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Regio-, Stereo-, and Enantioselective Alternating Copolymerization of Propene with Carbon Monoxide

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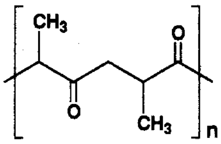
ABSTRACT: Essentially complete regioselectivity and good catalytic activity can be achieved in the copolymerization of propene with carbon monoxide using palladium-containing catalytic systems modified by the basic diphosphine ligand $CH_2\{CH_2P(C_2H_5)_2\}_2$. With (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) a stereoregular poly(1-oxo-2-methyltrimethylene) was obtained. When the optically pure ligand was used, the produced copolymer showed an intense band in the circular dichroism spectrum in the region around 275 nm as expected for a prevailingly isotactic structure. In most cases the copolymers can be isolated as a poly[spiro-2,5-(3-methyltetrahydrofuran)]. NMR analysis of the regioregular copolymers and comparison with model compounds suggest that the insertion of the propene units during the growth process takes place with primary regioselectivity.

Introduction

Cationic palladium systems modified with $CH_2\{CH_2P(C_6H_5)_2\}_2$ have allowed the alternating copolymerization of ethene and of substituted ethenes with carbon monoxide.[1] For propene the use of different chiral and achiral diphosphine ligands has been recently reported.[1–3] The produced material was in every case regioirregular.[2–5] Regioregular poly(1-oxo-2-methyltrimethylene) (1) has



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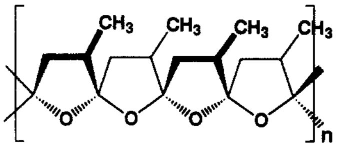
then become accessible either through ring opening radical polymerization of 2,2-diphenyl-4-methylene-5-methyl-1,3-dioxolane[6] or through copolymerization of propene and carbon monoxide using the aforementioned palladium catalysts modified by 1,3-propanediylbis(diisopropylphosphine) or 1,3-propanediylbis(dicyclohexylphosphine).[7,8] The latter method, besides being the only one economically acceptable, also allows the control of the stereochemistry of the produced copolymer. We succeeded indeed in synthesizing 1 having a seemingly good stereoregularity using a palladium catalytic system modified by (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine).[8] Under the reaction conditions applied the copolymer grows exclusively as a poly[spiro-2,5-(3-methyltetrahydrofuran)] (2)[9–11] which is transformed into the poly(1-oxo-2-methyltrimethylene) (structure 1) either thermally[10] or by dissolution in hexafluoro-2-propanol and reprecipitation with methanol.[9]



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There are three main reasons of interest in this product: (i) it represents the first regio- and stereoregular copolymer of an α-olefin with carbon monoxide, (ii) it grows in a quite unexpected atropoisomeric structure, and (iii) it is one of the very few polymers which can have optical activity deriving from the presence of asymmetric carbon atoms in the main chain.[12] We report herein on further investigations directed to a better understanding of the copolymerization mechanism as well as on a more complete characterization of the produced poly(1-oxo-2-methyltrimethylene).

Results and Discussion

Regioregular copolymers with a rather low molecular weight between propene and carbon monoxide were obtained using a catalytic system formed by $Pd(CH_3COO)_2$ modified by either 1,3-propanediylbis(diisopropylphosphine) or 1,3-propanediylbis(dicyclohexylphosphine).[7,8] In fact, the analogous system containing the similarly basic but less sterically hindered 1,3-propanediylbis(di-*n*-butylphosphine) had been reported to give copolymers with about 90% of regular head-to-tail enchainment.[8] We now surprisingly find that, using 1,3-propanediylbis(diethylphosphine) as the ligand, regioregular copolymers are formed. This regularity is easily recognized from the ^{13}C-NMR spectra in hexafluoro-2-propanol in the region of resonances of the carbonyl groups (Figure 1). The signals attributable to head-to-head and tail-to tail enchainment (Figure 1, ~222 and 216 ppm)[7] have an intensity of about 1%. The new catalyst has much higher catalytic activity causing a productivity of about 125 (g/g·h) and permits a remarkable increase of the molecular weight (about $M_n \sim 33000$), particularly when the presence of methanol in the reaction mixture is avoided. From a steric point of view the copolymer is quite similar to those previously obtained using the sterically more hindered ligands.[7,8] The intensity of the main signal in the region of the methyl resonances amounts to about 50% of the total intensity; this signal seems to be assignable to the isotactic triads.[7,8] According to ^{13}C-NMR and to IR analysis in the solid state, the copolymer is recovered with a partial (~25%) spiroketal structure.[9] When the reaction is carried out using 1,3-propanediylbis(dicyclohexylphosphine) as the ligand, the

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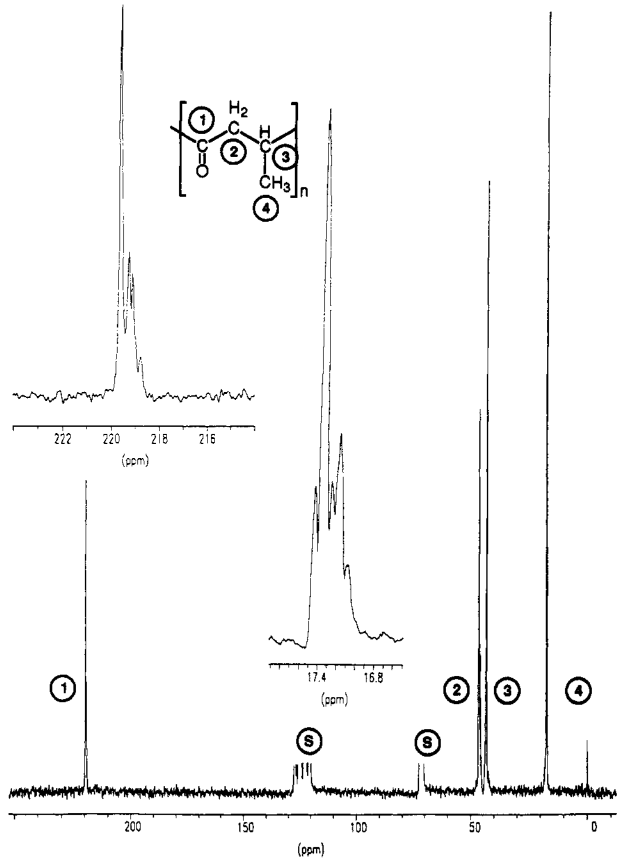


Figure 1. ^{13}C-NMR spectrum (125.8 MHz, $(CF_3)_2CDOD$ as the solvent) of poly(1-oxo-2-methyltrimethylene) obtained with palladium catalysts modified by 1,3-propanediylbis(diethylphosphine) (assignments according to the formula; S indicates solvent signals).

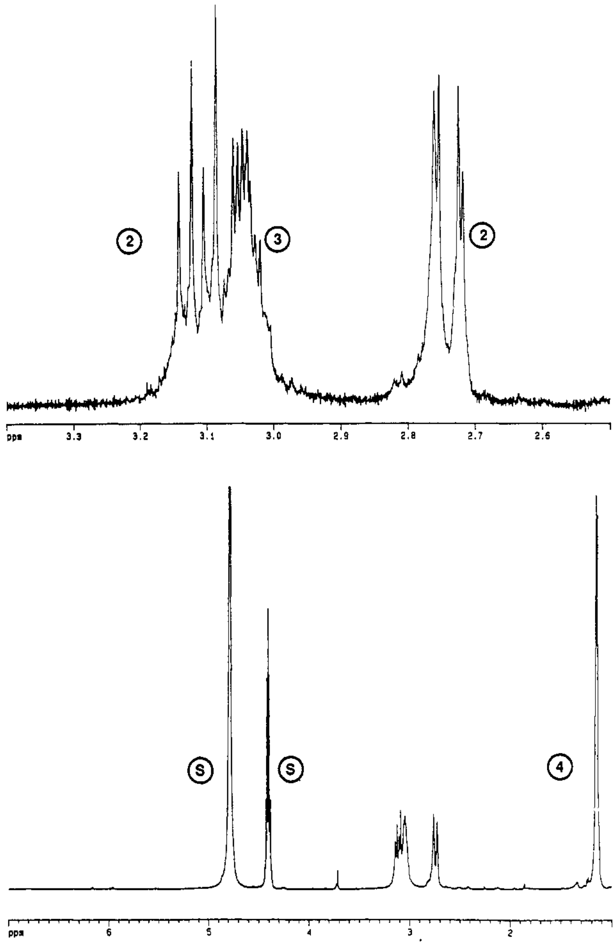


Figure 2. ^{1}H-NMR spectrum (500 MHz, $(CF_3)_2CDOD$ as the solvent) of poly(1-oxo-2-methyltrimethylene) obtained with palladium catalysts modified by racemic (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) (the assignments parallel those for ^{13}C reported in Figure 1).

copolymer is formed overwhelmingly (or exclusively when methanol is present in the reaction mixture) with structure 2.

Better results from the point of view of the stereochemical control were obtained when either racemic or optically pure ((*S*)-antipode) (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) was used as the ligand. The copolymer recovered in the case of the optically pure ligand was always isolated in the form of a poly[spiro-2,5-(3-methyltetrahydrofuran)], as previously reported.[8] When the racemic ligand was used to modify the palladium catalyst under otherwise identical reaction conditions, the copolymer was reproducibly isolated as poly(1-oxo-2-methyltrimethylene). We suspected that this could be due to some phosphine oxide impurities present in the ligand used. In fact, a copolymerization experiment was carried out with the optically pure ligand which was intentionally contaminated by the same amount (~10% from ^{31}P-NMR) of the oxide impurities. The produced copolymer was isolated as usually and showed only a partial (~50% from ^{13}C-NMR in the solid state) spiroketal structure. However, in no case were significant differences recognized in the ^{13}C- and ^{1}H-NMR spectra in hexafluoro-2-propanol of the three materials. Thus the use of the ligand either in the optically active or in the racemic form has no consequence on the stereochemistry of the produced polyketone. This fact suggests that the catalytic species responsible for the copolymerization reaction contain either only one ligand molecule or homochiral ligand molecules.

The previously suggested prevailingly isotactic structure for this copolymer[8] is nicely confirmed by the chiroptical properties of the material obtained with the optically pure ligand. In fact, the circular dichroism spectrum in the region of the n–π* transition shows a quite intense band. The intensity of this band ($\Delta\epsilon = -1.56$ L·mol^{-1}·cm^{-1} at 275 nm in hexafluoro-2-propanol) is much larger than that observed in the same region for the low molecular weight model compound (*S*)-3-methylpentan-2-one ($\Delta\epsilon = +0.123$, methanol as the solvent)[13] and has a magnitude comparable to that reported for isotactic poly[(*S*)-1-methylpropyl vinyl ketone].[14] DSC analysis shows a rather sharp melting point at 245.5 °C for this stereo- and regioregular copolymer.

The high regio- and stereoregularity of the copolymer is easily recognized also in the ^{1}H-NMR spectrum (Figure 2). In fact, the coupling constants for the diastereotopic methylene protons (signals at δ 2.75 and 3.10) can be easily evaluated in spite of some overlapping of the signal at lower field with that of the methine proton. The values of those constants (δ 18.0 and 3.0; δ 18.2 and 9.4) suggest a conformational homogeneity for the copolymer in solution, in keeping with the aforementioned intense dichroic band. In fact, of the three limiting conformations that can be expected (Chart 1) only I and II imply large differences (as those observed) for the two vicinal coupling constants. The conformational aspect is particularly interesting due to its possible relation with the photochemical degradation of this copolymer according to the Norrish II mechanism.[15] This mechanism requires a hydrogen atom in the γ-position with respect to the carbonyl group and implies a 6-member-ring transition state. Such a mechanism would be accessible for the less

Chart 1

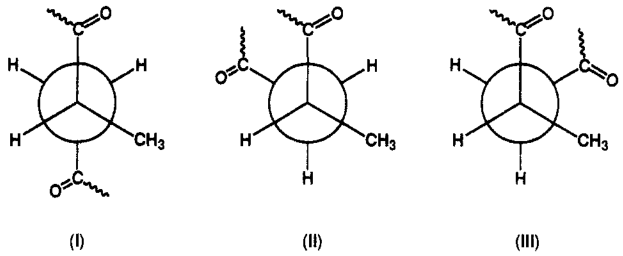
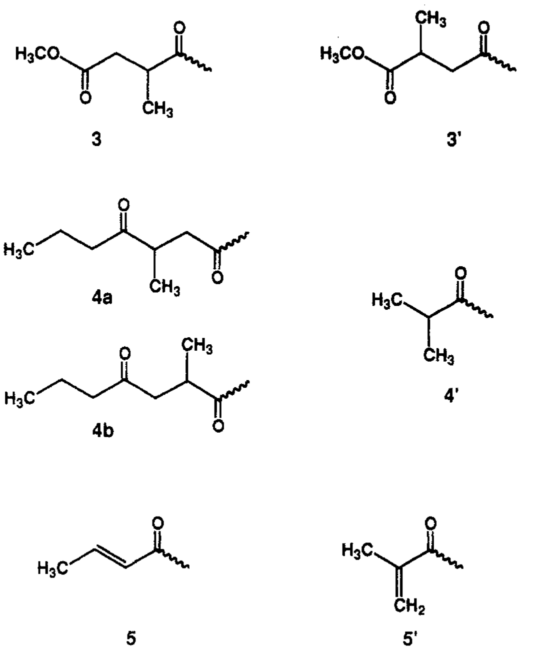


Chart 2



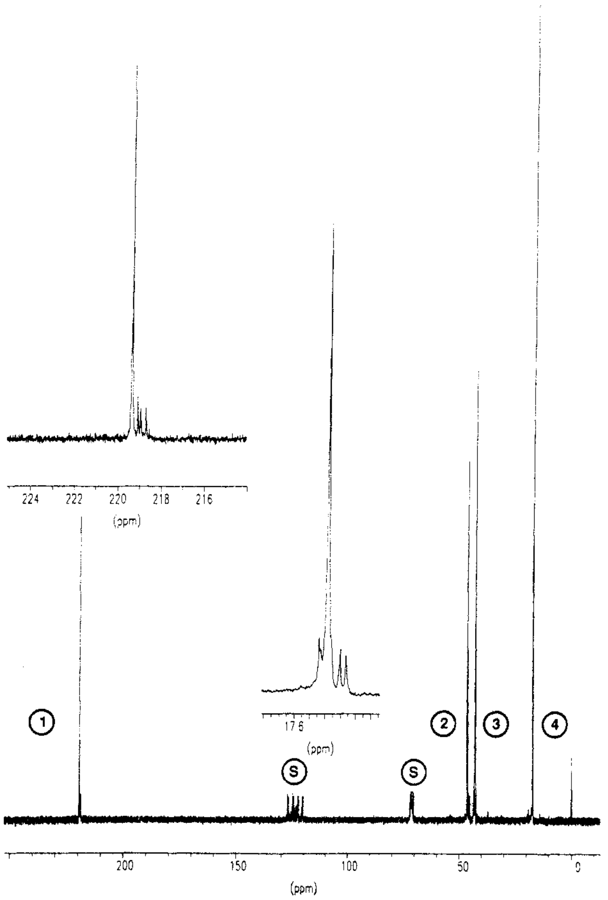


Figure 3. ^{13}C-NMR spectrum (125.8 MHz, $(CF_3)_2CDOD$ as the solvent) of poly(1-oxo-2-methyltrimethylene) obtained with palladium catalysts modified by racemic (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) (same assignments as in Figure 1).

probable conformation III as well as for conformation I.

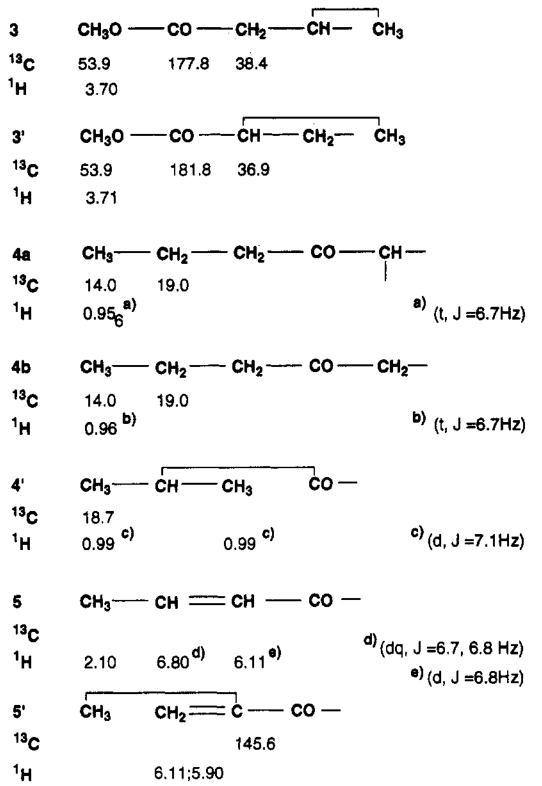
The complete ^{13}C-NMR spectrum (Figure 3) also suggests the high stereoregularity of the copolymer. We have previously proposed an assignment of the main bands in the region of the methyl and of the carbonyl groups based on a statistical approach.[7]

End group analysis for a regioirregular copolymer between propene and carbon monoxide has already been reported.[4] For the regioregular material disclosed in this paper this analysis is even more significant since it can give information about the regioselectivity of the propagation step and about the influence of the nature of the ligand used on the regioselectivity of the insertion. The assignment is based on the comparison of the observed and calculated chemical shift and on DEPT and ^{13}C–^{1}H-correlated NMR experiments. The assignments for the end groups shown in Chart 2 are summarized in Table 1.

For the copolymer obtained using (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) as the ligand among the possible end groups that could have been expected according to previous literature data on this type of material (Chart 2), we could recognize the two possible carbomethoxy moieties **3** and **3′**. The latter group always gives more intense signals. Of the two possible alkyl terminations (4 and 4′) only the *n*-propyl end group **4** could be unambiguously recognized in the ^{13}C-NMR spectrum. However, the doublet centered at 0.99 ppm in the ^{1}H-NMR spectrum shows that also the isopropyl termination **4′** is present even though in lower concentration. Furthermore, we could also clearly identify the unsaturated termination **5′** and **5**, the end group **5** having a much smaller concentration. For the copolymer obtained using 1,3-propanediylbis(diethylphosphine), its concentration is somewhat larger (**5′**/**5** = ~4/1). In this case terminal isopropyl groups are clearly recognized. The end groups **5′** and **5** are assigned to termination reactions via β-hydrogen elimination[3,4,16] after a primary and a secondary insertion of propene, respectively.

The regioselectivity in the insertion of the unsaturated terminal groups is much smaller than that observed during the growth of the chain. The overwhelming type of regioselectivity in the insertion reaction of the olefin in the growing chain cannot be unambiguously determined at this time. However, a tentative inference could be drawn from the analysis of the terminal *n*-propyl groups in the copolymers obtained with the cyclohexyl ligands (chiral and achiral). In both materials two different methyl triplets (Table 1) can be recognized. This splitting must therefore be due to a difference in the regiochemistry of the penultimate propene unit inserted (Chart 2, **4a** vs **4b**). The signal at higher field prevails by a factor of ~2 and is assigned to structure **4a** based on the NMR parameters of model compounds (heptan-4-one and 2-methylhexan-3-one, respectively). For the copolymer obtained using the achiral diphosphine ligand, depending on the reaction conditions the only other end groups which can be recognized are the unsaturated ones. Therefore the signal at higher field could identify the start of the chain and the regiochemistry of the second inserted propene unit. As a consequence of the regular structure of the copolymer, the regioselectivity of the insertion of the olefin could, hence, be determined as primary insertion. It is also noteworthy that 1,3-insertion of propene can be excluded in contrast to cyclopentene[17] for which overwhelming 1,3-

Table 1. Diagnostic ^{13}C- and ^{1}H-NMR Chemical Shifts (in Dideuteriohexafluoro-2-propanol) for the Various End Groups



3	CH_3O —	CO —	CH_2 —	CH —	CH_3	
^{13}C	53.9	177.8	38.4			
^{1}H	3.70					
3'	CH_3O —	CO —	CH —	CH_2 —	CH_3	
^{13}C	53.9	181.8	36.9			
^{1}H	3.71					
4a	CH_3 —	CH_2 —	CH_2 —	CO —	CH —	
^{13}C	14.0	19.0				
^{1}H	0.95_6 [a]					[a] (t, J =6.7Hz)
4b	CH_3 —	CH_2 —	CH_2 —	CO —	CH_2 —	
^{13}C	14.0	19.0				
^{1}H	0.96 [b]					[b] (t, J =6.7Hz)
4'	CH_3 —	CH —	CH_3	CO —		
^{13}C	18.7					
^{1}H	0.99 [c]		0.99 [c]			[c] (d, J =7.1Hz)
5	CH_3 —	CH =	CH —	CO —		
^{13}C						
^{1}H	2.10	6.80 [d]	6.11 [e]			[d] (dq, J =6.7, 6.8 Hz) [e] (d, J =6.8Hz)
5'	CH_3	CH_2 =	C —	CO —		
^{13}C			145.6			
^{1}H		6.11;5.90				

insertion is observed. A secondary regioselectivity for the insertion of the olefin unit was reported in the case of copolymerization of styrene[16] or substituted styrenes.[18] These regioselectivities parallel those observed in the polymerization of styrene and propene with soluble Ziegler–Natta catalytic systems.[19]

Conclusions

The reported results disclose systems able to catalyze the regio- and stereoregular alternating copolymerization of carbon monoxide with propene. In particular, basic diphosphine ligands with less hindered substituents give very active systems still maintaining a good regioregularity in the copolymerization process. The fact that the copolymer can form in the unexpected spiroketal structure appears not to depend on the presence of chiral ligands in the catalytic system.[8b] Furthermore, it appears that chiral optically active ligands having less sterically demanding substituents should give active systems able to give copolymers with high regio- and stereoregularity.

Experimental Section

General Procedures. $Ni(ClO_4)_2$ and 1,4-naphthoquinone were purchased from Fluka. $Pd(O_2CCH_3)_2$ was purchased from Aldrich. Dppe[20] and $Pd(Dppe)(O_2CCH_3)_2$ were prepared according to the literature.[17c] The solvents used were dried according to normal procedures and distilled under nitrogen.

Spectroscopically pure (*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) (^{31}P-NMR −8.73 ppm in C_6D_6)[21] and racemic (*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) containing ~10% impurity of the corresponding oxide (^{31}P-NMR 46.75 ppm in C_6D_6) were kindly given by Dr. E. Broger (F. Hoffmann-La Roche AG). The NMR spectra were measured on Bruker AMX 400 (solid state) and Bruker AMX 500 (in dideuteriohexafluoro-2-propanol solution) spectrometers with tetramethylsilane as the internal standard. IR spectra were recorded on a Mattson Instruments 6020 Galaxy Series FTIR as KBr pellets. CD spectra were recorded on a Jasco 600 in hexafluoro-2-propanol as the solvent. Light scattering, GPC, and viscosimetry measurements were carried out on a Knauer HPLC system equipped with a KMX-6 Chromatix (laser light source at 633 nm), a Knauer DRI refractometer, and a Viscotek differential viscosimeter Model 502. DTA measurements were obtained with a Mettler DSC 30 instrument.

Copolymerization Experiments. (a) A mixture of $[Pd(CH_3COO)_2(Dppe)]$ (0.06 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (0.3 mmol) in 151.5 mL of tetrahydrofuran, 8.5 mL of methanol, and 2 mL of methyl orthoformate was introduced under nitrogen in a 500 mL stainless steel rocking autoclave. After evacuation 39 g of propene was introduced through cooling at −60 °C. After heating at 50 °C, 80 bar of carbon monoxide was introduced, and the autoclave was kept at that temperature for 67 h. After cooling at room temperature and releasing the unreacted gases, the suspension was added to 500 mL of cold methanol and left at 5 °C for 24 h. The copolymer was filtered, washed with methanol, and dried. A total of 14.85 g of copolymer was obtained; the productivity was 34.7 g/gPd·h. M_w = 28000 (light scattering); M_p = 20000 (viscosimetry); M_n = 15000 (GPC). T_m = 225 °C.

(b) In the same manner $[Pd(CH_3COO)_2(Dppe)]$ (0.06 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (0.3 mmol) and 1,4-naphthoquinone (3 mmol) in 151.5 mL of tetrahydrofuran, 2 mL of methyl orthoformate, and 39 g of propene were introduced into the autoclave. The reaction temperature was 50 °C, the initial carbon monoxide pressure was 80 bar, and the reaction time was 42 h. The reaction mixture was treated as above. A total of 10.53 g of copolymer was obtained; the productivity was 39.3 g/gPd·h. M_w = 37000 (light scattering); M_p = 25000 (viscosimetry); M_n = 30000 (NMR).

(c) In the same way $[Pd(CH_3COO)_2(Dppe)]$ (0.06 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (0.3 mmol) and 1,4-naphthoquinone (3 mmol) in 130 mL of *tert*-butyl alcohol, 12.5 mL of methanol, 20 mL of toluene, and 39 g of propene were introduced into the autoclave. The reaction temperature was 40 °C, the initial carbon monoxide pressure was 90 bar, and the reaction time was 68 h. The reaction mixture was treated as above. A total of 54.32 g of copolymer was obtained; the productivity was 125.1 g/gPd·h. M_w = 66000 (light scattering); M_p = 30000 (viscosimetry).

(d) In an analogous manner $Pd(CH_3COO)_2$ (0.06 mmol), ((*S*)-6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) (0.07 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (0.3 mmol) and 1,4-naphthoquinone (3 mmol) in 151.5 mL o tetrahydrofuran, 8.5 mL of methanol, 39 g of propene, and carbon monoxide up to 85 bar were introduced into the autoclave. The reaction temperature was 42 °C and the reaction time was 192 h. A total of 6.9 g of copolymer was obtained; the productivity was 5.6 g/gPd·h. For the determination of the optical activity the copolymer was dissolved in hexafluoro-2-propanol and the solution was filtered. Addition of methanol caused precipitation of a white material, which was washed with methanol and dried. $[\alpha]^{20}_{D}$ = +26 (*c* = 0.97). CD in hexafluoro-2-propanol: $\Delta\epsilon = -1.56$ L·mol^{-1}·cm^{-1} at 275 nm. UV in hexafluoro-2-propanol: $\epsilon = 53$ L·mol^{-1}·cm^{-1} at 272 nm. M_n = 3400 (NMR).

(e) Similarly, $Pd(CH_3COO)_2$ (0.06 mmol), racemic (6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) (0.07 mmol), $Ni(ClO_4)_2{\cdot}6H_2O$ (0.3 mmol) and 1,4-naphthoquinone (3 mmol) in 151.5 mL of tetrahydrofuran, 8.5 mL of methanol, 39 g of propene, and carbon monoxide up to 85 bar were introduced into the autoclave. The reaction temperature was 42 °C and the reaction time was 141 h. A total of 1.83 g of copolymer was obtained; the productivity was 4.5 g/gPd·h. M_n = 4100 (vapor phase osmometry in 2-chlorophenol). T_m = 245.5 °C.

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