Macromolecules 1993, *26*, 911-915

Palladium(II)-Catalyzed Alternating Copolymerization and Terpolymerization of Carbon Monoxide with α-Olefins: Formation of Syndiotactic Copolymers as Well as Terpolymers with *both* Syndiotactic and Atactic Segments

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Received August 11, 1992; Revised Manuscript Received November 4, 1992

ABSTRACT: $[Pd(1,10\text{-phenanthroline})(MeCN)_2](BF_4)_2$ and related complexes were found to catalyze the alternating copolymerization of styrene derivatives with carbon monoxide to form syndiotactic copolymers with strictly head-to-tail arrangement in the polymer backbone. The polymers, as formed, were highly crystalline although the crystallinity (but not the stereoregularity) was lost upon dissolution in acids followed by reprecipitation. The Pd(II) catalysts were also found to catalyze the terpolymerization of ethylene, propylene, ω-undecylenyl alcohol, and ω-methyl undecylenate with styrene and carbon monoxide. At high ratios of styrene to the second olefin, the terpolymers formed had structures consisting of syndiotactic alternating styrene–CO blocks randomly separated by atactic spacers formed by the alternating second olefin–CO units. The tactic styrene–CO blocks were lost with increasing content of the second olefin.

The syntheses of new tactic polymers continues to be a challenging problem. From a practical standpoint, the interest in tactic polymers derives from their superior mechanical properties, higher crystallinity, and higher melting points when compared to the corresponding atactic analogs.[1] We[2] and others[3] have reported on the palladium(II)-catalyzed alternating copolymerization of carbon monoxide with α-olefins. Very recently, it has been shown that the alternating styrene–CO copolymer (S–CO copolymer) formed was syndiotactic.[4] Herein, we report our results encompassing the synthesis and characterization of syndiotactic copolymers of styrene derivatives with CO, as well as terpolymers of other α-olefins with styrene and CO that have *both* syndiotactic and atactic segments in the polymer chain. The syndiotactic segments consist of alternating S–CO blocks. To our knowledge, this is the first example of metal-catalyzed synthesis of copolymers where one monomer is incorporated into the tactic segments which are linked by atactic spacers formed by a second monomer.

Results and Discussion

The catalyst used for the alternating copolymerization and terpolymerization of carbon monoxide with α-olefins, $[Pd(1,10\text{-phenanthroline})(MeCN)_2](BF_4)_2$ (1), was formed in situ by codissolving a 1:1 molar ratio of $[Pd(MeCN)_4](BF_4)_2$ and 1,10-phenanthroline in a nitromethane/methanol mixture. 1,4-Benzoquinone was added to promote the reaction.[3a]

Copolymers. Compound 1 catalyzed the alternating copolymerization of carbon monoxide with ethylene, as well as styrene derivatives, and the molecular weights and polydispersities for the latter are summarized in Table I. Because of their high tacticity and resultant crystallinity (vide infra), the copolymers of carbon monoxide with styrene derivatives were insoluble in the common organic solvents. Therefore, in order to measure molecular weights, the solubility of two of the derivatives was enhanced by an epimerization procedure involving treatment with the sodium salt of 2-chlorophenol in 2-chlorophenol. This procedure has been described previously.[4b]

Table I
Molecular Weights and Their Distributions for the Alternating α-Olefin–Carbon Monoxide Copolymers and Terpolymers[a]

polymer	M_p[b]	M_w/M_n[b]
styrene–CO (epimerized)	1.7×10^5	4.1
p-methylstyrene–CO (epimerized)	2.1×10^5	2.6
styrene–ethylene–CO (E–CO = 52%)	5.0×10^4	2.3
styrene–ethylene–CO (E–CO = 11%)	1.3×10^5	1.6
styrene–propylene–CO (P–CO = 69%)	4.1×10^4	1.9
styrene–propylene–CO (P–CO = 12%)	1.1×10^5	2.4
styrene–ω-undecylenyl alcohol–CO (ω-undecylenyl alcohol–CO = 14%)	5.9×10^4	1.8
styrene–ω-methyl undecylenate–CO (ω–methyl undecylenate–CO = 14%)	5.0×10^4	2.1

[a] The styrene–ethylene–CO terpolymers were prepared using $[Pd(5\text{-methyl-}1,10\text{-phenanthroline})(MeCN)_2](BF_4)_2$ as catalyst. Other polymers were synthesized using $[Pd(1,10\text{-phenanthroline})(MeCN)_2](BF_4)_2$ as catalyst. [b] Molecular weights and their distributions measured by GPC relative to polystyrene standards.

NMR spectra indicated that the ethylene–CO copolymer (E–CO copolymer) had an alternating structure and those of carbon monoxide with styrene derivatives were tactic alternating copolymers with strictly head-to-tail arrangement in the polymer backbone. For example, the copolymers of carbon monoxide with styrene derivatives showed a single carbonyl absorption at ~210 ppm in their ^{13}C-NMR spectra due exclusively to a head-to-tail structure. Single dominant resonances for the CH_2 (~42 ppm) and CH (~53 ppm) groups in the backbone supported the presence of high stereoregularity in the polymers. The alternating structure of the copolymers was also consistent with the results of elemental analysis.

The yield and the stereoregularity of the S–CO copolymers formed were found to depend on the ligand attached to the Pd(II) center, and the results are shown in Table II. The highest yield and tacticity were achieved by using nitro-substituted 1,10-phenanthroline as the ligand. For the S–CO copolymer, the percentage of stereoregularity could be calculated from the resonance at approximately 134.57 ppm (ipso carbon in the phenyl group) (Figure 1). An important point to note is that, unlike α-olefin homopolymers, the alternating α-olefin–CO copolymers have truly asymmetric carbons in the polymer backbone. In the *syndiotactic* alternating α-olefin–CO copolymer the chiral sense of the asymmetric centers in the backbone

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Table II
Ligand Effect on the Copolymerization of Styrene with CO[a]

ligand	1,10-phenanthroline	5-methyl-1,10-phenanthroline	3,4,7,8-tetramethyl-1,10-phenanthroline	5-nitro-1,10-phenanthroline	2,9-dimethyl-1,10-phenanthroline
yield,[b] % (g)	37 (0.85)	48 (1.1)	23 (0.52)	74 (1.7)	0
percentage of tacticity,[c] %	80	80	73	90	

[a] All reactions were run at 60 °C for 48 h using 2.0 mL (17.5 mmol) of styrene, 1000 psi of CO, 6.8×10^{-2} mmol of 1, 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. [b] Yield is based on styrene. [c] The percentage of tacticity was calculated from the ^{13}C-NMR resonances at approximately 134.57 ppm of the copolymer.

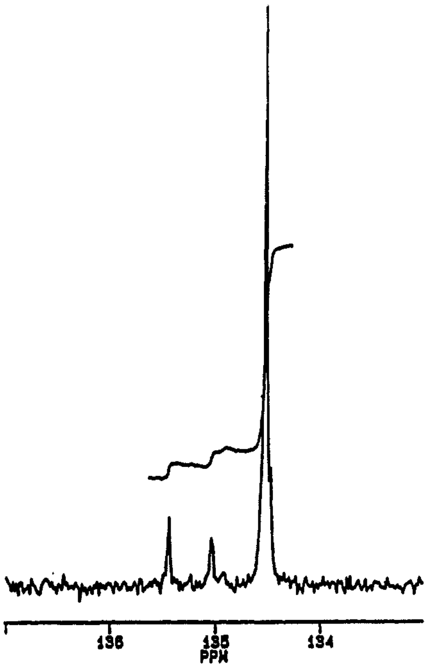

Figure 1. $^{13}C\{^1H\}$-NMR spectrum of the ipso carbons of the predominantly syndiotactic alternating styrene–carbon monoxide copolymer.

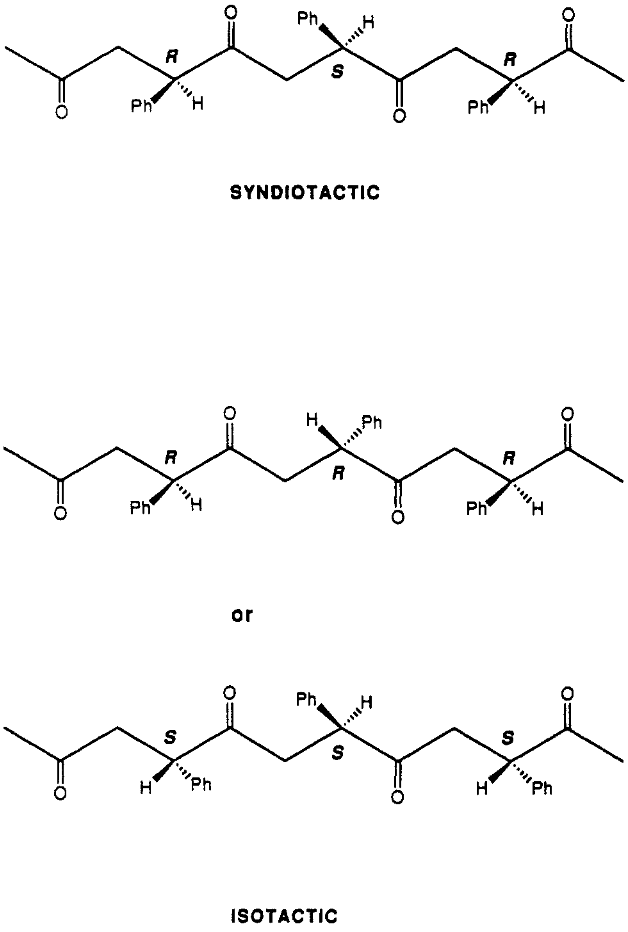

Figure 2. Syndiotactic and isotactic structures for the alternating copolymer of styrene with carbon monoxide.

alternate (i.e., ...*RSRSRS*...) (see Figure 2). On the other hand, all the asymmetric centers in the individual *isotactic* alternating α-olefin–CO copolymer chains have the *same* chiral sense (i.e., ...*RRRRRR*... or ...*SSSSSS*...) (see Figure 2). It is therefore not appropriate to use the terms "meso" and "racemic" in descriptions of polymer stereoregularity. Using the *R*,*S* convention instead, the diads 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*. A comparison of the NMR and XRD spectra of our S–CO copolymers with those reported recently[4] indicated a syndiotactic stereochemistry for the former. Therefore, the most intense absorbance in Figure 1 can be ascribed to the *RSR*/*SRS* triad, while the two minor absorbances of approximately equal intensity are due to the *RSS*/*SRR* and *RRS*/*SSR* triads.

The copolymers of carbon monoxide with styrene derivatives were highly crystalline solids, and sharp peaks were observed in the X-ray powder diffraction (XRD) spectra (Figure 3). DSC analysis of the S–CO copolymer indicated that the polymer had a T_g of 94 °C and a T_m of 290 °C. The high crystallinity rendered the copolymers insoluble in common organic solvents such as chloroform, methylene chloride, and THF. However, they slowly dissolved in acidic solvents such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol and 2-chlorophenol. The crystallinity of the copolymers could be destroyed by dissolving in an acidic solvent and reprecipitating by adding a nonsolvent. For example, the precipitation of *p*-methylstyrene–CO copolymer by addition of methanol to its solution in 2-chlorophenol resulted in the formation of a noncrystalline polymer that was soluble in chloroform and methylene chloride. The lack of crystallinity was shown by XRD experiments. The ^{13}C-NMR spectrum of the precipitated polymer indicated, however, that the tacticity of the polymer was *unaffected* during this procedure and that the solubility change was *not* due to a decrease of the stereoregularity.

Terpolymers. Compound 1 or its analog, $[Pd(5\text{-methyl-1,10-phenanthroline})(MeCN)_2](BF_4)_2$, was also found to catalyze the terpolymerization of α-olefins with styrene and CO (Table I). In the case of ethylene and propylene, at a high styrene to ethylene or propylene feed ratio, the terpolymers formed had structures comprised of tactic alternating S–CO blocks randomly separated by alternating ethylene–CO (E–CO) or propylene–CO (P–CO) units. For example, the ^1H-NMR spectrum of a E–S–CO terpolymer with 11 mol % E–CO content exhibited absorptions at 4.13 (t), 3.08 (dd), and 2.60 (dd) ppm due to the $-CH(Ph)CH_2-$ group of the S–CO unit. The coupling among the three protons is an indication of the presence of stereoregular (syndiotactic[4b]) structure since the base-epimerized atactic S–CO copolymer showed only broad resonances at the corresponding frequencies. The ^{13}C-

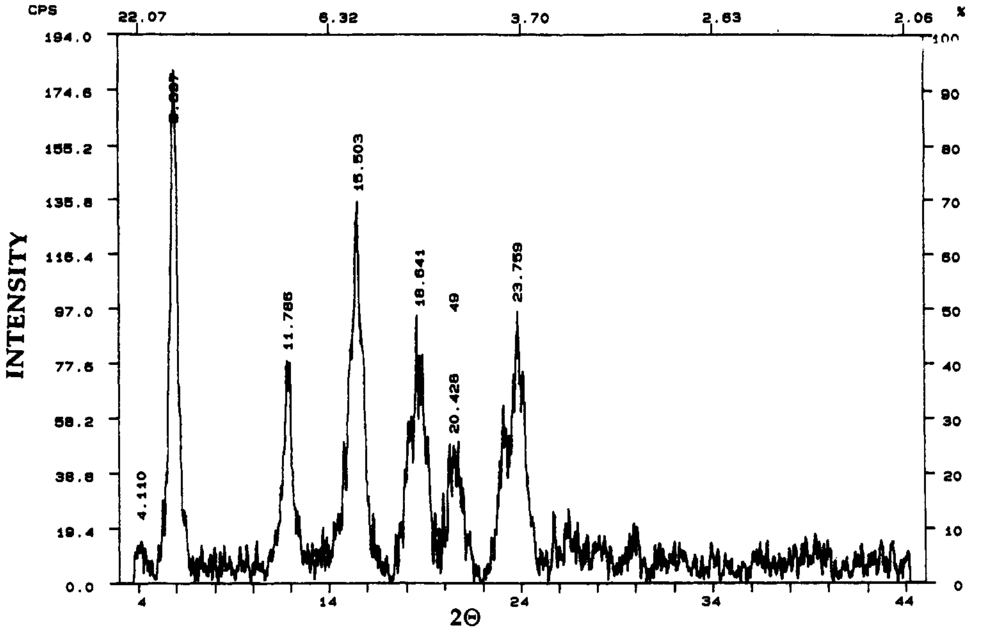

Figure 3. X-ray (Cu Kα) powder diffraction pattern for the syndiotactic alternating styrene–carbon monoxide copolymer.

NMR spectra had single dominant resonances at 206.34, 136.80, 128.60, 128.16, 126.92, 53.31, and 43.31 ppm due to stereoregular S–CO blocks, and three small absorptions at 206.74, 36.15, and 35.17 ppm due to E–CO units flanked by two S–CO units. This terpolymer was also highly crystalline, and its XRD spectrum was essentially identical to that of the alternating S–CO copolymer, thereby indicating that the type of tacticity (i.e., syndiotacticity) of the S–CO blocks was not altered upon the incorporation of a second olefin into the polymer. As expected, with increasing ethylene content, the S–CO units became more and more isolated, resulting in the loss of the tactic S–CO blocks. For example, the ^{1}H-NMR spectrum of the terpolymer with 52 mol % E–CO content showed broad absorptions, and the ^{13}C-NMR resonances at 207.5, 53.2, and 44.5 ppm turned into multiplets.

As with the E–S–CO terpolymers, P–S–CO terpolymer with a low P–CO content (12 mol %) possessed tactic S–CO blocks. On the other hand, the tactic S–CO blocks were absent in the terpolymer with 69 mol % P–CO content. The tactic P–S–CO terpolymer had a glass transition temperature (94 °C) very similar to that exhibited by the S–CO copolymer and showed proton absorptions at 4.13 (t), 3.08 (dd), and 2.62 (dd) ppm due to the –CH(Ph)-CH_2–group of the stereoregular (syndiotactic[4b]) S–CO blocks. The ^{13}C-NMR spectrum of the polymer exhibited single dominant resonances at 206.34, 136.84, 128.80, 128.62, 128.18, 126.94, 53.35, and 43.34 ppm due to the S–CO blocks and small absorptions at 210.63, 44.25, 41.12, and 16.26 ppm attributable to P–CO units. In comparison, all proton resonances of the atactic terpolymer were broad and multiplets were observed for most of its ^{13}C-NMR absorptions. Also, while the tactic P–S–CO terpolymer was crystalline solid (T_m = 227 °C), the atactic terpolymer was amorphous with T_g = 23 °C. Rather surprisingly, only two carbonyl resonances at 211.59 and 207.45 ppm were found for the atactic terpolymer. The lack of absorption at 215 ppm excluded the presence of head-to-head (and, hence, also tail-to-tail) structure in the P–CO units in the polymer backbone,[2] thereby indicating predominantly a head-to-tail configuration in these units. It is worth noting that there is only one previously reported synthesis[3i] of a predominantly regioregular alternating P–CO copolymer and, in that instance, a chelating diphosphine rather than a nitrogen-based ligand was used for the metal. Additionally, it was postulated[3i,4a] that the regioregularity of the P–CO copolymer obtained increased with increasing basicity and steric size of the chelating diphosphine employed. Clearly, this argument cannot be valid for our system given the low basicity and flat shape of the 1,10-phenanthroline ligand.

The solubility of the E–S–CO and the P–S–CO terpolymers largely depended on the ratio of styrene to the second olefin in the polymers. For example, the E–S–CO terpolymer containing 11 mol % E–CO content and the P–S–CO terpolymer with 12 mol % P–CO content were soluble in chloroform and methylene chloride but insoluble in acetone. However, the E–S–CO terpolymer with 52 mol % E–CO content and the P–S–CO terpolymer with 69 mol % P–CO content were soluble in both chloroform and acetone. The E–S–CO terpolymer with 80 mol % E–CO content was totally insoluble in common organic solvents and was found to dissolve only in acidic solvents such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol and 2-chlorophenol.

Finally, for the first time, functional α-olefins were also successfully terpolymerized with styrene and CO. Terpolymers of ω-undecylenyl alcohol, styrene, and CO, as well as ω-methyl undecylenate, styrene, and CO, containing 14 mol % functional α-olefin–CO units and tactic S–CO blocks in the terpolymer backbone, were obtained. The latter terpolymer was prepared starting with ω-undecylenic acid. The methyl ester groups were presumably formed through the reaction of the carboxylic acid groups of the monomer with the methanol solvent during the terpolymerization reaction. The presence of tactic S–CO blocks in the terpolymers was indicated by the NMR spectra. Both terpolymers showed ^{1}H-NMR absorptions at 4.12, 3.08 (dd), and 2.62 (dd) ppm and dominating single ^{13}C-NMR resonances at 206.33, 136.78, 128.58, 128.14, 126.90, 53.30, and 43.28 ppm. The presence of small ^{13}C-NMR resonances at 210.4, 46.1, and 44.2 ppm was consistent with alternating ω-undecylenyl alcohol–CO units or ω-methyl undecylenate–CO units incorporated into the terpolymers. The hydroxymethyl terminal groups of the ω-undecylenyl alcohol–CO units exhibited ^{1}H-NMR absorptions at 3.63 (–CH_2O–), and ^{13}C-NMR absorptions at 62.93 ppm, which were identical to those of ω-undecylenyl alcohol monomer. The methyl ester terminal groups of the ω-methyl undecylenate–CO units exhibited a ^{1}H-NMR resonance at 3.66 (s) ppm and ^{13}C-NMR resonances at 174.22 and 51.38 ppm. The ^{13}C-NMR absorption of the ester carbonyl groups was shifted 6.3 ppm upfield compared to that of the carboxylic acid groups of ω-undecylenic acid monomer. The conversion of the acid to ester was quantitative by NMR spectra.

Although they terpolymerize with styrene and CO, the functional α-olefins did not appear to copolymerize alone with CO. In the absence of styrene, isomerization to internal olefins occurred. During the terpolymerization of the α-olefins with styrene and CO, slow isomerization was observed as a side reaction. However, the isomerized products (internal olefins) were found to be inactive in the terpolymerization reaction.

Experimental Section

a. Materials. C.P.-grade chemicals were used as received unless otherwise stated. Styrene was dried over CaH_2, distilled, and stored under dry nitrogen in a refrigerator before use. $[Pd(MeCN)_4](BF_4)_2$ was prepared according to a literature method.[5] Nitromethane was dried over CaH_2 and vacuum-transferred. Methanol was treated with sodium methoxide and distilled.

b. Analysis. Preparation of catalyst solutions was performed in a dry-nitrogen-filled glovebox. However, all reactions were set up in air. ^{1}H- and ^{13}C-NMR spectra were recorded on an AM 300 FT-NMR spectrometer. The chemical shifts were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency. IR spectra were measured on a Perkin-Elmer Model 281B spectrometer using KBr pellets. X-ray powder diffraction experiments were carried out on a Scintag X-ray diffractometer, and the obtained data were analyzed on a Vax 3000 data station. The glass transition temperature and melting point of the polymers were measured on a DSC 2910 differential scanning calorimeter equipped with a Du Pont Thermal Analyst 2000. Elemental analyses were performed by Galbraith Laboratories, Inc.

c. Copolymerization of Ethylene and Carbon Monoxide. In a typical reaction, a mixture of 30 mg (6.8×10^{-2} mmol) of $[Pd(MeCN)_4](BF_4)_2$, 12.2 mg (6.8×10^{-2} mmol) of 1,10-phenanthroline, and 10 mg (9.3×10^{-2} mmol) of 1,4-benzoquinone was dissolved in 4.0 mL of nitromethane and was followed by the addition of 2.0 mL of methanol. The mixture was placed in a 125-mL Parr bomb and then charged with 500 psi ethylene and 500 psi of CO, bringing the total pressure to 1000 psi. After stirring at 60 °C for 19 h, the unreacted gases were released and the formed insoluble polymer (4.2 g) was washed with acetone and dried under vacuum.

Ethylene–CO copolymer. ^{1}H NMR (CF_3COOD, ppm): 3.02. $^{13}C\{^1H\}$ NMR (CF_3COOD, ppm): 217.02, 38.03.

d. Copolymerization of Styrene and Carbon Monoxide. The reaction was carried out according to a procedure analogous to that described above. To a catalyst solution containing 6.8×10^{-2} mmol of $[Pd(MeCN)_4](BF_4)_2$, 6.8×10^{-2} mmol of 1,10-phenanthroline, 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 2.0 mL (17.5 mmol) of styrene. The resultant solution was placed in a Parr bomb and charged with 1000 psi of CO. After the reaction mixture was stirred at 60 °C for 48 h, a crystalline polymer precipitate (0.85 g, 40% yield based on olefin) was formed. It was washed with acetone and vacuum-dried.

Styrene–CO copolymer. ^{1}H NMR [$(CF_3)_2CHOH$, ppm]: 7.15–6.55 (5 H, m), 4.08 (1 H, br), 2.92 (2 H, br). $^{13}C\{^1H\}$ NMR [$(CF_3)_2CHOH$, ppm]: 210.79, 134.57, 129.02, 127.79, 127.65, 53.80, 42.18. IR (KBr): 1690 cm^{-1}. Anal. Calcd for $C_6H_5CHCH_2$–CO: C, 81.8; H, 6.1. Found: C, 82.1; H, 6.0. $T_g = 94.1$ °C, $T_m = 290$ °C. The above reaction was repeated using other 1,10-phenanthroline derivatives. The resultant styrene–carbon monoxide copolymers had identical structures except for the degree of the tacticity, as confirmed by NMR spectra. The results are summarized in Table II.

e. Copolymerization of Carbon Monoxide with Substituted Styrenes. The reactions were performed following a procedure analogous to the one employed for styrene. Para-substituted styrenes (2.0 mL) were used instead of styrene. The reactions were run at 60 °C for 40 h, and the following yields (based on olefin) were obtained: *p*-methoxystyrene, 19%; *p*-methylstyrene, 54%; *p*-chlorostyrene, 11%. The copolymers formed were crystalline solids that were insoluble in common organic solvents. Sharp peaks were observed in the X-ray powder diffraction spectra of the *p*-methylstyrene–CO copolymer and the styrene–CO copolymer described above. However, the crystalline *p*-methylstyrene–CO copolymer was converted to an amorphous form through precipitation by addition of methanol to its solution in 2-chlorophenol. The loss of crystallinity was indicated by substantial broadening of the XRD spectrum.

p-Methylstyrene–CO copolymer. (a) Crystalline form. ^{1}H NMR [$(CF_3)_2CHOH$, ppm]: 6.72 (2 H, d, $J = 7.8$ Hz), 6.38 (2 H, d, $J = 7.8$ Hz), 4.00 (1 H, br), 2.86 (2 H, br), 2.20 (3 H, s). $^{13}C\{^1H\}$ NMR [$(CF_3)_2CHOH$, ppm]: 211.23, 138.18, 131.12, 129.48, 127.67, 53.59, 42.06, 19.23. IR (KBr): 1690 cm^{-1}. Anal. Calcd for $CH_3C_6H_4CHCH_2$–CO: C, 82.2; H, 6.9. Found: C, 82.7; H, 6.8. (b) Amorphous form. ^{1}H NMR ($CDCl_3$, ppm): 6.74 (2 H, d, $J = 7.8$ Hz), 6.55 (2 H, d, $J = 7.8$ Hz), 4.03 (1 H, t), 3.01 (1 H, dd, $J = 17.5$, 6.6 Hz), 2.59 (1 H, dd, $J = 17.5$, 6.6 Hz), 2.19 (3 H, s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 206.62, 136.35, 133.82, 129.14, 128.09, 53.07, 43.21, 20.98.

p-Methoxystyrene–CO copolymer. ^{1}H NMR [$(CF_3)_2CHOH$, ppm]: 6.52 (4 H, br), 4.06 (1 H, br), 3.78 (3 H, s), 2.91 (2 H, br). $^{13}C\{^1H\}$ NMR [$(CF_3)_2CHOH$, ppm]: 210.65, 158.09, 129.23, 127.87, 114.42, 55.02, 52.94, 42.21.

p-Chlorostyrene–CO copolymer. ^{1}H NMR (2-chlorophenol, ppm, selected absorptions): 4.20 (1 H, br), 3.20 (1 H, br), 2.83 (1 H, br). $^{13}C\{^1H\}$ NMR (2-chlorophenol, ppm, selected absorptions): 207.33, 52.77, 42.83. IR (KBr): 1685 cm^{-1}.

f. Terpolymerization of Ethylene, Styrene, and Carbon Monoxide. To a solution containing 6.8×10^{-2} mmol of $[Pd(MeCN)_4](BF_4)_2$, 6.8×10^{-2} mmol of 5-methyl-1,10-phenanthroline, 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 6.0 mL of styrene. The mixture was placed in a 125-mL Parr bomb and charged with 0.10 g of ethylene and 1000 psi of CO. After stirring at 60 °C for 22 h, a polymer precipitate (1.7 g) was obtained by adding methanol into the reaction mixture. The polymer product was washed with acetone and dried under vacuum.

Ethylene–styrene–CO terpolymer (molar ratio of E–CO units/S–CO units = 0.12). ^{1}H NMR ($CDCl_3$, ppm): 7.16–6.70 (5 H, br m), 4.13 (1 H, br t), 3.08 (1 H, dd, $J = 17.6$, 6.9 Hz), 2.60 (1.47 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 206.34, 136.80, 128.60, 128.16, 126.92, 53.31, 43.31, and additional small resonances at 206.74, 36.15, 35.17. IR (KBr): 1700 cm^{-1}.

By varying the feed ratio of ethylene versus styrene, terpolymers containing more ethylene units were obtained. Ethylene–styrene–CO terpolymer (molar ratio of E–CO units/S–CO units = 1.1). ^{1}H NMR ($CDCl_3$, ppm): 7.3–7.0 (5 H, br), 4.16 (1 H, br), 3.26 (1 H, br), 2.65 (5.3 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 207.46 (m), 137.51 (m), 129.11–127.10 (m), 53.21, 53.01, 45.69–43.44 (m), 36.01, 35.26.

Ethylene–styrene–CO terpolymer (molar ratio of E–CO units/S–CO units = 4.1). ^{1}H NMR [$(CF_3)_2CHOH$, ppm]: 7.4–7.2 (5 H, br), 4.24 (1 H, br), 3.0–2.70 (18.5 H, br). $^{13}C\{^1H\}$ NMR [$(CF_3)_2CHOH$, ppm]: 213.05, 212.89, 212.58, 212.48, 136.23, 129.38–127.52 (m), 53.49, 44.57, 35.40, 34.76.

g. Terpolymerization of Propylene, Styrene, and Carbon Monoxide. The reactions were carried out according to a procedure analogous to the one employed for the terpolymerization of ethylene, styrene, and carbon monoxide. 1,10-Phenanthroline was used as the ligand, and propylene was used instead of ethylene. Depending on the reaction conditions, propylene–styrene–CO terpolymers with different P–CO content were prepared.

Propylene–styrene–CO terpolymer (molar ratio of P–CO units/S–CO units = 0.14). ^{1}H NMR ($CDCl_3$, ppm): 7.1–6.7 (5 H, m), 4.13 (1 H, t), 3.08 (dd, $J = 17.7$, 6.9 Hz), 2.62 (dd, $J = 17.7$, 6.9 Hz), 3.2–2.3 (br), 1.1–0.88 (0.42 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 206.34, 136.84, 128.80, 128.62, 128.18, 126.94, 53.35, 43.34, and additional small resonances at 210.63 (m), 44.25 (m), 41.12 (m), 16.26 (m). IR (KBr): 1705 cm^{-1}. $T_g = 93.8$ °C, $T_m = 227$ °C.

Propylene–styrene–CO terpolymer (molar ratio of P–CO units/S–CO units = 2.2). ^{1}H NMR ($CDCl_3$, ppm): 7.4–7.0 (5 H, br m), 4.17 (1 H, br), 3.24–2.30 (8.1 H, br m), 1.05–0.87 (6.5 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 211.59 (m), 207.45 (m), 137.45, 128.9–127.2 (br m), 53.14, 44.18 (m), 40.90 (m), 16.44 (m). T_g = 23 °C.

h. Terpolymerization of Styrene, ω-Undecylenyl Alcohol, 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 1,10-phenanthroline, 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 were added 2.0 mL of styrene and 1.0 mL of ω-undecylenyl alcohol. The resultant mixture was placed in a Parr bomb, and 900 psi of CO was charged. After stirring at 60 °C for 67 h, the bomb was vented and Et_2O/pentane was added to the reaction mixture. The polymer precipitate (1.20 g) was washed with acetone/Et_2O/pentane and Et_2O/pentane and dried in vacuo. The terpolymer was soluble in chloroform and methylene chloride.

Styrene–ω-undecylenyl alcohol–CO terpolymer (molar ratio of S–CO units/ω-undecylenyl alcohol–CO units = 6.1). ^1H NMR ($CDCl_3$, ppm): 7.25–6.68 (5.0 H, br m), 4.12 (1.0 H, br), 3.63 (0.33 H, br), 3.08 (1.2 H, dd, br), 2.62 (1.3 H, dd, br). 1.72 (0.17 H, br), 1.55 (0.34 H, br), 1.40–0.89 (2.3 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): S–CO units, 206.33, 136.78, 128.58, 128.14, 126.90, 53.30, 43.28; ω-undecylenyl alcohol–CO units, 210.44, 62.93, 46.17, 44.20, 33.87, 32.74, 30.89, 29.36 (br), 26.55, 25.69.

i. Terpolymerization of Styrene, ω-Undecylenic Acid, 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 1,10-phenanthroline, 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 2.1 mL of styrene and 1.1 g of ω-undecylenic acid. The resultant mixture was placed in a Parr bomb, and 900 psi of CO was charged. After stirring at 60 °C for 18 h, the bomb was vented and the final solution was filtered. A polymer was obtained after removal of solvent from the filtrate. The terpolymer (0.60 g) was washed with acetone and Et_2O/pentane and dried in vacuo. Its NMR spectra revealed that the carboxylate group of the incorporated ω-undecylenic acid–CO units had been totally converted to corresponding methyl ester.

Styrene–ω-methyl undecylenate–CO terpolymer (ratio of S–CO units/ω-methyl undecylenate–CO units = 6.0). ^1H NMR ($CDCl_3$, ppm): 7.25–6.68 (5.0 H, br m), 4.13 (1.0 H, br), 3.66 (0.50 H, s), 3.06 (1.2 H, dd, br), 2.64 (1.3 H, dd, br), 2.29 (0.32 H, br), 1.58 (0.33 H, br), 1.40–0.90 (2.0 H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): S–CO units, 206.31, 136.76, 128.56, 128.11, 126.89, 53.27, 43.27; ω-methyl undecylenate–CO units, 210.40, 174.22, 51.38, 46.06, 44.16, 34.03, 30.87, 29.01 (br), 26.51, 24.88.

Acknowledgment. We thank Professor Earle Ryba for help with the XRD experiments and Mr. James Yeh for help with DSC measurements. This research was supported by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295). We also thank Johnson Matthey, Inc., for a generous loan of palladium.

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