $c = 13\text{ mg/mL}$). Epimerization of the poly(1,5-ketone) with sodium 2-chlorophenolate in 2-chlorophenol at 100°C for 48 h caused substantial broadening of its ^1H -NMR absorbances, and the $^{13}\text{C}\{^1\text{H}\}$ -NMR resonances of the oligomer turned into multiplets at the corresponding frequencies.

Three end groups ($-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, and $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CHCH}_3$) were identified by NMR spectroscopy. The ^1H -NMR spectrum of the oligomer showed small absorbances at 1.30 (sextet, $J = 7.3\text{ Hz}$) and 0.90 (t, $J = 7.3\text{ Hz}$) ppm due to the ethyl end of $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and resonances at 6.82 (q, $J = 6.8\text{ Hz}$) and 1.73 (s) ppm due to CH and CH_3 (adjacent to carbonyl) groups of the $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CHCH}_3$ terminus. The absorption due to the methyl (adjacent to CH_2) of the $-\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ end group overlapped with the CH_3 of the $-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ terminus. The presence of the $-\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CHCH}_3$ end group was also indicated in the ^1H -coupled ^{13}C -NMR spectrum by small resonances at 201.36 (s), 138.44 (s), and 138.15 (d, $J = 158\text{ Hz}$) ppm due to the carbonyl and the two vinylic carbons. The ten sp^3 carbons of the three terminal groups resonated at 41.13, 34.83, 28.33, 26.32, 24.25, 22.86, 14.94, 14.23, 11.85, and 11.15 ppm. The molecular weight of the oligomer was calculated on the basis of the ^1H -NMR spectrum to be $M_n = 600$ (number of repeating units 7).

The novel poly(1,5-ketone) structure formed in the alternating cooligomerization of *cis*-2-butene with carbon monoxide was presumably due to metal migration from secondary alkyl to the adjacent methyl group after the insertion of the *cis*-2-butene monomer into a Pd-acyl intermediate (Scheme 2). As shown in Scheme 2, the isomerization can occur by a β -H abstraction

Scheme 2. Proposed Mechanism for the Alternating Isomerization Cooligomerization of 2-Butene with CO

step followed by reinsertion of the resultant olefin in the opposite sense. The isomerization from a branched alkyl to a linear alkyl complex has been observed previously,¹³ and the reduction of steric interaction between the bulky phosphine ligand and the alkyl group on the metal would be the driving force.^{13b}

The cooligomerization reaction appears to be initiated by a Pd-H species, the formation of which in methanol has been described previously.^{3a} Initiation by Pd-OCH₃ species is ruled out since no terminal methoxy group was detected by NMR spectroscopy. The -C(O)CH₂CH₂CH₂CH₃ end group was formed through the insertion of *cis*-2-butene into a Pd-H species followed by metal migration and CO insertion. The formation of the -C(O)CH(CH₃)CH₂CH₃ terminus may result either from the insertion of 2-butene into a Pd-H bond followed by CO insertion or from the proton cleavage of a Pd-CH(CH₃)-CH(CH₃)-COR intermediate. However, the -C(O)C(CH₃)=CHCH₃ terminus can only arise through β -H abstraction from a Pd-CH(CH₃)CH(CH₃)COR intermediate. Scheme 2 summarizes the initiation, propagation, and termination steps for the alternating isomerization cooligomerization of 2-butene with carbon monoxide.

Finally, it should be pointed out that control experiments showed that compound **1** in CD₃NO₂ at 70 °C was able to catalyze the isomerization of *cis*-2-butene to the unreactive *trans*-2-butene but not to 1-butene. This was the reason for the absence of any 1,4-keto repeating units in the cooligomer that were derived from the reaction of 1-butene formed in situ.

Conclusion

The compound [Pd(Me-DUPHOS)(MeCN)₂](BF₄)₂, **1**, has been found to be an effective catalyst for the highly enantioselective, alternating copolymerization of α -olefins with carbon monoxide to form optically active, isotactic polymers. The α -olefin-CO copolymers, as synthesized in CH₃NO₂/CH₃OH,

(13) (a) Brief review: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 99. (b) Specific examples involving Pd(II)-phosphine complexes: Brumbaugh, J. S.; Sen, A. *J. Am. Chem. Soc.* **1988**, *110*, 803.

had a mixture of 1,4-ketone and spiroketal repeating units in the backbone. The interchange between 1,4-keto and spiroketal units was observed even in the absence of any added metal catalyst.

The temperature dependence of the molar optical rotation of the isotactic poly(1,4-ketone)s indicated that the chirality of the copolymers was due to the presence of stereogenic tertiary carbons in the polymer backbone rather than due to polymer conformation. The degree of enantioselectivity in the formation of chiral, isotactic P-CO copolymer was found to be >90%. The isotactic α -olefin-CO copolymers can serve as excellent starting materials for the synthesis of other classes of chiral polymers. For example, the complete reduction of the P-CO copolymer resulted in the formation of a novel, optically active poly(1,4-alcohol), (-CH₂CH(CH₃)CH(OH)-)_n.

Finally, **1** was also found to be a catalyst for the novel alternating isomerization cooligomerization of 2-butene with carbon monoxide to form optically active, isotactic poly(1,5-ketone). This unprecedented observation opens up the possibility of using γ -, δ -, ... olefins in the alternating isomerization cooligomerization/copolymerization reaction to form poly(1,6-, 1,7-, ... ketone)s as shown in Scheme 3.

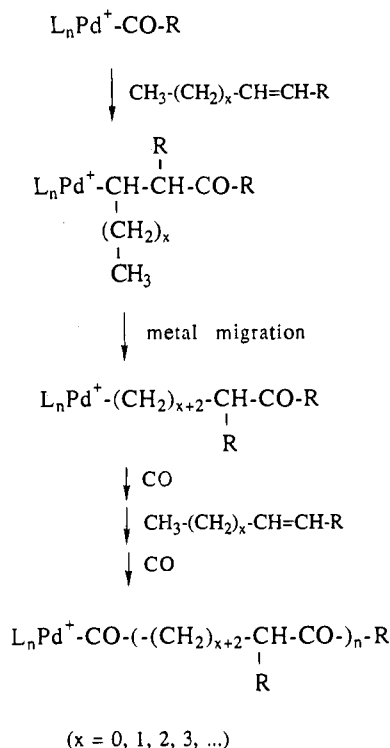
Experimental Section

Materials. C.P. grade chemicals were used as received unless otherwise stated. (-)-1,2-Bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene ((*R,R*)-Me-DUPHOS),⁶ (+)-1,2-bis((2*S*,5*S*)-2,5-dimethylphospholano)benzene ((*S,S*)-Me-DUPHOS),⁶ and 1,2-bis(dicyclohexylphosphino)ethane were purchased from Strem Chemicals. (*S*)-(+)-2-Methylbutyric acid, (*S*)-(+)-2-phenylbutyric acid, tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III), and LiAlH₄ (1 M solution in THF) were obtained from Aldrich. [Pd(MeCN)₄](BF₄)₂ was prepared according to the literature method.¹⁴ Nitromethane, THF, 1-heptene, and allylbenzene were dried over CaH₂ and either vacuum-transferred or vacuum-distilled. Methanol was treated with sodium methoxide and distilled.

General Methods. All catalyst solutions were prepared in a dry nitrogen-filled glovebox. The copolymerization of olefins with carbon

(14) Thomas, R. R.; Sen, A. *Inorg. Synth.* **1989**, *26*, 128; **1990**, *28*, 63.

Scheme 3. Alternating Isomerization Cooligomerization/
Copolymerization of β -, γ -, δ -, ... Olefins with CO To Yield
Poly(1,5-, 1,6-, 1,7-, ... Ketone)s



monoxide was performed under nitrogen atmosphere due to the sensitivity of the catalyst to air. 1H -, ^{13}C -, and ^{31}P -NMR spectra were recorded on a Bruker AM300 FT-NMR spectrometer. The chemical shifts of 1H - and ^{13}C -NMR resonances were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency, and those of ^{31}P -NMR resonances were referenced to external phosphoric acid. Solid state ^{13}C -NMR spectra and IR spectra were recorded on a Chemagnetics CMX300 FT-NMR spectrometer and a Perkin-Elmer 1600 FT-IR spectrophotometer, respectively. Molecular weights of polymers were measured on a Water Associates liquid/gel permeation chromatograph using a Microstyrigel column 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. Elemental analysis of the catalyst **1** and the polymers was carried out by Galbraith Laboratories, Inc.

Isolation and Structural Characterization of the Catalyst [Pd-(Me-DUPHOS)(MeCN)₂](BF₄)₂, **1.** A 1:1 molar ratio mixture of [Pd-(MeCN)₄](BF₄)₂ (100 mg, 0.225 mmol) and (*R,R*)-Me-DUPHOS (69.0 mg, 0.225 mmol) was codissolved in 5 mL of dry nitromethane, and the resultant solution was allowed to stir at ambient temperature under nitrogen for 3 h. A solid precipitate was obtained after the solution was concentrated under vacuum followed by addition of diethyl ether. The palladium(II) complex (144 mg) was washed with Et₂O and dried under vacuum. $^{31}P\{^1H\}$ -NMR (CD₃NO₂) (ppm): 83.66 (s). Anal. Calcd for PdC₂₂H₃₄N₂P₂B₂F₈: C, 39.5; H, 5.1. Found: C, 39.4; H, 5.4.

Preparation of Optically Active, Isotactic, Alternating Propylene-Carbon Monoxide Copolymer. A solution containing 4.5×10^{-2} mmol of [Pd(MeCN)₄](BF₄)₂ and 4.5×10^{-2} mmol of (*R,R*)-Me-DUPHOS in 9 mL of a 2:1 (v/v) CH₃NO₂/CH₃OH mixture was placed in a Parr bomb under nitrogen and charged with 30 g of propylene and 1500 psi of CO. The reaction mixture was stirred at 50 °C for 23 h. The resultant white solid (7.0 g) was washed with methanol and dried under vacuum. The formed polymer was found to have a mixture of 1,4-ketone and spiroketal repeating units in the polymer backbone. Reprecipitation of the poly(spiroketal/1,4-ketone) in (CF₃)₂CHOH/CH₃-OH changed its structure to pure poly(1,4-ketone).

P-CO Poly(spiroketal/1,4-ketone) Copolymer. Solid state $^{13}C\{^1H\}$ -NMR (ppm): 211.4, 114.3, 41.8, 39.7 (br), 17.2, 14.1 (br). IR

(KBr) (cm⁻¹): 1710, 832 (C-O-C). Anal. Calcd for C₃H₆-CO: C, 68.6; H, 8.6. Found: C, 68.0; H, 8.6.

P-CO Pure Poly(1,4-ketone) Copolymer. Solid state $^{13}C\{^1H\}$ -NMR (ppm): 211.4, 44.4, 41.2, 16.7. IR (KBr): 1708 cm⁻¹. 1H -NMR ((CF₃)₂CHOH) (ppm): 3.11-3.19 (2H, m), 2.80 (1H, d, *J* = 15.2 Hz), 1.20 (3H, d, *J* = 6.5 Hz). 1H -NMR (CDCl₃) (ppm): 2.92-3.09 (2H, m), 2.53 (1H, d, *J* = 17.3 Hz), 1.04 (3H, d, *J* = 6.5 Hz). $^{13}C\{^1H\}$ -NMR (CDCl₃) (ppm): 212.42, 44.74, 40.04, 16.41. $^{13}C\{^1H\}$ -NMR {2:1 (v/v) CDCl₃/(CF₃)₂CHOH} (ppm): 217.27, 44.79, 41.08, 15.88. ^{13}C -NMR ((CF₃)₂CHOH) (ppm): 217.49 (s), 44.31 (t, *J* = 127 Hz), 40.93 (d, *J* = 130 Hz), 15.17 (q, *J* = 127 Hz). Molar optical rotation: $[\Phi]^{25}_D = +49.0^\circ$ (*c* = 3.22 mg/mL, CHCl₃), $[\Phi]^{25}_D = -21^\circ$ (*c* = 18.1 mg/mL, (CF₃)₂CHOH). Molecular weight: 3.6×10^4 versus polystyrene standards, *M_w/M_n* = 2.4. The above copolymerization reaction was repeated using (*S,S*)-Me-DUPHOS as the ligand instead of the (*R,R*)-enantiomer. The resultant polymer was identical to the one formed with (*R,R*)-Me-DUPHOS as the ligand, except for the molar optical rotation (see Table 1).

Preparation of Atactic, Alternating Propylene-Carbon Monoxide Copolymer with Exclusively Head-to-Tail Arrangement in the Polymer Backbone. A catalyst solution containing 0.112 mmol of [Pd(MeCN)₄](BF₄)₂ and 0.112 mmol of 1,2-bis(dicyclohexylphosphino)ethane in 3 mL of a 2:1 (v/v) CH₃NO₂/CH₃OH mixture was placed in a Parr bomb under nitrogen and charged with 40 g of propylene and 1300 psi of CO. The reaction mixture was stirred at 40 °C for 3 days. The polymer (2.0 gm) formed was reprecipitated in CH₂Cl₂/CH₃OH, washed with methanol, and vacuum-dried.

Atactic, Head-to-Tail, Alternating P-CO Copolymer. 1H -NMR (CDCl₃) (ppm): 2.98 (2H, br), 2.53 (1H, br), 1.06 (3H, br). $^{13}C\{^1H\}$ -NMR (CDCl₃) (ppm): 211.79, 44.20, 40.70, 16.45. Molecular weight: 7200 versus polystyrene standards, *M_w/M_n* = 2.9.

Preparation of Optically Active, Isotactic, Alternating 1-Butene-Carbon Monoxide Copolymer. The reaction was performed following a procedure analogous to the one employed for propylene. 1-Butene (22 g) was used instead of propylene. The reaction was run at 34 °C for 20 h. The formed white solid (7.1 g) was washed with CH₃OH and dried in vacuo. The B-CO copolymer was found to have a mixture of 1,4-ketone and spiroketal units in the solid state and changed to pure poly(1,4-ketone) upon dissolution in CHCl₃ or after reprecipitation in (CF₃)₂CHOH/CH₃OH.

B-CO Poly(spiroketal/1,4-ketone) Copolymer. Solid state $^{13}C\{^1H\}$ -NMR (ppm): 211.90, 113.78, 45.93, 42.28, 22.96, 13.57. IR (KBr) (cm⁻¹): 1710, 810 (vs, C-O-C). Anal. Calcd for C₄H₈-CO: C, 71.4; H, 9.5. Found: C, 71.0; H, 9.7.

The B-CO Polyketone Copolymer. 1H -NMR (CDCl₃) (ppm): 2.98 (1H, dd, *J* = 17.6, 10.3 Hz), 2.88 (1H, m, br), 2.66 (1H, d, *J* = 17.6 Hz), 1.57 (1H, m), 1.36 (1H, m), 0.86 (3H, t, *J* = 7.3 Hz). $^{13}C\{^1H\}$ -NMR (CDCl₃) (ppm): 212.73, 46.57, 44.26, 24.46, 11.35. ^{13}C -NMR {2:1 (v/v) CDCl₃/(CF₃)₂CHOH} (ppm): 216.79 (s), 47.40 (d, *J* = 132 Hz), 43.79 (t, *J* = 127 Hz), 24.44 (t, *J* = 129 Hz), 10.58 (q, *J* = 126 Hz). IR (KBr) (cm⁻¹): 1707. Molecular weight: 3.8×10^4 versus polystyrene standards, *M_w/M_n* = 2.8. The molar optical rotations of the B-CO copolymers prepared using (*S,S*)-Me-DUPHOS and (*R,R*)-Me-DUPHOS ligands are listed in Table 1.

Preparation of Optically Active, Isotactic, Alternating 1-Heptene-Carbon Monoxide Copolymer. The reaction was carried out following a procedure analogous to the one employed for propylene. 1-Heptene (8 mL) was used instead of propylene. The reaction was run at 50 °C for 23 h under 1000 psi of CO. The resultant copolymer (4.5 g) was washed with CH₃OH and dried in vacuo. The formed H-CO copolymer was found to contain a mixture of 1,4-keto and spiroketal units in the polymer backbone. Reprecipitation of the polymer in CHCl₃-(CF₃)₂CHOH/CH₃OH changed its structures to pure poly(1,4-ketone).

H-CO Poly(spiroketal/1,4-ketone) Copolymer. $^{13}C\{^1H\}$ -NMR (CDCl₃) (ppm): 212.86, 113.61, 45.27, 44.70, 44.12, 40.75, 32.48, 31.84, 31.35, 29.00, 28.20, 26.58, 22.65, 22.43, 14.10, 14.01. IR (KBr) (cm⁻¹): 1709, 825 (C-O-C). Anal. Calcd for C₇H₁₄-CO: C, 76.1; H, 11.2. Found: C, 75.5; H, 11.1.

H-CO Poly(1,4-ketone) Copolymer. 1H -NMR (CDCl₃) (ppm): 2.92 (2H, m, br), 2.68 (1H, d, *J* = 16.5 Hz), 1.49 (1H, br), 1.25 (7H, br), 0.88 (3H, t, br). $^{13}C\{^1H\}$ -NMR (CDCl₃) (ppm): 212.86, 45.26,

44.75, 31.84, 31.36, 26.56, 22.41, 13.99. ^{13}C -NMR {2:1 (v/v) $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$ } (ppm): 216.22 (s), 45.93 (d, $J = 131$ Hz), 44.25 (t, $J = 128$ Hz), 31.77 (t, $J = 127$ Hz), 31.29 (t, $J = 127$ Hz), 26.68 (t, $J = 126$ Hz), 22.36 (t, $J = 125$ Hz), 13.62 (q, $J = 124$ Hz). IR (KBr) (cm^{-1}): 1708 cm^{-1} . Molecular weight: 8700 versus polystyrene standards, $M_w/M_n = 2.2$. The molar optical rotations of the H-CO copolymers formed using (*S,S*)-Me-DUPHOS and (*R,R*)-Me-DUPHOS ligands are listed in Table 1.

Preparation of Optically Active, Isotactic, Alternating Allylbenzene-Carbon Monoxide Copolymer. The reaction was performed following a procedure analogous to the one employed for propylene. Allylbenzene (8.9 gm) was used instead of propylene. The reaction was run at 50 °C for 20 h using 800 psi of CO. The formed white solid (8.3 g) was washed with acetone and dried in vacuo. The resultant allylbenzene-CO copolymer was found to have a mixture of 1,4-keto and spiroketal units in the polymer backbone. The polymer was converted to pure poly(1,4-ketone) by dissolution of the polymer in a $(\text{CF}_3)_2\text{CHOH}/\text{CHCl}_3$ mixture and reprecipitation of the concentrated polymer solution into CH_3OH . Note that the spiroketal to keto structural isomerization may take as long as 4 d.

A-CO Poly(spiroketal/1,4-ketone) Copolymer. Solid state ^{13}C - $\{^1\text{H}\}$ -NMR (ppm): 210.86, 140.92, 128.91 (br), 113.78, 47.49, 41.75, 36.01. IR (KBr) (cm^{-1}): 1706, 816 (C-O-C). Anal. Calcd for $\text{C}_9\text{H}_{10}\text{-CO}$: C, 82.2; H, 6.8. Found: C, 82.1; H, 6.9, Pd, 0.031.

A-CO Pure Poly(1,4-ketone) Copolymer. ^1H -NMR {1:1 (v/v) $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$ } (ppm): 7.14 (3H, m), 6.95 (2H, d, $J = 7.0$ Hz), 2.99 (1H, m), 2.66 (1H, dd, $J = 13.8, 6.2$ Hz), 2.51 (2H, m), 2.33 (1H, dd, $J = 13.8, 7.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) (ppm): 211.22, 138.45, 128.91, 128.49, 126.49, 47.24, 44.33, 37.16. ^{13}C -NMR {1:1 (v/v) $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$ } (ppm): 214.65 (s), 138.10 (s), 129.10 (d, $J = 160$ Hz), 128.95 (d, $J = 160$ Hz), 127.11 (d, $J = 167$ Hz), 47.87 (d, $J = 132$ Hz), 44.31 (t, $J = 127$ Hz), 37.22 (t, $J = 130$ Hz). IR (KBr) (cm^{-1}): 1706. Molecular weight: 7100 versus polystyrene standards, $M_w/M_n = 2.0$. The molar optical rotation of the A-CO poly(1,4-ketone) copolymer formed using (*R,R*)-Me-DUPHOS ligand is shown in Table 1.

Isospecific Alternating Isomerization Cooligomerization of *cis*-2-Butene with Carbon Monoxide. A solution containing 4.5×10^{-2} mmol of $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ and 4.5×10^{-2} mmol of (*R,R*)-Me-DUPHOS in 9 mL of a 2:1 (v/v) $\text{CH}_3\text{NO}_2/\text{CH}_3\text{OH}$ mixture was placed in a Parr bomb under nitrogen and charged with 18 g of *cis*-2-butene and 1400 psi of CO. The reaction mixture was stirred at 70 °C for 36 h. At the end of this period, a viscous liquid was obtained upon the removal of the solvent. The product was dissolved in 2-propanol, and the solution was run through a short-stem silica gel chromatograph column to remove the catalyst. The pure oligomers (1.6 g) were isolated by distilling off the 2-propanol solvent and low boiling organics at 120 °C under a high vacuum.

Stereoregular Poly(1-oxo-2-methyltetramethylene), $(-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})-)_n$. ^1H -NMR (2-propanol- d_8) (ppm): 2.58 (1H, m), 2.48

(2H, t, br), 1.86 (1H, m), 1.56 (1H, m), 1.05 (3H, d, $J = 6.7$ Hz), and small resonances at 6.82 (q, $J = 6.8$ Hz), 1.73 (s), 1.30 (sextet, $J = 7.3$ Hz), 0.90 (t, $J = 7.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (2-propanol- d_8) (ppm): 213.73, 45.63, 38.57, 26.91, 16.75, and small absorbances at 201.36, 138.44, 138.15, 41.13, 34.83, 28.33, 26.32, 24.25, 22.86, 14.94, 14.23, 11.85, 11.15. ^{13}C -NMR (2-propanol- d_8) (ppm): 213.73 (s), 45.63 (d, $J = 129$ Hz), 38.57 (t, $J = 125$ Hz), 26.91 (t, $J = 130$ Hz), 16.75 (q, $J = 127$ Hz). IR (neat) (cm^{-1}): 1705. Molar optical rotation: $[\Phi]^{25}_D = -22.2^\circ$ ($c = 12.9$ mg/mL, 2-propanol).

Reduction of Optically Active, Isotactic, Alternating P-CO Poly(1,4-ketone) with LiAlH_4 . The starting P-CO poly(1,4-ketone) was synthesized using (*R,R*)-Me-DUPHOS as the ligand. To a suspension of the P-CO copolymer (0.20 g) in 15 mL of dry THF was added 5.3 mL of 1 M LiAlH_4 solution (in THF) under nitrogen, and the resultant mixture was stirred at ambient temperature for 8 h, resulting in the complete dissolution of the polymer. The solution was stirred at 63 °C for additional 4 h to ensure 100% conversion of the ketone groups to the hydroxyl functionality. After the unreacted excess of LiAlH_4 was deactivated by dropwise addition of CH_3OH , the solvent was removed. The remaining solid was washed with aqueous hydrochloric acid, and the polyalcohol (0.18 g) was purified by reprecipitation in $\text{CH}_3\text{OH}/\text{HCl}$ acidified H_2O and washed with water.

Chiral Poly(1,4-alcohol), $(-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{OH})-)_n$. ^1H -NMR (CD_3OD) (ppm): 4.87 (1H, s), 3.58–3.68 (1H, br), 1.62–1.75 (2H, br), 1.15–1.35 (1H, m, br), 0.94 (3H, m). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_3OD) (ppm): 72.18–75.15 (m), 36.82–39.36 (m), 17.13, 16.37, 15.20, 14.53. IR (KBr) (cm^{-1}): 3405, 2961, 1459, 1381, 1017, 934, 861, 626. Molar optical rotation: $[\Phi]^{25}_D = +12.8^\circ$ ($c = 3.21$ mg/mL, CH_3OH).

Hydrogenation of Atactic, Exclusively Head-to-Tail, Alternating P-CO Copolymer with LiAlH_4 . Into a 15 mL THF solution containing 0.20 g of the atactic P-CO copolymer was added 5.3 mL of 1 M LiAlH_4 solution (in THF) under nitrogen. The resultant mixture was stirred at 65 °C for 5 h. After the addition of CH_3OH to decompose the excess unreacted LiAlH_4 , the solvent was removed. The polyalcohol (0.15 g) was purified by reprecipitation in $\text{CH}_3\text{OH}/\text{HCl}$ acidified H_2O and washed with water.

Achiral Poly(1,4-alcohol), $(-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{OH})-)_n$. ^1H -NMR (CD_3OD) (ppm): 4.87 (1H, s), 3.56 (1H, br), 1.59–1.76 (2H, br), 1.19–1.39 (1H, br), 0.92 (3H, br). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_3OD) (ppm): 72.17–74.60 (m), 36.35–38.90 (m), 17.07, 16.78, 16.31, 16.00, 15.18, 14.42, 13.79, 13.64. IR (KBr): no carbonyl band at ~ 1710 cm^{-1} .

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